2

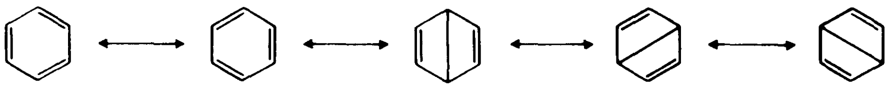
DELOCALIZED CHEMICAL BONDING

Although the bonding of many compounds can be adequately described by a single Lewis structure (page 12), this is not sufficient for many other compounds. These compounds contain one or more bonding orbitals that are not restricted to two atoms, but that are spread out over three or more. Such bonding is said to be *delocalized*.[1] In this chapter we shall see which types of compounds must be represented in this way.

The two chief general methods of approximately solving the wave equation, discussed in Chapter 1, are also used for compounds containing delocalized bonds.[2] In the valence-bond method, several possible Lewis structures (called *canonical forms*) are drawn and the molecule is taken to be a weighted average of them. Each ψ in Eq. (3), Chapter 1,

$$\Psi = c_1\psi_1 + c_2\psi_2 + \cdots$$

represents one of these structures. This representation of a real structure as a weighted average of two or more canonical forms is called *resonance*. For benzene the canonical forms are **1** and **2**. Double-headed arrows are used to indicate resonance. When the wave equation is solved, it is found that the energy value obtained by considering that **1** and **2** participate equally is lower than that for **1** or **2** alone. If **3**, **4**, and **5** (called *Dewar structures*) are also considered, the value is lower still. According to this method, **1** and **2** each contribute 39% to the actual molecule and the others 7.3% each.[3] The carbon–carbon bond order is 1.463 (not 1.5, which would be the case if only **1** and **2** contributed). In the valence-bond method, the *bond order* of a particular bond is the sum of the weights of those canonical forms in which the bonds is double plus 1 for the single bond that is present in all of them.[4] Thus, according to this picture, each C—C bond is not halfway between a single and a double bond but somewhat less. The energy of the actual molecule is obviously less than that of any one Lewis structure, since otherwise it would have one of those structures. The difference in energy between the actual molecule and the Lewis structure of lowest energy is call the *resonance energy*. Of course, the Lewis structures are not real, and their energies can only be estimated.



1 **2** **3** **4** **5**

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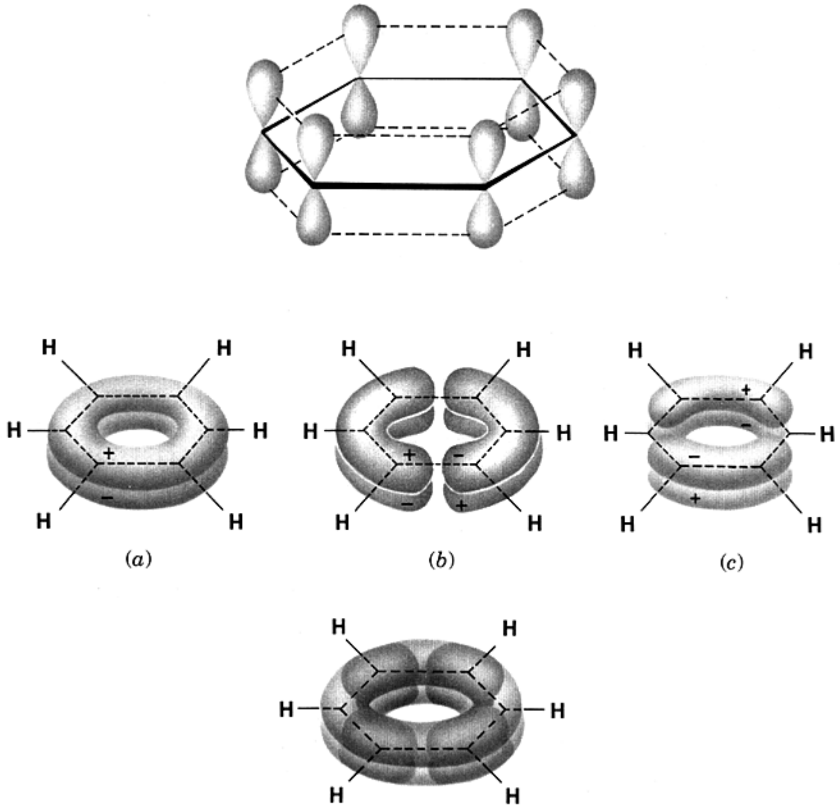
[1] The classic work on delocalized bonding is Wheland *Resonance in Organic Chemistry*; Wiley: New York, 1955.

[2] There are other methods. For a discussion of the free-electron method, see Streitwieser *Molecular Orbital Theory for Organic Chemists*; Wiley: New York, 1961, pp. 27-29. For the nonpairing method, in which benzene is represented as having three electrons between adjacent carbons, see Hirst; Linnett *J. Chem. Soc.* **1962,** 1035; Firestone *J. Org. Chem.* **1969,** *34*, 2621.

[3] Pullman; Pullman *Prog. Org. Chem.* **1958,** *4*, 31-71, p. 33.

[4] For a more precise method of calculating valence-bond orders, see Clarkson; Coulson; Goodwin *Tetrahedron* **1963,** *19*, 2153. See also Herndon; Párkányi *J. Chem. Educ.* **1976,** *53*, 689.

Qualitatively, the resonance picture is often used to describe the structure of molecules, but quantitative valence-bond calculations become much more difficult as the structures become more complicated (e.g., naphthalene, pyridine, etc.). Therefore the molecular-orbital method is used much more often for the solution of wave equations.[5] If we look at benzene by this method (qualitatively), we see that each carbon atom, being connected to three other atoms, uses sp^2 orbitals to form σ bonds, so that all 12 atoms are in one plane. Each carbon has a *p* orbital (containing one electron) remaining and each of these can overlap equally with the two adjacent *p* orbitals. This overlap of six orbitals (see Figure 2.1) produces six new orbitals, three of which (shown) are bonding. These three (called π orbitals) all occupy approximately the same space.[6] One of the three is of lower energy than



(*a*) (*b*) (*c*)

Superposition of (*a*), (*b*), and (*c*).

(*d*)

FIGURE 2.1 The six *p* orbitals of benzene overlap to form three bonding orbitals, (*a*), (*b*), and (*c*). The three orbitals superimposed are shown in (*d*).

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[5] For a review of how mo theory explains localized and delocalized bonding, see Dewar *Mol. Struct. Energ.* **1988,** *5*, 1-61.

[6] According to the explanation given here, the symmetrical hexagonal structure of benzene is caused by both the σ bonds and the π orbitals. It has been contended, based on mo calculations, that this symmetry is caused by the σ framework alone, and that the π system would favor three localized double bonds: Shaik, Hiberty; Lefour; Ohanessian *J. Am. Chem. Soc.* **1987,** *109*, 363; Stanger; Vollhardt *J. Org. Chem.* **1988,** *53*, 4889. See also Cooper; Wright; Gerratt; Raimondi *J. Chem. Soc., Perkin Trans. 2* **1989,** 255, 263; Jug; Köster *J. Am. Chem. Soc.* **1990,** *112*, 6772; Aihara *Bull. Chem. Soc. Jpn.* **1990,** *63*, 1956.

the other two, which are degenerate. They each have the plane of the ring as a node and so are in two parts, one above and one below the plane. The two orbitals of higher energy (Figure 2.1*b* and *c*) also have another node. The six electrons that occupy this torus-shaped cloud are called the *aromatic sextet*. The carbon–carbon bond order for benzene, calculated by the molecular-orbital method, is 1.667.[7]

For planar unsaturated and aromatic molecules, many molecular-orbital calculations (*mo calculations*) have been made by treating the σ and π electrons separately. It is assumed that the σ orbitals can be treated as localized bonds and the calculations involve only the π electrons. The first such calculations were made by Hückel; such calculations are often called *Hückel molecular-orbital* (HMO) *calculations*.[8] Because electron–electron repulsions are either neglected or averaged out in the HMO method, another approach, the *self-consistent field* (SCF), or *Hartree–Fock*, method, was devised.[9] Although these methods give many useful results for planar unsaturated and aromatic molecules, they are often unsuccessful for other molecules; it would obviously be better if all electrons, both σ and π, could be included in the calculations. The development of modern computers has now made this possible.[10] Many such calculations have been made[11] using a number of methods, among them an extension of the Hückel method (EHMO)[12] and the application of the SCF method to all valence electrons.[13]

One type of mo calculation that includes all electrons is called *ab initio*.[14] Despite the name (which means "from first principles") this type does involve assumptions, though not very many. It requires a large amount of computer time, especially for molecules that contain more than about five or six atoms other than hydrogen. Treatments that use certain simplifying assumptions (but still include all electrons) are called *semi-empirical* methods.[15] One of the first of these was called CNDO (Complete Neglect of Differential Overlap),[16] but as computers have become more powerful, this has been superceded by more modern methods, including MINDO/3 (Modified Intermediate Neglect of Differential Overlap),[17] MNDO (Modified Neglect of Diatomic Overlap),[17] and AM1 (Austin Model 1), all of which were introduced by M. J. Dewar and co-workers.[18] Semi-empirical calculations are generally regarded as less accurate than ab initio methods,[19] but are much faster and cheaper. Indeed,

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[7] The molecular-orbital method of calculating bond order is more complicated than the valence-bond method. See Ref. 3, p. 36; Clarkson; Coulson; Goodwin, Ref. 4.

[8] See Yates *Hückel Molecular Orbital Theory*; Academic Press: New York, 1978; Coulson; O'Leary; Mallion *Hückel Theory for Organic Chemists*; Academic Press: New York, 1978; Lowry; Richardson *Mechanism and Theory in Organic Chemistry*, 3rd ed., Harper and Row: New York, 1987, pp. 100-121.

[9] Roothaan *Rev. Mod. Phys.* **1951,** *23*, 69; Pariser; Parr *J. Chem. Phys.* **1952,** *21*, 466, 767; Pople *Trans. Faraday Soc.* **1953,** *49*, 1375, *J. Phys. Chem.* **1975,** *61*, 6; Dewar *The Molecular Orbital Theory of Organic Chemistry*; McGraw-Hill: New York, 1969; Dewar, in *Aromaticity*, *Chem. Soc. Spec. Pub.* no. 21, 1967, pp. 177-215.

[10] For discussions of the progress made in quantum chemistry calculations, see Ramsden *Chem. Br.* **1978,** *14*, 396-403; Hall *Chem. Soc. Rev.* **1973,** *2*, 21-28.

[11] For a review of molecular-orbital calculatons on *saturated* organic compounds, see Herndon, *Prog. Phys. Org. Chem.* **1972,** *9*, 99-177.

[12] Hoffmann *J. Chem. Phys.* **1963,** *39*, 1397. See Yates, Ref. 8, pp. 190-201

[13] Dewar *The Molecular Orbital Theory of Chemistry*, Ref. 9; Jaffé *Acc. Chem. Res.* **1969,** *2*, 136-143; Kutzelnigg; Del Re; Berthier *Fortschr. Chem. Forsch.* **1971,** *22*, 1-222.

[14] Hehre; Radom; Schleyer; Pople *Ab Initio Molecular Orbital Theory*; Wiley: New York, 1986; Clark *A Handbook of Computational Chemistry*; Wiley: New York, 1985, pp. 233-317; Richards; Cooper *Ab Initio Molecular Orbital Calculations for Chemists*, 2nd ed., Oxford University Press: Oxford, 1983.

[15] For a review, see Thiel, *Tetrahedron* **1988,** *44*, 7393-7408.

[16] Pople; Santry; Segal *J. Chem. Phys.* **1965,** *43*, S129; Pople; Segal *J. Chem. Phys.* **1965,** *43*, S136; **1966,** *44*, 3289; Pople; Beveridge *Approximate Molecular Orbital Theory*; McGraw-Hill: New York, 1970.

[17] For a discussion of MNDO and MINDO/3, and a list of systems for which these methods have been used, with references, see Clark, Ref. 14, pp. 93-232. For a review of MINDO/3, see Lewis, *Chem. Rev.* **1986,** *86*, 1111-1123.

[18] First publications are, MINDO/3: Bingham; Dewar; Lo *J. Am. Chem. Soc.* **1975,** *97*, 1285; MNDO: Dewar; Thiel *J. Am. Chem. Soc.* **1977,** *99*, 4899; AM1: Dewar; Zoebisch; Healy; Stewart *J. Am. Chem. Soc.* **1985,** *107*, 3902.

[19] See however, Dewar; Storch *J. Am. Chem. Soc.* **1985,** *107*, 3898.

calculations for some very large molecules are possible only with the semi-empirical methods.[20]

Molecular orbital calculations, whether by ab initio or semi-empirical methods, can be used to obtain structures (bond distances and angles), energies (such as heats of formation), dipole moments, ionization energies, and other properties of molecules, ions, and radicals—not only of stable ones, but also of those so unstable that these properties cannot be obtained from experimental measurements.[21] Many of these calculations have been performed on transition states (p. 210); this is the only way to get this information, since transition states are not, in general, directly observable. Of course, it is not possible to check data obtained for unstable molecules and transition states against any experimental values, so that the reliability of the various mo methods for these cases is always a question. However, our confidence in them does increase when (1) different mo methods give similar results, and (2) a particular mo method works well for cases that can be checked against experimental methods.

Both the valence-bond and molecular-orbital methods show that there is delocalization in benzene. For example, each predicts that the six carbon–carbon bonds should have equal lengths, which is true. Since each method is useful for certain purposes, we shall use one or the other as appropriate.

Bond Energies and Distances in Compounds Containing Delocalized Bonds

If we add the energies of all the bonds in benzene, taking the values from a source like Table 1.7, the value for the heat of atomization turns out to be less than that actually found in benzene (Figure 2.2). The actual value is 1323 kcal/mol (5535 kJ/mol). If we use *E* values for a C═C double bond obtained from cyclohexene (148.8 kcal/mol; 622.6 kJ/mol), a C—C single bond from cyclohexane (81.8 kcal/mol, 342 kJ/mol), and C—H bonds from methane (99.5 kcal/mol, 416 kJ/mol), we get a total of 1289 kcal/mol (5390 kJ/mol) for structure **1** or **2**. By this calculation the resonance energy is 34 kcal/mol (145 kJ/mol). Of course, this is an arbitrary calculation since, in addition to the fact that we are calculating a heat of atomization for a nonexistent structure (**1**), we are forced to use *E* values that themselves do not have a firm basis in reality. The resonance energy can never be measured, only estimated, since we can measure the heat of atomization of the real molecule but can only make an intelligent guess at that of the Lewis structure of lowest energy. Another method frequently used for estimation of resonance energy involves measurements of heats of hy-

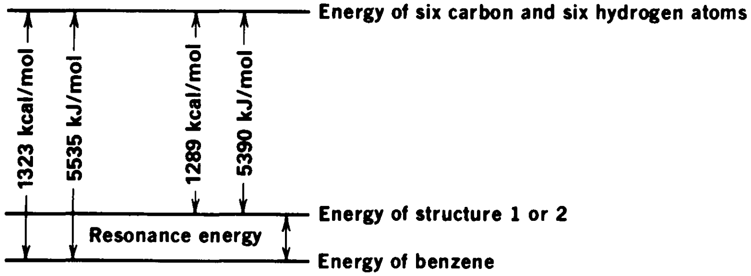


FIGURE 2.2 Resonance energy in benzene.

[20] Clark, Ref. 14, p. 141.

[21] Another method of calculating such properies is molecular mechanics (p. 149).

drogenation.[22] Thus, the heat of hydrogenation of cyclohexene is 28.6 kcal/mol (120 kJ/mol), so we might expect a hypothetical **1** or **2** with three double bonds to have a heat of hydrogenation of about 85.8 kcal/mol (360 kJ/mol). The real benzene has a heat of hydrogenation of 49.8 kcal/mol (208 kJ/mol), which gives a resonance energy of 36 kcal/mol (152 kJ/mol). By any calculation the real molecule is more stable than a hypothetical **1** or **2**.

The energies of the six benzene orbitals can be calculated from HMO theory in terms of two quantities, α and β. α is the amount of energy possessed by an isolated $2p$ orbital before overlap, while β (called the *resonance integral*) is an energy unit expressing the degree of stabilization resulting from π-orbital overlap. A negative value of β corresponds to stabilization, and the energies of the six orbitals are (lowest to highest): $\alpha + 2\beta$, $\alpha + \beta$, $\alpha + \beta$, $\alpha - \beta$, $\alpha - \beta$, and $\alpha - 2\beta$.[23] The total energy of the three occupied orbitals is $6\alpha + 8\beta$, since there are two electrons in each orbital. The energy of an ordinary double bond is $\alpha + \beta$, so that structure **1** or **2** has an energy of $6\alpha + 6\beta$. The resonance energy of benzene is therefore 2β. Unfortunately, there is no convenient way to calculate the value of β from molecular-orbital theory. It is often given for benzene as about 18 kcal/mol (76 kJ/mol); this number being half of the resonance energy calculated from heats of combustion or hydrogenation.

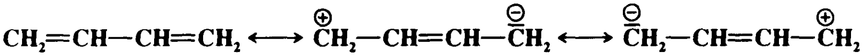
We might expect that bond distances in compounds exhibiting delocalization would lie between the values gives in Table 1.5. This is certainly the case for benzene, since the carbon–carbon bond distance is 1.40 Å,[24] which is between the 1.48 Å for an sp^2–sp^2 C—C single bond and the 1.32 Å of the sp^2–sp^2 C═C double bond.[25]

Kinds of Molecules That Have Delocalized Bonds

There are three main types of structure that exhibit delocalization:

1. *Double (or triple) bonds in conjugation.*[26] Benzene is, of course, an example, but the simplest is butadiene. In the molecular orbital picture (Figure 2.3), the overlap of four orbitals gives two bonding orbitals that contain the four electrons and two vacant antibonding orbitals. It can be seen that each orbital has one more node than the one of next lower energy. The energies of the four orbitals are (lowest to highest): $\alpha + 1.618\beta$, $\alpha + 0.618\beta$, $\alpha - 0.618\beta$, and $\alpha - 1.618\beta$; hence the total energy of the two occupied orbitals is $4\alpha + 4.472\beta$. Since the energy of two isolated double bonds is $4\alpha + 4\beta$, the resonance energy by this calculation is 0.472β.

In the resonance picture, these structures are considered to contribute:



$$\mathrm{CH_2{=}CH{-}CH{=}CH_2} \longleftrightarrow \overset{\oplus}{\mathrm{C}}\mathrm{H_2{-}CH{=}CH{-}}\overset{\ominus}{\mathrm{C}}\mathrm{H_2} \longleftrightarrow \overset{\ominus}{\mathrm{C}}\mathrm{H_2{-}CH{=}CH{-}}\overset{\oplus}{\mathrm{C}}\mathrm{H_2}$$

6 **7** **8**

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[22] For a review of heats of hydrogenation, with tables of values, see Jensen *Prog. Phys. Org. Chem.* **1976,** *12*, 189-228.

[23] For the method for calculating these and similar results given in this chapter, see Higasi; Baba; Rembaum *Quantum Organic Chemistry*; Interscience: New York, 1965. For values of calculated orbital energies and bond orders for many conjugated molecules, see Coulson; Streitwieser *Dictionary of π Electron Calculations*; W.H. Freeman: San Francisco, 1965.

[24] Bastiansen; Fernholt; Seip; Kambara; Kuchitsu *J. Mol. Struct.* **1973,** *18*, 163; Tamagawa; Iijima; Kimura *J. Mol. Struct.* **1976,** *30*, 243.

[25] The average C—C bond distance in aromatic rings is 1.38 Å: Allen; Kennard; Watson; Brammer; Orpen; Taylor *J. Chem. Soc., Perkin Trans. 2* **1987,** p. S8.

[26] For reviews of conjugation in open-chain hydrocarbons, see Simmons *Prog. Phys. Org. Chem.* **1970,** *7*, 1-50; Popov; Kogan *Russ. Chem. Rev.* **1968,** *37*, 119-141.

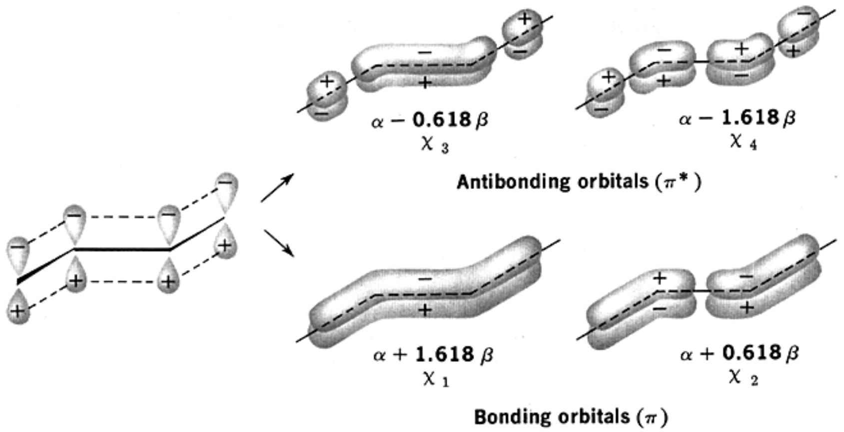


FIGURE 2.3 The four π orbitals of butadiene, formed by overlap of four *p* orbitals.

In either picture the bond order of the central bond should be higher than 1 and that of the other carbon–carbon bonds less than 2, although neither predicts that the three bonds have equal electron density. Molecular-orbital bond orders of 1.894 and 1.447 have been calculated.[27]

Since about 1959 doubt has been cast on the reality of delocalization in butadiene and similar molecules. Thus, the bond lengths in butadiene are 1.34 Å for the double bonds and 1.48 Å for the single bond.[28] Since the typical single-bond distance of a bond that is not adjacent to an unsaturated group is 1.53 Å (p. 20), it has been argued that the shorter single bond in butadiene provides evidence for resonance. However, this shortening can also be explained by hybridization changes (see p. 20); and other explanations have also been offered.[29] Resonance energies for butadienes, calculated from heats of combustion or hydrogenation, are only about 4 kcal/mol (17 kJ/mol), and these values may not be entirely attributable to resonance. Thus, a calculation from heat of atomization data gives a resonance energy of 4.6 kcal/mol (19 kJ/mol) for *cis*-1,3-pentadiene, and −0.2 kcal/mol (−0.8 kJ/mol), for 1,4-pentadiene. These two compounds, each of which possesses two double bonds, two C—C single bonds, and eight C—H bonds, would seem to offer as similar a comparison as we could make of a conjugated with a nonconjugated compound, but they are nevertheless not strictly comparable. The former has three sp^3 C—H and five sp^2 C—H bonds, while the latter has two and six, respectively. Also, the two single C—C bonds of the 1,4-diene are both sp^2–sp^3 bonds, while in the 1,3-diene, one is sp^2–sp^3 and the other sp^2–sp^2. Therefore, it may be that some of the already small value of 4 kcal/mol (17 kJ/mol) is not resonance energy but arises from differing energies of bonds of different hybridization.[30]

[27] Coulson *Proc. R. Soc. London, Ser. A* **1939,** *169,* 413.

[28] Marais; Sheppard; Stoicheff *Tetrahedron* **1962,** 17, 163.

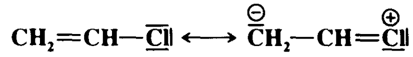
[29] Bartell *J. Am. Chem. Soc.* **1959,** *81,* 3497, *Tetrahedron* **1962,** *17,* 177, **1978,** *34,* 2891, *J. Chem. Educ.* **1968,** *45,* 754-767; Wilson *Tetrahedron,* **1962,** *17,* 191; Hughes *Tetrahedron* **1968,** *24,* 6423; Politzer; Harris *Tetrahedron* **1971,** *27,* 1567.

[30] For negative views on delocalization in butadiene and similar molecules, see Dewar; Gleicher *J. Am. Chem. Soc.* **1965,** *87,* 692; Dewar; Schmeising *Tetrahedron* **1959,** *5,* 166, **1960,** *11,* 96; Brown *Trans. Faraday Soc.* **1959,** *55,* 694; Somayajulu *J. Chem. Phys.* **1959,** *31,* 919; Mikhailov *Bull. Acad. Sci. USSR, Div. Chem. Sci.* **1960,** 1284; *J. Gen. Chem. USSR* **1966,** *36,* 379. For positive views, see Miyazaki; Shigetani; Shinoda *Bull. Chem. Soc. Jpn.* **1971,** *44,* 1491; Berry *J. Chem. Phys.* **1962,** *30,* 936; Kogan; Popov *Bull. Acad. Sci. USSR, Div. Chem. Sci.* **1964,** 1306; Altmann; Reynolds *J. Mol. Struct.* **1977,** *36,* 149. In general, the negative argument is that resonance involving excited structures, such as **7** and **8**, is unimportant. See rule 6 on p. 35. An excellent discussion of the controversy is found in Popov; Kogan Ref. 26, pp. 119-124.

Although bond distances fail to show it and the resonance energy is low, the fact that butadiene is planar[31] shows that there is some delocalization, even if not as much as previously thought. Similar delocalization is found in other conjugated systems (e.g., $C{=}C{-}C{=}O$[32] and $C{=}C{-}C{=}N$), in longer systems with three or more multiple bonds in conjugation, and where double or triple bonds are conjugated with aromatic rings.

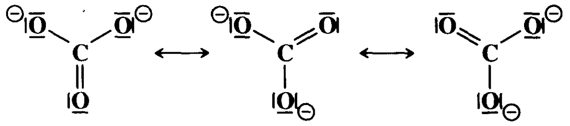
2. *Double (or triple) bonds in conjugation with a p orbital on an adjacent atom.* Where a *p* orbital is on an atom adjacent to a double bond, there are three parallel *p* orbitals that overlap. As previously noted, it is a general rule that the overlap of *n* atomic orbitals creates *n* molecular orbitals, so overlap of a *p* orbital with an adjacent double bond gives rise to three new orbitals, as shown in Figure 2.4. The middle orbital is a *nonbonding orbital* of zero bonding energy. The central carbon atom does not participate in the nonbonding orbital.

There are three cases: the original *p* orbital may have contained two, one, or no electrons. Since the original double bond contributes two electrons, the total number of electrons accommodated by the new orbitals is four, three, or two. A typical example of the first situation is vinyl chloride $CH_2{=}CH{-}Cl$. Although the *p* orbital of the chlorine atom is filled, it still overlaps with the double bond. The four electrons occupy the two molecular orbitals of lowest energies. This is our first example of resonance involving overlap between unfilled orbitals and a *filled* orbital. Canonical forms for vinyl chloride are:



$$CH_2{=}CH{-}\overline{\underline{Cl}}| \longleftrightarrow \overset{\ominus}{\overline{C}}H_2{-}CH{=}\overset{\oplus}{\underline{Cl}}|$$

Any system containing an atom that has an unshared pair and that is directly attached to a multiple-bond atom can show this type of delocalization. Another example is the carbonate ion:



The bonding in allylic carbanions, e.g., $CH_2{=}CH{-}\overline{C}H_2^{\ominus}$, is similar.

The other two cases, where the original *p* orbital contains only one or no electron, are generally found only in free radicals and cations, respectively. Allylic free radicals have one electron in the nonbonding orbital. In allylic cations this orbital is vacant and only the bonding orbital is occupied. The orbital structures of the allylic carbanion, free radical, and cation differ from each other, therefore, only in that the nonbonding orbital is filled, half-filled, or empty. Since this is an orbital of zero bonding energy, it follows that the bonding π energies of the three species relative to electrons in the $2p$ orbitals of free atoms are the same. The electrons in the nonbonding orbital do not contribute to the bonding energy, positively or negatively.[33]

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[31] Ref. 28; Fisher; Michl *J. Am. Chem. Soc.* **1987,** *109*, 1056; Wiberg; Rosenberg; Rablen *J. Am. Chem. Soc.* **1991,** *113*, 2890.

[32] For a treatise on $C{=}C{-}C{=}O$ systems, see Patai; Rappoport *The Chemistry of Enones*, two parts; Wiley: New York, 1989.

[33] It has been contended that here too, as with the benzene ring (Ref. 6), the geometry is forced upon allylic systems by the σ framework, and not the π system: Shaik; Hiberty; Ohanessian; Lefour *Nouv. J. Chim.* **1985,** *9*, 385. It has also been suggested, on the basis of ab initio calculations, that while the allyl cation has significant resonance stabilization, the allyl anion has little stabilization: Wiberg; Breneman; LePage *J. Am. Chem. Soc.* **1990,** *112*, 61.

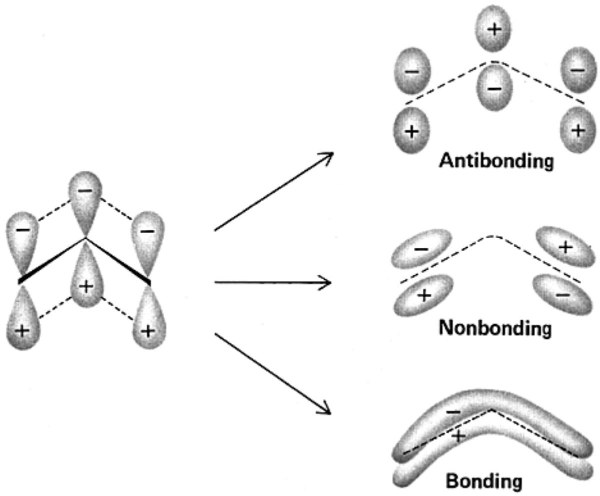


FIGURE 2.4 The three orbitals of an allylic system, formed by overlap of three *p* orbitals.

By the resonance picture, the three species may be described as having double bonds in conjugation with, respectively, an unshared pair, an unpaired electron, and an empty orbital (see Chapter 5):

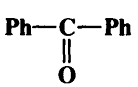
$$CH_2{=}CH{-}\overset{\ominus}{\bar{C}}H_2 \longleftrightarrow \overset{\ominus}{C}H_2{-}CH{=}CH_2$$
$$CH_2{=}CH{-}\dot{C}H_2 \longleftrightarrow \dot{C}H_2{-}CH{=}CH_2$$
$$CH_2{=}CH{-}\overset{\oplus}{C}H_2 \longleftrightarrow \overset{\oplus}{C}H_2{-}CH{=}CH_2$$

3. *Hyperconjugation.* The third type of delocalization, called *hyperconjugation*, is discussed on p. 68.

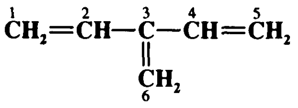
We shall find examples of delocalization which cannot be strictly classified as belonging to any of these types.

Cross Conjugation[34]

In a cross-conjugated compound, three groups are present, two of which are not conjugated with each other, although each is conjugated with the third. Some examples[35] are



$$Ph{-}\underset{\underset{O}{\|}}{C}{-}Ph$$



$$\overset{1}{C}H_2{=}\overset{2}{C}H{-}\underset{\underset{\underset{6}{CH_2}}{\|}}{\overset{3}{C}}{-}\overset{4}{C}H{=}\overset{5}{C}H_2$$

9

$CH_2{=}CH{-}O{-}CH{=}CH_2$

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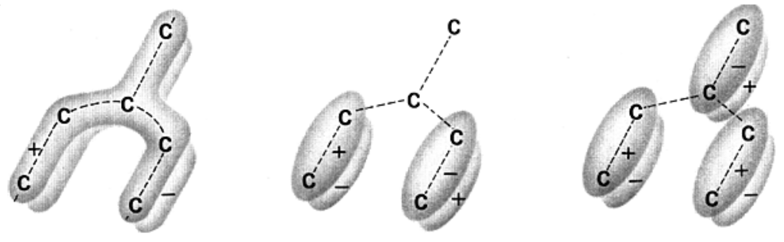
[34] For a discussion, see Phelan; Orchin *J. Chem. Educ.* **1968**, *45*, 633-637.

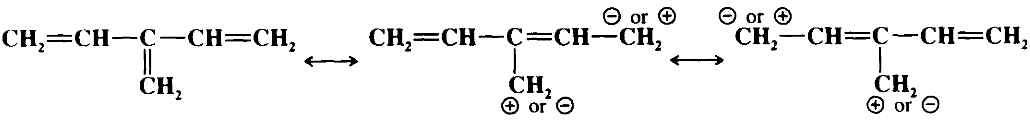
[35] **9** is the simplest of a family of cross-conjugated alkenes, called *dendralenes*. For a review of these compounds, see Hopf *Angew. Chem. Int. Ed. Engl.* **1984**, *23*, 948-960 [*Angew. Chem.* *96*, 947-958].



$\alpha + 1.932\beta$ $\alpha + \beta$ $\alpha + 0.518\beta$

FIGURE 2.5 The three bonding orbitals of 3-methylene-1,4-pentadiene (**9**).

Using the molecular-orbital method, we find that the overlap of six *p* orbitals in **9** gives six molecular orbitals, of which the three bonding orbitals are shown in Figure 2.5, along with their energies. Note that two of the carbon atoms do not participate in the $\alpha + \beta$ orbital. The total energy of the three occupied orbitals is $6\alpha + 6.900\beta$, so the resonance energy is 0.900β. Molecular-orbital bond orders are 1.930 for the C-1,C-2 bond, 1.859 for the C-3,C-6 bond and 1.363 for the C-2,C-3 bond.[34] Comparing these values with those for butadiene (p. 31), we see that the C-1,C-2 bond contains more and the C-3,C-6 bond less double-bond character than the double bonds in butadiene. The resonance picture supports this conclusion, since each C-1,C-2 bond is double in three of the five canonical forms, while the



$$CH_2{=}CH{-}\underset{\underset{CH_2}{\|}}{C}{-}CH{=}CH_2 \longleftrightarrow CH_2{=}CH{-}\underset{\underset{\underset{\oplus \text{ or } \ominus}{CH_2}}{|}}{C}{=}CH{-}\overset{\ominus \text{ or } \oplus}{CH_2} \longleftrightarrow \overset{\ominus \text{ or } \oplus}{CH_2}{-}CH{=}\underset{\underset{\underset{\oplus \text{ or } \ominus}{CH_2}}{|}}{C}{-}CH{=}CH_2$$

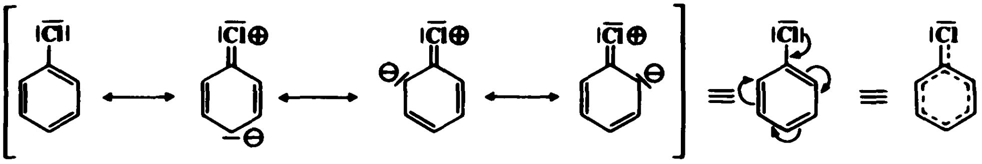
C-3,C-6 bond is double in only one. In most cases it is easier to treat cross-conjugated molecules by the molecular-orbital method than by the valence-bond method.

The Rules of Resonance

We have seen that one way of expressing the actual structure of a molecule containing delocalized bonds is to draw several possible structures and to assume that the actual molecule is a hybrid of them. These canonical forms have no existence except in our imaginations. The molecule does *not* rapidly shift between them. It is *not* the case that some molecules have one canonical form and some another. All the molecules of the substance have the same structure. That structure is always the same all the time and is a weighted average of all the canonical forms. In drawing canonical forms and deriving the true structures from them, we are guided by certain rules, among them the following:

1. All the canonical forms must be bona fide Lewis structures (see p. 12). For instance, none of them may have a carbon with five bonds.

2. The positions of the nuclei must be the same in all the structures. This means that all we are doing when we draw the various canonical forms is putting the *electrons* in in different ways. For this reason, shorthand ways of representing resonance are easy to devise:



10 **11**

The resonance interaction of chlorine with the benzene ring can be represented as shown in **10** or **11** and both of these representations have been used in the literature to save space. However, we shall not use the curved-arrow method of **10** since arrows will be used in this book to express the actual movement of electrons in reactions. We will use representations like **11** or else write out the canonical forms. The convention used in dashed-line formulas like **11** is that bonds that are present in all canonical forms are drawn as solid lines while bonds that are not present in all forms are drawn as dashed lines. In most resonance, σ bonds are not involved, and only the π or unshared electrons are put in in different ways. This means that if we write one canonical form for a molecule, we can then write the others by merely moving π and unshared electrons.

3. All atoms taking part in the resonance, i.e., covered by delocalized electrons, must lie in a plane or nearly so (see p. 36). This, of course, does not apply to atoms that have the same bonding in all the canonical forms. The reason for planarity is maximum overlap of the *p* orbitals.

4. All canonical forms must have the same number of unpaired electrons. Thus $\dot{C}H_2{-}CH{=}CH{-}\dot{C}H_2$ is not a valid canonical form for butadiene.

5. The energy of the actual molecule is lower than that of any form, obviously. Therefore, delocalization is a stabilizing phenomenon.[36]

6. All canonical forms do not contribute equally to the true molecule. Each form contributes in proportion to its stability, the most stable form contributing most. Thus, for ethylene, the form $\bar{C}H_2{-}\overset{+}{C}H_2$ has such a high energy compared to $CH_2{=}CH_2$ that it essentially does not contribute at all. We have seen the argument that such structures do not contribute even in such cases as butadiene.[30] Equivalent canonical forms, such as **1** and **2**, contribute equally. The greater the number of significant structures that can be written and the more nearly equal they are, the greater the resonance energy, other things being equal.

It is not always easy to decide relative stabilities of imaginary structures; the chemist is often guided by intuition.[37] However, the following rules may be helpful:

a. Structures with more covalent bonds are ordinarily more stable than those with fewer (compare **6** and **7**).

b. Stability is decreased by an increase in charge separation. Structures with formal charges are less stable than uncharged structures. Structures with more than two formal charges usually contribute very little. An especially unfavorable type of structure is one with two like charges on adjacent atoms.

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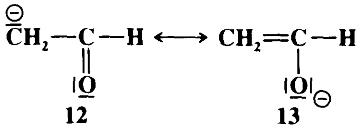
[36] It has been argued that resonance is not a stabilizing phenomenon in all systems, especially in acyclic ions: Wiberg *Chemtracts: Org. Chem.* **1989,** *2,* 85. See also Ref. 120 in Chapter 8.

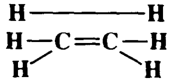
[37] A quantitative method for weighting canonical forms has been proposed by Gasteiger; Saller *Angew. Chem. Int. Ed. Engl.* **1985,** *24,* 687 [*Angew. Chem. 97,* 699].

c. Structures that carry a negative charge on a more electronegative atom are more stable than those in which the charge is on a less electronegative atom. Thus, **13** is more stable than **12**. Similarly, positive charges are best carried on atoms of low electronegativity.



$$\overset{\ominus}{\bar{C}}H_2-\underset{\underset{\underline{O}}{\|}}{C}-H \longleftrightarrow CH_2=\underset{\underset{\underline{O}^{\ominus}}{|}}{C}-H$$

12 **13**

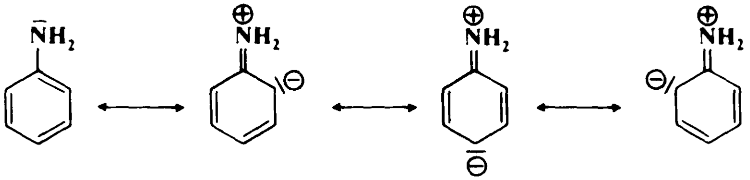


14

d. Structures with distorted bond angles or lengths are unstable, e.g., the structure **14** for ethane.

The Resonance Effect

Resonance always results in a different distribution of electron density than would be the case if there were no resonance. For example, if **15** were the actual structure of aniline, the two unshared electrons of the nitrogen would reside entirely on that atom. Since the real structure is not **15** but a hybrid that includes contributions from the other canonical forms shown, the electron density of the unshared pair does not reside entirely on the nitrogen, but is spread over the ring. This decrease in electron density at one position (and corresponding increase elsewhere) is called the *resonance* or *mesomeric effect.* We loosely say that the NH_2 contributes or donates electrons to the ring by a resonance effect, although no actual contribution takes place. The "effect" is caused by the fact that the electrons are in a different place from that we would expect if there were no resonance. In ammonia, where resonance is absent, the unshared pair *is* located on the nitrogen atom. As with the field effect (p. 18), we think of a certain molecule (in this case ammonia) as a substrate and then see what happens to the electron density when we make a substitution. When one of the hydrogen atoms of the ammonia molecule is replaced by a benzene ring, the electrons are "withdrawn" by the resonance effect, just as when a methyl group replaces a hydrogen of benzene, electrons are "donated" by the field effect of the methyl. The idea of donation or withdrawal merely arises from the comparison of a compound with a closely related one or a real compound with a canonical form.



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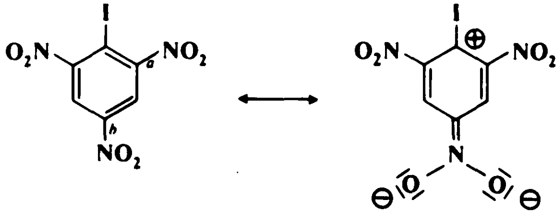
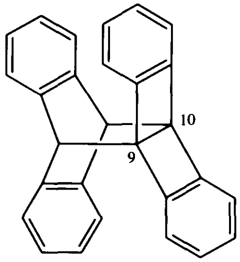
Steric Inhibition of Resonance

Rule 3 states that all the atoms covered by delocalized electrons must lie in a plane or nearly so. Many examples are known where resonance is reduced or prevented because the atoms are sterically forced out of planarity.

Bond lengths for the *o*- and *p*-nitro groups in picryl iodide are quite different.[38] Distance *a* is 1.45 Å, whereas *b* is 1.35 Å. The obvious explanation is that the oxygens of the *p*-nitro group are in the plane of the ring and thus in resonance with it, so that *b* has partial double-bond character, while the oxygens of the *o*-nitro groups are forced out of the plane by the large iodine atom.



The Dewar-type structure for the central ring of the anthracene system in **16** is possible only because the 9,10 substituents prevent the system from being planar.[39] **16** is the actual structure of the molecule and is not in resonance with forms like **17**, although in anthracene itself, Dewar structures and structures like **17** both contribute. This is a consequence of rule 2 (p. 34). In order for a **17**-like structure to contribute to resonance in **16**, the nuclei would have to be in the same positions in both forms.



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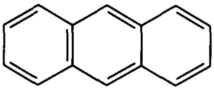
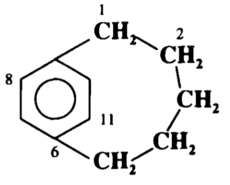


17

Even the benzene ring can be forced out of planarity.[40] In [5]paracyclophane[41] (**18**) the presence of a short bridge (this is the shortest para bridge known for a benzene ring) forces the benzene ring to become boat-shaped. The parent **18** has so far not proven stable enough



18

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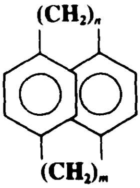
[38] Wepster, *Prog. Stereochem.* **1958,** *2*, 99-156, p. 125. For another example of this type of steric inhibition of resonance, see Exner; Folli; Marcaccioli; Vivarelli *J. Chem. Soc., Perkin Trans. 2* **1983,** 757.

[39] Applequist; Searle *J. Am. Chem. Soc.* **1964,** *86*, 1389.

[40] For a review of planarity in aromatic systems, see Ferguson; Robertson *Adv. Phys. Org. Chem.* **1963,** *1*, 203-281.

[41] For a monograph, see Keehn; Rosenfeld *Cyclophanes*, 2 vols.; Academic Press: New York, 1983. For reviews, see Bickelhaupt, *Pure Appl. Chem.* **1990,** *62*, 373-382; Vögtle; Hohner *Top. Curr. Chem.* **1978,** *74*, 1-29; Cram; Cram *Acc. Chem. Res.* **1971,** *4*, 204-213; Vögtle; Neumann *Top. Curr. Chem.* **1974,** *48*, 67-129; and reviews in *Top. Curr. Chem.* **1983,** *113*, 1-185; *115*, 1-163.

for isolation, but a uv spectrum was obtained and showed that the benzene ring was still aromatic, despite the distorted ring.[42] The 8,11-dichloro analog of **18** is a stable solid, and x-ray diffraction showed that the benzene ring is boat-shaped, with one end of the boat bending about 27° out of the plane, and the other about 12°.[43] This compound too is aromatic, as shown by uv and nmr spectra. [6]Paracyclophanes are also bent,[44] but in [7]paracyclophanes the bridge is long enough so that the ring is only moderately distorted. Similarly, [*n*,*m*]paracyclophanes (**19**), where *n* and *m* are both 3 or less (the smallest yet prepared is [2.2]paracyclophane), have bent (boat-shaped) benzene rings. All these compounds have properties that depart significantly from those of ordinary benzene compounds.



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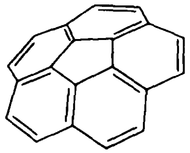

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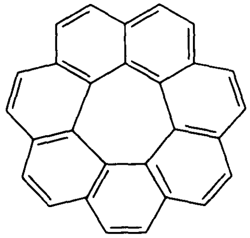

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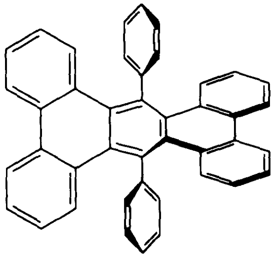

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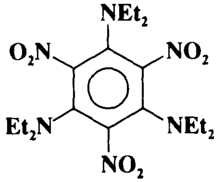

23

Other molecules in which benzene rings are forced out of planarity are corannulene (**20**),[45] (also called 5-circulene), 7-circulene (**21**),[46] **22**,[47] and **23**[48] (see also p. 161).

pπ–dπ Bonding. Ylides

We have mentioned (p. 9) that, in general, atoms of the second row of the periodic table do not form stable double bonds of the type discussed in Chapter 1 (π bonds formed by

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[42] Jenneskens; de Kanter; Kraakman; Turkenburg; Koolhaas; de Wolf; Bickelhaupt; Tobe; Kakiuchi; Odaira *J. Am. Chem. Soc.* **1985,** *107,* 3716. See also Tobe; Kaneda; Kakiuchi; Odaira *Chem. Lett.* **1985,** 1301; Kostermans; de Wolf; Bickelhaupt *Tetrahedron Lett.* **1986,** *27,* 1095; van Zijl; Jenneskens; Bastiaan; MacLean; de Wolf; Bickelhaupt *J. Am. Chem. Soc.* **1986,** *108,* 1415; Rice; Lee; Remington; Allen; Clabo; Schaefer *J. Am. Chem. Soc.* **1987,** *109,* 2902.

[43] Jenneskens; Klamer; de Boer; de Wolf; Bickelhaupt; Stam *Angew. Chem. Int. Ed. Engl.* **1984,** *23,* 238 [*Angew. Chem.* *96,* 236].

[44] See, for example, Liebe; Wolff; Krieger; Weiss; Tochtermann *Chem. Ber.* **1985,** *118,* 4144; Tobe; Ueda; Kakiuchi; Odaira; Kai; Kasai *Tetrahedron* **1986,** *42,* 1851.

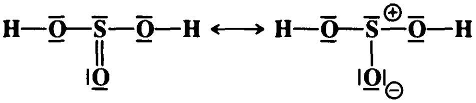
[45] Barth; Lawton *J. Am. Chem. Soc.* **1971,** *93,* 1730; Scott; Hashemi; Meyer; Warren *J. Am. Chem. Soc.* **1991,** *113,* 7082.

[46] Yamamoto; Harada; Okamoto; Chikamatsu; Nakazaki; Kai; Nakao; Tanaka; Harada; Kasai *J. Am. Chem. Soc.* **1988,** *110,* 3578.

[47] Pascal; McMillan; Van Engen; Eason *J. Am. Chem. Soc.* **1987,** *109,* 4660.

[48] Chance; Kahr; Buda; Siegel *J. Am. Chem. Soc.* **1989,** *111,* 5940.

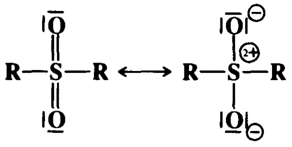
overlap of parallel *p* orbitals). However, there is another type of double bond that is particularly common for the second row atoms, sulfur and phosphorus. For example, such a double bond is found in the compound H_2SO_3, as written on the left. Like an ordinary



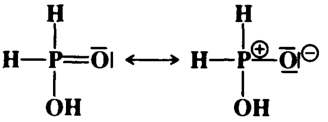
double bond, this double bond contains one σ orbital, but the second orbital is not a π orbital formed by overlap of half-filled *p* orbitals; instead it is formed by overlap of a filled *p* orbital from the oxygen with an empty *d* orbital from the sulfur. It is called a *pπ–dπ orbital*.[49] Note that we can represent this molecule by two canonical forms but the bond is nevertheless localized, despite the resonance. Some other examples of $p\pi$–$d\pi$ bonding are

$$R_3P{=}\overline{O}| \longleftrightarrow R_3\overset{\oplus}{P}{-}\overset{\ominus}{\underline{\overline{O}}}|$$

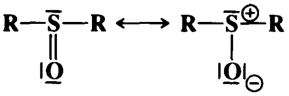
Phosphine oxides



Sulfones



Hypophosphorous acid



Sulfoxides

Nitrogen analogs are known for some of these phosphorus compounds, but they are less stable because the resonance is lacking. For example, amine oxides, analogs of phosphine oxides, can only be written $R_3\overset{\oplus}{N}{-}\overset{\ominus}{O}$. The $p\pi$–$d\pi$ canonical form is impossible since nitrogen is limited to eight outer-shell electrons.

In all the examples given above the atom that donates the electron pair is oxygen and, indeed, oxygen is the most common such atom. But in another important class of compounds, called *ylides*, this atom is carbon.[50] There are three main types of ylides—phosphorus,[51]

$$R_3P{=}CR_2 \longleftrightarrow R_3\overset{\oplus}{P}{-}\overset{\ominus}{\overline{C}}R_2$$

Phosphorus ylides

$$R_2S{=}CR_2 \longleftrightarrow R_2\overset{\oplus}{S}{-}\overset{\ominus}{\overline{C}}R_2 \qquad R_3\overset{\oplus}{N}{-}\overset{\ominus}{\overline{C}}R_2$$

Sulfur ylides Nitrogen ylides

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[49] For a monograph, see Kwart; King *d-Orbitals in the Chemistry of Silicon, Phosphorus, and Sulfur*; Springer: New York, 1977.

[50] For a monograph, see Johnson *Ylid Chemistry*; Academic Press: New York, 1966. For reviews, see Morris, *Surv. Prog. Chem.* **1983**, *10*, 189-257; Hudson *Chem. Br.* **1971**, *7*, 287-294; Lowe *Chem. Ind.* (*London*) **1970**, 1070-1079. For a review on the formation of ylides from the reaction of carbenes and carbenoids with heteroatom lone pairs, see Padwa; Hornbuckle *Chem. Rev.* **1991**, *91*, 263-309.

[51] Although the phosphorus ylide shown has three R groups on the phosphorus atom, other phosphorus ylides are known where other atoms, e.g., oxygen, replace one or more of these R groups. When the three groups are all alkyl or aryl, the phosphorus ylide is also called a *phosphorane*.

nitrogen,[52] and sulfur ylides,[53] although arsenic,[54] selenium, etc., ylides are also known. Ylides may be defined as compounds in which a positively charged atom from group 15 or 16 of the periodic table is connected to a carbon atom carrying an unshared pair of electrons. Because of $p\pi$–$d\pi$ bonding, two canonical forms can be written for phosphorus and sulfur, but there is only one for nitrogen ylides. Phosphorus ylides are much more stable than nitrogen ylides (see also p. 957). Sulfur ylides also have a low stability.

In almost all compounds that have $p\pi$–$d\pi$ bonds, the central atom is connected to four atoms or three atoms and an unshared pair and the bonding is approximately tetrahedral. The $p\pi$–$d\pi$ bond, therefore, does not greatly change the geometry of the molecule in contrast to the normal π bond, which changes an atom from tetrahedral to trigonal.

AROMATICITY

In the nineteenth century it was recognized that aromatic compounds[55] differ greatly from unsaturated aliphatic compounds,[56] but for many years chemists were hard pressed to arrive at a mutually satisfactory definition of aromatic character.[57] Qualitatively, there has never been real disagreement. Definitions have taken the form that aromatic compounds are characterized by a special stability and that they undergo substitution reactions more easily than addition reactions. The difficulty arises because these definitions are vague and not easy to apply in borderline cases. In 1925 Armit and Robinson[58] recognized that the aromatic properties of the benzene ring are related to the presence of a closed loop of electrons, the *aromatic sextet* (aromatic compounds are thus the arch examples of delocalized bonding), but it still was not easy to determine whether rings other than the benzene ring possessed such a loop. With the advent of magnetic techniques, most notably nmr, it is possible to determine experimentally whether or not a compound has a closed ring of electrons; aromaticity can now be defined as the *ability to sustain an induced ring current.* A compound with this ability is called *diatropic.* Although this definition also has its flaws,[59] it is the one most commonly accepted today. There are several methods of determining whether a compound can sustain a ring current, but the most important one is based on nmr chemical

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[52] For a review of nitrogen ylides, see Musker *Fortschr. Chem. Forsch.* **1970,** *14,* 295-365.

[53] For a monograph on sulfur ylides, see Trost; Melvin *Sulfur Ylides*; Academic Press: New York, 1975. For reviews, see Fava in Bernardi; Csizmadia; Mangini *Organic Sulfur Chemistry;* Elsevier: New York, 1985, pp. 299-354; Belkin; Polezhaeva *Russ. Chem. Rev.* **1981,** *50,* 481-497; Block, in Stirling *The Chemistry of the Sulphonium Group,* part 2, Wiley: New York, 1981, pp. 680-702; Block *Reactions of Organosulfur Compounds*; Academic Press: New York, 1978, pp. 91-127.

[54] For reviews of arsenic ylides, see Lloyd; Gosney; Ormiston *Chem. Soc. Rev.* **1987,** *16,* 45-74; Yaozeng; Yanchang *Adv. Organomet. Chem.* **1982,** *20,* 115-157.

[55] For books on aromaticity, see Lloyd *The Chemistry of Conjugated Cyclic Compounds*; Wiley: New York, 1989; *Non-Benzenoid Conjugated Carbocyclic Compounds*; Elsevier: New York, 1984; Garratt *Aromaticity*; Wiley: New York, 1986; Balaban; Banciu; Ciorba *Annulenes, Benzo-, Hetero-, Homo-Derivatives and their Valence Isomers,* 3 vols.; CRC Press: Boca Raton, FL, 1987; Badger *Aromatic Character and Aromaticity*; Cambridge University Press: Cambridge, 1969; Snyder *Nonbenzenoid Aromatics,* 2 vols.; Academic Press: New York, 1969-1971; Bergmann; Pullman *Aromaticity, Pseudo-Aromaticity, and Anti-Aromaticity*; Israel Academy of Sciences and Humanities: Jerusalem, 1971; *Aromaticity*; *Chem. Soc. Spec. Pub.* no. 21, 1967. For reviews, see Gorelik *Russ. Chem. Rev.* **1990,** *59,* 116-133; Stevenson *Mol. Struct. Energ.* **1986,** *3,* 57-83; Sondheimer *Chimia* **1974,** *28,* 163-172; Cresp; Sargent *Essays Chem.* **1972,** *4,* 91-114; Figeys *Top. Carbocyclic Chem.* **1969,** *1,* 269-359; Garratt; Sargent *Adv. Org. Chem.* **1969,** *6,* 1-108; and papers in *Top. Curr. Chem.* **1990,** *153* and *Pure Appl. Chem.* **1980,** *52,* 1397-1667.

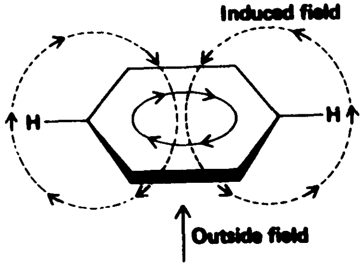
[56] For an account of the early history of aromaticity, see Snyder, in Snyder, Ref. 55, vol. 1, pp. 1-31. See also Balaban *Pure Appl. Chem.* **1980,** *52,* 1409.

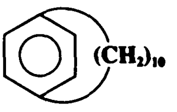
[57] For a review of the criteria used to define aromatic character, see Jones *Rev. Pure Appl. Chem.* **1968,** *18,* 253-280. For methods of assigning aromaticity, see Jug; Köster *J. Phys. Org. Chem.* **1991,** *4,* 163; Zhou; Parr *J. Am. Chem. Soc.* **1989,** *111,* 7371; Katritzky; Barczynski; Musumarra; Pisano; Szafran *J. Am. Chem. Soc.* **1989,** *111,* 7; Schaad; Hess *J. Am. Chem. Soc.* **1972,** *94,* 3068, *J. Chem. Educ.* **1974,** *51,* 640. See also Ref. 85.

[58] Armit; Robinson *J. Chem. Soc.* **1925,** *127,* 1604.

[59] Jones, Ref. 57, pp. 266-274; Mallion *Pure Appl. Chem.* **1980,** *52,* 1541.

shifts.[60] In order to understand this, it is necessary to remember that, as a general rule, the value of the chemical shift of a proton in an nmr spectrum depends on the electron density of its bond; the greater the density of the electron cloud surrounding or partially surrounding a proton, the more upfield is its chemical shift (a lower value of δ). However, this rule has several exceptions; one is for protons in the vicinity of an aromatic ring. When an external magnetic field is imposed upon an aromatic ring (as in an nmr instrument), the closed loop of aromatic electrons circulates in a diamagnetic ring current, which sends out a field of its own. As can be seen in the diagram, this induced field curves around and in the area of the proton is parallel to the external field, so the field "seen" by the aromatic protons is greater than it would have been in the absence of the diamagnetic ring current. The protons are moved downfield (to higher δ) compared to where they would be if electron density were the only factor. Thus ordinary olefinic hydrogens are found at approximately 5 to 6 δ, while the hydrogens of benzene rings are located at about 7 to 8 δ. However, if there were protons located above or within the ring, they would be subjected to a *decreased* field and should appear at lower δ values than normal CH_2 groups (normal δ for CH_2 is approximately 1 to 2). The nmr spectrum of [10]paracyclophane (**24**) showed that this was indeed the case[61] and that the CH_2 peaks were shifted to lower δ the closer they were to the middle of the chain.





24

It follows that aromaticity can be determined from an nmr spectrum. If the protons attached to the ring are shifted downfield from the normal olefinic region, we can conclude that the molecule is diatropic and hence aromatic. In addition, if the compound has protons above or within the ring (we shall see an example of the latter on p. 60), then if the compound is diatropic, these will be shifted upfield. One drawback to this method is that it cannot be applied to compounds that have no protons in either category, e.g., the dianion of squaric acid (p. 66). Unfortunately, ^{13}C nmr is of no help here, since these spectra do not show ring currents.[62]

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[60] For a review of nmr and other magnetic properties with respect to aromaticity, see Haddon; Haddon; Jackman *Fortschr. Chem. Forsch.* **1971,** *16*, 103-220. For an example of a magentic method other than nmr, see Dauben; Wilson; Laity, in Snyder, Ref. 55, vol. 2, pp. 167-206.

[61] Waugh; Fessenden *J. Am. Chem. Soc.* **1957,** *79*, 846. See also Shapiro; Gattuso; Sullivan *Tetrahedron Lett.* **1971,** 223; Pascal; Winans; Van Engen *J. Am. Chem. Soc.* **1989,** *111*, 3007.

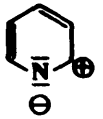
[62] For a review of ^{13}C spectra of aromatic compounds, see Günther; Schmickler *Pure Appl. Chem.* **1975,** *44*, 807-828.

It should be emphasized that the old and new definitions of aromaticity are not necessarily parallel. If a compound is diatropic and therefore aromatic under the new definition, it is more stable than the canonical form of lowest energy, but this does not mean that it will be stable to air, light, or common reagents, since *this* stability is determined not by the resonance energy but by the difference in free energy between the molecule and the transition states for the reactions involved; and these differences may be quite small, even if the resonance energy is large. A unified theory has been developed that relates ring currents, resonance energies, and aromatic character.[63]

The vast majority of aromatic compounds have a closed loop of six electrons in a ring (the aromatic sextet), and we consider these compounds first.[64]

Six-Membered Rings

Not only is the benzene ring aromatic, but so are many heterocyclic analogs in which one or more hetero atoms replace carbon in the ring.[65] When nitrogen is the hetero atom, little difference is made in the sextet and the unshared pair of the nitrogen does not participate in the aromaticity. Therefore, derivatives such as N-oxides or pyridinium ions are still aromatic. However, for nitrogen heterocycles there are more significant canonical forms (e.g., **25**) than for benzene. Where oxygen or sulfur is the hetero atom, it must be present in its ionic form (**26**) in order to possess the valence of 3 that participation in such a system demands. Thus, pyran (**27**) is not aromatic, but the pyrylium ion (**26**) is.[66]



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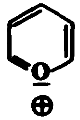

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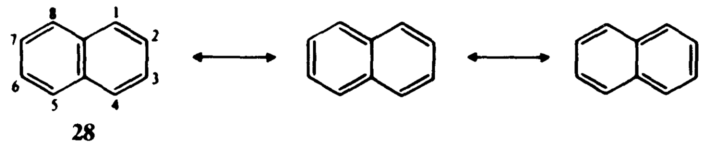
27

In systems of fused six-membered aromatic rings,[67] the principal canonical forms are usually not all equivalent. **28** has a central double bond and is thus different from the other two canonical forms of naphthalene, which are equivalent to each other.[68] For naphthalene,



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[63] Haddon *J. Am. Chem. Soc.* **1979,** *101,* 1722; Haddon; Fukunaga *Tetrahedron Lett.* **1980,** *21,* 1191.

[64] Values of molecular-orbital energies for many aromatic systems, calculated by the HMO method, are given in Coulson; Streitwieser, Ref. 23. Values calculated by a variation of the SCF method are given by Dewar; Trinajstić *Collect. Czech. Chem. Commun.* **1970,** *35,* 3136, 3484.

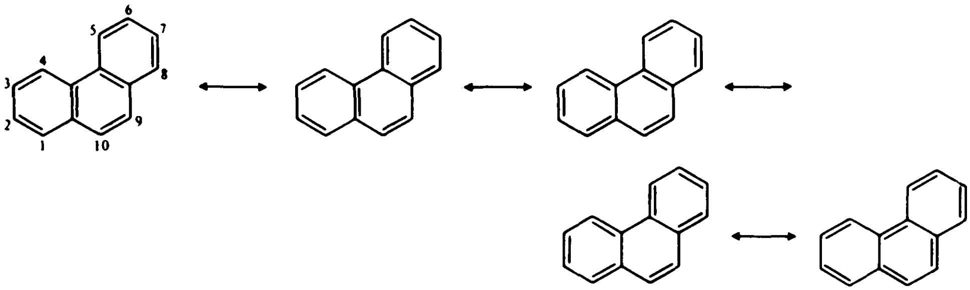
[65] For reviews of aromaticity of heterocycles, see Katritzky; Karelson; Malhotra *Heterocycles* **1991,** *32,* 127-161; Cook; Katritzky; Linda *Adv. Heterocycl. Chem.* **1974,** *17,* 255-356.

[66] For a review of pyrylium salts, see Balaban; Schroth; Fischer *Adv. Heterocycl. Chem.* **1969,** *10,* 241-326.

[67] For books on this subject, see Gutman; Cyvin *Introduction to the Theory of Benzenoid Hydrocarbons*; Springer: New York, 1989; Dias *Handbook of Polycyclic Hydrocarbons—Part A: Benzenoid Hydrocarbons*; Elsevier: New York, 1987; Clar *Polycyclic Hydrocarbons*, 2 vols.; Academic Press: New York, 1964. For a "periodic table" that systematizes fused aromatic hydrocarbons, see Dias *Acc. Chem. Res.* **1985,** *18,* 241-248; *Top. Curr. Chem.* **1990,** *253,* 123-143, *J. Phys. Org. Chem.* **1990,** *3,* 765.

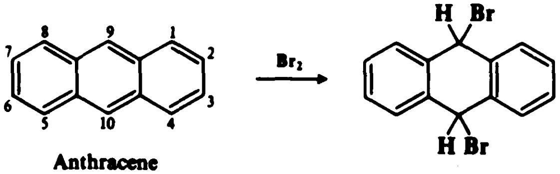
[68] As the size of a given fused ring system increases, it becomes more difficult to draw all the canonical forms. For discussions of methods for doing this, see Herndon *J. Chem. Educ.* **1974,** *51,* 10-15; Cyvin; Cyvin; Brunvoll; Chen *Monatsh. Chem.* **1989,** *120,* 833; Fuji; Xiaofeng; Rongsi *Top. Curr. Chem.* **1990,** *153,* 181; Wenchen; Wenjie *Top. Curr. Chem.* **1990,** *153,* 195; Sheng *Top. Curr. Chem.* **1990,** *153,* 211; Rongsi; Cyvin; Cyvin; Brunvoll; Klein *Top. Curr. Chem.* **1990,** *153,* 227, and references cited in these papers. For a monograph, see Cyvin; Gutman *Kekulé Structures in Benzenoid Hydrocarbons*; Springer, New York, 1988.

these are the only forms that can be drawn without consideration of Dewar forms or those with charge separation.[69] If we assume that the three forms contribute equally, the 1,2 bond has more double-bond character than the 2,3 bond. Molecular-orbital calculations show bond orders of 1.724 and 1.603, respectively (compare benzene, 1.667). In agreement with these predictions, the 1,2 and 2,3 bond distances are 1.36 and 1.415 Å, respectively,[70] and ozone preferentially attacks the 1,2 bond.[71] This nonequivalency of bonds, called *partial bond fixation*,[72] is found in nearly all fused aromatic systems. In phenanthrene, where the 9,10 bond is a single bond in only one of five forms, bond fixation becomes extreme and this bond is readily attacked by many reagents:[73]



In general there is a good correlation between bond distances in fused aromatic compounds and bond orders. Another experimental quantity that correlates well with the bond order of a given bond in an aromatic system is the nmr coupling constant for coupling between the hydrogens on the two carbons of the bond.[74]

The resonance energies of fused systems increase as the number of principal canonical forms increases, as predicted by rule 6 (p. 35).[75] Thus, for benzene, naphthalene, anthracene, and phenanthrene, for which we can draw, respectively, two, three, four, and five principal canonical forms, the resonance energies are, respectively, 36, 61, 84, and 92 kcal/mol (152, 255, 351, and 385 kJ/mol), calculated from heat-of-combustion data.[76] Note that when phenanthrene, which has a total resonance energy of 92 kcal/mol (385 kJ/mol), loses the 9,10 bond by attack of a reagent such as ozone or bromine, two complete benzene rings remain, each with 36 kcal/mol (152 kJ/mol) that would be lost if benzene was similarly attacked. The fact that anthracene undergoes many reactions across the 9,10 positions can



Anthracene

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[69] For a modern valence bond description of naphthalene, see Sironi; Cooper; Gerratt; Raimondi *J. Chem. Soc., Chem. Commun.* **1989**, 675.

[70] Cruickshank *Tetrahedron* **1962**, *17*, 155.

[71] Kooyman *Recl. Trav. Chim. Pays-Bas* **1947**, *66*, 201.

[72] For a review, see Efros *Russ. Chem. Rev.* **1960**, *29*, 66-78.

[73] See also Lai *J. Am. Chem. Soc.* **1985**, *107*, 6678.

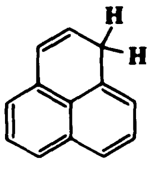
[74] Jonathan; Gordon; Dailey *J. Chem. Phys.* **1962**, *36*, 2443; Cooper; Manatt *J. Am. Chem. Soc.* **1969**, *91*, 6325.

[75] See Herndon *J. Am. Chem. Soc.* **1973**, *95*, 2404; Herndon; Ellzey *J. Am. Chem. Soc.* **1974**, *96*, 6631.

[76] Ref. 1, p. 98.

be explained in a similar manner. Resonance energies for fused systems can be estimated by counting canonical forms.[77]

Not all fused systems can be fully aromatic. Thus for phenalene (**29**) there is no way double bonds can be distributed so that each carbon has one single and one double bond.[78]



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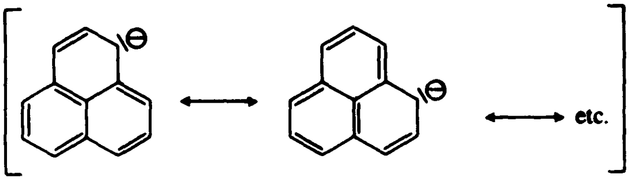

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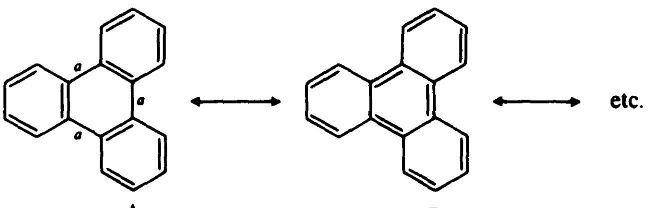
However, phenalene is acidic and reacts with potassium methoxide to give the corresponding anion (**30**), which is completely aromatic. So are the corresponding radical and cation, in which the resonance energies are the same (see p. 50)[79]

In a fused system there are not six electrons for each ring.[80] In naphthalene, if one ring is to have six, the other must have only four. One way to explain the greater reactivity of the ring system of naphthalene compared with benzene is to regard one of the naphthalene rings as aromatic and the other as a butadiene system.[81] This effect can become extreme, as in the case of triphenylene.[82] For this compound, there are eight canonical forms like **A**,



A **B**

in which none of the three bonds marked *a* is a double bond and only one form (**B**) in which at least one of them is double. Thus the molecule behaves as if the 18 electrons were distributed so as to give each of the outer rings a sextet, while the middle ring is "empty." Since none of the outer rings need share any electrons with an adjacent ring, they are as stable as benzene; triphenylene, unlike most fused aromatic hydrocarbons, does not dissolve in concentrated sulfuric acid and has a low reactivity.[83] This phenomenon, whereby some rings in fused systems give up part of their aromaticity to adjacent rings, is called *annellation* and can be demonstrated by uv spectra[67] as well as reactivities.

In this book we will use a circle to represent single aromatic rings (as, for example, in **24**), but will show one canonical form for fused ring compounds (e.g., **28**). It would be misleading to use two circles for naphthalene, for example, because that would imply 12 aromatic electrons, although naphthalene has only ten.[84]

[77] Swinborne-Sheldrake; Herndon *Tetrahedron Lett.* **1975**, 755.

[78] For reviews of phenalenes, see Murata *Top. Nonbenzenoid Aromat. Chem.* **1973**, *1*, 159-190; Reid *Q. Rev., Chem. Soc.* **1965**, *19*, 274-302.

[79] Pettit *J. Am. Chem. Soc.* **1960**, 82, 1972.

[80] For discussions of how the electrons in fused aromatic systems interact to form 4*n* + 2 systems, see Glidewell; Lloyd *Tetrahedron* **1984**, *40*, 4455, *J. Chem. Educ.* **1986**, *63*, 306; Hosoya *Top. Curr. Chem.* **1990**, *153*, 255.

[81] Meredith; Wright *Can. J. Chem.* **1960**, *38*, 1177.

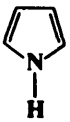
[82] For a review of triphenylenes, see Buess; Lawson *Chem. Rev.* **1960**, *60*, 313-330.

[83] Clar; Zander *J. Chem. Soc.* **1958**, 1861.

[84] See Belloli *J. Chem. Educ.* **1983**, *60*, 190.

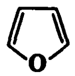
Five, Seven, and Eight-Membered Rings

Aromatic sextets can also be present in five- and seven-membered rings. If a five-membered ring has two double bonds and the fifth atom possesses an unshared pair of electrons, the ring has five *p* orbitals that can overlap to create five new orbitals—three bonding and two antibonding (Figure 2.6). There are six electrons for these orbitals: the four *p* orbitals of the double bonds each contribute one and the filled orbital contributes the other two. The six electrons occupy the bonding orbitals and constitute an aromatic sextet. The heterocyclic compounds pyrrole, thiophene, and furan are the most important examples of this kind of aromaticity, although furan has a lower degree of aromaticity than the other two.[85] Resonance energies for these three compounds are, respectively, 21, 29, and 16 kcal/mol (88, 121, and 67 kJ/mol).[86] The aromaticity can also be shown by canonical forms, e.g., for pyrrole:

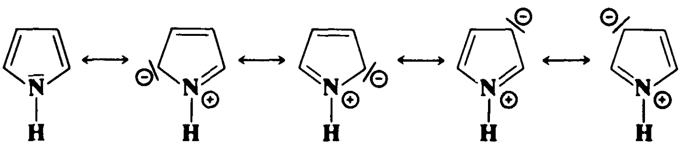


Pyrrole

Thiophene



Furan



A

In contrast to pyridine, the unshared pair in canonical structure **A** in pyrrole is needed for the aromatic sextet. This is why pyrrole is a much weaker base than pyridine.

The fifth atom may be carbon if it has an unshared pair. Cyclopentadiene has unexpected acidic properties ($pK_a \approx 16$) since on loss of a proton, the resulting carbanion is greatly

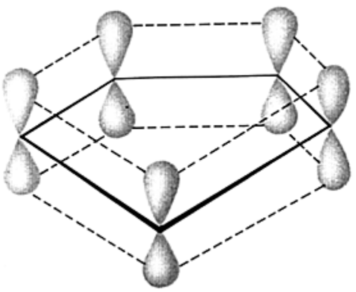


FIGURE 2.6 Overlap of five *p* orbitals in molecules such as pyrrole, thiophene, and the cyclopentadienide ion.

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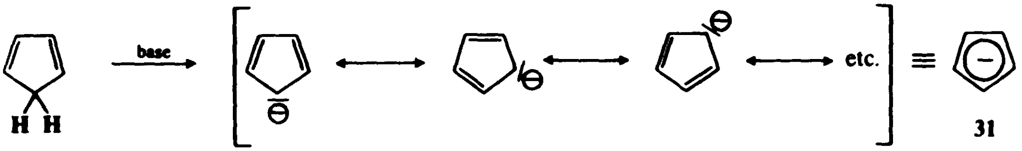
[85] The order of aromaticity of these compounds is benzene > thiophene > pyrrole > furan, as calculated by an aromaticity index based on bond distance measurements. This index has been calculated for 5- and 6-membered monocyclic and bicyclic heterocycles: Bird *Tetrahedron* **1985**, *41*, 1409; **1986**, *42*, 89; **1987**, *43*, 4725.

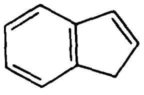
[86] Ref. 1, p 99. See also Calderbank; Calvert; Lukins; Ritchie *Aust. J. Chem.* **1981**, *34*, 1835.

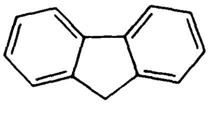
stabilized by resonance although it is quite reactive. The cyclopentadienide ion is usually represented as in **31**. Resonance in this ion is greater than in pyrrole, thiophene, and furan,



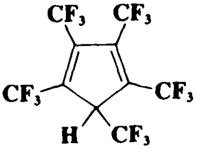
31

since all five forms are equivalent. The resonance energy for **31** has been estimated to be 24-27 kcal/mol (100-113 kJ/mol).[87] That all five carbons are equivalent has been demonstrated by labeling the starting compound with ^{14}C and finding all positions equally labeled when cyclopentadiene was regenerated.[88] As expected for an aromatic system, the cyclopentadienide ion is diatropic[89] and aromatic substitutions on it have been successfully carried out.[90] Indene and fluorene are also acidic ($pK_a \approx 20$ and 23, respectively) but less so than cyclopentadiene, since annellation causes the electrons to be less





Fluorene



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available to the five-membered ring. On the other hand, the acidity of 1,2,3,4,5-pentakis(trifluoromethyl)cyclopentadiene (**32**) is greater than that of nitric acid,[91] because of the electron-withdrawing effects of the triflouromethyl groups (see p. 264).

In sharp contrast to cyclopentadiene is cycloheptatriene (**33**), which has no unusual acidity. This would be hard to explain without the aromatic sextet theory, since, on the

33 **34**

35

basis of resonance forms or a simple consideration of orbital overlaps, **34** should be as stable as the cyclopentadienyl anion (**31**). While **34** has been prepared in solution,[92] it is less stable than **31** and far less stable than **35**, in which **33** has lost not a proton but a hydride ion. The six double-bond electrons of **35** overlap with the empty orbital on the seventh carbon and there is a sextet of electrons covering seven carbon atoms. **35**, known as the *tropylium ion*, is quite stable.[93] Tropylium bromide, which could be completely covalent if the electrons of the bromine were sufficiently attracted to the ring, is actually an ionic compound:[94]

[87] Bordwell; Drucker; Fried *J. Org. Chem.* **1981,** *46*, 632.

[88] Tkachuk; Lee *Can. J. Chem.* **1959,** *37*, 1644.

[89] Bradamante; Marchesini; Pagani *Tetrahedron Lett.* **1971,** 4621.

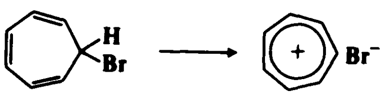
[90] Webster *J. Org. Chem.* **1967,** *32*, 39; Rybinskaya; Korneva *Russ. Chem. Rev.* **1971,** *40*, 247-255.

[91] Laganis; Lemal *J. Am. Chem. Soc.* **1980,** *102*, 6633.

[92] Dauben; Rifi *J. Am. Chem. Soc.* **1963,** *85*, 3041; also see Breslow; Chang *J. Am Chem. Soc.* **1965,** *87*, 2200.

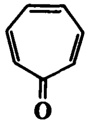
[93] For reviews, see Pietra *Chem. Rev.* **1973,** *73*, 293-364; Bertelli *Top. Nonbenzenoid Aromat. Chem.* **1973,** *1*, 29-46; Kolomnikova; Parnes *Russ. Chem. Rev.* **1967,** *36*, 735-753; Harmon, in Olah; Schleyer, *Carbonium Ions*, vol. 4; Wiley: New York, 1973, pp. 1579-1641.

[94] Doering; Knox *J. Am. Chem. Soc.* **1954,** *76*, 3203.



Just as with **31**, the equivalence of the carbons in **35** has been demonstrated by isotopic labeling.[95]

Another seven-membered ring that shows some aromatic character is tropone (**36**). This molecule would have an aromatic sextet if the two C=O electrons stayed away from the ring and resided near the electronegative oxygen atom. In fact, tropones are stable compounds, and tropolones (**37**) are found in nature.[96] However, analyses of dipole moments, nmr spectra, and x-ray diffraction measurements show that tropones and tropolones display appreciable bond alternations.[97] These molecules must be regarded as essentially nonaromatic, although with some aromatic character. Tropolones readily undergo aromatic substitution, emphasizing that the old and the new definitions of aromaticity are not always parallel. In sharp contrast to **36**, cyclopentadienone (**38**) has been isolated only in an argon matrix below 38 K.[98] Above this temperature it dimerizes. Many earlier attempts to prepare it were unsuccessful.[99] As in **36**, the electronegative oxygen atom draws electron to itself, but in this case it leaves only four electrons and the molecule is unstable. Some derivatives of **38** have been prepared.[99]



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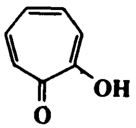

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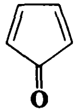

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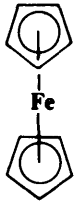

Ferrocene

Another type of five-membered aromatic compound is the *metallocenes* (also called *sandwich compounds*), in which two cyclopentadienide rings form a sandwich around a metallic ion. The best known of these is ferrocene, although others have been prepared

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[95] Vol'pin; Kursanov; Shemyakin; Maimind; Neiman *J. Gen. Chem. USSR* **1959**, *29*, 3667.

[96] For reviews of tropones and tropolones, see Pietra *Acc. Chem. Res.* **1979**, *12*, 132-138; Nozoe *Pure Appl. Chem.* **1971**, *28*, 239-280.

[97] Bertelli; Andrews *J. Am. Chem. Soc.* **1969**, *91*, 5280; Bertelli; Andrews; Crews *J. Am. Chem. Soc.* **1969**, *91*, 5286; Schaefer; Reed *J. Am. Chem. Soc.* **1971**, *93*, 3902; Watkin; Hamor *J. Chem. Soc. B* **1971**, 2167; Barrow; Mills; Filippini *J. Chem. Soc., Chem. Commun.* **1973**, 66.

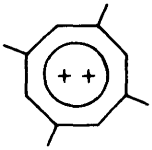
[98] Maier; Franz; Hartan; Lanz; Reisenauer *Chem. Ber.* **1985**, *118*, 3196.

[99] For a review of cyclopentadienone derivatives and of attempts to prepare the parent compound, see Ogliaruso; Romanelli; Becker *Chem. Rev.* **1965**, *65*, 261-367.

with Co, Ni, Cr, Ti, V, and many other metals.[100] Ferrocene is quite stable, subliming above 100°C and unchanged at 400°C. The two rings rotate freely.[101] Many aromatic substitutions have been carried out on metallocenes.[102] Metallocenes containing two metal atoms and three cyclopentadienyl rings have also been prepared and are known as *triple-decker sandwiches*.[103] Even tetradecker, pentadecker, and hexadecker sandwiches have been reported.[104]

The bonding in ferrocene may be looked upon in simplified molecular-orbital terms as follows.[105] Each of the cyclopentadienide rings has five molecular orbitals—three filled bonding and two empty antibonding orbitals (p. 45). The outer shell of the Fe atom possesses nine atomic orbitals, i.e., one 4*s*, three 4*p*, and five 3*d* orbitals. The six filled orbitals of the two cyclopentadienide rings overlap with the *s*, three *p*, and two of the *d* orbitals of the Fe to form twelve new orbitals, six of which are bonding. These six orbitals make up two ring-to-metal triple bonds. In addition further bonding results from the overlap of the empty antibonding orbitals of the rings with additional filled *d* orbitals of the iron. All told, there are eighteen electrons (ten of which may be considered to come from the rings and eight from iron in the zero oxidation state) in nine orbitals; six of these are strongly bonding and three weakly bonding or nonbonding.

The tropylium ion has an aromatic sextet spread over seven carbon atoms. An analogous ion, with the sextet spread over eight carbon atoms, is 1,3,5,7-tetramethylcyclooctatetraene dictation (**39**). This ion, which is stable in solution at −50°C, is diatropic and approximately planar. **39** is not stable above about −30°C.[106]



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Other Systems Containing Aromatic Sextets

Simple resonance theory predicts that pentalene (**40**), azulene (**41**), and heptalene (**42**) should be aromatic, although no nonionic canonical form can have a double bond at the

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[100] For a monograph on metallocenes, see Rosenblum *Chemistry of the Iron Group Metallocenes*; Wiley: New York, 1965. For reviews, see Lukehart *Fundamental Transition Metal Organometallic Chemistry*; Brooks/Cole: Monterey, CA, 1985, pp. 85-118; Lemenovskii; Fedin *Russ. Chem. Rev.* **1986,** *55*, 127-142; Sikora; Macomber; Rausch *Adv. Organomet. Chem.* **1986,** *25*, 317-379; Pauson, *Pure Appl. Chem.* **1977,** *49*, 839-855; Nesmeyanov; Kochetkova *Russ. Chem. Rev.* **1974,** *43*, 710-715; Shul'pin; Rybinskaya *Russ. Chem. Rev.* **1974,** *43*, 716-732; Perevalova; Nikitina *Organomet. React.* **1972,** *4*, 163-419; Bublitz; Rinehart *Org. React.* **1969,** *17*, 1-154; Leonova; Kochetkova *Russ. Chem. Rev.* **1973,** *42*, 278-292; Rausch *Pure Appl. Chem.* **1972,** *30*, 523-538. For a bibliography of reviews on metallocenes, see Bruce *Adv. Organomet. Chem.* **1972,** *10*, 273-346, pp. 322-325.

[101] For a discussion of the molecular structure, see Haaland *Acc. Chem. Res.* **1979,** *12*, 415-422.

[102] For a review on aromatic substitution on ferrocenes, see Plesske *Angew. Chem. Int. Ed. Engl.* **1962,** *1*, 312-327, 394-399 [*Angew. Chem. 74*, 301-316, 347-352].

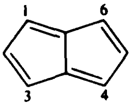
[103] For a review, see Werner *Angew. Chem. Int. Ed. Engl.* **1977,** *16*, 1-9 [*Angew. Chem. 89*, 1-10].

[104] See, for example, Siebert *Angew. Chem. Int. Ed. Engl.* **1985,** *24*, 943-958 [*Angew. Chem. 97*, 924-939].

[105] Rosenblum, Ref. 100, pp. 13-28; Coates; Green; Wade *Organometallic Compounds*, 3rd ed., vol. 2; Methuen: London, 1968, pp. 97-104; Grebenik; Grinter; Perutz *Chem. Soc. Rev.* **1988,** *17*, 453-490; pp. 460-464.

[106] This and related ions were prepared by Olah; Staral; Liang; Paquette; Melega; Carmody *J. Am. Chem. Soc.* **1977,** *99*, 3349. See also Radom; Schaefer *J. Am. Chem. Soc.* **1977,** *99*, 7522; Olah; Liang *J. Am. Chem. Soc.* **1976,** *98*, 3033; Willner; Rabinovitz *Nouv. J. Chim.* **1982,** *6*, 129.

ring junction. Molecular-orbital calculations show that azulene should be stable but not the other two, and this is borne out by experiment. Heptalene has been prepared[107] but reacts readily with oxygen, acids, and bromine, is easily hydrogenated, and polymerizes on standing. Analysis of its nmr spectrum shows that it is not planar.[108] The 3,8-dibromo and 3,8-dicarbomethoxy derivatives of **42** are stable in air at room temperature but are not diatropic.[109]A number of methylated heptalenes and dimethyl 1,2-heptalenedicarboxylates have also been prepared and are stable nonaromatic compounds.[110] Pentalene has not been prepared,[111] but the hexaphenyl[112] and 1,3,5-tri-*t*-butyl derivatives[113] are known. The former is air-sensitive in solution. The latter is stable, but x-ray diffraction and photoelectron spectral data show bond alternation.[114] Pentalene and its methyl and dimethyl derivatives have been formed in solution, but they dimerize before they can be isolated.[115] Many other attempts to prepare these two systems have failed.



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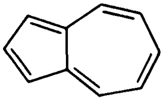

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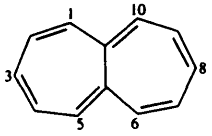
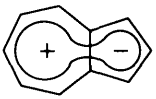
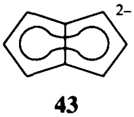


42

In sharp contrast to **40** and **42**, azulene, a blue solid, is quite stable and many of its derivatives are known.[116] Azulene readily undergoes aromatic substitution. Azulene may be regarded as a combination of **31** and **35** and, indeed, possesses a dipole moment of 0.8 D.[117] Interestingly, if two electrons are added to pentalene, a stable dianion (**43**) results.[118] It can be concluded that an aromatic system of electrons will be spread over two rings only if 10 electrons (not 8 or 12) are available for aromaticity.





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[107] Dauben; Bertelli *J. Am. Chem. Soc.* **1961,** *83*, 4659; Vogel; Königshofen; Wassen; Müllen; Oth *Angew. Chem. Int. Ed. Engl.* **1974,** *13*, 732 [*Angew. Chem. 86*, 777]; Paquette; Browne; Chamot *Angew. Chem. Int. Ed. Engl.* **1979,** *18*, 546 [*Angew. Chem. 91*, 581]. For a review of heptalenes, see Paquette *Isr. J. Chem.* **1980,** *20*, 233-239.

[108] Bertelli, in Bergmann; Pullman, Ref. 55, p. 326. See also Stegemann; Lindner *Tetrahedron Lett.* **1977,** 2515.

[109] Vogel; Ippen *Angew. Chem. Int. Ed. Engl.* **1974,** *13*, 734 [*Angew. Chem. 86*, 778]; Vogel; Hogrefe *Angew. Chem. Int. Ed. Engl.* **1974,** *13*, 735 [*Angew. Chem. 86*, 779].

[110] Hafner; Knaup; Lindner *Bull. Soc. Chem. Jpn.* **1988,** *61*, 155.

[111] Metal complexes of pentalene have been prepared: Knox; Stone *Acc. Chem. Res.* **1974,** 7, 321-328.

[112] LeGoff *J. Am. Chem. Soc.* **1962,** *84*, 3975. See also Hafner; Bangert; Orfanos *Angew. Chem. Int. Ed. Engl.* **1967,** *6*, 451 [*Angew. Chem. 79*, 414]; Hartke; Matusch *Angew. Chem. Int. Ed. Engl.* **1972,** *11*, 50 [*Angew. Chem. 84*, 61].

[113] Hafner; Süss *Angew. Chem. Int. Ed. Engl.* **1973,** *12*, 575 [*Angew. Chem. 85*, 626]. See also Hafner; Suda *Angew. Chem. Int. Ed. Engl.* **1976,** *15*, 314 [*Angew. Chem. 88*, 341].

[114] Kitschke; Lindner *Tetrahedron Lett.* **1977,** 2511; Bischof; Gleiter; Hafner; Knauer; Spanget-Larsen; Süss *Chem. Ber.* **1978,** *111*, 932.

[115] Bloch; Marty; de Mayo *J. Am. Chem. Soc.* **1971,** *93*, 3071; *Bull. Soc. Chim. Fr.* **1972,** 2031; Hafner; Dönges; Goedecke; Kaiser *Angew. Chem. Int. Ed. Engl.* **1973,** *12*, 337 [*Angew. Chem. 85*, 362].

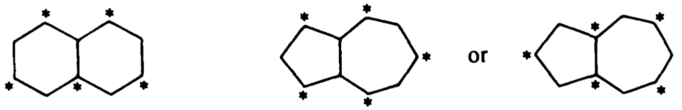
[116] For a review on azulene, see Mochalin; Porshnev *Russ. Chem. Rev.* **1977,** *46*, 530-547.

[117] Tobler; Bauder; Günthard *J. Mol. Spectrosc.* **1965,** *18*, 239.

[118] Katz; Rosenberger; O'Hara *J. Am. Chem. Soc.* **1964,** *86*, 249. See also Willner; Becker; Rabinovitz *J. Am. Chem. Soc.* **1979,** *101*, 395.

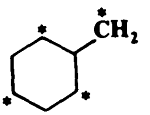
Alternant and Nonalternant Hydrocarbons[119]

Aromatic hydrocarbons can be divided into two types. In alternant hydrocarbons, the conjugated carbon atoms can be divided into two sets such that no two atoms of the same set are directly linked. For convenience one set may be starred. Naphthalene is an alternant and azulene a nonalternant hydrocarbon:



In alternant hydrocarbons, the bonding and antibonding orbitals occur in pairs; i.e., for every bonding orbital with an energy $-E$ there is an antibonding one with energy $+E$ (Figure 2.7[120]). Even-alternant hydrocarbons are those with an even number of conjugated atoms, i.e., an equal number of starred and unstarred atoms. For these hydrocarbons all the bonding orbitals are filled and the π electrons are uniformly spread over the unsaturated atoms.

As with the allylic system, odd-alternant hydrocarbons (which must be carbocations, carbanions, or radicals) in addition to equal and opposite bonding and antibonding orbitals also have a nonbonding orbital of zero energy. When an odd number of orbitals overlap, an odd number is created. Since orbitals of alternant hydrocarbons occur in $-E$ and $+E$ pairs, one orbital can have no partner and must therefore have zero bonding energy. For example, in the benzylic system the cation has an unoccupied nonbonding orbital, the free radical has one electron there and the carbanion two (Figure 2.8). As with the allylic system,



all three species have the same bonding energy. The charge distribution (or unpaired-electron distribution) over the entire molecule is also the same for the three species and can be calculated by a relatively simple process.[119]

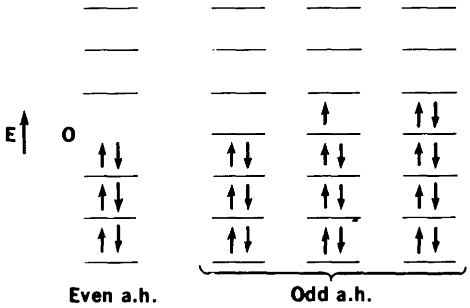


FIGURE 2.7 Energy levels in odd- and even-alternant hydrocarbons.[120] The arrows represent electrons. The orbitals are shown as having different energies, but some may be degenerate.

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[119] For discussions, see Jones *Physical and Mechanistic Organic Chemistry*, 2nd ed.; Cambridge University Press: Cambridge, 1984, pp. 122-129; Dewar *Prog. Org. Chem.* **1953**, *2*, 1-28.

[120] Taken from Dewar, Ref. 119, p. 8.

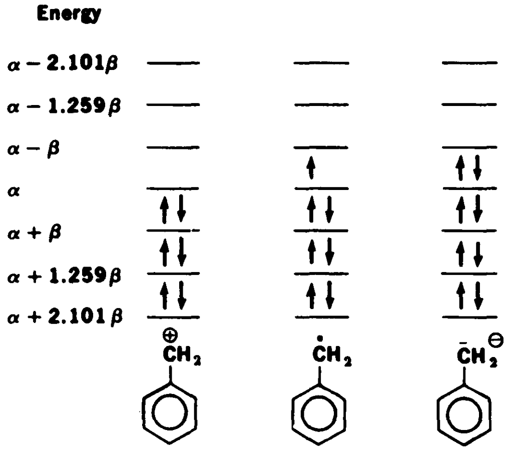


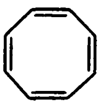
FIGURE 2.8 Energy levels for the benzyl cation, free radical, and carbanion. Since α is the energy of a *p* orbital (p. 30), the nonbonding orbital has no bonding energy.

For nonalternant hydrocarbons the energies of the bonding and antibonding orbitals are not equal and opposite and charge distributions are not the same in cations, anions, and radicals. Calculations are much more difficult but have been carried out.[121]

Aromatic Systems with Electron Numbers Other than Six

Ever since the special stability of benzene was recognized, chemists have been thinking about homologous molecules and wondering whether this stability is also associated with rings that are similar but of different sizes, such as cyclobutadiene (**44**), cyclooctatetraene (**45**), cyclodecapentaene[122] (**46**), etc. The general name *annulene* is given to these compounds, benzene being [6]annulene, and **44** to **46** being called, respectively, [4], [8], and [10]annulene. By a naïve consideration of resonance forms, these annulenes and higher ones should be as aromatic as benzene. Yet they proved remarkably elusive. The ubiquitous benzene ring is found in thousands of natural products, in coal and petroleum, and is formed by strong treatment of many noncyclic compounds. None of the other annulene ring systems has ever been found in nature and, except for cyclooctatetraene, their synthesis is not simple. Obviously, there is something special about the number six in a cyclic system of electrons.

44



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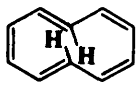

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Hückel's rule, based on molecular-orbital calculations,[123] predicts that electron rings will constitute an aromatic system only if the number of electrons in the ring is of the form

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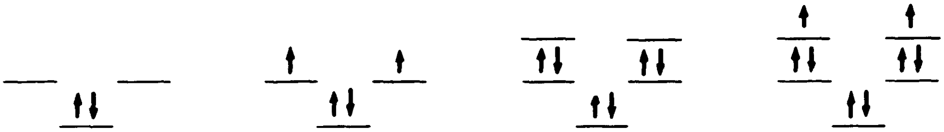
[121] Peters *J. Chem. Soc.* **1958,** 1023, 1028, 1039; Brown; Burden; Williams *Aust. J. Chem.* **1968,** *21,* 1939. For reviews, see Zahradnik, in Snyder, Ref. 55, vol. 2, pp. 1-80; Zahradnik *Angew. Chem. Int. Ed. Engl.* **1965,** *4,* 1039-1050 [*Angew. Chem. 77,* 1097-1109].

[122] The cyclodecapentaene shown here is the cis-trans-cis-cis-trans form. For other stereoisomers, see p. 58.

[123] For reviews of molecular-orbital calculations of nonbenzenoid cyclic conjugated hydrocarbons, see Nakajima *Pure Appl. Chem.* **1971,** *28,* 219-238; *Fortschr. Chem. Forsch.* **1972,** *32,* 1-42.

$4n + 2$, where n is zero or any position integer. Systems that contain 4n electrons are predicted to be nonaromatic. The rule predicts that rings of 2, 6, 10, 14, etc., electrons will be aromatic, while rings of 4, 8, 12, etc., will not be. This is actually a consequence of Hund's rule. The first pair of electrons in an annulene goes into the π orbital of lowest energy. After that the bonding orbitals are degenerate and occur in pairs of equal energy.



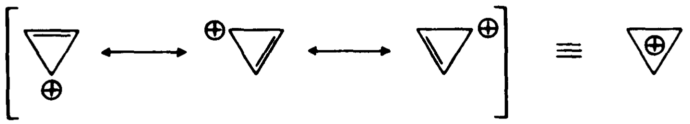
Duet (aromatic) **Quartet (diradical)** **Sextet (aromatic)** **Octet (diradical)**

When there is a total of four electrons, Hund's rule predicts that two will be in the lowest orbital but the other two will be unpaired, so that the system will exist as a diradical rather than as two pairs. The degeneracy can be removed if the molecule is distorted from maximum molecular symmetry to a structure of lesser symmetry. For example, if **44** assumes a rectangular rather than a square shape, one of the previously degenerate orbitals has a lower energy than the other and will be occupied by two electrons. In this case, of course, the double bonds are essentially separate and the molecule is still not aromatic. Distortions of symmetry can also occur when one or more carbons are replaced by hetero atoms or in other ways.[124]

In the following sections systems with various numbers of electrons are discussed. When we look for aromaticity we look for: (1) the presence of a diamagnetic ring current; (2) equal or approximately equal bond distances, except when the symmetry of the system is disturbed by a hetero atom or in some other way; (3) planarity; (4) chemical stability; (5) the ability to undergo aromatic substitution.

Systems of Two Electrons[125]

Obviously, there can be no ring of two carbon atoms though a double bond may be regarded as a degenerate case. However, in analogy to the tropylium ion, a three-membered ring with a double bond and a positive charge on the third atom (the *cyclopropenyl cation*) is a $4n + 2$ system and hence is expected to show aromaticity. The unsubstituted **47** has been prepared,[126] as well as several derivatives, e.g., the trichloro, diphenyl, and dipropyl derivatives, and these are stable despite the angles of only 60°. In fact, the tripropylcyclopropenyl[127]



47

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[124] For a discussion, see Hoffmann *Chem. Commun.* **1969,** 240.

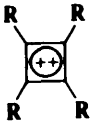
[125] For reviews, see Billups; Moorehead, in Rappoport *The Chemistry of the Cyclopropyl Group*, pt. 2; Wiley: New York, 1987, pp. 1533-1574; Potts; Baum *Chem. Rev.* **1974,** *74*, 189-213; Yoshida *Top. Curr. Chem.* **1973,** *40*, 47-72; D'yakonov; Kostikov *Russ. Chem. Rev.* **1967,** *36*, 557-563; Closs *Adv. Alicyclic Chem.* **1966,** *1*, 53-127, pp. 102-126; Krebs *Angew. Chem. Int. Ed. Engl.* **1965,** *4*, 10-22 [*Angew. Chem.* *77*, 10-22].

[126] Breslow; Groves; Ryan *J. Am. Chem. Soc.* **1967,** *89*, 5048; Farmum, Mehta; Silberman *J. Am. Chem. Soc.* **1967,** *89*, 5048; Breslow; Groves *J. Am. Chem. Soc.* **1970,** *92*, 984.

[127] Breslow; Höver; Chang *J. Am. Chem. Soc.* **1962,** *84*, 3168.

and tricyclopropylcyclopropenyl[128] cations are among the most stable carbocations known, being stable even in water solution. The tri-*t*-butylcyclopropenyl cation is also very stable.[129] In addition, cyclopropenone and several of its derivatives are stable compounds,[130] in accord

Cyclopropenone



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with the corresponding stability of the tropones.[131] The ring system **47** is nonalternant and the corresponding radical and anion (which do not have an aromatic duet) have electrons in antibonding orbitals, so that their energies are much higher. As with **31** and **35**, the equivalence of the three carbon atoms in the triphenylcyclopropenyl cation has been demonstrated by ^{14}C labeling experiments.[132] The interesting dications **48** (R = Me or Ph) have been prepared,[133] and they too should represent aromatic systems of two electrons.[134]

Systems of Four Electrons. Antiaromaticity

The most obvious compound in which to look for a closed loop of four electrons is cyclobutadiene (**44**).[135] Hückel's rule predicts no aromatic character here, since 4 is not a number of the form $4n + 2$. There is a long history of attempts to prepare this compound and its simple derivatives, and, as we shall see, the evidence fully bears out Hückel's prediction—cyclobutadienes display none of the characteristics that would lead us to call them aromatic. More surprisingly, there is evidence that a closed loop of four electrons is actually *antiaromatic*.[136] If such compounds simply lacked aromaticity, we would expect them to be about as stable as similar nonaromatic compounds, but both theory and experiment show that they are *much less stable*.[137] An antiaromatic compound may be defined as a compound that is destabilized by a closed loop of electrons.

After years of attempts to prepare cyclobutadiene, the goal was finally reached by Pettit and co-workers.[138] It is now clear that **44** and its simple derivatives are extremely unstable

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[128] Komatsu; Tomioka; Okamoto *Tetrahedron Lett.* **1980,** *21*, 947; Moss; Shen; Krogh-Jespersen; Potenza; Shugar; Munjal *J. Am. Chem. Soc.* **1986,** *108*, 134.

[129] Ciabattoni; Nathan *J. Am. Chem. Soc.* **1968,** *90*, 4495.

[130] See, for example, Kursanov; Vol'pin; Koreshkov *J. Gen. Chem. USSR* **1960,** *30*, 2855; Breslow; Oda *J. Am. Chem. Soc.* **1972,** *94*, 4787; Yoshida; Konishi; Tawara; Ogoshi *J. Am. Chem. Soc.* **1973,** 95, 3043; Ref. 129.

[131] For a reveiw of cyclopropenones, see Eicher; Weber *Top. Curr. Chem. Soc.* **1975,** *57*, 1-109. For discussions of cyclopropenone structure, see Shäfer; Schweig; Maier; Sayrac; Crandall *Tetrahedron Lett.* **1974,** 1213; Tobey, in Bergmann; Pullman, Ref. 55, pp. 351-362; Greenberg; Tomkins; Dobrovolny; Liebman *J. Am. Chem. Soc.* **1983,** *105*, 6855.

[132] D'yakonov; Kostikov; Molchanov *J. Org. Chem. USSR* **1969,** *5*, 171; **1970,** *6*, 304.

[133] Freedman; Young *J. Am. Chem. Soc.* **1964,** *86*, 734; Olah; Bollinger; White *J. Am. Chem. Soc.* **1969,** *91*, 3667; Olah; Mateescu *J. Am. Chem. Soc.* **1970,** *92*, 1430; Olah; Staral *J. Am. Chem. Soc.* **1976,** *98*, 6290. See also Lambert; Holcomb *J. Am. Chem. Soc.* **1971,** *93*, 2994; Seitz; Schmiedel; Mann *Synthesis* **1974,** 578.

[134] See Pittman; Kress; Kispert *J. Org. Chem.* **1974,** *39*, 378. See, however, Krogh-Jespersen; Schleyer; Pople; Cremer *J. Am. Chem. Soc.* **1978,** *100*, 4301.

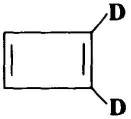
[135] For a monograph, see Cava; Mitchell *Cyclobutadiene and Related Compounds*; Academic Press: New York, 1967. For reviews, see Maier *Angew. Chem. Int. Ed. Engl.* **1988,** *27*, 309-332 [*Angew. Chem. 100*, 317-341]; **1974,** *13*, 425-438 [*Angew. Chem. 86*, 491-505]; Bally; Masamune *Tetrahedron* **1980,** *36*, 343-370; Vollhardt *Top. Curr. Chem.* **1975,** *59*, 113-136.

[136] For reviews of antiaromaticity, see Glukhovtsev; Simkin; Minkin; *Russ. Chem. Rev.* **1985,** *54*, 54-75; Breslow *Pure Appl. Chem.* **1971,** *28*, 111-130; *Acc. Chem. Res.* **1973,** *6*, 393-398; *Chem. Br.* **1968,** *4*, 100; *Angew. Chem. Int. Ed. Engl.* **1968,** *7*, 565-570 [*Angew. Chem. 80*, 573-578].

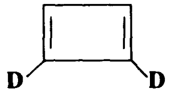
[137] For a discussion, see Bauld; Welsher; Cessac; Holloway *J. Am. Chem. Soc.* **1978,** *100*, 6920.

[138] Watts; Fitzpatrick; Pettit *J. Am. Chem. Soc.* **1965,** *87*, 3253, **1966,** *88*, 623. See also Cookson; Jones *J. Chem. Soc.* **1965,** 1881.

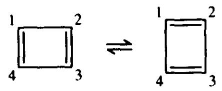
compounds with very short lifetimes (they dimerize by a Diels–Alder reaction; see **5-47**) unless they are stabilized in some fashion, either at ordinary temperatures embedded in the cavity of a hemicarcerand[138a] (see the structure of a carcerand, **30** on p. 89), or in matrices at very low temperatures (generally under 35 K). In either of these cases, the cyclobutadiene molecules are forced to remain apart from each other, and other molecules cannot get in. The structures of **44** and some of its derivatives have been studied a number of times using the low-temperature matrix technique.[139] The ground-state structure of **44** is a rectangular diene (not a diradical) as shown by the infrared (ir) spectra of **44** and deuterated **44** trapped in matrices[140] as well as by a photoelectron spectrum.[141] Molecular-orbital calculations agree.[142] The same conclusion was also reached in an elegant experiment in which 1,2-dideuterocyclobutadiene was generated. If **44** is a rectangular diene, the dideutero compound should exist as two isomers:



and

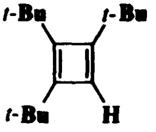


The compound was generated (as an intermediate that was not isolated) and two isomers were indeed found.[143] The cyclobutadiene molecule is not static, even in the matrices. There are two forms (**44a** and **44b**) which rapidly interconvert.[144]



47a **47b**

There are some simple cyclobutadienes that are stable at room temperature for varying periods of time. These either have bulky substituents or carry certain other stabilizing substituents. Examples of the first type are tri-*t*-butylcyclobutadiene (**49**)[145] and the dithia



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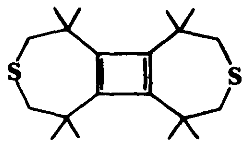


50

[138a] Cram; Tanner; Thomas *Angew. Chem. Int. Ed. Engl.* **1991,** *30,* 1024 [*Angew. Chem. 103,* 1048].

[139] See, for example, Lin; Krantz *J. Chem. Soc., Chem. Commun.* **1972,** 1111; Chapman; McIntosh; Pacansky *J. Am. Chem. Soc.* **1973,** *95,* 614; Maier; Mende *Tetrahedron Lett.* **1969,** 3155. For a review, see Sheridan *Org. Photochem.* **1987,** *8,* 159-248; pp. 167-181.

[140] Masamune; Souto-Bachiller; Machiguchi; Bertie *J. Am. Chem. Soc.* **1978,** *100,* 4889.

[141] Kreile; Münzel; Schweig; Specht *Chem. Phys. Lett.* **1986,** *124,* 140.

[142] See, for example, Borden; Davidson; Hart *J. Am. Chem. Soc.* **1978,** *100,* 388; Kollmar; Staemmler *J. Am. Chem. Soc.* **1978,** *100,* 4304; Jafri; Newton *J. Am. Chem. Soc.* **1978,** *100,* 5012; Ermer; Heilbronner *Angew. Chem. Int. Ed. Engl.* **1983,** *22,* 402 [*Angew. Chem. 95,* 414; Voter; Goddard *J. Am. Chem. Soc.* **1986,** *108,* 2830.

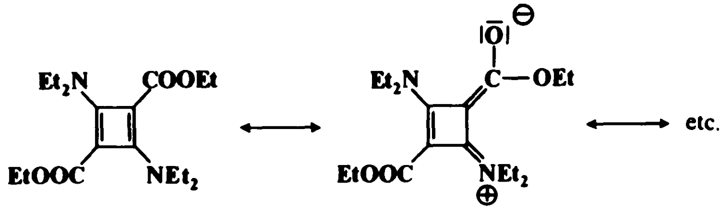
[143] Whitman; Carpenter *J. Am. Chem. Soc.* **1980,** *102,* 4272. See also Whitman; Carpenter *J. Am. Chem. Soc.* **1982,** *104,* 6473.

[144] Carpenter *J. Am. Chem. Soc.* **1983,** *105,* 1700; Huang; Wolfsberg *J. Am. Chem. Soc.* **1984,** *106,* 4039; Dewar; Merz; Stewart *J. Am. Chem. Soc.* **1984,** *106,* 4040; Orendt; Arnold; Radziszewski; Facelli; Malsch; Strub; Grant; Michl *J. Am. Chem. Soc.* **1988,** *110,* 2648. See, however, Arnold; Radziszewski; Campion; Perry; Michl *J. Am. Chem. Soc.* **1991,** *113,* 692.

[145] Masamune; Nakamura; Suda; Ona *J. Am. Chem. Soc.* **1973,** *95,* 8481; Maier; Alzérreca *Angew. Chem. Int. Ed. Engl.* **1973,** *12,* 1015 [*Angew. Chem. 85,* 1056]. For a discussion, see Masamune *Pure Appl. Chem.* **1975,** *44,* 861-884.

compound **50**.[146] These compounds are relatively stable because dimerization is sterically hindered. Examination of the nmr spectrum of **49** showed that the ring proton ($\delta = 5.38$) was shifted *upfield*, compared with the position expected for a nonaromatic proton, e.g., cyclopentadiene. As we shall see on p. 64, this indicates that the compound is antiaromatic. A similar investigation cannot be made for **50** because it has no ring proton, but x-ray crystallography showed that the central ring is a rectangular diene (as shown) with single and double-bond lengths of 1.59–1.60 and 1.34 Å, respectively.[147] The unusually long single-bond distance may be due to repulsion between the methyl groups. Photoelectron spectroscopy showed that **50** is not a diradical.[148]

The other type of stable cyclobutadiene has two electron-donating and two electron-withdrawing groups,[149] and is stable in the absence of water.[150] An example is **51**. The stability of these compounds is generally attributed to the resonance shown, a type of resonance stabilization called the *push–pull* or *captodative effect*,[151] although it has been concluded from a photoelectron spectroscopy study that second order bond fixation is more important.[152] An x-ray crystallographic study of **51** has shown[153] the ring to be a distorted square with bond lengths of 1.46 Å and angles of 87° and 93°.



51

It is clear that simple cyclobutadienes, which could easily adopt a square planar shape if that would result in aromatic stabilization, do not in fact do so and are not aromatic. The high reactivity of these compounds is not caused merely by steric strain, since the strain should be no greater than that of simple cyclopropenes, which are known compounds. It is probably caused by antiaromaticity.[154]

The unfused cyclobutadiene system is stable in complexes with metals[155] (see Chapter 3), but in these cases electron density is withdrawn from the ring by the metal and there is

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[146] Krebs; Kimling; Kemper *Liebigs Ann. Chem.* **1978,** 431.

[147] Irngartinger; Nixdorf; Riegler; Krebs; Kimling; Pocklington; Maier; Malsch; Schneider *Chem. Ber.* **1988,** *121*, 673. This paper also includes an x-ray structure of tetra-*t*-butylcyclobutadiene. See also Irngartinger; Nixdorf *Chem. Ber.* **1988,** *121*, 679; Dunitz; Krüger; Irngartinger; Maverick; Wang; Nixdorf *Angew. Chem. Int. Ed. Engl.* **1988,** *27*, 387 [*Angew. Chem. 100*, 415].

[148] Lauer; Müller; Schulte; Schweig; Krebs *Angew. Chem. Int. Ed. Engl.* **1974,** *13*, 544 [*Angew. Chem. 86*, 597]. See also Brown; Masamune *Can. J. Chem.* **1975,** *53*, 972; Lauer; Müller; Schulte; Schweig; Maier; Alzérreca *Angew. Chem. Int. Ed. Engl.* **1975,** *14*, 172 [*Angew. Chem. 87*, 194]; Irngartinger; Hase; Schulte; Schweig *Angew. Chem. Int. Ed. Engl.* **1977,** *16*, 187 [*Angew. Chem. 89*, 194].

[149] The presence of electron-donating and withdrawing groups on the same ring stabilizes $4n$ systems and destabilizes $4n + 2$ systems. For a review of this concept, see Gompper; Wagner *Angew. Chem. Int. Ed. Engl.* **1988,** *27*, 1437-1455 [*Angew. Chem. 100*, 1492-1511].

[150] Gompper; Seybold *Angew. Chem. Int. Ed. Engl.* **1968,** *7*, 824 [*Angew. Chem. 80*, 804]; Neuenschwander; Niederhauser *Chimia* **1968,** *22*, 491, *Helv. Chim. Acta* **1970,** *53*, 519; Gompper; Mensch; Seybold *Angew. Chem. Int. Ed. Engl.* **1975,** *14*, 704 [*Angew. Chem. 87*, 711]; Gompper; Kroner; Seybold; Wagner *Tetrahedron* **1976,** *32*, 629.

[151] Manatt; Roberts *J. Org. Chem.* **1959,** *24*, 1336; Breslow, Kivelevich, Mitchell, Fabian; Wendel *J. Am. Chem. Soc.* **1965,** *87*, 5132; Hess; Schaad *J. Org. Chem.* **1976,** *41*, 3058.

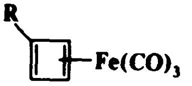
[152] Gompper; Holsboer; Schmidt; Seybold *J. Am. Chem. Soc.* **1973,** *95*, 8479.

[153] Lindner; Gross *Chem. Ber.* **1974,** *107*, 598.

[154] For evidence, see Breslow; Murayama; Murahashi; Grubbs *J. Am. Chem. Soc.* **1973,** *95*, 6688; Herr *Tetrahedron* **1976,** *32*, 2835.

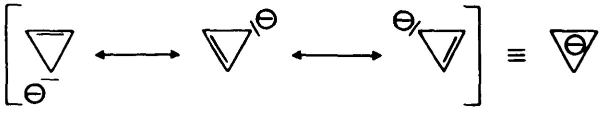
[155] For reviews, see Efraty *Chem. Rev.* **1977,** *77*, 691-744; Pettit *Pure Appl. Chem.* **1968,** *17*, 253-272; Maitlis *Adv. Organomet. Chem.* **1966,** *4*, 95-143; Maitlis; Eberius, in Snyder, Ref. 55, vol. 2. pp. 359-409.

no aromatic quartet. In fact, these cyclobutadiene–metal complexes can be looked upon as systems containing an aromatic duet. The ring is square planar,[156] the compounds undergo

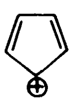


aromatic substitution,[157] and nmr spectra of monosubstituted derivatives show that the C-2 and C-4 protons are equivalent.[157]

Two other systems that have been studied as possible aromatic or antiaromatic four-electron systems are **52** and **53**.[158] In these cases also the evidence supports antiaromaticity, not aromaticity. With respect to **52**, HMO theory predicts that an unconjugated



54 **52**



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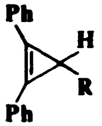
54 (i.e., a single canonical form) is more stable than a conjugated **52**,[159] so that **54** would actually lose stability by forming a closed loop of four electrons. The HMO theory is supported by experiment. Among other evidence, it has been shown that **55** (R = COPh) loses its proton in hydrogen-exchange reactions about 6000 times more slowly than **56**



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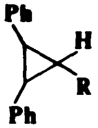

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(R = COPh).[160] Where R = CN, the ratio is about 10,000.[161] This indicates that **55** are much more reluctant to form carbanions (which would have to be cyclopropenyl carbanions) than **56**, which form ordinary carbanions. Thus the carbanions of **55** are less stable than corresponding ordinary carbanions. Although derivatives of cyclopropenyl anion have been prepared as fleeting intermediates (as in the exchange reactions mentioned above), all attempts to prepare the ion or any of its derivatives as relatively stable species have so far met with failure.[162]

In the case of **53**, the ion has been prepared and has been shown to be a diradical in the ground state,[163] as predicted by the discussion on p. 52.[164] Evidence that **53** is not only

[156] Dodge; Schomaker *Acta Crystallogr.* **1965,** *18,* 614; *Nature* **1960,** *186,* 798; Dunitz; Mez; Mills; Shearer *Helv. Chim. Acta* **1962,** *45* 647; Yannoni; Ceasar; Dailey *J. Am. Chem. Soc.* **1967,** 89, 2833.

[157] Fitzpatrick; Watts; Emerson; Pettit *J. Am. Chem. Soc.* **1965,** *87,* 3255. For a discussion, see Pettit *J. Organomet. Chem.* **1975,** *100,* 205-217.

[158] For a review of cyclopentadienyl cations, see Breslow *Top. Nonbenzenoid Aromat. Chem.* **1973,** *1,* 81-94.

[159] Clark *Chem. Commun.* **1969,** 637; Ref. 136.

[160] Breslow; Brown; Gajewski *J. Am. Chem. Soc.* **1967,** *89,* 4383.

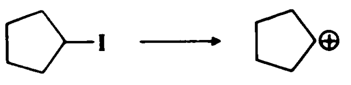
[161] Breslow; Douek *J. Am. Chem. Soc.* **1968,** *90,* 2698.

[162] See, for example, Breslow; Cortés; Juan; Mitchell *Tetrahedron Lett.* **1982,** *23,* 795. A triphenylcyclopropyl anion has been prepared in the gas phase, with a lifetime of 1-2 seconds: Bartmess; Kester; Borden; Köser *Tetrahedron Lett.* **1986,** *27,* 5931.

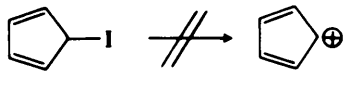
[163] Saunders; Berger; Jaffe; McBride; O'Neill; Breslow; Hoffman; Perchonock; Wasserman; Hutton; Kuck *J. Am. Chem. Soc.* **1973,** *95,* 3017.

[164] Derivatives of **53** show similar behavior; Breslow; Chang; Yager *J. Am. Chem. Soc.* **1963,** *85,* 2033; Volz *Tetrahedron Lett.* **1864,** 1899; Breslow; Hill; Wasserman *J. Am. Chem. Soc.* **1964,** *86,* 5349; Breslow; Chang; Hill; Wasserman *J. Am. Chem. Soc.* **1967,** *89,* 1112; Gompper; Glöckner *Angew. Chem. Int. Ed. Engl.* **1984,** *23,* 53 [*Angew. Chem.* *96,* 48].

nonaromatic but also antiaromatic comes from studies on **57** and **59**.[165] When **57** is treated with silver perchlorate in propionic acid, the molecule is rapidly solvolyzed (a reaction in which the intermediate **58** is formed; see Chapter 5). Under the same conditions, **59** undergoes no solvolysis at all; i.e., **53** does not form. If **53** were merely nonaromatic, it should be about as stable as **58** (which of course has no resonance stabilization at all). The fact that it is so much more reluctant to form indicates that **53** is much less stable than **58**.



57 **58**



59 **53**

It is strong evidence for Hückel's rule that **52** and **53** are not aromatic while the cyclopropenyl cation (**47**) and the cyclopentadienyl anion (**31**) are, since simple resonance theory predicts no difference between **52** and **47** or **53** and **31** (the same number of equivalent canonical forms can be drawn for **52** as for **47** and for **53** as for **31**).

In compounds in which overlapping parallel *p* orbitals form a closed loop of $4n + 2$ electrons, the molecule is stabilized by resonance and the ring is aromatic. But the evidence given above (and additional evidence discussed below) indicates that when the closed loop contains $4n$ electrons, the molecule is *destabilized* by resonance. In summary, **44**, **52**, and **53** and their simple derivatives are certainly not aromatic and are very likely antiaromatic.

Systems of Eight Electrons

Cyclooctatetraene[166] (**45**) is not planar but tub-shaped.[167] Therefore we would expect that it is neither aromatic nor antiaromatic, since both these conditions require overlap of parallel *p* orbitals. The reason for the lack of planarity is that a regular octagon has angles of 135°, while sp^2 angles are most stable at 120°. To avoid the strain, the molecule assumes a nonplanar shape, in which orbital overlap is greatly diminished.[168] Single- and double-bond distances in **45** are, respectively, 1.46 and 1.33 Å, which is expected for a compound made up of four individual double bonds.[167] The reactivity is also what would be expected for a linear polyene. However, the cyclooctadiendiynes **60** and **61** are planar conjugated eight-electron systems (the four extra triple-bond electrons do not participate), which nmr evidence show to be

45

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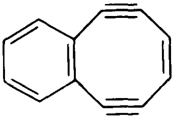
[165] Breslow; Mazur *J. Am. Chem. Soc.* **1973**, *95*, 584; Breslow; Hoffman *J. Am. Chem.Soc.* **1972**, *94*, 2110. For further evidence, see Lossing; Treager *J. Am. Chem. Soc.* **1975**, *97*, 1579. See also Breslow; Canary *J. Am. Chem. Soc.* **1991**, *113*, 3950.

[166] For a monograph, see Fray; Saxton *The Chemistry of Cyclo-octatetraene and its Derivatives*; Cambridge University Press: Cambridge, 1978. For a review, see Paquette *Tetrahedron* **1975**, *31*, 2855-2883. For reviews of heterocyclic 8π systems, see Kaim *Rev. Chem. Intermed.* **1987**, *8*, 247-286; Schmidt *Angew. Chem. Int. Ed. Engl.* **1975**, *14*, 581-591 [*Angew. Chem. 87*, 603-613].

[167] Bastiansen; Hedberg; Hedberg *J. Chem. Phys.* **1957**, *27*, 1311.

[168] The compound perfluorotetracyclobutacyclooctatetraene has been found to have a planar cyclooctatetraene ring, although the corresponding tetracyclopenta analog is nonplanar: Einstein; Willis; Cullen; Soulen *J. Chem. Soc., Chem. Commun.* **1981**, 526. See also Paquette; Wang; Cottrell *J. Am. Chem. Soc.* **1987**, *109*, 3730.

antiaromatic.[169] There is evidence that part of the reason for the lack of planarity in **45** itself is that a planar molecular would have to be antiaromatic.[170] The cycloheptatrienyl anion (**34**) also has eight electrons but does not behave like an aromatic system.[92] The nmr spectrum of the benzocycloheptatrienyl anion (**62**) shows that, like **49, 60,** and **61,** this compound is antiaromatic.[171]



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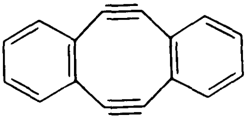

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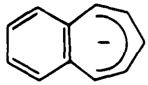

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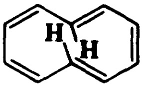
Systems of Ten Electrons[172]

There are three geometrically possible isomers of [10]annulene—the all-cis (**63**), the mono-trans (**64**), and the cis–trans–cis–cis–trans (**46**). If Hückel's rule applies, they should be planar. But it is far from obvious that the molecules would adopt a planar shape, since they must overcome considerable strain to do so. For a regular decagon (**63**) the angles would have to be 144°, considerably larger than the 120° required for sp^2 angles. Some of this strain would also be present in **64** but this kind of strain is eliminated in **46** since all the angles are 120°. However, it was pointed out by Mislow[173] that the hydrogens in the 1 and 6 positions should interfere with each other and force the molecule out of planarity.



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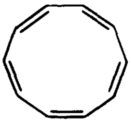

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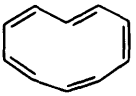

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Compounds **63** and **64** have been prepared[174] as crystalline solids at −80°C. Nmr spectra show that all the hydrogens lie in the olefinic region and neither compound is aromatic. From ^{13}C and proton nmr spectra it has been deduced that neither is planar. However, that the angle strain is not insurmountable has been demonstrated by the preparation of several compounds that have large angles but that are definitely planar 10-electron aromatic systems.

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[169] For a review, see Huang; Sondheimer *Acc. Chem. Res.* **1982,** *15*, 96-102. See also Dürr; Klauck; Peters; von Schnering *Angew. Chem. Int. Ed. Engl.* **1983,** *22*, 332 [*Angew. Chem.* *95*, 321]; Chan; Mak; Poon; Wong; Jia; Wang *Tetrahedron* **1986,** *42*, 655.

[170] Figeys; Dralants *Tetrahedron Lett.* **1971,** 3901; Buchanan *Tetrahedron Lett.* **1972,** 665.

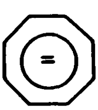
[171] Staley; Orvedal *J. Am. Chem. Soc.* **1973,** *95*, 3382.

[172] For reviews, see Kemp-Jones; Masamune *Top. Nonbenzenoid Aromat. Chem.* **1973,** *1*, 121-157; Masamune; Darby *Acc. Chem. Res.* **1972,** *5*, 272-281; Burkoth; van Tamelen, in Snyder, Ref. 55, vol. 1, pp. 63-116; Vogel, in *Aromaticity*, Ref. 55, pp. 113-147.

[173] Mislow *J. Chem. Phys.* **1952,** *20*, 1489.

[174] Masamune; Hojo; Hojo; Bigam; Rabenstein *J. Am. Chem. Soc.* **1971,** *93*, 4966. [10]Annulenes had previously been prepared, but it was not known which ones: van Tamelen; Burkoth *J. Am. Chem. Soc.* **1967,** *89*, 151; van Tamelen; Greeley *Chem. Commun.* **1971,** 601; van Tamelen; Burkoth; Greeley *J. Am. Chem. Soc.* **1971,** *93*, 6120.

Among these are the dianion **65**, the anions **66** and **67**, and the azonine **68**.[175] **65**[176] has angles of about 135°, while **66**[177] and **67**[178] have angles of about 140°, which are not very far



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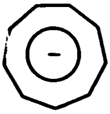

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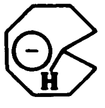

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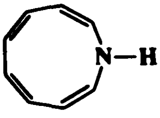
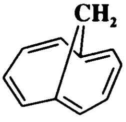


68

from 144°. The inner proton in **67**[179] (which is the mono-trans isomer of the all-cis **66**) is found far upfield in the nmr (−3.5 δ). For **63** and **64**, the cost in strain energy to achieve planarity apparently outweighs the extra stability that would come from an aromatic ring. To emphasize the delicate balance between these factors, we may mention that the oxygen analog of **68** (oxonin) and the N-carbethoxy derivative of **68** are nonaromatic and nonplanar, while **68** itself is aromatic and planar.[180]

So far **46** has not been prepared, despite many attempts. However, there are various ways of avoiding the interference between the two inner protons. The approach that has been most successful involves bridging the 1 and 6 positions.[181] Thus, 1,6-methano[10]annulene (**69**)[182] and its oxygen and nitrogen analogs **70**[183] and **71**[184] have been prepared and are stable compounds that undergo aromatic substitution and are diatropic.[185] For example, the perimeter protons of **69** are found at 6.9 to 7.3 δ, while the



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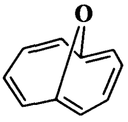

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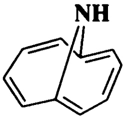

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[175] For reviews of **68** and other nine-membered rings containing four double bonds and a hetero atom (*heteronins*), see Anastassiou *Acc. Chem. Res.* **1972,** *5*, 281-288, *Top. Nonbenzenoid Aromat. Chem.* **1973,** *1*, 1-27, *Pure Appl. Chem.* **1975,** *44*, 691-749. For a review of heteroannulenes in general, see Anastassiou; Kasmai *Adv. Heterocycl. Chem.* **1978,** *23*, 55-102.

[176] Katz *J. Am. Chem. Soc.* **1960,** *82*, 3784, 3785; Goldstein; Wenzel *J. Chem. Soc., Chem. Commun.* **1984,** 1654; Garkusha; Garbuzova; Lokshin; Todres *J. Organomet. Chem.* **1989,** *371*, 279. See also Noordik; van den Hark; Mooij; Klaassen *Acta Crystallogr. Sect. B.* **1974,** *30*, 833; Goldberg; Raymond; Harmon; Templeton *J. Am. Chem. Soc.* **1974,** *96*, 1348; Evans; Wink; Wayda; Little *J. Org. Chem. Soc.* **1981,** *46*, 3925; Heinz; Langensee; Müllen *J. Chem. Soc., Chem.Commun.* **1986,** 947.

[177] Katz; Garratt *J. Am. Chem. Soc.* **1964,** *86*, 5194; LaLancette; Benson *J. Am. Chem. Soc.* **1965,** *87*, 1941; Simmons; Chesnut; LaLancette *J. Am. Chem. Soc.* **1965,** *87*, 982; Paquette; Ley; Meisinger; Russell; Oku *J. Am. Chem. Soc.* **1974,** *96*, 5806; Radlick; Rosen *J. Am. Chem. Soc.* **1966,** *88*, 3461.

[178] Anastassiou; Gebrian *Tetrahedron Lett.* **1970,** 825.

[179] Boche; Weber; Martens; Bieberbach *Chem. Ber.* **1978,** *111*, 2480. See also Anastassiou; Reichmanis *Angew. Chem. Int. Ed. Engl.* **1974,** *13*, 728 [*Angew. Chem. 86*, 784]; Boche; Bieberbach *Tetrahedron Lett.* **1976,** 1021.

[180] Anastassiou; Cellura *Chem. Commun.* **1969,** 903; Anastassiou; Gebrian *J. Am. Chem. Soc.* **1969,** *91*, 4011; Anastassiou; Cellura; Gebrian *Chem. Commun.* **1970,** 375; Anastassiou; Yamamoto *J. Chem. Soc., Chem. Commun.* **1972,** 286; Chiang; Paul; Anastassiou; Eachus *J. Am. Chem. Soc.* **1974,** *96*, 1636.

[181] For reviews of bridged [10]-, [14]-, and [18]annulenes, see Vogel *Pure Appl. Chem.* **1982,** *54*, 1015-1039; *Isr. J. Chem.* **1980,** *20*, 215-224; *Chimia* **1968,** *22*, 21-32; Vogel; Günther *Angew. Chem. Int. Ed. Engl.* **1967,** 6, 385-401 [*Angew. Chem. 79*, 429-446].

[182] Vogel; Roth *Angew. Chem. Int. Ed. Engl.* **1964,** *3*, 228 [*Angew. Chem. 76*, 145]; Vogel; Böll *Angew. Int. Ed. Engl.* **1964,** *3*, 642 [*Angew. Chem. 76*, 784]; Vogel; Böll; Biskup *Tetrahedron Lett.* **1966,** 1569.

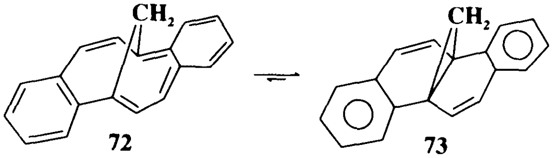
[183] Vogel; Biskup; Pretzer; Böll *Angew. Chem. Int. Ed. Engl.* **1964,** *3*, 642 [*Angew. Chem. 76*, 785]; Sondheimer; Shani *J. Am. Chem. Soc.* **1964,** *84*, 3168; Shani; Sondheimer *J. Am. Chem. Soc.* **1967,** *89*, 6310; Bailey; Mason *Chem. Commun.* **1967,** 1039.

[184] Vogel; Pretzer; Böll *Tetrahedron Lett.* **1965,** 3613. See also the first paper of Ref. 183.

[185] For another type of bridged diatropic [10]annulene, see Lidert; Rees *J. Chem. Soc., Chem. Commun.* **1982,** 499; Gilchrist; Rees; Tuddenham *J. Chem. Soc., Perkin Trans. 1* **1983,** 83; McCague; Moody; Rees *J. Chem. Soc., Perkin Trans. 1* **1984,** 165, 175; Gibbard; Moody; Rees *J. Chem. Soc., Perkin Trans. 1* **1985,** 731, 735.

bridge protons are at −0.5 δ. The crystal structure of **69** shows that the perimeter is nonplanar, but the bond distances are in the range 1.37 to 1.42 Å.[186] It has therefore been amply demonstrated that a closed loop of 10 electrons is an aromatic system, although some molecules that could conceivably have such a system are too distorted from planarity to be aromatic. A small distortion from planarity (as in **69**) does not prevent aromaticity, at least in part because the σ orbitals so distort themselves as to maximize the favorable (parallel) overlap of *p* orbitals to form the aromatic 10-electron loop.[187]

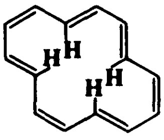
In **72**, where **69** is fused to two benzene rings in such a way that no canonical form can be written in which both benzene rings have six electrons, the aromaticity is reduced by annellation, as shown by the fact that the molecule rapidly converts to the more stable **73**,



in which both benzene rings can be fully aromatic[188] (this is similar to the cycloheptatriene–norcaradiene conversions discussed on p. 1135).

Systems of More than Ten Electrons: 4*n* + 2 Electrons[189]

Extrapolating from the discussion of [10]annulene, we expect larger 4*n* + 2 systems to be aromatic if they are planar. Mislow[173] predicted that [14]annulene (**74**) would possess the same type of interference as **46**, although in lesser degree. This is borne out by experiment. **74** is aromatic (it is diatropic; inner protons at 0.00 δ, outer protons at 7.6 δ),[190] but is completely destroyed by light and air in one day. X-ray analysis shows that although there are no alternating single and double bonds, the molecule is not planar.[191]



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[186] Bianchi; Pilati; Simonetta *Acta Crystallogr., Sect. B* **1980,** *36*, 3146. See also Dobler; Dunitz *Helv. Chim Acta* **1965,** *48*, 1429.

[187] For a discussion, see Haddon *Acc. Chem. Res.* **1988,** *21*, 243-249.

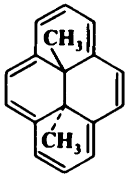
[188] Hill; Giberson; Silverton *J. Am. Chem. Soc.* **1988,** *110*, 497. See also McCague; Moody; Rees; Williams *J. Chem. Soc., Perkin Trans. 1* **1984,** 909.

[189] For reviews of annulenes, with particular attention to their nmr spectra, see Sondheimer *Acc. Chem. Res.* **1972,** *5*, 81-91, *Pure Appl. Chem.* **1971,** *28*, 331-353, *Proc. R. Soc. London. Ser. A* **1967,** *297*, 173-204; Sondheimer; Calder; Elix; Gaoni; Garratt; Grohmann; di Maio; Mayer; Sargent; Wolovsky, in *Aromaticity*, Ref. 55, pp. 75-107; Haddon; Haddon; Jackman, Ref. 60. For a review of annulenoannulenes (two annulene rings fused together), see Nakagawa *Angew. Chem. Int. Ed. Engl.* **1979,** *18*, 202-214 [*Angew. Chem. 91*, 215-226]. For a review of reduction and oxidation of annulenes; that is, formation of radical ions, dianions, and dications, see Müllen *Chem. Rev.* **1984,** *84*, 603-646. For a review of annulene anions, see Rabinovitz *Top. Curr. Chem.* **1988,** *146*, 99-169.

[190] Gaoni; Melera; Sondheimer; Wolovsky *Proc. Chem. Soc.* **1964,** 397.

[191] Bregman *Nature* **1962,** *194*, 679; Chiang; Paul *J. Am. Chem. Soc.* **1972,** *94*, 4741. Another 14-electron system is the dianion of [12]annulene, which is also apparently aromatic though not planar: Oth; Schröder *J. Chem. Soc. B* **1971,** 904. See also Garratt; Rowland; Sondheimer *Tetrahedron* **1971,** *27*, 3157; Oth; Müllen, Königshofen; Mann; Sakata; Vogel *Angew. Chem. Int. Ed. Engl.* **1974,** *13*, 284 [*Angew. Chem. 86*, 232]. For some other 14-electron aromatic systems, see Anastassiou, Elliott; Reichmanis *J. Am. Chem. Soc.* **1974,** *96*, 7823; Wife; Sondheimer *J. Am. Chem. Soc.* **1975,** *97*, 640; Ogawa; Kubo; Saikachi *Tetrahedron Lett.* **1971,** 4859; Oth; Müllen; Königshofen; Wassen; Vogel *Helv. Chim. Acta* **1974,** *57*, 2387; Willner; Gutman; Rabinovitz *J. Am. Chem. Soc.* **1977,** *99*, 4167; Röttele; Schröder *Chem. Ber.* **1982,** *115*, 248.

However, a number of stable bridged [14]annulenes have been prepared,[192] e.g., *trans*-15,16-dimethyldihydropyrene (**75**),[193] *syn*-1,6:8,13-diimino[14]annulene (**76**),[194] and *syn*- and *anti*-1,6:8,13-bismethano[14]annulene (**77** and **78**).[195] The dihydropyrene **75** (and its diethyl and dipropyl homologs) is undoubtedly aromatic: the π perimeter is approximately planar,[196] the bond distances are all 1.39 to 1.40 Å, and the molecule undergoes aromatic substitution[193] and is diatropic.[197] The outer protons are found at 8.14 to 8.67 δ, while the CH_3 protons are at −4.25 δ. **76** and **77** are also diatropic,[198] although x-ray crystallography indicates that the π periphery in at least **76** is not quite planar.[199] However, **78**, in which the geometry of the molecule greatly reduces the overlap of the *p* orbitals at the bridgehead positions with adjacent *p* orbitals, is definitely not aromatic,[200] as shown by nmr spectra[195] and x-ray crystallography, from which bond distances of 1.33 to 1.36 Å for the double bonds and 1.44 to 1.49 Å for the single bonds have been obtained.[201] In contrast, all the bond distances in **76** are ~1.38 to 1.40 Å.[199]



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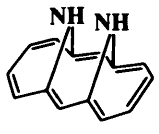

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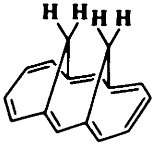

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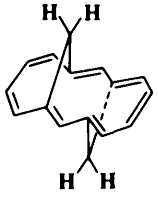

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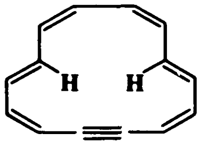
Another way of eliminating the hydrogen interferences of [14]annulene is to introduce one or more triple bonds into the system, as in dehydro[14]annulene (**79**).[202] All five known



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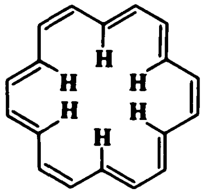

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[192] For a review, see Vogel *Pure Appl. Chem.* **1971,** *28,* 355-377.

[193] Boekelheide; Phillips *J. Am. Chem. Soc.* **1967,** *89,* 1695; Boekelheide; Miyasaka *J. Am. Chem. Soc.* **1967,** *89,* 1709. For reviews of dihydropyrenes, see Mitchell *Adv. Theor. Interesting Mol.* **1989,** *1,* 135-199; Boekelheide *Top. Nonbenzoid Arom. Chem.* **1973,** *1,* 47-79, *Pure Appl. Chem.* **1975,** *44,* 807-828.

[194] Vogel; Kuebart; Marco; Andree; Günther; Aydin *J. Am. Chem. Soc.* **1983,** *105,* 6982; Destro; Pilati; Simonetta; Vogel *J. Am. Chem. Soc.* **1985,** *107,* 3185, 3192. For the di —O— analog of **76**, see Vogel; Biskup; Vogel; Günther *Angew. Chem. Int. Ed. Engl.* **1966,** *5,* 734 [*Angew. Chem. 78,* 755].

[195] Vogel; Haberland; Günther *Angew. Chem. Int. Ed. Engl.* **1970,** *9,* 513 [*Angew. Chem. 82,* 510]; Vogel; Sombroek; Wagemann *Angew. Chem. Int. Ed. Engl.* **1975,** *14,* 564 [*Angew. Chem. 87,* 591].

[196] Hanson *Acta Crystallogr.* **1965,** *18,* 599, **1967,** *23,* 476.

[197] A number of annellated derivatives of **75** are less diatropic, as would be expected from the discussion on p. 44: Mitchell; Williams; Mahadevan; Lai; Dingle *J. Am. Chem. Soc.* **1982,** *104,* 2571 and other papers in this series.

[198] As are several other similarly bridged [14]annulenes; see, for example, Vogel; Reel *J. Am. Chem. Soc.* **1972,** *94,* 4388; Flitsch; Peeters *Chem. Ber.* **1973,** *106,* 1731; Huber; Lex; Meul; Müllen *Angew. Chem. Int. Ed. Engl.* **1981,** *20,* 391 [*Angew. Chem. 93,* 401]; Vogel; Nitsche; Krieg *Angew. Chem. Int. Ed. Engl.* **1981,** *20,* 811 [*Angew. Chem. 93,* 818]; Mitchell; Anker *Tetrahedron Lett.* **1981,** *22,* 5139; Vogel; Wieland; Schmalstieg; Lex *Angew. Chem. Int. Ed. Engl.* **1984,** *23,* 717 [*Angew. Chem. 96,* 717]; Neumann; Müllen *J. Am. Chem. Soc.* **1986,** *108,* 4105.

[199] Ganis; Dunitz *Helv. Chim. Acta* **1967,** *50,* 2369.

[200] For another such pair of molecules, see Vogel; Nitsche; Krieg, Ref. 198. See also Vogel; Schieb; Schulz; Schmidt; Schmickler; Lex *Angew. Chem. Int. Ed. Engl.* **1986,** *25,* 723 [*Angew. Chem. 98,* 729].

[201] Gramaccioli; Mimun; Mugnoli; Simonetta *Chem. Commun.* **1971,** 796. See also Destro; Simonetta *Tetrahedron* **1982,** *38,* 1443.

[202] For a review of dehydroannulenes, see Nakagawa *Top. Nonbenzenoid Aromat. Chem.* **1973,** *1,* 191-219.

dehydro[14]annulenes are diatropic. **79** can be nitrated or sulfonated.[203] The extra electrons of the triple bond do not form part of the aromatic system but simply exist as a localized bond. [18]Annulene (**80**) is diatropic:[204] the 12 outer protons are found at about $\delta = 9$ and the 6 inner protons at about $\delta = -3$. X-ray crystallography[205] shows that it is nearly planar, so that interference of the inner hydrogens is not important in annulenes this large. **80** is reasonably stable, being distillable at reduced pressures, and undergoes aromatic substitutions.[206] The C—C bond distances are not equal, but they do not alternate. There are 12 inner bonds of about 1.38 Å and 6 outer bonds of about 1.42 Å.[205] **80** has been estimated to have a resonance energy of about 37 kcal/mol (155 kJ/mol), similar to that of benzene.[207]

The known bridged [18]annulenes are also diatropic[208] as are most of the known dehydro[18]annulenes.[209] The dianions of open and bridged [16]annulenes[210] are also 18-electron aromatic systems.[211]

[22]Annulene[212] and dehydro[22]annulene[213] are also diatropic. In the latter compound there are 13 outer protons at 6.25 to 8.45 δ and 7 inner protons at 0.70 to 3.45 δ. Some aromatic bridged [22]annulenes are also known.[214] [26]Annulene has not yet been prepared, but several dehydro[26]annulenes are aromatic.[215] Furthermore, the dianion of 1,3,7,9,13,15,19,21-octadehydro[24]annulene is another 26-electron system that is aromatic.[216] Ojima and co-workers have prepared bridged dehydro derivatives of [26], [30], and [34] annulenes.[217] All of these are diatropic. The same workers prepared a bridged tetradehydro[38]annulene,[217] which showed no ring current. On the other hand, the dianion of the cyclophane **81** also has 38 perimeter electrons, and this species is diatropic.[218]

There is now no doubt that $4n + 2$ systems are aromatic if they can be planar, although **63** and **78** among others, demonstrate that not all such systems are in fact planar enough

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[203] Gaoni; Sondheimer *J. Am. Chem. Soc.* **1964,** *86*, 521.

[204] Jackman; Sondheimer; Amiel; Ben-Efraim; Gaoni; Wolovsky; Bothner-By *J. Am. Chem. Soc.* **1962,** *84*, 4307; Gilles; Oth; Sondheimer; Woo *J. Chem. Soc. B* **1971,** 2177. For a thorough discussion, see Baumann; Oth *Helv. Chim. Acta* **1982,** *65*, 1885.

[205] Bregman; Hirshfeld; Rabinovich; Schmidt *Acta Crystallogr.* **1965,** *19*, 227; Hirshfeld; Rabinovich *Acta Crystallogr.* **1965,** *19*, 235.

[206] Calder; Garratt; Longuet-Higgins; Sondheimer; Wolovsky *J. Chem. Soc. C* **1967,** 1041; Woo; Sondheimer *Tetrahedron* **1970,** *26*, 3933.

[207] Oth; Bünzli; de Julien de Zélicourt *Helv. Chim. Acta* **1974,** *57*, 2276.

[208] For some examples, see DuVernet; Wennerström; Lawson; Otsubo; Boekelheide *J. Am. Chem. Soc.* **1978,** *100*, 2457; Ogawa; Sadakari; Imoto; Miyamoto; Kato; Taniguchi *Angew. Chem. Int. Ed. Engl.* **1983,** *22*, 417 [*Angew. Chem. 95*, 412]; Vogel; Sicken; Röhrig; Schmickler; Lex; Ermer *Angew. Chem. Int. Ed. Engl.* **1988,** *27*, 411 [*Angew. Chem. 100*, 450].

[209] Okamura; Sondheimer *J. Am. Chem. Soc.* **1967,** *89*, 5991; Ojima; Ejiri; Kato; Nakamura; Kuroda; Hirooka; Shibutani *J. Chem. Soc., Perkin Trans. 1* **1987,** 831; Sondheimer, Ref. 189. For two that are not, see Endo; Sakata; Misumi *Bull. Chem. Soc. Jpn.* **1971,** *44*, 2465.

[210] For a review of this type of polycyclic ion, see Rabinovitz; Willner; Minsky *Acc. Chem. Res.* **1983,** *16*, 298-304.

[211] Oth; Anthoine; Gilles *Tetrahedron Lett.* **1968,** 6265; Mitchell; Boekelheide *Chem. Commun.* **1970,** 1557; Oth; Baumann; Gilles; Schröder *J. Am. Chem. Soc.* **1972,** *94*, 3948. See also Brown; Sondheimer *Angew. Chem Int. Ed. Engl.* **1974,** *13*, 337 [*Angew. Chem. 86*, 346]; Cresp; Sargent *J. Chem. Soc., Chem. Commun.* **1974,** 101; Schröder; Plinke; Smith; Oth *Angew. Chem. Int. Ed. Engl.* **1973,** *12*, 325 [*Angew. Chem. 85*, 350]; Rabinovitz; Minsky *Pure Appl. Chem.* **1982,** *54*, 1005-1014.

[212] McQuilkin; Metcalf; Sondheimer *Chem. Commun.* **1971,** 338.

[213] McQuilkin; Sondheimer *J. Am. Chem. Soc.***1970,** *92*, 6341; Iyoda; Nakagawa *J. Chem. Soc., Chem. Commun.* **1972,** 1003. See also Kabuto; Kitahara; Iyoda; Nakagawa *Tetrahedron Lett.* **1976,** 2787; Akiyama; Nomoto; Iyoda; Nakagawa *Bull. Chem. Soc. Jpn.* **1976,** *49*, 2579.

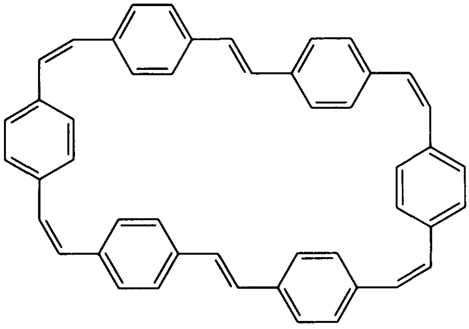
[214] For example see Broadhurst; Grigg; Johnson *J. Chem. Soc., Perkin Trans. 1* **1972,** 2111; Ojima et al., Ref. 209; Yamamoto; Kuroda; Shibutani; Yoneyama; Ojima; Fujita; Ejiri; Yanagihara *J. Chem. Soc., Perkin Trans. 1* **1988,** 395.

[215] Metcalf; Sondheimer *J. Am. Chem. Soc.* **1971,** *93*, 5271; Iyoda; Nakagawa *Tetrahedron Lett.* **1972,** 4253; Ojima; Fujita; Matsumoto; Ejiri; Kato; Kuroda; Nozawa; Hirooka; Yoneyama; Tatemitsu *J. Chem. Soc., Perkin Trans. 1* **1988,** 385.

[216] McQuilkin; Garratt; Sondheimer *J. Am. Chem. Soc.* **1970,** *92*, 6682. See also Huber; Müllen; Wennerström *Angew. Chem. Int. Ed. Engl.* **1980,** *19*, 624 [*Angew. Chem. 92*, 636].

[217] Ojima et al., Ref. 215.

[218] Müllen; Unterberg; Huber; Wennerström; Norinder; Tanner; Thulin *J. Am. Chem. Soc.* **1984,** *106*, 7514.



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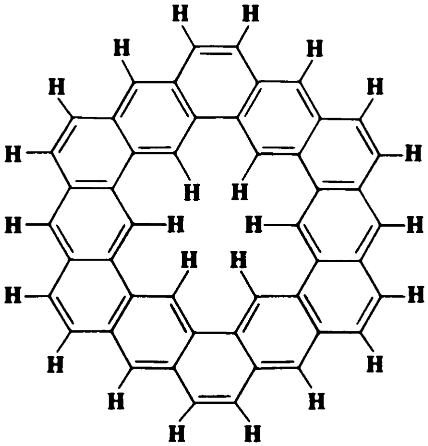
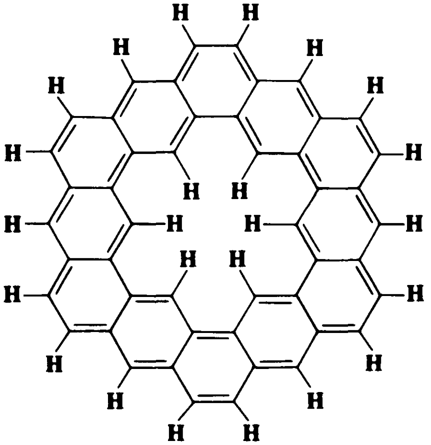
for aromaticity. The cases of **74** and **76** prove that absolute planarity is not required for aromaticity, but that aromaticity decreases with decreasing planarity.

The proton nmr spectrum of **82** (called kekulene) showed that in a case where electrons can form either aromatic sextets or larger systems, the sextets are preferred.[219] The 48 π electrons of **82** might, in theory, prefer structure **82a**, where each ring is a fused benzene



82a



82b

ring, or **82b**, which has a [30]annulene on the outside and an [18]annulene on the inside. The proton nmr spectrum of this compound shows three peaks at δ = 7.94, 8.37, and 10.45 in a ratio of 2:1:1. It is seen from the structure that **82** contains three groups of protons. The peak at 7.94 δ is attributed to the 12 ortho protons and the peak at 8.37 δ to the six external para protons. The remaining peak comes from the six inner protons. If the molecule preferred **82b**, we would expect to find this peak upfield, probably with a negative δ, as in the case of **80**. The fact that this peak is far downfield indicates that the electrons prefer to be in benzenoid rings. Note that in the case of the dianion of **81**, we have the opposite situation. In this ion, the 38-electron system is preferred even though 24 of these must come from the six benzene rings, which therefore cannot have aromatic sextets.

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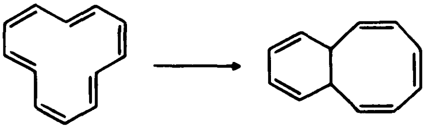
[219] Staab; Diederich *Chem. Ber.* **1983**, *116*, 3487; Staab; Diederich; Krieger; Schweitzer *Chem. Ber.* **1983**, *116*, 3504. For a similar molecule with 10 instead of 12 rings, see Funhoff; Staab *Angew. Chem. Int. Ed. Engl.* **1986**, *25*, 742 [*Angew. Chem. 98*, 757].

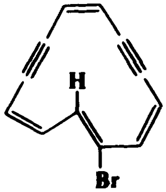
Systems of More than Ten Electrons: 4*n* Electrons[189]

As we have seen (p. 53), these systems are expected to be not only nonaromatic but actually antiaromatic. The chief criterion for antiaromaticity in annulenes is the presence of a *paramagnetic* ring current,[220] which causes protons on the outside of the ring to be shifted *upfield* while any inner protons are shifted *downfield*, in sharp contrast to a diamagnetic ring current, which causes shifts in the opposite directions. Compounds that sustain a paramagnetic ring current are called *paratropic*; we have already seen such behavior in certain four- and eight-electron systems. As with aromaticity, we expect that antiaromaticity will be at a maximum when the molecule is planar and when bond distances are equal.

The [12]annulene **83** has been prepared.[221] In solution this molecule undergoes rapid conformational mobility (as do many other annulenes),[222] so that above a certain temperature, in this case −150°C, all protons are magnetically equivalent. However, at −170°C the mobility is greatly slowed and the three inner protons are found at about 8 δ while the nine outer protons are at about 6 δ. **83** suffers from hydrogen interference and is certainly not planar. It is very unstable and above −50°C rearranges to **84**. Several bridged and dehydro[12]annulenes are known, e.g., 5-bromo-1,9-didehydro[12]annulene (**85**),[223] cycl[3.3.3]azine (**86**),[224] 9b-methyl-9b*H*-benzo[*cd*]azulene (**87**),[225] and 1,7-methano[12]-annulene (**88**).[226] In these compounds both hydrogen interference and conformational mobility are prevented. In **86, 87,** and **88,** the bridge prevents conformational changes, while in **85** the bromine atom is too large to be found inside the ring. Nmr spectra show that all four compounds are paratropic, the inner proton of **85** being found at 16.4 δ. The dication of **77**[227] and the dianion of **69**[228] are also 12-electron paratropic species.



83 **84**



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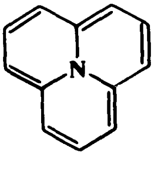

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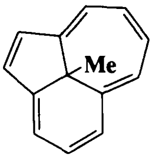

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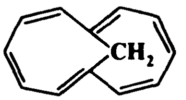

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[220] Pople; Untch *J. Am. Chem. Soc.* **1966,** *88,* 4811; Longuet-Higgins, in *Aromaticity,* Ref. 55. pp. 109-111.

[221] Oth; Röttele; Schröder *Tetrahedron Lett.* **1970,** 61; Oth; Gilles; Schröder *Tetrahedron Lett.* **1970,** 67.

[222] For a review of conformational mobility in annulenes, see Oth *Pure Appl. Chem.* **1971,** *25,* 573-622.

[223] Untch; Wysocki *J. Am. Chem. Soc.* **1967,** *89,* 6386.

[224] Farquhar; Leaver *Chem. Commun.* **1969,** 24. For a review, see Matsuda; Gotou *Heterocycles* **1987,** *26,* 2757-2772.

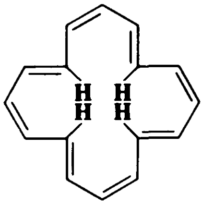
[225] Hafner; Kühn *Angew. Chem. Int. Ed. Engl.* **1986,** *25,* 632 [*Angew. Chem. 98,* 648]. For a similar system, see Kohnz; Düll; Müllen *Angew. Chem. Int. Ed. Engl.* **1989,** *28,* 1343 [*Angew. Chem. 101,* 1375].

[226] Vogel; Königshofen; Müllen; Oth *Angew. Chem. Int. Ed. Engl.* **1974,** *13,* 281 [*Angew. Chem. 86,* 229]. See also Mugnoli; Simonetta *J. Chem. Soc., Perkin Trans. 2* **1976,** 822; Scott; Kirms; Günther; von Puttkamer *J. Am. Chem. Soc.* **1983,** *105,* 1372; Destro; Ortoleva; Simonetta; Todeschini *J. Chem. Soc., Perkin Trans. 2* **1983,** 1227.

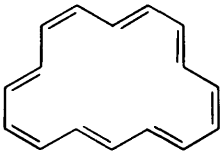
[227] Müllen; Meul; Schade; Schmickler; Vogel *J. Am. Chem. Soc.* **1987,** *109,* 4992. This paper also reports a number of other bridged paratropic 12-, 16-, and 20-electron dianions and dications. See also Hafner; Thiele *Tetrahedron Lett.* **1984,** *25,* 1445.

[228] Schmalz; Günther *Angew. Chem. Int. Ed. Engl.* **1988,** *27,* 1692 [*Angew. Chem. 100,* 1754].

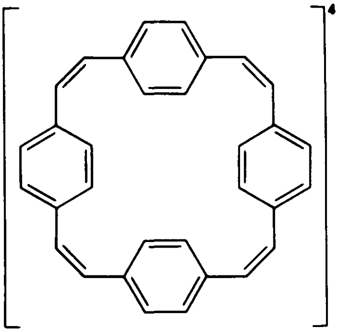
The results for [16]annulene are similar. The compound was synthesized in two different ways,[229] both of which gave **89**, which in solution is in equilibrium with **90**. Above −50°C there is conformational mobility, resulting in the magnetic equivalence of all protons, but at −130°C the compound is clearly paratropic: there are four protons at 10.56 δ and twelve at 5.35 δ. In the solid state, where the compound exists entirely as **89**, x-ray crystallography[230] shows that the molecules are nonplanar with almost complete bond alternation: the single bonds are 1.44 to 1.47 Å and the double bonds 1.31 to 1.35 Å. A number of dehydro and bridged [16]annulenes are also paratropic,[231] as are [20]annulene,[232] [24]annulene,[233] and **91**, a 28-electron system that is the tetraanion of [2_4]paracyclophanetetraene.[234] However, a bridged tetradehydro[32]annulene was atropic.[217]



89

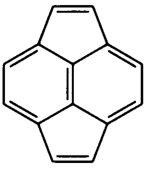


90



91

Both peracyclene (**92**)[235] (which because of strain is stable only in solution) and dipleiadiene (**93**)[236] are paratropic, as shown by nmr spectra. These molecules might have been expected to behave like naphthalenes with outer bridges, but instead, the outer π frameworks (12 and 16 electrons, respectively) constitute antiaromatic systems with an extra central double bond.



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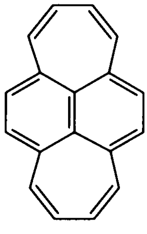

93

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[229] Schröder; Oth *Tetrahedron Lett.* **1966,** 4083; Sondheimer; Gaoni *J. Am. Chem. Soc.* **1961,** *83*, 4863; Oth; Gilles *Tetrahedron Lett.* **1968,** 6259; Calder; Gaoni; Sondheimer *J. Am. Chem. Soc.* **1968,** *90*, 4946. For monosubstituted [16]annulenes, see Schröder; Kirsch; Oth *Chem. Ber.* **1974,** *107*, 460.

[230] Johnson; Paul; King *J. Chem. Soc. B* **1970,** 643.

[231] For example, see Calder; Garratt; Sondheimer *J. Am. Chem. Soc.* **1968,** *90*, 4954; Murata; Okazaki; Nakazawa *Angew. Chem. Int. Ed. Engl.* **1971,** *10*, 576 [*Angew. Chem. 83*, 623]; Ogawa; Kubo; Tabushi *Tetrahedron Lett.* **1973,** 361; Nakatsuji; Morigaki; Akiyama; Nakagawa *Tetrahedron Lett.* **1975,** 1233; Elix *Aust. J. Chem.* **1969,** *22*, 1951; Vogel; Kürshner; Schmickler; Lex; Wennerström; Tanner; Norinder; Krüger *Tetrahedron Lett.* **1985,** *26*, 3087.

[232] Metcalf; Sondheimer *J. Am. Chem. Soc.* **1971,** *93*, 6675. See also Oth; Woo; Sondheimer *J. Am. Chem. Soc.* **1973,** *95*, 7337; Nakatsuji; Nakagawa *Tetrahedron Lett.* **1975,** 3927; Wilcox; Farley **1984,** *106*, 7195.

[233] Calder; Sondheimer *Chem. Commun.* **1966,** 904. See also Stöckel; Sondheimer *J. Chem. Soc., Perkin Trans.1* **1972,** 355; Nakatsuji; Akiyama; Nakagawa *Tetrahedron Lett.* **1976,** 2623; Yamamoto et al., Ref. 214.

[234] Huber; Müllen; Wennerström, Ref. 216.

[235] Trost; Bright; Frihart; Brittelli *J. Am. Chem. Soc.* **1971,** *93*, 737; Trost; Herdle *J. Am. Chem. Soc.* **1976,** *98*, 4080.

[236] Vogel; Neumann; Klug; Schmickler; Lex *Angew. Chem. Int. Ed. Engl.* **1985,** *24*, 1046 [*Angew. Chem. 97*, 1044].

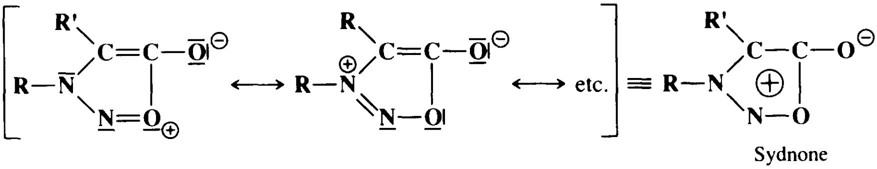
The fact that many $4n$ systems are paratropic even though they may be nonplanar and have unequal bond distances indicates that if planarity were enforced, the ring currents might be even greater. That this is true is dramatically illustrated by the nmr spectrum of the dianion of **75**[237] (and its diethyl and dipropyl homologs).[238] We may recall that in **75**, the outer protons were found at 8.14 to 8.67 δ with the methyl protons at −4.25 δ. For the dianion, however, which is forced to have approximately the same planar geometry but now has 16 electrons, the outer protons are shifted to about −3 δ while the methyl protons are found at about 21 δ, a shift of about 25 δ! We have already seen where the converse shift was made, when [16]annulenes that were antiaromatic were converted to 18-electron dianions that were aromatic.[211] In these cases, the changes in nmr chemical shifts were almost as dramatic. Heat-of-combustion measures also show that [16]annulene is much less stable than its dianion.[239]

We can therefore conclude that in $4n$ systems antiaromaticity will be at a maximum where a molecule is constrained to be planar (as in **52** or the dianion of **75**) but, where possible, the molecule will distort itself from planarity and avoid equal bond distances in order to reduce antiaromaticity. In some cases, such as cyclooctatraene, the distortion and bond alternation are great enough for antiaromaticity to be completely avoided. In other cases, e.g., **83** or **89**, it is apparently not possible for the molecules to avoid at least some *p*-orbital overlap. Such molecules show paramagnetic ring currents and other evidence of antiaromaticity, although the degree of antiaromaticity is not as great as in molecules such as **52** or the dianion of **75**.

Other Aromatic Compounds

We shall briefly mention three other types of aromatic compounds.

1. *Mesoionic compounds*[240] cannot be satisfactorily represented by Lewis structures not involving charge separation. Most of them contain five-membered rings. The most common are the *sydnones*, stable aromatic compounds that undergo aromatic substitution when R′ is hydrogen.



Sydnone

2. *The dianion of squaric acid.*[241] The stability of this system is illustrated by the fact that the pK_1 of squaric acid[242] is about 1.5 and the pK_2 is about 3.5,[243] which means that

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[237] For a review of polycyclic dianions, see Rabinovitz; Cohen *Tetrahedron* **1988**, *44* 6957-6994.

[238] Mitchell; Klopfenstein; Boekelheide *J. Am. Chem. Soc.* **1969**, *91*, 4931. For another example, see Deger; Müllen; Vogel *Angew. Chem. Int. Ed. Engl.* **1978**, *17*, 957 [*Angew. Chem. 90*, 990].

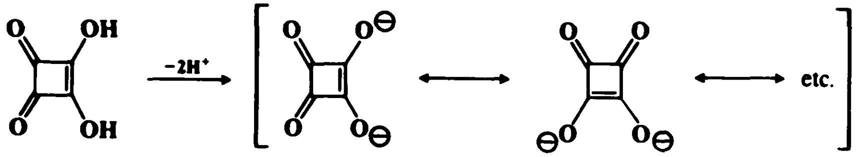
[239] Stevenson; Forch *J. Am. Chem. Soc.* **1980**, *102*, 5985.

[240] For reviews, see Newton; Ramsden *Tetrahedron* **1982**, *38*, 2965-3011; Ollis; Ramsden *Adv. Heterocycl. Chem.* **1976**, *19*, 1-122; Ramsden *Tetrahedron* **1977**, *33*, 3203-3232; Yashunskii; Kholodov *Russ. Chem. Rev.* **1980**, *49*, 28-45; Ohta; Kato, in Snyder, Ref. 55, vol. 1, pp. 117-248.

[241] West; Powell *J. Am. Chem. Soc.* **1963**, *85*, 2577; Ito; West *J. Am. Chem. Soc.* **1963**, *85*, 2580.

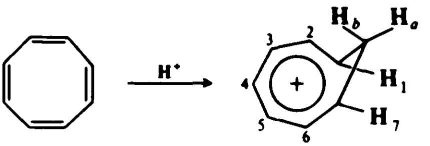
[242] For a review of squaric acid and other nonbenzenoid quinones, see Wong; Chan; Luh, in Patai; Rappoport *The Chemistry of the Quinonoid Compounds*, vol. 2, pt. 2; Wiley: New York, 1988, pp. 1501-1563.

[243] Ireland; Walton *J. Phys. Chem.* **1967**, *71*, 751; MacDonald *J. Org. Chem.* **1968**, *33*, 4559.



even the second proton is given up much more readily than the proton of acetic acid, for example.[244] The analogous three-,[245] five-, and six-membered ring compounds are also known.[246]

3. *Homoaromatic compounds.* When cyclooctatetraene is dissolved in concentrated H_2SO_4, a proton adds to one of the double bonds to form the homotropylium ion **94**.[247] In this species an aromatic sextet is spread over seven carbons, as in the tropylium ion. The



94

eighth carbon is an sp^3 carbon and so cannot take part in the aromaticity. Nmr spectra show the presence of a diatropic ring current: H_b is found at $\delta = -0.3$; H_a at 5.1 δ; H_1 and H_7 at 6.4 δ; H_2–H_6 at 8.5 δ. This ion is an example of a ***homoaromatic*** compound, which may be defined as a compound that contains one or more[248] sp^3-hybridized carbon atoms in an otherwise conjugated cycle.[249] In order for the orbitals to overlap most effectively so as to close a loop, the sp^3 atoms are forced to lie almost vertically above the plane of the aromatic atoms.[250] In **94**, H_b is directly above the aromatic sextet and so is shifted far upfield in the nmr. All homoaromatic compounds so far discovered are ions, and it is questionable[251] as to whether homoaromatic character can exist in uncharged systems.[252] Homoaromatic ions of two and ten electrons are also known.

[244] There has been a controversy as to whether this dianion is in fact aromatic. See Aihara *J. Am. Chem. Soc.* **1981**, *103*, 1633.

[245] Eggerding; West *J. Am. Chem. Soc.* **1976**, *98*, 3641; Pericás; Serratosa *Tetrahedron Lett.* **1977**, 4437; Semmingsen; Groth *J. Am. Chem. Soc.* **1987**, *109*, 7238.

[246] For a monograph, see West *Oxocarbons*; Academic Press: New York, 1980. For reviews, see Serratosa *Acc. Chem. Res.* **1983**, *16*, 170-176; Schmidt *Synthesis* **1980**, 961-994; West *Isr. J. Chem.* **1980**, *20*, 300-307; West; Niu in Snyder, Ref. 55, vol. 1, pp. 311-345, and in Zabicky *The Chemistry of the Carbonyl Group*, vol. 2; Wiley: New York, 1970, pp. 241-275; Maahs; Hegenberg *Angew. Chem. Int. Ed. Engl.* **1966**, *5*, 888-893 [*Angew. Chem. 78*, 927-931].

[247] Rosenberg; Mahler; Pettit *J. Am. Chem. Soc.* **1962**, *84*, 2842; Keller; Pettit *J. Am. Chem.Soc.* **1966**, *88*, 604, 606; Winstein; Kaesz; Kreiter; Friedrich *J. Am. Chem. Soc.* **1965**, *87*, 3267; Winstein; Kreiter; Brauman *J. Am. Chem. Soc.* **1966**, *88*, 2047; Haddon *J. Am. Chem. Soc.* **1988**, *110*, 1108. See also Childs; Mulholland; Varadarajan; Yeroushalmi *J. Org. Chem.* **1983**, *48*, 1431.

[248] If a compound contains two such atoms it is *bishomoaromatic*; if three, *trishomoaromatic*, etc. For examples see Paquette, Ref. 249.

[249] For reviews, see Childs *Acc. Chem. Res.* **1984**, *17*, 347-352; Paquette *Angew. Chem. Int. Ed. Engl.* **1978**, *17*, 106-117 [*Angew. Chem. 90*, 114-125]; Winstein *Q. Rev., Chem. Soc.* **1969**, *23*, 141-176; *Aromaticity*, Ref. 55, pp. 5-45; and in Olah; Schleyer, *Carbonium Ions*; Wiley: New York, vol. 3, 1972, the reviews by Story; Clark, 1007-1098, pp. 1073-1093; Winstein 965-1005. (The latter is a reprint of the *Q. Rev., Chem. Soc.* review mentioned above.)

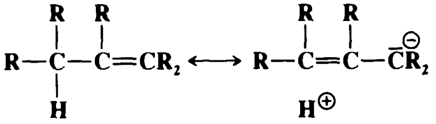
[250] Calculations show that only about 60% of the chemical shift difference between H_a and H_b is the result of the aromatic ring current, and that even H_a is shielded; it would appear at $\delta = \sim 5.5$ without the ring current: Childs; McGlinchey; Varadarajan *J. Am. Chem. Soc.* **1984**, *106*, 5974.

[251] Houk; Gandour; Strozier; Rondan; Paquette *J. Am. Chem. Soc.* **1979**, *101*, 6797; Paquette; Snow; Muthard; Cynkowski *J. Am. Chem. Soc.* **1979**, *101*, 6991. See however, Liebman; Paquette; Peterson; Rogers *J. Am. Chem. Soc.* **1986**, *108*, 8267.

[252] Examples of uncharged homo*anti*aromatic compounds have been claimed: Wilcox; Blain; Clardy; Van Duyne; Gleiter; Eckert-Maksić *J. Am. Chem. Soc.* **1986**, *108*, 7693; Scott; Cooney; Rogers; Dejroongruang *J. Am. Chem. Soc.* **1988**, *110*, 7244.

HYPERCONJUGATION

All of the delocalization discussed so far involves π electrons. Another type, called *hyperconjugation*, involves σ electrons.[253] When a carbon attached to at least one hydrogen is attached to an unsaturated atom or one with an unshared orbital, canonical forms such as **95** can be drawn. In such canonical forms there is no bond at all between the carbon and hydrogen. The effect of **95** on the actual molecule is that the electrons in the C—H bond are closer to the carbon than they would be if **95** did not contribute at all.



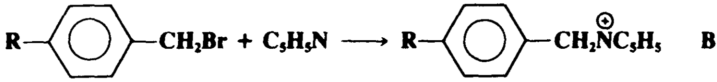
$$R{-}\overset{R}{\underset{H}{C}}{-}\overset{R}{C}{=}CR_2 \longleftrightarrow R{-}\overset{R}{C}{=}\overset{R}{C}{-}\overset{\ominus}{C}R_2 \quad H^{\oplus}$$

95

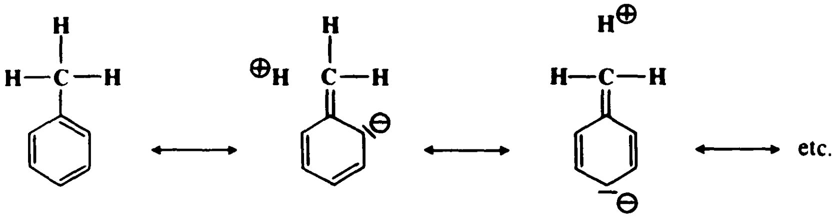
Hyperconjugation in the above case may be regarded as an overlap of the σ orbital of the C—H bond and the π orbital of the C—C bond, analogous to the π–π-orbital overlap previously considered. As might be expected, those who reject the idea of resonance in butadiene (p. 31) believe it even less likely when it involves no-bond structures.

The concept of hyperconjugation arose from the discovery of apparently anomalous electron-release patterns for alkyl groups. By the field effect alone, the order of electron release for simple alkyl groups connected to an unsaturated system is *t*-butyl > isopropyl > ethyl > methyl, and this order is observed in many phenomena. Thus, the dipole moments in the gas phase of $PhCH_3$, PhC_2H_5, $PhCH(CH_3)_2$, and $PhC(CH_3)_3$ are, respectively, 0.37, 0.58, 0.65 and 0.70 D.[254]

However, Baker and Nathan observed that the rates of reaction with pyridine of *p*-substituted benzyl bromides (see reaction **0-43**) were about opposite that expected from electron release by the field effect.[255] That is, the methyl-substituted compound reacted fastest and the *t*-butyl-substituted compounded reacted slowest.



This came to be called the *Baker–Nathan effect* and has since been found in many processes. Baker and Nathan explained it by considering that hyperconjugative forms contribute to the actual structure of toluene:



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[253] For monographs, see Baker *Hyperconjugation*; Oxford University Press: Oxford, 1952; Dewar *Hyperconjugation*; Ronald Press: New York, 1962. For a review, see de la Mare *Pure Appl. Chem.* **1984**, *56*, 1755-1766.

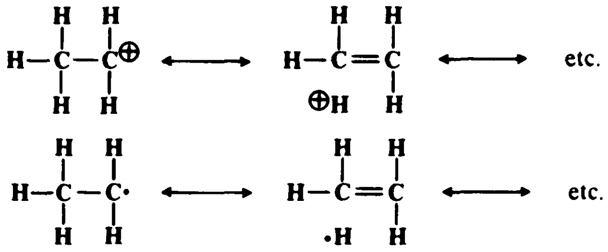
[254] Baker; Groves *J. Chem. Soc.* **1939**, 1144.

[255] Baker; Nathan *J. Chem. Soc.* **1935**, 1840, 1844.

For the other alkyl groups, hyperconjugation is diminished because the number of C—H bonds is diminished and in *t*-butyl there are none; hence, with respect to this effect, methyl is the strongest electron donor and *t*-butyl the weakest.

However, the Baker–Nathan effect has now been shown not to be caused by hyperconjugation, but by differential solvation.[256] This was demonstrated by the finding that in certain instances where the Baker–Nathan effect was found to apply in solution, the order was completely reversed in the gas phase.[257] Since the molecular structures are unchanged in going from the gas phase into solution, it is evident that the Baker–Nathan order in these cases is not caused by a structural feature (hyperconjugation) but by the solvent. That is, each alkyl group is solvated to a different extent.[258]

At present the evidence is against hyperconjugation in the ground states of neutral molecules.[259] However, for carbocations and free radicals[260] and for excited states of molecules,[261] there is evidence that hyperconjugation is important. In hyperconjugation in the ground state of neutral molecules, which Muller and Mulliken call *sacrificial hyperconjugation*,[262] the canonical forms involve not only no-bond resonance but also a charge separation not possessed by the main form. In free radicals and carbocations, the canonical forms display no more charge separation than the main form. Muller and Mulliken call this *isovalent hyperconjugation*:



Even here the main form contributes more to the hybrid than the others.

TAUTOMERISM

There remains one topic to be discussed in our survey of chemical bonding in organic compounds. For most compounds all the molecules have the same structure, whether or not this structure can be satisfactorily represented by a Lewis formula. But for many other compounds there is a mixture of two or more structurally distinct compounds that are in rapid equilibrium. When this phenomenon, called *tautomerism*,[263] exists, there is a rapid shift back and forth among the molecules. In most cases, it is a proton that shifts from one atom of a molecule to another.

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[256] This idea was first suggested by Schubert; Sweeney *J. Org. Chem.* **1956,** *21*, 119.

[257] Hehre; McIver; Pople; Schleyer *J. Am. Chem. Soc.* **1974,** *96*, 7162; Arnett; Abboud *J. Am. Chem. Soc.* **1975,** *97*, 3865; Glyde; Taylor *J. Chem. Soc., Perkin Trans. 2* **1977,** 678. See also Taylor *J. Chem. Res. (S)* **1985,** 318.

[258] For an opposing view, see Cooney; Happer *Aust. J. Chem.* **1987,** *40*, 1537.

[259] For some evidence in favor, see Laube; Ha *J. Am. Chem. Soc.* **1988,** *110*, 5511.

[260] Symons *Tetrahedron* **1962,** *18*, 333.

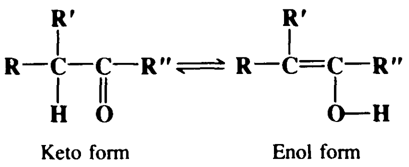
[261] Rao; Goldman; Balasubramanian *Can. J. Chem.* **1960,** *38*, 2508.

[262] Muller; Mulliken *J. Am. Chem. Soc.* **1958,** *80*, 3489.

[263] For reviews, see Toullec *Adv. Phys. Org. Chem.* **1982,** *18*, 1-77; Kol'tsov; Kheifets *Russ. Chem. Rev.* **1971,** *40*, 773-788, **1972,** *41*, 452-467; Forsén; Nilsson in Zabicky, Ref. 246, vol. 2, pp. 157-240.

Keto-Enol Tautomerism[264]

A very common form of tautomerism is that between a carbonyl compound containing an α hydrogen and its enol form:[264a]



$$R-\underset{H}{\overset{R'}{C}}-\underset{O}{\overset{\|}{C}}-R'' \rightleftharpoons R-\overset{R'}{C}=\underset{O-H}{C}-R''$$

In simple cases (R″ = H, alkyl, OR, etc.) the equilibrium lies well to the left (Table 2.1). The reason can be seen by examining the bond energies in Table 1.7. The keto form differs from the enol form in possessing a C—H, a C—C, and a C=O bond where the enol has a C=C, a C—O, and an O—H bond. The approximate sum of the first three is 359 kcal/mol (1500 kJ/mol) and of the second three is 347 kcal/mol (1452 kJ/mol). The keto form is therefore thermodynamically more stable by about 12 kcal/mol (48 kJ/mol) and enol forms cannot normally be isolated.[272a] In certain cases, however, a larger amount of the enol form

TABLE 2.1 The enol content of some carbonyl compounds

Compound	Enol content, %	Ref.
Acetone	6×10^{-7}	265
$PhCOCH_3$	1.1×10^{-6}	266
Cyclopentanone	1×10^{-6}	267
CH_3CHO	6×10^{-5}	268
Cyclohexanone	4×10^{-5}	267
Butanal	5.5×10^{-4}	269
$(CH_3)_2CHCHO$	1.4×10^{-2}	270
Ph_2CHCHO	9.1	271
CH_3COOEt	No enol found[a]	267
CH_3COCH_2COOEt	8.4	272
$CH_3COCH_2COCH_3$	80	272
$PhCOCH_2COCH_3$	89.2	267
$EtOOCCH_2COOEt$	7.7×10^{-3}	267
$NCCH_2COOEt$	2.5×10^{-1}	267

[a] Less than 1 part in 10 million.

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[264] The mechanism for conversion of one tautomer to another is discussed in Chapter 12 (reaction **2-3**).

[264a] For a treatise, see Rappoport *The Chemistry of Enols*; Wiley: New York, 1990.

[265] Tapuhi; Jencks *J. Am. Chem. Soc.* **1982,** *104*, 5758; Chiang; Kresge; Tang; Wirz *J. Am. Chem. Soc.* **1984,** *106*, 460. See also Hine; Arata *Bull. Chem. Soc. Jpn.* **1976,** *49*, 3089; Guthrie *Can. J. Chem.* **1979,** *57*, 797, 1177; Dubois; El-Alaoui; Toullec *J. Am. Chem. Soc.* **1981,** *103*, 5393; Toullec *Tetrahedron Lett.* **1984,** *25*, 4401; Chiang; Kresge; Schepp *J. Am. Chem. Soc.* **1989,** *111*, 3977.

[266] Keeffe; Kresge; Toullec *Can. J. Chem.* **1986,** *64*, 1224.

[267] Gero *J. Org. Chem.* **1954,** *19*, 469, 1960; Keeffe, Kresge; Schepp *J. Am. Chem. Soc.* **1990,** *112*, 4862. See these papers for values for other simple compounds.

[268] Chiang; Hojatti; Keeffe; Kresge; Schepp; Wirz *J. Am. Chem. Soc.* **1987,** *109*, 4000.

[269] Bohne; MacDonald; Dunford *J. Am. Chem. Soc.* **1986,** *108*, 7867.

[270] Chiang; Kresge; Walsh *J. Am. Chem. Soc.* **1986,** *108*, 6314; Ref. 269.

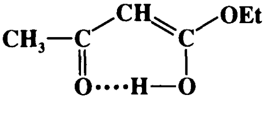
[271] Chiang; Kresge; Krogh *J. Am. Chem. Soc.* **1988,** *110*, 2600.

[272] Moriyasu; Kato; Hashimoto *J. Chem. Soc., Perkin Trans. 2* **1986,** 515.

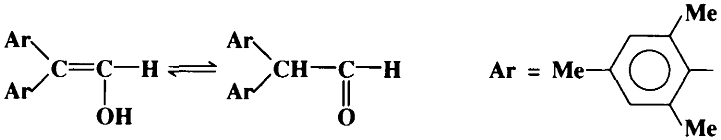
[272a] For reviews on the generation of unstable enols, see Kresge *Pure Appl. Chem.* **1991,** *63*, 213-221; Capon, in Rappoport, Ref. 264a, pp. 307-322.

is present, and it can even be the predominant form.[273] There are three main types of the more stable enols:[274]

1. Molecules in which the enolic double bond is in conjugation with another double bond. Some of these are shown in Table 2.1. As the table shows, carboxylic esters have a much smaller enolic content than ketones. In molecules like acetoacetic ester, the enol is also stabilized by internal hydrogen bonding, which is unavailable to the keto form:



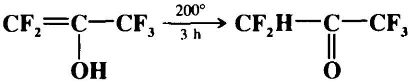
2. Molecules that contain two or three bulky aryl groups.[275] An example is 2,2-dimesitylethenol (**96**). In this case the keto content at equilibrium is only 5%.[276] In cases



96 **97**

such as this steric hindrance (p. 161) destabilizes the keto form. In **96** the two aryl groups are about 120° apart, but in **97** they must move closer together (~109.5°). Such compounds are often called *Fuson-type enols*.[277]

3. Highly fluorinated enols, an example being **98**.[278]



$$\underset{\mathbf{98}}{CF_2{=}\underset{\displaystyle OH}{\underset{|}{C}}{-}CF_3} \xrightarrow[3\ h]{200^\circ} \underset{\mathbf{99}}{CF_2H{-}\underset{\displaystyle O}{\underset{\|}{C}}{-}CF_3}$$

In this case the enol form is not more stable than the keto form (it is less stable, and converts to the keto form upon prolonged heating). It can however be kept at room temperature for long periods of time because the tautomerization reaction (**2-3**) is very slow, owing to the electron-withdrawing power of the fluorines.

Frequently, when the enol content is high, both forms can be isolated. The pure keto form of acetoacetic ester melts at −39°C, while the enol is a liquid even at −78°C. Each can be kept at room temperature for days if catalysts such as acids or bases are rigorously excluded.[279] Even the simplest enol, vinyl alcohol $CH_2{=}CHOH$, has been prepared in the

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[273] For reviews of stable enols, see Kresge *Acc. Chem. Res.* **1990,** *23,* 43-48, *CHEMTECH,* **1986,** 250-254; Hart; Rappoport; Biali, in Rappoport, Ref. 264a, pp. 481-589; Hart, *Chem. Rev.* **1979,** *79,* 515-528; Hart; Sasaoka *J. Chem. Educ.* **1980,** *57,* 685-688.

[274] For some examples of other types, see Pratt; Hopkins *J. Am. Chem. Soc.* **1987,** *109,* 5553; Nadler; Rappoport; Arad; Apeloig *J. Am. Chem. Soc.* **1987,** *109,* 7873.

[275] For a review, see Rappoport; Biali *Acc. Chem. Res.* **1988,** *21,* 442-449. For a discussion of their structures, see Kaftory; Nugiel; Biali; Rappoport *J. Am. Chem. Soc.* **1989,** *111,* 8181.

[276] Biali; Rappoport *J. Am. Chem. Soc.* **1985,** *107,* 1007. See also Kaftory; Biali; Rappoport *J. Am. Chem. Soc.* **1985,** *107,* 1701; Nugiel; Rappoport *J. Am. Chem. Soc.* **1985,** *107,* 3669; Nadler; Rappoport *J. Am. Chem. Soc.* **1987,** *109,* 2112; O'Neill; Hegarty *J. Chem. Soc., Chem. Commun.* **1987,** 744; Becker; Andersson *Tetrahedron Lett.* **1987,** *28,* 1323.

[277] First synthesized by Fuson; see for example Fuson; Southwick; Rowland *J. Am. Chem. Soc.* **1944,** *66,* 1109.

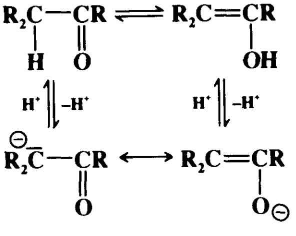
[278] For a review, see Bekker; Knunyants *Sov. Sci. Rev. Sect. B* **1984,** *5,* 145-182.

[279] For an example of particularly stable enol and keto forms, which could be kept in the solid state for more than a year without significant interconversion, see Schulenberg *J. Am. Chem. Soc.* **1968,** *90,* 7008.

gas phase at room temperature, where it has a half-life of about 30 min.[280] The enol $Me_2C{=}CCHOH$ is indefinitely stable in the solid state at −78°C and has a half-life of about 24 hours in the liquid state at 25°C.[281]

The extent of enolization[281a] is greatly affected by solvent,[282] concentration, and temperature. Thus, acetoacetic ester has an enol content of 0.4% in water and 19.8% in toluene.[283] In this case, water reduces the enol concentration by hydrogen bonding with the carbonyl, making this group less available for internal hydrogen bonding. As an example of the effect of temperature, the enol content of pentan-2,4-dione $CH_3COCH_2COCH_3$ was found to be 95, 68, and 44%, respectively, at 22, 180, and 275°C.[284]

When a strong base is present, both the enol and the keto form can lose a proton. The resulting anion (the *enolate ion*) is the same in both cases. Since **100** and **101** differ only in



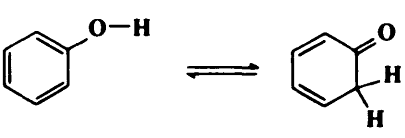
100 **101**

placement of electrons, *they* are not tautomers but canonical forms. The true structure of the enolate ion is a hybrid of **100** and **101** although **101** contributes more, since in this form the negative charge is on the more electronegative atom.

Other Proton-Shift Tautomerism

In all such cases, the anion resulting from removal of a proton from either tautomer is the same because of resonance. Some examples are:[285]

1. Phenol-keto tautomerism.[286]



Phenol Cyclohexadienone

[280] Saito *Chem. Phys. Lett.* **1976,** *42,* 399. See also Capon; Rycroft; Watson; Zucco *J. Am. Chem. Soc.* **1981,** *103,* 1761; Holmes; Lossing *J. Am. Chem. Soc.* **1982,** *104,* 2648; McGarritty; Cretton; Pinkerton; Schwarzenbach; Flack *Angew. Chem. Int. Ed. Engl.* **1983,** *22,* 405 [*Angew. Chem.* *95,* 426]; Rodler; Blom; Bauder *J. Am. Chem. Soc.* **1984,** *106,* 4029; Capon; Guo; Kwok; Siddhanta; Zucco *Acc. Chem. Res.* **1988,** *21,* 135-140.

[281] Chin; Lee; Park; Kim *J. Am. Chem. Soc.* **1988,** *110,* 8244.

[281a] For a review of keto-enol equilibrium constants, see Toullec, in Rappoport, Ref. 264a, pp. 323-398.

[282] For an extensive study, see Mills; Beak *J. Org. Chem.* **1985,** *50,* 1216.

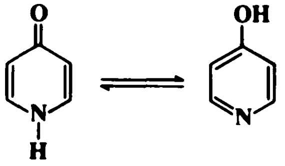
[283] Meyer *Leibigs Ann. Chem.* **1911,** *380,* 212. See also Ref. 272.

[284] Hush; Livett; Peel; Willett *Aust. J. Chem.* **1987,** *40,* 599.

[285] For a review of the use of x-ray crystallography to determine tautomeric forms, see Furmanova *Russ. Chem. Rev.* **1981,** *50,* 775-791.

[286] For reviews, see Ershov; Nikiforov *Russ. Chem. Rev.* **1966,** *35,* 817-833; Forsén; Nilsson, Ref. 263, pp. 168-198.

For most simple phenols this equilibrium lies well to the side of the phenol, since only on that side is there aromaticity. For phenol itself there is no evidence for the existence of the keto form.[287] However, the keto form becomes important and may predominate: (1) where certain groups, such as a second OH group or an N=O group, are present;[288] (2) in systems of fused aromatic rings;[289] (3) in heterocyclic systems. In many heterocyclic compounds in the liquid phase or in solution, the keto form is more stable,[290] although in vapor phase the positions of many of these equilibria are reversed.[291] For example, in the equilibrium between 4-pyridone (**102**) and 4-hydroxypyridine (**103**), **102** is the only form detectable in ethanolic solution, while **103** predominates in the vapor phase.[291]



102 **103**

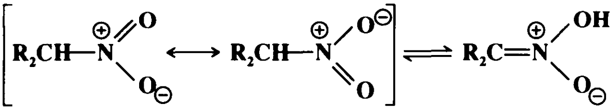
2. Nitroso-oxime tautomerism.

$$R_2CH{-}N{=}O \rightleftharpoons R_2C{=}N{-}OH$$

Nitroso Oxime

This equilibrium lies far to the right, and as a rule nitroso compounds are stable only when there is no α hydrogen.

3. Aliphatic nitro compounds are in equilibrium with aci forms.



$$\left[R_2CH{-}\overset{\oplus}{N}\begin{smallmatrix}\nearrow O\\ \searrow O^{\ominus}\end{smallmatrix} \longleftrightarrow R_2CH{-}\overset{\oplus}{N}\begin{smallmatrix}\nearrow O^{\ominus}\\ \searrow O\end{smallmatrix}\right] \rightleftharpoons R_2C{=}\overset{\oplus}{N}\begin{smallmatrix}\nearrow OH\\ \searrow O^{\ominus}\end{smallmatrix}$$

Nitro form Aci form

The nitro form is much more stable than the aci form, in sharp contrast to the parallel case of nitroso-oxime tautomerism, undoubtedly because the nitro form has resonance not found in the nitroso case. Aci forms of nitro compounds are also called nitronic acids and azinic acids.

4. Imine-enamine tautomerism.[292]

$$R_2CH{-}CR{=}NR \rightleftharpoons R_2C{=}CR{-}NHR$$

Imine Enamine

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[287] Keto forms of phenol and some simple derivatives have been generated as intermediates with very short lives, but long enough for spectra to be taken at 77 K. Lasne; Ripoll; Denis *Tetrahedron Lett.* **1980,** *21*, 463. See also Capponi; Gut; Wirz *Angew. Chem. Int. Ed. Engl.* **1986,** *25*, 344 [*Angew. Chem. 98*, 358].

[288] Ershov; Nikiforov, Ref. 286. See also Highet; Chou *J. Am. Chem. Soc.* **1977,** *99*, 3538.

[289] See, for example, Majerski; Trinajstić *Bull. Chem. Soc. Jpn.* **1970,** *43*, 2648.

[290] For a monograph on tautomerism in heterocyclic compounds, see Elguero; Marzin; Katrizky; Linda *The Tautomerism of Heterocycles*; Academic Press: New York, 1976. For reviews, see Katritzky; Karelson; Harris *Heterocycles* **1991,** *32*, 329-369; Beak *Acc. Chem. Res.* **1977,** *10*, 186-192; Katritzky *Chimia* **1970,** *24*, 134-146.

[291] Beak; Fry; Lee; Steele *J. Am. Chem. Soc.* **1976,** *98*, 171.

[292] For reviews, see Shainyan; Mirskova *Russ. Chem. Rev.* **1979,** *48*, 107-117; Mamaev; Lapachev *Sov. Sci. Rev. Sect. B.* **1985,** *7*, 1-49. The second review also includes other closely related types of tautomerization.

Enamines are normally stable only when there is no hydrogen on the nitrogen ($R_2C{=}CR{-}NR_2$). Otherwise, the imine form predominates.[293]

Ring-chain tautomerism[294] (as in sugars) consists largely of cyclic analogs of the previous examples. There are many other highly specialized cases of proton-shift tautomerism.

Valence Tautomerism

This type of tautomerism is discussed on p. 1134.

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[293] For examples of the isolation of primary and secondary enamines, see Shin; Masaki; Ohta *Bull. Chem. Soc. Jpn.* **1971,** *44*, 1657; de Jeso; Pommier *J. Chem. Soc., Chem. Commun.* **1977,** 565.

[294] For a monograph, see Valters; Flitsch *Ring-Chain Tautomerism*; Plenum: New York, 1985. For reviews, see Valters *Russ. Chem. Rev.* **1973,** *42*, 464-476, **1974,** *43*, 665-678; Escale; Verducci *Bull. Soc. Chim. Fr.* **1974,** 1203-1206.