The Chemistry of Dienes and Polyenes. Volume 1
Edited by Zvi Rappoport

ISBN: 0-471-96512-X

CHAPTER 1

Contribution of quantum chemistry to the study of dienes and polyenes

V. BRANCHADELL, M. SODUPE, A. OLIVA and J. BERTRÁN

Departament de Química, Universitat Autònoma de Barcelona, 08193 Bellaterra, Spain
Fax: (34)35812920; e-mail: IQFI1@EBCCUAB1.bitnet

I. INTRODUCTION

Dienes and polyenes have been a subject of great interest due to their important role in biology, materials science and organic synthesis. The mechanism of vision involves *cis–trans* photoisomerization of 11-*cis*-retinal, an aldehyde formed from a linear polyene. Moreover, this kind of molecule exhibits high linear and non-linear electrical and optical properties. Short polyenes are also involved in pericyclic reactions, one of the most important classes of organic reactions.

A knowledge of the structure and properties of dienes and polyenes is necessary to understand the mechanisms of these processes. Quantum chemical calculations can be very helpful to achieve this goal. Several reviews have discussed the theoretical contributions to different aspects of dienes and polyenes[1–5]. Orlandi and coworkers[1] have reviewed the studies devoted to the ground state structure and spectra of linear polyenes. The molecular electrical properties of several organic molecules, including polyenes, have been considered by André and Delhalle[2]. Finally, the mechanism of pericyclic reactions has been discussed by Houk and coworkers[3,4] and Dewar and Jie[5].

The aim of this chapter is to present the most recent theoretical contributions to the study of structure, properties and reactivity of dienes and polyenes. Earlier stages in these areas are covered in the above-mentioned reports[1–5].

In this chapter we do not intend to carry out an exhaustive review of all the theoretical studies related to dienes and polyenes. Instead, we have selected those studies which we think may illustrate the present status of quantum chemical calculations in the study of these compounds. We will emphasize the significance and validity of the results rather than the methodological aspects. We will focus our attention on *ab initio* calculations, although some references to semiempirical results will also be included. In order to make the reading more comprehensive to the nontheoretician, we will briefly present in the next section a survey of the most common theoretical methods. In Section III we will present the studies dealing with the ground state structures and vibrations of linear polyenes. The excited states structures and electronic spectra will be considered in Section IV. Section V will be devoted to electrical and optical properties. Finally, the Diels–Alder reaction will be covered in Section VI, as a significant example of chemical reaction involving dienes.

II. SURVEY OF THEORETICAL METHODS

The purpose of most quantum chemical methods is to solve the time-independent Schrödinger equation. Given that the nuclei are much more heavier than the electrons, the nuclear and electronic motions can generally be treated separately (Born–Oppenheimer approximation). Within this approximation, one has to solve the electronic Schrödinger equation. Because of the presence of electron repulsion terms, this equation cannot be solved exactly for molecules with more than one electron.

The most simple approach is the Hartree–Fock (HF) self-consistent field (SCF) approximation, in which the electronic wave function is expressed as an antisymmetrized product of one-electron functions. In this way, each electron is assumed to move in the average field of all other electrons. The one-electron functions, or spin orbitals, are taken as a product of a spatial function (molecular orbital) and a spin function. Molecular orbitals are constructed as a linear combination of atomic basis functions. The coefficients of this linear combination are obtained by solving iteratively the Roothaan equations.

The number and type of basis functions strongly influence the quality of the results. The use of a single basis function for each atomic orbital leads to the minimal basis set. In order to improve the results, extended basis sets should be used. These basis sets are named double-ζ, triple-ζ, etc. depending on whether each atomic orbital is described by two, three, etc. basis functions. Higher angular momentum functions, called polarization functions, are also necessary to describe the distortion of the electronic distribution due to the bonding. Although increasing the size of the basis set is expected to improve the description of the system, the exact result will never be achieved with such a monoconfigurational wave function. This is due to the lack of electron correlation in the Hartree–Fock approximation.

Two different correlation effects can be distinguished. The first one, called dynamical electron correlation, comes from the fact that in the Hartree–Fock approximation the instantaneous electron repulsion is not taken into account. The nondynamical electron correlation arises when several electron configurations are nearly degenerate and are strongly mixed in the wave function.

Several approaches have been developed to treat electron correlation. Most of these methods start from a single-reference Hartree–Fock wave function. In the configuration interaction (CI) method, the wave function is expanded over a large number of configurations obtained by exciting electrons from occupied to unoccupied orbitals. The coefficients of such an expansion are determined variationally. Given that considering all possible excitations (Full CI) is not computationally feasible for most of the molecules, the expansion is truncated. The most common approach is CISD, where only single and double excitations are considered. The Møller–Plesset (MP) perturbation theory is based on a perturbation expansion of the energy of the system. The nth-order treatment is denoted MPn. MP2 is the computationally cheapest treatment and MP4 is the highest order normally used. Finally, other methods for including dynamical electron correlation are those based on the coupled cluster (CC) approach.

When the HF wave function gives a very poor description of the system, i.e. when nondynamical electron correlation is important, the multiconfigurational SCF (MCSCF) method is used. This method is based on a CI expansion of the wave function in which both the coefficients of the CI and those of the molecular orbitals are variationally determined. The most common approach is the Complete Active Space SCF (CASSCF) scheme, where the user selects the chemically important molecular orbitals (active space), within which a full CI is done.

An alternative approach to conventional methods is the density functional theory (DFT). This theory is based on the fact that the ground state energy of a system can be expressed as a functional of the electron density of that system. This theory can be applied to chemical systems through the Kohn–Sham approximation, which is based, as the Hartree–Fock approximation, on an independent electron model. However, the electron correlation is included as a functional of the density. The exact form of this functional is not known, so that several functionals have been developed.

The inclusion of electron correlation is generally necessary to get reliable results. However, the use of methods that extensively include electron correlation is limited by the computational cost associated with the size of the systems.

Even *ab initio* Hartree–Fock methods can become very expensive for large systems. In these cases, the semiempirical methods are the ones generally applied. In these methods, some of the integrals are neglected and others are replaced using empirical data.

Up to now, we have only considered the computation of the electronic energy of the system. To get a thorough description of the structure of a molecule, it is necessary to know the potential energy surface of the system, i.e. how the energy depends on the geometry parameters. Optimization techniques allow one to locate stationary points, both minima and saddle points on the potential energy surface. These methods require the derivatives of the energy with respect to the geometry parameters. Second derivatives are necessary to obtain the harmonic frequencies. Higher-order derivatives are much more difficult to obtain.

In this section we have surveyed the most common methods of quantum chemistry on which are based the studies presented in the next sections. A more extensive description of these methods can be found in several excellent textbooks and reports[6–11].

III. GROUND STATE STRUCTURE AND VIBRATIONAL SPECTRA

The structure of the ground state of linear polyenes has been the subject of several theoretical studies[12–37]. Molecular geometries and vibrational frequencies for polyenes up to $C_{18}H_{20}$ have been reported. Much emphasis has been placed on the calculation of force constants that can be used in the construction of force fields.

We will first discuss results corresponding to 1,3-butadiene. This molecule is the simplest of the series, so that several levels of calculation have been used, thus permitting one to establish the minimum requirements of the theoretical treatment. The extension to trienes, tetraenes and longer polyenes will be discussed in further subsections.

A. Butadiene

The ground state structure of butadiene has been extensively studied using different kinds of theoretical methods[19,21,23,31,34,36]. For this molecule, several conformations associated with rotation around the single C−C bond are possible. Experimental evidence shows that the most stable one is the planar *s-trans* conformation. All theoretical calculations agree with this fact.

1. Geometry

Figure 1 shows schematically the structure of *s-trans*-1,3-butadiene. Several studies show that proper geometry parameters are only obtained with a basis set of at least double-ζ quality, including polarization functions for carbon atoms. Table 1 presents a selection of the results obtained at several levels of calculation, using a basis set of this kind.

At the HF level, the value of the C=C bond length is clearly underestimated. The inclusion of electron correlation at different levels of calculation leads to values in closer agreement with experiment. The value of the C−C bond length is less sensitive to the inclusion of electron correlation. As a consequence of this fact, the CC bond alternation (the difference between CC single and double bond lengths) is overestimated at the HF level. The inclusion of dynamical electron correlation through MP*n* calculations corrects this error. A very similar result is obtained at the CASSCF level of calculation[31].

The values of the C−H bond lengths also change with the inclusion of electron correlation, leading to a better agreement with the experimental values. On the other hand, the values of the CCC and CCH bond angles are less sensitive to the level of calculation. These results show that the inclusion of electron correlation is necessary to obtain geometry parameters within the range of the experimental results. However, some of the geometry parameters are already well reproduced at lower levels of calculation.

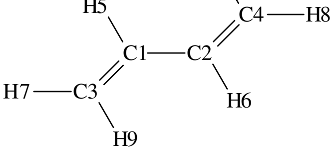


FIGURE 1. Schematic representation of the structure of *s-trans*-1,3-butadiene

TABLE 1. Geometry[a] (in Å and degrees) of *s-trans*-1,3-butadiene at several levels of calculation[b]

	HF[c]	MP2[c]	MP3[c]	MP4[d]	exp[e]
C1C3	1.323	1.342	1.338	1.349	1.337–1.349
C1C2	1.468	1.456	1.463	1.464	1.463–1.467
C1H5	1.078	1.090	1.090	1.094	1.093–1.108
C3H7	1.075	1.084	1.085	1.089	1.093–1.108
C3H9	1.077	1.086	1.087	1.091	1.093–1.108
C1C2C4	124.1	123.7	123.7	123.8	122.8–124.4
C1C2H6	116.6	116.7	116.5	116.5	114.7–117.7
C2C4H10	121.7	121.4	121.6	121.5	119.5–120.9
C2C4H8	121.1	121.7	121.8	121.8	119.5–102.5

[a] See Figure 1 for numeration.

[b] A basis set of double-ζ+polarization quality is used in all cases.

[c] Reference 23.

[d] Reference 35.

[e] Reference 38.

TABLE 2. Selected vibrational frequencies (cm^{-1}) of *s-trans*-1,3-butadiene computed at several levels of calculation[a]

Symmetry	Description	HF[b]	MP2[b]	MP4[c]	exp[d]
a_g	CH str	3242	3200	3165	3025
	CH_2 str	3325	3217	3149	3014
	C=C str	1898	1745	1721	1644
	C−C str	1326	1265	1250	1206
	CCC bend	550	522	515	513
b_u	CH str	3343	3207	3165	3062
	CH_2 str	3331	3216	3156	2986
	C=C str	1818	1678	1657	1579
	CCC bend	319	298	295	301
a_u	CCCC tors	167	160	160	163[e]

[a] A basis set of double-ζ+polarization quality is used in all cases.

[b] Reference 23.

[c] Reference 35.

[d] Reference 39.

[e] Reference 40.

2. Vibrational frequencies and force field

Harmonic vibrational frequencies for *s-trans* butadiene have also been calculated at several levels of calculation[19,21,23,24,31,35]. Table 2 presents the computed values of some of the vibrational frequencies.

HF frequencies are generally larger than the corresponding experimental data. The inclusion of electron correlation improves the results, but the theoretical frequencies are still higher than the experimental ones. Both the introduction of electron correlation and the size of the basis set seem to be important in order to obtain reliable results.

In order to obtain better agreement between theory and experiment, computed frequencies are usually scaled. Scale factors can be obtained through multiparameter fitting towards experimental frequencies. In addition to limitations on the level of calculation, the discrepancy between computed and experimental frequencies is also due to the fact that experimental frequencies include anharmonicity effects, while theoretical frequencies are computed within the harmonic approximation. These anharmonicity effects are implicitly considered through the scaling procedure.

TABLE 3. Selected force constants (mdyn $Å^{-1}$) computed for *s-trans* butadiene at several levels of calculation[a]

	HF[a]	MP2[b]	MP4[c]	exp[d]
C=C	11.259	9.591	9.263	8.886
C−C	5.859	5.687	5.491	5.428
C=C/C−C	0.398	0.414	0.409	
C=C/C=C	−0.093	−0.110	−0.116	

[a] A basis set of double-ζ+polarization quality is used in all cases.
[b] Reference 23.
[c] Reference 35.
[d] Reference 39.

A knowledge of the force field for the ground state of a molecule is essential for understanding its static and dynamical properties. The characterization of the potential surfaces from vibrational data alone is not possible for most molecules, even when the harmonic approximation is assumed. The large number of adjustable parameters in the force constants matrix requires information from different isotopic species which are very difficult to obtain in a highly purified form for many molecules. The number of parameters can be reduced by truncation of the off-diagonal interaction constants. However, this approximation introduces great uncertainty in the derivation of accurate force fields. Force constants can be computed from theoretical calculations without any assumption regarding the off-diagonal coupling terms. Scaled force constants can be generally transferred from one molecule to another and allow the construction of accurate force fields. These force fields are necessary to interpret the vibrational spectra of more complex molecules.

Table 3 presents the values of the force constants corresponding to the C skeleton vibrations of *s-trans*-1,3-butadiene obtained at several levels of calculation. The computed values are very sensitive to the inclusion of electron correlation. Stretching C=C and C−C force constants decrease when electron correlation is taken into account. This effect is generally larger for basis sets without polarization functions than for those with polarization functions[23]. On the contrary, the values of the C=C/C−C and C=C/C=C coupling constants do not vary much upon increasing the level of calculation of electron correlation.

3. Conformational equilibrium

The potential energy function corresponding to the rotation around the C−C bond of butadiene has been studied in detail by Guo and Karplus[23]. The second stable isomer corresponds to a *gauche* conformation, with a CCCC torsion angle between 35 and 40 degrees. At the MP3/6-31G* level of calculation, this conformation is 2.6 kcal mol^{-1} higher than the most stable *s-trans* conformation, in excellent agreement with the experimental value of 2.7 kcal mol^{-1}[41], and 0.9 kcal mol^{-1} lower in energy than the planar *s-cis* conformation, which would correspond to the transition state linking two different *gauche* structures.

The form of the torsional potential in the region between CCCC = 0−120 degrees is not sensitive to the addition of polarization functions or inclusion of electron correlation. The effects are somewhat larger in the region between 120 and 180 degrees. The C−C and C=C bond lengths are very sensitive to a change in the torsional angle. This behavior can be related to the change in the degree of π bond delocalization[22,23]. Finally, the C=C−C bond angle remains almost constant when the torsional angle varies from 0 to 135 degrees, but dramatically increases in going from 135 to 180 degrees, due to the repulsion between two methylene groups.

A density functional calculation reported by Oie and coworkers[34] shows that the potential energy surface between the *s-cis* and *gauche* regions is extremely flat, so that the potential energy surface should be considered of a *cis–trans* type rather than of a *gauche–trans* type.

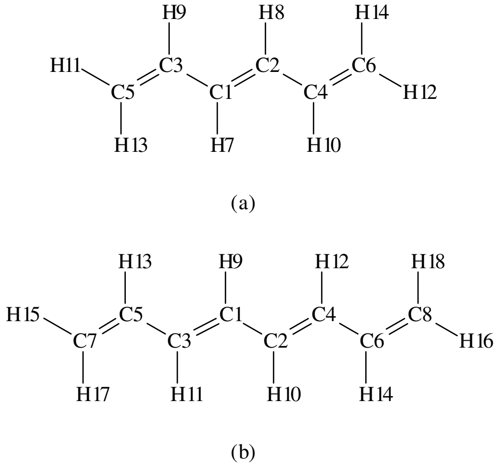
Several studies have considered the role of substituents on the conformational equilibrium in butadiene[19,27,28,32,33]. Guo and Karplus[27] have studied the structures of stable conformations and potential energy functions about the central C−C bond for 18 different methylated butadienes. They showed that methyl substitution at the (*E*)-4-position has little effect on the potential function, while the methyl substitution at the (*Z*)-4-position has a larger effect on the shape of the potential function. All the three trimethylated derivatives of butadiene have a global potential energy minimum at the *gauche* conformation, while for 2,4-dimethylpentadiene there is a second stable structure corresponding to the *s-trans* conformation. The stable conformations of 1,3-dienes and the shapes of potential functions can be determined from two basic interactions: conjugation and steric repulsion. Conjugation tends to stabilize the planar conformations (*s-cis* or *s-trans*), while steric repulsion is normally strongest in the planar conformations and weakest in the nonplanar ones. The changes in the shape of the potential function produced by methyl substitution are mainly due to the increase of steric interactions.

B. Trienes and Tetraenes

We will now consider the studies devoted to the next two linear polyenes: 1,3,5-hexatriene and 1,3,5,7-octatetraene. First, we will present the results corresponding to geometries and conformational energies computed for these compounds. We will then discuss the computed frequencies and force fields.

1. Geometries and conformations

The most stable conformation of both hexatriene and octatetraene is the all-*s-trans* one. Figure 2 represents these structures schematically.



(a)

(b)

FIGURE 2. Schematic representation of the structure of: (a) all-*trans*-1,3,5-hexatriene and (b) all-*trans*-1,3,5,7-octatetraene

TABLE 4. Selected geometrical parameters[a] (Å) of all-*trans*-hexatriene computed at several levels of calculation[b]

Bond	HF[c]	ACPF[d]	CASSCF[d]	exp[e]
C1=C2	1.325	1.350	1.353	1.368
C3=C5	1.319	1.341	1.347	1.337
C1−C3	1.460	1.451	1.459	1.458

[a] see Figure 2 for numeration.
[b] A basis set of double-ζ+polarization quality is used in all cases.
[c] Reference 21.
[d] Reference 31.
[e] Reference 38a.

TABLE 5. Selected geometrical parameters[a] (Å) of all-*trans*-octatetraene computed at several levels of calculation[b]

Bond	HF[c]	CASSCF[c]	MP2[d]	exp[e]
C1−C2	1.461	1.457	1.442	1.451
C1=C3	1.335	1.355	1.355	1.327
C3−C5	1.465	1.461	1.448	1.451
C5=C7	1.330	1.350	1.345	1.336

[a] See Figure 2 for numeration.
[b] A basis set of double-ζ+polarization quality is used in all cases.
[c] Reference 30.
[d] Reference 36.
[e] Reference 42.

Several theoretical studies have been devoted to the ground state structure of all-*trans*-1,3,5-hexatriene[21,25,31] and all-*trans*-1,3,5,7-octatetraene[18,21,26,30,31,36]. Tables 4 and 5 present the values of the CC bond lengths obtained in some selected theoretical calculations.

The introduction of electron correlation produces the same kind of effects on the CC bond lengths as those observed for butadiene. For hexatriene and octatetraene the inner C=C bonds are predicted to be longer than the outer C=C bonds. This result is in excellent agreement with experimental data corresponding to hexatriene, but differs from the experimental result in the case of octatetraene. This discrepancy has been suggested to be due to an important experimental error in the reported values[42].

When these results are compared with those corresponding to butadiene (Table 1), one can observe that bond alternation decreases upon increasing the chain length at all levels of calculation, in excellent agreement with experimental results.

High energy stable rotamers of hexatriene have also been theoretically studied[25,29]. Two possible *Cis/Trans* isomers are possible with respect to the C1=C2 bond (see Figure 2). For each of them, the rotation around the C1−C3 and C2−C4 bonds can lead to *s-trans* and *gauche* conformations. The *gauche-Trans-trans*, *trans-Cis-trans* and *gauche-Cis-trans* conformers have been found to be 3.0, 2.0 and 5.1 kcal mol^{-1} above the most stable all-*trans* conformation, respectively[25].

For *trans-Cis-trans*-hexatriene Liu and Zhou[29] have found a planar C_{2v} structure at the HF, MP2 and CASSCF levels of calculation, while the experimental data[43] suggest a nonplanar structure with a dihedral angle of 10 degrees around the central C1=C2 double bond. The calculated torsional potential curves around both the central C1=C2 double bond and the C1−C3 single bond are very flat in the range between −10 and 10 degrees.

This fact allows the effective relaxation of steric repulsion. The potential barrier for the motion around the C−C single bonds is smaller than that corresponding to the motion around the central C=C bond. Using the potential functions computed for these motions, and assuming a Boltzmann distribution, average torsional angles of 7.7 and 7.1, at 300 K, are obtained for rotations around C1−C3 and C1=C2, respectively. This torsional motion seems to be due to the nonplanar structure observed experimentally.

Panchenko and Bock[26] have studied three high energy rotamers of octatetraene: *g,T,t,T,t-*, *t,T,t,C,t-* and *g,T,t,C,t-* where *C* and *T* refer to *Cis/Trans* isomerism around the C1=C3 and C2=C4 double bonds, while *g* and *t* refer to *gauche* and *s-trans* conformations around C5−C3, C1−C2 and C4−C6 single bonds (see Figure 2). The most stable structure is *t,T,t,C,t-*, which lies 1.9 kcal mol^{-1} above the all-*trans* conformer. The *g,T,t,T,t-* and *g,T,t,C,t-* conformations are 3.0 and 5.0 kcal mol^{-1} higher in energy than the all-*trans* structure, respectively. These conformational energies are very similar to those computed for hexatriene and butadiene.

2. Vibrational frequencies and force constants

Vibrational frequencies of hexatriene and octatetraene have been reported by several authors[21,24–26,36]. The increase in the size of these molecules with respect to butadiene limits the use of highly accurate levels of calculation, so that a good choice of scaling factors is necessary to obtain useful results. Kofraneck and coworkers[21] have shown that employing scale factors determined from vibrational data for *trans* structures alone does not give a balanced description of *cis* and *trans* structures.

The experimental vibrational spectra of hexatrienes are complicated by the overlapping of the vibronic coupling, which manifests itself in a decrease of the experimental value of the total symmetric vibration of the C=C double bonds. This is the result of an interaction between the ground and the lowest excited state frequencies of the dominant double bond stretching modes. In order to take into account this effect, Panchenko and coworkers[25] have used a special scale factor for the central C=C double bond stretching coordinate. For the rest of the modes, the scale factors transferred from butadiene are used. This treatment has been extended to all-*trans*-octatetraene[26] and a complete assignment of its experimental spectra has been achieved.

Liu and Zhou[29] have computed the quadratic force field of *cis*-hexatriene by a systematic scaling of *ab initio* force constants calculated at the planar C_{2v} structure. Their results reproduce satisfactorily the observed spectral features of this molecule.

Lee and colleagues[36] have computed the vibrational frequencies of all-*trans*-octatetraene. They have found that the mean absolute percentage deviation for frequencies is 12% at the HF level, while it decreases to 4% at the MP2 level. Among the low-frequency modes, the frequencies of the in- and out-of-plane CCC skeletal bends are lower than the experimental values by 16%. When d basis functions on each carbon atom are added, the frequencies of some of the low-frequency modes approach the observed frequencies.

When the electron correlation level improves from HF to MP4, the C=C/C=C coupling constant remains basically unchanged in the DZ and 6-31G basis sets. The coupling constants of MP4/DZ, MP4/6-31G* and MP2/6-311G(2d,p) increase no more than 23% from the HF/DZ value. The C−C/C=C coupling constant does not vary appreciably upon increasing the correlation level.

C. Longer Polyenes

The possibility that the results obtained for short polyenes can be extrapolated to longer polyenes and to polyacetylene has been discussed by several authors[21,24,31,37].

It is generally assumed that increasing the degree of polymerization of any polymer leads to a number of very regular and systematic trends, provided that the backbone conformation does not change in the course of this process. The latter condition is fulfilled for all-*trans*-polyenes. However, how fast the convergence to bulk and convergence to edge effects is reached for a particular mode depends very much on the system under consideration. In the case of the all-*trans*-polyenes, the most prominent feature that has been observed in the vibrational spectra is the decrease of the lowest totally symmetric C=C double bond stretching frequency. A correct description of the C=C stretching region of the vibrational spectra requires good estimates of the off-diagonal force constants, that can only be achieved when electron correlation is taken into account in the computation of the force field. For this reason, the use of calculations at the Hartree–Fock level and conventional scaling techniques is insufficient to obtain a good description of the vibrational spectra of long polyenes.

Kofraneck and coworkers[24] have used the geometries and harmonic force constants calculated for *trans*- and *gauche*-butadiene and for *trans*-hexatriene, using the ACPF (Average Coupled Pair Functional) method to include electron correlation, to compute scaled force fields and vibrational frequencies for *trans*-polyenes up to 18 carbon atoms and for the infinite chain.

Complete harmonic force fields have been computed up to $C_{10}H_{12}$. For $C_{14}H_{16}$ only the in-plane force field has been calculated while for $C_{18}H_{20}$ calculations have been restricted to that part of the force field directly related to the carbon backbone. The results obtained show that diagonal force constants for C=C decrease as the length of the chain increases, whereas the opposite occurs for C–C. For a polyene of a specified chain length, the force constant corresponding to a C=C is lower in the center of the chain than it is at the edge of the molecule. C–C force constants behave oppositely. An almost linear correlation is observed between equilibrium distances and diagonal force constants. Faster convergence is observed for force constants corresponding to bonds at the edge of a polyene than for force constants of central bonds.

Structural features of the methylene end group converge very fast upon chain length extension. A similar fast convergence is obtained for the methine C–H bond lengths and all bond angles. On the other hand, a slower convergence is obtained for the central CC single and double bonds[24,31,37]. The reduction of the bond alternation is the most important geometry change accompanying the increase in the chain length.

For most of the force constants, extrapolation to the infinite length polyene is unnecessary because convergence is practically already achieved for $C_{14}H_{16}$. The only slowly converging part of the force field is connected with carbon–carbon single and double bond stretches and the coupling between them. According to these results, we could expect that the knowledge of an accurate force field for butadiene and hexatriene will allow a rather safe extrapolation to longer polyenes and to polyacetylene for very large portions of their force fields. However, the pending problem is the determination of the CC stretching diagonal and off-diagonal force constants and, eventually, a few further coupling constants between CC stretching and other internal coordinates.

IV. EXCITED STATES

Understanding the nature of the low-lying excited states of short polyenes has presented a formidable challenge for both experimentalists and theoreticians[1]. Most of the discussion has been focused on the relative ordering of the two lowest $2\,^1A_g$ and $1\,^1B_u$ singlet states. The excited $1\,^1B_u$ state can be described as a single excitation from the highest occupied orbital (HOMO) to the lowest unoccupied orbital (LUMO). The $2\,^1A_g$ state is characterized by a large component of the HOMO,HOMO → LUMO,LUMO double excitation.

It is currently accepted that for long polyenes starting with octatetraene, the lowest excited singlet state corresponds to the 2 ^1A_g state[44]. Because the X $^1A_g \rightarrow 2\,^1A_g$ electronic transition is dipole forbidden, the 2 ^1A_g state is difficult to characterize experimentally. The X $^1A_g \rightarrow 1\,^1B_u$ electronic transition is dipole-allowed and it appears in the spectra as a very intense band. This 1 ^1B_u state undergoes very rapid internal conversion to the 2 ^1A_g state, which then decays to the X ^1A_g state by fluorescence[1]. For the shorter polyenes, butadiene and hexatriene, the lack of fluorescence suggested that the above mechanism does not hold[45]. Because of that, the ordering of these two states in the shorter polyenes has been a subject of great controversy for a long time. Recently, experimental results have suggested that the 2 ^1A_g state lies below the 1 ^1B_u state[46–48].

The two lowest triplet states are the 1 ^3B_u and 1 ^3A_g states. The former is mainly described by the HOMO → LUMO single excitation while the latter is a mixture of single excitations of proper symmetry, i.e. HOMO$-$1 → LUMO and HOMO → LUMO $+$ 1.

The determination of accurate relative excitation energies by *ab initio* methods has been shown to present great difficulties and to require extensive calculations[49,50]. First, extended basis sets are needed to account for the diffuse character of some of the excited states. Second, electron correlation effects have to be treated in a balanced way. Moreover, while the most important correlation effects (nondynamic) are described by configurations within the π space, inclusion of dynamic correlation effects is important to obtain quantitative results for the excitation energies. Especially important is the dynamic polarization of the σ orbitals in the excited states which are dominated by ionic valence structures. Finally, low-lying Rydberg states can interact with nearby valence excited states. Because of the different correlation effects, the extent of this mixing is highly sensitive to the theoretical method used.

Recent calculations using the multiconfiguration second-order perturbation (CASPT2) method have been shown to yield accurate excitation energies for a number of organic molecules[49,50]. This method is based on the Complete Active Space Self-Consistent-Field (CASSCF) procedure, which is used to calculate the molecular orbitals and the reference wave function. This step accounts for the most important interactions such as the mixing of nearly degenerate configurations, which is commonly found in excited states. In a second step, the dynamical correlation effects are added using the second-order perturbation theory. This method represents a very efficient alternative to the multireference configuration interaction (MRCI) method which becomes impracticable for large molecules due to the size of bottleneck inherent in this approach. The CASPT2 vertical excitation energies to the low-lying valence excited states of butadiene, hexatriene and octatetraene are given in Table 6. These values will be discussed in the next subsections.

A. Butadiene

Because butadiene is the smallest polyene, its low-lying electronic states have been extensively studied theoretically[49,51–62]. Most of the studies have been performed for the most stable *trans* isomer.

It is now generally agreed that the first allowed transition in *s-trans* butadiene corresponds to the X $^1A_g \rightarrow {}^1B_u$ excitation, the experimental vertical excitation energy being determined to be 5.92 eV[63,64]. There has been, however, some disagreement on the location of the 2 ^1A_g state. That is, while Doering and McDiarmid suggested the vertical energy to be 7.3 eV[65], the results of Chadwick and coworkers[47,48], based on resonance Raman spectroscopy, placed the 2 ^1A_g state 0.25 eV below the 1 ^1B_u state. For the two lowest triplet states, 1 ^3B_u and 1 ^3A_g, the experimental vertical excitation energies are found to be 3.2 and 4.91 eV, respectively[63].

TABLE 6. CASPT2 vertical excitation energies (eV) for the low-lying excited states of butadiene, hexatriene and octatetraene[a]

State	*trans*-Butadiene[b]	*trans*-Hexatriene[b]	*trans*-Octatetraene[c]
1 ^1B_u	6.23(5.92)	5.01(4.95)	4.42(4.41)
2 ^1A_g	6.27	5.19(5.21)	4.38
1 ^3B_u	3.20(3.22)	2.55(2.61)	2.17(2.10)
1 ^3A_g	4.89(4.91)	4.12(4.11)	3.39(3.55)
	cis-Butadiene[d]	*cis*-Hexatriene[d]	
1 $^1B_2$	5.58(5.49)	5.00(4.92)	
2 $^1A_1$	6.04	5.04	
1 $^3B_2$	2.81	2.57	
1 $^3A_1$	4.74	3.94	

[a] Experimental values in parentheses.
[b] Reference 49.
[c] Reference 30.
[d] Reference 62.

Theoretical calculations have also shown discrepancies in the relative vertical excitation energies of the two 2 ^1A_g and 1 ^1B_u singlet states. Early calculations[51] placed the 2 ^1A_g state below the 1 ^1B_u state, while more recent theoretical studies show the reversed order when the ground state X ^1A_g geometry is used[49].

It can be observed in Table 6 that the CASPT2 method gives accurate vertical excitation energies. In particular, it can be observed that the vertical transitions to the two lowest triplet states are in excellent agreement with the experimental results. For the singlet states of *s-trans* butadiene the CASPT2 method shows the largest errors for the states of B_u symmetry, due to valence–Rydberg mixing[49]. However, these errors are still smaller than 0.4 eV, which demonstrates the adequacy of the method. Other accurate calculations have been performed for the vertical excitation energies of butadiene. In particular, Graham and Freed[60] have reported results for the excited states of *trans*-butadiene using an effective valence Hamiltonian (EVSH) method, obtaining similar accuracy to that of the CASPT2 method.

Particularly interesting is the relative ordering of the 2 ^1A_g and 1 ^1B_u states. CASPT2 results indicate that both states are very close in energy with the 1 ^1B_u state lying below the 2 ^1A_g state. The CASPT2 energy difference between the two states is computed to be 0.04 eV, in good agreement with the EVSH results[60] which place the 1 ^1B_u state 0.05 eV below the 2 ^1A_g state. Because of valence–Rydberg mixing in the 1 ^1B_u state, the error in the computed excitation energy is expected to be larger for this state than for the 2 ^1A_g state, which is clearly of valence character. Based on earlier experience, Serrano-Andrés and coworkers estimate the vertical transition to the 2 ^1A_g state to be above the 1 ^1B_u state by around 0.3 eV[49].

The computed vertical excitation energies of *cis*-butadiene are shifted down compared to those of *s-trans*-butadiene. The ordering of the lowest singlet states (1 $^1B_2$ and 2 $^1A_1$) is equivalent to the one found in the *trans* isomer. That is, the 1 $^1B_2$ state (1 ^1B_u for *trans*) lies below the 2 $^1A_1$ state (2 ^1A_g for *trans*). However, the computed energy difference (0.46 eV) in the *cis* isomer is larger than that of the *trans* structure (0.04 eV). It is interesting to note that valence–Rydberg mixing in *cis*-butadiene is smaller than in *trans*-butadiene, and so the error in the excitation energy to the 1 $^1B_2$ state is expected to be smaller than the one corresponding to the equivalent 1 ^1B_u state.

The relative ordering of the two lowest singlet states is in contrast to the resonance Raman scattering experiments[47,48], which seem to indicate that the 2 ^1A_g state is 0.25 eV below the 1 ^1B_u state. However, it is not clear that the reported ordering corresponds to the vertical excitation energies. Thus, this discrepancy might be attributed to the fact that the 2 ^1A_g state is more sensitive to geometry relaxation than the 1 ^1B_u state[52,54,55]. As a consequence, the adiabatic excitation energies show the reversed order, the 2 ^1A_g state being now more stable than the 1 ^1B_u state.

Ab initio calculations on the geometry optimization of the 2 ^1A_g state of *s-trans*-butadiene have shown that the C_{2h} planar structure is not stable since it presents several imaginary frequencies associated to out-of-plane vibrations. Three nonplanar structures are found to be stable minima on the potential energy surface. The nonplanarity of this state makes the out-of-plane vibrations effective accepting modes. This fact strongly increases the rate of 2 $^1A_g \rightarrow 1\ ^1A_g$ internal conversion, which would explain the lack of fluorescence in butadiene[56].

B. Hexatriene

Ab initio calculations for hexatriene are less numerous than for butadiene due to its larger size[49,52,62,66–71]. However, CASPT2 results for hexatriene[49] have shown that the study of this molecule present less difficulties than that of butadiene or ethene. This is due to the fact that in hexatriene there is no significant mixing between valence and Rydberg states. Thus, correlation effects are treated in a more balanced way and consequently the vertical excitation energies are more accurate (Table 6).

Similarly to *s-trans*-butadiene, the 1 ^1B_u state lies below the 2 ^1A_g state in *trans*-hexatriene. The CASPT2 vertical excitation energies of these two states are in excellent agreement with the experimental results. The computed energy difference (0.2 eV) between the 1 ^1B_u and 2 ^1A_g states is slightly smaller than the estimated value (0.3 eV) for *s-trans*-butadiene[49,30]. In *cis*-hexatriene the lowest singlet state is also the 1 $^1B_2$ state, although for this isomer the two singlet states are very close in energy[62].

The effect of geometrical relaxation on the relative excitation energies has been studied by Cave and Davidson, who performed *ab initio* CI calculations using semiempirical optimized geometries of the ground and excited states[52]. Their results showed that the 2 ^1A_g state is again more affected by the geometrical changes than the 1 ^1B_u state. As a consequence, the adiabatic excitation energies show the reversed order, in agreement with recent experimental results for *cis*-hexatriene which indicate that the 2 ^1A_g state lies 5270 cm^{-1} below the 1 ^1B_u state[46].

CASSCF calculations for *cis*-[68] and *trans*-hexatriene[67] have also shown that the planar structure in the 2 ^1A_g state is not stable, since it presents two imaginary frequencies. For *cis*-hexatriene[68], the release of symmetry constraints leads to two stable minima, one of C_2 symmetry and one of C_s symmetry, corresponding to out-of-plane deformations of the terminal hydrogen atoms. These results are in agreement with the experimental spectrum which could only be interpreted as arising from two non-planar configurations in the 2 ^1A_g state. However, the stabilization energy associated with the distortion from planarity is small, thus indicating that this molecule is extremely flexible with respect to the out-of-plane distortions. As in the case of butadiene, the non-planarity of hexatriene in the 2 ^1A_g state could account for the absence of fluorescence due to a strong increase of radiationless decay to the ground state.

C. Octatetraene

Octatetraene is the shortest unsubstituted polyene that exhibits fluorescence. The X $^1A_g \rightarrow 2\,^1A_g$ transition is clearly seen in one- and two-photon absorption spectra and the 2 ^1A_g is unambiguously identified to be the lowest singlet state[1].

Few *ab initio* studies have been performed for *trans*-octatetraene[30,67,72]. All these studies, except the more recent calculations at the CASPT2 level[30], locate the 2 ^1A_g state above the 1 ^1B_u state. The CASPT2 vertical energies corresponding to both states are very close and show the reverse ordering (Table 6). The computed vertical energy to the 2 ^1A_g state (4.38 eV) is somewhat larger than the value estimated from vertical absorption (3.97 eV)[44] which confirms previous indications that this estimated value is too low[67,72]. The computed vertical energy to the dipole allowed 1 ^1B_u state (4.42 eV) is in excellent agreement with the experimental result (4.41 eV)[30].

In addition to the CASPT2 vertical excitation energies, Serrano-Andrés and coworkers also reported the adiabatic excitation energies and the fluorescence maxima at the same level of calculation[30]. The geometries of the ground and low-lying 2 ^1A_g and 1 ^1B_u states have been obtained at the CASSCF level using a large basis set. Since both experiments and theoretical calculations have indicated that the structure of octatetraene in these states is planar, calculations were performed assuming a C_{2h} symmetry. Similarly to shorter polyenes, the lengths of the double bonds in the excited states increase while those of the single bonds decrease. The effect of geometry changes on the excitation energies appears to be also more important for the 2 ^1A_g state than for the 1 ^1B_u one. That is, the difference between the vertical (4.38 eV) and adiabatic energy (3.61 eV) for the 2 ^1A_g state is 0.77 eV, while for the 1 ^1B_u state the adiabatic excitation energy (4.35 eV) is only 0.07 eV less than the vertical (4.42 eV) one. These results are in good agreement with experimental observations, which estimate an energy difference of 0.79 eV[73] between the 0–0 transitions of the 2 ^1A_g and 1 ^1B_u states. Also, the computed value of 2.95 eV for the fluorescence maximum agrees very well with the experimental one, 3.1 eV[74].

D. Longer Polyenes

Because highly accurate, correlated *ab initio* methods are still computationally very expensive for large molecules, most of the theoretical studies on longer polyenes have been performed using the Parriser–Parr–Pople (PPP) method or other semiempirical methods[4,75–78]. These studies have provided an important insight on the dependence of vibrational, geometrical and excitation energy features with increasing length of the polyene.

Similarly to shorter polyenes, calculations of the excited states of longer polyenes have shown that the lengths of the double bonds increase upon excitation while those of the single bonds decrease[75–78]. However, these changes are not equally distributed along the chain. Instead, they tend to localize in the central region of the molecule and are more pronounced in the 2 ^1A_g state, for which calculations indicate a reversal of the bond alternation pattern.

Calculations have also given a better understanding of the anomalous frequency increase of the C=C stretch mode upon excitation to the 2 ^1A_g state in polyenes[1,67,78]. By comparing the calculated adiabatic and diabatic frequencies, this increase is explained in terms of the vibronic coupling between the 1 ^1A_g and 2 ^1A_g states. As the polyenes get longer, the frequency of the C=C stretch mode decreases in the ground state and increases slightly in the 2 ^1A_g state, due to the decrease of the X ^1A_g–2 ^1A_g energy gap which leads to a more effective vibronic coupling.

As has already been mentioned, the lowest singlet state has been unambiguously identified to be the 2 ^1A_g state for long polyenes, the energy difference between the 2 ^1A_g and 1 ^1B_u states increasing with the length of the polyene. It has also been shown that the longer the polyene, the smaller the excitation energy for the X $^1A_g \rightarrow 2\ ^1A_g$ transition[1], thus explaining the observed decrease in the fluorescence quantum yield, due to the increase in the rate of internal conversion. Therefore, the lack of fluorescence in the shorter polyenes, butadiene and hexatriene, and in *trans*-polyacetylene, arise from different sources. That is, while in the shorter polyenes the increase in the rate of radiationless decay is due to the nonplanarity of the 2 ^1A_g state, in very long polyenes it is due to the small energy gap between the X ^1A_g and 2 ^1A_g states[1,56].

V. MOLECULAR ELECTRIC PROPERTIES

Conjugated polyenes exhibit large linear and nonlinear optical properties due to the mobility of electrons in extended π-orbital systems. Hence, this is another reason for the growing interest shown in these molecules in recent years[2,79–89].

Molecular electric properties give the response of a molecule to the presence of an applied field E. Dynamic properties are defined for time-oscillating fields, whereas static properties are obtained if the electric field is time-independent. The electronic contribution to the response properties can be calculated using finite field calculations[90], which are based upon the expansion of the energy in a Taylor series in powers of the field strength. If the molecular properties are defined from Taylor series of the dipole moment μ, the linear response is given by the polarizability α, and the nonlinear terms of the series are given by the nth-order hyperpolarizabilities (β and γ).

The various response tensors are identified as terms in these series and are calculated using numerical derivatives of the energy. This method is easily implemented at any level of theory. Analytic derivative methods have been implemented using self-consistent-field (SCF) methods for α, β and γ, using multiconfiguration SCF (MCSCF) methods for β and using second-order perturbation theory (MP2) for γ[90]. The response properties can also be determined in terms of 'sum-over-states' formulation, which is derived from a perturbation theory treatment of the field operator $-\mu E$, which in the static limit is equivalent to the results obtained by SCF finite field or analytic derivative methods.

The static electronic dipole polarizability and second hyperpolarizability tensors have been computed for a series of conjugated polyenes using the *ab initio* SCF method[79,88]. Results for polyenes from C_4H_6 to $C_{22}H_{24}$ were reported by Hurst and coworkers[79] while longer polyenes up to $C_{44}H_{46}$ have recently been reported by Kirtman and coworkers[88]. The basis set dependence was analyzed in the study of Hurst and coworkers, who showed that for the shorter polyenes, such as C_4H_6, extra diffuse functions and diffuse polarization functions are important for describing the second hyperpolarizability. However, it was also shown that as the length of the polyene increases, the size of the basis set becomes less important. Therefore, the calculations up to $C_{44}H_{46}$ have been performed using the split-valence 6-31G basis set[88].

The computed 6-31G values for the longitudinal polarizability and longitudinal hyperpolarizability per unit cell are given in Table 7. It can be observed that the longitudinal polarizability and longitudinal hyperpolarizability increase with the chain length. However, the rate of variation of these magnitudes decreases with N, in such a way that α_L/N

TABLE 7. Static longitudinal polarizabilities α_L (in a.u.) and longitudinal hyperpolarizabilities γ_L (in 10^4 a.u.) per unit for linear $C_{2n}H_{2n+2}$ polyenes[a]

	α_L/N	γ_L/N		α_L/N	γ_L/N
C_4H_6	37.4	0.3	$C_{26}H_{28}$	112.3	151.5
C_6H_8	47.3	1.8	$C_{28}H_{30}$	115.6	171.4
C_8H_{10}	57.2	5.4	$C_{30}H_{32}$	118.5	190.7
$C_{10}H_{12}$	66.4	12.0	$C_{32}H_{34}$	121.1	209.7
$C_{12}H_{14}$	74.7	21.9	$C_{34}H_{36}$	123.3	226.5
$C_{14}H_{16}$	82.2	35.2	$C_{36}H_{38}$	125.5	243.4
$C_{16}H_{18}$	88.9	51.3	$C_{38}H_{40}$	127.4	260.1
$C_{18}H_{20}$	94.8	69.7	$C_{40}H_{42}$	129.2	273.5
$C_{20}H_{22}$	100.0	89.4	$C_{42}H_{44}$	130.8	287.9
$C_{22}H_{24}$	104.6	110.0	$C_{44}H_{46}$	132.3	301.1
$C_{24}H_{26}$	108.7	130.9			

[a] Reference 88.

and γ_L/N approach an asymptotic limit. The results for the finite polyenes are extrapolated to predict the unit-cell longitudinal polarizability and longitudinal hyperpolarizability of infinite polyacetylene. Kirtman and coworkers[88] using an improved extrapolation procedure have predicted the asymptotic polyacetylene limit of α_L/N to be 166 a.u. $\pm$ 3% and of γ_L/N to be 691×10^4 a.u. $\pm 5.6\%$.

The results reported in Table 7 correspond to the static electronic contribution to the response properties. However, when a molecule is placed under the effect of an electric field, not only the electronic cloud is modified but also the nuclei positions are changed and the vibrational motion is perturbed[91–93]. Thus, aside from the electronic response to the applied field there is a vibrational contribution which arises from the relaxation (deformation) of the nuclear frame upon the application of an external electric field, and also from the change in the vibrational energy. Recently, Champagne and coworkers have reported *ab initio* calculations on the vibrational polarizability of polyacetylene chains[87]. The results obtained show that the vibrational contribution to the polarizability is about 10% of the electronic contribution. The vibrational longitudinal polarizability per unit cell increases with the chain length as does the corresponding electronic contribution until saturation is reached, the extrapolated value being approximately one order of magnitude smaller than the electronic one.

The experimental measures of these molecular electric properties involve oscillating fields. Thus, the frequency-dependence effects should be considered when comparing the experimental results[90]. Currently, there are fewer calculations of the frequency-dependent polarizabilities and hyperpolarizabilities than those of the static properties. Recent advances have enabled one to study the frequency dispersion effects of polyatomic molecules by *ab initio* methods[90,94]. In particular, the frequency-dependent polarizability α and hyperpolarizability γ of short polyenes have been computed by using the time-dependent coupled perturbed Hartree–Fock method. The results obtained show that the dispersion of α increases with the increase in the optical frequency[81,94]. At a given frequency, α and its relative dispersion increase with the chain length. Also, like α, the hyperpolarizability γ values increase with the chain length[81]. While the electronic static polarizability is smaller than the dynamic one, the vibrational contribution is smaller at optical frequencies[87].

Further work on long polyenes, including vibrational distortion, frequency dispersion effects and electron correlation, would be important for evaluating more accurate asymptotic longitudinal polarizabilities and hyperpolarizabilities.

VI. CHEMICAL REACTIVITY

The dienes and polyenes are compounds which intervene in a large number of organic reactions, as will be seen in different chapters of this book. Several excellent reviews have been devoted to theoretical studies about their reactivity, with special emphasis on the mechanism of pericyclic reactions[3–5]. As was mentioned in the introduction, this section will only treat, as an example, the Diels–Alder reaction, since it has been the most studied one by theoreticians. Our goal is not to cover all aspects, but instead to show the high potential and usefulness of theoretical methods in order to interpret and rationalize the experimental results. In the rest of the chapter we will concentrate on the last *ab initio* calculations.

A. The Diels–Alder Reaction

The Diels–Alder reaction is among the most useful tools in organic chemistry. It has been the object of a great number of theoretical studies[95–131] dealing with almost every one of the experimental aspects: reactivity, mechanism, selectivity, solvent effects, catalysis and so on.

1. Reaction mechanism

The most simple Diels–Alder reaction, that between butadiene and ethylene, represented schematically in Figure 3, has been extensively studied employing several methods of calculation. The results obtained have initiated some controversy regarding the nature of the reaction mechanism[3–5,95].

High-level *ab initio* calculations reported by Li and Houk[96] show that two different mechanisms can coexist: a one-step concerted mechanism and a two-step mechanism. In the one-step mechanism the reaction takes place through a symmetrical transition state, while in the two-step mechanism the reaction takes place through a biradical intermediate, the rate-determining step being the formation of this intermediate. The proper description of biradical or biradicaloid structures requires the use of a MCSCF method. With this kind of calculation the nondynamic electron correlation is taken into account. At the CASSCF/6-31G* level of calculation the concerted mechanism is more favorable than the two-step mechanism by only 1.9 kcal mol^{-1}. However, the lack of dynamic correlation leads to an overestimation of the stability of biradicaloid structures. When the energies of the concerted transition state and of the transition state leading to the formation of the biradical are recomputed at the QCISD(T) level (Quadratic CI with single and double excitations with the perturbational inclusion of triple excitations), which is

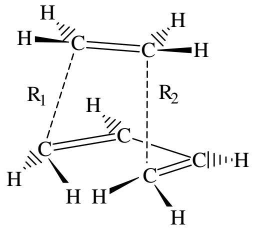


FIGURE 3. Schematic representation of the transition state of the Diels–Alder reaction between butadiene and ethylene

supposed to describe properly all correlation effects, the difference between both mechanisms rises to 10.2 kcal mol^{-1}, in favor of the concerted mechanism. At this point, it seems clear that the reaction between butadiene and ethylene takes place through a concerted mechanism.

In addition to conventional *ab initio* methods, techniques based on the density functional theory (DFT) have also been used to study the Diels–Alder reaction between butadiene and ethylene[97–99]. With these kinds of methods, a concerted mechanism through a symmetric transition state is also predicted. Several kinds of density functionals have been used. The simplest one is based on the Local Density Approach (LDA), in which all the potentials depend only on the density. More sophisticated functionals include a dependence on the gradient of the density, such as that of Becke, Lee, Yang and Parr (BLYP).

Table 8 presents the values of the length of the forming C–C bonds (R) at the concerted transition state, and of the potential energy barrier computed at several levels of calculation, for the reaction between butadiene and ethylene. MP4, QCISD(T) and BLYP yield reasonable energy barriers. LDA greatly underestimates the barrier, while CASSCF overestimates it. This is due probably to an overestimation of the correlation energy at the LDA level and to the lack of dynamic correlation at the CASSCF level. The value of the bond length of the forming C–C bonds does not change very much with the level of calculation. These results show that reliable energy barriers are only obtained with a proper inclusion of dynamic electron correlation.

Reactions of unsymmetrical dienes and/or dienophiles have also been studied[101,103,104]. For these reactions *ab initio* calculations predict concerted non-synchronous mechanisms. The values of the potential energy barriers are very sensitive to the level of calculation and reasonable values are only obtained when electron correlation is included up to the MP3 level[103].

The possibility of a biradical mechanism was suggested using the MNDO and AM1 semiempirical methods, for the addition of protoanemonin (5-methylene-2(5*H*)-furanone) to butadiene[105] and to several substituted dienes[106]. Experimental evidence for this kind of mechanism has recently been published[133]. A biradical mechanism has also been considered for the dimerization of butadiene[96]. For this reaction, CASSCF calculations

TABLE 8. Values of the length (Å) of the forming C–C bonds (R) and of the energy barrier (ΔE) (in kcal mol^{-1}) for the concerted transition state of the butadiene + ethylene reaction computed at several levels of calculation[a]

	R	ΔE
MP2[b]	2.285	17.6
MP4[b]		22.1
CASSCF[c]	2.223	43.8
QCISD(T)[c]		25.5
LDA[d]	2.298	4.5
B-LYP[e]	2.294	21.3
exp[f]		24.2–27.5

[a] A basis set of double-ζ+polarization quality is used in all cases.
[b] Reference 131.
[c] Reference 96.
[d] Reference 97.
[e] Reference 98.
[f] Reference 132.

predict the two-step mechanism as the most favorable by 1.3 kcal mol^{-1}. The stability of biradicaloid structures is probably overestimated at this level of calculation, but the size of the system makes difficult the use of higher-level *ab initio* methods.

2. Selectivity

Diels–Alder reactions with unsymmetrical dienes and/or dienophiles can lead to the formation of different isomers. One of the most interesting aspects in these systems is stereoselectivity, observed in reactions involving cyclic dienes. In these cases, two different stereoisomers can be formed: *endo* and *exo*.

Experimental observations show that in most of the cases the *endo* product is predominant over the *exo* one. Theoretical calculations devoted to this topic[103,107–110] do not always agree with the experimentally observed *endo/exo* selectivity. The discrepancy has been attributed to effects of the medium in which real reactions take place, that are not included in most theoretical calculations. Jorgensen and coworkers[103] have shown that the computed *endo/exo* selectivity is dependent on the level of calculation. In this way, for the reaction of methyl vinyl ketone with cyclopentadiene, calculations using small basis sets predict the preferential formation of the *exo* product, while the *endo* one is shown to be kinetically favored when larger basis sets are used. A similar dependence has been observed by Ruiz-López and coworkers[109] for the reaction between methyl acrylate and cyclopentadiene, and by Sbai and coworkers[110] for the additions of chiral butenolides to cyclopentadiene.

Very recent work[111] has shown that the predominant formation of the *endo* adduct in the reaction between cyclopropene and isotopically substituted butadiene could be attributed to an attractive interaction between a C—H bond of cyclopropene and the π bond being formed in the diene moiety.

Other theoretical studies on the selectivity of Diels–Alder reaction refer to regioselectivity[108,112,113], site-selectivity[105,112,114] and diastereofacial selectivity[110,117]. The latter is presently the subject of much interest in recent years, since this kind of selectivity is very important in the synthesis leading to manifold families of carbocyclic amino acids and nucleosides. Earlier proposals by Cherest and Felkin[115] and Anh and Eisenstein[116] suggested that the controlling factor might be the interaction between the bonding orbital being formed and the antibonding orbitals of adjacent bonds. These suggestions have been criticized by Frenking and coworkers[118], Wong and Paddon-Row[119] and Wu, Houk and coworkers[120,121]. Dannenberg and colleagues[123] have shown, using an extension of FMO theory, that diastereofacial selectivity is influenced by both steric and electronic factors in a complex way. Recent *ab initio* calculations[110], using the 3-21G and 6-31G* basis sets, of the Diels–Alder reaction between crotonolactone and β-angelica lactone have correctly reproduced the experimental *anti* preference, the steric hindrance produced by the methyl group of β-angelica lactone being in this case the controlling factor. The inclusion of zero-point vibrational energies, thermal contributions to the energy and the entropy term do not appreciably change the difference between *syn* and *anti* energy barriers.

3. Solvent effect and catalysis

Another aspect that has been theoretically studied[109,124,129] is experimental evidence that Diels–Alder reactions are quite sensitive to solvent effects in aqueous media. Several models have been developed to account for the solvent in quantum chemical calculations. They may be divided into two large classes: discrete models, where solvent molecules are explicitly considered; and continuum models, where the solvent is represented by its macroscopic magnitudes. Within the first group noteworthy is the Monte Carlo study of Jorgensen and coworkers[124–126] of the reaction of cyclopentadiene with methyl vinyl ketone. They find that the main factor which intervenes in the acceleration of this reaction by the solvent is not the hydrophobic effect, but the influence of hydrogen bonding. Although the number of hydrogen bonds to the carbonyl oxygen remains constant during the process, the strength of each bond is 1–2 kcal mol^{-1} greater at the transition state. This interpretation through enhanced hydrogen bonding has been recently confirmed using the supermolecule approach. On the other hand, Ruiz-López and coworkers[109], using a continuum model, have shown two other important aspects. First, the solvent increases the asynchronicity of the process. Second, the *endo/exo* selectivity and the facial selectivity increase with the polarity of the solvent.

Theoretical calculations have also permitted one to understand the simultaneous increase of reactivity and selectivity in Lewis acid catalyzed Diels–Alder reactions[101–130]. This has been traditionally interpreted by frontier orbital considerations through the destabilization of the dienophile's LUMO and the increase in the asymmetry of molecular orbital coefficients produced by the catalyst. Birney and Houk[101] have correctly reproduced, at the RHF/3-21G level, the lowering of the energy barrier and the increase in the *endo* selectivity for the reaction between acrolein and butadiene catalyzed by BH_3. They have shown that the catalytic effect leads to a more asynchronous mechanism, in which the transition state structure presents a large zwitterionic character. Similar results have been recently obtained, at several *ab initio* levels, for the reaction between sulfur dioxide and isoprene[130].

As a final remark in this section, we expect that the results presented herein have shown how theoretical methods allow us to obtain some insight into a great variety of experimental facts, even in the complex case of chemical reactivity.

VII. CONCLUDING REMARKS

All along this chapter, we have covered some of the most significant and recent contributions of Quantum Chemistry to the study of dienes and polyenes.

We have shown that theoretical calculations are a complementary tool to experiment in the comprehension of the behavior of such systems. In certain aspects, specially for the smaller systems, quantum chemical calculations already provide sufficiently accurate results. However, for larger molecules and time-dependent phenomena the results have not yet achieved the same level of accuracy.

The enormous development of powerful computers and the implementation of new theoretical methods continuously extends the field in which theory can provide results with chemical accuracy. This fact allows us to foresee that in the near future the structure and properties of dienes and polyenes will be more thoroughly understood.

VIII. REFERENCES

1. G. Orlandi, F. Zerbetto and M. Z. Zgierski, *Chem. Rev.*, **91**, 867 (1991).
2. J. M. André and J. Delhalle, *Chem. Rev.*, **91**, 84 (1991).
3. K. N. Houk, Y. Li and J. D. Evanseck, *Angew. Chem., Int. Ed. Engl.*, **31**, 682 (1992).
4. K. N. Houk, J. González and Y. Li, *Acc. Chem. Res.*, **28**, 81 (1995).
5. M. J. S. Dewar and C. Jie, *Acc. Chem. Res.*, **25**, 537 (1992).
6. W. H. Hehre, L. Radom, P. v. R. Schleyer and J. A. Pople, *Ab Initio Molecular Orbital Theory*, Wiley, New York, 1986.
7. K. P. Lawley (Ed.), *Ab Initio Methods in Quantum Chemistry*, Parts I and II, *Adv. Chem. Phys.*, Vols. 67 and 69, Wiley, New York, 1987.
8. A. Hinchliffe, *Computational Quantum Chemistry*, Wiley, New York, 1988.
9. A. Szabo and N. S. Oslund, *Modern Quantum Chemistry: Introduction to Advanced Electronic Structure Theory*, 1st edition, revised, Macmillan, New York, 1989.

10. C. W. Bauschlicher, S. R. Langhoff and P. R. Taylor, *Adv. Chem. Phys.*, **77**, 103 (1990).
11. J. Simons, *J. Phys. Chem.*, **95**, 1017 (1991).
12. H. O. Villar, M. Dupous, J. D. Watts, G. J. B. Hurst and E. Clementi, *J. Chem. Phys.*, **88**, 1003 (1988).
13. J. E. Rice, B. Liu, T. J. Lee and C. Rohlfing, *Chem. Phys. Lett.*, **161**, 277 (1989).
14. T. P. Hamilton and P. Pulay, *J. Phys. Chem.*, **93**, 2341 (1989).
15. I. A. Alberts and H. F. Schaeffer III, *Chem. Phys. Lett.*, **161**, 375 (1989).
16. P. G. Szalay, H. Lishka and A. Karpfer, *J. Phys. Chem.*, **93**, 6629 (1989).
17. C. X. Cui, M. Kertesz and M. Dupous, *J. Chem. Phys.*, **93**, 5890 (1990).
18. M. Aoyagi, I. Ohmine and B. E. Kohler, *J. Phys. Chem.*, **94**, 3922 (1990).
19. C. W. Bock, Y. N. Panchenko and V. I. Pupyshev, *J. Comput. Chem.*, **11**, 623 (1990).
20. C. W. Bock, *J. Mol. Struct.*, **221**, 159 (1990).
21. M. Kofraneck, A. Karpfen and H. Lischka, *Int. J. Quantum. Chem., Sym.*, **24**, 721 (1990).
22. K. B. Wiberg, R. E. Rosenberg and P. R. Rablen, *J. Am. Chem. Soc.*, **113**, 2890 (1991).
23. H. Guo and M. Karplus, *J. Chem. Phys.*, **94**, 3679 (1991).
24. M. Kofraneck, H. Lischka and A. Karpfen, *J. Chem. Phys.*, **96**, 982 (1992).
25. Y. N. Panchenko, S. V. Krasnoshchiokov, P. George and C. W. Bock, *Struct. Chem.*, **3**, 15 (1992).
26. Y. N. Panchenko and C. W. Bock, *Struct. Chem.*, **3**, 27 (1992).
27. H. Guo and M. Karplus, *J. Mol. Struct. Theochem.*, **260**, 347 (1992).
28. N. H. Werstiuk, G. Timmins, J. Ma and T. A. Wildmon, *Can. J. Chem.*, **70**, 1971 (1992).
29. R. Liu and X. Zhou, *J. Phys. Chem.*, **97**, 1850 (1993).
30. L. Serrano-Andrés, R. Lindh, B. O. Roos and M. Merchán, *J. Phys. Chem.*, **97**, 9360 (1993).
31. G. Fogarasi, R. Liu and P. Pulay, *J. Phys. Chem.*, **97**, 4036 (1993).
32. M. Traetteberg, H. Hopf, H. Lipka and R. Hänel, *Chem. Ber.*, **127**, 1459 (1994).
33. M. Traetteberg, P. Bakken, H. Hopf and R. Hänel, *Chem. Ber.*, **127**, 1469 (1994).
34. T. Oie, I. A. Topol and S. K. Burt, *J. Phys. Chem.*, **99**, 905 (1995).
35. J. Y. Lee, O. Hahn, S. J. Lee, S. Choi, H. Shim, B. J. Mhin and K. S. Kim, *J. Phys. Chem.*, **99**, 1913 (1995).
36. J. Y. Lee, O. Hahn, S. J. Lee, B. J. Mhin, M. S. Lee and K. S. Kim, *J. Phys. Chem.*, **99**, 2262 (1995).
37. B. Kirtman, J. L. Toto, K. A. Robins and M. Hasan, *J. Chem. Phys.*, **102**, 5350 (1995).
38. (a) W. Haugen and M. Traetteberg, *Acta Chem. Scand.*, **20**, 1726 (1966).
    (b) K. Kuchitsu, T. Fukuyama and Y. Mosher, *J. Mol. Struct.*, **1**, 463 (1967).
    (c) K. Kveseth, R. Seip and D. A. Kohl, *Acta Chem. Scand.*, **A34**, 31 (1980).
    (d) W. Caminati, G. Grassi and A. Bauder, *Chem. Phys. Lett.*, **148**, 13 (1988).
39. Y. Furukawa, H. Takenchi, F. Harada and M. Tasumi, *Bull. Chem. Soc. Jpn.*, **56**, 392 (1983).
40. A. R. H. Cole, A. A. Green and G. A. Osborne, *J. Mol. Spectrosc.*, **48**, 212 (1973).
41. J. R. Durig, N. E. Bucy and R. H. Cole, *Can J. Phys.*, **53**, 1832 (1975).
42. R. H. Baughman, B. E. Kohler, I. J. Levy and C. Spangler, *Synth. Met.*, **11**, 37 (1985).
43. M. Traetteberg, *Acta Chem. Scand.*, **22**, 2294 (1968).
44. B. S. Hudson, B. E. Kohler and K. Schulten, In *Excited States* (Ed. E. C. Lim), Vol. 6, Academic Press, New York, 1982, p. 1.
45. R. McDiarmid, *Int. J. Quantum. Chem.*, **29**, 875 (1986).
46. W. J. Buma, B. E. Kohler and K. Song, *J. Chem. Phys.*, **92**, 4622 (1990).
47. R. R. Chadwick, D. P. Gerrily and B. S. Hudson, *Chem. Phys. Lett.*, **115**, 24 (1985).
48. R. R. Chadwick, M. Z. Zgierski and B. S. Hudson, *J. Chem. Phys.*, **95**, 7204 (1991).
49. L. Serrano-Andrés, M. Merchán, I. Nebot-Gil, R. Lindh and B. O. Roos, *J. Chem. Phys.*, **98**, 3151 (1993).
50. B. O. Roos, L. Serano-Andrés and M. Merchán, *Pure Appl. Chem.*, **65**, 1693 (1993).
51. R. J. Buenker and J. L. Whitten, *J. Chem. Phys.*, **49**, 5381 (1968).
52. R. J. Cave and E. R. Davidson, *Chem. Phys. Lett.*, **148**, 190 (1988).
53. V. Galasso, *J. Chem. Phys.*, **89**, 4529 (1988).
54. P. G. Szalay, A. Karpfen and H. Lischka, *Chem. Phys.*, **130**, 219 (1989).
55. P. G. Szalay, A. Karpfen and H. Lischka, *Chem. Phys.*, **141**, 355 (1990).
56. F. Zerbetto and M. Z. Zgierski, *J. Chem. Phys.*, **93**, 1235 (1990).
57. R. J. Cave, *J. Chem. Phys.*, **92**, 2450 (1990).
58. F. Zerbetto and M. Z. Zgierski, *Chem. Phys. Lett.*, **176**, 7 (1991).

59. L. Serrano-Andrés, J. Sánchez-Marín and I. Nebot-Gil, *J. Chem. Phys.*, **97**, 7499 (1992).
60. R. L. Graham and K. F. Freed, *J. Chem. Phys.*, **96**, 1304 (1992).
61. K. B. Wiberg, C. M. Hadad, G. B. Ellison and J. B. Foresman, *J. Phys. Chem.*, **97**, 13586 (1993).
62. L. Serrano-Andrés, B. O. Roos and M. Merchán, *Theoret. Chim. Acta*, **87**, 387 (1994).
63. O. A. Mosher, W. M. Flicker and A. Kuppermann, *J. Chem. Phys.*, **59**, 6502 (1973).
64. J. P. Doering, *J. Chem. Phys.*, **70**, 3902 (1979).
65. J. P. Doering and R. McDiarmid, *J. Chem. Phys.*, **73**, 3617 (1980).
66. R. J. Cave and E. R. Davidson, *J. Phys. Chem.*, **92**, 614 (1988).
67. M. Aoyagi, I. Ohmine and B. E. Kohler, *J. Phys. Chem.*, **94**, 3922 (1990).
68. W. J. Buma, B. E. Kohler and K. Song, *J. Chem. Phys.*, **94**, 6367 (1991).
69. H. Torii and M. Tasumi, *J. Chem. Phys.*, **101**, 4496 (1994).
70. F. Zerbetto and M. Z. Zgierski, *J. Chem. Phys.*, **98**, 4822 (1993).
71. C. H. Martin and K. F. Freed, *J. Phys. Chem.*, **99**, 2701 (1995).
72. R. J. Cave and E. R. Davidson, *J. Phys. Chem.*, **92**, 2173 (1988).
73. R. M. Garin, C. Weisman, J. K. McVey and S. A. Rice, *J. Chem. Phys.*, **68**, 522 (1978).
74. H. Petek, A. J. Bell, Y. S. Choi, K. Yoshihara, B. A. Tounge and R. L. Christensen, *J. Chem. Phys.*, **98**, 3777 (1993).
75. P. Tavan and K. Schulten, *Phys. Rev. B*, **36**, 4337 (1987).
76. J. L. Brédas and J. M. Toussaint, *J. Chem. Phys.*, **92**, 2624 (1990).
77. F. Zerbetto and M. Z. Zgierski, *Chem. Phys. Lett.*, **143**, 153 (1988).
78. F. Negri, G. Orlandi, F. Zerbetto and M. Z. Zgierski, *J. Chem. Phys.*, **91**, 6215 (1989).
79. G.J.B. Hurst, M. Dupuis and E. Clementi, *J. Chem. Phys.*, **89**, 385 (1988).
80. G. P. Das and D. S. Dudis, *Chem. Phys. Lett.*, **185**, 151 (1991).
81. S. P. Karna, G. B. Talapatra, W. M. K. P. Wijekoon and P. N. Prasad, *Phys. Rev. A*, **45**, 2763 (1992).
82. A. J. Grant and B. T. Pickup, *J. Chem. Phys.*, **97**, 3521 (1992).
83. S. P. Karna, *Chem. Phys. Lett.*, **214**, 186 (1993).
84. B. Champagne, J. G. Fripiat and J. M. Andrés, *J. Chem. Phys.*, **96**, 8330 (1992).
85. G. P. Das, A. T. Yeates and D. Dudis, *Chem. Phys. Lett.*, **212**, 671 (1993).
86. N. Matsuawa and D. A. Dixon, *J. Phys. Chem.*, **98**, 2545 (1994).
87. B. Champagne, E. A. Perpète and J. M. André, *J. Chem. Phys.*, **101**, 10796 (1994).
88. B. Kirtman, J. L. Toto, K. A. Robins and M. Hasan, *J. Chem. Phys.*, **102**, 5350 (1995).
89. I.D.L. Albert, J. O. Morley and D. Pugh, *J. Chem. Phys.*, **102**, 237 (1995).
90. D. P. Shelton and J. E. Rice, *Chem. Rev.*, **94**, 3 (1994).
91. D. M. Bishop, *Rev. Mod. Phys.*, **62**, 343 (1990).
92. C. E. Dykstra, *J. Chem. Educ.*, **65**, 198 (1988).
93. J. Martí, J. L. Andrés, J. Bertrán and M. Duran, *Mol. Phys.*, **80**, 623 (1993).
94. H. Sekino and R. J. Bartlett, *J. Chem. Phys.*, **94**, 3665 (1991).
95. F. Bernardi, A. Bottoni, M. J. Field, M. F. Guest, I. H. Hillier, M. A. Robb and A. Venturini, *J. Am. Chem. Soc.*, **110**, 3050 (1988).
96. Y. Li and K. N. Houk, *J. Am. Chem. Soc.*, **115**, 7478 (1993).
97. R. V. Stanton and K. M. Merz, *J. Chem. Phys.*, **100**, 434 (1994).
98. J. Baker, M. Muir and J. Andzelm, *J. Chem. Phys.*, **102**, 2036 (1995).
99. J. E. Carpenter and C. P. Sosa, *J. Mol. Struct. Theochem.*, **311**, 325 (1994).
100. K. N. Houk, R. J. Loncharich, J. F. Blake and W. L. Jorgensen, *J. Am. Chem. Soc.*, **111**, 9172 (1989).
101. D. M. Birney and K. N. Houk, *J. Am. Chem. Soc.*, **112**, 4127 (1990).
102. J. González and K. N. Houk, *J. Org. Chem.*, **57**, 3033 (1992).
103. W. L. Jorgensen, D. Lim and J. F. Blake, *J. Am. Chem. Soc.*, **115**, 2936 (1993).
104. J. W. Storer, L. Raimondi and K. N. Houk, *J. Am. Chem. Soc.*, **116**, 9675 (1994).
105. V. Branchadell, J. Ortí, R. M. Ortuño, A. Oliva, J. Font, J. Bertrán and J. J. Dannenberg, *J. Org. Chem.*, **56**, 2190 (1991).
106. J. Ortí, V. Branchadell, R. M. Ortuño, A. Oliva, J. Font, J. Bertrán and J. J. Dannenberg, *J. Mol. Struct., Theochem.*, **284**, 37 (1993).
107. M. Sodupe, A. Oliva, J. Bertrán and J. J. Dannenberg, *J. Org. Chem.*, **54**, 2488 (1989).
108. V. Branchadell, M. Sodupe, R. M. Ortuño, A. Oliva, D. Gómez-Pardo, A. Guingant and J. d'Angelo, *J. Org. Chem.*, **56**, 4135 (1991).
109. M. F. Ruiz-López, X. Assfeld, J. I. García, J. A. Mayoral and L. Salvatella, *J. Am. Chem. Soc.*, **115**, 8780 (1993).

110. A. Sbai, V. Branchadell and A. Oliva, *J. Org. Chem.*, **61**, 621 (1996).
111. M. Sodupe, R. Rios, V. Branchadell, A. Nicholas, A. Oliva and J. J. Dannenberg, submitted.
112. D. Alonso, J. Ortí, V. Branchadell, A. Oliva, R.M. Ortuño, J. Bertrán and J. Font, *J. Org. Chem.*, **55**, 3060 (1990).
113. V. Branchadell, A. Oliva. R. M. Ortuño, S. Rafel and M. Ventura, *Tetrahedron*, **48**, 9001 (1992).
114. V. Branchadell, J. Font, A. Oliva, J. Ortí, R. M. Ortuño, J. Rafel, A. Terris and M. Ventura, *Tetrahedron*, **47**, 8775 (1991).
115. M. Cherest, H. Felkin and N. Prudent, *Tetrahedron Lett.*, 2201 (1968).
116. N. T. Anh and O. Eisenstein, *Nouv. J. Chim.*, **1**, 62 (1977).
117. N. Kaila, R. W. Franck and J. J. Dannenberg, *J. Org. Chem.*, **54**, 4206 (1989).
118. G. Frenking, K. F. Koehler and M. T. Reetz, *Angew. Chem.*, **103**, 1167 (1991).
119. S. S. Wong and M. Paddon-Row, *J. Chem. Soc., Chem. Commun.*, 456 (1990).
120. Y. D. Wu, K. N. Houk and B. M. Trost, *J. Am. Chem. Soc.*, **109**, 5560 (1987).
121. Y. D. Wu, J. A. Tucker and K. N. Houk, *J. Am. Chem. Soc.*, **113**, 5018 (1991).
122. R. Casas, T. Parella, V. Branchadell, A. Oliva. R. M. Ortuño and A. Guingant, *Tetrahedron*, **48**, 2659 (1992).
123. X. L. Huang, J. J. Dannenberg, M. Duran and J. Bertrán, *J. Am. Chem. Soc.*, **115**, 4024 (1993).
124. J. F. Blake and W. L. Jorgensen, *J. Am. Chem. Soc.*, **113**, 7430 (1991).
125. J. F. Blake, D. Lim and W. L. Jorgensen, *J. Org. Chem.*, **59**, 803 (1994).
126. W. L. Jorgensen, J. F. Blake, D. Lim and D. L. Severance, *J. Chem. Soc., Faraday Trans.*, 1727 (1994).
127. T. Karcher, W. Sicking, J. Sauer and R. Sustmann, *Tetrahedron Lett.*, **33**, 8027 (1992).
128. R. Sustmann and W. Sicking, *Tetrahedron*, **48**, 10293 (1992).
129. C. Cativiela, V. Dillet, J. I. García, J. A. Mayoral, M. F. Ruiz-López and L. Salvatella, *J. Mol. Struct. Theochem.*, **331**, 37 (1995).
130. D. Suárez and T. L. Sordo, *J. Am. Chem. Soc.*, **116**, 763 (1994).
131. R. Herges, H. Jiao and P. v. R. Schleyer, *Angew. Chem., Int. Ed. Engl.*, **36**, 749 (1995).
132. (a) M. Uchiyama, T. Tomioka and A. Amano, *J. Phys. Chem.*, **68**, 1879 (1964).
    (b) W. J. Tsang, *J. Chem. Phys.*, **42**, 1805 (1965).
    (c) D. C. Tardy, R. Ireton and A. S. Gordon, *J. Am. Chem. Soc.*, **101**, 1508 (1979).
133. C. Ochoa de Echagüen and R. M. Ortuño, *Tetrahedron Lett.*, **36**, 749 (1995).

The Chemistry of Dienes and Polyenes. Volume 1
Edited by Zvi Rappoport

ISBN: 0-471-96512-X

CHAPTER **2**

Structural chemistry of dienes and polyenes

JORDI BENET-BUCHHOLZ, ROLAND BOESE and THOMAS HAUMANN

Institut für Anorganische Chemie, Universität Essen, Universitätsstrasse 3–5,
D-45117 Essen, Germany
Fax: int+49-201-1832535; e-mail: boese@structchem.uni-essen.de

and

MARIT TRAETTEBERG

Department of Chemistry, Norwegian University of Science and Technology, N-7055
Trondheim, Norway
Fax: int+47-73-59-6255; e-mail: martra@alfa.itea.ntnu.no

I. INTRODUCTION

The structural chemistry of dienes and polyenes is extremely diverse and intricate since about 12% of all determined structures of organic compounds contain two or more double bonds. This topic must therefore be restricted to generalized systems which have common features. The structural features of some polyene groups, for example that of metal complexes or of polyenes with heteroatoms directly linked to the double bonds, are so divergent that it is difficult to present a unified view of the structures within such classes of compounds. They are therefore not included in the present discussion.

Consequently, we had to confine ourselves to the groups outlined in the following, also excluding neighboring double bonds (allenes) as well as those systems containing triple bonds and aromatic systems even if there is a significant bond localization which converts, for example, benzene to cyclohexatriene. Because in most cases the large molecules, such as macrocycles, have the same structural characteristics in detail as the comparable smaller molecules, these are also omitted in the following sections. Some of the small molecules, however, display a variety of mutual influences in terms of different electronic and steric effects, so these will be discussed in more detail as representatives of others which have similar characteristics. For a series of molecules also the *ab initio* calculated geometries are presented for comparison without claiming to be comprehensive. They demonstrate the strength of present day computational methods even with basis sets and methods which can be no longer considered as 'high level' calculations. In a few cases these comparisons also display the deficiencies of the methods, calling for either more sophisticated techniques or extended considerations of the models. Restrictions also do not allow one to discuss the discrepancies in detail, as well as the methodological differences of the methods of structure determinations.

II. DIENES AND POLYENES

A. Linear and Branched Dienes and Polyenes

The linear polyenes are divided into the following three groups:

1. Nonconjugated acyclic dienes and polyenes.
2. Conjugated acyclic dienes and polyenes.
3. Sterically strained conjugated acyclic dienes and polyenes.

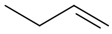
1. Nonconjugated acyclic dienes and polyenes

Rotational isomerism normally complicates the study of gaseous nonconjugated dienes and polyenes because many conformers appear simultaneously, and hence only few structures of free molecules in this category have been studied.

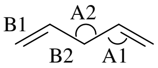
1,4-Pentadiene **(1,4-PD)** is the smallest diene with isolated double bonds. It is also the simplest hydrocarbon molecule capable of '*homoconjugation*', a condition that may occur when two π-systems are separated by a single methylene group. The idea is that there may exist considerable overlap of the π-orbitals across this group (for certain torsion angles), and that this circumstance should facilitate some interesting chemistry, as for example the di-π-methane photorearrangement[1]. The structure and conformations of **1,4-PD** has been studied by gas electron diffraction[2] (GED) as well as by microwave spectroscopy[3] (MW) (see Table 1), and in both studies a mixture of conformers with C_1, C_2 and C_S symmetry was observed. The most recent single-crystal diffraction X-ray data show **1,4-PD** very close to ideal C_2 symmetry[4] (see Figure 1). The C=C−C−C torsion angle is 117.1° (T, mean value) and the central bond angle 112.2°, in good agreement with the calculated *ab initio* values (see Table 1).

The fragment of **1,4-PD** is also present in 1,1-divinylcyclopropane **(DVC)**, where the central methylene group is replaced by a three-membered ring. For this strained molecule a strong interaction between cyclopropane *Walsh* and vinyl π-orbitals was expected. The photoelectron spectra of **DVC**[5] could be best understood with the assumption of optimal

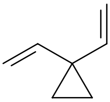
TABLE 1. Structural parameters for 1-butene (**1-BU**) and nonconjugated acyclic dienes and polyenes (distances in Å, angles in degrees)



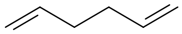
(1-BU)



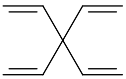
(1,4-PD)



(DVC)



(1,5-HD)



(TVM)

	Symmetry	B1	B2	A1	A2	T1[a]	Method[b]
1-BU	C_1	1.336	1.499	125.6	111.65	119.9	GED$^{(S2)7}$
		1.336	1.507	126.7	114.8	(0.0)	MW$^{(S3)8}$
1,4-PD	C_S	1.339	1.511	125.5	113.1	4.3	GED$^{(S1)2}$
	C_2	1.339	1.511	125.5	108.9	122.2	GED$^{(S1)2}$
		1.324	1.502	125.2	112.2	117.1	XR$^{(S1)4}$
		1.318	1.509	125.1	112.0	118.5	HF^{4}
		1.339	1.504	124.4	111.1	116.4	MP2^{4}
	C_S	1.318	1.509	125.1	112.4	122.6	HF^{4}
DVC	C_1	1.319	1.489	126.3	116.5	127.4	XR$^{(S1)9}$
		1.331^d	1.483^d	125.6^d		−10.3^d	
	C_1	1.339	1.487	125.2	116.2	116.3	MP2^{9}
		1.340^d	1.484^d	125.2^d		−10.4^d	
1,5-HD	*c*	1.340	1.508	124.6	111.5	—	GED$^{(S3)6}$
TVM	C_1	1.326 to 1.328	1.515 to 1.526	125.9 to 126.7	105.5 to 111.8	—	XR$^{(S1)4}$
	C_1	1.318	1.518 to 1.530	127.2	106.0 to 111.1	—	HF^{4}
	S_4	1.319	1.523	127.1	105.5 to 111.5	—	HF^{4}
	D_{2d}	1.317	1.538	126.0	108.7 to 109.9	90/180	HF^{4}

[a] Torsion angle T1 is C=C−C−C.

[b] HF = RHF/6-31G(d), MP2 = MP2/6-31G(d). GED = gas electron diffraction, MW = microwave, XR = single-crystal X-ray diffraction, esd's for bond lengths and angles in the last digit S1: 1−3, S2: 3−10, S3: >10.

[c] Averaged values for the conformers.

[d] Vinyl group with *anti* conformation.

orbital interactions, which result from bisected *syn* conformations of both vinyl groups in highest molecular symmetry C_{2v}. In the crystal the molecule has asymmetric C_1 form, where only one vinyl group interacts in terms of cyclopropyl conjugation (see Figure 2). The cyclopropane bonds are affected by this interaction, where the *vicinal* bonds (C1−C2, C1−C3) are significantly elongated by 0.02 Å (mean value) 1.515(1)/1.524(1) Å compared to the *distal* bond C2−C3 [1.499(1) Å]. This observation is in agreement with the electron donor properties of cyclopropane (see also Section II.C.1).

Ab initio calculations at the MP2/6-31G(d) level provide the same asymmetric conformation found in the crystal as the global minimum structure, whereas one vinyl group is nearly in *anti* bisected orientation to the ring and the other vinyl group is strongly twisted into *gauche* conformation. The higher symmetric form in C_2, where both vinyl groups

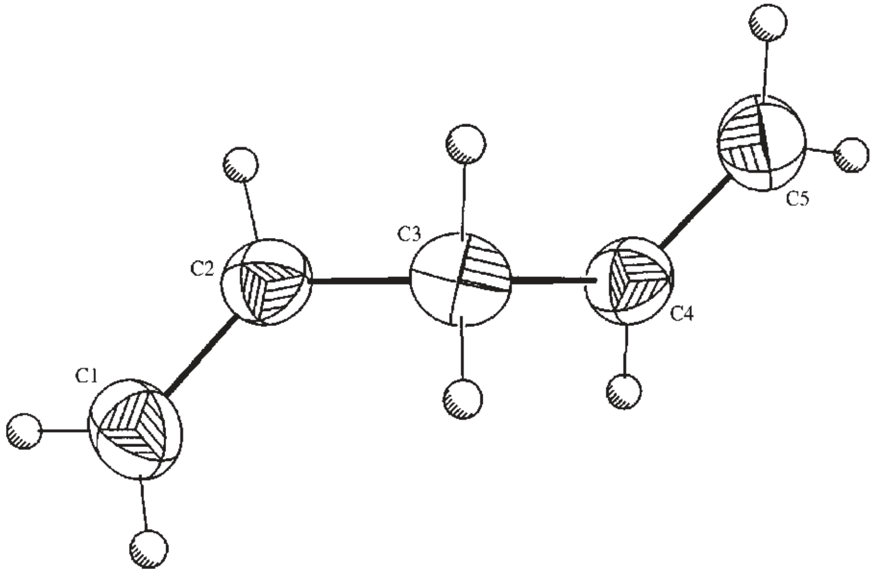
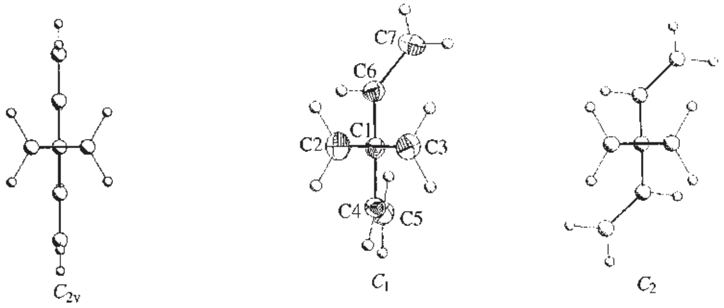


FIGURE 1. Molecular structure of 1,4-pentadiene **(1,4-PD)**; presentation with thermal probability plots of 50%

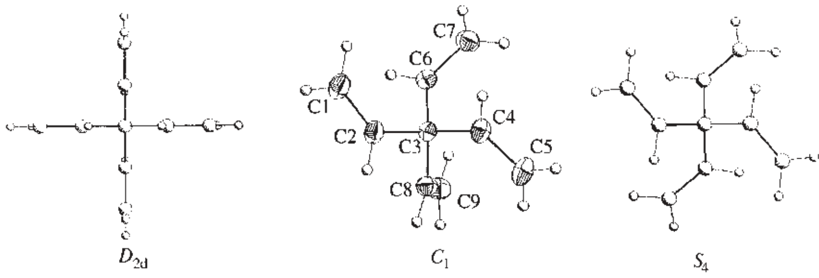
are *gauche* orientated (see C_2 form of **1,4-PD**) is 3.3 kJ mol^{-1} [MP2/6-31G(d)//MP2/6-31G(d)] higher in energy than the C_1 form. The symmetric form of **DVC** in C_{2v} is destabilized by 10.0 kJ mol^{-1}, mainly due to steric reasons with intramolecular H- - -H repulsions involved, which occur between vinyl and ring H-atoms.

The next homolog, 1,5-hexadiene **(1,5-HD)**, is of special chemical interest because the molecule is capable of undergoing the so-called Cope rearrangement. A GED study of **1,5-HD** was also recently reported[6]. Because of the increased conformational complexity of this molecule compared to that of **1,4-PD**, the structural details of the various conformers could not be resolved and only averaged structure parameters were determined from the gas phase. Molecules in the solid state are frozen, mostly in only one conformation, which may but must not represent the conformational ground state. Therefore, conformational isomerization is usually not discussed with X-ray structures presented in the literature.

In Table 1 the structure parameters obtained for the unconjugated dienes/polyenes are compared with data for 1-butene (**1-BU**)[7]. There is nothing in the ground-state molecular structure of either **1,4-PD** or **1,5-HD** that indicates the presence of interaction between the two π-systems of the molecules. The structure parameters are very similar to those observed for **1-BU** by GED[7] and by MW[8]. The bond lengths are approximately the same in all three molecules, and the small differences between the C−C−C angles may be attributed to differences in steric strain between an ethylenic group on one side and a methylene, methyl group or a second ethylenic group, respectively, on the other. In all conformers of the **1,4-PD**, **1,5-HD** and **1-BU** molecules the C=C bonds approximately eclipse a methylene C−H (all molecules) or a C−C (**1,4-PD; 1-BU**) bond. Two recent high-resolution X-ray crystal structures[9], of 1,1-divinylcyclopropane (**DVC**) and tetravinylmethane (**TVM**), both included in Table 1, show slight but significant differences in distances and angles of the respective vinyl groups and are discussed below.



1,1-Divinylcyclopropane **(DVC)**



Tetravinylmethane **(TVM)**

FIGURE 2. Calculated high symmetry conformations (C_{2v}, C_2 and D_{2d}, S_4, respectively) and experimentally determined molecular structures of 1,1-divinylcyclopropane **(DVC)** and tetravinylmethane **(TVM)** in C_1; presentation with thermal probability plots of 50%

Tetravinylmethane **(TVM)** is a very interesting compound with respect to its conformational and structural parameters. All the assumptions on the symmetry of **TVM** are based on D_{2d} and S_4 conformations[10,11]. Surprisingly, none of these conformations is observed in the crystalline state; instead, C_1 symmetry was found in an orthorhombic crystal lattice (space group Pbca). If one of the vinyl groups (C3-C8-C9) is rotated by *ca* 150°, the C_1 symmetry can be transferred to S_4 symmetry (or vice versa). This is evident from Figure 2 where **DVC** is also shown in the same projection which demonstrates that the C_1 symmetry is no coincidence of packing effects.

The calculation of the three conformations of **TVM** on *ab initio* level 6-31G(d)//6-31G(d) (Hartree–Fock) showed that the S_4 symmetric form represents an energetical minimum but the C_1 form is only 1.51 kJ mol^{-1} higher in energy (local minimum, established by frequency calculations). The D_{2d} symmetric form is 56.4 kJ mol^{-1} higher in energy than the S_4 conformation and represents a transition state.

The small difference in energy between S_4 and C_1 forms caused speculations as to whether a second crystalline form might exist which has S_4 symmetry. These assumptions were fed by the fact that an X-ray powder diffractogram revealed another orthorhombic lattice with half of the volume. This polymorphic form emerged when cooling below the melting point at *ca* 170 K and crystallizing with slower speeds in a capillary by means of a miniature zone melting procedure. Further extensive experiments with the aim of growing a single crystal of the second polymorph finally resulted in another surprise: the same C_1 symmetry was found for the molecules but now existing in an acentric crystal lattice ($P2_12_12_1$). This means that in the first lattice two racemic molecules with C_1 and C_1' symmetry crystallize together; in the second lattice all molecules are identical. During the nucleation process only C_1 forms started to crystallize together, either for the whole bulk and the other material converted to this form, or racemic twins, probably in domains, remained undetected. It seems that the interconversion from C_1 to C_1' is energetically rather likely. The change from S_4 symmetry to C_1 can be carried out by rotation of each of the four vinyl groups. Therefore, statistically more of the C_1 symmetric molecules exist in the melt than those with S_4 symmetry and, although the latter represents the energetic minimum, it more probably crystallizes in the less stable C_1 conformation for entropic reasons. However, a more favorable crystal packing of the C_1 form may overcome the small energy difference between C_1 and S_4. A transformation from S_4 to S_4' is expected via C_1 and C_1' but not via D_{2d}. Figure 3 gives a rough survey of the energy relations of the discussed conformations in C_1, S_4 and D_{2d}.

The structural features of **TVM** in C_1 are a result of complex interplay between through-bond (hyperconjugation) and through-space interaction (homoconjugation). While all four independent double-bond lengths are nearly equivalent [1.332(1)–1.335(1) Å], the single bonds show significant differences [1.515(1)–1.526(1) Å]. This observation is correlated with the degree of hyperconjugation of the σ(C–C) single bond and the surrounding π-systems. For all single bonds the orientation of the π-orbital axis of the remaining three vinyl groups are different relative to the σ(C–C) bonding orbital of the considered bond.

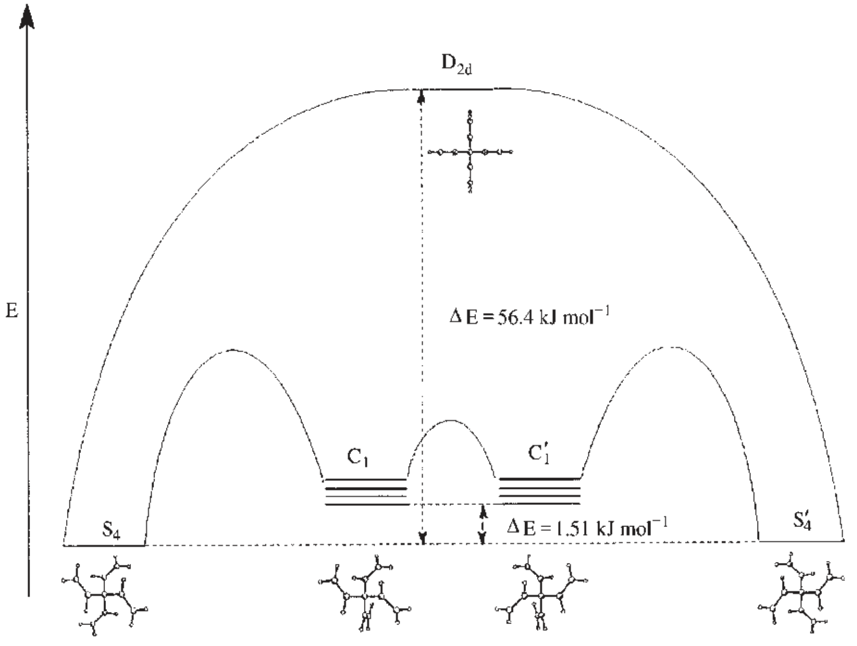


FIGURE 3. Conformational transformations of **TVM** and relative energies of calculated geometries in D_{2d}, S_4 and C_1

Homoconjugational interactions and nonbonding intramolecular contacts of the four π-systems are responsible for the observed distribution of bond angles at the central atom, which are also significantly inequivalent [105.1(1)° to 111.8(1)°].

2. Conjugated acyclic dienes and polyenes

When the π-systems of two or more double bonds overlap, as in conjugated dienes and polyenes, the π-electrons will be delocalized. This has chemical consequences, which implies that the range of possible chemical reactions is vastly extended over that of the alkenes. Examples are various pericyclic reactions or charge transport in doped polyacetylenes. A detailed understanding of the electronic structure of polyenes is therefore of utmost importance for development within this field. We will first discuss the structure of dienes and polyenes based on theoretical studies. Thereafter the results from experimental studies are presented and discussed.

The electron distribution in dienes and polyenes has been the subject of numerous studies that encompass a wide range of experimental[12–14] and theoretical methods[15–19], and the CC bond alternation between double bonds of *ca* 1.34 Å and single bonds of *ca* 1.46 Å in these molecules has been clearly established. The extent of bond alternation in long polyenes is central to the understanding of electronic interactions in π-systems. It has been suggested[20] that a chain-length increase will systematically increase the length of the double bond and decrease the length of the single bond in such a way that the distinction between single and double bonds vanishes for infinitely long polyenes. This would have dramatic effects on the chemical properties, as polyacetylenes with equal carbon–carbon bonds would have metallic properties[17].

A multiconfigurational self-consistent field (MCSCF) study by Villar and Dupuis[17], including the conjugated polyenes C_4H_6, C_6H_8, C_8H_{10} and $C_{10}H_{12}$, showed, however, that a correct description of bond alternacy in polyenes requires the inclusion of electron correlation, and that even large polyene molecules will retain a structure with alternating short (double) and long (single) CC bonds, when electron correlation is properly accounted for. Table 2 gives the optimized parameters for the four smallest conjugated polyenes, as calculated by Villar and Dupuis, using the π-CAS-MCSCF approach. The RHF (Restricted Hartree–Fock) results for $C_{10}H_{12}$ are also shown in order to compare the single bond/double bond alternacy obtained with and without the inclusion of electron correlation. The results obtained using the CAS-MCSCF wave function show a decrease in the single bond/double bond alternacy compared to the RHF results. The difference in bond length between a double and a single bond from the π-CAS-MCSCF calculations is close to the experimental values for polyacetylene[21], where the observed difference is 0.08 Å, in good agreement with the computed values at the MCSCF level for the central unit of $C_{10}H_{12}$.

TABLE 2. Geometrical parameters for 1,3-butadiene (C_4H_6), 1,3,5-hexatriene (C_6H_8), 1,3,5,7-octatetraene (C_8H_{10}) and 1,3,5,7,9-decapentaene ($C_{10}H_{12}$) from π-CAS-MCSCF calculations with 6-31G basis set[17]

Distance (Å)	C_4H_6	C_6H_8	C_8H_{10}	$C_{10}H_{12}$	$C_{10}H_{12}$[a]
$C^1{=}C^2$	1.349	1.350	1.351	1.350	(1.329)
$C^2{-}C^3$	1.463	1.459	1.457	1.458	(1.459)
$C^3{=}C^4$		1.356	1.357	1.357	(1.336)
$C^4{-}C^5$			1.454	1.452	(1.453)
$C^5{=}C^6$				1.359	(1.337)

[a] RHF/6-31G(d).

Villar and Dupuis explain the decrease in bond alternacy, when electron correlation is included, in terms of occupation numbers of the highest occupied (HOMO) and lowest unoccupied (LUMO) orbitals. The calculated HOMO occupation numbers decrease with polyene chain length; for C_4H_6, C_6H_8, C_8C_{10} and $C_{10}H_{12}$ these are 1.869, 1.846, 1.828 and 1.815, while the corresponding LUMO occupation numbers increase: 0.135, 0.160, 0.179 and 0.193, respectively. For all these conjugated alternate hydrocarbons, the HOMO and LUMO orbitals have opposite bonding properties for any two adjacent C atoms. An increase in the occupation of the LUMOs will therefore result in an elongation of the double bonds and a shortening of the single bonds.

The relationship between π-electron delocalization and the length of CC bonds was originally described in 1939 by Schomaker and Pauling[22], and for a period of 20 years this description was generally accepted. In 1959 Dewar and Schmeising discussed this theory and claimed that the length of any C−C bond is determined by the state of hybridization of the carbon atoms involved in the bonding[23]. Together with *ab initio* calculations it is now possible to carry out natural bond orbital (NBO) analyses[24], which produce — among other quantities — the state of hybridization of all bonding orbitals.

In order to elucidate the possible effect from differences in hybridization states, we have — for the purpose of writing this chapter — carried out NBO analyses for MP2/6-31G(d,p) optimized structures[25] of some relevant molecules, using a CRAY Y-MP supercomputer (Table 3). The orbitals of the $C^3{=}C^4$ σ-bond of the hexatrienes are calculated to have higher % p-character than those of the $C^1{=}C^2$ bond. Hybridization differences appear therefore to offer an alternative explanation for the bonding pattern in conjugated hydrocarbons. The hybridization of the orbitals constituting the single bonds remain, however, practically the same for all carbons in the unsaturated compounds presented in Table 2, while the C−C single bond lengths, according to the MCSCF calculation, show variations of the same order of magnitude as the double bonds. An explanation based on hybridization differences is therefore dubious.

The calculated hybridization of the carbon atom orbitals in the terminal C−H bonds of the conjugated dienes/polyenes is generally equal to those calculated for ethylene ($sp^{2.27}$), corresponding to 69.3% p-character. The angle between two such bonds (∠H−C−H) should accordingly be somewhat smaller than 120°, which is the optimum angle between two sp^2 hybridized carbon orbitals. This is in agreement with experimentally determined terminal H−C−H angles in dienes/polyenes. The p-character of carbon orbitals of nonterminal C−H bonds is generally calculated to be larger than those of the terminal C−H bonds, in agreement with the general observation that the C=C(H)−C angle (in 1,3-butadiene $\geqslant 124°$) is normally larger than the terminal C=C−H angles. This implies

TABLE 3. Hybridizations of bonding orbitals for σ-bonds from NBO (Natural Bond Orbital) analyses based on MP2/6-31G(d,p) optimized structures

Molecule	$C^1{=}C^2$	C−C	$C^3{=}C^4$	$C^2{-}H$[a]
Ethane		$sp^{2.57}$-$sp^{2.57}$		$sp^{3.16}$-s
Ethylene	$sp^{1.57}$-$sp^{1.57}$			$sp^{2.27}$-s
1,3-Butadiene[b]	$sp^{1.55}$-$sp^{1.61}$	$sp^{2.02}$-$sp^{2.02}$		$sp^{2.49}$-s
trans-1,3,5-Hexatriene[c]	$sp^{1.55}$-$sp^{1.61}$	$sp^{2.00}$-$sp^{1.96}$	$sp^{1.63}$-$sp^{1.63}$	$sp^{2.51}$-s
cis-1,3,5-Hexatriene[d]	$sp^{1.55}$-$sp^{1.63}$	$sp^{2.01}$-$sp^{1.99}$	$sp^{1.61}$-$sp^{1.61}$	$sp^{2.48}$-s

[a] For hybridization of the C−H orbitals in the other C−H bonds, see footnotes *b*, *c* and *d*,

[b] C^1(*cis*):$sp^{2.26}$; C^1(*trans*):$sp^{2.31}$,

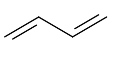
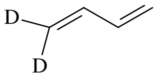
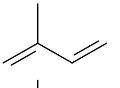
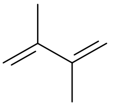
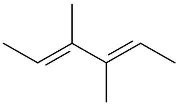
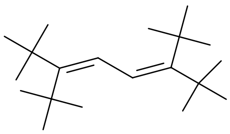
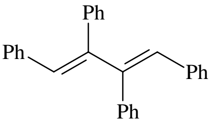
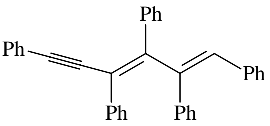
[c] C^1(*cis*):$sp^{2.25}$; C^1(*trans*):$sp^{2.31}$; C^3: $sp^{2.53}$,

[d] C^1(*cis*):$sp^{2.25}$; C^1(*trans*):$sp^{2.32}$; C^3: $sp^{2.54}$

smaller CCH angles, in agreement with the relatively large p-character of the C−H carbon orbital.

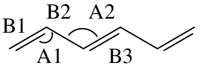
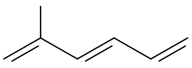
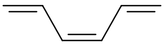
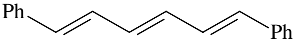
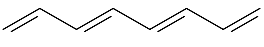
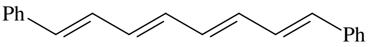
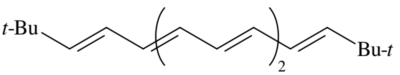
We will now consider the experimental structure data available for acyclic conjugated dienes and polyenes. Tables 4 and 5 list the most relevant structural data for 1,3-dienes and for larger conjugated polyenes. The experimental data shown in Table 4 are generally in agreement with the theoretical description of the bonding properties of 1,3-butadiene, as described above; see Table 2. The X-ray data of 1,3-butadiene could give very accurate geometry parameters[4] in good agreement with the GED investigation[26]. The C=C−C angles in 2-methyl-1,3-butadiene deviate considerably from those in the parent compound. This is, however, reasonable when the need for space of the methyl group is taken into consideration. The enlarged C=C−C angles in *cis*,*cis*-1,2,3,4-tetramethyl-1,3-butadiene may be attributed to the same cause. In the similarly substituted molecule

TABLE 4. Structural parameters determined for acyclic 1,3-dienes (distances in Å, angles in degrees)

	B1	B2	A1	A2	Method[a]
	1.349	1.467	124.4	124.4	GED[26]
	1.335	1.456	123.9	123.9	XR$^{(S1)4}$
	1.337	(1.467)	123.5	123.5	MW[30]
	1.340	1.463	121.4	127.3	GED[31]
	1.349	1.491	122.0	122.0	GED[32]
	1.350	1.473	126.6	126.6	GED[33]
	1.346	1.353	142.3	142.3	XR$^{(S2)27}$
	1.349	1.458	131.1	131.1	XR$^{(S1)28}$
	1.357	1.493	121.3	121.3	XR[34]
	1.363	1.405	129.4	126.3	XR[35]

[a] In parentheses, esd's for bond lengths and angles in the last digit S1: 1−3, S2: 3−10.

TABLE 5. Structural parameters determined for acyclic conjugated polyenes (distances in Å, angles in degrees)

	B1	B2	B3	A1	A2	Method[a]
	1.338	1.451	1.348	124.0	123.8	XR(S1)[4]
	1.337	1.458	1.368	121.7	124.4	GED[36]
	1.348	1.456	(1.348)	119.1	124.8	GED[37]
	1.336	1.462	1.326	122.1	125.9	GED[38]
	1.328	1.433	1.328	124.7	125.5	XR[39]
	1.327	1.451/ 1.451	1.336	125.3	125.1/ 124.7	XR[40]
	1.334	1.442/ 1.445	1.336	122.9	123.8/ 123.5	XR[41]
	1.337	1.433/ 1.437	1.341	125.3	125.2/ 125.5	XR[42]

[a] In parentheses esd's for bond lengths and angles in the last digit S1: 1–3.

cis,*cis*-1,2,3,4-tetraphenyl-1,3-butadiene the C=C−C angles are unusually small. This might be explained by the spacial needs of the *cis*-substituted phenyl groups at each of the C=C bonds. Totally unexpected was the result of an X-ray structure of 1,1,4,4-tetra-*tert*-butyl-1,3-butadiene from 1994 which had amazingly large C=C−C angles and a too short central single bond distance of 1.353 Å[27]. A redetermination by the same authors[28] reconciliated this unusual structure and a value of 1.458 Å is quite in the range of the other 1,3-butadienes. The substance taken for the structure determination was apparently contaminated with a [3]cumulene and cocrystallized with the 1,3-butadiene; the overlap and merge of the electron densities of both molecules lead to the wrong structure which should be seen as a warning of the care needed if totally unexpected and contradictory results are obtained.

The bonding pattern of the last molecule in Table 4 is rather different from that of 1,3-butadiene, a fact which is probably connected to the ethynyl substituent that allows a further delocalization of the π-electrons in this molecule.

The amount of high precision experimental structural data on conjugated polyenes is limited. Some structure results are presented in Table 5. In gas electron diffraction studies it is difficult to determine closely spaced bond distances accurately, because these parameters are highly correlated with the corresponding vibrational amplitudes. Today it is possible to calculate the vibrational amplitudes accurately, if the vibrational frequencies are known. This was, however, not the case when the GED studies presented in Table 5 were carried out. The observed differences between the terminal and central C=C bonds in the GED studies of *trans*-1,3,5-hexatriene and *cis*-1,3,5-hexatriene are probably too large[29]. A very accurate X-ray study of *trans*-1,3,5-hexatriene has, however, been carried out also in connection with the preparation of this chapter[4]. Figure 4 shows the molecular structures of *trans*-1,3-butadiene and *trans*-1,3,5-hexatriene as found in the crystal lattice.

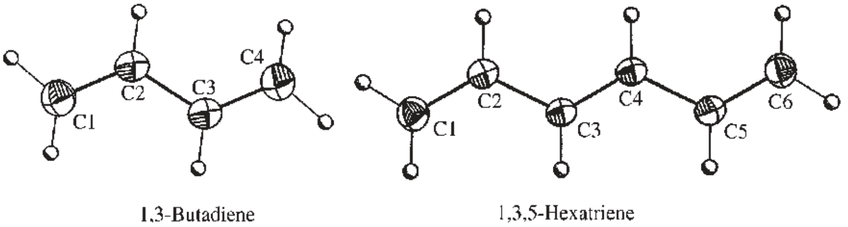


FIGURE 4. Molecular structures of 1,3-butadiene and *trans*-1,3,5-hexatriene; presentation with thermal probability plots of 50%

In this study a C=C bond length difference of 0.010 Å is determined, compared with the theoretically calculated difference of 0.006 Å; see Table 2[17]. The single-bond double-bond alternation and the C=C−C valence angles are also quite similar in the two studies.

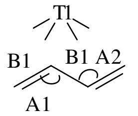
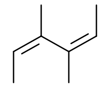
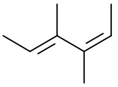
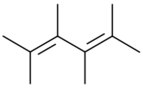
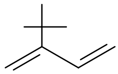
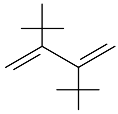
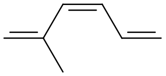
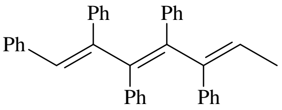
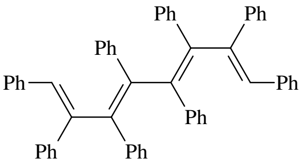
3. Sterically strained linear conjugated dienes and polyenes

Steric strain in conjugated dienes and polyenes generally occurs when the molecules are substituted with spacious groups. Among the di-*tert*-butyl-substituted 1,3-butadienes, the 1,1-substituted isomer is the sterically most heavily strained[43] example. This type of strain is, however, analogous to the strain present in similarly 1,1-disubstituted 1-alkenes and is therefore not connected to the special properties of the diene system. We will limit our discussion on this subject to dienes and polyenes that are sterically strained in a way that influences the delocalized π-system. We have therefore selected dienes/polyenes with conformations deviating by more than 20° from the generally preferred *anti* orientation of adjacent C=C bonds. Table 6 shows relevant structural data observed for such molecules. These data indicate that dienes substituted with moderately large substituents, such as methyl groups, in 1-*cis* and 3- (or 2- and 4-*cis*) positions are destabilized in *anti* conformation because the substituents will be 1,3 parallel oriented, resulting in substantial nonbonded repulsion. For larger substituents, such as *tert*-butyl groups, one substituent in 2- (or 3-) position is sufficient to destabilize an *anti* conformation because of repulsions between the substituent and the C^4 methylene group.

The minimum energy conformation of a conjugated diene will primarily depend on the nonbonded steric interactions and on the interaction between the two π-systems. Both these effects will depend on the dihedral angle at the single bond connecting the two double bonds. For dienes, in which the *anti* conformation becomes unfavorable because of steric strain, the energy contribution of the π-system is analogous to that of the high-energy form of 1,3-butadiene. There has been much discussion about whether the metastable form of 1,3-butadiene has a planar *syn* or a nonplanar *gauche* conformation. Polarized infrared spectra of the matrix isolated metastable isomer provide strong evidence for a planar *syn* structure[44,45]. All recent quantum chemical calculations[46], on the other hand, find the *gauche* structure, characterized by a dihedral angle between 30° and 41°, to be more stable than the planar *syn* form by about 4 $\mathrm{kJ\,mol^{-1}}$, and the energy variation in the torsional region 0–*ca* 65° is of a similar magnitude. The relation between nonbonded repulsions and the dihedral angle will of course depend on the nature of the substituents.

The molecules in Table 6 may be divided into three groups based on their dihedral angles. For most of these molecules the dihedral angle is close to 60°. In 2,3-di-*tert*-butyl-1,3-butadiene (**2,3-TB**) the dihedral angle is close to 90°, corresponding to an approximately perpendicular conformation, while the dihedral angle in 2-*tert*-butyl-1,3-butadiene (**2-TB**) is determined to be 32.1°.

TABLE 6. Structural parameters observed for sterically strained dienes and polyenes (distances in Å, angles in degrees)

	B1	B2	A1	A2	T1	Method^{a}
	1.349	1.479	123.5	123.5	66.7	GED$^{(S3)47}$
	1.359	1.460	120.6	123.3	65.7	GED$^{(S3)47}$
	1.349	(1.487)	125.0	125.0	60.0	GED$^{(S1)48}$
	1.345	1.485	121.7	126.2	32.1	GED$^{(S2)49}$
	1.346 1.326	1.543 1.506	118.3 119.1	118.3 119.1	101.5 96.6	GED$^{(S3)49}$ XR$^{(S1)50}$
	1.345	1.463	123–128	—	58.0/180	GED$^{(S2)51}$
	1.347^{b}	1.493	122.4–126.0	—	59.3/60.9	XR^{52}
	1.347^{b}	1.462; 1.487	118.6–120.1	—	62.8/62.3	XR^{53}

[a] In parentheses esd's for bond lengths and angles in the last digit S1: 1–3, S2: 3–10, S3: >10.

[b] Average value.

All the molecules with dihedral angles close to 60° will experience some steric strain also in conformations close to planar *syn*. It seems therefore reasonable that the minimum energy conformation to a large extent is determined by the torsional potential connected to the sp^2-sp^2 single bond, as the torsional energy rises sharply for torsional angles larger than *ca* 65° toward a maximum at around 120°^{46}. The approximately perpendicular minimum energy conformation of **2,3-TB** must, however, be almost exclusively a result of minimization of the van der Waals steric energy.

When a **2-TB** conformer has a C=C−C=C dihedral angle within the region ±65°, the steric repulsions involving the *tert*-butyl group and the C^4 methylene group will be negligible, and the preferred conformation of the π-system is therefore probably governed by the same factors that are primarily responsible for the preferred conformation of the high-energy conformer of 1,3-butadiene, namely the torsional potential at the C^2-C^3 bond and the nonbonded repulsions between the C^1 and C^4 methylene groups. The concentration of the high-energy form of 1,3-butadiene is very small, and thus it is difficult to study the structure of this conformer experimentally, while the analogous conformer of **2-TB** is present in 100%. The observed conformation for **2-TB** therefore gives strong support to the results obtained by the quantum chemical calculations for metastable 1,3-butadiene.

B. Monocyclic Dienes and Polyenes

In small and medium-sized monocyclic dienes the C=C double bonds are necessarily *cis* connected to the adjacent ring atoms. For rings with at least ten carbon ring atoms *trans* double bonds may be present, without causing high strain energy in the molecule. The existing relevant structural data available for monocyclic dienes/polyenes are therefore presented in two tables. In Table 7 molecular structures for molecules with a maximum of eight ring atoms are shown, while Table 8 gives similar data for larger monocyclic dienes and polyenes. We restrict our discussion to monocyclic dienes and polyenes with no heteroatomic substituents. The available structural data for such molecules are rather limited.

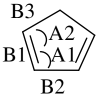
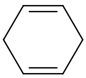
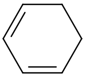
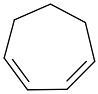
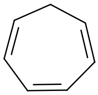
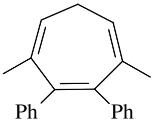
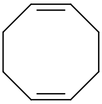
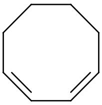
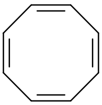
The smallest conceivable conjugated monocyclic diene is 1,3-cyclobutadiene. Several complexes involving cyclobutadiene are known. The compound itself is unstable and has not been studied by structural methods. It will therefore not be included in the present discussion. 1,3-Cyclobutadiene has, however, been isolated in argon matrices, and it has been established that the molecule has D_{2h} symmetry[54]. For the tetra-*tert*-butyl derivative an envelope conformation (twist angle 7°) was found by X-ray methods[55], however the distances in the ring were obviously too similar for an antiaromatic system [1.464(3) and 1.483(3) Å]. A redetermination at even lower temperatures gave more reasonable results (1.441 and 1.527 Å)[56] and a further analysis of the anisotropic parameters revealed that some residual disorder is still responsible for some equilibration and distances of 1.34 and 1.60 Å were assumed to be the correct ones[57].

The next cyclic alkadiene, 1,3-cyclopentadiene, has been experimentally studied by MW, GED and XR methods. The carbon skeleton is planar (C_{2v} symmetry), and the small C=C−C angles compared to those in 1,3-butadiene (124.3°) or *cis*-1-butene (126.4°)[58] do not seem to influence noticeably the lengths of the CC bonds, although other effects, such as π-electron delocalization, might have an opposite effect. The apparently 'normal' structure parameters observed for 1,3-cyclopentadiene might therefore be a result of different forces having opposite effects on the structure parameters.

In Table 7 the *six-membered monocyclic dienes* are represented by the conjugated 1,3-cyclohexadiene and its isomer 1,4-cyclohexadiene. 1,3-Cyclohexadiene has a nonplanar equilibrium conformation that is primarily influenced by three factors: π-electron interaction (optimal for a planar conformation); angle strain and torsion strain (both optimal for a planar conformation). The reduced overlap between the two π-orbital systems is, for the observed C=C−C=C angle of 18°, estimated at *ca* 10% and should therefore not influence the conjugation stabilization drastically, compared to a conformation with coplanar C=C bonds.

It is reasonable to assume that the 1,3-cyclohexadiene molecule is stabilized by its conjugated π-system, relative to the nonconjugated 1,4-isomer. Existing experimental and theoretical information about these two molecules indicate, however, that other forces, in

TABLE 7. Experimentally determined and calculated structure parameters for monocyclic dienes and polyenes; maximum 8 ring atoms (distances in Å, angles in degrees)

	B1	B2 (B3)	A1	A2	T1[b]	Method[a]
	1.340	1.469	109.3	109.4	0.0	GED^{59}
	1.342	1.465	109.3	109.3	0.0	MW^{60}
	1.344	1.460	109.6	109.1	0.0	XR$^{(S1)4}$
	1.354	1.465	109.2	109.1	0.0	MP2^{c4}
	1.347	(1.511)	122.7	122.7	~0	GED$^{(S2)61}$
	1.334	(1.496)	123.4	123.4	~0	GED$^{(S1)62}$
	1.318	(1.468)	123.4	123.5	0.0	XR$^{(S1)63}$
	1.339	1.468	118.2	121.6	17.0	GED$^{(S2)64}$
	1.348	1.464	120.3	120.3	18.0	GED$^{(S1)65}$
	1.350	1.468	120.1	120.1	18.3	GED$^{(S3)61}$
	1.347	1.450	129.1	129.1	0.0	GED$^{(S2)66}$
	1.345	1.470	128.5	125.0	0.0	MP2^{d67}
	1.356	1.446	121.8	127.2	α: 40.5^{e,f,g} β: 36.5^{e}	GED$^{(S2)68}$
	1.337/ 1.357	1.471^{h}	121.4^{h}	125.1^{h}	α: 52.6^{e} β: 34.3^{e}	XR^{69}
	1.340	1.514	130.6	130.6	~0	GED$^{(S2)70}$
	1.347	1.475/ (1.501)	129.0	129.0	38.0	GED$^{(S2)71}$
	1.340	1.476	126.1	126.1	α: 43.1^{g}	GED$^{(S1)72}$
	1.333	1.468	126.6	126.6		XR$^{(S1)73}$

[a] In parentheses, esd's for bond lengths and angles in the last digit S1: 1–3, S2: 3–10, S3: >10.

[b] C=C–C=C torsion angle.

[c] MP2/6-31G(d).

[d] MP2/6-31G(d,p).

[e] α is the angle between the $C^2C^3C^4C^5$ and $C^1C^2C^5C^6$ planes; β is the angle between the $C^1C^6C^7$ and $C^1C^2C^5C^6$ planes.

[f] C^1=C^2–C^3–C^4: −86.5°, C–C–C–C: 63.8°, C^3–C^4–C^5=C^6: 8.1°, C–C=C–C: 6.2°.

[g] 'Bath tub' angles.

[h] Average value.

addition to the π-electron distribution, contribute to the overall energies of the two isomers. They do, for example, appear to have nearly equal enthalpies of formation[74]. Skancke and coworkers[75] have recently performed *ab initio* calculations at different levels of theory for a number of molecules, including the two cyclohexadienes. Optimized structures of the two isomers at the HF/6-31G(d) level favored the 1,4- over the 1,3-isomer by 1.1 $\mathrm{kJ\,mol^{-1}}$. Contrary to this, MP2/6-31G(d) and MP2/6-31G(d,p) optimizations found the 1,3-isomer to have the lowest energy of the two, the differences being 1.2 $\mathrm{kJ\,mol^{-1}}$ and 0.1 $\mathrm{kJ\,mol^{-1}}$, respectively. At a still more advanced level of calculation, MP4dq/6-31G(d,p)//MP2/6-31G(d,p), the 1,4-isomer was again calculated to be the more stable, by 1.1 $\mathrm{kJ\,mol^{-1}}$. If a conclusion should be drawn from the partly conflicting information presented above, it must be that the energies of the 1,3- and 1,4-cyclohexadiene molecules are nearly the same.

We have already pointed to one effect that should contribute to lowering the relative energy of 1,3-cyclohexadiene, namely the π-electron conjugation. If the energies of the 1,3- and 1,4-cyclohexadiene molecules are approximately equal, this might imply that the 1,3-isomer is destabilized, or the 1,4-isomer stabilized, by other causes. The distribution of torsion angles in the two molecules might give a possible explanation. In a planar 1,4-cyclohexadiene molecule all C−C torsion angles correspond to potential energy minima (although not generally the lowest ones). In the conjugated nonplanar 1,3-isomer none of the torsion angles at the formal single bonds has a value corresponding to the expected potential energy minima. The total effect from the torsions in the two isomers might therefore destabilize the 1,3- relative to the 1,4-isomer by an energy amount comparable to that of the additional π-electron stabilization in the conjugated 1,3-cyclohexadiene molecule.

The next molecules to be discussed are the *seven-membered monocyclic dienes and polyenes*. 1,3-Cycloheptadiene has been studied by GED (Table 7). The molecule has also been studied by MW[76]. This study did not include a complete structure determination, but it was concluded that the carbon skeleton is planar, except for the C^6 carbon, corresponding to C_S symmetry. This is in agreement with the GED results. *Ab initio* calculation at the MP2 level, utilizing the 6-31G(d,p) basis set, has recently been carried out[77]. Both the C_S and C_2 conformers of 1,3-cycloheptadiene were considered, and the MP3/6-31G(d,p)//MP2/6-31G(d,p) calculations predict the C_S conformer to be 3.3 $\mathrm{kJ\,mol^{-1}}$ lower in energy than the C_2 conformer. It was concluded that the calculated C_S conformer at the MP2 level is in excellent agreement with the available MW and GED data. The MP2 and MP3 energetics results allow, however, for the possibility of the presence of a C_2 conformer, as evidenced by NMR data[78]. The experimental results do not rule out the presence of small amounts of a C_2 conformer that is twisted about the diene region.

On the basis of the NMR spectrum of *1,3,5-cycloheptatriene* Doering and Coworkers[79] suggested in 1956 that the molecule has a pseudo-aromatic structure with a planar carbon skeleton. The supposed aromatic structure is reflected in the commonly used name tropylidene for this molecule. There is, however, no doubt that the 1,3,5-cycloheptatriene[68] molecule has a boat-shaped conformation with alternating double and single bonds. A recent MP2/6-31G(d)//MP2/6-31G(d) calculation by Skancke[75] gave almost identical bond lengths and valence angles to those in the GED study; the 'bath tub' angles differed, however, somewhat (α, 27.7°; β, 57.3°). The corresponding angles observed in the X-ray study of 2,5-dimethyl-3,4-diphenyl-1,3,5-cycloheptatriene[69] are, however, similar to those observed by GED for the parent compound.

The final entries in Table 7 concern *eight-membered monocyclic dienes and polyenes*. The unconjugated *1,5-cyclooctadiene* was observed to have twist-boat conformation and C_2 symmetry. In accordance with what is very often the case in GED studies of cyclic compounds, amounts less than about 10% could not be ruled out. The GED study is in agreement with molecular mechanics calculations[80], which found the twist-boat form to be lower in potential energy than the regular boat by 29 kJ mol^{-1} and the chair lower by 17 kJ mol^{-1}. The twist-boat conformation adopted by the free molecules appears to be a result of minimizing torsional strain and nonbonded repulsions.

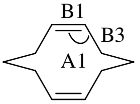
The GED results obtained for *1,3-cyclooctadiene* should be regarded with caution, as the data in Table 7 refer to a 25-year-old study, where it was assumed that only one conformer is present. The structure of 1,3-cyclooctadiene should therefore be reinvestigated.

The observed geometry of *1,3,5,7-cyclooctatetraene* (**COT**) is strikingly similar in the solid state and in the gas phase. The molecule is found to be boat-shaped with D_{2d} symmetry. Single and double bonds are as expected for a nonplanar compound with isolated double bonds and no significant π-orbital overlap. Addition of substituents results in differences in the ring geometry, e.g. repulsion of the methyl groups in octamethyl-**COT** causes significant flattening of the ring[81]. The NMR spectrum of cyclooctatetraenyl dianion is, however, in agreement with a planar aromatic eight-membered ring, with a high degree of resonance stabilization in association with a closed shell of $(4n + 2)$ π-electrons for $n = 2$[82]. As a dianionic ligand the **COT** skeleton is also planar and has aromatic character[83].

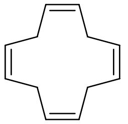
Table 8 presents structures observed for monocyclic dienes and polyenes with rings large enough to accommodate *trans* C=C double bonds. In a cyclodecadiene molecule strain-free carbon skeletons can only be derived when two double bonds are diametrically placed and have the same configuration (*cis*, *cis* or *trans*,*trans*). *Cis*,*cis*-Cyclodeca-1,6-diene **(1,6-CD**D) may exist in *twelve* different conformations, and it is therefore noteworthy that it almost exclusively prefers one of these, namely the one indicated in Table 8. This conformer does not have the repulsive transannular HH interactions that destabilize the corresponding saturated molecule in all conceivable conformers.

The *all-cis-1,4,7,10-cyclodecatetraene* (**1,4,7,10-CDT**) molecule is of special interest as a tetrahomo-8π-system, when all four π-bonds are arranged in a way where maximum interaction is guaranteed. This arrangement is realized in the crown conformation, which is also the conformer observed in an X-ray study of the molecule. The mean C=C bond

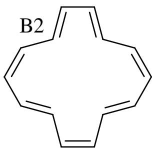
TABLE 8. Experimentally determined structure parameters for monocyclic dienes and polyenes; minimum 10 ring atoms (distances in Å, angles in degrees)



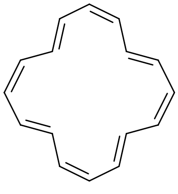
(1,6-CDD)



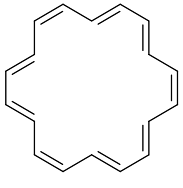
(1,4,7,10-CDT)



(14-ANN)



(16-ANN)



(18-ANN)

	B1	B2 (B3)	A1	Method[a]
1,6-CDD	1.326	(1.506)	128.2	GED(S2)[84]
1,4,7,10-CDT	1.324[b]	(1.503)[b]	127.4[b]	XR[85]
14-ANN	1.378[b]	1.378[b]		XR(S3)[86]
16-ANN	1.337[b]	1.454[b]		XR[87]
18-ANN	1.371–1.429	1.371–1.429		XR[88]

[a] In parentheses, esd's for bond lengths and angles in the last digit S2: 3–10, S3: >10.

[b] Average value.

lengths correspond approximately to those in planar 1,4-cyclohexadiene (see Table 7), whereas the single bonds are somewhat longer. The distances between hydrogen atoms pointing toward the center of the ring, *ca* 2.01 Å, are clearly shorter than the sum of the van der Waals radii of 2.4 Å. As the molecule prefers a conformation in which all the double bonds are coplanar, this is interpreted as an absence of homoantiaromatic destabilization.

Results from X-ray studies of three annulenes are presented In Table 8. According to Hückel's rule [14]annulene **(14-ANN)** and [18]annulene **(18-ANN)** should be aromatic and most probably planar molecules, while [16]annulene **(16-ANN)**, as a [4*n*]annulene, should be antiaromatic. The [14]annulene molecule is nonplanar, with a structure that approaches C_{2h} symmetry. The cause of the nonplanarity is the steric overcrowding in the center of the molecule. While the spread of the individual bond lengths implies possible significant differences, there is no significant pattern to the values obtained.

The [16]annulene is nonplanar, with almost complete bond alternation. The single bonds (1.454 Å) are alternately *trans* and *gauche*, and the double bonds (1.337 Å) *cis* and *trans*. The average torsion angle at a *gauche* C−C bond is 41°. The molecule is therefore relatively flat with S_4 noncrystallographic symmetry, and the structure confirms the lack of aromaticity in this [4*n*]annulene.

The investigation of [18]annulene is the oldest of the X-ray annulene studies reported, and it was stated that the hydrogens have not been reliably located. The molecular structure closely resembles that of coronene[89]. This rules out the possibility of a structure with alternate long and short C−C bonds. The observed spread of CC distances in [14]annulene and in [18]annulene is *ca* 0.06 Å, while that in [16]annulene is twice as large, *ca* 0.12 Å. The annulene molecules therefore have structures that are similar to what is expected on the basis of Hückel's rule.

C. Polycyclic Dienes and Polyenes

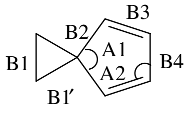
The largest contribution and variety in the family of polyenes is to be found in the group of bicyclic and polycyclic compounds. For this chapter we selected those compounds which represent the most important prototypes of different kinds of interaction, namely cyclopropyl-conjugation, spiroconjugation, hyperconjugation and homoconjugation.

1. Spiropolyenes

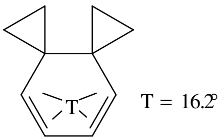
In respect to the similar chemical behavior of alkenes and cyclopropanes but different MO and bonding situations, the determination of exact geometries of cyclopropyl-conjugated hydrocarbons can supply important information. As reported in the literature, the three-membered ring in a substituted cyclopropane derivative is rather sensitive to bond length distortions caused by conjugation effects[90]. The electron-withdrawing effect of a neighboring double bond leads to a lengthening of the *vicinal* bonds and a shortening of the *distal* bond in the three-membered ring if the bisected conformation is fulfilled. In small spirocyclic dienes the conformation is fixed in the bisected form where the best orbital overlap can be achieved.

Table 9 shows the geometrical features of compounds, where strong cyclopropyl conjugation takes place. In spiro[2.4]hepta-4,6-diene (**SHD**) this interaction has an important contribution to the molecular dipole moment, 0.95 Debye measured by microwave analysis[91]. The structural influences are mainly taking place in the three-membered ring, where a strong bond length splitting is observed for most of the experimental and theoretical methods. However, the ED investigation could not distinguish between the cyclopropane bonds. The same problem occurs in the gas-phase structure determination of the dispiro compound **(DSD1)**; unfortunately there are no further

TABLE 9. Experimentally determined and calculated structure parameters for spiro[2.*n*]dienes (distances in Å, angles in degrees)

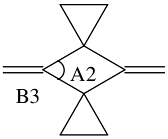


(SHD)



(DSD1)

(DSD2)



(DSOD)

	B1 (B1')	B2	B3	B4	A1	A2	Method^{a}
SHD	1.494 (1.546)	1.462	1.361	1.467	107.0	108.9	MW$^{(S1)91}$
	1.486 (1.533)	1.467	1.338	1.448	104.8	109.1	XR$^{(S1)9}$
	1.510^{b}	1.509	1.340	1.460	102.6	109.5	GED$^{(S2)59}$
	1.484 (1.528)	1.473	1.360	1.460	105.7	109.0	MP2^{9}
DSD1	1.508^{b}	1.518	1.345	1.459	117.4	121.6	GED$^{(S2)92}$
DSD2	1.498 (1.526)	1.482	1.335	—	114.6	122.7	XR$^{(S1)9}$
	1.496 (1.521)	1.479	1.354	—	114.6	122.7	MP2^{9}
DSOD	1.492 (1.504)	1.518	1.318	—	90.1	89.9	XR$^{(S1)93}$

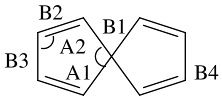
[a] In parentheses, esd's for bond lengths and angles in the last digit S1: 1–3, S2: 3–10. MP2 = MP2/6-31G(d).
[b] Mean values for cyclopropane bonds.

structural data available so far. The dispirodecadiene **(DSD2)** has been analyzed by X-ray and *ab initio* methods; both results are in good agreement with respect to the different models of investigation. The dispiro compound (**DSOD**) can be considered as a derivative of [4]rotane. While the cyclobutane ring is square and planar in **DSOD**, additional strain and rehybridization shortens the vicinal cyclopropane bond and the double bond.

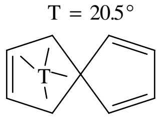
Compounds with two perpendicular π-systems joined by a common spiro-atom exhibit through-space *spiroconjugation*[94]. One important representative of spiroconjugated systems is spiro[4.4]nonatetraene **(SN4)**[95]. The molecular structures of spiro[4.4]nona-1,3,7-triene **(SN3)** and **SN4** have been determined by X-ray diffraction in order to detect the slight distortions expected by spiroconjugation. Comparison of bond lengths and angles reveals a slight shortening of the double bonds and a small lengthening of the single bonds connecting the spiro atom in **SN4**. The same effect is also found by *ab initio* calculations at the Hartree–Fock level 6-31G(d), although to a minor extent[96]. Table 10 shows the most important geometrical features of **SN3** and **SN4** together with the data of spirotetraenedione **(STD)**.

While **SN4** and **STD** exhibit essentially D_{2d} symmetry, **SN3** has C_S symmetry with a planar diene ring and an envelope-shaped cyclopentene ring. The maximum torsion in the folded ring of **SN3** is 20.2°. The spiro-connection of two five-membered ring systems leads to some strain at the spiroatom (101.4° to 101.8° at A1 compared to 109.5° for tetrahedral

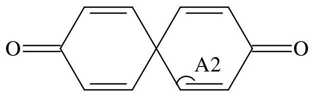
TABLE 10. Experimentally determined and calculated structure parameters for spiro[4.n]polyenes (distances in Å, angles in degrees)



(SN4)



(SN3)



(STD)

	B1	B2	B3	B4	A1	A2	Method[a]
SN4	1.516	1.338	1.469	—	101.7	109.6	$\mathrm{XR}^{(\mathrm{S1})96}$
	1.519	1.326	1.479	—	101.4	109.2	RHF/6-31G(d)[96]
SN3	1.505 1.514	1.347 1.343	1.470	1.334	101.8	108.9	$\mathrm{XR}^{(\mathrm{S1})96}$
	1.511 1.516	1.326 1.326	1.479	1.319	101.3	108.9	RHF/6-31G(d)[96]
STD	1.497	1.323	1.451	1.227	111.7	121.2	$\mathrm{XR}^{(\mathrm{S2})97}$

[a] In parentheses, esd's for bond lengths and angles in the last digit S1: 1–3, S2: 3–10.

environment). Derived from these data the structural effects of spiroconjugation seem to be extremely small, since bond lengths and angles are in normal ranges.

2. Annulated cyclopolyenes

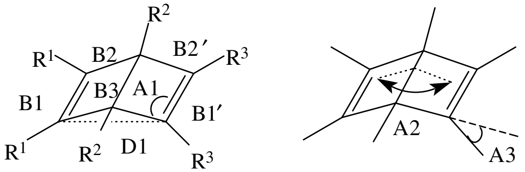
Two rings linked by sharing the same bond instead of the same atom lead to annulated bicyclic or tricyclic compounds, the propellanes. In the case of poly-unsaturated molecules, an interesting case is represented by the bicyclo[2.2.0] type. The parent compound Dewar benzene (bicyclo[2.2.0]hexa-2,5-diene) **(DEW)** is the smallest bicyclic diene which is an often discussed valence isomer of aromatic benzene C_6H_6. Unsubstituted **DEW** is a very small and strained molecule which is prepared photochemically. It is the first valence bond isomer of benzene ever isolated. The molecule is not planar; the interplanar angle of both adjacent four-membered rings varies between 115° and 118° (see Table 11). In this butterfly shape the π-systems are bent toward each other and can perform homoconjugation as well as hyperconjugation.

Very obvious is the long central single bond B3 observed by all experimental methods (1.57 to 1.63 Å). The double bonds reveal pyramidalization[98] (see Figure 5) which is defined by the angle A3 and describes the *out-of-plane* deviation of the substituents (1.5° to 2°). Hyperconjugational effects bias the sp^2–sp^3 single bond lengths which appear to be elongated. The effects of hyperconjugation and pyramidalization are illustrated in Figure 5.

If cyclohexa-1,3-diene is annulated with a three-membered ring at the 5,6- single bond, the norcaradiene system results. An opening of the cyclopropane ring at the common bond is observed by thermal rearrangement yielding cycloheptatriene. In the case of bisnorcaradiene **(BNOR)**, which is a [4.4.1]propellane, the ring opening leads to an energetically more favorable aromatic [10]annulene system. Substitution at the cyclopropane has an essential influence on the [10]annulene $\rightleftharpoons$ bisnorcaradiene equilibrium (Figure 6).

In contrast to the effect of π-systems in the cyclohexadiene systems, the introduction of π-acceptor substituents at the cyclopropane unit shortens the central bond. In the case of the cyano group, the influence of two substituents leads to a central bond B4 which

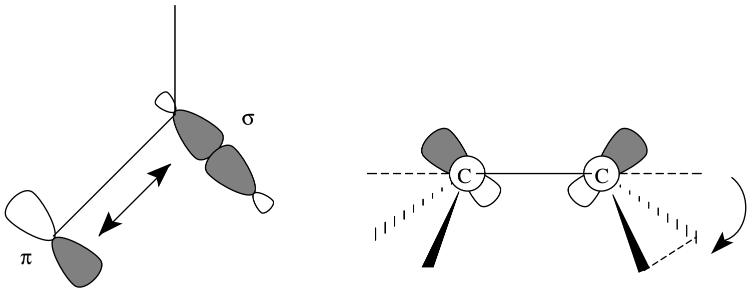
TABLE 11. Experimentally determined structure parameters for bicyclo[2.2.0]dienes (distances in Å, angles in degrees)



(DEW)

		B1 (B1’)	B2 (B2’)	B3	D1	A1 (A2)	Method[a]
DEW	$R^1 = R^2 = R^3 = H$	1.345	1.524	1.574	2.595	(117.3)	$GED^{(S3)99}$
	$R^1 = R^2 = R^3 = Me$	1.352	1.523	1.629		(124.5)	$GED^{(S2)100}$
	$R^1 = R^2 = H$ $R^3 = CN$	1.328 (1.336)	1.529 (1.531)	1.575	2.569	(114.9)	$XR^{(S1)101}$
	$R^1 = R^3 = H$ $R^2 = cy^b$	1.346	1.531	1.594		95.1 (115.9)	XR^{101}
	$R^1 = R^3 = H$ $R^2 = cy^b$	1.311 (1.319)	1.521 (1.524)	1.565		94.8 (116.6)	$XR^{(S1)102}$
	$R^1 = R^3 = H$ $R^2 = cy^b$	1.316	1.533	1.572		(117.7)	$XR^{(S1)104}$

[a] In parentheses, esd’s for bond lengths and angles in the last digit S1: 1–3, S2: 3–10, S3: >10.
[b] cy = cyclic bridged.



(A) **(B)**

FIGURE 5. Hyperconjugation **A** (π–σ(C–C)) and pyramidalization **B** of a C=C double bond

is even shorter than B5 (Table 12). In this case the norcaradiene form **C** is stabilized. A combination of a cyano and a methyl group has a weaker effect and, in the case of two methyl groups, the central bond is almost cleaved (1.771 Å and 1.827 Å for two independent molecules in the crystal lattice) and a significant equalization of the double and single bonds occurs in the rest of the molecule (form **B**). If there is no substitution, the bridged [10]annulene system **A** is observed with a distance of 2.235 Å for the former

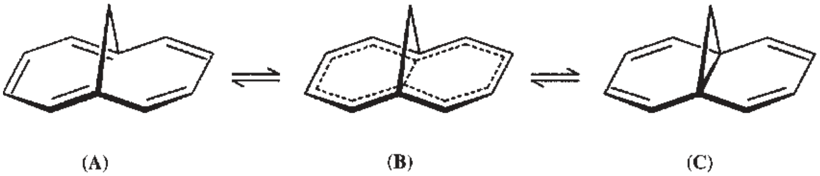
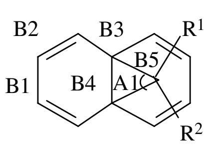
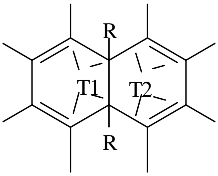

(A) (B) (C)

FIGURE 6. Equilibrium of CH_2-bridged [10]annulene **A** and bisnorcaradiene **C**

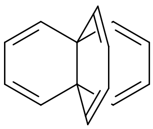
TABLE 12. Experimentally determined and calculated structure parameters for bisnorcaradienes and annulated polyenes (distances in Å, angles in degrees)



(BNOR)



(DHN)



(PRO)

		B1	B2	B3	B4	B5 (T1)[b]	A1 (T2)	Method[a]
BNOR	$R^1 = R^2 = CN$	1.450	1.343	1.475	1.539	1.569 (151.0)	58.8 (4.3)	$XR^{(S1)105}$
	$R^1 = CN$ $R^2 = Me$	1.444	1.342	1.472	1.640	1.527 (145.7)	63.9 (5.8)	$XR^{(S1)106}$
	$R^1 = R^2 = Me$	1.419	1.335	1.458	1.771	1.508 (140.2)	71.8 (7.9)	$XR^{(S2)107}$
		1.431	1.348	1.453	1.827	1.507 (139.9)	74.6 (8.3)	$XR^{(S2)107}$
	$R^1 = R^2 = H$	1.418	1.377	1.405	2.235	1.486 (139.3)	97.6 (15.9)	$XR^{(S2)108}$
DHN	$R = Me$	1.470	1.337	1.537	1.553	(55.2)	(21.6)	$XR^{(S2)109}$
	$R = COOMe$	1.481	1.345	1.540	1.557	(53.2)	(20.5)	$XR^{(S2)109}$
PRO		1.457	1.341	1.528	1.567	(40.5)	(9.8)	$XR^{(S3)110}$

[a] In parentheses, esd's for bond lengths and angles in the last digit S1: 1–3, S2: 3–10, S3: >10.

[b] for **BNOR**: T1 = torsion angle C=C–C–C.

central bond. The aromatic character of the CH_2-bridged [10]annulene is weakened by folding of the conjugated system (see T1 and T2). Higher-level *ab initio* calculations on the MP2/6-31G(d) level could not predict a stable bisnorcaradiene form **C** as a minimum on the potential energy surface. The electron-withdrawing effect of both π-systems weakens the central bond in such a way that the energetic barrier between both forms disappears and the annulene structure is the only alternative. Table 12 shows geometrical parameters of different substituted bisnorcaradienes and related molecules.

Substituted 9,10-dihydronaphthalenes **(DHN)** adopt essentially C_2 symmetry, whereas the diene systems are strongly twisted (see torsion angles T1 and T2). The bond lengths are in normal ranges. [4.4.4]Propellahexaene **(PRO)** has a remarkable propeller-like shape, close to D_3 symmetry. The torsion angles in the annulated six-membered rings are smaller than in the **(DHN)** structures. The central bond (1.567 Å) is only slightly longer than the normal value for sp^3-sp^3 single bonds.

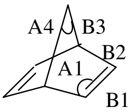
3. Bridged polyenes

Norbornadiene (bicyclo[2.2.1]hepta-2,5-diene) **(NOR)** appears also as a strained olefinic bicyclic molecule. The interplanar angle is smaller than in **DEW** with 113.9° to 115.1° (see Table 11). The same homoconjugational and hyperconjugational effects can be observed in **NOR**, whereas influences of homoconjugation mainly bias the electronic structure[111,112] and hyperconjugation biases the geometrical properties. The additive hyperconjugational interactions between π- and σ(C−C)-systems have a significant elongational effect on the single bonds (see Figure 5). The bond B2 is 0.024 Å (mean value) longer than a normal sp^2-sp^3 C−C single bond and B3 is observed about 0.013 Å (mean value) longer than normal C−C bonds of this type (sp^3-sp^3).

Bicyclic olefins of the **NOR** type were often discussed in terms of high reactivity and *exo*-selectivity in Diels-Alder reactions. A straightforward explanation for this effect can be given by the observed pyramidalization of the double bond into the *exo*-region of the unsaturated center (see Tables 13 and 14, angle A3). Another characteristic property of the bicylic systems of the **NOR** type is related to the globular shape of the molecules[113]. The nonpolarity and regular shape of molecules often lead to plastic phases[114] and polymorphism. The investigation of the molecular structure in the plastic high-temperature phase is not possible, caused by local disorder and inner rotation of the molecules. With the special method of *in situ* crystallization from solution using an IR laser beam[115] it is possible to circumvent the plastic phases. A single crystal of **NOR** in the ordered low-temperature phase could be achieved by this method; the X-ray data are given in Table 13.

In 7-isopropylidene-norbornene (**INOR1**) hyperconjugation also has a significant influence on the geometrical parameters. All single bonds which interact with the π-systems

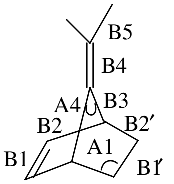
TABLE 13. Experimentally determined and calculated structure parameters for bicyclo[2.2.1]hepta-2,5-diene (distances in Å, angles in degrees)

	B1	B2	B3	A1 (A3)^b	A2^b (A4)	Method^a
NOR	1.337	1.536	1.555	107.2 (∼ 4.5)	114.4 (92.5)	XR$^{(S1)116}$
	1.339	1.533	1.571	—	— (92.2)	GED$^{(S1)117}$
	1.336	1.530	1.557	107.1	— (91.9)	MW$^{(S1)118}$
	1.319	1.539	1.550	107.7 (2.7)	115.1 (92.3)	RHF/6-31G(d)[116]
	1.345	1.533	1.552	107.0 (3.7)	114.8 (92.3)	MP2/6-31G(d)[116]

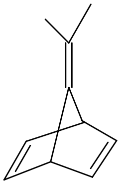
[a] In parentheses, esd's for bond lengths and angles in the last digit S1: 1–3.

[b] For the definition of A2 and A3, see Table 11.

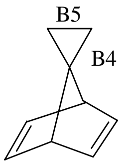
TABLE 14. Experimentally determined and calculated structure parameters for 7-substituted bicyclo[2.2.1]dienes and -polyenes (distances in Å, angles in degrees)



(INOR1)



(INOR2)



(SNOR)

	B1 (B1')	B2 (B2')	B3	B4 (B5)	A1 (A3)^b	A2^b (A4)	Method^a
INOR1	1.342 (1.553)	1.521 (1.566)	1.519	1.333	107.5 (~ 4.2)	111.3 (96.0)	XR$^{(S1)116}$
INOR2	1.337	1.538	1.533	1.330	107.6 (~ 1.9)	114.5 (94.4)	XR$^{(S1)116}$
	1.320	1.539	1.533	1.318	107.3 (1.7)	115.3 (93.7)	RHF/6-31G(d)^{116}
	1.346	1.533	1.533	1.339	107.1 (2.4)	115.2 (94.4)	MP2/6-31G(d)^{116}
SNOR	1.332	1.535	1.537	1.485 (1.525)	107.0 (~ 2.9)	114.3 (93.7)	XR$^{(S1)116}$
	1.320	1.539	1.537	1.483 (1.514)	107.2 (2.3)	114.9 (93.0)	RHF/6-31G(d)^{116}
	1.346	1.533	1.537	1.489 (1.522)	107.0 (3.1)	114.9 (93.7)	MP2/6-31G(d)^{116}

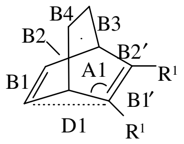
[a] In parentheses, esd's for bond lengths and angles in the last digit S1: 1–3.

[b] For the definition of A2 and A3, see Table 11.

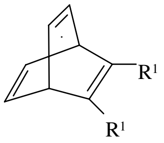
show longer bonds than usual. The six-membered ring is more puckered, with an interplanar angle of 111.3°, than in the cyclohexadiene system in **NOR**. The exocyclic double bond B4 shortens the central single bonds B3 and widens the angle A4 by hybridization effects and strain compared to **NOR**.

Strong homoconjugation effects are discussed for **INOR2**, where destabilizing interactions of the norbornadiene system and the exocyclic π-system take place[111]. As a consequence there is a slight tendency to achieve a bicycloaromatic state, in agreement with the observed polarization of the exocyclic bond B4 (obtained from ^{13}C-NMR data[112]). Structural influences, caused by pure homoconjugation, are hard to detect. They cannot be separated from the strong hyperconjugation effects, which again alter the σ(C−C) single bond system of **INOR2**. In **SNOR** the norbornadiene fragment is nearly identical to that in **INOR2**; here the spiro cyclopropane unit is part of the homoconjugated system[119]. Cyclopropyl homoconjugation in **SNOR** has a significant influence on the rather sensitive (bent) bonds of the three-membered ring. In addition to the effects of strain and hybridization, the vicinal bonds B4 are shortened and the distal bond B5 is elongated by electronic interactions with the π-systems. In contrast to cyclopropyl conjugation, this effect weakens the distal bond and the cyclopropyl group acts as an electron acceptor rather than an electron donor.

TABLE 15. Experimentally determined and calculated structure parameters for bicyclo[2.2.2]dienes and -polyenes (distances in Å, angles in degrees)



(DBAR)



(BAR)

		B1 (B1')	B2 (B2')	B3 B4	D1	A1	Method^a
DBAR	$R^1 = H$	1.339	1.521	1.553		113.5	GED$^{(S2)121}$
	$R^1 = CN$	1.325 (1.346)	1.512 (1.517)	1.559	2.444	111.8	XR$^{(S1)101}$
BAR	$R^1 = H$	1.335	1.538			112.9	GED$^{(S1)122}$
	$R^1 = CN$	1.311 (1.334)	1.531 (1.536)		2.430	111.4	XR$^{(S1)101}$

[a] In parentheses, esd's for bond lengths and angles in the last digit S1: 1–3, S2: 3–10.

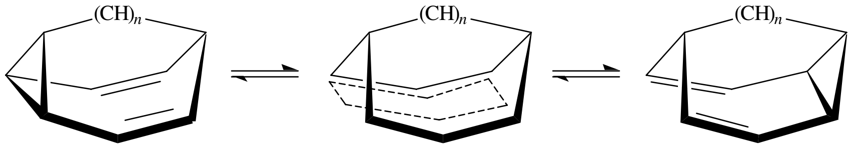
For **INOR1**, **INOR2** and **SNOR** a significant pyramidalization of the endocyclic double bonds can be observed by all methods. The out-of-plane deviations appear to be around 1.9° to 3.1° (see Table 14).

Barrelene **(BAR)** is an interesting molecule with high symmetry (D_{3h}) and three homoconjugated π-systems. The synthesis of the unsubstituted hydrocarbon **BAR** (which is rather stable at room temperature) was first reported by Zimmermann and Paufler in 1960[120]. The structural parameters of **BAR** (Table 15) show unusually long single bonds B2 (1.512–1.538 Å). In a direct comparison of bond B2 with dihydrogenated **DBAR** the difference caused by hyperconjugation is about 0.018 Å (Table 15), in good agreement with the observations from the bicyclo[2.2.1]systems.

4. Polycyclic polyenes

One of the most interesting small polycyclic hydrocarbons is tricyclodecatriene, better known as bullvalene **(BUL)**. It can be considered as a 1,2,3-trivinylcyclopropane, where the vinyl groups are linked by a common carbon (bridgehead) atom at each end. Undergoing Cope rearrangement, the molecule is able to transform a cyclopropyl atom into a bridgehead atom, and the bridgehead atom with two adjacent atoms into cyclopropyl atoms (see Figure 7). Several rapid rearrangements transfers each of the ten carbon atoms into a bridgehead atom, leading to a constant change of the π-bond positions in the molecule.

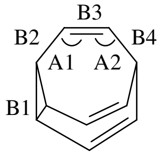
The molecular structure of the parent compound was investigated in the vapor and in the solid phase using X-ray, XN and GED methods. The reported data are shown in Table 16. In both phases a clear bond length separation could be detected with a localized three-membered ring and its three adjacent double bonds. The symmetry-equivalent cyclopropane bonds are rather long in C_{3v}-symmetric **BUL** (1.533–1.542 Å), which can be explained by the common electron-withdrawing effect of the π-systems in a *syn*-clinal conformation. For comparison, the unaffected bonds in unsubstituted cyclopropane are 1.499 Å in the crystal and 1.510 Å in the gas phase. Therefore, the bond lengths in **BUL**



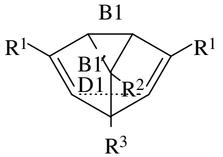
(A) **(B)** (C)

FIGURE 7. Cope rearrangement of bullvalene **(BUL)** ($n = 2$) and semibullvalene **(SEM)** ($n = 0$)

TABLE 16. Experimentally determined structure parameters for small polycyclic polyenes (distances in Å, angles in degrees)



(BUL)



(SEM, SEM1, SEM2)

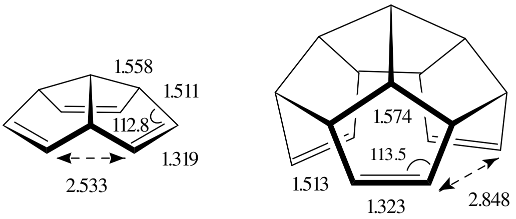
		B1 (B1')	B2	B3	B4 (D1)	A1	A2	Method[a,b]
BUL		1.542	1.465	1.346	1.523	122.6	126.3	GED$^{(S2)123}$
		1.539	1.452	1.319	1.508	124.1	126.7	XR$^{(S1)124}$
		1.533	1.473	1.342	1.516	123.7	126.5	XN$^{(S1)125}$
SEM	$R^1 = R^2 = R^3 = H$	1.600 (1.530)	1.531	1.350	1.531	107.4	113.5	GED$^{(S2)126}$
SEM1	$R^1 = R^3 = H$ $R^2 = CN$	1.577 (1.508)	1.475	1.375	1.524 (2.349)	111.0	111.8	XR^{127}
SEM2	$R^1 = CN$ $R^2 = R^3 = Me$	1.835 (1.487)	1.402	1.354	1.498 (2.048)	110.7	111.2	XR$^{(S1)128}$

[a] In parentheses, esd's for bond lengths and angles in the last digit S1: 1–3, S2: 3–10.

[b] XN = neutron diffraction.

are mainly influenced by cyclopropyl conjugation, where the weakening of the cyclopropane bonds is very helpful in terms of ring opening and the rearrangement mechanism.

In the related molecule tricyclooctadiene, which is also described as semibullvalene **(SEM)**, one vinyl group has been replaced by a direct bond to the former bridgehead atom ($n = 0$, see Figure 7). In **SEM** a very rapid Cope rearrangement also occurs, but in this case only two tautomeric forms are available. The structure of **SEM** could be investigated by GED; in the crystalline phase, however, only data of substituted derivatives are known. In the unsubstituted molecule the cyclopropane bonds are significantly different because of the interaction with both π-systems. In the case of bond B1, which is in the vicinal position for both double bonds, the cyclopropyl conjugation lengthens this bond to 1.600 Å, whereas for the other bonds vicinal and distal effects essentially cancel out each other (1.530 Å). In the rest of the molecule the single and double bonds are well localized and reveal normal values.



(1) **(2)**

FIGURE 8. Structures of triquinacene (**1**) and hexaquinacene (**2**) (distances in Å, angles in degrees)

Substitution of a single hydrogen atom by an electron acceptor group can show a very dramatic effect on the molecular structure of the **SEM** fragment. This is shown in Table 16. A cyano group at the central cyclopropane atom leads to a strengthening of bond B1; now the distal effect of the cyano group works in the opposite direction to that of the double bonds. As a result, the **SEM1** molecule is stabilized in its ground state for this tautomeric form. Double substitution at the double bonds **(SEM2)** by cyano groups has a destabilizing effect. The electron-withdrawing influence of the π-systems is now stronger and weakens the cyclopropane bond B1. The rearrangement is pushed forward by this substitution, leading to the same C_S symmetric molecule with substituents at the same positions for both tautomeric forms. The structural data reveal a very long ring bond B1 (1.835 Å) and, on the other side of the molecule, a shorter distance (D1) between the nonbonded atoms (2.048 Å). The bishomoaromatic character of this structure is also obvious by the other bond lengths of the molecule. The difference between the double bond length and the adjacent single bond length is only 0.056 Å. For this kind of substitution, there is an essential contribution of tautomeric form **B** (Figure 7).

The structure of the $C_{10}H_{10}$ hydrocarbon triquinacene (**1**), in which three multiply fused rings build a cup-shaped geometry with p–π orbitals projected toward the center of the concave face, was investigated by X-ray analysis. The C_{3v}-symmetric hydrocarbon was discussed in terms of strong through-space interaction of the π-systems (homoconjugation) and homoaromatic character. The nonbonded distances of the almost-planar cyclopentene rings are 2.533 Å and are therefore too long for a π–π overlap which leads to peripheral delocalization (see Figure 8). The bond distances for double and single bonds are quite normal. The fusion of three additional five-membered rings leads to the C_{16} hydrocarbon hexaquinacene (**2**), which represents a large fragment of a closed cage-like dodecahedrane ($C_{20}H_{20}$). The central cyclopentane rings are planar within the experimental error, but the cyclopentene rings are very slighty puckered outward. Analogous to **1**, the hydrocarbon **2** reveals C_{3v} symmetry but with the p–π axes almost in the same plane. With nonbonded distance (2.848 Å) the magnitude of the p–p overlap integral is very small. Again, no essential homoaromatic influence can be detected by any distortion of the molecular geometry.

D. Alkylidenecycloalkanes and -alkenes

Exocyclic double bonds at cyclic systems, which contain cross-conjugated double bonds, cannot be considered as a subgroup of radialenes and shall therefore be treated separately, although many of the structural features are comparable. However, in these systems the exocyclic and endocyclic double bonds are competing with each other as sites for Diels–Alder reactions, cycloadditions and electrophilic attacks. The double bond character of both, as measured by its distance, can provide some evidence for the selectivities. If no strain and conjugation are expected, the double bonds should be comparable to those found in ethene [1.314(1) Å XR[129] and 1.339(1) Å, GED[130]] or better in tetramethylethene [1.348(1) Å, XR[131] and 1.353(4) Å GED[132]]; the single bond distances are 1.507 Å and 1.511 Å. The H−C−H angle in ethene is 117.7°[129] and 117.4(1)[130]; the corresponding C−C−C angle in tetramethylethene is 112.1(1)°[131] and 112.2(5)°[132]. For isobutene, the GED values are in between these data: C=C 1.342(3), C−C 1.508(2) Å and C−C−C 115.8°[132]. Consequently, we expect for the exocyclic double bond at small cycloalkanes, such as in the extreme of a three-membered ring, the highest influence on the double bond distance. However, in methylenecyclopropane **(MCPA)** having an innercyclic angle at the central carbon atom of about 60°[133], this distance [1.316(1) Å] is almost unaffected compared to ethene (XR data), and even only slightly shortened if the gas-phase structures are taken. Here, it should be taken into account that both structure determinations deviate significantly. The same is found if the methylene double bonds of the GED structures of **MCPA** and methylenecyclobutane are compared (Table 17).

This comparison demonstrates that the exocyclic double bond length is little affected by the cyclic strain, which was also found for the radialenes; see Section II.E. However, significant deviations were found for conjugated systems, and the same holds for the linear and branched dienes and polyenes.

The smallest member of the family of alkylidenecycloalkenes is the highly sensitive methylenecyclopropene or triafulvalene **(MCPE)**, which was expected to exhibit either pseudoaromatic[136], nonaromatic[137] or antiaromatic[138] character. From the microwave spectrum of this compound only a 20% contribution of the zwitterionic state was suggested[139]. Surprisingly, the exocyclic bond distance was determined to be 1.332 Å, which is the same as in methylenecyclopropane **(MCPA)** determined by GED but significantly longer as determined by XR and MW. Because of the different electronic situation in the benzocyclopropa- and naphthocyclopropa-annulated systems[133], these will not be discussed further here although the exocyclic bond distances compare very well with those mentioned above and are in the range of 1.329–1.347 Å for a series of compounds[133].

1,2-Dimethylenecyclobutane, with the exocyclic double bonds as depicted in Table 18, should be comparable with butadiene. The double bond distances are virtually the same

TABLE 17. Structural parameters of ethene derivatives and small ring methylenecycloalkanes (distances in Å, angles in degrees)

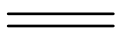
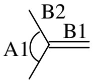
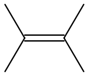
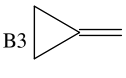
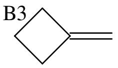
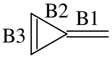
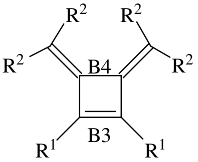
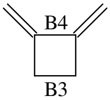
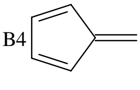
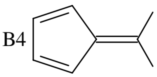
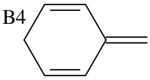
	B1	B2	B3	A1	Method
	1.314	—	—	117.7	XR[129]
	1.339	—	—	117.4	GED[130]
	1.342	1.508	—	115.5	GED[132]
	1.348	1.507	—	112.1	XR[131]
	1.353	1.511	—	112.2	GED[132]
	1.316	1.460	1.526	63.0	XR[133]
	1.322	1.457	1.542	63.9	MW[134]
	1.332	1.457	1.542		GED[135]
	1.331	1.517	1.565		GED[135]

TABLE 18. Structure parameters for free alkylidenecycloalkenes and -alkanes (distances in Å, angles in degrees)

		B1	B2	B3	B4	Method
		1.332	1.441	1.323	—	MW[139]
		1.332	1.446	1.328	—	MP2/6-31G(d)
	$R^1=R^2=H$	1.335	1.488	1.357	1.516	GED[142]
	$R^1=R^2=H$[15]	1.338	1.480	1.366	1.509	MP2/6-31G(d)
	$R^1=$ *t*-Bu $R^2=$ Me	1.340	1.500	1.373	1.503[a]	XR[143]
		1.343	1.530	1.575	1.486	GED/MW[140]
		1.349	1.470	1.355	1.476	MW[144]
		1.349	1.468	1.357	1.476	MW[145]
		1.349	1.468	1.359	1.469	MP2/6-31G(d)[75]
		1.347	1.476	1.340	1.462	GED[146]
		1.354	1.433	1.343	1.460	XR[147]
		1.343	1.439	1.346	1.435	XR[148]
		MW spectrum consistent with planar ring				MW[149]

[a] Torsion angle C=C−C=C = 57.4°.

(1.343[140] and 1.349[26]) and again the highest distortion is found in the sp^2–sp^2 single bond (1.486 and 1.467 Å), which suffers the most from the ring strain and rehybridization. A spirocyclic substituted[141] derivative, determined by X-ray methods, shows the same features, 1.328[141] and 1.335 Å[4] for the double bonds and 1.479[141] and 1.456 Å[4] for the single bond.

3,4-Dimethylenecyclobut-1-ene has shortened exocyclic double bonds (1.335 Å[142]), which compare well with those of **MCPE** as a result of cross-conjugation. The difference between **MCPA** and **MCPE** for the exocyclic double bond, both determined by GED methods (0.010 Å), is the same as the difference between the ring-saturated dimethylenecyclobutane and the ring-unsaturated dimethylenecyclobutene (0.008 Å). Because of an enhanced conjugation of the methylene π-orbitals with the cyclic π-orbitals in the dimethylenecyclobutene, the conjugation between both methylene groups is reduced, leading to a longer distance in the bond between these groups (1.486 vs 1.516 Å, see Table 18). However, increased ring strain in the unsaturated ring has the same effect. For a derivative, the 1,2-di-*tert*-butyl-3,4-diisopropylidenecyclobut-1-ene[143], this conjugation is reduced due to a torsion of the ring system because of the bulky substituents, which leads to almost equalized single bonds in the ring (see Table 18).

The parent fulvene, 5-methylene-1,3-cyclopentadiene, was the subject of numerous calculations and conformational considerations. Both structures derived from microwave spectra[144,145] agree with the *ab initio* data[75], the cross-conjugation from both sides reduces the length of the exocyclic double bond which is even shorter than the endocyclic double bonds. The consistency of two experimental and the *ab initio* data underline the reliability of the assumption that the exocyclic double bond should be shorter than the endocyclic ones. X-ray data from numerous derivatives, e.g. the 1,2,3,4,6-pentaphenylfulvene[150] or bicyclo[3.3.1]nonane-9-fulvene[151], however, give a nonuniform picture of the difference of the endocyclic and exocyclic bond distances. For the first mentioned, the exocyclic bond is 0.012 Å longer than the endocyclic double bond, and for the latter it is 0.008 Å shorter. Therefore these data are not considered for further discussion.

The GED data of isopropylidenecyclopentadiene or dimethylfulvene[146] deviate essentially from those of the parent compound; the exocyclic double bond is 0.007 Å longer than the endocyclic double bond. In an old X-ray determination[148] it is 0.003 Å shorter, and a very recent and accurate X-ray structure[147] gives a 0.011 Å longer distance, which is consistent with the inductive effect of the two methyl groups. The greatest discrepancy between the two X-ray determinations is found in the distal bond (0.025 Å), which is even shorter than the vicinal bond in the old crystal structure.

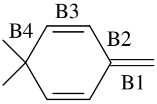
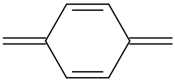
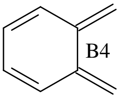
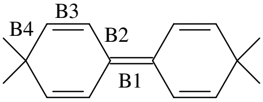
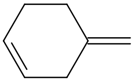
For the parent 6-methylene-1,4-cyclohexadiene a planar structure was found[149]; the 4,4′-dimethyl derivative, however, gave a dihedral angle of 8°[152], which should diminish slightly the cross-conjugation.

For the dimer, the bis(4,4-dimethyl-2,5-cyclohexadiene-1-ylidene), also referred to as pentaene, a second 'biphenyl case' exists, however not such a dramatic one. Biphenyl was found in the gas phase to be twisted by *ca* 42°[153] because of the repulsions of the *ortho*-hydrogen atoms. In favor of the molecular packing in the solid, these repulsions are overcome and a planar structure was found[154]. This example was frequently taken as a textbook example for the so-called 'packing effects' and considered as one of the most prominent examples for differences of structures in the gas phase and in the solid state. For pentaene, however, the central bond is even shorter than in biphenyl and therefore the *ortho*-hydrogen atoms should be even closer in a planar configuration. A torsion as in biphenyl is less likely, and therefore the structure as found in the gas phase[152] in a 'boat' — or 'chair' — fashion-like conformation with dihedral angles of about 9° is quite understandable. Semiempirical calculations confirm a chair-like structure[155] for the complete molecule, but the solid-state X-ray investigation[156] gave an essentially coplanar structure (slight 'stepped' form) with C_i symmetry and slender 'boat'-shaped phenyl rings (maximum torsion angles in the rings, 5.1°). Consequently, the central bond distance is longer than the double bonds in the rings (see Table 19).

p-Xylylene is very much related to the pentaene and polymerizes easily to poly-*p*-xylylene; the monomer should serve as a prototype for a biradical with the gain of aromaticity for the ring as the driving force. Although good *R*-values are achieved, the results from the GED experiments were claimed by the authors to be less reliable[157], endocyclic and exocyclic double bonds seem to be equal (1.381 Å) and the *ab initio* data reveal almost the same length (1.355, 1.358 Å). However, the difference between single and double bonds is much larger for the *ab initio* data (0.10 Å) than for the experiment (0.07 Å), which means that the conjugation is much less than originally anticipated from the experiment. This structure compares well with **DSD2** (Table 9), which has two spiroconnected cyclopropane rings instead of the exomethylene groups. There, the experimental difference between the single and double bond is larger (0.147 Å) than the calculated difference (0.125 Å).

4-Methylenecyclohex-1-ene (Table 19) is not planar and the MW data do not allow any detailed discussion on the distances because of the conformational behavior, which is consistent with a high barrier to ring conversion[159]. No X-ray structures

TABLE 19. Structure parameters for six-membered ring alkylidenecycloalkenes (distances in Å)

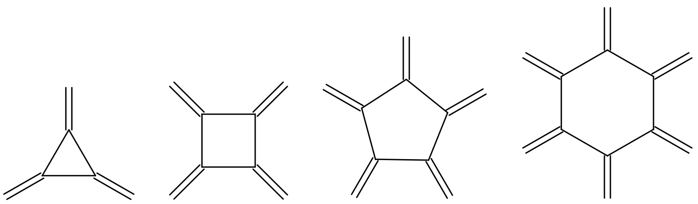
	B1	B2	B3	B4	Method[a]
	1.357	1.478	1.352	1.493	GED[152]
	1.381 1.358	1.451 1.458	1.381 1.355	— —	GED[157] MP2[75]
	1.356	1.458	1.357	1.484	MP2[75]
	1.382 1.37 1.374	1.472 1.46 1.462	1.350 1.33 1.327	1.496 1.50 1.499	GED[152] XR[156] XR[158]
	MW spectrum consistent with higher barrier to ring inversion				MW[159]

[a] MP2 = MP2/6-31G(d)

were found which provide more detailed information on the parent structure. For the 5,6-dimethylenecyclohexa-1,3-diene structure type (Table 19) no experimental data are available which give some idea about the delocalization in the ring. The *ab initio* data reveal a larger difference in bond distances (0.128 Å), which means that the conjugation in the ring should be even smaller than in the *p*-xylylene.

E. Radialenes

Radialenes are a class of compounds that have only relatively recently been synthesized and described[160–162]. They may also be described as all-*exo*-methylene-cycloalkanes, and the first four members of this group of molecules, which we for the convenience of the reader, will refer to by the number of ring atoms, are presented in Figure 9.



(3) **(4)** **(5)** **(6)**

FIGURE 9. Structures of radialenes

Numerous heteroradialenes, in which the *exo*-methylene groups are replaced by oxygen, nitrogen or sulfur atoms, have also been synthesized and studied because of their interesting electrical and magnetic properties. Heteroradialenes are, however, not included in this review.

Two questions related to the structure of radialenes are of special interest:

1. What kind of interaction exists between the π-electrons of the exocyclic C=C bonds?
2. Which factors determine the conformation of the radialene rings?

The radialene double bonds in a planar radialene ring will have overlapping π-orbitals, and it is reasonable to assume that the π-electrons in such a case will be delocalized and that this will have some influence on the lengths of the C−C and C=C bonds. Among the parent **3**–**6** radialene molecules **5** is not known, and so far only the planar molecule **3** has been the subject of an experimental structure investigation. It is therefore at present not possible to obtain experimental evidence about the structure and conformation of the parent **4**, **5** and **6** radialenes. For all these hydrocarbons a number of substituted species are known and have been studied (see below), but as the substituents result in increased nonbonded repulsions between the enlarged exocyclic groups, the preferred conformations of these species will probably differ from those of the parent compounds. In order to gain insight into the conformations of the parent radialene rings, one is therefore limited to information available from theoretical calculations. We have carried out MP2/6-31G(d,p) calculations with full geometry optimization for the parent radialene molecules **3**, **4**, **5** and **6**, and some of the results are shown in Table 20.

According to these calculations the minimum energy conformations of [3]- and [4]radialenes are planar, that of **5** is nearly planar, while the minimum energy conformer of **6** is a chair, which is flattened compared to that of cyclohexane (ring dihedral angles: 40.48°, vs 54°). It is reasonable to assume that coplanar structures might be advantageous for radialenes, if the total π-system of a ring is considered separately. The nonbonded repulsions involving hydrogen atoms of adjacent methylene groups will, however, be substantial for planar conformers of rings larger than **5**. The H---H distance for planar [6]radialene is, for example, estimated to be approximately 1.7 Å. The effect of nonbonded repulsions is illustrated by the calculated H---H distances presented in Table 20. In **3** this distance (3.8 Å) is so large that negligible interaction will occur. Also, in planar **4** this distance is

TABLE 20. Structure parameters obtained from MP2/6-31G(d,p) calculations (distances in Å, angles in degrees). Some similarly calculated data for 1,3-butadiene are shown for comparison

	3	**4**	**5**[e]	**5**[f]	**6**	**1,3-Butadiene**
$C-C_{ring}$	1.4448	1.4925	1.4848	1.4834	1.4829	1.4569
C=C	1.3387	1.3408	1.3456	1.3453	1.3456	1.3431
C−H	1.0813	1.0817	1.0810	1.0812[h]	1.0812	1.083[h]
∠C=C−H	121.04	121.26	121.59	121.53	120.97	121.45[h]
H··H[a]	3.808	2.875	2.241	2.3450[c]	2.805	
$C-C-C-C_{ring}$	0.0	0.0	0.0 (Ass.)	12.06[d]	40.48	
Bond bending[g]	27.8	14.0		5.6	1.3	
E[b]	−231.35543	−308.55248	−385.74467	−385.74552	−462.90302	

[a] Distance between nearest hydrogens in adjacent methylene groups.

[b] Total energies in Hartrees.

[c] Average value of 2.295; 2.295; 2.364; 2.406; 2.364[Å].

[d] Average absolute value of −5.75; 15.08; −18.64; 15.08; −5.75 (deg).

[e] Planar conformer.

[f] Twist-envelope conformer.

[g] Deviation between orbital direction and line of nuclear centers in the ring.

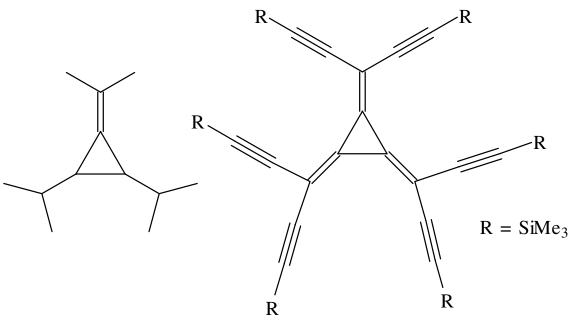
[h] Average value.

clearly larger than the sum of the Van der Waals radii of the two hydrogen atoms. The latter quantity is an ill-defined quantity that may be derived in a number of ways, and the results are not always consistent. We will here use Pauling's Van der Waals radius for hydrogen, 1.20 Å[163]. For a planar conformer of **5** the calculated shortest H---H distance, 2.24 Å, is somewhat smaller than the sum of the Van der Waals radii, while these distances are only slightly smaller than this value in the minimum energy twist-envelope conformer. A reasonable interpretation of these data is that a planar ring is preferred by the [5]radialene π-system, but since this conformation implies a certain degree of nonbonded repulsion between hydrogens on adjacent methylene groups, the total minimum energy conformation is achieved for a conformer based on a compromise between maximum π-orbital overlap and minimum nonbonded repulsion. The calculated energy is thereby reduced by *ca* 2.1 $\mathrm{kJ\,mol^{-1}}$, relative to a planar **5** conformer.

The reason for the minimum energy conformer of **6** cannot be as simple as that proposed for **5**, as the former is far more puckered than what is necessary for minimizing the H---H nonbonded repulsions. Valence angle strain is another factor that might be important in this case. The similarity to the chair conformer of cyclohexane is striking, although the calculated [6]radialene conformation is less puckered.

The calculated difference between single and double CC bond lengths (**3**, 0.106 Å; **4**, 0.152 Å; **5**, 0.139 Å; **6**, 0.137 Å) is, with the exception of **3**, larger for the radialenes than for 1,3-butadiene (0.113 Å). This might indicate that the π-electron delocalization in the radialenes is reduced compared to that in 1,3-butadiene. An alternative explanation for the calculated bond length differences could be attributed to the deviations between the carbon orbital directions in the ring C−C bonds and the line connecting two neighboring ring carbon atoms in the radialenes (Table 20). The CC orbital overlap in a ring will be reduced proportionally to the magnitude of such deviations, resulting in increased C−C ring bond lengths. The electronic structure of **3** is sufficiently different from that of 1,3-butadiene to render a comparison between the structures of these two molecules meaningless.

Relatively few structural studies of radialenes have been carried out, and most of these are X-ray crystallographic studies. The first structure study of a radialene was, however, a gas electron diffraction study of **3** that appeared in 1968[164]. The molecule was found to be planar with $D_{3\mathrm{h}}$ symmetry, in agreement with information from IR and Raman spectroscopic measurements[165]. To the best of our knowledge only two structures of substituted [3]radialene have been reported since then. In both molecules all six hydrogens are equally substituted: in one case with methyl groups[166] **(7)** and in the other with trimethylsilylethynyl groups[167] **(8)**; see Figure 10. In hexamethyl[3]radialene **(7)** the $D_{3\mathrm{h}}$



(7) **(8)**

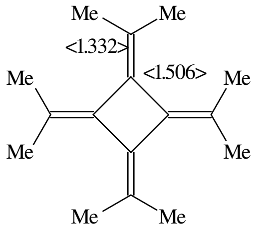
FIGURE 10. Structures of substituted [3]radialenes

symmetry of the parent system is not noticeably perturbed, while the deviation from this ideal symmetry is larger in the trimethylsilylethynyl **(8)** derivative, presumably because of crystal packing effects. The lengths of the C−C bonds in the ring are: **3**, 1.453(20) Å; **7**, 1.451(11) Å and **8**, 1.420(5)−1.431(3) Å. It therefore appears that the C−C bond in the hexakis(trimethylsilylethynyl) derivative is smaller than in the parent molecule. However, this cannot be stated with certainty, as the two structures have been obtained with different methods and because the GED results[164] have rather large error limits. The exocyclic double bonds of the three studies are: **3**, 1.343(20) Å; **7**, 1.331(1) Å; **8**, 1.350(4) Å, 1.355(4) Å, 1.358(3) Å. The exocyclic CC double bonds in **8** appear to be significantly longer than in **7**. This is, however, not surprising, as the exocyclic double bonds in **8** are cross-conjugated with the ethynyl substituents. The experimental results available for [3]radialenes are in good agreement with the calculated results for the parent compound (Table 20).

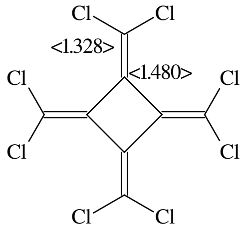
Considerably more structure data are available for [4]radialenes than for their smaller homologs[168−177]. The structure of the parent molecule **4** has not been determined yet, but its vibrational spectrum is in agreement with a planar molecule of $D_{4\mathrm{h}}$ symmetry[178]. Most [4]radialene structures are, however, found to be puckered: **9**, 22.1°[168]; **10**, 26.5°[172]; **11**, 19.2°[173]; **12**, 34.7°[174]. These include, for example the molecules shown in Figure 11.

The nonplanarity of these [4]radialene molecules is obviously caused by nonbonded repulsions between the substituents on the methylene groups. On the other hand, the three [4]radialenes in Figure 12 are observed to have planar radialene systems **13**[169], **14**[170], **15**[166].

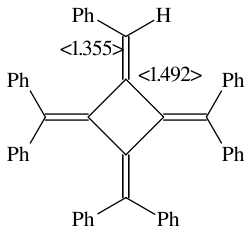
These molecules also have large substituents, and it might seem surprising that the radialene rings avoid puckered conformations in these species. The nonbonded repulsions are, however, reduced in these molecules because of external ring closures **(13)** or because two of the exocylic CC double bonds involve cumulated double bond systems (**14** and



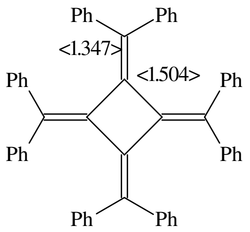
(9)



(10)

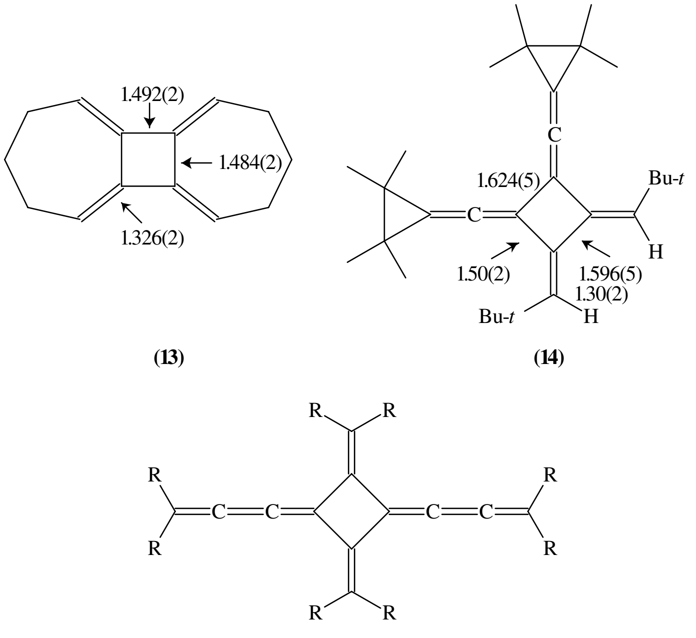


(11)



(12)

FIGURE 11. Structures of substituted puckered [4]radialenes (distances in Å)



(13) **(14)**

(15)

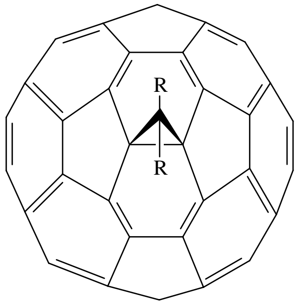
FIGURE 12. Structures of substituted planar [4]radialenes (distances in Å)

15), where the 'substituents' are pointing away from the adjacent methylene groups. Based on the available experimental information for [4]radialenes and the theoretically derived structure for **4**, one might therefore conclude that the preferred conformation for [4]radialene is planar, and that the ring is easily distorted by substitution due to nonbonded repulsions.

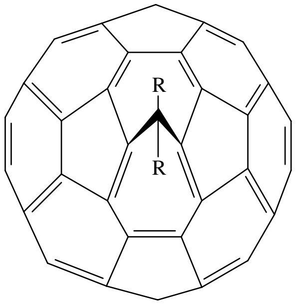
The parent [5]radialene **(5)** has so far evaded preparation. The decamethyl derivative is, however, known, and this molecule is found to have a half-chair conformation, with approximately C_2 symmetry[179]. There are, however, observations indicating that [5]radialene is a more interesting structural system than these meager data suggest. A [5]radialene-type bonding pattern is, for example, present in the newly discovered C_{60} molecule (buckminsterfullerene). A PM3 computational and experimental study of the [6,6]-closed **(16a)** and [6,5]-open **(17a)** methanofullerenes[180] demonstrated that the electronic basis for the experimentally preferred formation of **16a** and **17a** over the [6,6]-open **(16b)** and [6,5]-closed **(17b)** isomers of methanofullerenes (see Figure 13) is the preservation of the [5]radialene-type bonding pattern by these two structures.

The [6]radialenes are normally observed to have chair conformations[164,168,181,182], although a twist-boat conformation has been observed for a very highly substituted [6]radialene molecule[183]. A planar [6]radialene system has also been observed for thiophene-annulated cyclohexane **18**[184] and **19**[185] (Figure 14).

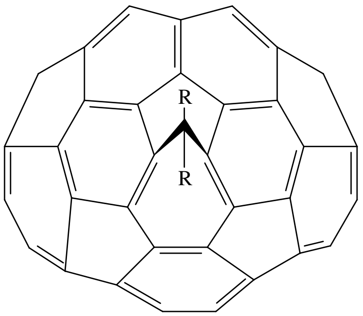
The latter two molecules are, however, special cases, where forces other than those inherent in the [6]radialene system are determining the preferred conformation. Hexakis(ethylidene)cyclohexane is the only radialene molecule where structure results obtained in the solid state[181], as well as in the gas phase[182], are available for comparison (Table 21).



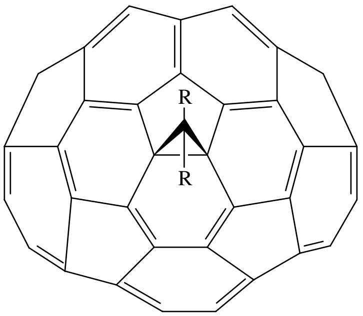
(16a)



(16b)

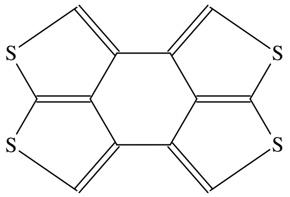


(17a)

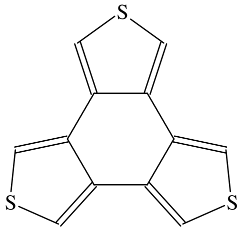


(17b)

FIGURE 13. Structures of methanofullerenes: [6,6]-closed (**16a**), [6,6]-open **(16b)**, [6,5]-closed **(17b)** and [6,5]-open **(17a)**



(18)

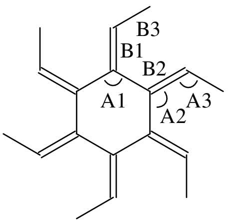


(19)

FIGURE 14. Substituted [6]radialene (planar)

The molecule is found to be somewhat less puckered in the solid state than in the gas phase, presumably because of crystal packing effects. Apart from this, the structure parameters from the two studies are in excellent agreement. The C−C−C−C dihedral ring angles are observed to be ±46.2° in the crystal and ±53.0(6)° in the gas phase. The small differences in some of the angle parameters resulting from the two studies may generally be attributed to the flattening of the ring in the crystal state. The observed

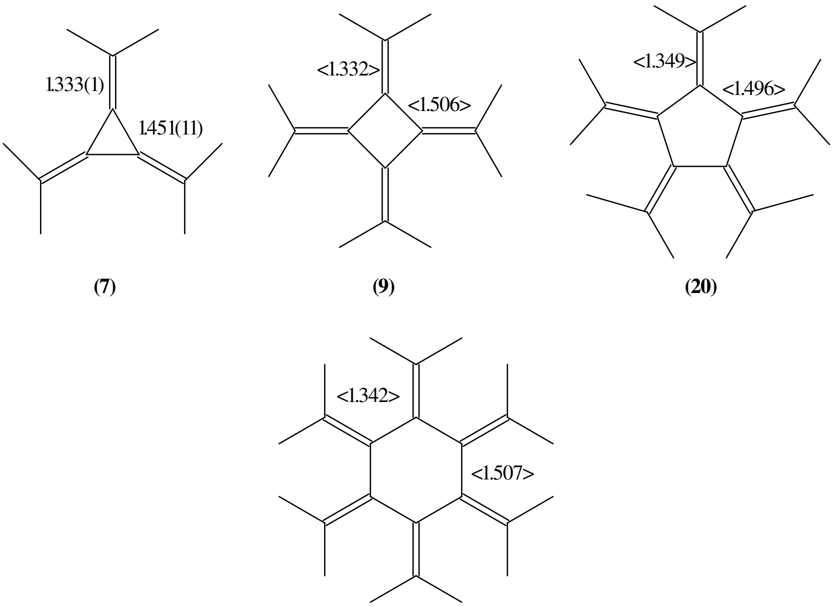
TABLE 21. Structural parameters for hexakis(ethylidene)-cyclohexane from gas electron diffraction (GED) and X-ray crystallography (XR) (distances in Å, angle in degrees)

	Parameter	GED[182]	XR[181]
	B1	1.347(1)	1.334(3)
	B2	1.494(2)	1.495(3)
	B3	1.508(3)	1.497(3)
	A1	112.1(2)	114.1(2)
	A2	121.3(4)	121.1(2)
	A3	127.0(6)	128.1(2)
	T1[a]	176.4	174.0
	T2[b]	±53.0	±46.2

[a] T1 = torsion angle C—C=C—CH_3.
[b] T2 = torsion angle $(C—C—C—C)_{ring}$

C—C—C—C dihedral angle in gaseous hexakis(ethylidene)cyclohexane is 12.5° larger than the corresponding angle calculated for the parent radialene (**6**). This seems reasonable when the increased nonbonded repulsion due to the methyl substituents in the former is taken into account.

In order to get insight into the preferred orientations of the various radialene systems, we might consider the permethylated derivatives of the parent compounds, since



(7) **(9)** **(20)**

(21)

FIGURE 15. Structures of all-methyl substituted radialenes (distances in Å)

some structure data are available for all of them: **7**[166,171], **9**[164,168], **20**[179] and **21**[164,168] (Figure 15).

The endocyclic CC bonds in [3]radialenes are generally found to be about 0.05 Å shorter than those in the higher radialenes. This effect is also reproduced by the *ab initio* calculations (see Table 20), and is primarily attributed to the special bonding pattern in a three-membered ring. For exocyclic C=C bonds the correlation between ring size and bond length is more questionable. Hexamethyl[3]radialene is the only permethylated radialene with a planar radialene system. The nonplanarity of the other radialenes is clearly due to repulsions between neighboring methyl groups. The shortest distances between methyl carbon atoms on adjacent CC double bonds in planar conformations may be estimated to be 3.80, 2.56, 1.80 and 1.30 Å for permethylated [3]-, [4]-, [5]- and [6]radialenes (**7**, **9**, **20** and **21**), respectively. Only in the methylated [3]radialene (**7**) is a planar structure therefore possible without severe steric repulsions between the substituents.

Planar conformations of radialenes with five or more ring atoms will always be more or less destabilized due to nonbonded repulsions, unless special structural effects that stabilize a planar conformation are present. The available experimental data indicate, however, that radialene systems generally prefer planar conformations, if steric effects are not taken into account.

III. ACKNOWLEDGMENTS

The authors (RB, JBB, TH) gratefully acknowledge the help of A. Müller, the Fonds der Chemischen Industrie and the Deutsche Forschungsgemeinschaft for financial help and for the donation of several compounds which could be structurally investigated for the purpose of this chapter which came from H. Hopf (Braunschweig), F.-G. Klärner (Essen), S. Kozhushkov (Göttingen) and A. de Meijere (Göttingen). MT has received support from the Alexander von Humboldt Foundation and from the Norwegian Supercomputing Committee through a grant of computing time.

IV. REFERENCES

1. See, for example: D. O. Cowan and R. L. Drisko, *Elements of Photochemistry*, Chap. 8, Plenum Press, New York, 1976.
2. B. W. McClelland and K. Hedberg, *J. Am. Chem. Soc.*, **109**, 7404 (1987).
3. B. Cadioli and E. Gallinella, *J. Mol. Struct.*, **31**, 199 (1976).
4. J. Benet-Buchholz, T. Haumann and R. Boese, unpublished results.
5. M. Eckert-Maksic, R. Gleiter, N. S. Zefirov, S. I. Kozhushkov and T. S. Kuznetsova, *Chem. Ber.*, **124**, 371 (1991).
6. G. Schultz and I. Hargittai, *J. Mol. Struct.*, **346**, 63 (1995).
7. D. Van Hemelrijk, L. Van den Enden, H. Geise, H. Sellers and L. Schäfer, *J. Am. Chem. Soc.*, **102**, 2189 (1980).
8. S. Kondo, E. Hirota and Y. Morino, *J. Mol. Spectrosc.*, **28**, 471 (1968).
9. T. Haumann, R. Boese, S. I. Kozhushkov and A. de Meijere, unpublished results.
10. A. Schweig, U. Weidner, J. G. Berger and W. Grahn, *Tetrahedron Lett.*, 557 (1973).
11. R. Gleiter, R. Haider, P. Bischof and H.-J. Lindner, *Chem. Ber.*, **116**, 3736 (1983).
12. F. W. Langkilde, R. Wilbrandt and A. M. Brouwer, *J. Phys. Chem.*, **94**, 4809 (1990).
13. W. Tang and T. Bally, *J. Phys. Chem.*, **97**, 4365 (1993).
14. F. W. Langkilde, B. Amstrup, R. Wilbrandt and A. M. Brouwer, *Spectrochim. Acta*, **45**, 883 (1989).
15. H. O. Villar, M. Dupuis and E. Clementi, *Phys. Rev.*, **B37**, 2520 (1988).
16. H. O. Villar, M. Dupuis, J. D. Watts and E. Clementi, *J. Chem. Phys.*, **88**, 1003 (1988).
17. H. O. Villar and M. Dupuis, *Theor. Chim. Acta*, **83**, 155 (1992).
18. G. Orlandi, F. Zerbetto and M. Z. Zgierski, *Chem. Rev.*, **91**, 887 (1991).
19. E. Kraka and D. Cremer, in *Theoretical Models of Chemical Bonding, Part 2* (Ed. Z. Maksić), Springer-Verlag, Berlin, 1990, p. 453.

20. L. Rimai, M. E. Heyde and D. Gill, *J. Am. Chem. Soc.*, **95**, 4493 (1973).
21. C. R. Fincher, C. E. Chen, A. J. Heeger, A. G. McDiarmid and J. B. Hastings, *Phys. Rev. Lett.*, **48**, 100 (1982).
22. V. Schomaker and L. Pauling, *J. Am. Chem. Soc.*, **61**, 1769 (1939).
23. M. J. S. Dewar and H. N. Schmeising, *Tetrahedron*, **5**, 166 (1959).
24. E. D. Glendening, A. E. Reed, J. E. Carpenter and F. Weinhold: *NBO 3.0 Program Manual*, Department of Chemistry, University of California-Irvine, California 92717.
25. M. J. Frisch, G. W. Trucks, H. B. Schlegel, P. M. W. Gill, B. G. Johnson, M. A. Robb, J. R. Cheeseman, T. A. Keith, G. A. Petersson, J. A. Montgomery, K. Raghavachari, M. A. Al-Laham, V. G. Zakrzewski, J. V. Ortiz, J. B. Foresman, J. Cioslowski, B. B. Stefanov, A. Nanayakkara, M. Challacombe, C. Y. Peng, P. Y. Ayala, W. Chen, M. W. Wong, J. L. Andres, E. S. Replogle, R. Gomperts, R. L. Martin, D. J. Fox, J. S. Binkley, D. J. Defrees, J. Baker, J. P. Stewart, M. Head-Gordon and J. A. Pople, *Gaussian 94* (Revision A.1), Gaussian, Inc., Pittsburgh PA, 1995.
26. K. Kveseth, R. Seip and D. Kohl, *Acta Chem. Scand.*, **A34**, 31 (1980).
27. H. Hopf, R. Hänel, P. G. Jones and P. Bubenitschek, *Angew. Chem., Int. Ed. Engl.*, **33**, 1369 (1994).
28. H. Hopf, R. Hänel, P. G. Jones and P. Bubenitschek, *Angew. Chem., Int. Ed. Engl.*, **35**, 337 (1996).
29. GED reinvestigations of *cis* and *trans* isomers of 1,3,5-hexatriene have been started by one of the authors (MT).
30. W. Caminati, G. Grassi and A. Bauder, *Chem. Phys. Lett.*, **148**, 13 (1988).
31. M. Traetteberg, G. Paulen, S. J. Cyvin, Y. N. Panchenko and V. I. Mochaklov, *J. Mol. Struct.*, **116**, 141 (1984).
32. C. F. Aten, L. Hedberg and K. Hedberg, *J. Am. Chem. Soc.*, **90**, 2463 (1968).
33. M. Traetteberg, *Acta Chem. Scand.*, **24**, 2295 (1970).
34. I. L. Karle and K. S. Dragonette, *Acta Crystallogr.*, **19**, 500 (1965).
35. H.-F. Klein, M. Mager, S. Isringhausen-Bley, U. Flörke and H.-J. Haupt, *Organometallics*, **11**, 3174 (1992).
36. M. Traetteberg, *Acta Chem. Scand.*, **22**, 628 (1968).
37. M. Traetteberg and G. Paulen, *Acta Chem. Scand.*, **A28**, 1150 (1974).
38. M. Traetteberg, *Acta Chem. Scand.*, **22**, 2294 (1968).
39. T. Hall, S. M. Bachrach, C. W. Spangler, L. S. Sapochak, C. T. Lin, H. W. Guan and R. D. Rogers, *Acta Crystallogr.*, **C45**, 1541 (1989).
40. R. H. Baughman, B. E. Kohler, I. J. Levy and C. Spangler, *Synthetic Metals*, **11**, 37 (1985).
41. W. Drenth and E. E. H. Wiebenga, *Acta Crystallogr.*, **8**, 755 (1955).
42. A. Kiehl, A. Eberhardt, M. Adam, V. Enkelman and K. Mullen, *Angew. Chem., Int. Ed. Engl.*, **31**, 1588 (1992).
43. M. Traetteberg, P. Bakken, H. Hopf and R. Hänel, *Chem. Ber.*, **127**, 1469 (1994).
44. J. J. Fisher and J. Michl, *J. Am. Chem. Soc.*, **109**, 1056 (1987).
45. B. R. Arnold, V. Balaji and J. Michl, *J. Am. Chem. Soc.*, **112**, 1808 (1990).
46. (a) I. L. Alberts and H. F. Schaefer III, *Chem. Phys. Lett.*, **161**, 375 (1989).
    (b) J. E. Rice, B. Liu, T. J. Lee and C. M. Rohlfing, *Chem. Phys. Lett.*, **161**, 277 (1989).
    (c) C. W. Bock, P. George and G. P. Trachtman, *Theor. Chim. Acta*, **64**, 293 (1984).
    (d) G. R. De Maré, *J. Mol. Struct. (THEOCHEM)*, **107**, 127 (1984).
    (e) K. B. Wiberg and R. E. Rosenberg, *J. Am. Chem. Soc.*, **112**, 1509 (1990).
    (f) H. Guo and M. Karplus, *J. Chem. Phys.*, **94**, 3679 (1991).
47. M. Traetteberg, *Acta Chem. Scand.*, **24**, 2295 (1970).
48. M. Traetteberg and L. K. Sydnes, *Acta Chem. Scand.*, **B31**, 387 (1977).
49. M. Traetteberg, H. Hopf, H. Lipka and R. Hänel, *Chem. Ber.*, **127**, 1459 (1994).
50. W. R. Roth, O. Adamczak, R. Breuckmann, H.-W. Lennartz and R. Boese, *Chem. Ber.*, **124**, 2499 (1991).
51. M. Traetteberg and G. Paulen, *Acta Chem. Scand.*, **A28**, 1 (1974).
52. N. F. Woolsey, L. J. Radonovich, F. M. Saad and M. Brostrom, *J. Org. Chem.*, **49**, 1937 (1984).
53. A. L. Rheingold, D. L. Staley, R. F. Heck and L. Silverberg, *Acta Crystallogr.*, **C46**, 144 (1990).
54. G. Maier, *Angew. Chem., Int. Ed. Engl.*, **27**, 309 (1988).
55. H. Irngartinger, N. Riegler, K. D. Malsch, K.-A. Schneider and G. Maier, *Angew. Chem., Int. Ed. Engl.*, **19**, 211 (1980).

56. H. Irngartinger and M. Nixdorf, *Angew. Chem., Int. Ed. Engl.*, **22**, 403 (1983).
57. J. D. Dunitz, C. Krüger, H. Irngartinger, E. F. Maverick, Y. Wang and M. Nixdorf, *Angew. Chem., Int. Ed. Engl.*, **27**, 387 (1988).
58. D. van Hemelrijk, L. van den Enden, H. J. Geise, H. L. Sellers and L. Schäfer, *J. Am. Chem. Soc.*, **102**, 2189 (1980).
59. J. F. Chiang and C. F. Wilcox, Jr., *J. Am. Chem. Soc.*, **95**, 2885 (1973).
60. D. Damiani, L. Ferretti and E. Gallinella, *Chem. Phys. Lett.*, **37**, 265 (1976).
61. H. Oberhammer and S. H. Bauer, *J. Am. Chem. Soc.*, **91**, 10 (1969).
62. G. Dallinga and L. H. Toneman, *J. Mol. Struct.*, **1**, 117 (1967).
63. G. A. Jeffrey, J. Buschmann, C. W. Lehmann and P. Luger, *J. Am. Chem. Soc.*, **110**, 7218 (1988).
64. G. Dallinga and L. H. Toneman, *J. Mol. Struct.*, **1**, 11 (1967).
65. M. Traetteberg, *Acta Chem. Scand.*, **22**, 2305 (1968).
66. K. Hagen and M. Traetteberg, *Acta Chem. Scand.*, **26**, 3643 (1972).
67. N. Nevins, E. L. Stewart, N. L. Allinger and J. P. Bowen, *J. Phys. Chem.*, **98**, 2056 (1994).
68. M. Traetteberg, *J. Am. Chem. Soc.*, **86**, 4265 (1964).
69. J. Stegemann and H. J. Lindner, *Acta Crystallogr.*, **B35**, 2161 (1979).
70. K. Hagen, L. Hedberg and K. Hedberg, *J. Phys. Chem.*, **86**, 117 (1982).
71. M. Traetteberg, *Acta Chem. Scand.*, **24**, 2285 (1970).
72. W. Haugen and M. Traetteberg, in *Selected Topics in Structure Chemistry* (Eds. P. Andersen, O. Bastiansen and S. Furberg), Universitetsforlaget, Oslo, 1967.
73. K. H. Claus and C. Krüger, *Acta Crystallogr.*, **C44**, 1632 (1988).
74. See J. Liebman, Chapter 3, *'Thermochemistry of Dienes and Polyenes'*, in the present volume.
75. A. Skancke, Personal communication.
76. T. K. Avirah, T. B. Malloy Jr. and R. L. Cook, *J. Chem. Phys.*, **71**, 2194 (1979).
77. N. Nevins, E. L. Stewart, N. L. Allinger and J. P. Bowen, *J. Phys. Chem.*, **98**, 2056 (1994).
78. P. O. Crews, *Chem. Commun.*, **11**, 583 (1971).
79. W. v. E. Doering, G. Laber, R. Vonderwahl, N. F. Chamberlain and R. B. Williams, *J. Am. Chem. Soc.*, **78**, 5448 (1956).
80. O. Ermer, *J. Am. Chem. Soc.*, **98**, 3964 (1976).
81. J. Bordener, R. G. Parker and R. H. Stanford Jr., *Acta Crystallogr.*, **B28**, 1069 (1972).
82. T. J. Katz, *J. Am. Chem. Soc.*, **82**, 3784 (1960).
83. N. Rösch and A. Streitwieser Jr., *J. Organomet. Chem.*, **145**, 195 (1978).
84. A. Almenningen, G. G. Jacobsen and H. M. Seip, *Acta Chem. Scand.*, **23**, 1495 (1969).
85. A. Krause, H. Musso, W. Boland, R. Ahlrichs, R. Gleiter, R. Boese and M. Bär, *Angew. Chem., Int. Ed. Engl.*, **28**, 1379 (1989).
86. C. C. Chiang and I. C. Paul, *J. Am. Chem. Soc.*, **94**, 4741 (1972).
87. S. M. Johnson, I. C. Paul and G. S. D. King, *J. Chem. Soc. (B)*, 643 (1970).
88. J. Bregman, F. L. Hirshfeld, D. Rabinovich and G. M. J. Schmidt, *Acta Crystallogr.*, **19**, 227 (1965).
89. J. M. Robertson and J. G. White, *J. Chem. Soc.*, 607 (1945).
90. F. H. Allen, *Acta Crystallogr.*, **B36**, 81 (1980).
91. M. D. Harmony, S. N. Mathur, J.-I. Choe, M. Kattija-Ari, A. E. Howard and S. W. Staley, *J. Am. Chem. Soc.*, **103**, 2961 (1981).
92. A. Almenningen, P. Bakken, A. de Meijere and M. Traetteberg, *Acta Chem. Scand.*, **44**, 470 (1990).
93. R. Boese, in *Advances in Strain in Organic Chemistry*, Vol. II (Ed. B. Halton), JAI Press, Greenwich, Connecticut, 1992, pp. 191–254.
94. H. E. Simmons and T. Fukunaga, *J. Am. Chem. Soc.*, **89**, 5208 (1967).
95. M. F. Semmelhack, J. S. Foos and S. Katz, *J. Am. Chem. Soc.*, **95**, 7325 (1973).
96. T. Haumann, J. Benet-Buchholz and R. Boese, *J. Mol. Struct.*, **374**, 299 (1996).
97. D. L. Cullen, B. Hass, D. G. Klunk, T. V. Willoughby, C. N. Morimoto, E. F. Meyer Jr., G. Farges and A. Dreiding, *Acta Crystallogr.*, **B32**, 555 (1976).
98. (a) R. Huisgen, *Pure Appl. Chem.*, **53**, 171 (1981).
    (b) J. Spanget-Larsen and R. Gleiter, *Tetrahedron Lett.*, **23**, 2435 (1982).
    (c) K. N. Houk, N. G. Rondan, F. K. Brown, W. L. Jorgensen, J. D. Madura and D. C. Spellmeyer, *J. Am. Chem. Soc.*, **105**, 5980 (1983).
99. E. A. McNeill and F. R. Scholer, *J. Mol. Struct.*, **31**, 65 (1976).
100. M. J. Cardillo and S. H. Bauer, *J. Am. Chem. Soc.*, **92**, 2399 (1970).

101. H. Irngartinger, T. Oeser, R. Jahn and D. Kallfaβ, *Chem. Ber.*, **125**, 2067 (1992).
102. H. Irngartinger and J. Deuter, *Chem. Ber.*, **123**, 341 (1990).
103. K. Weinges, J. Klein, W. Sipos, P. Günther, U. Huber-Patz, H. Rodenwald, J. Deuter and H. Irngartinger, *Chem. Ber.*, **119**, 1540 (1986).
104. K. Weinges, W. Sipos, J. Klein, J. Deuter and H. Irngartinger, *Chem. Ber.*, **120**, 5 (1987).
105. R. Bianchi, T. Pilati and M. Simonetta, *Acta Crystallogr.*, **C39**, 378 (1983).
106. R. Bianchi, T. Pilati and M. Simonetta, *J. Am. Chem. Soc.*, **103**, 6426 (1981).
107. R. Bianchi, G. Morosi, A. Mugnoli and M. Simonetta, *Acta Crystallogr.*, **B29**, 1196 (1973).
108. R. Bianchi, T. Pilati and M. Simonetta, *Acta Crystallogr.*, **B36**, 3146 (1980).
109. G. Maier, N. H. Wiegand, S. Baum, R. Wüllner, W. Mayer and R. Boese, *Chem. Ber.*, **122**, 767 (1989).
110. L. A. Paquette, S. Liang, L. Waykole, G. DeLucca, H. Jendralla, R. D. Rogers, D. Kratz and R. Gleiter, *J. Org. Chem.*, **55**, 1598 (1990).
111. E. Heilbronner and H.-D. Martin, *Helv. Chim. Acta*, **55**, 1490 (1972).
112. R. W. Hoffmann, R. Schüttler, W. Schäfer and A. Schweig, *Angew. Chem., Int. Ed. Engl.*, **11**, 512 (1972).
113. J. H. Strange, *Acta Crystallogr.*, **B28**, 1645 (1972).
114. J. Timmermans, *J. Phys. Chem. Solids*, **18**, 1 (1961).
115. R. Boese and M. Nussbaumer, in *Correlations, Transformations and Interactions in Organic Crystal Chemistry*, Vol. VII (Eds. D. W. Jones and A. Katrusiak), Oxford University Press, Oxford, 1994, p. 20.
116. J. Benet-Buchholz, T. Haumann, R. Boese and F.-G. Klärner, unpublished results.
117. A. Yokozeki and K. Kuchitsu, *Bull. Chem. Soc. Jpn.*, **44**, 2536 (1971).
118. G. Knuchel, G. Grassi, B. Vogelsanger and A. Bauder, *J. Am. Chem. Soc.*, **115**, 10845 (1993).
119. F. Brogli, E. Heilbronner and J. Ipaktschi, *Helv. Chim. Acta*, **55**, 2447 (1972).
120. H. E. Zimmermann and R. Paufler, *J. Am. Chem. Soc.*, **82**, 1514 (1960).
121. A. Yokozeki and K. Kuchitsu, *Bull. Chem. Soc. Jpn.*, **44**, 1783 (1971).
122. S. Yamamoto, M. Nakata, T. Fukuyama, K. Kuchitsu, D. Hasselmann and O. Ermer, *J. Phys. Chem.*, **86**, 529 (1982).
123. B. Andersen and A. Marstrander, *Acta Chem. Scand.*, **25**, 1271 (1971).
124. A. Amit, R. Huber and W. Hoppe, *Acta Crystallogr.*, **B24**, 865 (1968).
125. P. Luger, J. Buschmann, R. K. McMullan, J. R. Ruble, P. Matias and G. A. Jeffrey, *J. Am. Chem. Soc.*, **108**, 7825 (1986).
126. Y. C. Wang and S. H. Bauer, *J. Am. Chem. Soc.*, **94**, 5652 (1972).
127. G. G. Christoph and M. A. Beno, *J. Am. Chem. Soc.*, **100**, 3156 (1978).
128. I. Sellner, H. Schuster, H. Sichert, J. Sauer and H. Nöth, *Chem. Ber.*, **116**, 3751 (1983).
129. G. J. H. van Nes and A. Vos, *Acta Crystallogr.*, **B35**, 2593 (1979).
130. E. Hirota, Y. Endo, S. Saito, K. Yoshida, I. Yamaguchi and K. Machida, *J. Mol. Spectrosc.*, **89**, 223 (1981).
131. R. Boese, N. Niederprüm and D. Bläser, *Struct. Chem.*, **3**, 399 (1992).
132. I. Tokue, T. Fukuyama and K. Kuchitsu, *J. Mol. Struct.*, **23**, 33 (1974).
133. (a) R. Boese, in *Advances in Strain in Organic Chemistry*, Vol. II (Ed. B. Halton), JAI Press, Greenwich, Connecticut, 1992, p. 219.
    (b) R. Boese, D. Bläser, E. W. Billups and M. M. Haley, in preparation.
134. V. W. Laurie and W. M. Stigliani, *J. Am. Chem. Soc.*, **92**, 1485 (1970).
135. L. V. Vilkov, V. S. Mastryukov and N. I. Sadova, *Determination of the Geometrical Structure of Free Molecules*, Mir Publishers, Moscow, 1983, p. 125.
136. (a) W. J. Hehre and J. A. Pople, *J. Am. Chem. Soc.*, **97**, 6941 (1975).
    (b) A. Sabljić and N. Trinajstic, *Croat. Chem. Acta*, **51**, 249 (1978).
    (c) W. C. Herndon, *Pure Appl. Chem.*, **52**, 1459 (1980).
    (d) K. Jug, *J. Org. Chem.*, **48**, 1344 (1983).
137. (a) B. A. Hess Jr. and L. J. Schaad, *J. Org. Chem.*, **37**, 4179 (1972).
    (b) J. Aihara, *Bull. Chem. Soc. Jpn.*, **56**, 1935 (1983).
    (c) P. H. M. Buzelaar, E. Kraka, D. Cremer and P. v. R. Schleyer, *J. Am. Chem. Soc.*, **108**, 561 (1986).
138. F. Fratev, D. Bonchev and V. Enchev, *Croat. Chem. Acta*, **54**, 545 (1981).
139. T. D. Norden, S. W. Staley, W. H. Taylor and M. D. Harmony, *J. Am. Chem. Soc.*, **108**, 7912 (1986).

140. L. K. Montgomery, C. A. Wilson and J. D. Wieser, *J. Mol. Struct.*, **129**, 69 (1985).
141. D. S. Yufit, Yu. T. Struchkov, S. I. Kozhushkov and A. De Meijere, *Acta Crystallogr.*, **C49**, 1517 (1993).
142. A. Skancke, *Acta Chem. Scand.*, **22**, 3239 (1968).
143. H. J. Bruins Slot, J. Kroon, J. M. Oostveen, H. J. T. Bos and P. Vermeer, *Acta Crystallogr.*, **C11**, 741 (1982).
144. P. A. Baron, R. D. Brown, F. R. Burden, P. J. Domaille and J. E. Kent, *J. Mol. Spectrosc.*, **43**, 401 (1972).
145. R. D. Suenram and M. D. Harmony, *J. Chem. Phys.*, **58**, 5842 (1973).
146. J. F. Chiang and S. H. Bauer, *J. Am. Chem. Soc.*, **92**, 261 (1970).
147. R. Boese and Th. Haumann, unpublished results.
148. N. Norman and B. Post, *Acta Crystallogr.*, **14**, 503 (1961).
149. W. Hutter, H.-K. Bodenseh and A. Koch, *J. Mol. Struct.*, **319**, 73 (1994).
150. G. Wu, A. L. Rheingold, S. J. Geib and R. F. Heck, *Organometallics*, **6**, 1941 (1987).
151. F. R. Fronczek, J. G. Garcia and M. L. McLaughlin, *Acta Crystallogr.*, **C46**, 1181 (1990).
152. M. Traetteberg, P. Bakken, A. Almenningen, W. Lüttke and J. Janssen, *J. Mol. Struct.*, **81**, 87 (1982).
153. L. A. Carreira and T. G. Towns, *J. Mol. Struct.*, **41**, 1 (1977).
154. G. P. Charbonneau and Y. Delugeard, *Acta Crystallogr.*, **B33**, 1586 (1977).
155. J. Janssen and W. Lüttke, *J. Mol. Struct.*, **81**, 73 (1982).
156. M. Noltemeyer, J. Janssen and W. Lüttke, *J. Mol. Struct.*, **81**, 105 (1982).
157. P. G. Mahaffy, J. D. Wieser and L. K. Montgomery, *J. Am. Chem. Soc.*, **99**, 4514 (1977).
158. R. Boese, D. Bläser and W. v. E. Doering, unpublished results.
159. R. Cervellati, D. Damiani, L. Dore and D. G. Lister, *J. Mol. Spectrosc.*, **139**, 328 (1990).
160. H. Hopf, *Angew. Chem., Int. Ed. Engl.*, **23**, 948 (1984).
161. A. Nickon and E. F. Silversmith, in *Organic Chemistry; The Name Game*, Pergamon, New York, 1987, p. 84.
162. H. Hopf and G. Maas, *Angew. Chem., Int. Ed. Engl.*, **31**, 931 (1992).
163. L. Pauling, *The Nature of the Chemical Bond*, Cornell University Press, New York, 1960, p. 260.
164. E. A. Dorko, J. L. Henscher and S. H. Bauer, *Tetrahedron*, **24**, 2425 (1968).
165. (a) J. C. Burr Jr., E. A. Dorko and J. A. Merritt, *J. Chem. Phys.*, **45**, 3877 (1966).
    (b) K. H. Ree and F. A. Miller, *Spectrochim. Acta*, **A27**, 1 (1971).
    (c) E. A. Dorko, R. Scheps and S. A. Rice, *Z. Phys. Chem. (Munich)*, **78**, 565 (1974).
166. H. Dietrich, *Acta Crystallogr.*, **B26**, 44 (1970).
167. T. Lange, V. Gramlich, W. Amrein, F. Diederich, M. Gross, C. Boudon and J.-P. Gisselbrecht, *Angew. Chem., Int. Ed. Engl.*, **34**, 805 (1995).
168. G. Wilke, *Angew. Chem., Int. Ed. Engl.*, **27**, 185 (1988).
169. S. Hashmi, K. Polborn and G. Szeimies, *Chem. Ber.*, **122**, 2399 (1989).
170. A. E. Learned, A. M. Arif and P. J. Stang, *J. Org. Chem.*, **53**, 3122 (1988).
171. M. Iyoda, M. Oda, Y. Kai, N. Kanehisa and N. Kasai, *Chem. Lett.*, 2149 (1990).
172. F. P. van Remorrtere and F. B. Boer, *J. Am. Chem. Soc.*, **92**, 3355 (1970).
173. H. Hart, D. L. Ward, K. Tanaka and F. Toda, *Tetrahedron Lett.*, **23**, 2125 (1982).
174. M. Iyoda, H. Otani, Y. Kai, Y. Baba and N. Kasai, *J. Am. Chem. Soc.*, **108**, 5371 (1986).
175. F. W. Nader, C.-D. Wacker, H. Irngartinger, U. Huber-Patz, R. Jahn and H. Rodewald, *Angew. Chem., Int. Ed. Engl.*, **24**, 852 (1985).
176. T. Sugimoto, H. Awaji, Y. Masaki, Z. Yoshida, Y. Kai, H. Nakagawa and N. Kasai, *J. Am. Chem. Soc.*, **107**, 5792 (1985).
177. A. Fronda and G. Maas, *Angew. Chem., Int. Ed. Engl.*, **28**, 1663 (1989).
178. F. A. Miller, F. R. Brown and K. H. Rhee, *Spectrochim. Acta*, **A28**, 1467 (1972).
179. M. Iyoda, H. Otani, M. Oda, Y. Kai, Y. Baba and N. Kasai, *J. Chem. Soc., Chem. Commun.*, 1794 (1986).
180. F. Diederich, L. Isaacs and D. Philp, *J. Chem. Soc., Perkin Trans., 2*, 391 (1994).
181. W. Marsch and J. D. Dunitz, *Helv. Chim. Acta*, **58**, 707 (1975).
182. H. Hopf and M. Traetteberg, to appear (1997).
183. T. Sugimoto, Y. Misaki, T. Kajita, Z. Yoshida and N. Kasai, *J. Am. Chem. Soc.*, **109**, 4106 (1987).
184. F. Wudl, R. C. Haddon, E. T. Zellers and F. B. Bramwell, *J. Org. Chem.*, **44**, 2491 (1979).
185. P. Rademacher, R. Boese and W. A. Brett, in preparation.

The Chemistry of Dienes and Polyenes. Volume 1
Edited by Zvi Rappoport

ISBN: 0-471-96512-X

CHAPTER **3**

Thermochemistry of dienes and polyenes

JOEL F. LIEBMAN

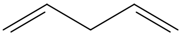
Department of Chemistry and Biochemistry, University of Maryland, Baltimore County Campus, 1000 Hilltop Circle, Baltimore, Maryland 21250, USA
Fax: 001 410-455-2608; e-mail: JLIEBMAN@UMBC2.UMBC.EDU

This study is dedicated to the memory of Prof. Thomas L. Jacobs who first introduced the author to cyclic acetylenes, dienes and cumulenes on an examination in 1963

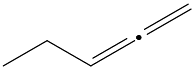
I. INTRODUCTION: SCOPE AND DEFINITIONS

A. What Do We Mean By Dienes and Polyenes?

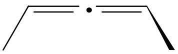
For this chapter we will define a diene as any organic compound that contains two carbon–carbon double bonds, whether the double bonds are nonconjugated as in 1,4-pentadiene, **1**; cumulated or ‘allenic’ as in 1,2- and 2,3-pentadiene, **2** and **3**; or conjugated as in (*Z*)- and (*E*)-1,3-pentadiene, **4** and **5**. Relatedly, a triene contains three carbon–carbon double bonds, a tetraene has four carbon–carbon double bonds, etc. We will use the generic term polyene to encompass trienes, tetraenes, etc., even though we admit now that the thermochemistry of tetraenes and more unsaturated species is sparse enough to make polyene and triene nearly synonymous in the current context. We will largely avoid discussion of ‘buried’ polyenes, since it does not particularly benefit our understanding of polyenes to include discussion of the numerous derivatives of benzene **(6)**, of naphthalene **(7)** or of any other polynuclear aromatic hydrocarbon, even though they could be named systematically as polyenes. Nonetheless, some of these compounds will appear occasionally in our chapter.



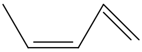
(1)



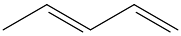
(2)



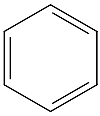
(3)



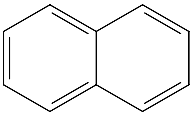
(4)



(5)

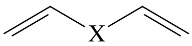


(6)

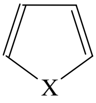


(7)

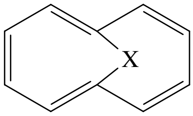
We will also forego discussion of any substituted polyene wherein the substituent is not hydrocarbyl (i.e. composed of any elements other than hydrogen and carbon). This decision does not arise out of lack of interest in these species *per se*, but rather, that discussion of many of the relevant compounds has been presented in earlier thermochemistry chapters elsewhere in other volumes in the 'Functional Groups' series. For example, the energetics of the $X = O$ containing divinyl ether, **8**; furan, **9**; and 1,6-oxido[10]annulene (also known as 11-oxa-bicyclo[4.4.1]deca-1,3,5,7,9-pentaene), **10**; have been recently discussed in the Supplement E2 volume of this series[1] and therein were explicitly compared with those of their corresponding hydrocarbon analogs with $X = CH_2$, 1,4-pentadiene, cyclopentadiene and 1,6-methano[10]annulene, respectively. The $-O-$ vs $-CH_2-$ comparison was shown to be generally interesting and informative where it can be made. The available thermochemical data are disappointingly sparse. For example, there are no thermochemical data for either pyran isomer, **11** or **12** with $X = O$, to include with discussions of the corresponding $X = CH_2$ species, the isomeric 1,3- and 1,4-cyclohexadienes that are discussed at some length in Section V.D of the current chapter. Indeed, not even all hydrocarbyl substituents and their ancillary functionalities and features will be discussed in the current chapter. We now acknowledge we will largely omit discussion of homoaromatic species such as cyclopropanated species and their comparison with the formally related compounds having C=C bonds. Inclusion of this interrelation is quite superfluous in the current chapter since it figured prominently in a recent review of the thermochemistry of cyclopropanes[2].



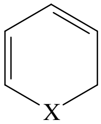
(8)



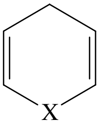
(9)



(10)



(11)



(12)

B. What Do We Mean By Thermochemistry?

As has been the approach for most of the author's other reviews on organic thermochemistry, the current chapter will be primarily devoted to the relatively restricted scope of 'enthalpy of formation' (more commonly and colloquially called heat of formation) and write this quantity as ΔH_f, instead of the increasingly more commonly used and also proper $\Delta H_f{}^\circ$ and $\Delta_f H_m{}^\circ$. No discussion will be made in this chapter on other thermochemical properties such as Gibbs energy, entropy, heat capacity and excess enthalpy. Additionally (following thermochemical convention), the temperature and pressure are tacitly assumed to be 25 °C ('298 K') and 1 atmosphere (taken as either 101,325 or 100,000 Pa) respectively[3] and the energy units are chosen to be kJ mol^{-1} instead of kcal mol^{-1} (where $4.184 \text{ kJ} \equiv 1 \text{ kcal}$, $1 \text{ kJ} = 0.2390 \text{ kcal}$).

Again, following our earlier chapters as precedent, we continue to view intermolecular forces as 'complications' and 'nuisances'. We consider the molecule *per se* to be of sole interest and thus, unless explicitly noted to the contrary, any species discussed in this chapter is to be assumed in the (ideal) gas phase. Admittedly, most organic compounds are 'naturally' liquids or solids under the thermochemically idealized conditions. They are likewise found in the condensed phase for most studies by synthetically or mechanistically inclined chemists. 'Corrections' to the gas are definitionally made by using enthalpies of vaporization (ΔH_v) and of sublimation (ΔH_s), defined by equations 1 and 2:

$$\Delta H_v \equiv \Delta H_f(g) - \Delta H_f(lq) \tag{1}$$

$$\Delta H_s \equiv \Delta H_f(g) - \Delta H_f(s) \tag{2}$$

where g, lq and s refer to gas, liquid and solid, respectively. Phase change enthalpies were obtained from whatever source available: our choice to maximize the use of gas phase data and minimize that from the liquid or solid requires numerous expediencies. In the absence of data from experimental measurements, enthalpies of vaporization for hydrocarbons will usually be estimated using the generally accurate (± 2 kJ mol^{-1}) two-parameter equation of Reference 4. We admit that the procedures for estimating enthalpies of sublimation are generally dependent on values obtained from experimental measurements (either those of enthalpies of fusion[5] or melting point[6]). Nonetheless, some effort will still be made to estimate enthalpies of sublimation.

C. Sources of Data

We have already acknowledged our intent to use relevant estimation approaches to enthalpies of vaporization and sublimation to maximize the usefulness of the data available. That dienes and polyenes have multiple double bonds that are potentially hydrogenatable to the totally saturated aliphatic or alicyclic hydrocarbons allows the employment of two other assumptions. The first assumption argues that the enthalpy of hydrogenation, ΔH_{H_2} measured in a nonpolar solvent is essentially equal to that which would be obtained in the gas phase[7]. The second assumption[8], implicitly employing the first, legitimizes the use of estimation techniques and even molecular mechanics to derive the enthalpy of formation of the totally saturated species. From this last number, the enthalpy of formation of the unsaturated diene or polyene of interest can be derived by equation 3 and simple arithmetic.

$$\Delta H_f\ (\text{unsaturated}) + \Delta H_{H_2} = \Delta H_f\ (\text{saturated}) \tag{3}$$

These latter assumptions make use of thermochemical data ancillary to the enthalpy of hydrogenation. These data are not just the enthalpies of formation of CO_2(g) and H_2O(lq), needed for his/her counterpart who measures enthalpies of combustion. The use of ancillary thermochemical information becomes imperative, e.g. the enthalpy of formation of an alkane that is the product of hydrogenating a diene of interest. It is an easy conceptual step to go from ancillary information to secondary sources of thermochemical data. This is consonant with our own bibliographic preferences and prejudices. In this paper we tacitly choose to cite secondary sources[9] over primary sources. This strongly simplifies the writing and reading of our text at the risk of offending an occasional author of an uncited primary research paper.

II. NONCONJUGATED DIENES AND POLYENES

A. Acyclic Species

It may appear that nonconjugated, acyclic dienes are the simplest and least interesting of all the classes of compounds to be discussed in the current chapter. The reader may wish to ask of the current author who has written numerous earlier reviews on organic thermochemistry: 'Don't you get bored reading hour after hour, day after day, numbers and their derived problems?' To which, he responds 'Yes, and when I do I ask myself 'Why am I bored?' and then I have an interesting project'[10].

The simplest nonconjugated, acyclic diene is 1,4-pentadiene **(1)**, with its enthalpy of formation of 105.6 kJ mol^{-1}. The obvious question is whether the two double bonds are truly independent. If they are, then the enthalpy of hydrogenation of one double bond as in (the identical) reactions 4a and 4b would be precisely one half of that of the hydrogenation of both as in reaction 5.

$$CH_2{=}CHCH_2CH{=}CH_2 + H_2 \longrightarrow CH_3CH_2CH_2CH{=}CH_2 \qquad (4a)$$

$$CH_2{=}CHCH_2CH{=}CH_2 + H_2 \longrightarrow CH_2{=}CHCH_2CH_2CH_3 \qquad (4b)$$

$$CH_2{=}CHCH_2CH{=}CH_2 + 2H_2 \longrightarrow CH_3CH_2CH_2CH_2CH_3 \qquad (5)$$

We would likewise deduce that the formal reaction in equation 6

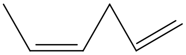
$$CH_2{=}CHCH_2CH{=}CH_2 + CH_3CH_2CH_2CH_2CH_3 \longrightarrow 2CH_3CH_2CH_2CH{=}CH_2 \qquad (6)$$

would then be thermoneutral. In fact, it is exothermic by merely 1.3 ± 2.1 kJ mol^{-1}, a result equal to the expected precise value of 0 within the experimental error bars.

We now turn to the isomeric hexadienes, of which three species qualify for consideration: the 1,5- and the (*Z*)- and (*E*)-1,4- compounds, species **13**, **14** and **15**, respectively. If interaction between the two double bonds in 1,4-pentadiene is so small, we expect this as well for the 1,5-hexadiene. One test of this is to consider reaction 7 by analogy to reaction 6.

$$CH_2{=}CH(CH_2)_2CH{=}CH_2 + CH_3CH_2(CH_2)_2CH_2CH_3 \longrightarrow 2CH_3CH_2(CH_2)_2CH{=}CH_2 \qquad (7)$$

(13)



(14)

(15)

To do so, one can take the enthalpy of formation of *n*-hexane from Pedley, and with the phase independence assumptions in Reference 7, employ the enthalpies of hydrogenation of 1-hexene and 1,5-hexadiene from References 11 and 12 respectively. Alternatively[13], one can forget about the first quantity altogether and simply take the difference of the enthalpies of hydrogenation of the diene and twice that of the monoene. This reaction is endothermic by 1.1 ± 1.8 kJ mol^{-1}, a value statistically indistinguishable from the absence of any interolefin interaction in the diene. Relatedly, for the isomeric 1,4-hexadienes **14** and **15**, equation 8 may be used.

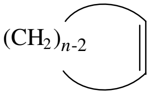
$$CH_3CH{=}CHCH_2CH{=}CH_2 + CH_3(CH_2)_4CH_3 \longrightarrow CH_3CH{=}CH(CH_2)_2CH_3 + CH_3(CH_2)_3CH{=}CH_2 \qquad (8)$$

Again, one may take the difference of the enthalpies of hydrogenation of the diene and the sum of those for the two monoenes. Doing this separately for **14** and **15**, we find the reaction enthalpies for the *Z*- and *E*-dienes are −1.9 ± 1.2 and −1.8 ± 1.1 kJ mol^{-1}. These values are effectively zero. A stabilizing — or destabilizing — interaction was not expected for nonconjugated acyclic dienes and none was found.

B. Acyclic, Polymeric Polyenes

In this section we will discuss the thermochemistry of a collection of polymeric species of the generic repeat or monomeric formula [$-CH{=}CH-(CH_2)_{n-2}-$]. We admit that the state of many of the compounds at 298 K is ambiguous, or more precisely, that the sample's degree of crystallinity (cf the polymer chemist's terms 'amorphous solid' or even vaguer 'highly elastic') is ill-defined. As such, any attempts to correct for intermolecular interactions are suspect. We recall that it is easier to predict enthalpies of vaporization than of sublimation, and so conclude that general predictions for liquids are more reliable than for solids. As such, we will study the polymer in its liquid state even if the relevant temperature is not 298 K. No temperature corrections will be made and, given all of the above uncertainties, it seems an unnecessary additional effort to concern ourselves with the precise Z/E composition of the polymer[14]. The desired numbers in this section are enthalpies of hydrogenation and the final products are $n/2$ moles of polyethylene, i.e. $(CH_2CH_2)_{poly}$, with its derived enthalpy of formation[15] of *ca* -52 kJ mol^{-1}.

Starting with the $n = 4$ case, the desired polymer can be obtained by polymerization of either cyclobutene (**16**, $n = 4$) or butadiene. Using the cyclobutene polymerization enthalpy from Reference 16 and of the enthalpy of formation of monomer from Pedley, we find the enthalpy of formation of [$-CH{=}CH-(CH_2)_2-$] is 12 kJ mol^{-1}. We conclude that the enthalpy of hydrogenation is -116 kJ mol^{-1}.



(16)

For the $n = 5$ case there is the unique starting material of cyclopentene (**16**, $n = 5$) and polymerization enthalpy[16] from which the enthalpy of formation of [$-CH{=}CH-(CH_2)_3-$] is found to be -14 kJ mol^{-1}. The enthalpy of hydrogenation is thus *ca* -121 kJ mol^{-1}. Likewise, for $n = 6$, 7 and 8, the respective enthalpies of hydrogenation of [$-CH{=}CH-(CH_2)_{n-2}$] are seen to be *ca* -83, -120 and -121 kJ mol^{-1}. Except for the $n = 6$ case, the various enthalpies of hydrogenation are around -120 kJ mol^{-1}, a value comparable to those found for numerous simple internal olefins reported in References 11 and 14. We can think of no reason why the $n = 6$ case should be so different from the others[17].

III. CUMULATED OR ALLENIC DIENES AND POLYENES (CUMULENES)

A. Allene

We start with a discussion of allene (propadiene), the simplest diene of all. Its gas phase enthalpy of formation is 190.5 ± 1.2 kJ mol^{-1}. We wish to compare this quantity with that of related monoenes. The first comparison addresses the 'relative stability' of one and two double bonds in a 3-carbon chain. Conceptually, this may be expressed as the enthalpy of the formal reaction 9

$$2MeCH{=}CH_2 \longrightarrow C_3H_8 + CH_2{=}C{=}CH_2 \qquad (9)$$

We find that allene is destabilized by *ca* 46 kJ mol^{-1}. Is this destabilization also found for other species with cumulated, or allenic, double bonds?

B. Dienes

Let us start with 1,2-butadiene. A particularly simple analysis is the comparison of allene and 1,2-butadiene using the formal methylation reaction 10

$$CH_2{=}C{=}CH_2 + MeCH{=}CH_2 \longrightarrow MeCH{=}C{=}CH_2 + CH_2{=}CH_2 \qquad (10)$$

This reaction has an accompanying endothermicity of *ca* 4 $kJ\,mol^{-1}$. Said differently, methylation of ethylene is some 4 $kJ\,mol^{-1}$ more exothermic than of allene. How general is this greater exothermicity of alkylation of monoolefins over that of related allenes? Proceeding to the three cumulated 5-carbon dienes, we may consider the reactions

$$CH_2{=}C{=}CH_2 + EtCH{=}CH_2 \longrightarrow EtCH{=}C{=}CH_2 + CH_2{=}CH_2 \qquad (11a)$$

$$CH_2{=}C{=}CH_2 + 2MeCH{=}CH_2 \longrightarrow MeCH{=}C{=}CHMe + 2CH_2{=}CH_2 \qquad (11b)$$

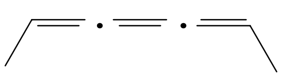
$$CH_2{=}C{=}CH_2 + Me_2C{=}CH_2 \longrightarrow Me_2C{=}C{=}CH_2 + CH_2{=}CH_2 \qquad (11c)$$

Using standard references and protocol, we find the three reactions are respectively endothermic by *ca* 2, 8 and 6 $kJ\,mol^{-1}$, or *ca* 2, 4 and 3 $kJ\,mol^{-1}$ once one remembers to divide by 2 the last two numbers because the allene is dialkylated. So doing, from equations 10 and 11 we find an average *ca* 3 $kJ\,mol^{-1}$ (per alkyl group) lessened stability for alkylated allenes than the correspondingly alkylated alkenes. This is a small difference that fits most naturally in the study of substituted cumulenes such as ketenes and ketenimines, i.e. not in this chapter. But it is also a guideline for the understanding of polyenes with more cumulated double bonds.

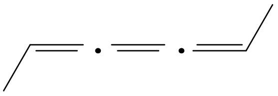
C. Trienes

The thermochemistry of totally cumulated trienes, i.e. species with the C=C=C=C substructure, is very limited. Indeed, the sole examples we know are those reported by Roth, namely (*Z*)- and (*E*)-2,3,4-hexatrienes MeCH=C=C=CHMe, species **17** and **18**. Their enthalpies of formation are identical to within experimental error, 265 $kJ\,mol^{-1}$. This equality is altogether reasonable given the small Me•••Me interaction across the 4-carbon, linear, cumulene chain in contradistinction to the 4.3 $kJ\,mol^{-1}$ difference that is found for the isomeric (*Z*)-and (*E*)-2-butenes with their significantly smaller Me•••Me distance. Are cumulated trienes 'unstable' relative to cumulated dienes much as cumulated dienes are unstable relative to simple olefins? Briefly regressing to cumulated dienes, this assertion is corroborated by the finding that species **3**, i.e. 1,3-dimethylallene, has an enthalpy of 'decarbonization'[18] of 144.5 $kJ\,mol^{-1}$ (reaction 12)

$$\mathbf{3} \longrightarrow (E)\text{-}MeCH{=}CHMe(g) + C(s) \qquad (12)$$



(17)



(18)

while the related reactions 13 of the two monosubstituted (R = Me and Et) and the unsubstituted allene (R = H)

$$RCH{=}C{=}CH_2 \longrightarrow RCH{=}CH_2(g) + C(s) \qquad (13)$$

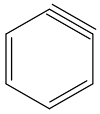
have enthalpies of 142.3, 140.6 and 139.0 kJ mol^{-1}. All of these decarbonization reactions are exothermic by *ca* 140 kJ mol^{-1}. Returning to the trienes, the related reaction 14

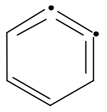
$$(\mathbf{17} \text{ or } \mathbf{18}) \longrightarrow \mathbf{3} + \mathrm{C(s)} \tag{14}$$

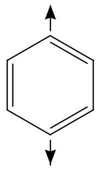
has the contrasting endothermicity of but 123 kJ mol^{-1}. Are the trienes so different from the dienes? These two sets of results become consonant once we observe the conjugated — and hence stabilizing — diene substructure (note the $\Delta^{2,3}$–$\Delta^{4,5}$ interaction) that is lying within the cumulated double bonds of **17** and **18**.

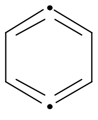
D. Tetraenes

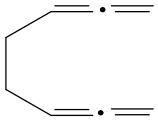
We know of no substance containing four completely cumulated double bonds for which the enthalpy of formation is available, and but few species that fill that structural description at all. Likewise, we know of no substance containing three cumulated double bonds and an either affixed conjugated or nearby, but unconjugated, double bond for which enthalpy of formation data are available except for the disingenuous benzyne **(19)** recognized if it is drawn in its unconventional resonance structure **20**. However, besides the equally inappropriate *p*-benzyne (**21**, **22**), we find in Roth the desired thermochemical numbers for three other tetraenes. All of these latter species are bis-allenes, the acyclic 1,2,6,7-octatetraene **(23)** and 4,4-dimethyl-1,2,5,6-heptatetraene **(24)**, and the cyclic 1,2,6,7-cyclodecatetraene **(25)**. There is no reason to believe that either **23** or **24** is particularly strained. Table 1 documents our optimism by numerically taking one-half of the difference of the enthalpies of formation of these acyclic bis-allenes and more 'conventional' species[19], namely the corresponding olefins and acetylenes. Nearly constant differences were found. We should expect both the cumulene **25** and its olefin counterpart, 1,5-cyclooctadiene, **26**, to be strained, and their comparison is further complicated by the ambiguity of having to choose between the *meso* or *dl* isomers for the former (**27** and **28**, respectively), and among the (*Z*,*Z*), (*E*,*Z*) or (*E*,*E*) isomers for the latter (**29**–**31**, respectively). There are two measurements from which one can derive the desired enthalpy of formation of the cumulene. The first is Roth's enthalpy of hydrogenation that results in a value of 360 kJ mol^{-1} for explicitly the *meso* compound, **27**. The second is the nearly contemporaneous determination of the enthalpies[20] of combustion and of vaporization (for what appears to be isomer **27** as well) resulting in 356.1 ± 3.8 kJ mol^{-1}. We have arbitrarily decided to consider the (*Z*,*Z*) isomer of **26**, species **29**, because it is the most stable of the 1,5-cyclooctadienes (see Section V.F). So doing, the desired difference quantity is

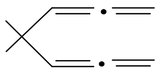

(19)


(20)


(21)


(22)


(23)


(24)

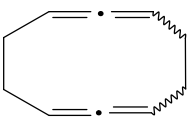

(25)

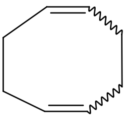
TABLE 1. Enthalpies of formation of bis-allenes, the related bis-olefins and bis-acetylenes and their acyclic analogs

$-$R$-$	2Et$-$	$-CH_2CH_2-$	$Me_2C<$
ΔH_f (CH_2=CH$-$R$-$CH=CH_2)	0	84	52[a]
1/2δ (bis-allene, bis-olefin)	141	142	139
ΔH_f (CH_2=C=CH$-$R$-$CH=C=CH_2)	282	368	330
ΔH_f (HC≡C$-$R$-$C≡CH)	330	415[b]	382[b]
1/2δ (bis-allene, bis-acetylene)	-24	-23	-26

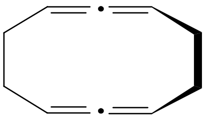
[a] The necessary enthalpy of formation of Me_2C ($CH=CH_2$)$_2$ was derived by assuming the reaction $Me_2CEt_2 + CH_2(CH=CH_2)_2 \xrightarrow{\quad} Me_2C(CH=CH_2)_2 + CH_2Et_2$ is thermoneutral.

[b] The liquid phase enthalpy of formation of this species is from Pedley; the necessary enthalpy of vaporization was estimated.

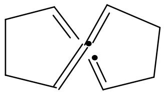
found to be *ca* 130 kJ mol^{-1}. Considering all of the above uncertainties and the relatively exotic structure of **25**, we conclude that the bis-allene **25** is *not* so strange after all[21].



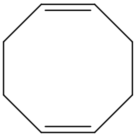
(26)



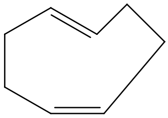
(27)



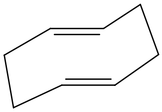
(28)



(29)



(30)

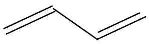


(31)

IV. CONJUGATED ACYCLIC DIENES

A. Consequences of Conjugation

It is part of the folklore of organic chemistry that the conjugated 1,3-butadiene, **32**, enjoys stabilization beyond that were there no interaction between the two double bonds. Indeed, conjugated dienes represent an archetypical example for organic chemists when discussing resonance stabilization accompanying the interaction of two functional groups, and so it may be argued that a new functional group arises.



(32)

What is relevant to this chapter is that a conjugated diene has higher thermodynamic stability than one would expect in the absence of conjugation. Leaving off all hydrogens and substituents in the name of simplicity, several interrelated definitions that document this stabilization are apparent. The first compares the enthalpy of hydrogenation corresponding to total saturation of the diene; cf reaction 15a with the hydrogenation enthalpies of the related monoenes, cf reactions 15b and 15c. The difference of the first enthalpy, ΔH_r (equation 15a), and the sum of the second and third [ΔH_r(equation 15b) + ΔH_r (equation 15c)], provides a definition for the conjugation energy, E_{16} (equation 16).

$$\text{C=C–C=C} + 2\text{H}_2 \longrightarrow \text{C–C–C–C} \tag{15a}$$

$$\text{C=C–C–C} + \text{H}_2 \longrightarrow \text{C–C–C–C} \tag{15b}$$

$$\text{C–C–C=C} + \text{H}_2 \longrightarrow \text{C–C–C–C} \tag{15c}$$

$$E_{16} \equiv \Delta H_r(\text{equation 15a}) - [\Delta H_r(\text{equation 15b}) + \Delta H_r(\text{equation 15c})] \tag{16}$$

We immediately recognize this quantity (E_{16}) as equal to the exothermicity of reaction 17:

$$\text{C–C–C=C} + \text{C=C–C–C} \longrightarrow \text{C=C–C=C} + \text{C–C–C–C} \tag{17}$$

The result for 1,3-butadiene is -15.7 ± 1.9 kJ mol^{-1}, a value comparable to conventional expectations save the sign[22]. We can now define the difference of the value for an arbitrary conjugated diene of interest and this 15.7 kJ mol^{-1} as E_{18} (equation 18).

$$E_{18} = -15.7 - E_{17} \tag{18}$$

That is, we can compare the 'new diene' with the archetypical 1,3-butadiene where a positive number suggests that it is more stabilized than the paradigm.

The above definition of the enthalpic effects of conjugation is not unique. A second definition decouples the two double bonds by an alternative hydrogenation process (equation 19).

$$\text{C=C–C=C} + \text{H}_2 \longrightarrow \text{C=C–H} + \text{H–C=C} \tag{19}$$

It is found that this reaction, more properly called a hydrogenolysis than a hydrogenation, is only *ca* 5 kJ mol^{-1} exothermic for simple species such as 1,3-butadiene and its mono and dimethylated derivatives[12,23,24]. This is surprisingly close to thermoneutrality. Nonetheless, we have decided to define E_{20} by equation 20,

$$E_{20} = 5.1 - E_{19} \tag{20}$$

where 5.1 ± 1.2 kJ mol^{-1} is the precise hydrogenolysis value for 1,3-butadiene. Again, comparison can be made with 1,3-butadiene where a positive number for E_{20} implies the new diene is more stable than the archetype. A third definition totally hydrogenates the diene to the saturated hydrocarbon (cf equation 15a), and the difference of this enthalpy and that for the unsubstituted butadiene results in E_{21} (equation 21):

$$E_{21} = -225.7 - E_{20} \tag{21}$$

In this equation the -225.7 ± 1.3 kJ mol^{-1} is the hydrogenation enthalpy of 1,3-butadiene to *n*-butane. This last expression speaks to substituent/diene interactions and to substituent–substituent interactions. Both electronic and steric effects contribute. Again, this allows calibration of a substituted diene with 1,3-butadiene itself. A positive sign can be interpreted as the substituted species being more stabilized than the archetype.

TABLE 2. Conjugation enthalpies of gaseous substituted butadienes relative to butadiene itself

Substituents	E_{18}	E_{20}	E_{21}
(*E*) 1-Me	6	2	3
(*Z*) 1-Me	−3	−3	−3
2-Me	0	3	−4
(*E*) 1-Et[a]	7[b]	3	4
(*Z*) 1-Et[a]	7[b]	−1	0
2-Et[c]	−12[d]	−6	−10
(*E*, *E*) 1,4-Me_2[e]	5[b]	1	14
(*E*, *Z*) 1,4-Me_2[e]	5[b]	−3	11
(*Z*, *Z*) 1,4-Me_2[e]	−2[b]	−7	6
2,3-Me_2	−5[b]	0	2
(*E*, *E*) 1,2,3,4-Me_4[f]		−7	15
(*E*, *Z*) 1,2,3,4-Me_4[f]		−14	17
(*Z*, *Z*) 1,2,3,4-Me_2[f]		−15	10
2,3-*t* − Bu_2[g]		−44[h]	−12[i]

[a] The enthalpies of formation of the isomeric 1-ethylbutadienes (or more properly named 1,3-hexadienes) are taken from Reference 12.

[b] The enthalpies of formation of the monoolefin hexene products are derived from Reference 11.

[c] The enthalpy of formation of the 2-ethylbutadiene is taken from Reference 8.

[d] The enthalpy of formation of the monoolefin products, 3-methyl-1-pentene and 2-ethyl-1-butene, are derived from Reference 11.

[e] The enthalpies of formation of the isomeric dimethylbutadienes (or more properly named 2,4-hexadienes) are taken from Reference 12.

[f] The enthalpies of formation of the isomeric tetramethylbutadienes (or more properly named 3,4-dimethyl-2,4-hexadienes) are taken from Reference 23.

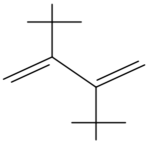
[g] The enthalpy of formation of the di-*t*-butylbutadiene is taken from Reference 23.

[h] This is the solvent and vaporization-corrected enthalpy of hydrogenation of the diene from Reference 23. There is no need in the current context for the enthalpy of formation of the hydrogenation product 2,3-di-*t*-butylbutane (or more properly named 2,2,3,4,5,5-hexamethylhexane), unlisted in our archives, and derived in Reference 23 by molecular mechanics.

[i] The enthalpy of formation of the hydrogenolysis product, 3,3-dimethyl-1-butene, was derived from the data in Reference 11b.

However, because a given alkyl group replacing hydrogen on saturated and unsaturated carbon results in different enthalpy of formation changes, we hesitate to compare dienes with different number of substituents on the butadiene backbone. Indeed, that 1,3-butadiene is a di-terminal double-bond system allows for the conclusion that butadiene is not a good species for comparison. Indeed, Table 2 presents the accumulated values of E_{18}, E_{20} and E_{21} for all of the acyclic dienes (all unsystematically named therein as substituted derivatives of butadiene) that are known to the author for which there is relevant gas phase enthalpic data[25]. It is very disconcerting that these definitions and descriptions of conjugation energy and substituent effects for our set of dienes result in no obvious generalities or guidelines.

The description of conjugated dienes as shown by equation 17 and the associated comparison with butadiene in equation 18 corresponds most closely to the conventional definition. The results are plausible in that groups on one double bond that are *cis*-situated relative to the other encourage nonplanarity, cause destabilization and result in lessened conjugation energy. Or so we say. The biggest debit of this approach is that the thermochemistry of the monoenes related by single addition of H_2 is often absent. An example is the case of 2,3-di-*t*-butylbutadiene **33**, and so the energetics of this species could not be examined in the current light.



(33)

Because reaction 19 is so close to thermoneutrality for unstrained olefins and dienes, it represents a convenient way of estimating and benchmarking enthalpies of formation for dienes and polyenes[26] even if it is not isodesmic[27] whereas reaction 17 is. However, it is 'full of surprises' such as the finding that the related oxygen reaction (equation 22) involving α-dicarbonyl compounds is also nearly thermoneutral[24,28].

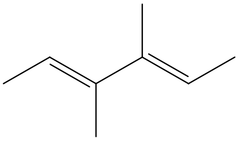
$$2\text{RCHO} \longrightarrow \text{RCOCOR} + \text{H}_2 \tag{22}$$

However, it is not obvious how much understanding the energetics of this last reaction will provide a key to understanding of dienes.

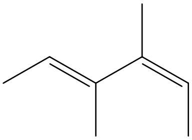
Reaction 14 is the simplest process associated with the measurement of the hydrogenation of the diene. No other unsaturated compounds such as the monoolefins formed by addition of a single equivalent of H_2, not reactions 7a, 7b or 12, need be considered. This is a virtue from the vantage points of not having to 'interrupt' the reaction, analyze the products or needing to synthesize any additional species. However, all comparison with monoolefins has been lost and that is the interrelationship conjugation energy speaks to. Perhaps with more data we will gain greater understanding.

B. What Other Data Are There

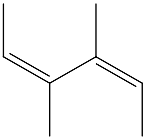
We admit to comparatively little experience in quantitatively understanding solvent and entropic effects. For example, consider the 1,2,3,4-tetramethylbutadienes presented in Table 2. From Reference 23, we find the relative solution phase Gibbs energies for the (*E*,*E*)-, (*E*,*Z*)- and (*Z*,*Z*)-isomers (**34**–**36**, respectively) increase in the order $(E,E) < (E,Z) \approx (Z,Z)$. By contrast, the gas phase enthalpies of formation increase in the order $(Z,Z) < (E,E) < (E,Z)$. Somehow it seems inappropriate to include the other C_8H_{14} hydrocarbons of Reference 23 in the current study when we only know their relative Gibbs energies in solution[29].



(34)



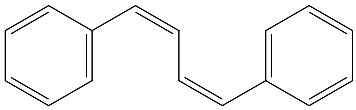
(35)



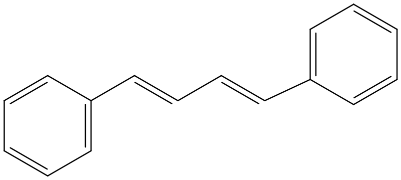
(36)

Data are sparse. Let us thus relax the earlier phase restriction to the gas phase. We therefore briefly discuss some conjugated dienes for which we have enthalpy of formation data solely in the condensed phase. The first pair of species are the isomeric (*Z*,*Z*)-and

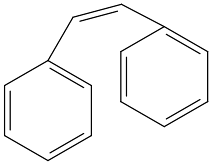
(*E*,*E*)-1,4-diphenylbutadienes, **37** and **38**. Pedley tells us that the difference of enthalpies of formation is *ca* 20 kJ mol^{-1} in the solid. Pedley's chronicled data to the contrary, we would have thought that the value should be larger than the comparable archival difference for **39** and **40**, the (*Z*)- and (*E*)-diphenylethylenes (stilbenes)[30]. We likewise find that solid 1,2,3,4-tetraphenylbutadiene, **41**, is *ca* 30 kJ mol^{-1} less stable than its 1,1,4,4-isomer, **42**. One natural comparison is with the saturated tetraphenylbutanes but there are seemingly no data available for 1,2,3,4-tetraphenylbutane. Another comparison involves formal cleavage of the central single bond to form two molecules of diphenylethylene, but the absence of Z/E assignments for the double bonds in 1,2,3,4-tetraphenylbutadiene makes this approach irrelevant.



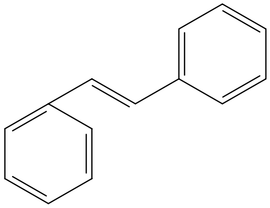
(37)



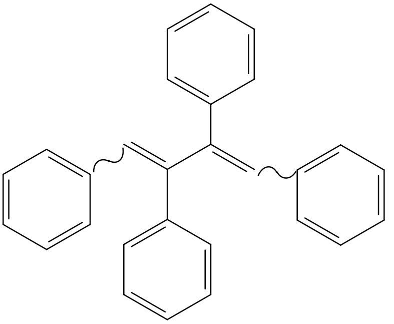
(38)



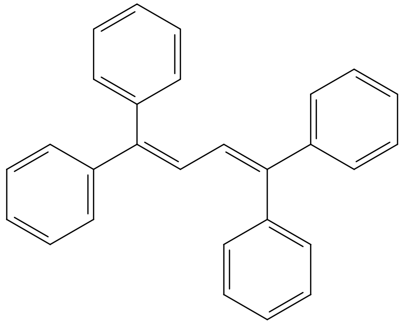
(39)



(40)



(41)



(42)

V. CYCLIC DIENES

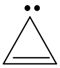
A. What Types of Species Qualify?

There are three generic types of species with this description: those cyclic dienes in which both double bonds are found totally within, or *endo* to, the ring; those in which both double bonds are found *exo* to the ring, and those with one *endo* and one *exo* double bond. We start with the first class of compounds.

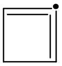
B. Doubly *Endo* Micro-rings

The first member of this class of compounds would appear to be cyclopropadiene, **43**, but it is immediately recognized that this species is more accurately drawn with the alternative resonance structure corresponding to cyclopropenylidene, **44**. As such, this C_3H_2 species does not truly belong in the current chapter and so will be ignored here[31]. There are two isomers for cyclobutadiene, the 1,2- and 1,3-, species **45** and **46** respectively. We are not surprised there are no enthalpy of formation data for the former and it is tempting to conclude that this cyclic allene is seemingly 'too small' to even allow for reaction calorimetry of any kind. There are no enthalpy of formation data for the latter or for any of its derivatives either[32], although the generally believed antiaromaticity of cyclobutadienes would have argued against inclusion of the data even had we found it much as the thermochemistry of cyclohexatrienes (i.e. substituted benzenes) is all but ignored in this chapter.

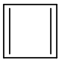
(43)



(44)



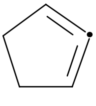
(45)



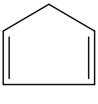
(46)

C. Cyclopentadiene

Turning now to cyclopentadienes, there are the isomeric 1,2-and 1,3-cyclopentadiene [**47** and **48** (**9**, $X = CH_2$)]. The thermochemical community has ignored **47**, a cyclic allene, and indeed, it has seemingly ignored all cyclic allenes[33] despite the reasonable number of reasonable, i.e. isolable and isolated, species[34]. The latter is among the most normal looking species in this chapter: **48** is customarily called cyclopentadiene without any locants for the two double bonds. Pedley chronicles its enthalpy of formation to be $134.3 \pm 1.5\ \text{kJ mol}^{-1}$ from measurements of its enthalpy of a gas phase hydrogenation reaction resulting in cyclopentane. Roth cites this value and also one derived of their own from solution phase hydrogenation measurements, $138.9\ \text{kJ mol}^{-1}$, that resulted in the same product. The $4.6\ \text{kJ mol}^{-1}$ discrepancy is quite disconcerting because:



(47)



(48)

(a) if it really reflects a difference of gas phase and condensed phase enthalpies of hydrogenation, the earlier enunciated assumption that results from nonpolar media mimic those in the gas phase is suspect;

(b) most compounds have never been studied by thermochemists. Those compounds that have been investigated have rarely been studied by more than one group;

(c) we may define the conjugative stabilization in cyclopentadiene as the exothermicity of the cyclopentene 'disproportionation' (reaction 23).

$$2\text{cyclo-}[(CH_2)_3(CH)_2] \longrightarrow \mathbf{48} + \text{cyclo-}[(CH_2)_5] \tag{23}$$

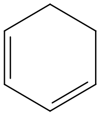
Using Pedley's suggested enthalpy of formation, this reaction is seen to be exothermic by 9.9 kJ mol^{-1}. This number is quite small noting that a related but strain-free reaction (an alternative acyclic paradigm for conjugation), i.e. reaction 24

$$2(E)\text{-MeCH=CHPr} \longrightarrow (E,E)\text{-MeCH=CHCH=CHMe} + n - C_6H_{14} \qquad (24)$$

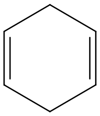
is exothermic by nearly 20 kJ mol^{-1}. Indeed, this result would appear to reflect the oft-asserted instability of *cis*-oid (alternatively written *Z*- or s-*cis*) dienes[35]. Using Roth's value for the enthalpy of formation of cyclopentadiene, the exothermicity of reaction 23 has now shrunk to 5.3 kJ mol^{-1}. If this value is taken, the conjugative stabilization of cyclopentadiene has all but vanished[36].

D. 1,3- and 1,4-Cyclohexadiene

It is perhaps unexpected to have an entire section devoted solely to two normal-looking cyclic dienes, 1,3- and 1,4-cyclohexadiene, species **49** and **50** (**11** and **12** with $X = CH_2$). While an entire volume has been written on stereochemical aspects of substituted cyclohexadienes[37], this interest alone would not suggest that more than a perfunctory discussion of the enthalpies of formation of the parent species need be made. Our expectations are simple. The former diene is conjugated; the latter is not. A difference of *ca* 15 kJ mol^{-1} favoring the former is expected. Our archives are surprisingly mute: Pedley gives us the enthalpy of formation of only the 1,3-species, 106.2 ± 0.9 kJ mol^{-1}, derived from a 60-year-old gas phase enthalpy of hydrogenation measurement[38]. Roth gives us that value as well as one derived from a 23-year-old solution hydrogenation enthalpy measurement[39]. As with cyclopentadiene, this latter value differs from the earlier one by some 5 kJ mol^{-1}. Though more recent, that measurement which was made in the polar solvent, glacial AcOH, requires the need for solvent effect corrections. This suggests that the earlier value is preferable. Interestingly, the latter reference[39] also reports the hydrogenation enthalpy of 1,4-cyclohexadiene. This value is *ca* 1 kJ mol^{-1} higher than the corresponding enthalpy found for its 1,3-isomer. Since the hydrogenation product is the same for both dienes, in the absence of any particular solvent effect for **49** or **50**, we conclude that the enthalpies of formation of these two cyclohexadienes are nearly the same with the formally conjugated species the slightly more stable. Direct equilibration of **49** and **50** showed[40] the former 1,3-isomer to be more stable by 1.6 ± 0.8 kJ mol^{-1}. Disappointingly, this reaction was performed in polar media (*t*-BuOK in DMSO) and so the same skepticism enunciated for the solution phase hydrogenation study could be enunciated here[41].



(49)



(50)

What about measurements of enthalpies of combustion of condensed phase species **49** and **50** and accompanying enthalpies of vaporization? Enthalpies of formation of the gaseous hydrocarbons can be directly obtained from these studies as well. There are two recent studies that provide us with useful information. The first[42] results in the values of 104.6 ± 0.6 and 104.8 ± 0.6 kJ mol^{-1} respectively. The second accompanies the earlier cited cyclic bisallene (and polycyclic monoolefin) study, in which the authors[20] reported the value of 100.4 ± 3.1 kJ mol^{-1} for the 1,4-isomer. This value is quite different from what was reported above and so, regrettably, we find no corresponding combustion measurements on its isomer in Reference 20 as well. It is tempting to ignore this last result because the comparison of the stabilities of the 1,3- and 1,4-cyclohexadienes cannot be directly addressed from this latter paper.

Summarizing all of the above, it would appear that 1,3- and 1,4-cyclohexadiene have nearly identical enthalpies of formation. Does this mean that the 1,3-isomer is destabilized and/or that the 1,4-isomer is stabilized? Let us accept an enthalpy of formation of *ca* 105 kJ mol^{-1} for the enthalpy of formation of both isomers. In the absence of any stabilization or destabilization, we would expect the cyclohexene 'disproportionation' reaction 25

$$2\text{cyclo-}[(\mathrm{CH_2})_4(\mathrm{CH})_2] \longrightarrow (\mathbf{49} \text{ or } \mathbf{50}) + \text{cyclo-}[(\mathrm{CH_2})_6] \qquad (25)$$

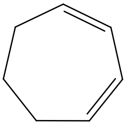
to be nearly thermoneutral. In fact, our analysis suggests that this reaction is exothermic by 8 kJ mol^{-1}. Accordingly, 1,3-cyclohexadiene is less stable than we would have derived from results of 2,4-hexadiene (but again remember *cis*-oid conjugated dienes). Conversely, 1,4-cyclohexadiene is more stable on the basis of conventional assumptions about the thermochemistry of nonconjugated dienes and acyclic paradigms.

E. Cycloheptadienes

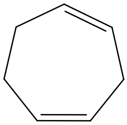
As was seen for 1,3-cyclohexadiene, the data in Pedley and Roth report conflicting measurements for the enthalpy of formation of 1,3-cycloheptadiene, **51**. The values differ by some 3 kJ mol^{-1}. This is often a non-negligible difference, but either result is plausible: the disproportionation reaction 26

$$2\text{cyclo-}[(\mathrm{CH_2})_5(\mathrm{CH})_2] \longrightarrow \mathbf{51} + \text{cyclo-}[(\mathrm{CH_2})_7] \qquad (26)$$

corresponding to earlier reactions 23 and 25, is exothermic by either *ca* 6 or 9 kJ mol^{-1}. However, the difference becomes almost irrelevant when comparing these findings with those for 1,4-cycloheptadiene, **52**. As with the isomeric cyclohexadienes **49** and **50**, Reference 39 presents solution phase hydrogenation (glacial AcOH solvent) for the two cycloheptadienes. Remembering that the difference of the solution phase enthalpies of hydrogenation, and hence of formation, difference of the isomeric cyclohexadienes was within a kJ mol^{-1} of that found from the chosen combustion measurements, encourages us to trust the difference found for **51** and **52**. But here, the conjugated isomer is reported to be more stable than its unconjugated counterpart by almost 30 kJ mol^{-1}. This difference is significantly larger than the acyclic paradigm for the stabilization effects due to conjugation of double bonds. We strongly suggest reinvestigation of the thermochemistry of the cycloheptadienes — and the cyclohexadienes as well.



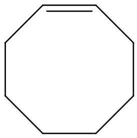
(51)



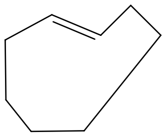
(52)

F. Cyclooctadienes

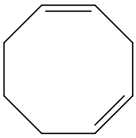
As with the isomeric cyclohexadienes, there are a variety of data to present. Let us start with the 1,5-isomer, **26** and remind the reader there are three 'forms' of this species, the (*Z*,*Z*), (*E*,*Z*) and (*E*,*E*) isomers, **29–31**, respectively. Pedley presents enthalpy of formation data for only the first. By contrast, Roth enigmatically gives data only for the last two. Taken as a totality, the three numbers are 101.1 ± 1.3 kJ mol^{-1}, 158.2 and 196.2 kJ mol^{-1}. When there are two double bonds in an 8-membered ring, at least for the 1,5-isomer, changing from a (*Z*)-conformation to (*E*) seems to be accompanied by *ca* 50 ± 10 kJ mol^{-1} per double bond increase in enthalpy of formation. This is consistent with isomerization of the monoolefin, cyclooctene, as well. Pedley suggests the enthalpy of formation of (*Z*)-cyclooctene, **53**, to be −27.0 ± 4.2 kJ mol^{-1}. Roth cites enthalpies of formation of (*E*)-cyclooctene, **54**, ranging from 9.2 to 20.1 kJ mol^{-1} based on three distinct hydrogenation measurements. We thus deduce a E/Z difference of 42±6 kJ mol^{-1}. Likewise, using numbers from Roth, we find that (*Z*,*Z*)-1,3-cyclooctadiene, **55a**, is some 60 kJ mol^{-1} more stable than its (*E*,*Z*)-isomer, **55b**.



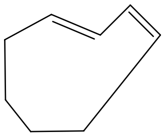
(53)



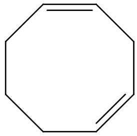
(54)



(55a)



(55b)



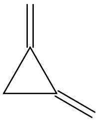
(56)

From a consistent set of hydrogenation enthalpies in glacial AcOH, the cyclooctadienes decrease in stability 1,5- (**29**) < 1,4- (**56**) < 1,3- (**55a**) with sequential differences of 13.0 **(29**, **55a)** and 6.7 **(55a**, **56)** kJ mol^{-1}. For comparison — despite our earlier enunciated skepticism about isomerization reactions performed in polar media (*t*-BuOK in DMSO) — the following enthalpies of reaction, and thus enthalpies of formation, differences were found[43]: 16.4 ± 1.4 and 2.8 ± 0.8 kJ mol^{-1}. Consistency, if not precise numerical agreement, is found for the energetics of the isomeric cyclooctadienes.

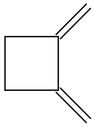
G. Doubly *Exo* Cyclic Dienes

Except for the still thermochemically uninvestigated 1,2-bismethylenecyclopropane[44], **57**, all bismethylenecycloalkanes can further be divided into two categories — those in which the *exo*-methylene groups are on adjacent carbons and those further apart. The two isomeric bismethylenecyclobutanes have been studied. Roth presents an enthalpy of formation for the 1,2-isomer, **58**, of 204.2 kJ mol^{-1}. In the absence of any additional strain-induced destabilization or conjugative/delocalization-induced stabilization, we would expect the disproportionation reaction 27 of methylenecyclobutane **(59)**

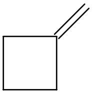
$$2[\mathbf{59}] \longrightarrow \mathbf{58} + \text{cyclo-}[(\mathrm{CH_2})_4] \qquad (27)$$



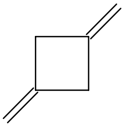
(57)



(58)



(59)



(60)

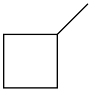
to be thermoneutral. In fact it is exothermic by *ca* 10 kJ mol^{-1}, reflecting — as in our earlier discussion of cyclopentadiene — the destabilization induced by forcing a *cis*-oid conformation on a conjugated diene. Reaction 28

$$2[\mathbf{59}] \longrightarrow \mathbf{60} + \text{cyclo-}[(\text{CH}_2)_4] \tag{28}$$

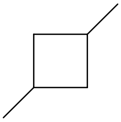
relatedly for the 1,3-bismethylene isomer, **60**, would also be expected to be thermoneutral in the absence of additional stabilization or destabilization effects. No direct enthalpy of formation measurements exist for **60**. Reaction 28 may be roughly recast in terms of hydrogenation enthalpies. Twice this quantity for the singly methylenated **59** would equal that of **60** in the absence of any other significant stabilizing or destabilizing factor, if we make the reasonable assumption that the saturated counterpart, reaction 29, is essentially thermoneutral.

$$2[\mathbf{61}] \longrightarrow \mathbf{62} + \text{cyclo-}[(\text{CH}_2)_4] \tag{29}$$

In fact, using data for **59** and **60** with the same solvent and *a fortiori* from the same paper[45], we deduce that **60** is seemingly destabilized by 5 kJ mol^{-1}.



(61)

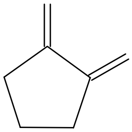


(62)

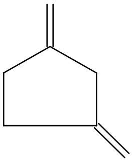
Does the 10 kJ mol^{-1} stabilization for adjacent exomethylene groups in cyclobutane arise from conjugative interactions? Is the 5 kJ mol^{-1} destabilization for nonadjacent exomethylenes in cyclobutane general for other cycloalkane derivatives?

Consider now other bismethylenecycloalkanes. We start with 1,2-dimethylenecyclopentane, **63**, and acknowledge there are no accompanying thermochemical data for its 1,3-isomer, **64**. We can write the formal reaction 30

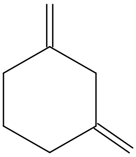
$$2\text{cyclo} - [(\text{CH}_2)_4\text{C}{=}\text{CH}_2] \longrightarrow \mathbf{64} + \text{cyclo-}[(\text{CH}_2)_5] \tag{30}$$



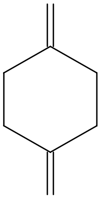
(63)



(64)



(65)



(66)

From enthalpy of formation data of **63** from Roth, and for the other species from Pedley, we find reaction 30 is exothermic by 6 $\mathrm{kJ\,mol^{-1}}$. Consider now the isomeric 1,3-and 1,4-dimethylenecyclohexane, **65** and **66**; no thermochemical data for its 1,2-isomer are seemingly available. We can write the related formal reactions 31a and 31b.

$$2\text{cyclo} - [(\mathrm{CH_2})_5\mathrm{C{=}CH_2}] \longrightarrow \mathbf{65} + \text{cyclo-}[(\mathrm{CH_2})_6] \qquad (31\text{a})$$

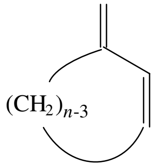
$$2\text{cyclo} - [(\mathrm{CH_2})_5\mathrm{C{=}CH_2}] \longrightarrow \mathbf{66} + \text{cyclo-}[(\mathrm{CH_2})_6] \qquad (31\text{b})$$

From enthalpy of formation data of **65** from Roth, of **66** from Reference 46, and for the other species from Pedley, we find reactions 31a and 31b are exothermic by nearly 19 and 9 $\mathrm{kJ\,mol^{-1}}$ respectively. We have no understanding of why 1,3-dimethylenecyclohexane is so stable relative to its 1,4-isomer, or how to predict stabilization of any bismethylenecycloalkane as a function of ring size.

H. *Endo, Exo* Cyclic Species

As the ring size gets bigger, there are an increasing number of isomers of this general description. For the sake of brevity, we will consider only the formally conjugated species, generically **67** where n is the ring size[47]. No problems or surprises are expected here: consider thus the straightforward hydrogenation reaction 32

$$\mathbf{67} + 2\mathrm{H_2} \longrightarrow \text{cyclo-}[(\mathrm{CH_2})_{n-1}\mathrm{CHMe}] \qquad (32)$$



(67)

Taking the enthalpy of formation of **67** with $n = 5$ from Roth and the product methylcyclopentane from Pedley, this reaction is found to be 222 $\mathrm{kJ\,mol^{-1}}$ exothermic. This result is consonant with that of the acyclic reaction 33

$$\mathrm{CH_2{=}CHC(Me){=}CH_2} \longrightarrow \mathrm{CH_3CH_2CHMe_2} \qquad (33)$$

which has an exothermicity of 228 $\mathrm{kJ\,mol^{-1}}$, some 6 $\mathrm{kJ\,mol^{-1}}$ higher. It is not, however, consonant with the enthalpy of reaction 32 with $n = 6$ for which a reaction enthalpy of some 177 $\mathrm{kJ\,mol^{-1}}$ is found using numbers from Pedley[48]. Other than assuming that an experimental measurement is wrong, no explanation is apparent[49].

I. Bicyclic Dienes and ‘Beyond’

There are many bicyclic dienes and polyenes. If for no other reason than to show that seemingly homologous series often show profound complications, in Table 3 we present the enthalpies of formation of the bicyclo[2.2.n]alka-2,5-dienes, bicyclo[2.2.n]alk-2-enes and bicyclo[2.2.n]alkanes, species **68**, **69** and **70**, respectively, wherein we limit our attention to the cases of $n = 0$, 1 and 2. It is seen that the enthalpies of formation of the bicycloalkadiene, bicycloalkene and bicycloalkane always become more negative in that

TABLE 3. Recommended enthalpies of formation of bicyclo[2.2.n]alka-2,5-dienes, bicyclo[2.2.n]alk-2-enes and bicyclo[2.2.n]alkanes for $n = 0$, 1 and 2

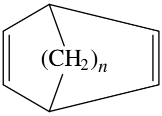
	$n = 0^a$	$n = 1^b$	$n = 2^c$
Bicycloalkadiene	335	240	141
Bicycloalkene	261	90	35
Bicycloalkane	125	−52	−99

[a] See Reference 50.
[b] See Reference 51.
[c] See Reference 52.

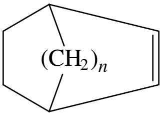
order and that, for a given degree of unsaturation, the enthalpies of formation also always become more negative in the order $n = 0$, 1 and 2. These results are sensible. It is the exceptional double bond[53] for which saturation (hydrogenation) is an endothermic reaction. Recognizing the monocyclic structural fragments amidst the bicycles, we also expect the strain energies to decrease in the order of 4-membered ring > 5-membered ring > 6-membered ring. The deviation from thermoneutrality of the formal reaction 34

$$2[\mathbf{69}] \longrightarrow \mathbf{68} + \mathbf{70} \qquad (34)$$

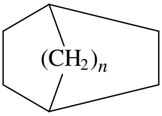
speaks to the interaction of the two double bonds in the bicycloalkadiene[54]. For $n = 0$, 1 and 2, these reactions are respectively 62 *endo*, 2 *exo* and 28 kJ mol^{-1} *exo*-thermic.



(68)

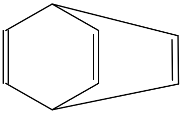


(69)

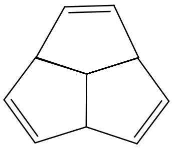


(70)

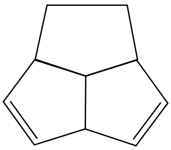
Hardly feigning completeness under the general rubric of 'beyond', we now briefly discuss bicyclo[2.2.2]octatriene or barrelene, **71**, with its recommended[52] enthalpy of formation of 303 kJ mol^{-1}. The difference of this enthalpy of formation and the bicyclic species with one fewer double bond (**68**, $n = 2$) is 162 kJ mol^{-1}, *ca* 20 kJ mol^{-1} less than any other difference we find in Table 3. It is thus clear that this bicyclic triene is considerably destabilized. By contrast, the corresponding difference for **72**, the tricyclic triquinacene, and the corresponding diene **73**, is *ca* 20 kJ mol^{-1} lower[55] than for the diene as well as for **74**, a related bicyclic diene[56]. Having promised to avoid discussion of homoaromaticity in the beginning of this chapter and other exotic interactions of double bonds, we avoid mention of the mechanisms of seeming stabilization, destabilization and normalcy for **72**, **71**, and of **73** and **74**, respectively.



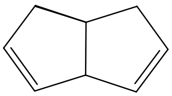
(71)



(72)



(73)

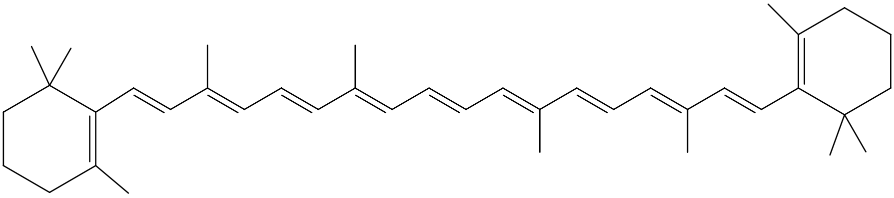


(74)

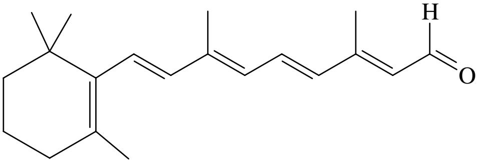
VI. CONJUGATED POLYENES

A. What Sparse Data Are There

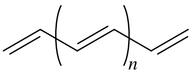
We have earlier discussed the thermochemistry of acyclic conjugated dienes. In this section the enthalpy of formation of conjugated trienes will be discussed along with a few compounds with more than three double bonds. For all of the activity in the chemical and biochemical community in conjugated polyenes — whether derived from interest in antioxidants (e.g. β-carotene, **75**), the visual process (e.g. retinal, **76**) or conducting polymers (e.g. polyacetylene, **77**) — there are surprisingly little thermochemical data for species with conjugated three or more double bonds. Nonetheless, we remind the reader that following our earlier enunciated prejudices, we will still ignore substituted species such as the partially conjugated ergosterol, **78**, with its solid and gaseous phase enthalpies of formation of -789.8 ± 24.7 and -670.9 ± 25.5 kJ mol^{-1}, respectively.



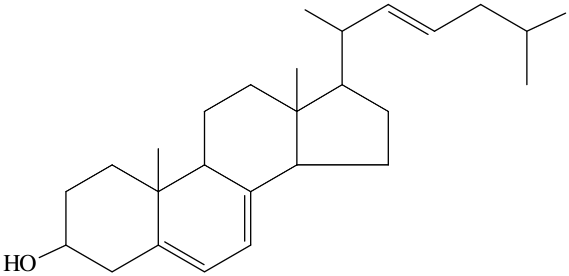
(75)



(76)



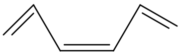
(77)



(78)

B. Acyclic Species

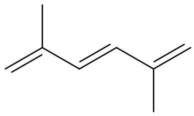
We start with the simplest conjugated triene, 1,3,5-hexatriene, for which there are the two isomers, the (*Z*)- and (*E*)-, species **79** and **80**, respectively. Nearly 30 years ago[57], the enthalpy of combustion of the former, as liquid, was reported. From this number, the customary ancillary values of the enthalpies of formation of H_2O and CO_2, and our standard estimation approach for enthalpies of vaporization, we obtain the desired enthalpy of formation of gaseous **80** as 175 ± 14 kJ mol^{-1}. Somewhat later, considerably more precise enthalpies of hydrogenation[39] were reported for both compounds. These studies were performed in glacial AcOH with an unmeasured correction for solvent effects. Ignoring this solvent correction and accepting these enthalpies of hydrogenation and of formation of the common hydrogenation product, gaseous *n*-hexane, we derive the desired enthalpies of formation of **79** and **80** to be 169.7 ± 1.1 and 165.1 ± 1.5 kJ mol^{-1}. The two results for (*E*)-1,3,5-hexatriene are in agreement. One can do better than merely ignore the solvent correction for the hydrogenation measurement by positing[56] a constant correction per double bond of *ca* 2.9 kJ mol^{-1}, and thereby result in the modified value of *ca* 174 kJ mol^{-1} for the (*E*)-triene. Needless to say, it would be more correct to measure the solvent correction directly[12]. Alternatively, one can perform the hydrogenation in a nonpolar solvent and so mimic the gas phase result[7]. Within the last few years, this quasi-gas-phase hydrogenation measurement were reported[12] albeit on a **79/80** (or Z/E-hexatriene) mixture of known stoichiometry. Accepting the earlier difference of enthalpies for the two isomers results in the enthalpies of formation of **79** and **80** of 172.0 ± 2.5 and 167.8 ± 2.5 kJ mol^{-1} respectively. Admitting some numerical ‘sloppiness’, a corollary of the earlier observation[37,38] that the enthalpy of formation of a strainless conjugated diene is *ca* 5 kJ mol^{-1} more than the sum of the component monoenes is that the enthalpy of formation of a strainless conjugated triene is *ca* 10 kJ mol^{-1} more than the sum of the component monoenes. A value of 167.5 kJ mol^{-1} is ‘predicted’ in good agreement with experiment for the (*E*)-isomer; we may understand the *ca* 5 kJ mol^{-1} discrepancy for the (*Z*)-isomer in terms of strain in the latter as a 3.2 ± 1.1 kJ mol^{-1} difference is found[11] for the Z/E difference for 3-hexene, the related monoolefin with an internal double bond.



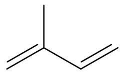
(79)

(80)

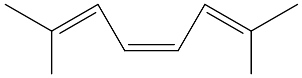
Agreement is somewhat poorer for substituted hexatrienes. Consider now the (*E*)-isomer of 2,5-dimethyl-1,3,5-hexatriene **(81)** for which Roth gives an enthalpy of formation of 95.8 kJ mol^{-1}. Simple olefin additivity, as done above for the parent hexatriene, results in a value of 103 kJ mol^{-1}. Modifying the above 5 to 3.5 kJ mol^{-1} as found for the relatedly branched conjugated diene (isoprene, **82**) gives a new value of *ca* 100 kJ mol^{-1} for the enthalpy of formation of **81**. The discrepancy has shrunk to *ca* 4 kJ mol^{-1}.



(81)



(82)



(83)

Consider now the 1,1,6,6-tetramethylated derivative of (*Z*)-1,3,5-hexatriene **(83)**, a species more properly named (*Z*)-2,6-dimethyl-2,4,6-octatriene and occasionally and trivially called ‘*cis*-allo-ocimene’. To estimate its enthalpy of formation, let us use simple olefin additivity along with:

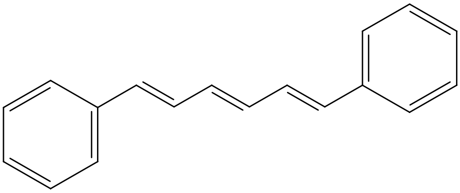
(a) the same 3.5 (instead of 5 kJ mol^{-1}) correction as above,

(b) the Z/E correction for the central hexatriene double bond as with the parent triene,

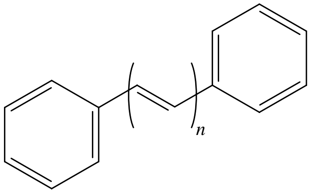
(c) the same Z/E difference as found for the substructure C=C−C=C−Me as found in the pentadienes **4** and **5**,

Numerically, the above sum to *ca* 40 kJ mol^{-1}. The experimentally measured enthalpy of formation for liquid **83**, derived from a combustion measurement, is −24 kJ mol^{-1}. Using our standard protocol to estimate the necessary enthalpy of vaporization results in an additional 50 kJ mol^{-1}. A value of 26 kJ mol^{-1} is thus predicted for the enthalpy of formation of gaseous **83**. The source of the 14 kJ mol^{-1} discrepancy evades us[58].

The final acyclic conjugated triene we will discuss is 1,6-diphenylhexatriene, presumed (*E*,*E*,*E*) and hence species **84**. Ignored by Pedley, an earlier archive[59] presented the enthalpy of formation of the solid to be 211 kJ mol^{-1}, a value *ca* 10 kJ mol^{-1} lower than that would be obtained by extrapolating from the enthalpies of formation of solid (*E*)-stilbene **(40)** and (*E*,*E*)-1,4-diphenylbutadiene **(38)**. Admitting the caveats given by a yet earlier compendium[60], we estimate with some callousness the necessary enthalpy of sublimation to obtain the desired gas phase enthalpy of formation. A value of *ca* 120 kJ mol^{-1} is found by averaging the values of other C_{18} hydrocarbons[61], while using only polynuclear aromatic hydrocarbons[62] would have given us 110 kJ mol^{-1}. This suggests that the enthalpy of formation of the gaseous species is between *ca* 320 and 330 kJ mol^{-1}. By contrast, the simple olefinic additivity logic would have resulted in *ca* 360 kJ mol^{-1}. The 30–40 kJ mol^{-1} difference is without explanation. Given the interest in α,ω-diphenylpolyenes (generically **85**), we recommend the remeasurement of the enthalpy of formation of **84**.



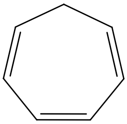
(84)



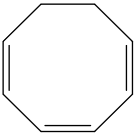
(85)

C. Totally Monocyclic Species

By this description we mean all of the conjugated double bonds are found in a single ring. Two thermochemically characterized examples we know of are tropilidene (1,3,5-cycloheptatriene) **(86)** and 1,3,5-cycloctatriene **(87)**. We have already mentioned that 1,3,5-cyclohexatriene and its derivatives will not be directly considered in this chapter because of the 'special' aromaticity of benzene and its derivatives. Were there no additional strain or resonance effects, then the enthalpy of formation of benzene and tropilidene would differ by −20.6 kJ mol^{-1}, the so-called 'universal' methylene increment[63]. Ignoring an uncertainty of *ca* 5 kJ mol^{-1} inherent in deciding between Pedley's (180.9 kJ mol^{-1}) and Roth's (186.6 kJ mol^{-1}) recommended values of the enthalpy of formation of tropilidene, the difference for benzene and tropilidene is *ca* 100 kJ mol^{-1} with benzene having the less positive value. It is unequivocal that the 120 kJ mol^{-1} discrepancy reflects the aromatic stabilization of benzene — one cannot use this discrepancy to suggest tropilidene is markedly destabilized.



(86)

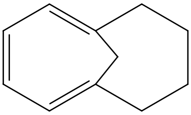


(87)

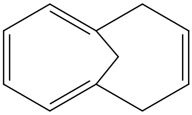
Relatedly, one would have expected 1,3,5-cyclooctatriene to have a more negative enthalpy of formation than tropilidene by the same $-20.6\ \mathrm{kJ\,mol^{-1}}$. By contrast, the difference for these enthalpies of formation of species **86** and **87** as derived from experimentally measured enthalpies of formation is *ca* $+12\ \mathrm{kJ\,mol^{-1}}$. From this we may deduce that tropilidene enjoys considerable stabilization due to homoaromatic interactions. While this conclusion is not new[64], nonetheless we find it encouraging to see it corroborated.

D. Totally Bicyclic Species

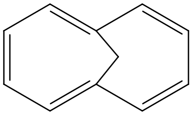
We also know the enthalpies of formation of the triene, 1,6-(butane-1,4-diyl)-tropilidene (bicyclo[4.4.1]undeca-1,3,5-triene, **88**) as well as of the related tetraene [1,6-(2-butene-1,4-diyl)-tropilidene, **89**] and pentaene [1,6-(1,3-butadiene-1,4-diyl)-tropilidene, **90**], respectively[65]. Choosing Roth's suggested value for the enthalpy of formation of the parent tropilidene so that all four species are taken from the same primary source[66], we find that attachment of these varying 4-carbon chains increase the enthalpy of formation by -40, 74 and 136 $\mathrm{kJ\,mol^{-1}}$, respectively. Upon affixing these same 4-carbon chains to benzene to form tetralin, 1,4-dihydronaphthalene and naphthalene (**91, 92** and **7**, respectively) the corresponding enthalpy of formation changes[67] by -57, 51 and 68 $\mathrm{kJ\,mol^{-1}}$.



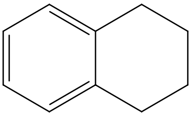
(88)



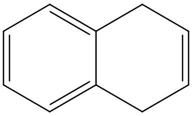
(89)



(90)



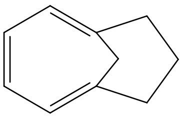
(91)



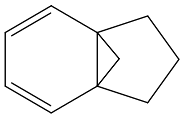
(92)

That there is less stabilization associated with attachment of $-(CH_2)_4-$ to tropilidene than to benzene suggests the greater sensitivity of homoaromatic species to distortion with concomitant loss of stabilization. This is not altogether surprising. Attachment of a propane-1,3-diyl chain to tropilidene does not result in the homoaromatic species **93** but instead the ring closes to the [4.3.1]-propelladiene, **94**. By contrast, we suspect few readers would want to consider the corresponding 1,2-(propane-1,3-diyl)-benzene, **95**, as non- or even homoaromatic. After all, this stable species has long been known as either indane or hydrindane. Relatedly, replacement of CH_2 by CF_2, CMe_2 or CH_2CH_2 shifts the equilibrium to the appropriate [4.3.1] or [4.3.2] propellane (species **96–98**, respectively).

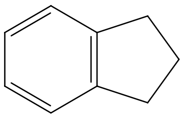
It is interesting that attachment of $-(CH_2)_4-$ and $-CH_2CH{=}CHCH_2-$ to benzene results in nearly the same enthalpy of formation change but it is not obvious how fortuitous this equality is: we have reasons for considerable skepticism of its validity[68]. That formation of naphthalene from benzene is accompanied by a lessened enthalpy of formation increase than that of 1,6-methano[10]annulene (yet another name for species **90**) from tropilidene would appear to be more of a strain than a resonance derived effect. From Roth, we find the resonance energy increase on going from tropilidene to 1,6-methano[10]annulene is 55 kJ mol^{-1} and from benzene to naphthalene the increase is nearly the same, nearly 59 kJ mol^{-1}. By contrast, the 1,5-methano[10]annulene **(99)** is less stable by 77 kJ mol^{-1} than the species it appears most naturally to be compared with, namely the isomeric **90**.



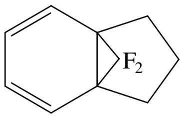
(93)



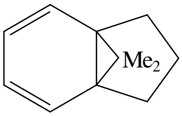
(94)



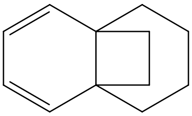
(95)



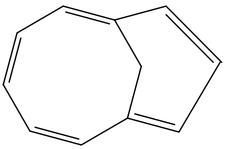
(96)



(97)



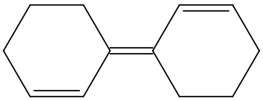
(98)



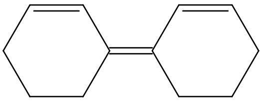
(99)

E. Semicyclic Species

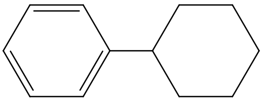
This class of compounds is defined to have some of the three conjugated double bonds found in the ring and others not. This class includes the isomeric 3,3′-bis(cyclohexenylidenes), **100** and **101**. Roth shows us that the two isomers have the same enthalpy of formation within *ca* 1 kJ mol^{-1}, a difference somewhat smaller than the 4 kJ mol^{-1} found for the totally acyclic 1,3,5-hexatrienes, **79** and **80** respectively. Naively these two sets of trienes should have the same $(E)/(Z)$ enthalpy difference. Given experimental uncertainties, we will not attempt to explain the difference[69]. We may compare **100** and **101** with phenylcyclohexane, **102**, an isomeric species which also has the same carbon skeleton. There is nearly a 110 kJ mol^{-1} enthalpy of formation difference between the semicyclic and cyclic trienes. We are not surprised, for the word ‘cyclic’ is customarily replaced by ‘aromatic’ when in the context of the previous sentence.



(100)



(101)



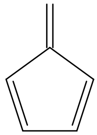
(102)

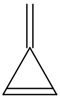
Strictly speaking, compounds such as fulvenes, isotoluenes and 3,4-dimethylenecyclobutene also qualify as semicyclic trienes. However, they will be discussed in the following section of this chapter because of their relation to aromatic hydrocarbons.

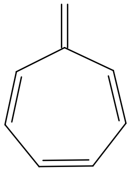
VII. CONJUGATED SPECIES WITH *EXO*-METHYLENE GROUPS: FULVENES, ISOTOLUENES, XYLYLENES AND RELATED SPECIES

A. Trivial Names and Nontrivial Compounds

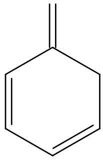
The classes of compounds discussed in this section have ‘trivial’ but ‘generic’ names that hark back to a more primitive understanding of organic chemistry. The class name ‘fulvenes’ addresses the yellow color of some of their initially discovered examples. Strictly speaking, these compounds are derivatives of methylenecyclopentadiene, **103**. In Section VII.C below on fulvenes we will extend the discussion to include the energetics of the ring-contracted methylenecyclopropene, **104**, and ring-expanded methylenecycloheptatriene, **105**, and thereby include the so-called triafulvenes and heptafulvenes. (These latter names suggest a more correct name for the derivatives of **103** is pentafulvenes, an alternative we will not use in this chapter.)

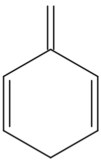

(103)

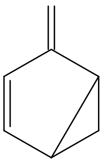

(104)

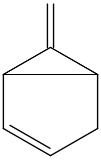

(105)

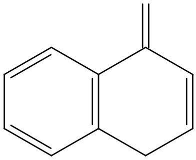
‘Isotoluenes’, discussed below in Section VII.D, are tautomeric isomers of alkylbenzenes wherein the aromatic ring has been sacrificed to form an exocyclic double bond, and so there is the archaic term ‘semibenzenes’ that has elsewhere been used for these species. Strictly speaking, the name ‘isotoluene’ itself refers to the two derivatives of cyclohexadiene (cf **49** and **50**) with a single exomethylene group, and so there are the *o*-, **106**, and *p*-, **107**, isomers. We also recognize the bicyclic species, **108** and **109**, that may both be casually considered *m*-isotoluenes, as well as tautomers of other alkylarenes such as **110** and **111**, that being suitably isomeric to 1-methylnaphthalene **(112)** and 9-methylanthracene **(113)** also qualify as isotoluenes.

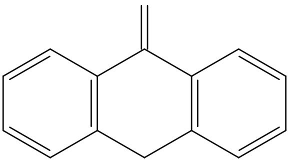

(106)

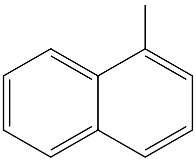

(107)

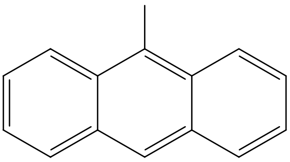

(108)


(109)

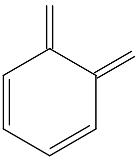

(110)


(111)

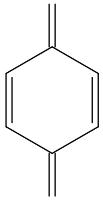

(112)


(113)

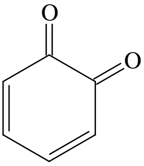
'Xylylenes', to be discussed in Section VII.E, have the same formal relation to xylenes as ethylene does to ethane, namely two fewer hydrogens with a compensatory, additional double bond. More properly then, *o*- and *p*-xylylene, **114** and **115**, are recognized as derivatives of 1,3- and 1,4-cyclohexadiene (**49** and **50**) with two exomethylene groups. (They are also recognized as derivatives of *o*- and *p*-benzoquinone, **116** and **117**, and so there is the alternative name of quinodimethans.) There is also a species called *m*-xylylene that has been alternatively drawn as **118, 119** and **120**. We will also consider the ring-contracted 3,4-dimethylenecyclobutene, **121**, under the generic category of xylylenes as well.



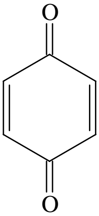
(114)



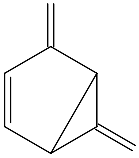
(115)



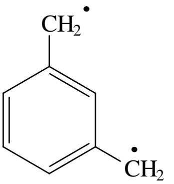
(116)



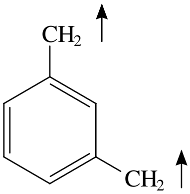
(117)



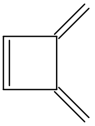
(118)



(119)



(120)



(121)

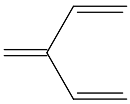
The compounds in this section — fulvenes, isotoluenes, xylylenes — are characterized by trivial names. Our various reference citations document their nontrivial chemistry: isomerization, polymerization and oxidation befall the unwary experimentalist who would study them.

B. Conjugation and Cross-conjugation

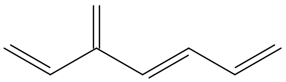
In the title to this section we referred to fulvenes, isotoluenes and xylylenes as conjugated species. Strictly speaking, we should have referred to them as cross-conjugated. Let us thus begin with a definition. By cross-conjugated, we mean species with the substructure $C{=}C({-}C{=}C)_2$ as opposed to $C{=}C{-}C{=}C{-}C{=}C$, that is, they are formal derivatives of 1,1-divinylethylene as opposed to 1,2-divinylethylene. It is a common assumption in the study of energetics of organic compounds that cross-conjugation results in less resonance stabilization than conventional conjugation. Is this assumption quantitatively corroborated by the thermochemical literature?

The simplest cross-conjugated polyene is **122**, 3-methylene-1,4-pentadiene or 1,1-divinylethylene itself. Accepting the analysis in Reference 2 that was made using Roth's data, we find this species to be some 23 kJ mol^{-1} less stable than the simplest conjugated polyene, **80**, (*E*)-1,3,5-hexatriene or 1,2-divinylethylene. The next simplest cross-conjugated polyenes are 3-methylene-1,4,6-heptatriene, **123**, and 3,4-dimethylene-1,5-hexadiene, **124**, that would naturally be compared with (*E*,*E*)-1,3,5,7-octatetraene,

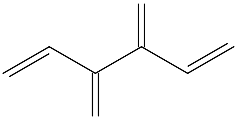
125. While we know of no experimental thermochemical data for **123**, Roth informs us that the enthalpy of formation of **124** is 259 kJ mol^{-1}. There are no experimental thermochemical data for **125** either, but it is easy to estimate the desired enthalpy of formation. We may either use the standard olefin approach with ethylene, 1,3-butadiene and (*E*)-1,3,5-hexatriene (i.e. with $CH_2{=}CH_2$, **33** and **79**) or linearly extrapolate these three unsaturated hydrocarbons. From either of these approaches, we find a value of *ca* 225 kJ mol^{-1}. Cross-conjugation costs some 35 kJ mol^{-1} in the current case. Interestingly, the directly measured cross-conjugated 1,1-diphenylethylene **(126)** is only *ca* 10 kJ mol^{-1} less stable than its directly measured conjugated (*E*)-1,2-isomer **(40)** despite the expected strain effects that would additionally destabilize the former species.



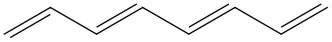
(122)



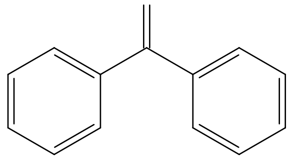
(123)



(124)



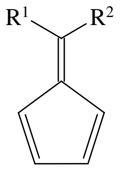
(125)



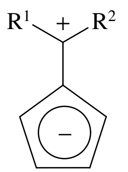
(126)

C. Fulvenes

Part of the folklore of nonbenzenoid hydrocarbons suggests fulvenes are on the nonaromatic/aromatic border. It is thus not obvious whether these species really belong in this chapter. Yet, because their aromaticity is so much less than that found for their isomeric benzenoid derivatives[70] we feel confident to proceed. Other than the parent hydrocarbon[71] species **103** [i.e. **127** wherein (R^1, R^2) = (H, H) most of the other thermochemically characterized fulvenes have substitution on the exomethylene carbon; cf (R^1, R^2) = (H, Me)[71], (Me, Me)[72] and (Ph, Ph)[73]: for reference, the suggested enthalpies of formation of the (H, H), (H, Me), (Me, Me) and (Ph, Ph) species are 224, 185, 144 and 402 kJ mol^{-1}, respectively. Were all differences in steric interactions and contributions from the dipolar resonance structures of the generic type **128** negligible, then ΔH_f (**127**, R^1, R^2) and $\Delta H_f(CH_2{=}CR^1R^2)$ would be linearly related. We find that a nearly perfect straight line



(127)



(128)

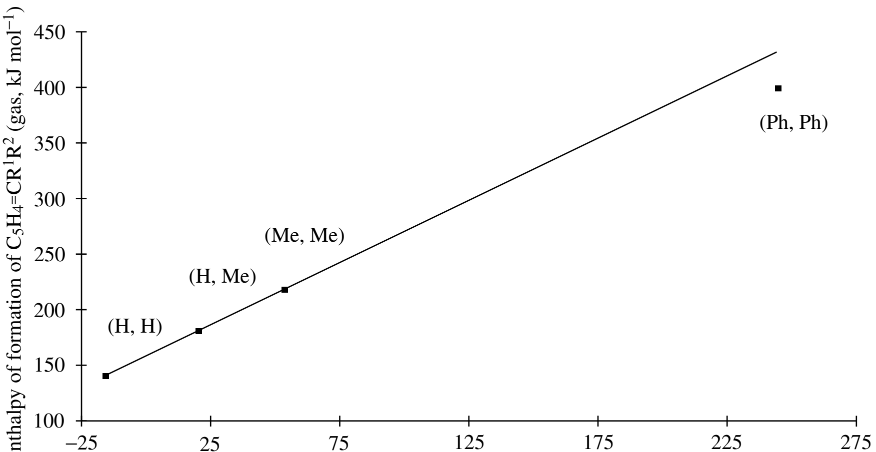


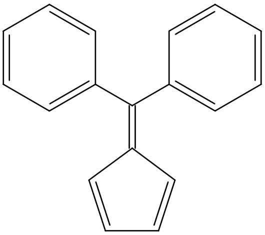
FIGURE 1. Enthalpies of formation of $C_5H_4{=}CR^1R^2$ vs $CH_2{=}CR^1R^2$

for olefins vs fulvenes (equation 35) can be drawn[74] through the (H, H), (H, Me) and (Me, Me) points:

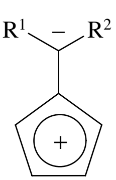
$$\Delta H_f(\mathbf{127}, R^1, R^2) \pm 1.3 = (1.152 \pm 0.026)\Delta H_f(CH_2{=}CR^1R^2) + (163.0 \pm 0.9) \quad (35)$$

The r^2 for this line is 0.9995 with a standard deviation of *ca* 0.9 kJ mol^{-1} (Figure 1). The deviation for $R^1 = R^2 =$ Ph **(129)** is some 43 kJ mol^{-1} below the line. If the *exo*-methylene/ring bond is quite polar and resonance structures **128** are significant (**130** is easily ignorable), then ΔH_f (**127**, R^1, R^2) and $\Delta H_f(O{=}CR^1R^2)$ would be more likely to be linearly related. Another nearly perfect line, that of carbonyls vs fulvenes, can be drawn through the (H,H), (H,Me) and (Me,Me) points (equation 36).

$$\Delta H_f(\mathbf{127}, R^1, R^2) \pm 2.7 = (0.734 \pm 0.075)\Delta H_f(O{=}CR^1R^2) + (304.8 \pm 5.9) \quad (36)$$



(129)



(130)

The r^2 is but 0.998 with a standard deviation of *ca* 1.0 kJ mol^{-1} (Figure 2). Again the diphenyl species **129** is sorely deviant, this time above the line by some 59 kJ mol^{-1}, i.e. in the opposite direction. Despite the nearly ±15 kJ mol^{-1} uncertainty reported for the measurement for enthalpy of formation of diphenylfulvene, these results suggest the

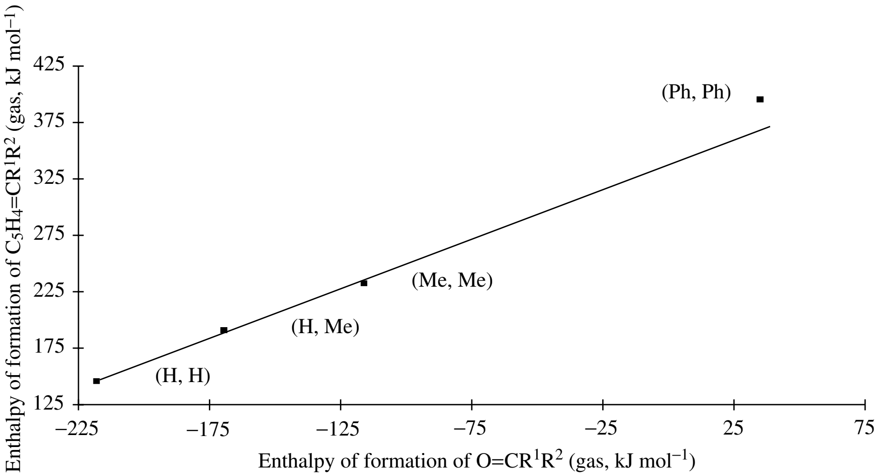


FIGURE 2. Enthalpies of formation of $C_5H_4{=}CR^1R^2$ vs $O{=}CR^1R^2$

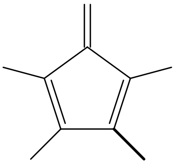
fulvene *exo*-methylene/ring bond is of polarity intermediate between those of 'normal' olefins and ketones. This conclusion is consistent with the general idea of some — but not 'that much' — polarity in fulvenes.

Consider now the one ring-substituted fulvene for which we have a measured enthalpy of formation, namely the ring tetramethylated derivative **131** with its value of 83 kJ mol^{-1}. If benzene is the appropriate paradigm for fulvene, then reaction 37 is expected to be essentially thermoneutral.

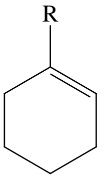
$$\mathbf{103} + 4\text{PhMe} \longrightarrow \mathbf{131} + 4\text{C}_6\text{H}_6 \qquad (37)$$

If an olefinic paradigm is appropriate for fulvene, then reaction 38 would be more likely to be thermoneutral.

$$\mathbf{103} + 4(\mathbf{132}, \text{R} = \text{Me}) \longrightarrow \mathbf{131} + 4(\mathbf{132}, \text{R} = \text{H}) \qquad (38)$$



(131)



(132)

From the enthalpies of formation from Roth for the fulvenes and from Pedley for the other hydrocarbons in equations 37 and 38, we find the former reaction is exothermic by 12 kJ mol^{-1} while the latter is endothermic by 12 kJ mol^{-1}. Ionic resonance structures analogous to **128** are expected to be of less importance for the ring alkylated species than for the parent species **103**: negatively charged carbon is destabilized by adjacent electron-donating groups. Nonbonded Me•••Me and Me•••CH_2 repulsion further destabilize the tetramethyl species. As such, reactions 37 and 38 are more endothermic than the above numbers suggest. We conclude that the understanding derived from equation 37 is untenable. Equivalently, fulvene is more olefinic than benzenoid, a result we have already concluded.

The parent triafulvene, **104**, is the sole representative of this hydrocarbon class for which there is a suggested enthalpy of formation[75], namely 423 kJ mol^{-1}. If the conjugative interactions of the *exo*-methylene with cyclopropene and cyclopentadiene were the same, then equation 39 would be thermoneutral.

$$\mathbf{103} + \text{cyclo-}[CH_2(CH)_2] \longrightarrow \mathbf{104} + \text{cyclo-}[CH_2(CH)_4] \qquad (39)$$

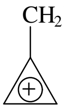
In fact, it is some 56 kJ mol^{-1} endothermic. Part of small ring folklore[76] asserts that introduction of trigonal carbons into 3-membered rings is energetically expensive compared to acyclic paradigms. In that 5-membered ring compounds are generally 'normal', much the same is expected when comparing the directly relevant 3- and 5-membered rings; cf equations 40 and 41:

$$\text{cyclo-}[(CH_2)_3] + \text{cyclo-}[(CH_2)_4C{=}CH_2] \longrightarrow \text{cyclo-}[(CH_2)_2C{=}CH_2] + \text{cyclo-}[(CH_2)_5] \qquad (40)$$

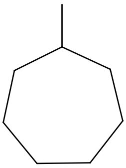
$$\text{cyclo-}[(CH_2)_2C{=}CH_2] + \text{cyclo} - [(CH_2)_3(CH)_2] \longrightarrow \text{cyclo-}[CH_2(CH)_2] + \text{cyclo-}[(CH_2)_4C{=}CH_2] \qquad (41)$$

These reactions, going from no sp^2 carbon to one in a 3-membered ring, and from one to two respectively, are endothermic by *ca* 59 and 55 kJ mol^{-1}. This suggests that going from two to three sp^2 carbons in a three-membered ring will also be endothermic by *ca* 50–60 kJ mol^{-1}. Correcting for this suggests equation 39 would be essentially thermoneutral were there no special strain effects in 3-membered rings. As such, we conclude that the conjugative effects of the *exo*-methylene on cyclopropene and cyclopentadiene in the formation of triafulvene and fulvene, respectively, are nearly the same. This is a surprising result given the reversed polarity of these hydrocarbons; cf ionic resonance structures **128** and **133**.

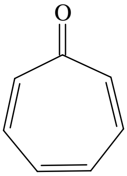
What, then, can be said about heptafulvene, **105**? No direct measurement of the enthalpy of formation of **105** has been reported. However, there are chronicled[77] measurements of its enthalpy of hydrogenation[78], −386 kJ mol^{-1}. The enthalpy of formation of the hydrogenation product, methylcycloheptane **(134)**, remains unmeasured. However, the difference of this value and of the demethylated counterpart, cycloheptane, is not likely to be significantly dissimilar from the differences found for the pairs methylcyclohexane and cyclohexane, methylcyclopentane and cyclopentane, and even the acyclic isobutane ('2-methylpropane') and propane. These last differences average *ca* 30 kJ mol^{-1} and thus we deduce $\Delta H_f(\mathbf{134}, g) = -148$ kJ mol^{-1} and $\Delta H_f(\mathbf{105}, g) = 238$ kJ mol^{-1}. Is this last value plausible? Let us compare **105** with tropone, **135**. The enthalpy of formation of **105** is found to be 194 kJ mol^{-1} more positive than that of **135**. By contrast, the difference of enthalpies of formation of methylenecyclohexane and cyclohexanone, methylenecyclopentane and cyclopentanone, and isobutene ('methylenepropane') and acetone (propanone) average some 203 kJ mol^{-1}. This does not make sense in that we might have thought that tropone would enjoy more resonance stabilization than heptafulvene. Yet we recall that conjugated α,β-unsaturated carbonyl compounds have less resonance stabilization than the sterically comparable and isoelectronically related dienes[79].



(133)



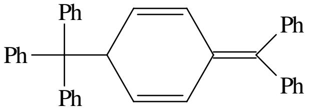
(134)



(135)

D. Isotoluenes

It is interesting to note that 100 years ago the first isotoluene was discovered[80] and 60 years ago its thermochemistry was investigated[81]. However, this compound has generally remained misnamed and so its interesting structural feature was ignored by most chemists. Then again, the incorrect name itself evinces interest (hexaphenylethane) — by contrast, the mere length (and, implicitly, the complexity) of its more 'systematic' name 4-(triphenylmethyl)-1-(diphenylmethylidene)-2,5-cyclohexadiene, **136**, disguises its unusual structural features[82]. Much more recently, the enthalpies of formation of both *o*- and *p*-isotoluene (**106** and **107**, respectively) have been determined: the former by both positive[83] and negative[84,85] ion chemistry, the latter only by the latter[84,85]. The positive ion experiment suggests an enthalpy of formation of 172 $\mathrm{kJ\,mol^{-1}}$. The negative ion experiments suggest the enthalpies of formation of the isotoluenes lie some 100 ± 17 $\mathrm{kJ\,mol^{-1}}$ above that of toluene and so are numerically *ca* 150 ± 17 $\mathrm{kJ\,mol^{-1}}$. Are any of these values reasonable? The following outlines our confusion.



(136)

The first observation is that the two isotoluenes have nearly the same enthalpy of formation as had been seen for the isomeric cyclohexadienes in Section V.C. This suggests that conjugation energy in both of these species is small because the *o*- and *p*-isotoluenes are formally conjugated and cross-conjugated trienes, respectively. Yet, there is considerable conjugation energy in the isotoluenes as demonstrated by the 25 (using data from Reference 83) or 50 $\mathrm{kJ\,mol^{-1}}$ (using data from Reference 84 and 85) exothermicity of the formal reactions 42a and 42b.

$$\mathbf{49} + \text{cyclo-}[(CH_2)_5C{=}CH_2] \longrightarrow \mathbf{106} + \text{cyclo-}[(CH_2)_6] \tag{42a}$$

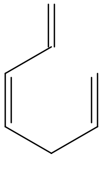
$$\mathbf{50} + \text{cyclo-}[(CH_2)_5C{=}CH_2] \longrightarrow \mathbf{107} + \text{cyclo-}[(CH_2)_6] \tag{42b}$$

Remembering that a typical endothermicity of very approximately 5 $\mathrm{kJ\,mol^{-1}}$ is found when there is no strain accompanying combination of two olefins to form a conjugated diene[23,24], the cyclization reaction of (*Z*)-1,3,6-heptatriene, **137** (equation 43)

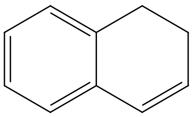
$$\mathbf{137} \longrightarrow \mathbf{107} + H_2 \tag{43}$$

is naively expected to be endothermic by that *ca* 5 $\mathrm{kJ\,mol^{-1}}$ as well. From a plausible enthalpy of formation of *ca* 162 $\mathrm{kJ\,mol^{-1}}$ for the acyclic triene, we deduce the enthalpy of formation of **106** to be 163 kJ mol^{-1}. Considering all the assumptions, it is not unreasonable that a value as small as 150 kJ mol^{-1} may arise[86].

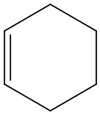
Finally, our earlier experience[87] suggests the difference of the enthalpy of formation of benzo-*p*-isotoluene, **110**, and *p*-isotoluene, **107**, should be comparable to that of the cyclohexadienes **49** and **50** to the dihydronaphthalenes, **138** and **92**, and to cyclohexene, **139**, to tetrahydronaphthalene, **91**, and thus to the *ca* 31 kJ mol^{-1} found for general benzoannelation. Admitting there are complications with the enthalpies of formation of the former pair of species (see Section V.C), let us use those of the latter pair and their difference of 31 kJ mol^{-1}. From Reference 85 (using both negative and positive ion chemical techniques and logic), we find **110** has an enthalpy of formation some 65 kJ mol^{-1} higher than that of 1-methylnaphthalene, **112**. From Reference 88, we find the latter number, 113 kJ mol^{-1}, and so derive the enthalpy of formation of **110** to be 180 kJ mol^{-1}. From this we conclude that the enthalpy of formation of *p*-isotoluene, **107**, is *ca* 150 kJ mol^{-1}. This is consistent with one of the suggested experimental numbers, but violates our intuition as noted above[89].



(137)



(138)

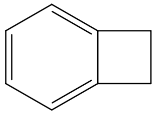


(139)

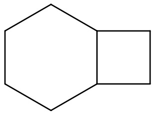
E. Xylylenes

As with the isotoluenes, there are two sets of independent, but also indirect, measurements from which the enthalpy of formation of *o*-xylylene, **114**, can be derived. One study interrelated this species by varied equilibration measurements involving the isomeric benzocyclobutene **140** and the hydrogenation enthalpy of the latter hydrocarbon to bicyclo[4.2.0]octane, **141**. The value of 254 kJ mol^{-1} was derived by Roth from this study. The second study[90] employed what are now relatively primitive quantum chemical calculations to assist in their understanding of ion–molecule reactions, most notably proton affinity measurements involving the 2-methylbenzyl cation, **142**. An alternative value of 234 ± 17 kJ mol^{-1} was initially derived here. One can be convinced these independent values are roughly consonant if the suggested error bars are employed. Yet it should be admitted that the authors of Reference 90 suggested a value of 230 ± 17 kJ mol^{-1} for the *p*-isomer, **115**, from related analysis involving the 4-methylbenzyl cation, **143**. However, this value was amended to 203 ± 17 kJ mol^{-1} in a relatively recent compendium[91] by use of experimentally measured enthalpies of halide transfer reactions[92]. In turn, use of a new and nearly completed proton affinity scale[93] results in a value somewhat less than 200 kJ mol^{-1} for ΔH_f **(115)**. The same analysis suggests a comparable enthalpy of formation for the *o*-isomer, **114**. So, which value is to be preferred for the enthalpy of formation of (either) xylylene, *ca* 200, 230 or 250 kJ mol^{-1}? The origin of the discrepancy evades us, as does any explanation for the observation that the two xylylenes should have nearly the same enthalpy of formation[94].

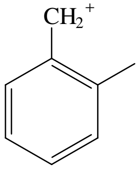
Let us now turn to the ring-contracted xylylene 3,4-dimethylenecyclobutene **(121)**. Does Roth's preferred enthalpy of formation value of 336 kJ mol^{-1} look plausible? In the absence of both 'special' strain and resonance energy contributions, the difference of the



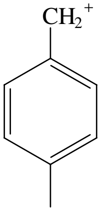
(140)



(141)



(142)



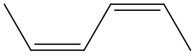
(143)

enthalpies of formation of **121** and benzene would equal the difference of the enthalpies of formation of 2,3-dimethyl-1,3-butadiene and 2,4-hexadiene. That is, the following reaction would be essentially thermoneutral;

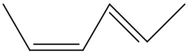
$$\mathbf{121} + \mathrm{MeCH{=}CHCH{=}CHMe} \longrightarrow \mathbf{6} + \mathrm{CH_2{=}CMeCMe{=}CH_2} \qquad (44)$$

Taking the former value from Pedley (45.1 ± 1.1 kJ mol^{-1}) and the average of the values for the (*Z*,*Z*)-, (*E*,*Z*)- and (*E*,*E*)-2,4-hexadienes (species **144, 145** and **146**, *ca* 48 kJ mol^{-1} from Reference 12), we derive the enthalpy of formation of **121** is 86 kJ mol^{-1}. The discrepancy is 250 kJ mol^{-1}, a large but mostly sensible number. That is, we recover all but *ca* 30 kJ mol^{-1} of this exothermicity by summing the new destabilization arising from the strain energy of a 4-membered ring (*ca* 109 kJ mol^{-1}) and the loss of resonance energy of benzene as defined by Roth (fortuitously also, *ca* 109 kJ mol^{-1}). Relatedly, the exothermicity of the formal reaction 45

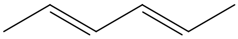
$$\mathbf{121} + \text{cyclo-}[(\mathrm{CH_2})_3(\mathrm{CH})_2] \longrightarrow \mathbf{103} + \text{cyclo-}[(\mathrm{CH_2})_3\mathrm{C{=}CH_2}] \qquad (45)$$



(144)



(145)



(146)

is *ca* 25 kJ mol^{-1}. Using the more classical calorimetric measured value for the enthalpy of formation of *o*-xylylene, a comparable exothermicity is found for the following putative thermoneutral reaction (equation 46) involving this species along with 1,3-cyclohexadiene and cyclobutene:

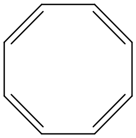
$$\mathbf{121} + \mathbf{49} \longrightarrow \mathbf{103} + \text{cyclo-}[(\mathrm{CH_2})_2(\mathrm{CH})_2] \qquad (46)$$

That equations 44, 45 and 46 find species **121** equally destabilized suggests either an error in the measurement and/or an error in our understanding of the energetics of 3,4-dimethylenecyclobutene.

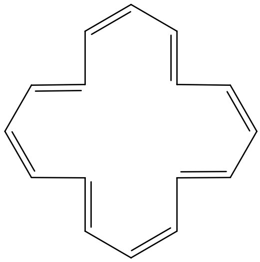
VIII. ANNULENES: AROMATICITY AND ANTIAROMATICITY

A. If We Study Cyclooctatetraene, Why Not Benzene?

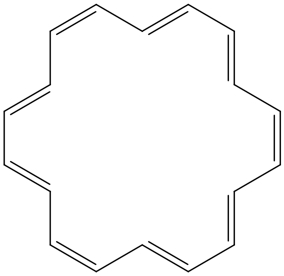
When starting this chapter we promised ourselves and the reader not to consider benzene and its derivatives. Cyclooctatetraene [or more properly (*Z*,*Z*,*Z*,*Z*)-1,3,5,7-cyclooctatetraene, **147**] is generally recognized as a polyene and so this latter compound would appear to belong here. How can we do one and not the other? Therefore, in this concluding section of the chapter, we briefly discuss the enthalpies of formation of some of the



(147)



(148)



(149)

[n]annulenes, those cyclic conjugated polyenes with the generic formula C_nH_n. There are experimentally determined values for $n = 6$ (benzene), 8 (cyclooctatetraene), 16 and 18, species **6, 147, 148** and **149**, respectively[95].

B. How Aromatic or Antiaromatic are [8] and [16]Annulenes?

Regardless of how we wish to define the resonance stabilization of the $n = 6$ case of benzene, it is unequivocal that this substance enjoys considerable stabilization relative to 'classical' expectations related to acyclic and/or less unsaturated precedent. Rather than discussing the plethora of models and even greater experimental evidence that documents this 'aromaticity', we consider benzene itself as the paradigm. We will return to olefinic paradigms later in this section.

More precisely, let us consider the enthalpies of reaction for the formal process 47:

$$n/6[C_6H_6] \longrightarrow C_nH_n \qquad (47)$$

We start with the $n = 8$ case and thus species **147**. For the liquid and gas, the enthalpies of reaction are 189.1 and 185.7 kJ mol^{-1} endothermic, respectively, while for the solid with temperature-uncorrected enthalpies of fusion, the reaction is found to be 189.9 kJ mol^{-1} endothermic. These numbers are essentially indistinguishable and this near-equality encourages us to consider data for reaction 47 from any of the three phases as equivalent to each other and equal to *ca* 188 kJ mol^{-1}. For the $n = 16$ case, there are thermochemical data only for the solid phase of [16]annulene, **148**. Using this enthalpy of formation of **148**, 547.5±11.7 kJ mol^{-1}, and that of solid benzene by use of a temperature-uncorrected enthalpy of fusion, this reaction is found to be some 373 kJ mol^{-1} endothermic. That 373 is greater than 188 does not mean that [16]annulene is more destabilized than its 8-carbon analog. Numbers associated with aromaticity and antiaromaticity have usually been normalized by dividing by the number of carbon atoms and/or π-electrons. Accordingly, dividing these two destabilization numbers by 16 and 8, respectively, results in the more significant stabilization per carbon (or per π-electron). These last two numbers, 23.3 and 23.6 kJ mol^{-1}, are essentially equal. We thus conclude that the aromaticity — more precisely, the antiaromaticity — of species **148** and **147**, [16] and [8]annulene, are essentially equal.

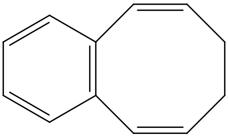
C. [18]Annulene and Acyclic Polyenes

Let us turn to [18]annulene, **149**, for which there are two sets of measurements. The first set consists of direct enthalpy of combustion and thus of formation[96]. From the latter datum, 163.4±16.7 kJ mol^{-1} for solid **149** and our phase change independence assumption, we find reaction 48 to be exothermic by some 46 kJ mol^{-1}. Equivalently, benzene is *ca* 2.5 kJ mol^{-1} more aromatic per carbon than [18]annulene. As noted by the authors of Reference 96, this difference seems too small: [18]annulene does not behave *that* aromatic. These latter authors redetermined the enthalpy of formation of **149** by analyzing the enthalpy of the decomposition reaction to form benzene and 1,2-benzo-1,3,7-cyclooctatriene, **150**, in reaction 48:

$$\mathbf{149} \longrightarrow \mathbf{6} + \mathbf{150} \tag{48}$$

On the basis of some judicious measurements and relevant estimations, the enthalpy of formation of gas phase [18]annulene was derived[97] to be *ca* 519±22 kJ mol^{-1}. From this we conclude that benzene is *ca* 15 kJ mol^{-1} more aromatic per carbon than [18]annulene. This value seems too large.

Although we cannot as yet converge on a desired enthalpy of formation of gaseous [18]annulene[98], it is quite apparent that this last number is suspect in terms of at least two acyclic paradigms for aromaticity. Recall the Dewar–Breslow definition[99] for aromaticity and antiaromaticity of an [n]annulene in terms of the corresponding acyclic polyene with $n/2$ double bonds. There is no experimental measurement of the enthalpy of formation of all-(E)-1,3,5,7,9,11,13,15,17-octadecanonaene, species **151**. However, we should be surprised if this value seriously differed from that of nine ethylenes and 8(5) kJ mol^{-1}, the 5 kJ mol^{-1} being taken as the enthalpy of reaction 19 for unstrained olefins and dienes[100]. The enthalpy of formation of **151** is thus *ca* 513 kJ mol^{-1}. This is somewhat less than the value for [18]annulene and so we would conclude that the cyclic species is essentially nonaromatic[101]. Alternatively, consider the series of acyclic polyenes, ethylene, 1,3-butadiene, 1,3,5-hexatriene, …. The gas phase enthalpies of formation are respectively 52.5, 110.0, 165.1, … corresponding to an enthalpy of formation of an acyclic and unstrained −CH=CH− (or alternatively =CH−CH=)[102] group of *ca* 56 kJ mol^{-1}. Were [18]annulene totally strainless and totally without aromaticity (as opposed to delocalization), one could say that it was composed of nine such groups. The enthalpy of formation of **151** would then equal *ca* 9•56 or 504 kJ mol^{-1}. This number is less positive than the recommended enthalpy of formation of [18]annulene. Do we want to consider this species to be antiaromatic[103]? The source of the error is not apparent.



(150)

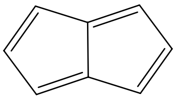
(151)

D. Annulenoannulenes

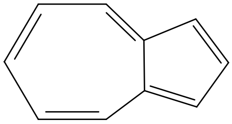
We close this chapter with a brief discussion of [n]annuleno[n']annulenes, those species composed of two *ortho*-fused annulenes. Using the same closed shell criterion as for

[*n*]annulenes themselves, we find that there are but five species that fulfill this description for which thermochemical data are derivable from experiment: pentalene **(152)**, naphthalene **(7)**, azulene **(153)**, bicyclo[6.2.0]deca-1,3,5,7,9-pentaene **(154)** and octalene **(155)**. We obtain the enthalpy of formation of **152** by assuming reaction 49 involving it and its 1,3,5-tri-*t*-butyl derivative, **156**, is thermoneutral,

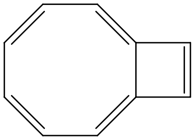
$$\mathbf{156} + 3\mathrm{PhH} \longrightarrow \mathbf{152} + 3^{t}\text{-}\mathrm{BuPh} \tag{49}$$



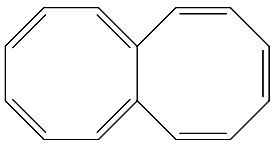
(152)



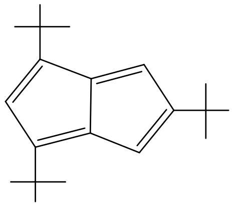
(153)



(154)



(155)

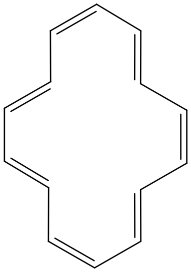


(156)

Is this value of 330 kJ mol^{-1} plausible? Were pentalene a normal polyene, we would anticipate an enthalpy of formation of *ca* $4\cdot 52.5+5\cdot 5$ or *ca* 235 kJ mol^{-1}. There is thus *ca* 100 kJ mol^{-1} of destabilization. Is this due to antiaromaticity since we recognize pentalene as a derivative of planar [8]annulene? We think not, for there are two five-membered rings in pentalene each contributing *ca* 30 kJ mol^{-1} of strain apiece[104].

The next three annulenoannulenes — species **7**, **153** and **154** — are isomers with enthalpies of formation 150.3, 307.5 and (from Roth) 514.2 kJ mol^{-1}. In terms of combining ethylenes to form polyenes, their shared acyclic reference energy[105] would be 293 kJ mol^{-1}. It is clear that naphthalene is aromatic and viewing it as a polyene is ill-advised. It is clear that species **154** is strained by at least *ca* 100 kJ mol^{-1} as befits the presence of a four-membered ring. We find further disentangling the competing roles of destabilizing strain and stabilizing aromatic delocalization is problematic.

Turning now to octalene, were species **155** a normal polyene, its enthalpy of formation would be *ca* 407 kJ mol^{-1}. Instead, the experimentally determined value is 551 kJ mol^{-1}. This suggests considerable destabilization much as found in its component cyclooctatetraene rings: after all, cyclooctatetraene itself is destabilized by *ca* 60 kJ mol^{-1} relative to the acyclic octatetraene. Octalene is not a simply modified derivative of [14]annulene **(157)** or even of all-(*E*)-1,3,5,7,9,11,13-tetradecaheptaene, **158**. Regrettably, it evades us how to make the necessary 'wiggle-worm corrections' to relate general polyenes, annulenes and annulenoannulenes. But we do not wring our hands. Perhaps in time to contribute to a future supplement to this volume we will have gained the necessary insights to make these interrelations, comparable in qualitative and quantitative understanding of the other dienes and polyenes that fill this chapter.



(157)

(158)

IX. ACKNOWLEDGMENTS

The author wishes to thank Suzanne W. Slayden for her numerous scientific and editorial comments on this study, and to the Chemical Science and Technology Laboratory of the US National Institute of Standards and Technology for partial support of his research.

X. REFERENCES AND COMMENTARY

1. S. W. Slayden and J. F. Liebman, in *The Chemistry of Functional Groups, Supplement E2*: *The Chemistry of Hydroxyl*, *Ether and Peroxide Groups* (Ed. S. Patai), Wiley, Chichester, 1993.
2. J. F. Liebman, in *The Chemistry of the Cyclopropyl Group*, Vol. 2 (Ed. Z. Rappoport), Wiley, Chichester, 1995.
3. D. D. Wagman, W. H. Evans, V. B. Parker, R. H. Schumm, I. Halow, S. M. Bailey, K. L. Churney and R. L. Nuttall, *The NBS Tables of Chemical Thermodynamic Properties*: *Selected Values for Inorganic and* C_1 *and* C_2 *Organic Substances in SI Units*, *J. Phys. Chem. Ref. Data*, **11** (1982), Supplement 2.
4. J. S. Chickos, A. S. Hyman, L. H. Ladon and J. F. Liebman, *J. Org. Chem.*, **46**, 4294 (1981).
5. J. S. Chickos, R. Annunziata, L. H. Ladon, A. S. Hyman and J. F. Liebman, *J. Org. Chem.*, **51**, 4311 (1986).
6. J. S. Chickos, D. G. Hesse and J. F. Liebman, in *Energetics of Organometallic Species* (Ed. J. A. Martinho Simões), NATO ASI, Series C, Vol. 367, Kluwer, Dordrecht, 1992.
7. D. W. Rogers, O. A. Dagdagan and N. L. Allinger, *J. Am. Chem. Soc.*, **101**, 671 (1979).
8. W. R. Roth, O. Adamczak, R. Breuckmann, H.-W. Lennartz and R. Boese, *Chem. Ber.*, **124**, 2499 (1991).
9. Unless otherwise said, our preferred sources for enthalpies of formation of hydrocarbons are Reference 8 by Roth and his coworkers, and J. B. Pedley, R. D. Naylor and S. P. Kirby, *Thermochemical Data of Organic Compounds* (2nd ed.), Chapman & Hall, New York, 1986. In this chapter these two sources will be referred to as ‘Roth’ and ‘Pedley’, respectively, with due apologies to their coworkers. We will likewise also occasionally take enthalpies of fusion from either E. S. Domalski, W. H. Evans and E. D. Hearing, ‘Heat Capacities and Entropies of Organic Compounds in the Condensed Phase’, *J. Phys. Chem. Ref. Data*, **13**, 1984, Supplement 1, or E. S. Domalski and E. D. Hearing, *J. Phys. Chem. Ref. Data*, **19**, 881 (1990), and refer to either work as ‘Domalski’.
10. This is a paraphrase of the dialogue involving the humanistic psychologist Carl Rogers: “being asked ‘Don’t you get bored listening hour after hour, day after day to people telling you their problems’, replied, ‘Yes, and when I do I ask myself “Why am I bored?” and then I have an interesting experiment’.” This episode was recounted by Irvin Greenberg, another humanistic psychologist, to the author of the current study.
11. (a) D. W. Rogers and E. L. Crooks, *J. Chem. Thermodyn.*, **15**, 1087 (1983).
    (b) D. W. Rogers, E. Crooks and K. Dejroongraung, *J. Chem. Thermodyn.*, **19**, 1209 (1987).
12. W. Fang and D. W. Rogers, *J. Org. Chem.*, **57**, 2297 (1992).
13. By Hess’s Law, these two approaches must yield the same energy of interaction between the two double bonds. The virtue of this latter approach is that enthalpy of formation data for the

hydrogenated or saturated species need not be available. The use of Hess's law discourages us from employing enthalpies of formation obtained by using molecular mechanics. So does our prior experience (e.g. References 1 and 2) in making estimates to accommodate for missing enthalpies of formation. In the current study we use molecular mechanics in the following, relatively limited sense. In Reference 8, Roth empirically measured enthalpies of hydrogenation and accompanied these numbers by molecular mechanically calculated enthalpies of formation of saturated hydrocarbons to derive the enthalpies of formation of the dienes and polyenes of direct interest in this chapter. The current author did not deem it necessary or even desirable to estimate *de novo* the enthalpies of formation of the saturated species.

14. For simple alkenes there is a *ca* 4 kJ mol^{-1} difference in the enthalpy of hydrogenation for their single internal double bond. See References 11 for the isomeric hexenes; D. W. Rogers and K. Dejoongruang, *J. Chem. Thermodyn.*, **20**, 675 (1988) for isomeric heptenes; and D. W. Rogers, K. Dejoongruang, S. D. Samuel, W. Fang and Y. Zhao, *J. Chem. Thermodyn.*, **24**, 561 (1992) for isomeric octenes.
15. We take here twice the 'universal methylene increment' (cf Reference 1) as found in the liquid state, i.e. $20.6 + 4.7$ where 20.6 is the usually proposed (gas phase) value and 4.7 is (within a sign) the enthalpy of vaporization or condensation per carbon for an arbitrary organic compound as suggested in Reference 4.
16. B. Lebedev and N. Smirnova, *Macromol. Chem. Phys.*, **195**, 35 (1994).
17. Said differently, in the absence of interolefin interactions within and between polymer molecules, the enthalpy of polymerization should reflect the release of strain energy of the precursor monomer cycloalkene. From our earlier knowledge of cycloalkenes [e.g. J. F. Liebman and A. Greenberg, *Chem. Rev.*, **76**, 311 (1976) and A. Greenberg and J. F. Liebman, *Strained Organic Molecules*, Academic Press, New York, 1978], we conclude cyclohexene is less strained than cyclobutene, cyclopentene, cycloheptene and cyclooctene. Another reason for suspicion is that the enthalpies of polymerization and of hydrogenation of cyclohexene and its 4-methyl derivative are not expected to be particularly different, yet the polymerization of the former is reported (under all conditions) to be some 30 kJ mol^{-1} more negative than the latter. Reference 27 gives us the enthalpies of formation and polymerization of 4-methylcyclohexene, -75 ± 4 and -1 kJ mol^{-1}, respectively: the enthalpy of formation of poly(4-methylcyclohexene) is thus -76 kJ mol^{-1}. We can roughly estimate the enthalpy of formation of the saturated counterpart of the polymer, i.e. $[-(CH_2)_5CHMe-]$ in two ways. The first starts with $[-(CH_2)_6-]$, the saturated counterpart of polymerized cyclohexene. We would predict its enthalpy of formation to be $-54{\bullet}6/2 = -162$ kJ mol^{-1}. From the values in Pedley, we find the average difference of the enthalpies of formation of liquid n-alkanes and arbitrary monomethyl derivatives is *ca* $- 31$ kJ mol^{-1} and so $\Delta H_f([-(CH_2)_5CHMe], lq) \approx -193$ kJ mol^{-1}. Alternatively, we can start with liquid $[-(CH_2)_7-]$ and its enthalpy of formation of $-54{\bullet}7/2 = -189$ kJ mol^{-1} and 'correct' it to -193 kJ mol^{-1} by the *ca* $- 4$ kJ mol^{-1} that accompanies isomerization of a $-CH_2CH_2-$ unit in a liquid n-alkane to $-CHMe-$. We thus find the hydrogenation enthalpy of poly(4-methylcyclohexene) is *ca* $- 117$ kJ mol^{-1}, an entirely reasonable and adequately precedented value. Summarizing, save the possibility of experimental error in the enthalpy of formation of the polymer of cyclohexene, the source of the discrepancy remains evasive.
18. The reader should not be bothered by the presence of solid carbon among the formal products of reaction 12. However, we can correct for it by explicitly considering the enthalpy of formation of 'gaseous graphite' or, equivalently, the sublimation enthalpy of graphite. One estimate of this quantity assumes a value of 6.1 kJ mol^{-1} as suggested for polynuclear aromatic hydrocarbons [S. E. Stein, D. M. Golden and S. W. Benson, *J. Phys. Chem.*, **81**, 314 (1977)]. [Alternatively, following from the estimate of the enthalpy of formation of 'gaseous diamond' [D. Van Vechten and J. F. Liebman, *Isr. J. Chem.*, **21**, 105 (1981)], we derive a value of between 4.7 and 9.4 kJ mol^{-1}.] Replacing C(s) by gaseous graphite results in endothermicity of reaction 12 of *ca* 135 kJ mol^{-1}.
19. We choose 'one-half' so that the difference quantity corresponds to the enthalpy difference for one allene unit, where we remind the reader that the difference of the enthalpies of formation of an allene and the corresponding olefin is the same as the enthalpy of the 'formal decarbonization' reaction of the allene that forms the olefin and solid, graphitic carbon.
20. V. A. Luk'yanova, L. P. Timofeeva, M. P. Kozina, V. N. Kirin and A. V. Tarakanova, *Russ. J. Phys. Chem.*, **65**, 439 (1991).

21. We can narrow the difference from 10 kJ mol^{-1} even further once it is remembered that in the comparison of *meso*-bisallene, **27**, and (Z,Z)-diene, **29**, there are two extra alkylallene and alkylolefin interactions for which a stabilization of *ca* 3 kJ mol^{-1} for the latter was already suggested. Admittedly, comparison with the corresponding 1,5-cyclooctadiyne suggests strain-derived anomalies. From the enthalpy of hydrogenation, and thus derived enthalpy of formation, of this diyne from W. R. Roth, H. Hopf and C. Horn, *Chem. Ber.*, **127**, 1781 (1994), we find $1/2\delta$ (bis-allene, bis-acetylene) equals *ca* − 80 kJ mol^{-1}. We deduce that the discrepancy of this last δ quantity from the others is due to strain in the cyclic diyne.
22. We can return to 'normalcy' by reversing the sign and speaking of 15.7 kJ mol^{-1} as the conjugation energy of butadiene. This seeming ambiguity of sign is very much like that electron affinity. 'Everyone knows' that butadiene enjoys stability over that of two ethylenes. 'Everyone knows' that atomic chlorine wants another electron to form Cl^-. Conjugation energies, like electron affinities, are thus naturally negative. Therefore, since we have but one sign to consider in the current context, it is often ignored.
23. W. R. Roth, H.-W. Lennartz, W. v. E. Doering, W. R. Dolbier, Jr. and J. C. Schmidhauser, *J. Am. Chem. Soc.*, **110**, 1883 (1988).
24. J. F. Liebman, *Struct. Chem.*, **3**, 449 (1992).
25. We admittedly ignore some of the dienes discussed in Reference 23 for which free energies are available. Not knowing entropies and solvent effects precisely, and acknowledging that rather small effects are relevant to the current discussion, we conclude that free energies are not free. More work is needed for the use of Gibbs energies than for enthalpies.
26. See References 12 and 23, and elsewhere in this chapter.
27. W. J. Hehre, R. Ditchfield, L. Radom and J. A. Pople, *J. Am. Chem. Soc.*, **92**, 4796 (1970).
28. We might have thought that α-diketones would have less stabilization by this definition than conjugated dienes. After all:
    (a) with its positive oxygen, the resonance structure $^{+}O{-}C{=}C{-}O^{-}$ looks less stabilizing than the one with positive carbon $^{+}C{-}C{=}C{-}C^{-}$;
    (b) the carbon oxygen bond in ketones is polarized $C^{\delta+}{-}O^{\delta-}$ and thus there is coulombic repulsion in the diketone;
    (c) to mollify (b) by decreasing the partial positive charge on carbon, the diketone 'enjoys' less ionic/covalent resonance than the monoketone fragments.
    We are surprised.
29. We admit some cowardice. Most of our earlier estimates of entropy invoked symmetry numbers and/or were studies of bond cleavage reactions dominated by translational effects. We hesitate to compare isomers with the same carbon or heavy atom skeleton when effects of a few kJ mol^{-1} are crucial.
30. We are being somewhat disingenuous in that we are taking the difference here of the enthalpy of formation of the 'naturally' liquid (Z)-isomer and of the liquid (E)-isomer obtained by summing the value for the solid and the *ca* 27 kJ mol^{-1} enthalpy of fusion (at 398 K) from Domalski. We know of no measurement of the enthalpy of fusion for (Z)-stilbene at any temperature from which to derive an enthalpy of formation for the solid.
31. Because of its carbene functionality, our decision to consider only the parent hydrocarbons would mean that cyclopropenylidene would be ignored here even if monoolefins were of relevance. This philosophy accounts for our ignoring the energetics of the isomeric carbenes, propargylene (HCCCH) and propenylidene (CH_2CC), in the earlier section on cumulenes in the current chapter.
32. It is interesting to note that there are enthalpy of formation data for solid and gaseous tetra-*t*-butyltetrahedrane, but not for its more stable valence isomer, tetra-*t*-butylcyclobutadiene; cf G. Maier, *Angew. Chem.*, *Int. Ed. Engl.*, **27**, 309 (1988). This review cites unpublished enthalpy of combustion measurements (M. Månsson) and enthalpy of sublimation measurements (C. Rüchardt, H.-D. Beckhaus and B. Dogan). We admit our surprise that details of these measurements remain unpublished.
33. The reader may recall that the enthalpy of formation of a cyclic bis-allene has been determined (see Section III.D).
34. See, for example, the two reviews with enticing compounds by R. P. Johnson:
    (a) in *Molecular Structure and Energetics*: *Studies of Organic Molecules* (Eds. J. F. Liebman and A. Greenberg), VCH, Deerfield Beach, 1986.
    (b) *Chem. Rev.*, **89**, 1111 (1989).

We now make the *a posteriori* 'obvious' suggestion that determinations of enthalpies of hydrogenation be made.

35. This has been quantitated for 1,3-butadiene itself:
 (a) M. E. Squillacote, R. S. Sheridan, O. L. Chapman and F. A. L. Anet, *J. Am. Chem. Soc.*, **101**, 3657 (1979).
 (b) P. W. Mui and E. Grunwald, *J. Am. Chem. Soc.*, **104**, 6562 (1982).
 (c) Y.-P. Sun, D. F. Sears, Jr. and J. Saltiel, *J. Am. Chem. Soc.*, **110**, 6277 (1988).
36. This seeming lack of stabilization is disconcerting when it is noticed that the antisymmetric combination of the two methylene C−H σ bonds is of the right symmetry to 'mix in' with the π system. As such, cyclopentadiene can be said to enjoy the possibility of 6π, and hence aromatic stabilization.
37. P. W. Rabideau (Ed.) *The Conformational Analysis of Cyclohexenes, Cyclohexadienes and Related Hydroaromatic Compounds*, VCH, New York, 1989.
38. G. B. Kistiakowsky, J. R. Ruhoff, H. A. Smith and W. E. Vaughn, *J. Am. Chem. Soc.*, **58**, 146 (1936).
39. R. B. Turner, B. J. Mallon, M. Tichy, W. von E. Doering, W. R. Roth and G. Schröder, *J. Am. Chem. Soc.*, **95**, 8605 (1973).
40. E. Taskinen and K. Nummelin, *J. Org. Chem.*, **50**, 4833 (1985). These authors performed the isomer equilibration at several temperatures and so could use the experimentally derived equilibrium constant to derive the enthalpy of rearrangement. There was no need for assuming the entropy of isomerization is 0 or just determined by symmetry number corrections.
41. Taskinen and Nummelin (op. cit.) reported many other isomer equilibria in their paper. Most of these used cyclohexane as the solvent and I_2 as the catalyst and so are not confounded by solvent effects. However, these authors noted that hydrogen atom transfer induced disproportionation (to form the aromatic benzene) dominates this reaction for the case of **49/50** isomerization and so they needed alternative reaction conditions.
42. (a) W. V. Steele, R. D. Chirico, A. Nguyen, I. A. Hossenlopp and N. K. Smith, *Determination of Some Pure Compound Ideal-Gas Enthalpies of Formation*, NIPER-319, IITRI, Bartlesville, OK, June 1989.
 (b) W. V. Steele, R. D. Chirico, A. Nguyen, I. A. Hossenlopp and N. K. Smith, *Am. Inst. Chem. Eng. Symp. Ser.*, **85** (271), 140 (1990).
43. E. Taskinen and K. Nummelin, *Acta Chem. Scand.*, **B39**, 791 (1985).
44. We know of three species containing the bismethylenecyclopropane substructure for which enthalpies of formation are available: the annelated benzocyclopropene and naphtho[*b*]cyclopropene, and the tris-methylene species, [3]-radialene [see J. F. Liebman and A. Greenberg, *Chem. Rev.*, **89**, 1225 (1989)]. However, none of these data seems particularly useful in the current context.
45. R. B. Turner, P. Goebel, B. J. Mallon, W. von E. Doering, J. F. Coburn, Jr. and M. Pomerantz, *J. Am. Chem. Soc.*, **90**, 4315 (1968).
46. W. R. Roth, F.-G. Klärner and H. W. Lennartz, *Chem. Ber.*, **113**, 1818 (1980).
47. To be honest, this self-imposed limitation was also employed because we lack the desired enthalpy of formation of any other type of *exo*, *endo*-cyclic dienes.
48. It is to be remembered that the cyclic diene contains a *cis*-/internal olefinic linkage while the acyclic diene contains a terminal one. Were the carbon skeleton the same, the difference in the enthalpies of hydrogenation of (*Z*)-/internal and terminal olefins should be reflected in the difference of their enthalpies of formation. For the isomeric butenes, the difference is 7.2 $\mathrm{kJ\,mol^{-1}}$ and for the pentenes, the difference is 9.6 $\mathrm{kJ\,mol^{-1}}$. Furthermore, strictly speaking, the data Pedley gives for the 3-methylenecyclohexene is for the liquid while for the methylcyclohexane we have enthalpies of formation of both the liquid and gas. The following strategies were employed here:
 (a) Estimate the enthalpy of formation of vaporization of the diene. This gives an enthalpy of formation of the gaseous diene of 23 $\mathrm{kJ\,mol^{-1}}$ and a hydrogenation enthalpy of 177 $\mathrm{kJ\,mol^{-1}}$.
 (b) Assume the diene and its hydrogenated product have the same enthalpy of vaporization. Equivalently, the enthalpy of hydrogenation of the liquid diene will be the same as that of the gaseous species. This also gives a hydrogenation enthalpy of 177 $\mathrm{kJ\,mol^{-1}}$.
49. We wish to argue that experimental error is the case. Pedley cites liquid phase enthalpies of formation of -12.7 and -58.7 $\mathrm{kJ\,mol^{-1}}$ for the isomeric 3-methylenecyclohexene and 2-methyl-1,3-cyclohexadiene. The difference of these two numbers, -46 $\mathrm{kJ\,mol^{-1}}$, is meaningfully

distinct from those of the related species with but one double bond, methylenecyclohexane and 1-methylcyclohexene, -20 kJ mol^{-1}. This is plausible: after all, we have seen unusual ring size effects with the *endo*, *endo* and *exo*, *exo* dienes presented earlier in this section. Consider now the 2-methyl-1,3-cyclohexadiene measurement. Regardless of the precise choice made for the enthalpy of formation of liquid 1,3-cyclohexadiene (cf the earlier discussion of the gas), a value of *ca* 70 kJ mol^{-1} appears plausible. This would imply that methylation affects the enthalpy of formation of a 1,3-cyclohexadiene by some -130 kJ mol^{-1}. The change upon methylation of liquid cyclohexene is -42.7 kJ mol^{-1}, while for liquid benzene the change is -36.6 kJ mol^{-1}. Something is seriously wrong with the archival enthalpy of formation of 2-methyl-1,3-cyclohexadiene, and by inference with the value of 3-methylenecyclohexene as well.

50. D. W. Rogers, F. J. McLafferty, W. Fang and Y. Qi, *Struct. Chem.*, **4**, 161 (1993).
51. D. W. Rogers, F. J. McLafferty, W. Fang, Q. Yang and Y. Zhao, *Struct. Chem.*, **3**, 53 (1992).
52. D. W. Rogers, F. J. McLafferty and K. Channamallu, *Struct. Chem.*, **3**, 291 (1992).
53. The only experimentally thermochemically characterized case we know of is benzene, which while formally valid is admittedly disingenuous.
54. We are not distinguishing between through-space, through-bond, or ‘simply’ steric mechanisms, nor discussing concepts such as homoantiaromaticity or any other ‘prefixed’ or ‘hyphenated’ aromaticity phenomena as explanations for stabilization or destabilization of any of the aforementioned species.
55. J. F. Liebman, L. A. Paquette, J. R. Peterson and D. W. Rogers, *J. Am. Chem. Soc.*, **108**, 8267 (1986).
56. D. W. Rogers, S. A. Loggins, S. D. Samuel, M. A. Finnerty and J. F. Liebman, *Struct. Chem.*, **1**, 481 (1990). Admittedly, the authors did not separate **74** from the isomeric bicyclo[3.3.0]octa-2,6-diene but it is unlikely that these two species are *that* different.
57. D. Kreysig, R. Friere, H. Aparowsky and J. Schirmer, *J. Prakt. Chem.*, **37**, 329 (1968).
58. Had the compound been less stable than we would predict the discrepancy would have been easier to explain. One could argue that the *gem*-dimethyl groups would have resulted in destabilization because of ‘buttressing’. It is tempting to argue that the triene was contaminated by ‘polymer’ and/or peroxide, both of which have lower enthalpies of formation. But we have no documentation of this.
59. D. R. Stull, E. F. Westrum, Jr. and G. C. Sinke, *The Chemical Thermodynamics of Organic Compounds*, Wiley, New York, 1969.
60. M. Kharasch, *Bur. Stands. J. Res.*, **2**, 359 (1929).
61. We used all of the C_{18} hydrocarbons in Pedley and derived their enthalpies of sublimation by subtracting the recommended enthalpies of formation of the solid and the corresponding gaseous species. There was considerable variation in the sublimation enthalpies, as seemingly befits the diverse choice of compounds (and associated crystal packing) including such species as naphthacene, 6,6-diphenylfulvene, 3,4,5,6-tetramethylphenanthrene, [3.3]paracyclophane and *n*-octadecane.
62. See Stein and coworkers cited in Reference 18.
63. While there is some dispute about how universal the ‘universal methylene increment’ really is (cf Reference 1), it is nonetheless generally conceded that a methylene group affixed to two carbons usually contributes *ca* -21 kJ mol^{-1} to the gas phase enthalpy of formation.
64. See W. R. Roth, F. G. Klärner, G. Siepert and H. W. Lennartz, *Chem. Ber.*, **125**, 217 (1992) and D. W. Rogers, A. Pododensin and J. F. Liebman, *J. Org. Chem.*, **58**, 2589 (1993) and many references cited therein.
65. Species **88–90** are also recognized to be bicyclo[4.4.1]undecane derivatives.
66. Roth gives two values for the enthalpy of formation of **90**. We adopt the value from his laboratory for our current study.
67. Pedley is the major source of information for all of these 4-carbon bridged benzenes, where we acknowledge that the enthalpy of the gaseous 1,4-dihydronaphthalene was found by combining Pedley’s value for the liquid with our estimated enthalpy of vaporization.
68. Our uncertainty is derived in part from the lack of a measured enthalpy of vaporization, cf Reference 67. However, what triggered our skepticism is the observation that the isomeric 1,2-and 1,4-dihydronaphthalenes have reported enthalpies of formation that differ by *ca* 13 kJ mol^{-1} while the corresponding species lacking the benzene ring, the isomeric 1,3- and 1,4-cyclohexadienes, are almost isoenergetic (see Section V.D of this chapter). From J. F. Liebman, in *The Cyclophanes* (Eds. P. M. Keehn and S. M. Rosenfeld), Academic Press, New York, 1983,

we find that benzoannelation normally has a quite constant effect on enthalpies of formation of nonaromatic species. For example, benzoannelation of cyclopentene, cyclopentadiene and cyclohexene are accompanied by increases of *ca* 27, 29 and 31 kJ mol^{-1}, respectively. Taking a value of *ca* 30 kJ mol^{-1} for the increase, we can think of no reason why the enthalpy of formation of either dihydronaphthalene should be outside the 130–140 kJ mol^{-1} range.

69. We recall that Fang and Rogers, op. cit., measured the enthalpy of hydrogenation of the acyclic trienes in a nonpolar solvent instead of acetic acid as earlier reported. However, they did not remeasure the Z- and E-isomers separately but instead assumed the earlier measured difference is correct. Said differently, they assumed that the effect on the enthalpy difference of the Z- and E-hexatriene is essentially independent of solvent. This is plausible but remains untested.
70. See, for example, R. S. Hosmane and J. F. Liebman, *Tetrahedron Lett.*, **33**, 2303 (1992). We additionally note that in the absence of any conjugative interaction, the difference of the enthalpies of formation of fulvene (*vide infra*) and benzene would very nearly equal the difference of the enthalpies of formation of methylenecyclopentane and cyclohexene. The former difference is 161 kJ mol^{-1} while the latter difference is but 17 kJ mol^{-1}.
71. The desired enthalpy of formation of fulvene and of its 6-methyl derivative were determined by Roth by measurement of the appropriate enthalpy of hydrogenation. The facile polymerization of this compound precludes conventional bomb calorimetry.
72. The desired enthalpy of formation of 6,6-dimethylfulvene was determined by Roth citing measurement of hydrogenation enthalpies, and chronicled by Pedley citing enthalpies of combustion and vaporization. The two results differ by 7 kJ mol^{-1}. We have opted for Roth's value because it is in better agreement with a value calculated using Roth's force field method. It is also to be noted that measurement cited by Pedley for the neat condensed phase could be flawed by the presence of partially polymerized fulvene and neither elemental abundance of the compound nor analysis of the combustion products would have disclosed this. Likewise, the measured enthalpy of vaporization would not have necessarily uncovered this contaminant.
73. As documented by Pedley, only enthalpies of combustion and sublimation have been reported for 6,6-diphenylfulvene. We recommend the measurement of the enthalpy of hydrogenation to form α-cyclopentyl diphenylmethane to acquire a more precise enthalpy of formation.
74. The author thanks Suzanne W. Slayden for suggesting and doing this statistical analysis, as well as providing the accompanying figures.
75. The number and requisite analysis used to derive it is taken from Liebman and Greenberg (Reference 44).
76. J. F. Liebman and A. Greenberg, in *The Chemistry of the Cyclopropyl Group*, Vol. 1 (Ed. Z. Rappoport), Wiley, Chichester, 1987.
77. R. B. Turner, W. R. Meador, W. von E. Doering, L. H. Knox, J. R. Mayer and D. W. Wiley, *J. Am. Chem. Soc.*, **79**, 4127 (1957).
78. Unlike many of the early hydrogenation studies, this measurement was made in a relatively nonpolar polyether solvent (with the admittedly misleading name 'diethylcarbitol'). Because the solvent is nonpolar, the results for this species are expected to adequately mimic those that would be found in the gaseous phase.
79. This conjugated enone/diene difference is more definitively seen in the 184 kJ mol^{-1} decrease in enthalpy of formation on going from 1-pentene to butanal, in contrast to the 177 kJ mol^{-1} going from (E)-1,3-pentadiene to *trans*-crotonaldehyde. For further discussion, see J. F. Liebman and R. M. Pollack, in *The Chemistry of Enones* (Eds. S. Patai and Z. Rappoport), Wiley, Chichester, 1989.
80. J. M. McBride, *Tetrahedron*, **38**, 2009 (1976).
81. H. E. Bent and G. R. Cuthbertson, *J. Am. Chem. Soc.*, **58**, 170 (1936).
82. Admittedly, $Ph_3C{-}CPh_3$ (literally, hexaphenylethane as drawn) has largely uncharacterized features as well. For example, the considerable weakness of the central C−C bond is not paralleled by the 'central' C−C bond in tetraphenylmethane and 1,1,1,2-tetraphenylethane, the sole thermochemically characterized species in which there is a $C{-}(C_B)_3$ (C*) structural group. [The enthalpy of formation of the latter species is from H.-D. Beckhaus, B. Dogan, J. Schaetzer, S. Hellmann and C. Rüchardt, *Chem. Ber.*, **133**, 137 (1990).]
83. T. Bally, D. Hasselmann and K. Loosen, *Helv. Chim. Acta*, **68**, 345 (1983).
84. J. E. Bartmess, *J. Am. Chem. Soc.*, **104**, 335 (1982).
85. J. E. Bartmess and S. S. Griffith, *J. Am. Chem. Soc.*, **112**, 2931 (1990).

86. This value was obtained by summing the enthalpies of formation of 1,4-pentadiene, ethylene and *ca* 5 kJ mol^{-1} as in References 23 and 24 and by assuming thermoneutrality for the reaction

$$\text{EtCH=CH}_2 + (Z)\text{–EtCH=CHCH=CH}_2 \longrightarrow \text{C}_3\text{H}_8 + \mathbf{137}$$

where the enthalpy of formation of the hexadiene is from Reference 12.
87. See J. F. Liebman cited in Reference 68.
88. R. Sabbah, R. Chastel and M. Laffitte, *Thermochim. Acta*, **10**, 353 (1974).
89. We feel it is about time that we quote the wondrous aphorism ‘things are counterintuitive only when you have intuition’ (Deborah Van Vechten, personal communication).
90. S. K. Pollack, B. C. Raine and W. J. Hehre, *J. Am. Chem. Soc.*, **103**, 6308 (1981).
91. S. G. Lias, J. E. Bartmess, J. F. Liebman, J. L. Holmes, R. D. Levin and W. G. Mallard, *Gas-Phase Ion and Neutral Thermochemistry*, *J. Phys. Chem. Ref. Data*, **17** (1988), Supplement 1.
92. R. B. Sharma, D. K. S. Sharma, K. Hiroaka and P. Kebarle, *J. Am. Chem. Soc.*, **107**, 3747 (1985).
93. E. P. Hunter, 1996 NIST Proton Affinity Scale, in preparation. We thank Edward Hunter for sharing his numbers with us.
94. We admit that the two isomeric cyclohexadienes have very nearly the same enthalpies of formation. However, it is doubtful that replacement of $>\text{CH}_2$ by $>\text{C=CH}_2$ is without significant steric and electronic consequences. The latter group is larger and both [intermethylene C–H] and [(1,4)-π-electron] antibonding derived repulsion suggests destabilization arising from vicinal $>\text{C=CH}_2$ groups. We thus expect *o*-xylylene to be significantly less stable than its *p*-isomer. We wonder if these two C_8H_8 species found with nearly the same enthalpy of formation are really the same compound, although it appears unlikely that it be either styrene or heptafulvene.
95. We naturally exclude here the cyclopropenyl, cyclopentadienyl and cycloheptatrienyl radicals, all of which can also be recognized as cyclic C_nH_n species much as we did not include in our discussion the enthalpies of formation of allyl and pentadienyl radical as part of our analysis of polyenes such as butadiene and hexatriene.
96. A. E. Beezer, C. T. Mortimer, H. D. Springall, F. Sondheimer and R. Wolovsky, *J. Chem. Soc.*, 216 (1965).
97. J. F. M. Oth, J.-C. Bünzli and Y. de Julien de Zélicourt, *Helv. Chim. Acta*, **58**, 2276 (1974).
98. We suspect fewer problems would have arisen had Oth and coworkers (see Reference 97) decided to perform enthalpy of hydrogenation measurements on [18]annulene. Nonetheless, we note that Oth's suggested value for the enthalpy of formation of benzo-1,3,5-cyclooctatriene is within 2 kJ mol^{-1} of that estimated summing Roth's enthalpy of formation of 1,3,5-cyclooctatriene and Liebman's (cited in Reference 68) benzoannelation constant.
99. (a) R. Breslow and E. Mohachsi, *J. Am. Chem. Soc.*, **85**, 431 (1963).
    (b) A. L. H. Chung and M. J. S. Dewar, *J. Chem. Phys.*, **42**, 756 (1965).
100. We admit to being somewhat sloppy because we are not distinguishing between (*Z*)- and (*E*)-polyene subunits. However, the reader will recall from Section VI.A that in Reference 23 it was shown that the difference in enthalpies of formation of (*Z*)- and (*E*)-1,3,5-hexatriene was *ca* 4 kJ mol^{-1}.
101. Benzene remains ‘safely’ aromatic by this definition. After all, its enthalpy of formation is 82.6 kJ mol^{-1} while that of the reference acyclic species is 167.5 kJ mol^{-1}, considerably higher.
102. In our own notes, we find that we have occasionally written the –CH=CH– group as <–CH=CH–> and where the < and > indicate it was a single bond that was deleted or ‘X'd’ out in the generation of the group. In a related way, =CH–CH=, $-\text{CH}_2-$ and $\text{CH}_2=$ are written <=CH–CH=>, $<-\text{CH}_2->$ and $\text{CH}_2=>$; Mahnaz Motevalli-Oliner and Joel F. Liebman, hitherto unpublished symbolism.
103. Benzene remains ‘safely’ aromatic by this definition as well. After all, its enthalpy of formation is 82.6 kJ mol^{-1} while that of the ‘real’ 1,3,5-hexatriene, the reference acyclic species, is 165.1 kJ mol^{-1}, considerably higher.
104. This is by analogy to cyclopentane, cyclopentene and methylenecyclopentane, all from References 17 by Greenberg and Liebman.
105. We have summed the enthalpy of formation of five ethylenes for the five formal double bonds and 6(5) for the six formal single bonds by analogy to our discussion of [18]annulene.