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Optical measurements of anthracene. By MAUREEN M. JULIAN and F. DONALD BLOSS, *Department of Geological Sciences, Virginia Polytechnic Institute and State University, Blacksburg, Virginia 24061, USA*

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Abstract

In biaxial crystals, measurement of the angle between the two optic axes, $2V$, is constant for a given crystal, at a given temperature, and for a given wavelength. A study of the optical properties of anthracene ($C_{14}H_{10}$) was done because of conflicting results in the literature and because recently developed techniques introduce computer and statistical methods into the practice of optical crystallography permitting greater accuracy. For anthracene at $20^\circ C$, $2V = 90.0 (1.8)^\circ$ at 540 nm, and $2V = 89.4 (1.8)^\circ$ at 900 nm. The work was complicated by the fact that the anthracene crystal rapidly dissolves in immersion media. Data were completed on four separate crystals, three at 540 nm and one at 900 nm. The data were analyzed by the Bloss–Reiss–Rohrer program *EXCALIBUR* with Joel's equation to find the optic axes, and refinement was done by least squares to calculate an accurate $2V$. The molecular refractivities are calculated from the crystalline refractivities. The optical and diamagnetic data are compared.

Introduction

In biaxial crystals, measurement of the angle between the two optic axes, $2V$, (Bloss, 1961, Fig. 9-2) is constant for a given crystal, at a given temperature, and for a given wavelength. For anthracene ($C_{14}H_{10}$) a wide range of principal refractive indices n_1 , n_2 and n_3 have been reported (Table 1). The standard formula

$$\cos V = \frac{n_1}{n_2} \left(\frac{n_3^2 - n_2^2}{n_3^2 - n_1^2} \right)^{1/2} \quad (1)$$

relates the optic axial angle, $2V$, to the principal refractive indices. The large discrepancy seen in Table 1 indicates significant error in the literature. A study of the optical properties of anthracene thus seemed in order, particularly because recently developed techniques introduce computer and statistical methods into the practice of optical crystallography and permit greater routine accuracy.

Table 1. *Optical data for anthracene*

λ (nm)	n_1	n_2	n_3	$2V$	Reference
546	1.556	1.786	1.959	107.8°	Sundararajan (1936)
546	1.43	1.79	2.04	115.0°	Sundararajan (1936)
546	1.57	1.817	2.22	90°	Winchell (1954)
490	1.59	1.86	2.26	95°	Winchell (1954)
420	1.64	2.07	2.41	113°	Winchell (1954)
589	1.959	1.485	1.837	129°	Lasheen & Abdeen (1972)
	(assumed)				
540	1.553	1.810	2.259	90.01°	This work

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Experimental

For anthracene crystals precipitated from amyl acetate, $2V$ was determined by mounting the crystal to be studied on a spindle stage that was fastened to the stage of a polarizing microscope. The techniques, described by Bloss & Riess (1973), involve rotation of the crystal about an axis parallel to the microscope stage – by varying the spindle setting (S settings) by 10° intervals between $S = 0$ and $S = 170^\circ$ – and, at each of these eighteen S settings determining the microscope stage setting (M) that produce crystal extinction. The data was analyzed by the Bloss–Reiss–Rohrer program *EXCALIBUR* with Joel's equation (Joel, 1966) to find the optic axes, and refinement was done by least squares to calculate $2V$ usually accurate to 1 or 2° . A further advantage of the technique is that, if crystal extinction is determined photometrically, values of $2V$ for wavelengths beyond the visible range can also be determined. The results for four separate crystals of anthracene are as follows:

crystal 1	$2V = 92.76^\circ$ e.s.d. 4.75° at $\lambda = 540$ nm
crystal 2	90.01° e.s.d. 1.80° 540 nm
crystal 3	90.27° e.s.d. 3.38° 540 nm

average of crystals 1, 2 and 3

	91.01° average of standard error
	of the mean 1.91° 540 nm
crystal 4	89.45° e.s.d. 1.77° 900 nm.

Crystals 2 and 4 have the best standard deviations and their values will be used.

Anthracene proved soluble in the Cargille immersion oils. During determination of $2V$ by the Bloss–Reiss method, this solubility necessitated collection of the crystal extinction data within 20 min, the time that usually elapsed before the solution caused the dissolving crystal to drop off the spindle and terminate its study. This time constraint did foster random experimental errors in the extinction measurements and thus caused e.s.d.'s for $2V$ to be as high as 4.75° whereas, for crystals whose extinctions can be measured without time pressure, the e.s.d.'s computed for $2V$ are usually 1° or less. The solubility of anthracene in the immersion media proved to be a more serious problem when determining the principal refractive indices of anthracene because such solution probably caused a significant change in the refractive index of the oil, particularly at the grain–oil faces where the Becke line tests are performed. The values found in this work are listed in Table 1.

Under ordinary circumstances – that is, insolubility of the crystals in the immersion media – the Bloss–Reiss method yields not only a value of $2V$ and its e.s.d. but also the settings of the spindle stage and the microscope stage that will correctly orient the crystal so that each of its principal refractive indices (n_1 , n_2 and n_3) can be tested relative to the

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oil. The result is that these principal refractive indices can be measured without appreciable error stemming from crystal misorientations. For anthracene it was necessary to deviate from these standard spindle stage methods. Instead, an anthracene crystal mounted on a spindle was first observed 'dry'. Fortunately the crystals were sufficiently large so that conoscopic interference figures could be obtained even with a medium power (20 \times) objective. Relating these interference figures to the morphology of the crystals showed that the principal vibration axis $\mathbf{Y} = \mathbf{b}$ which means that the (010) plane is the optic plane and the crystallographic b monoclinic axis is the optic normal. Experimentally it is observed that $\angle \mathbf{Zc} = 7.5^\circ$ (Winchell, 1954).

Commercially available oils (*i.e.* Cargille) are well standardized in the refractive index region between 1.300 to 2.00 where indices of refraction for most minerals lie. In this study the measured values for anthracene are $n_1 = 1.553$ and $n_2 = 1.810$ by the Becke line method at 540 nm. Extinction measurements gave $2V = 90.01^\circ$. With these values in (1), n_3 can be calculated to be 2.259, which is well outside the range of the oils. Since this value is difficult to check experimentally this would be a major source of error for the literature values.

Optical anisotropies

The relationship between the optical anisotropic properties and the molecular shape and packing supplies a good internal check on the optical and structural data and also gives information that can be correlated with the magnetic anisotropies.

J. M. Robertson (1933) determined the crystal structure of anthracene and D. W. J. Cruickshank (1956) and later R. Mason (1964) refined it with $a = 8.561$, $b = 6.035$, $c = 11.163$ Å, $\beta = 124^\circ 42'$, $Z = 2$, monoclinic, $P2_1/a$, $M = 178.2$ g mol $^{-1}$ and $D = 1.26$ Mg m $^{-3}$.

The Lorentz-Lorenz equation (Lonsdale, 1949) can be used to calculate the three orthogonal gram molecular refractivities R_i of any crystal along direction i .

$$R_i = \frac{(n_i^2 - 1)M}{(n_i^2 + 2)D}, \quad (2)$$

where n_i is the refractive index of the crystal in the i direction, M is molecular weight and D is density. The refractivity along the b monoclinic axis is 61.012 which according to the notation of Lonsdale & Krishnan (1936) is R_3 . R_1 and R_2 are chosen such that $R_1 < R_2$. For anthracene the crystalline refractivities calculated from (2) are

$$R_1 = 45.258 \quad R_2 = 81.696 \quad R_3 = 61.012.$$

Derivation of relationship between molecular and crystalline refractivities

The molecular refractivities r_L , r_M , r_N along molecular axes L , M , N (Fig. 1) can be calculated from a combination of the crystalline refractivities and information on the packing and shape of the molecules. In the case of anthracene there are two planar molecules in the unit cell. Choose orthogonal crystallographic axes a and b and a third axis c' per-

pendicular to both of them. Note c' is in the (010) plane. The nine direction cosines relative to these three axes a , b , and c' are:

	a	b	c'
L	-0.4960	-0.1248	0.8593
M	-0.3234	-0.8919	-0.3162
N	0.8059	-0.4347	0.4020

The direction cosines α_j , β_j , and γ_j where $j = L, M, N$ of the first molecule are related to those of the second molecule by α_j , $-\beta_j$, and γ_j . The two sets of tensors representing the two molecules can be combined to give the nine resultant components:

$$r_{aa} = r_L \alpha_L^2 + r_M \alpha_M^2 + r_N \alpha_N^2 \quad (3)$$

$$r_{bb} = r_L \beta_L^2 + r_M \beta_M^2 + r_N \beta_N^2 \quad (4)$$

$$r_{c'c'} = r_L \gamma_L^2 + r_M \gamma_M^2 + r_N \gamma_N^2 \quad (5)$$

$$r_{bc'} = r_{c'b} = 0 \quad (6)$$

$$r_{c'a} = r_{ac'} = r_L \alpha_L \gamma_L + r_M \alpha_M \gamma_M + r_N \alpha_N \gamma_N \quad (7)$$

$$r_{ab} = r_{ba} = 0. \quad (8)$$

r_{bb} is the component along the b monoclinic axis and as stated above will be defined as R_3 . In order to get R_1 and R_2 , a diagonalization is done to eliminate the cross terms. Since the trace is invariant,

$$R_1 + R_2 + R_3 = r_L + r_M + r_N = r_{aa} + r_{bb} + r_{c'c'}. \quad (9)$$

The angle φ that R_1 and R_2 have to be rotated in the (010) plane is

$$\tan 2\varphi = \frac{2r_{ac'}}{r_{aa} - r_{c'c'}}. \quad (10)$$

Also

$$R_1 = 0.5 \{ r_{aa} + r_{c'c'} \pm [(r_{aa} - r_{c'c'})^2 + 4r_{ac'}^2]^{1/2} \}$$

$$R_2 = 0.5 \{ r_{aa} + r_{c'c'} \mp [(r_{aa} - r_{c'c'})^2 + 4r_{ac'}^2]^{1/2} \}.$$

Since the crystalline refractivities R_1 , R_2 and R_3 can be measured, the above equations are solved for the molecular refractivities r_L , r_M and r_N and the angle μ . Mathematically there are two solutions:

$$r_L = 45.084, \quad r_M = 54.919, \quad r_N = 87.967, \quad \mu = 7.3^\circ \quad (11)$$

and

$$r_L = 81.988, \quad r_M = 65.470, \quad r_N = 40.507, \quad \mu = 6.6^\circ, \quad (12)$$

where $\mu = \angle \mathbf{Zc} = \beta - \pi/2 - \varphi$. The experimentally observed value for μ is 7.5° (Winchell, 1954), see Fig. 2.

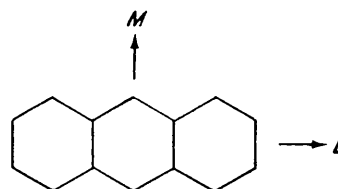


Fig. 1. Molecular axes for anthracene.

The calculations so far are not dependent on the shape of the molecule. If it is assumed that the *molecular* refractivity is directly proportional to the density, then it is implied that, for a large planar molecule, the refractivity normal to the plane would be less than the refractivities in the plane of the molecule, i.e. $r_N \ll r_L$ or r_M . (The opposite would be expected for the diamagnetic anisotropies K_L, K_M and K_N , i.e. $K_N \gg K_L$ or K_M .) In the limiting case where K_N completely dominates K_L and K_M or where $r_L = r_M$ and r_N essentially vanishes, then $\tan 2\varphi = 2\alpha_N \gamma_N / (\alpha_N^2 - \gamma_N^2)$. φ becomes a function only of the direction cosines. In the limiting case $\mu = 8.2^\circ$ for anthracene. Also in the limiting case $r_L \sim R_1$ or R_2 . In the anthracene case from (11), $r_L = 45.084$ and $R_1 = 45.258$, from (12), $r_L = 81.988$ and $R_2 = 81.696$.

Thus from density considerations the values from (12) ought to be chosen over (11) even though the experimental value of μ is closer in (11).

With the equation from Lasheen & Abdeen (1972) the molecular anisotropy can be calculated:

$$\Delta r = 0.5(r_L + r_M) - r_N = 33.51.$$

It is useful to compare the diamagnetic and optical effects. The diamagnetic anisotropies K_L, K_M and K_N are calculated from the magnetic susceptibilities χ_1, χ_2 , and χ_3 in a manner similar to the calculations of the molecular optical anisotropies r_L, r_M , and r_N from the gram molecular refractivities R_1, R_2 and R_3 . In the optical case r_N is chosen $\ll r_L$ or r_M whereas in the diamagnetic case K_N is chosen $\gg K_L$ or K_M .

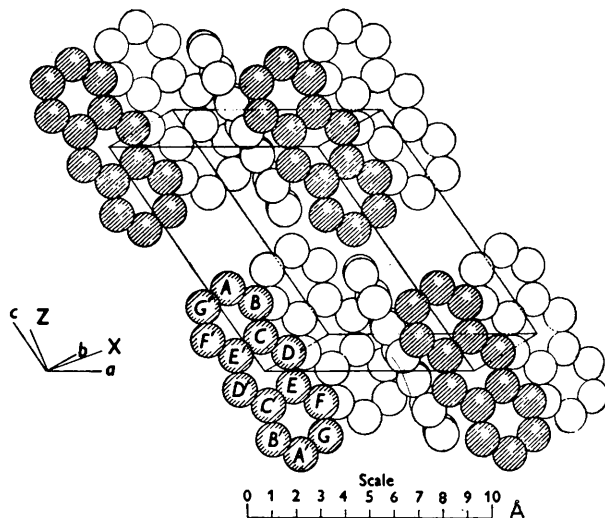


Fig. 2. (Adapted from Sinclair, Robertson & Mathieson, 1950.) Packing of anthracene molecules in the unit cell. Crystallographic axes a, b and c ; principal vibration axes $x, y = b$, and z .

The molecular data:

diamagnetic	$K_L = -910$ $\Delta K = 2181$	$K_M = -902$ $\mu_{\text{calc}} = 8.2^\circ$	$K_N = -3079$ $\mu_{\text{exp}} = 9.6^\circ$
optical	$r_L = 82.0$ $\Delta r = 33.5$	$r_M = 65.5$ $\mu_{\text{calc}} = 6.6^\circ$	$r_N = 40.5$ $\mu_{\text{exp}} = 7.5^\circ$

Calculated from the crystalline data:

diamagnetic	$\chi_1 = -910$	$\chi_2 = -2675$	$\chi_3 = -1317$
optical	$R_1 = 45.3$	$R_2 = 81.7$	$R_3 = 61.0$

The molar diamagnetic data are from Lasheen (1968) except for μ which was calculated from Lasheen's data. The units of molar diamagnetic susceptibility or anisotropy are $\text{m}^3 \text{mol}^{-1}$ and a factor of 10^{-12} has been omitted in the diamagnetic data. The Lasheen data have been converted to SI units. [For a useful discussion of the conversion see Pass & Sutcliffe (1971).]

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