

CHAPTER 9

Optical Crystallography

John A. Biles

SCHOOL OF PHARMACY
UNIVERSITY OF SOUTHERN CALIFORNIA
LOS ANGELES, CALIFORNIA

9.1 Introduction	337
9.2 Petrographic Microscope	339
9.3 Crystals	341
9.4 Crystallization	344
9.5 Polarization Colors—Anisotropy	344
9.6 Determination of Refractive Index	346
9.7 Indicatrix	350
9.8 Dispersion	364
9.9 Molecular Orientations in the Solid State.	365
Experimental Procedures	366
Questions	368
References	369

9.1 INTRODUCTION

About 1885 the petrographic microscope was introduced by geologists to give more adequate information regarding thin slices of rocks. In 1916 Wright¹ suggested that the petrographic microscope be used for the identification of chemical compounds. Winchell's *The Optical Properties of Organic Compounds* was first published in 1945 and has since been revised.² This text included the optical crystallographic data on all of the organic compounds reported in journals to which he had access at that time. At the present time there are several texts available to those interested in the use of optical crystallography.³⁻⁷ Today the petrographic microscope has assumed importance

in the various fields of chemistry including pharmaceutical chemistry, medicine, police and military intelligence, and the various scientific technologies. The use of optical crystallography has been emphasized in identification and determination of molecular orientations in the crystalline state. Its use often permits the evaluation of properties that cannot be determined by other means.

The use of optical crystallography developed with the theory of the interaction of light with the electrons of the molecules present in the crystal. The theory used in the explanation of optical crystallography is derived from the electromagnetic theory of light. Fletcher introduced the optical indicatrix to explain the effect of light passing through a nonopaque crystal.⁸ Early in the twentieth century, Barlow and Pope published an article on "The development of the atomic theory which correlates chemical and crystalline structure and leads to a demonstration of the nature of valency."⁹ Lewis¹⁰ stated that this was an extremely bold but carefully elaborated theory of the nature of valence and chemical structure based on the crystallographic study of chemical compounds. The theory leads to the idea that elements having the same valence occupy the same fraction of the total volume. Jaeger contributed to the theory of Barlow and Pope using saccharin and phthalimide as models.¹¹ Other investigators who contributed to the theory of Barlow and Pope were Rodd,¹² Drugman,¹³ and Colgate and Rodd.¹⁴

In 1918 Wherry published his work on the correlation of the axial ratios and refractive index ratios for compounds belonging to the tetragonal crystal system.¹⁵ Déverin investigated the relationship of symmetrically substituted aromatic compounds to threefold and sixfold symmetry.¹⁶ After Lorentz¹⁷ and Lorenz¹⁸ developed the formula for molecular refraction, calculations were made for the structural units in the molecule. Brühl found that conjugated unsaturated groups caused an increase of the molecular refractive and dispersive power.¹⁹ This optical exaltation was quantitative and dependent on the nature and number of unsaturated atomic groups. It has been shown that the mathematical relationship of the total induced polarization which is caused by the distortion of the electron shells in the molecule is equivalent to the molar refraction. Optical crystallographers have included the determination of the molar refraction of the molecules in the solid state in their publications.

Krishnan and other workers have studied the magnetic susceptibilities of solids.²⁰ The results of those studies showed that there was a correlation of magnetic and optical anisotropy. The investigators stated that

Optical measurements in theory have the same value, but owing to strong mutual influence of the optical dipoles induced in neighboring molecules in the crystal, even in those cases where the molecules happen to be oriented in the same manner, the birefringence of the crystal, as a whole, does not directly give that of the individual molecules. In order to correlate the optical constants of the crystal, the relative positions of the latter in the crystal have also to be considered; thus the problem is more complicated than in the corresponding magnetic case.

Lonsdale and Krishnan²¹ formulated mathematical relationships between crystal and molecular diamagnetic susceptibilities and molecular orientations for the different crystal systems. The abnormal susceptibilities of aromatic molecules led Pauling to the conclusion that three bond orbitals of the carbon atom in the benzene ring are coplanar and the fourth orbital possesses lobes above and below the benzene ring.²² The just mentioned studies led to the use of optical anisotropy in predicting molecular orientations. Wells²³ and Evans²⁴ have summarized these relationships.

Another area of microscopy was developed by the Kofler group and the McCrone group. The Kofler group has been responsible for the development of "Thermo-Mikro-Methoden" and the McCrone group has been responsible for the development of fusion methods in the United States. The work of McCrone may be appreciated by referring to his text.²⁵ Fusion methods have been utilized in the study of solids of pharmaceutical and medical importance, identification of explosives, study of insecticides, and the investigation of polymorphic crystal forms.

Most recently in the pharmaceutical field there has been considerable interest in the relationship of polymorphic forms as well as crystalline forms of solvated molecules to drug availability. The use of optical crystallography provides a convenient tool for the rapid identification of these various crystalline forms. Since a microscopic examination can be done with a minimum amount of material, positive and rapid identification and definite conclusions can be made and drawn utilizing optical crystallography.

Having introduced the reader to the historical and applied aspects of optical crystallography, a discussion of the tool, presentation of theory, and application of the knowledge are in order.

9.2 PETROGRAPHIC MICROSCOPE

The petrographic microscope, a polarizing microscope, differs from an ordinary compound microscope in that it has a rotating stage, a polarizer located in the condenser below the stage, an analyzer located in the body tube, and an Amici-Bertrand lens located in the body tube. Of importance also is the convergent lens and iris diaphragm located in the condenser. Just above the objective is a slot into which a quartz wedge, first-order test plate, or quarter-wavelength test plate may be inserted. A cross section of the petrographic microscope is shown in Fig. 9.1.

The polarizer and analyzer are either Nicol prisms or Polaroid lens. The polarizer is used to resolve all light into one plane of vibration. The analyzer is placed in the body tube so that its plane of vibration is perpendicular to that of the polarizer. When the planes are perpendicular, the Nicol prisms are crossed. The planes of vibration of the prisms coincide with the cross hairs in the ocular. The analyzer can be pushed in and out of the body tube. When

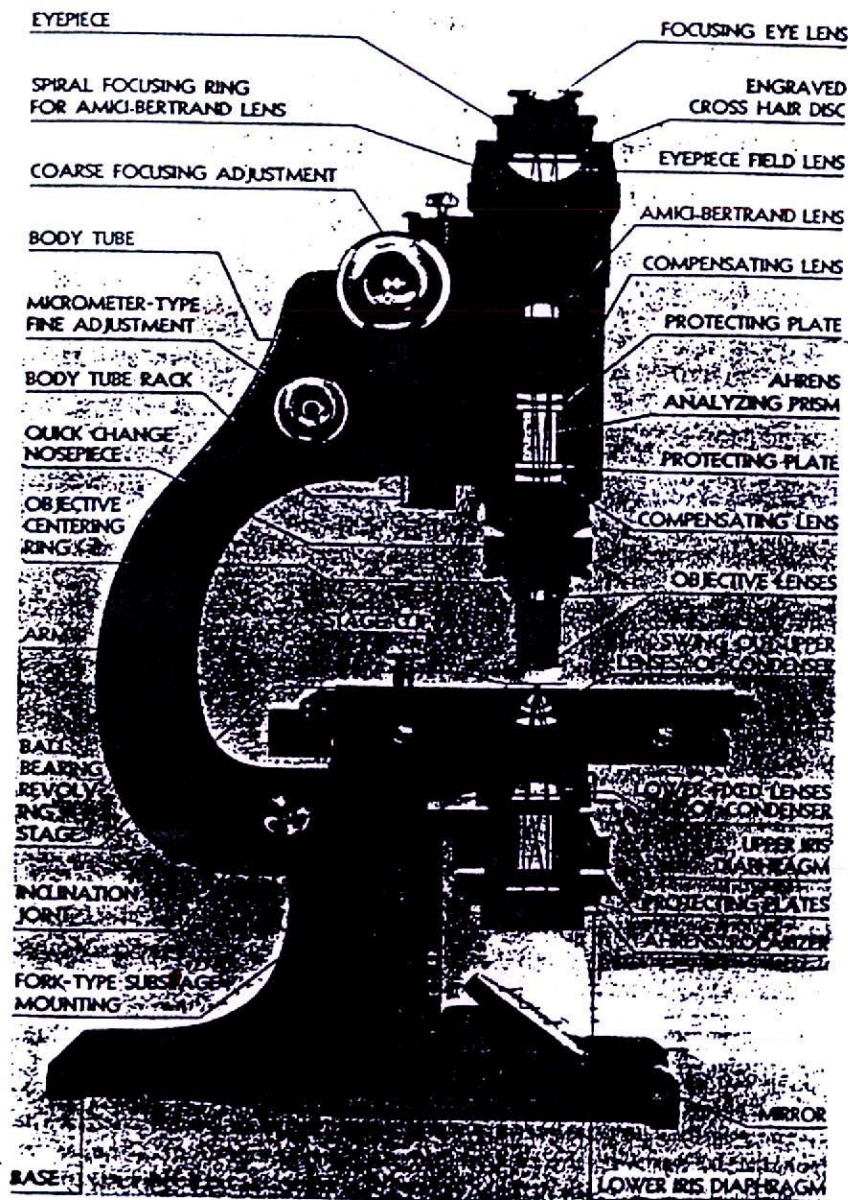


FIGURE 9.1: The Petrographic microscope. Courtesy of American Optical Company, Instrument Division.

is termed "extinction." If an anisotropic material is placed on the stage between the crossed nicols, light will pass through the analyzer provided the planes of vibration of the crystal are not parallel to the planes of vibration of the Nicol prisms. The light passing through may be colored, and these are called polarization colors. The intensity of the light in the optical system may be controlled by altering the diameter of the iris diaphragm.

The polarization colors may be made a great deal more intense by rotating the convergent lens into position above the condenser. If then the Amici-Bertrand lens is inserted into the body tube, the image will be focused at infinity. The resultant shadow or combination of colors and shadows is called an "interference figure." This figure is of great importance in determining almost all of the optical crystallographic properties of a given crystalline substance. Complete determination of the properties is made by inserting the test plates into the slot above the objective and observing the resulting effects on either the interference figure or crystal. A more detailed description of the petrographic microscope and the passage of light through the optical system is found in any suitable textbook on optical crystallography^{4,7} or chemical microscopy.⁵

9.3 CRYSTALS

An ideal crystal is a regular polyhedral solid bounded by plane faces which represents an extended array of atoms arranged in a definite order in all directions. Such a crystal contains a unit cell or a unit of structure, repetition of which in three dimensions produces the crystal. Each unit cell for a specific crystal is the same size and contains the same number of atoms similarly arranged. Even though size and shape of such a crystal may vary, the angles between the faces will remain constant. At times many of the crystal faces may not be evident, but there still remains an orderly internal arrangement of atoms.

Crystals vary in their angular relationships and symmetry. On this basis, a crystal is classified into one of six crystal systems. The systems, depending on the symmetry, are subdivided into 32 classes. Certain forms are characteristic of each class. A measurement of the interfacial angles reveals a number of faces of the same type. Faces of the same type are referred to as a "form." In some instances one form is all that is needed to define the three-dimensional solid. In other instances, and at times demanded, two or more forms are present.

Each system is defined in terms of the crystallographic axes, which are imaginary lines used to describe the position of the plane faces in space. The systems are defined as follows:

1. *Isometric System.* This system includes those crystals which are referred to three mutually perpendicular equal axes. The axes are identified as A_1 , A_2 ,

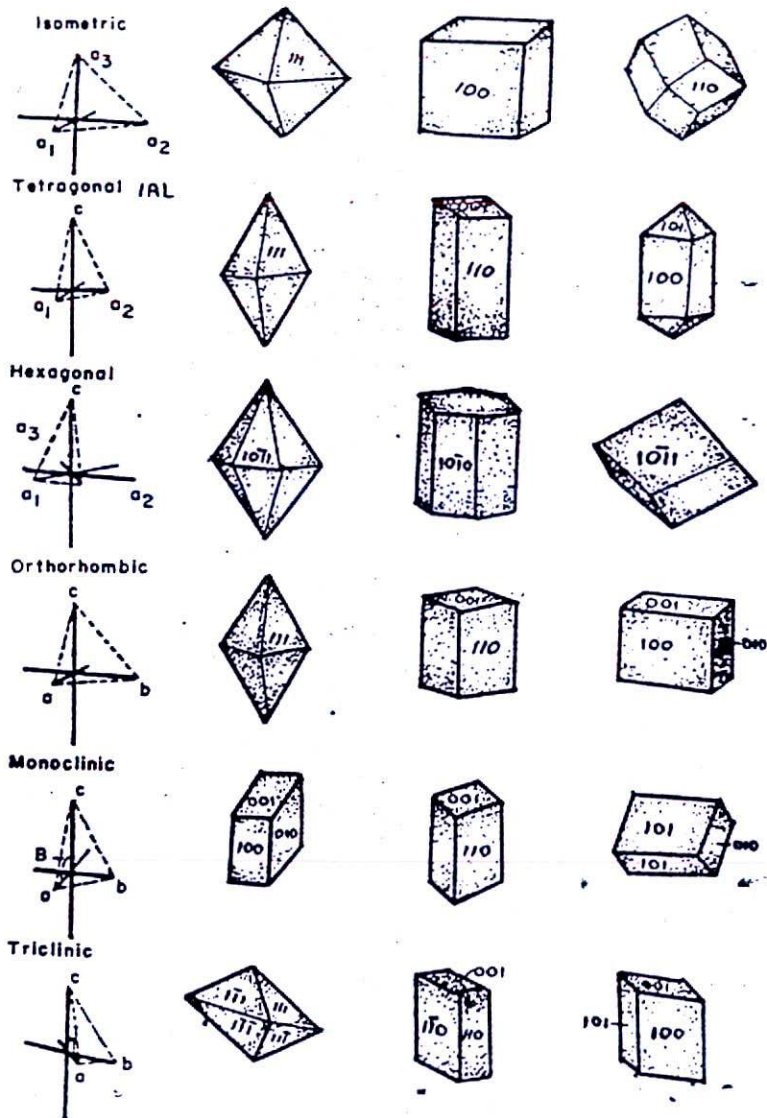


FIGURE 9.2: The crystal systems. Courtesy of John Wiley & Sons.

2. *Tetragonal System.* This system includes those crystals which are referred to three mutually perpendicular axes, two equal in length, and one longer or shorter. The equal axes are A_1 and A_2 . The third axis is C .

3. *Hexagonal System.* This system includes those crystals which are referred to three equal axes lying in one plane and intersecting at angles of sixty degrees, and a fourth axis, either longer or shorter and perpendicular to the plane of the other three. The equal axes are A_1 , A_2 , and A_3 . The perpendicular axis is C .

4. *Orthorhombic System.* This system includes those crystals which are referred to three mutually perpendicular axes of unequal length. The axes are a , b , and c .

5. *Monoclinic System.* This system includes those crystals which are referred to three unequal axes, two axes perpendicular to the third axis but not to each other. The two axes are a and c , the third axis is b .

6. *Triclinic System.* This system includes those crystals which are referred to three unequal axes intersecting at oblique and obtuse angles. The axes are a , b , and c .

The axes, simple forms, and combinations in the six crystal systems are illustrated in Fig. 9.2.

Crystals of a given substance may vary in size, relative development of a given face, and the number and kind of faces or forms present. Crystals showing such variations have different crystal habits. The habit acquired depends upon the solvent used, the temperature, pressure, concentration, impurities, and the rate of precipitation. If the crystal faces in the three dimensions are equidimensional, or nearly so, the habit is termed "equant." If a pair of opposite and parallel faces are larger, the crystal is flattened and is said to be "tabular." If this is carried to the extreme, the crystal is said to be "lamellar." If three or more faces all parallel to a line are larger and elongated, the crystal is said to be "columnar"; the extreme tendency of this type is termed "acicular."

The habit of a crystal can also vary because the crystal is easily cleaved. Cleavage occurs in the plane where the intramolecular forces are the weakest. A crystal may possess several cleavages which are parallel to common crystal faces. The cleavage may range from perfect to poor. Cleavage is of great help in suggesting intermolecular arrangement, particularly with aromatic organic substances.

Crystals of a given substance may also vary in crystal form. This means that the unit cell will vary, and the crystal exhibits polymorphism. Such substances are termed dimorphic, trimorphic, etc., according to whether they possess two, three, or more forms. On standing one of the forms may convert to another form. This form is termed "metastable." If the form conversion is reversible, the polymorphism is enantiotropic; if the form conversion is irreversible, the polymorphism is monotropic. Polymorphic conversions are dependent on pressure and temperature. In addition various polymorphic

forms may be isolated using different solvents. When different crystalline forms of a single substance are isolated, one must also consider the possibility of isolating solvated forms. Also a single substance may exist in two different species in the solid state. For example, two different species can exist because of tautomerism. This difference is called "dynamic isomerism" and should not be confused with polymorphism.

9.4 CRYSTALLIZATION

Macroscopic and microscopic procedures are valuable in obtaining crystals for microscopic study. Generally speaking well-formed crystals are obtained using microscopic methods. Such crystals should be used for detailed study. Pharmaceutical chemists are well aware of the macroscopic procedures. A clean microscope slide is used for microscopic procedures. About 2 drops of the solvent is added to the slide and a small amount of the solid material to be crystallized. A supersaturated solution is obtained at room temperature. To dissolve the small amount of excess solid, the slide is heated using a microburner. On heating the solvent will evaporate and solid will crystallize at the edge of the solution. A glass rod is used to push the crystals to the center of the drop of solution. As this crystallization begins and proceeds, the slide is removed from the microburner. To prevent further evaporation the solution containing crystallized solid is covered with a clean cover slip.

Macroscopic procedures are advantageous because the rate of crystallization may be carefully controlled. When necessary, large volumes of solvent may be used for crystallizing slightly soluble solute. Concentrations of more soluble solids may be carefully controlled. Temperature is more readily controlled. Crystallization on a microscopical scale has great advantages in that crystallization is rapid, the crystal growth may be followed directly, and physical-chemical changes which occur can be readily identified. Crystals from microscopic procedures may also be smaller and more nearly perfect. Application may be done by doing experiments 9.1-9.4.

9.5 POLARIZATION COLORS—ANISOTROPY

Substances in which the velocity of the transmission of light differs in different directions are called "anisotropic." Tetragonal, hexagonal, orthorhombic, monoclinic, and triclinic crystals are anisotropic. When white light, which has many planes of vibration, passes through an anisotropic crystal, it is resolved into two planes of vibration. The velocity of light in each plane of vibration is different. Since the refractive index is a measure of the velocity of light, it can be said that the anisotropic media shows double refraction. The

numerical difference between the two indices of refraction is a measure of the birefringence of the crystal.

The plane of vibration of the crystal may be located under the microscope with the aid of the polarizer and the analyzer. Should the plane of vibration of the crystal be parallel to the plane of vibration of the polarizer, light will pass through the crystal with no change in direction of vibration. The light vibrating in the plane of the polarizer will then be totally reflected in the analyzer. As a result, between crossed Nicol prisms the crystal will be extinct. If the crystal is rotated by moving the stage, the crystal will then take on a color. The intensity of the color reaches a maximum at 45° from the position of extinction. The color may be any in the visible spectrum. These are called polarization colors. With continued rotation of the stage, the crystal will then become extinct again. The extinction position is 90° from the previous extinction position. Thus, two different planes of vibration have been located. The refractive index of the crystal is determined when the crystal is in the position of extinction. The principal planes of vibration of the tetragonal, hexagonal, and orthorhombic systems parallel the crystallographic axes.

The principal indices of refraction are obtained by locating the principal planes of vibration. A principal index of refraction parallels the b axis of the monoclinic system. Principal indices of refraction may or may not parallel one of the crystallographic axes of the triclinic system.

If an observer looks down the c axis of a tetragonal or hexagonal crystal between crossed Nicol prisms, the crystal section will show complete extinction. If the observer looks at a section including the a and c crystallographic axes of the tetragonal or hexagonal system, extinction will occur when the long edge of the crystal is parallel to the cross hairs. This occurs because the plane of vibration is parallel to the crystallographic axis, which in turn is parallel to the long edge of the crystal. This extinction is called "parallel extinction." Orthorhombic crystals will show parallel extinction. However no complete extinction is observed, as is shown by tetragonal and hexagonal crystals. On close examination of the principal planes of vibration through the determination of the principal indices of refraction, one finds that orthorhombic crystals possess three different planes of vibration, all mutually perpendicular. Monoclinic and triclinic crystals possess three planes of vibration and therefore three different principal indices of refraction. When one looks at a section of a monoclinic crystal which includes the b axis, the extinction is parallel. When one looks down the b axis of this monoclinic crystal, extinction between crossed Nicol prisms occurs when the long edge of the crystal is at an angle to the cross hairs. This extinction is called "inclined" or "oblique." Triclinic crystals show oblique extinction. This discussion is summarized in Table 9.1. Experiments 9.5-9.9 allow one to observe the extinction, polarization colors, and habit of various crystalline substances.

TABLE 9.1: Effect of Crystals on Light

System	Velocity of transmission	Extinction	Principal indices of refraction
Isometric (cubic)	Isotropic	Complete	One
Tetragonal	Anisotropic	Parallel and complete	Two
Hexagonal	Anisotropic	Parallel and complete	Two
Orthorhombic	Anisotropic	Parallel	Three
Monoclinic	Anisotropic	Parallel and inclined	Three
Triclinic	Anisotropic	Inclined	Three

9.6 DETERMINATION OF REFRACTIVE INDEX

The refractive index governs the visibility of all transparent objects. It can be defined as the ratio of the velocity of light traveling in a vacuum to the light traveling in a given medium. The refractive index has also been defined as the ratio of the sine of the angle of incidence to the angle of refraction when incident light is refracted into a medium of less density to a medium of greater density. These ratios result because of the interaction of light with the electron shells of the lesser and denser media. The interaction of light with the electron cloud causes a distortion of the cloud. A measure of the ease of distortion is called the "polarizability." The refractive index is directly proportional to the polarizability. The distortion causes an optical dipole to be induced. The total polarization, which is a measure of the dielectric constant, is a function of the induced dipole and the permanent dipole. For light of long wavelength Maxwell showed that the dielectric constant was equal to the square of the refractive index. For this reason the molar polarization can be calculated knowing the refractive index.

The refractive index of liquids can be easily determined with the use of the Abbé refractometer. Knowing the refractive index of liquids, the refractive index of solids may be determined, since a nonopaque solid will not be seen in a liquid provided both solid and liquid have the same refractive index.

To determine the refractive index of solids, it is necessary to prepare a series of liquids having specific refractive-index values. On mixing mineral oil and α -bromnaphthalene in various proportions a series of liquids can be prepared having refractive-index values varying from 1.48 to 1.658. Usually the oils are prepared in which each oil varies from the next oil by 0.005. Equal volumes of mineral oil and α -bromnaphthalene provide a liquid having an index midway between 1.48 and 1.658. The series of oils may be continued by mixing α -bromnaphthalene with methylene iodide (1.74). Another oil

may be prepared by saturating methylene iodide with sulfur, iodoform, and iodides. This provides a liquid with a refractive index of 1.86. Mixing this latter oil with methylene iodide will provide various liquids having refractive indices between 1.74 and 1.86. Most organic solids are not sufficiently soluble in these oils. Thus, they may be used to determine the refractive index of the solids. The refractive index of the liquids will vary about 0.0004 units/ 1°C .

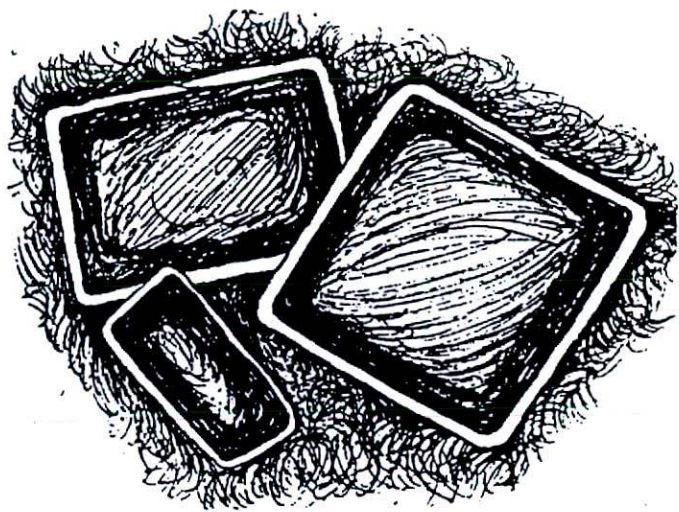


FIGURE 9.3: The Becke line is the bright band of light surrounding the crystal.

To determine the refractive index of an isometric crystal such as sodium chloride, freshly crystallized material is isolated and dried. A few crystals are placed in a microscope slide and immersed with a couple of drops of refractive-index oil. The slide is mounted on the revolving stage of the microscope and focused sharply. The Becke line is used to determine if the crystal has a higher or lower refractive index than the surrounding medium. The Becke line is a bright band of light which moves to the medium of higher index of refraction as the body tube is focused upward. The bright band of light will move to the medium of lower index of refraction as the body tube is focused downward. The Becke line is difficult to observe if the field is too well illuminated. Therefore, the iris diaphragm must be adjusted so that the field is not too bright; the field should have a slight touch of gray. The Becke line is illustrated in Fig. 9.3. The movement of the Becke line in opposite directions when the body tube is moved upward or downward may be explained with the use of Fig. 9.4. As the figure suggests the majority of rays from the light source is reflected when they hit the interface between the media of high

and low refractive index. The reader may do experiments 9.10 and 9.11 to familiarize himself with the determination of the refractive index of solids.

When a crystal is mounted in a chosen immersion oil, the Becke line is observed. If the Becke line moves toward the center of the crystal as the focus is raised, then the surrounding medium has the lower refractive index. In order to determine the refractive index of the crystal, a higher mounting oil

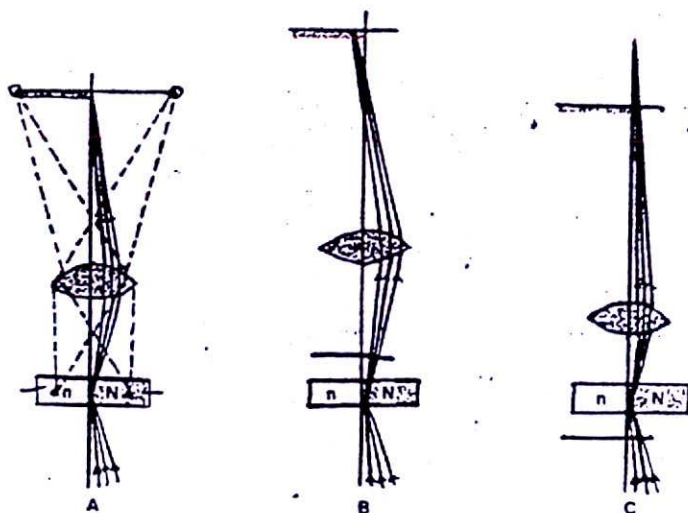


FIGURE 9.4: Movement of the Becke line. (A) Crystal in sharp focus. (B) Becke line within crystal as the body tube is focused upward. (C) Becke line outside crystal as the body tube is focused downward. Courtesy of John Wiley & Sons.

is chosen. After mounting the crystal in an oil of higher refractive index, it may be observed that the Becke line moves outward from the edge of the crystal as the focus is raised. With proper choice of oils, the crystal is found to disappear when mounted in one of the oils, or a mixture of two oils adjacent in refractive index. When crystals do disappear, it is concluded that the solid has the same refractive index as the liquid. Should the crystal be colored, then a filter of the same color may be placed between the condenser and the light source so that the field will have a similar color. In this manner the refractive index of the colored crystal may be easily determined.

When an isometric crystal is mounted in an oil having the same refractive index, the crystal will not be observed, even when the stage is rotated through 360° . If the difference between the refractive index of the liquid and solid is low, the contrast is low; when the difference is great, the contrast is high. When one mounts an anisotropic crystal in a liquid and focus on the solid sharply under the microscope, it can be observed that the contrast will vary

as the stage is rotated through 360° . This indicates that the refractive index of the crystal changes as the stage is rotated. This incidentally will occur only when the polarizer is in position in the condenser and when the analyzer is not inserted into the body tube.

In determining the refractive indices of an anisotropic crystal, the orientation of the crystal must be known. Thus the experience gained in observing the crystal as it is rolled in Canada balsam is most beneficial in determining the principal indices of refraction. Consider a columnar crystal which belongs to the tetragonal system. When looking at a face of this crystal (rectangular shaped) two principal indices of refraction can be determined. One index will be determined when the long edge is parallel to the vertical cross hair. A second index will be determined when the long edge is parallel to the horizontal cross hair. These positions represent extinction positions of the crystal.

To determine the refractive indices of the tetragonal or hexagonal crystal, a crystal showing the maximum polarization colors between crossed Nicol prisms is chosen for study. This crystal is rotated to a position of extinction. It is then noted whether the long edge of the crystal is parallel to the vertical or horizontal cross hair. The analyzer is then removed and the movement of the Becke line is noted. The crystals are mounted in the various immersion oils using the previously described procedure to determine the refractive index which corresponds to the chosen plane of vibration (as determined from the extinction position). Having determined the first refractive index, then the refractive index corresponding the plane of vibration at 90° is determined. This may be observed by performing experiment 9.12.

When Table 9.1 is examined, it will be observed that crystals belonging to the orthorhombic, monoclinic, and triclinic crystal systems possess three principal indices of refraction. These three indices are difficult to determine without the knowledge or use of the interference figures to determine the crystal orientation. Therefore, the procedure is somewhat "hit-and-miss." Generally speaking the orientation showing the highest polarization colors will yield the highest and lowest indices of refraction. If then the crystal is rolled 90° , the intermediate index may be obtained. These determinations, however, may not yield the three principal indices of refraction. If one is studying a crystal possessing a tabular habit, he may roll the crystal in Canada balsam to determine the planes of vibration and relate the polarization colors to each position studied. The planes of vibration may then be identified with the crystallographic axes. Then two orientations need be chosen to determine the three indices of refraction. One of the indices will be common to both orientations. This is illustrated in Fig. 9.5. The refractive indices for an orthorhombic crystal may be obtained by performing experiment 9.13.

If the higher index of refraction parallels the long edge of the crystal, then the elongation is positive. If the opposite occurs, then the elongation is negative. Elongation is not too significant since the habit of the crystal is quite susceptible to change.

The two indices of refraction in tetragonal and hexagonal crystals are identified as epsilon and omega. Omega parallels the a crystallographic axis and epsilon parallels the c crystallographic axis. The three indices of refraction in the orthorhombic, monoclinic, and triclinic crystals are referred to as alpha, beta, and gamma. Alpha is the lowest index value and gamma is the highest index value, beta therefore being the intermediate value.

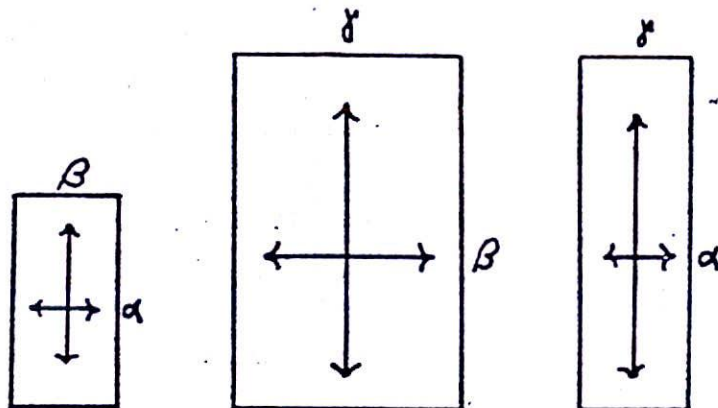


FIGURE 9.5: The three principal planes of vibration as observed from the three faces of the orthorhombic crystal. The refractive indices are alpha, beta, and gamma. The crystal shows positive elongation.

It is possible that omega can be a higher or lower value when compared to epsilon. When omega is the higher refractive index, the crystal by definition is optically negative. When epsilon is the higher refractive index, the crystal is optically positive. When the values for alpha, beta, and gamma are compared, one can conclude that beta, the intermediate value, may have an index value closer to alpha than gamma. If this occurs, one states the orthorhombic, monoclinic, or triclinic crystal is optically positive. The crystal is optically negative when beta has an index value closer to gamma than to alpha.

9.7 INDICATRIX

To understand the optic sign of anisotropic crystals more adequately and comprehend the effect of crystals on light, the indicatrix is used. By definition the indicatrix is a "three dimensional geometric figure showing the variation of the indices of refraction of a crystal for light waves in their directions of vibration. Each radius vector represents a vibration direction whose length measures the index of refraction of the crystal for waves vibrating parallel to

the direction." Consider a pinpoint source of light in the center of an isotropic crystal. Allow the light waves to propagate in all directions for an instant. Then draw wave normals perpendicular to the direction of propagation. The summation of all wave normals for the isotropic crystal would be a sphere. This sphere by definition is an isotropic indicatrix. This is illustrated in Fig. 9.6.

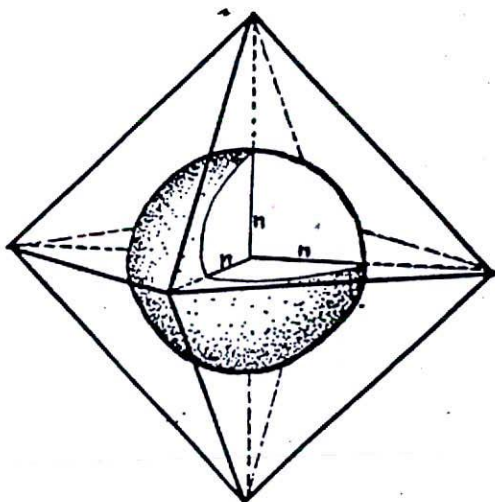


FIGURE 9.6: The isotropic indicatrix. Courtesy of John Wiley & Sons.

The radius of the sphere is equal to the refractive index of the crystal. Therefore, the refractive index of the isotropic crystal is constant.

When considering a tetragonal or hexagonal crystal, an indicatrix shaped like an oblate or prolate spheroid is formed. When light travels in the direction of the c crystallographic axis, it behaves as though the crystal is isotropic. Therefore, two radii of the spheroid are equal. When light travels in a direction perpendicular to the c axis, the velocity of light varies depending on the position of the section of the crystal. Therefore, the radii will vary. This direction, coinciding with the c axis, is called the "optic axis." Consequently in the three-dimensional section, the indicatrices appear as shown in Fig. 9.7.

The radius of the longer axis of the prolate spheroid corresponds to the refractive index for epsilon. As defined earlier, this corresponds to a uniaxial positive indicatrix. When the refractive index corresponding to epsilon coincides to the radius of the shorter axis of the oblate spheroid, the uniaxial indicatrix is negative. If one considers any section of the positive or negative indicatrix, one axis always corresponds to the refractive index for omega and the other axis will vary in length up to a maximum which corresponds to

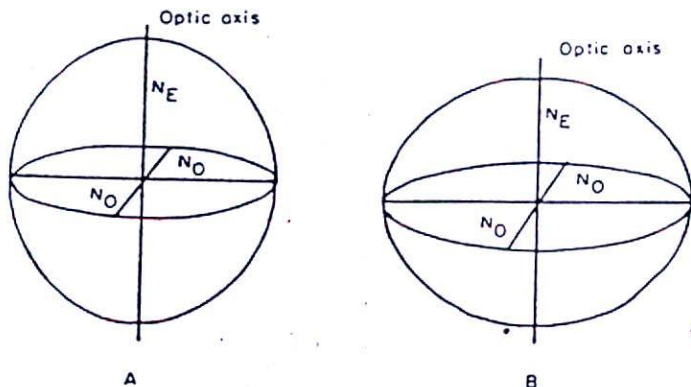


FIGURE 9.7: The uniaxial indicatrix for (A) a positive crystal and (B) a negative crystal.

epsilon. Consequently the value for omega will always be constant regardless of the position of the crystal (or position of the indicatrix). However, only the highest value for epsilon for a positive crystal and the lowest value for epsilon for a negative crystal should be reported. These values are called "principal indices of refraction." The exact positions of the indicatrices for

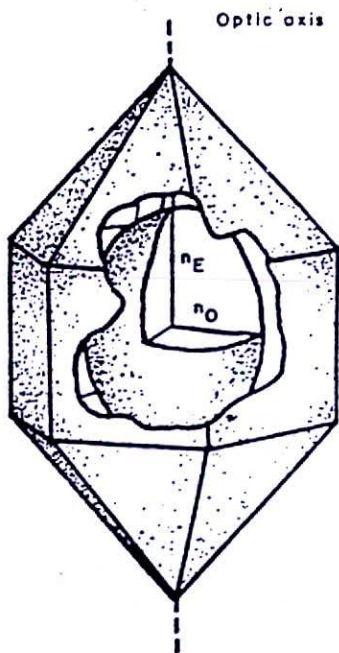


FIGURE 9.8: Uniaxial positive crystal (quartz). Courtesy of John Wiley & Sons.

quartz (positive crystal) and sodium nitrate (negative crystal) are illustrated in Figs. 9.8 and 9.9.

In the quartz and NaNO_3 crystal the section of the indicatrix perpendicular to the optic axis is circular. All other sections are elliptical. When looking at a section perpendicular to the optic axis, the crystal shows complete extinction between crossed Nicol prisms. This always holds true and is a convenient way

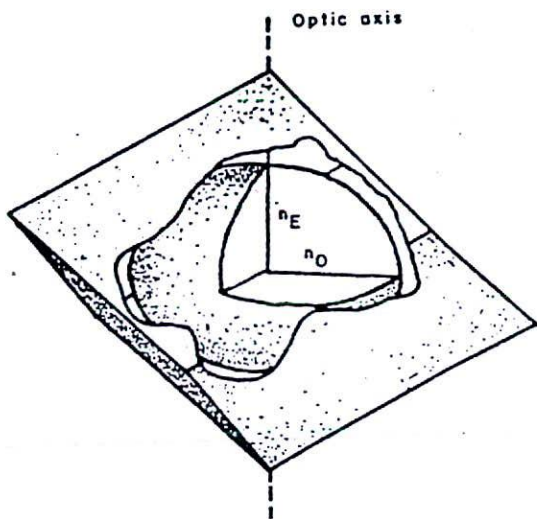


FIGURE 9.9: Uniaxial negative crystal (NaNO_3). Courtesy of John Wiley & Sons.

to locate the optic axis. All other observed sections of the crystal correspond to elliptical sections of the indicatrix and will show parallel extinction. That is, when looking at the crystal planes corresponding to the elliptical sections, one sees the crystal becoming alternately light and dark between crossed Nicol prisms. The crystal is extinct when one of the axes of the indicatrix is parallel to the plane of the polarizer. The greatest difference in the indices of refraction, i.e., the maximum birefringence, is obtained when a section is viewed parallel to the plane of the optic axis. This orientation gives the two principal indices of refraction. When a section is viewed perpendicular to the optic axis, the crystal shows complete extinction between crossed Nicol prisms. With this orientation only ω is obtained.

The orientation of tetragonal and hexagonal crystals and the optic sign are determined from interference figures. An interference figure is a telescopic image of convergent light passing through an anisotropic crystal between crossed Nicol prisms. The definition of the interference figure also represents the procedure by which the figure may be obtained. A crystal is focused sharply and placed at the intersection of the cross hairs in the ocular.

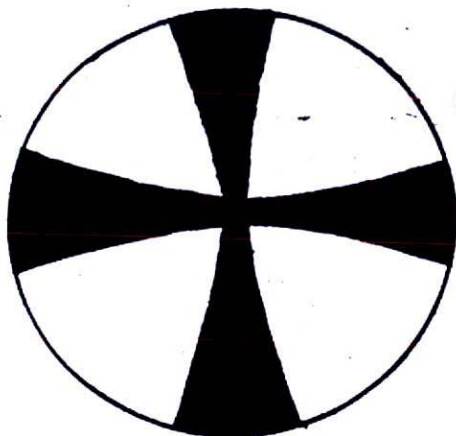


FIGURE 9.10: Centered uniaxial optic-axis interference figure.

The analyzer is then placed in position, the convergent lens is inserted into position and the Amici-Bertrand lens is placed in position so that the power of the ocular will be nullified. If one is looking at a section of a tetragonal or hexagonal crystal perpendicular to the c axis (i.e., looking down the c axis or looking down the optic axis) one sees an interference as shown in Fig. 9.10. This figure is called a centered optic-axis uniaxial interference figure. If one examines Figs. 9.8 or 9.9, one concludes that the crystal must rest on its apex to get the centered figure (i.e., in order to look down the optic axis). This is impossible unless the crystal is mounted in a viscous liquid such as Canada

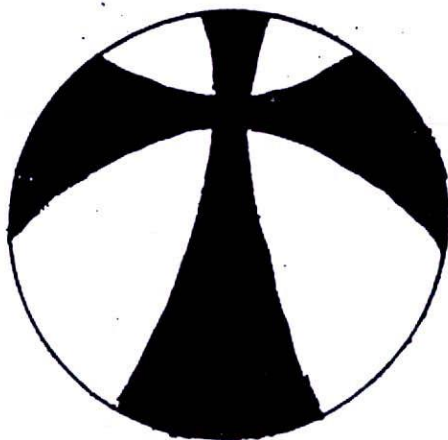


FIGURE 9.11: Off-centered uniaxial optic-axis interference figure.

balsam. It is more likely that the crystal will rest on one of its faces. If the direction of propagation of light is at an angle to the optic axis, then the figure will not be centered, as illustrated in Fig. 9.11.

The crystal may be lying on a predominant face and the optic axis is outside the field of the microscope. Then the cross will not be observed, only one of its brushes. This is illustrated in Fig. 9.12.

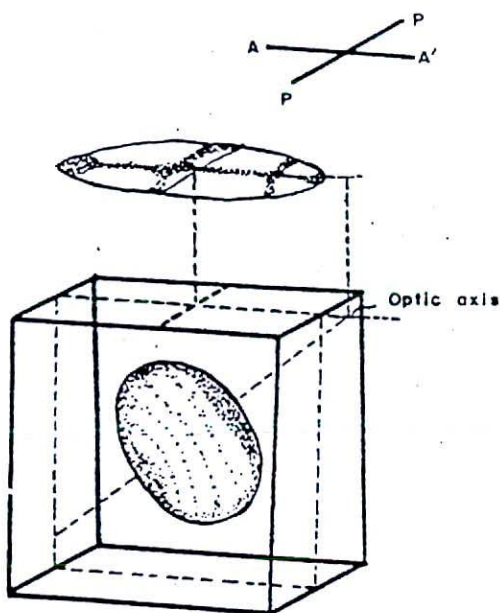


FIGURE 9.12: Off-centered optic-axis figure. Point of emergence of optic axis is outside the field of the microscope. Courtesy of John Wiley & Sons.

Should the crystal be lying on a face which represents a section including the a and c crystallographic axis and therefore including the optic axis, one will observe a flash figure. This interference figure is illustrated in Fig. 9.13.

The optic sign may be determined using the optic-axis interference. Before this procedure is described, a review of the interaction of light waves (electromagnetic wave theory) is necessary. Without any crystal under the microscope and with the polarizer and analyzer in position, different Newton colors are observed when the quartz wedge is inserted in the slot located above the objective. As the wedge is pushed in, some colors will reappear. On first appearance, the color is first order; on second appearance it is second order, etc. The colors of the first order include, in order: gray, gray blue, white, yellowish white, yellow, and red. Following the red color, include, in order,

the second-order colors, namely: violet, blue, green, yellow, orange, red. The third-order colors include violet, green, yellow, red. In reference to red color, it can be said that a color of lower order would be yellow or orange and a color of higher order would be blue or violet. The quartz wedge is so constructed that the fast ray vibrates in the direction of the long edge and the slow

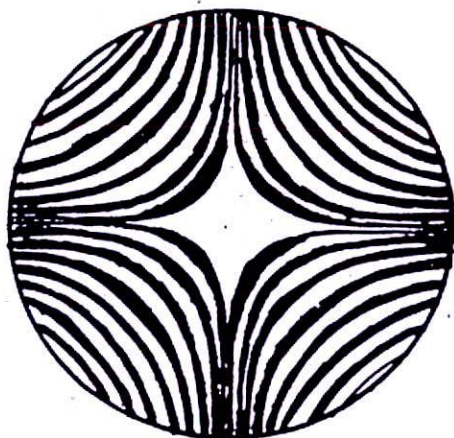


FIGURE 9.13: The uniaxial flash figure. Optic axis in the diagonal position.

ray vibrates in the direction of the width of the quartz wedge. The quartz wedge is illustrated in Fig. 9.14.

Another test plate used in determining the optic sign is the gypsum plate or selenite plate, which is ground to such a thickness that it gives a first-order red color. This test plate is shown in Fig. 9.15 and the planes of vibration of the fast and slow rays are identified.

Consider the anisotropic crystal to be of such thickness that its polarization or interference color is gray. If this anisotropic crystal is now placed under the microscope in its extinction position and the first-order red test plate is inserted, the field will appear red. When rotated 45° , the crystal may appear blue. If the stage is now rotated an additional 90° , the crystal will appear yellow or orange. These observations are explained as follows: when the slow and fast rays of the test plate and crystal are vibrating parallel reinforcement occurs. Thus, the color (red) will be reinforced to give a color of a higher order (blue). If the slow and fast rays of the test plate and crystal are vibrating perpendicularly, then compensation occurs and the result is a color of a lower order (i.e., color changes from red to yellow or orange). Reinforcement is called "constructive interference" and compensation is called "destructive interference."

When Fig. 9.10 is examined, one observes a cross, termed "isogyres."

which represents positions of complete extinction. The light areas in the four quadrants represent slow and fast rays of the crystal vibrating mutually perpendicular of such wavelength difference that destructive interference is not complete. Thus in the four quadrants rays are vibrating mutually perpendicular, one ray representing the radial ray, the other representing the tangent ray. The velocity of one of the rays does not change and is termed the "ordinary ray," the other ray velocity changes and is called the "extraordinary ray"

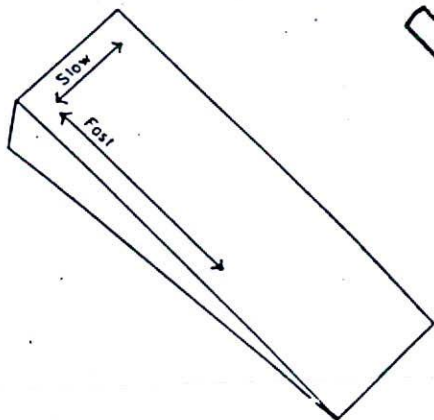


FIGURE 9.14: The quartz wedge.

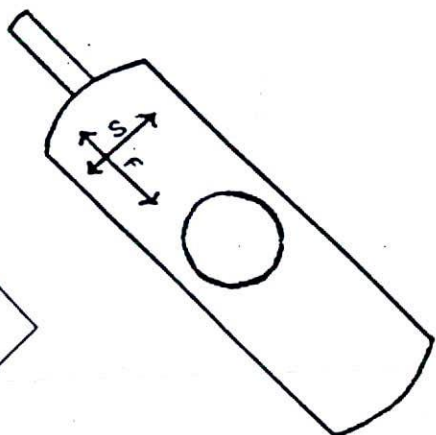


FIGURE 9.15: The first-order red test plate.

ray." The former ray is the tangent ray and the latter ray is the radial ray. The traces of the planes of vibration of the ordinary and extraordinary components in the optic-axis uniaxial interference figure are illustrated in Fig. 9.16. The optic axis interference figure is dashed in. If the first-order red test plate is inserted into the slot, the isogyres will appear red. The slow ray of the test plate (see Fig. 9.15) will vibrate parallel to the o ray in quadrants 2 and 4 and will vibrate parallel to the e ray in quadrants 1 and 3. Let us assume that the e ray is faster than the o ray. Then the optic sign may be determined from the interaction of the rays of the crystal with the rays of the test plate. Figure 9.17 illustrates the resulting effect. The isogyres will be red. In quadrants 1 and 3 adjacent to the isogyre a yellow color will appear. In quadrants 2 and 4 adjacent to the isogyre a blue color will appear. Using a first-order red test plate, blue appears when interference is constructive. This results when like rays (i.e., slow rays) vibrate parallel. Thus, in quadrants 2 and 4, the slow ray of the test plate is vibrating with the slow ray of the crystal. The o ray is the slow ray because its plane of vibration is parallel to that of the slow ray of the test plate. By definition, when the o ray is the slow

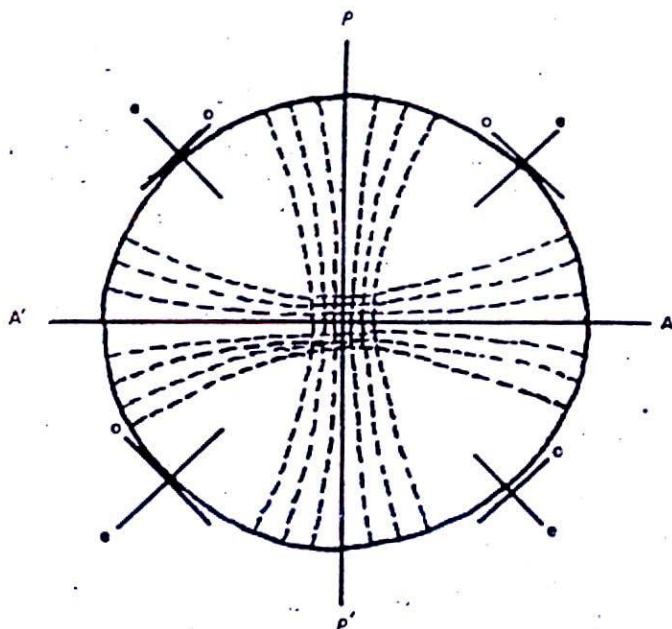


FIGURE 9.16: The uniaxial interference figure.

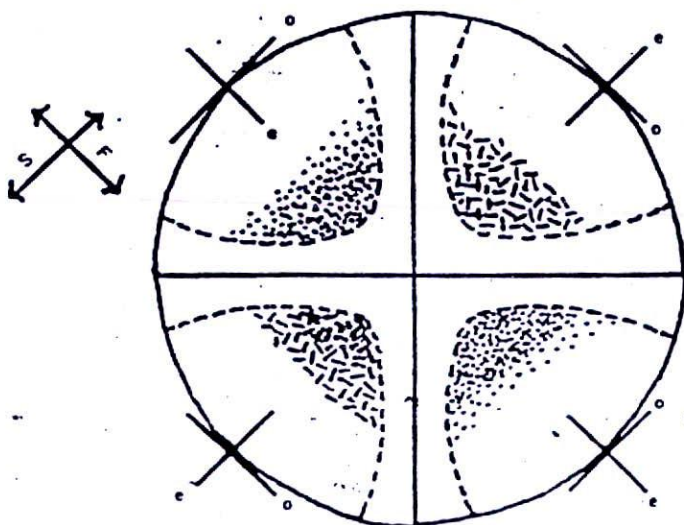


FIGURE 9.17: The uniaxial interference figure. When the first-order red plate is inserted into the body tube, blue color will appear, as represented by the dotted areas in quadrants 2 and 4. The similar areas in quadrants 1 and 3 will appear yellow.

ray and the e ray is the fast ray, the crystal is optically negative. Should the crystal have been optically positive (i.e., the optic sign is positive) blue would have appeared in quadrants 1 and 3, whereas yellow or orange would have appeared in quadrants 2 and 4. For a more detailed discussion of the determination of the optic sign of uniaxial crystals, using the various test plates, the reader is referred to texts in optical crystallography.

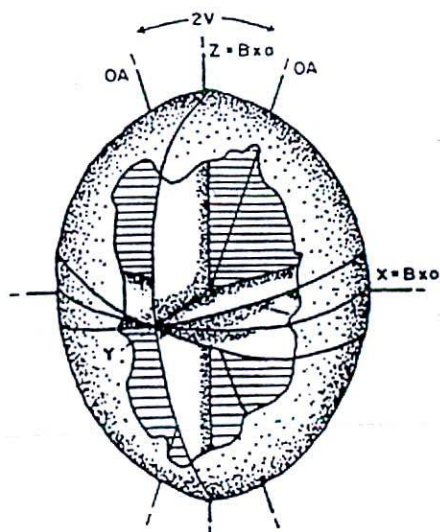


FIGURE 9.18: The positive biaxial indicatrix. OA is the optic axis. Courtesy of John Wiley & Sons.

Since the refractive index is inversely proportional to the velocity of the light, the refractive index for the ordinary ray (ω) is higher for a negative crystal than for a positive crystal.

The examination of the interference figures, the determination of the optic sign may be done by performing experiments 9.13 and 9.14.

The biaxial indicatrix is common to the orthorhombic, monoclinic, and triclinic crystal system. Biaxial indicates that this three-dimensional form contains two optic axes. This indicatrix corresponds to a triaxial ellipsoid. Just as the section perpendicular to the optic-axis of a uniaxial indicatrix is circular, so must the section perpendicular to the optic axis of the biaxial indicatrix. The radius of each of the three axes of the biaxial indicatrix corresponds to the numerical value of the refractive index. Thus the orthorhombic, monoclinic, and triclinic crystals possess three indices of refraction. The values are identified in increasing numerical numbers as alpha, beta, and gamma. The positive and negative biaxial indicatrices are illustrated in Figs. 9.18 and 9.19.

The three axes of the triaxial ellipsoid are XX' (shortest axis), YY' (intermediate axis), and ZZ' (longest axis). The optic axes lie in the XZ plane, and XX' or ZZ' will bisect the acute angle made between the optic axes. If XX' bisects the acute angle, the indicatrix is negative. If ZZ' bisects the acute angle, the indicatrix is positive. Respectively then the ZZ' or XX' will be the obtuse bisectrix. Perpendicular to the optical axes and to the XZ plane is YY' . This intermediate axis is termed the "optic normal." Perpendicular to each optic axis is a circular section, the diameter being equivalent to YY' .

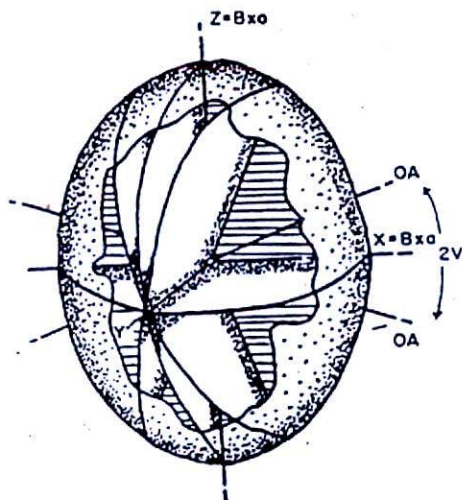


FIGURE 9.19: The negative biaxial indicatrix. OA is the optic axis. Courtesy of John Wiley & Sons.

Whereas the biaxial indicatrix as such is not observed under the microscope, observations are seen which can be correlated with the indicatrix. If the observer looks at a section parallel to the XZ plane, he is looking down the Y axis. An interference figure called the "optic normal figure" is seen. This figure is somewhat analogous to the flash figure observed with a uniaxial figure. When the crystal with the optic normal orientation is placed in the position of extinction, the interference figure is a cross. When the stage is rotated, the isogyres (black brushes) will rapidly leave the field in either the first and third quadrant or the second and fourth quadrant depending on what direction the stage is rotated. On continued rotation the isogyres will come back into the field in the alternate quadrants and form the cross at the position of extinction.

If the observer looks at a section perpendicular to the axis bisecting the acute angle made by the two optic axes (termed the "acute bisectrix" and

abbreviated as Bxa) in the position of extinction, a cross is observed. On rotating the stage, the isogyres separate and come together again during a 90° rotation. If the observer is looking at a section perpendicular to the obtuse bisectrix when the crystal is in the extinction position, a cross is observed and will separate on rotation of the stage. The obtuse bisectrix figure separates more rapidly when the stage is rotated than does the acute bisectrix figure. The optic normal separates the most rapidly on rotation of the stage. If the acute angle is small enough, the isogyres will not leave the field when the stage is rotated. With most microscopes, the isogyres will leave the field when the obtuse bisectrix figure is rotated. If one examines a crystal so oriented that the observed section corresponds to the circular section of the biaxial indicatrix, a cross is not observed—only a single brush. The interference figures corresponding to the various sections of the triaxial indicatrix are shown in Figs. 9.20 and 9.21.

When examining Fig. 9.20A-C and 9.21A-B, one observes concentric rings. The center of the concentric rings is the point of emergence of the optic axis. Therefore, the distance between the point of emergence of the two optic axes in Fig. 9.20A-C is a measure of the angle between the two optic axes (termed " $2V$ ").

In Fig. 9.22 the axes of the triaxial ellipsoid are located in the crystal. In Fig. 9.22A the crystal is located in the extinction position and in Fig. 9.22B the crystal is located in the 45° position. When the crystal is between crossed Nicol prisms, the convergent lens and Amici-Bertrand lens inserted, the interference figure is seen. In 9.22A the optic normal (YY') coincides with the vertical cross hair and the obtuse bisectrix coincides with the horizontal cross hair. When the crystal is rotated 45° so that the isogyres are located in quadrants 2 and 4, the optic normal (YY') is in the diagonal position in quadrants 1 and 3. The obtuse bisectrix is in the diagonal position in quadrants 2 and 4. The observer is looking down the acute bisectrix. Figure 9.22B corresponds to Fig. 9.20B or C.

By definition, the length of the semiaxis of the triaxial ellipsoid corresponding to the refractive index, XX' , YY' , and ZZ' , corresponding to alpha, beta, and gamma. It has been previously stated that the refractive index is inversely proportional to the velocity of the light. Therefore, the velocity of light vibrating in the XX' plane is the fastest, the velocity of light vibrating in the ZZ' plane the slowest, and the velocity of light vibrating in the YY' plane the intermediate. In Fig. 9.22B, the light vibrating in the diagonal plane in quadrants 1 and 3, represents rays parallel to the optic normal and the light vibrating in the diagonal plane in quadrants 2 and 4 represents the rays parallel to the Bxo.

This condition holds for that section between the convex sides of the isogyres.

With this knowledge, the optic sign of the crystal may be determined. Consider that a crystal fragment is so oriented that a centered acute bisectrix

figure is obtained. The observer places the crystal such that the isogyres are in quadrants 1 and 3 in the 45° position (see Fig. 9.20C). The plane of vibration of YY' is diagonal in quadrants 2 and 4. The plane of vibration of ZZ' is diagonal in quadrants 1 and 3. The planes of vibration of the fast and slow rays are therefore known. The first-order red test plate is then inserted in the slot above the objective. Yellow or orange spots are seen next to the optic axis on the convex side of the isogyres. As recalled, yellow or orange results

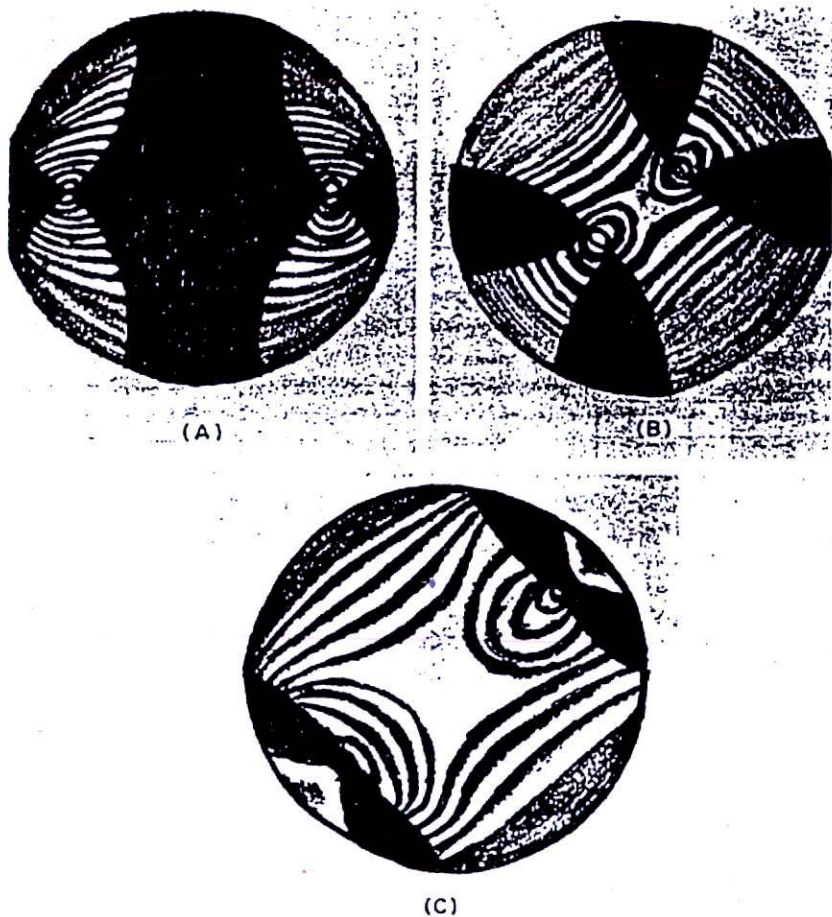


FIGURE 9.20: The acute bisectrix interference figure. (A) Crystal in extinction position. (B) Acute bisectrix with small $2V$. (C) Acute bisectrix with moderate $2V$.

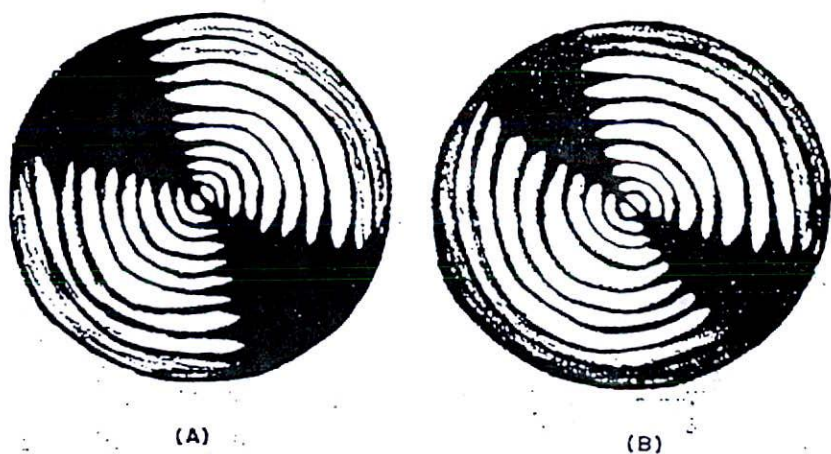


FIGURE 9.21: The biaxial optic axis interference figure. (A) Symmetrical isogyre indicating $2V$ to be 90° . (B) Nonsymmetrical isogyre indicating $2V$ to be less than 90° .

because the plane of vibration of the slow ray of the first-order red plate is vibrating parallel to the fast ray of the crystal fragment. Knowing the direction of vibration of the slow ray of the test plate, the direction of vibration of the fast ray of the crystal fragment is thus determined. If the crystal fragment is then rotated 90° so that the isogyres are in quadrants 2 and 4, one will observe a blue patch next to the point of emergence of the optic axis on the convex side of the isogyre.

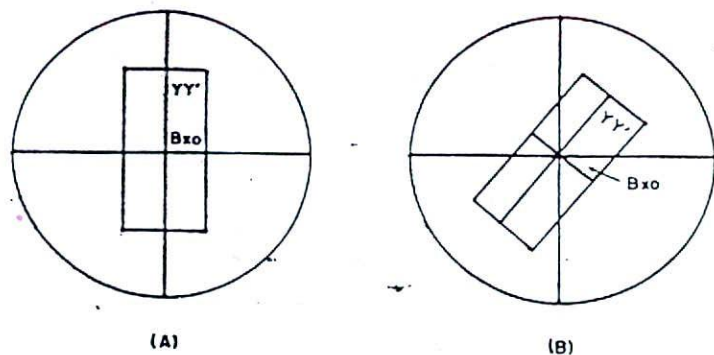


FIGURE 9.22: A section of an orthorhombic crystal including the optic normal and the obtuse bisectrix. (A) The section in the extinction position and (B) in the 45° position.

9.8 DISPERSION

In some instances, which is true of many organic compounds, there is an abnormal change of refractive index with different wavelengths of light. This condition is called the "dispersion of the indices of refraction." Dispersion is essentially the scattering of the components of white light along different paths. Dispersion of the refractive indices is possible in any of the six crystal systems. Rarely, if at all, is the dispersion of the indices in the anisotropic crystals regular.

In biaxial crystals there can be dispersion of the optic axes. In uniaxial crystals such dispersion does not occur because the optic axis for different wavelengths of light parallels the c axis. In orthorhombic crystals dispersion of the optic axes is termed "axial dispersion." The optic axes for different wavelengths of light lie in the XZ plane, but $2V$ changes with different wavelengths of light.

Axial dispersion is expressed by a dispersion formula which states that $2V$ for red light is less than or greater than $2V$ for violet light. Red and violet are chosen as these colors are most generally seen. When white light is used, violet light is cut out along the optic axis for this monochromatic light. The color at the opposite end of the spectrum, red, appears. At the point of emergence of the optic axis for red light, violet light will appear. If $2V$ for red light is greater than $2V$ for violet light, the dispersion formula is $r > v$. Some crystals will show axial dispersion, $v > r$. Another type of dispersion which may occur in orthorhombic crystals is crossed axial plane dispersion. In this instance the optic planes for red and violet light are perpendicular. At some intermediate wavelength of light, the crystal becomes uniaxial.

Three different types of dispersion may arise in monoclinic crystals, depending on the orientation of the triaxial ellipsoid. One of the planes of symmetry of the indicatrix is parallel to the plane of symmetry of the crystal. One of the axes of the indicatrix coincides with the b axis of the crystal.

When the acute bisectrix parallels the b axis, the obtuse bisectrix and the optic normal lie in the plane of symmetry. Dispersion takes place by the rotation of the optic plane around the b axis. The optic normal and the obtuse bisectrix lie in the plane of symmetry. In this instance the optic planes for different wavelengths of light are crossed. This condition is termed "crossed dispersion."

When the obtuse bisectrix parallels the b axis, the acute bisectrix and the optic normal lie in the plane of symmetry of the crystal. Dispersion takes place by rotation of the optic plane around the b axis. In the direction of the acute bisectrix the optic planes for different wavelengths of light are parallel to each other. This condition is termed "horizontal dispersion."

It is to be noted that when the B_{2m} shows crossed dispersion, the B_{2o} shows horizontal dispersion. Conversely, if the B_{2o} shows horizontal dispersion, the B_{2m} shows crossed dispersion.

A third type of dispersion is seen if the optic normal coincides with the b axis. The acute and obtuse bisectrices lie in the plane of symmetry. The dispersion arises from the rotation of the optic plane on the optic normal. The optic plane for different wavelengths of light are in the same plane. However, the optic axes for the different wavelengths of light are inclined to each other. This condition is termed "inclined dispersion".

In the three types of dispersion in monoclinic crystals, which are independent of the dispersion of the indices of refraction, there is always dispersion of the optic axes—namely, axial dispersion. Crossed axial plane dispersion may occur in monoclinic crystals.

The triclinic system has no plane of symmetry as the crystallographic axes are inclined to each other. None of the ellipsoidal axes corresponds to the crystallographic axes, so dispersion of the refractive indices, the optic axes, and the bisectrices are irregular.

Dispersion of the optic axes and the ellipsoid is seen when looking at an interference figure. When the crystal is in the extinction position, axial or inclined dispersion is not seen as the optic plane, for different wavelengths of light, is in the same plane as white light. When the crystal is in the extinction position, crossed or horizontal dispersion can be seen. With horizontal dispersion red light will appear in quadrants 1 or 2 or 3 and 4. Violet light will appear in quadrants 3 and 4 or 1 and 2, respectively. With crossed dispersion red light will appear in quadrants 1 and 3 or 2 and 4. Violet light will appear in 2 and 4 or 1 and 3, respectively.

Dispersion of the indices of refraction is observed when the source of light is white light and the image of the crystal is seen. In such instances the crystal may not disappear in immersion oils. However, when the index of refraction in question is obtained, a band of blue light and a band of yellow light around the edge of the crystal will move in opposite directions as the focus is raised.

9.9 MOLECULAR ORIENTATIONS IN THE SOLID STATE

Optical and magnetic studies led to the use of anisotropy in predicting molecular orientations. Wells and Evans have summarized these relationships.

In crystals containing planar atoms or groups with all their planes parallel, a large negative birefringence is expected with two high and comparable refractive indices for light polarized in the plane of the groups and one much lower index for vibrations at right angles to this plane. When planar groups are all parallel to a line but not parallel to each other, strong positive birefringence is expected, since the single vibration direction parallel to all the groups will be associated with a much smaller velocity than in any other direction. When planar groups are inclined in all directions, no large birefringence is to be expected.

Vibrations along the length of rod-shaped molecules or atom groups correspond to much greater polarization than vibrations in any other direction. A large positive birefringence is expected when the rod-shaped groups are all parallel to one direction. When the groups are all parallel to a plane but not to each other, a large negative birefringence is expected. If the rod-shaped groups are inclined in all directions, the resulting crystal is isotropic or approximately so.

EXPERIMENTAL PROCEDURES

- E9.1. Recrystallize sodium chloride from an aqueous solution using the microscopic procedure described previously. After placing the cover slip on the recrystallized sodium chloride in the solution, place the cooled slide on the stage of the microscope. Examine the crystals using white light. Examine the crystals between crossed Nicol prisms. It will be noted that all of the crystals examined show complete extinction between the crossed Nicol prisms. Sodium chloride is isomeric.
- E9.2. Recrystallize sodium chloride from an aqueous solution of urea and compare the habit obtained in this manner with the habit obtained by crystallization from distilled water. Cubic forms are obtained when crystallized from distilled water and octahedral forms are obtained when crystallized from a solution of urea.

Habit variations may also be observed by first crystallizing adipic acid from distilled water. Crystallize a second batch from 0.1% benzalkonium chloride. Finally crystallize a third batch from 0.1% sodium lauryl sulfate.

- E9.3. Recrystallize methylprednisolone (Medrol) from an oiling solution of *n*-butyl alcohol. Examine the crystals under the microscope obtained when crystallized above 117°C. Recrystallize the steroid at a temperature below 117°C. Also heat the solution above 120°C and allow to cool slowly. After standing for a few minutes examine the crystals under the microscope. Two forms should be evident. Allow the solution to stand for 24 hours and reexamine the crystals. The low temperature form should be present. The high temperature form is therefore metastable at room temperature and also more soluble than the low temperature form. Methylprednisolone is dimorphic.

Recrystallize diethylbarbituric acid (Barbital) from hot water. How many different forms can you identify? Repeat the microscopic study by crystallizing from concentrated ammonium solution and also after sublimation. Barbital is polymorphic.

- E9.4. Recrystallize ouabain from water at 4, 20, and 50°C. Examine the crystals under the microscope. They represent respectively the nonhydrate, octahydrate, and dihydrate of ouabain. The tetrahydrate may be obtained by recrystallizing from 97% methanol. The 4½ hydrate is obtained by recrystallizing from 95% ethanol.

The monoethanol solvate form of hydrocortisone *t*-butylacetate may be obtained by crystallization from 95% ethanol. When crystallized from 20% ethanol, the anhydrous form of the ester is obtained. Examine the two crystalline forms under the microscope.

- E9.5. Examination of tetragonal crystal with and without the use of crossed Nicol prisms. Recrystallize urea from water using the microscopic technique. Note the columnar crystals. The extinction is parallel. Between crossed Nicol prisms different crystals will show different polarization colors. The colors vary because the thickness of the crystals is different.
- Obtain some fluorocortisone acetate and crystallize from approximately 50% ethanol. Examine under the microscope with and without the analyzer in the body tube. Complete extinction should be observed with most of the crystals studied. Crystallize the fluorocortisone acetate using the macroscopic technique. Filter and dry the crystals. Place a few crystals on a microscope slide and suspend them in Canada balsam. Place a cover slip on the balsam. Focus on a crystal under the microscope. If the cover is gently moved, the crystal, if not too large, will roll. After balancing the fluorocortisone acetate crystal on its side, one will observe parallel extinction between crossed Nicol prisms. Danthron and potassium dihydrogen phosphate are tetragonal.
- E9.6. Examination of hexagonal crystals under the microscope. Repeat experiment 9.5 by (a) crystallizing lead iodide from water, (b) iodoform from water, (c) thymol from water-ethanol solution, (d) tartar emetic from water, (e) sodium nitrate from water. Examine crystals between crossed Nicol prisms, rolling the crystals in Canada balsam.
- E9.7. Examination of orthorhombic crystals under the microscope. Repeat experiment 9.5 by (a) crystallizing sulfacetamide from water-ethanol (b) sulfanilamide from water, (c) potassium nitrate or potassium sulfate from water, (d) *p*-aminohippuric acid from water, (e) codeine sulfate from water-ethanol. Examine between crossed Nicol prisms, rolling the crystals in Canada balsam.
- E9.8. Examination of monoclinic crystals under the microscope. Repeat experiment 9.5 by (a) crystallizing antipyrine, aprobarbital, ephedrine HCl, pheniramine maleate from water. Other monoclinic crystals include salicylamide, quinine dihydrochloride, *p*-aminobenzoic acid. Many organic medicinals are monoclinic substances.
- E9.9. Examination of triclinic crystals under the microscope. Repeat experiment 9.5 by (a) recrystallizing copper sulfate from water, (b) phenolphthalein from water or water-ethanol, (c) naphazoline hydrochloride from water.
- E9.10. Recrystallize sodium chloride so that suitable crystals are obtained. Dry the crystals well. Mount the crystals on a microscope slide using the following immersion oils (a) mineral oil, (b) Canada balsam or nitrobenzene and (c) α -bromnaphthalene or methylene iodide. Focus sharply on the crystals and then note the movement of the Becke line as focused upward and downward.
- E9.11. Using the refractive index oils, determine the refractive index of (a) NaCl, (b) NaBr, (c) NaI. Relating the refractive index to the polarizability, and knowing that the polarizability of the halides increases with molecular weight, is it surprising that the relationship of the refractive index to the sodium halides exist as found in this experiment?
- E9.12. Determine the two principal indices of refraction for urea. To gain experience, also determine the two principal indices of refraction for

- fluorocortisone acetate and lead iodide. With the latter two compounds, the habit is such that the common orientation is a section perpendicular to the *c* crystallographic axis. This orientation will show complete extinction. The crystals must then be crushed so that various random orientations will be obtained. Choose the orientation showing the greatest polarization colors.
- E9.13. Place a few crystals of sodium nitrate on a microscope slide. Cover the crystals with a cover slip. Heat the slide over a microburner until the crystals have liquified. Cool the slide and examine the fused material under the microscope. Insert the convergent lens, analyzer, and Amici-Bertrand lens. Move the slide around until an optic-axis uniaxial interference figure is obtained. With the aid of the first-order test plate, determine the optic sign. Also observe the movement of the isochromatic curves appearing in the four different quadrants when the quartz wedge is inserted.
- E9.14. Obtain some fluorocortisone acetate, crystallize from 50% ethanol, and determine the crystal system, optic sign, and the refractive indices. Repeat the procedure for iodoform, urea, and tartar emetic. The common orientation for the first two compounds is a centered optic-axis figure. The common orientation for the latter two compounds is the flash figure. You will observe that the two indices of refraction will be more difficult to determine when the common orientation is the optic-axis figure.
- E9.15. Obtain a small sheet of mica. Separate the sheet into thinner sections. Mount one of these sections on the petrographic stage. Examine the interference figure. This is an acute bisectric. Rotate the stage until the isogyres are in quadrants 2 and 4. Determine the optic sign using the first-order red test plate. Repeat the examination with the isogyres in quadrants 1 and 3.
- E9.16. Obtain some ouabain and crystallize from water at room temperature. The octahydrate is isolated. Mount isolated crystals in Canada balsam and examine the crystal. Determine what interference figure is common to this section. Then roll the crystal 90° so that you are looking at another section of the crystal. Determine the interference figure common to this new section. Having determined the orientation of the biaxial indicatrix by rolling the crystal, then determine the optic sign, dispersion, and principal indices of refraction for ouabain octahydrate.

QUESTIONS

- Q9.1. Compare and/or differentiate:
- isoaxial, uniaxial, and biaxial
 - dynamic isomerism and dimorphism
 - monoclinic and triclinic
 - dispersion in tetragonal and orthorhombic crystals
- Q9.2. Compare the refractive indices (handbook values) of NaCl, NaBr, and NaI. Explain the values. (*Hint*: Check the values with the specific refraction values of the halogens.)
- Q9.3. Crystals of aromatic molecules such as purines will cleave readily one in

- plane, but not in other planes of the crystals. The cleavage is parallel to the plane of the purine nucleus. Explain why this characteristic cleavage occurs.
- Q9.4. (a) Will the refractive index for isometric crystals change when different monochromatic light sources are used?
 (b) How would one determine the refractive index of a colored isometric crystal using the refractive index oils described?
- Q9.5. Under what conditions will optical crystallography be valuable to a structural crystallographer?
- Q9.6. (a) Assuming the orthorhombic crystal illustrated in Fig. 9.22 to be a negative crystal, what kind of an interference figure would be seen if:
 (i) the investigator looked at a section including the XX' and ZZ' axes?
 (ii) the investigator looked down the XX' axis?
 (b) Does the crystal illustrated in Fig. 9.22B show (+) or (-) elongation?

REFERENCES

1. F. E. Wright, *J. Am. Chem. Soc.*, **38**, 1647 (1916).
2. A. N. Winchell, *The Optical Properties of Organic Compounds*, Academic Press, New York, 2nd ed., 1954.
3. A. Johannsen, *Manual of Petrographic Methods*, McGraw-Hill, New York, 1918.
4. A. N. Winchell, *Elements of Optical Mineralogy*, Part I, Wiley, New York, 1937.
5. E. M. Chamot and C. W. Mason, *Handbook of Chemical Microscopy*, Vol. I, Wiley, New York, 2nd ed., 1938.
6. N. H. Hartshorne and A. Stuart, *Crystals and the Polarising Microscope*, Arnold, London, 1934.
7. E. E. Wahlstrom, *Optical Crystallography*, Wiley, New York, 1960.
8. L. Fletcher, *The Optical Indicatrix*, Frowde, London, 1892; quoted by E. E. Jelley, in *Physical Methods of Organic Chemistry*, (A. Weissberger, ed.), Wiley (Interscience), New York, 1945, p. 458.
9. W. Barlow and W. J. Pope, *J. Chem. Soc.*, **89**, 1675 (1906).
10. G. N. Lewis, *CA*, **1**, 1809 (1907).
11. F. M. Jaeger, *Z. Krist.*, **44**, 61 (n.d.); see *CA*, **2**, 498 (1908).
12. E. H. Rodd, *Proc. Roy. Soc. (London)*, **A292**, 313 (1913-1914).
13. J. Drugman, *Z. Kryst. Mineral*, **53**, 240 (n.d.); see *CA*, **8**, 1111 (1914).
14. R. T. Colgate and E. H. Rodd, *J. Chem. Soc.*, **97-98**, 1585 (1910).
15. E. T. Wherry, *J. Wash. Acad. Sci.*, **8**, 277, 319 (1918).
16. L. Déverin, *Chem. Zentr.*, **109**, 847 (1938, II).
17. H. A. Lorentz, *Ann. Physik.*, **9**, 641 (1880).
18. L. Lorentz, *Ann. Physik*, **11**, 70 (1880).
19. J. W. Brühl, *J. Chem. Soc.*, **91**, 115 (1907).
20. K. S. Krishna, B. C. Guha, and S. Banerjee, *Trans. Roy. Soc. (London)*, **A231**, 235 (1933).
21. K. Lonsdale and K. S. Krishnan, *Proc. Roy. Soc. (London)*, **A156**, 597 (1936).
22. L. Pauling, *J. Chem. Phys.*, **4**, 673 (1936).
23. A. F. Wells, *Structural Inorganic Chemistry*, Oxford, New York, 1945, p. 230.
24. R. C. Evans, *An Introduction to Crystal Chemistry*, Cambridge, New York, 2nd ed., 1964, p. 116.
25. W. C. McCrone, *Fusion Methods in Chemical Microscopy*, Wiley (Interscience), New York, 1957.