The Determination of the Orientation of Anthracene Molecules in the Unit Cell by a Refractivity Method

By Szu-Lin Chen, John C. Schug and Jimmy W. Viers

Department of Chemistry, VPI & SU, Blacksburg, VA 24061, USA

Abstract

The monoclinic anthracene crystal is used as an example to demonstrate the feasibility of optimizing the orientation of molecules in the unit cell by matching calculated and experimental refractivity ellipsoids using a simplex algorithm. The calculated refractivity ellipsoid is determined by use of an empirical formula using bond directional polarizabilities. Optimization of the molecular orientations to provide the best fit to the experimental ellipsoid starting from several assumed orientations results in fits for which the maximum deviation from the experimental molecular orientation was no more than 10°. The method can be applied to other monoclinic molecular crystals directly and could be extended to other crystal systems with anisotropic optical properties.

Introduction

The dependence of a crystal's refractive indices on the structure and orientation of its constituent molecules has been exploited in several different ways. Bragg (1924*a*, *b*) and Zachariasen (1933) calculated the refractive indices of calcite, aragonite and sodium bicarbonate crystals from their atomic arrangements. On the basis of the birefringence in calcite and sodium nitrate crystals Bragg (1924*b*) determined the bond distance for N–O. Bhagavantam (1929, 1930) determined the magnetic and optical properties of aromatic compounds and attempted to relate the properties to the orientation of the molecules in the crystal lattice. For anthracene, using the molecular structure and its orientation from X-ray diffraction, Julian & Bloss (1982) calculated the molecular refractivities from the refractive indices of the crystal. Bunn (1961) calculated its crystal refractive indices from the directional bond polarizabilities of the molecular bonds. The purpose of the present study is to illustrate the reverse procedure; we investigate the possibility of determining the molecular orientation in the unit cell by matching the macroscopic optical properties of the crystal to those calculated from a molecular structure.

The macroscopic directional refractivities of the crystal, the density, the point/space group of the

Table 1. *Parameters for bond polarizabilities (Bunn,* 1961, *p.* 313)

	$10^{25} P_l$ cm^{-3}	$10^{25} P_t$ cm^{-3}
C—C (aromatic)	22·5	4·8
C—H	8·2	6·0

crystal and the crystal constants as well as the molecular structure are assumed to be known. Starting with empirical bond polarizabilities, we use the simplex method to optimize the molecular orientation by matching the orientation and shape of the crystal refractivity ellipsoid found experimentally. Although the discussion here is confined to anthracene, the idea can be extended to any other monoclinic crystal without difficulty. In fact, except for the cubic system with isotropic properties, this method should also be capable of extension to other crystal systems.

Method

To illustrate the method we use an approximate molecular geometry for anthracene in which the aromatic rings are assumed to be regular hexagons, and all bond angles are taken to be 120°. Fig. 1 shows the idealized molecular geometry and indicates the directions (**l**, **m**, **n**) of the principal components of its polarizability tensor. We employ the standard longitudinal (P_l) and transverse (P_t) bond polarizabilities listed in Table 1 and calculate the three principal components of molecular polarizability by summing over all bonds, *b*:

$$p_i = \sum_b [P_l(b) \cos^2 A_{bi} + P_t(b) \sin^2 A_{bi}],$$
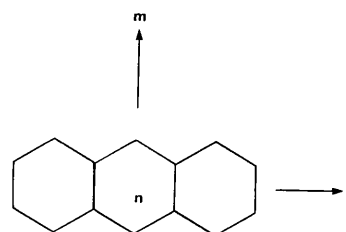
$$i = l, m, n, \qquad (1)$$

Fig. 1. The principal-axis system of anthracene.

where A_{bi} is the angle between the bth bond and the ith axis. The principal molar refractivities are then calculated from

$$r_{ii} = (4\pi/3)Np_i, \quad i = l, m, n, \tag{2}$$

where N is Avogadro's number. The values obtained for anthracene are:

$$r_{ll} = 76\cdot4, \quad r_{mm} = 69\cdot7, \quad r_{nn} = 34\cdot5 \text{ cm}^3 \text{ mol}^{-1}.$$

To describe the crystal refractivities, we use an orthogonal coordinate system (a', b', c'), where a' and b' are chosen parallel to the crystal axes a and b, and c' is taken perpendicular to a' and b'. For simplicity, (a, b, c') is used to express (a', b', c'). If we use u_{jk} to represent the direction cosine of unit vector j with respect to the direction k, and note that $u_{jk} = u_{kj}$, we have the following orthogonal transformation to transform the molecular refractivities to the (a, b, c') coordinate system:

$$R = \begin{bmatrix} u_{al} & u_{am} & u_{an} \\ u_{bl} & u_{bm} & u_{bn} \\ u_{c'l} & u_{c'm} & u_{c'n} \end{bmatrix} \begin{bmatrix} r_{ll} & 0 & 0 \\ 0 & r_{mm} & 0 \\ 0 & 0 & r_{nn} \end{bmatrix}$$
$$\times \begin{bmatrix} u_{la} & u_{lb} & u_{lc'} \\ u_{ma} & u_{mb} & u_{mc'} \\ u_{na} & u_{nb} & u_{nc'} \end{bmatrix}. \tag{3}$$

The anthracene crystal has symmetry $P2_1/a$. The two molecules in the unit cell differ in orientation only with respect to the signs of u_{lb}, u_{mb} and u_{nb}; the magnitudes of these as well as the magnitudes and signs of the other direction cosines are identical for the two molecules. When one averages the result of (3) for the two molecules in the unit cell the following is obtained for the molar refractivity of the crystal:

$$R = \begin{bmatrix} \sum_j r_{jj}u_{ja}^2 & 0 & \sum_j r_{jj}u_{ja}u_{jc'} \\ 0 & \sum_j r_{jj}u_{jb}^2 & 0 \\ \sum_j r_{jj}u_{ja}u_{jc'} & 0 & \sum_j r_{jj}u_{jc'}^2 \end{bmatrix}, \tag{4}$$

where $j = l, m, n$. The four zeros arise from the sign changes in u_{lb}, u_{mb} and u_{nb} noted earlier. The form of this matrix is typical of second-order tensor properties for monoclinic crystals (Sands, 1982). Diagonalization of this matrix yields three principal refractivities as the eigenvalues. The direction cosines of the principal axes relative to a, b and c' are obtained from the eigenvectors. The calculated matrix has a trace of 180·60, while the sum of the three principal refractivities from experiment (Julian & Bloss, 1982) is 187·97. The difference between these numbers reflects errors in the approximate molecular structure and in the empirical bond polarizabilities employed. This slight error will make exact predictions of molecular orientations impossible.

For each set of assumed molecular orientations a corresponding resultant ellipsoid can thus be calcu-

lated. For the monoclinic crystal the orientation of this ellipsoid in three-dimensional space is described by an angle between c' and the longest principal axis. The difference between the experimental and the calculated angles can be used as one standard for optimization of the molecular orientation in the unit cell. For anthracene $\beta = 124\cdot7$, $U = 7\cdot5°$ (the angle between the optical axis and the monoclinic c), so the experimental angle from c' is $27\cdot2°$. In addition, we can compare the shapes of the calculated and experimental ellipsoids as measured by the ratios R_2/R_1 and R_3/R_1. Here R_1 is the smallest eigenvalue and R_2 is the largest. For anthracene the ratios of the principal semi-axes of the experimental refractivity ellipsoid are $R_2/R_1 = 1\cdot805$ and $R_3/R_1 = 1\cdot348$.

A linear combination of these standards with different weighting factors (C_i) yields a function F, which can be minimized to determine the correct molecular orientation:

$$F = C_1|\Delta| + C_2|1\cdot805 - (R_2'/R_1')_{\text{cal}}|$$
$$+ C_3|1\cdot348 - (R_3'/R_1')_{\text{cal}}|. \tag{5}$$

Δ is the deviation between the experimental angle, $27\cdot2°$, and the calculated one.

Since the nine direction cosines for a molecule must satisfy the usual orthonormality conditions (Nye, 1957), only three out of the nine are independent. We chose u_{la}, u_{lb} and u_{ma} as the independent parameters. These must satisfy the consistency conditions:

$$u_{la}^2 + u_{lb}^2 \leq 1 \quad \text{and} \quad u_{la}^2 + u_{ma}^2 \leq 1,$$

to ensure that all direction cosines are real. For each choice of these three, we solved the orthonormality equations for the remaining direction cosines and used (4) to obtain the crystal refractivity tensor. Because of the quadratic nature of the orthonormality equations, this procedure gives eight different solutions, four of which refer to the orientation of each molecule in the unit cell. The four solutions for each molecule are related to one another by a reflection through the (a, b) plane and a second reflection through the (l, m) plane.

Optimization of the molecular orientation

A simplex algorithm (O'Neill, 1971) was used to minimize F [(5)] with respect to the orientation of the anthracene molecules. In practice, we found that there are an infinite number of ellipsoidal orientations with zero Δ, which indicates that the orientation condition as reflected in Δ is a weaker condition and the first term of (5) should receive relatively little weight. Best results were obtained with $C_1 = 0\cdot02$ and $C_2 = C_3 = 1\cdot0$.

Table 2 lists the three starting-angle sets and the optimized angle sets for several calculations. The actual orientation and the calculated orientation of

Table 2. *Optimized angle set of anthracene molecules in their monoclinic unit cell*

Start angles are l_a, l_b and m_a

Optimized angle set is expressed as following matrix form:

$$\begin{array}{ccc} l_a & l_b & l_{c'} \\ m_a & m_b & m_{c'} \\ n_a & n_b & n_{c'} \end{array}$$

The actual angle set for the first molecule in the unit cell is:

119·70	97·10	30·71
108·86	153·19	108·34
36·27	115·71	66·28

That for the second molecule in the unit cell is:

119·70	83·00	30·68
108·86	26·73	108·23
36·27	64·34	66·23

				Remarks
Start angles	5·00	87·00	85·00	
Step angles	30·00	30·00	30·00	
Weighting factors	0·02	1·00	1·00	
F	0·085			
Δ	0·000			
R2 R3 R1	76·400	59·803	44·397	
R2/R1 R3/R1 R2/R3	1·7208	1·3470	1·2775	
Optimized angle set	62·93	89·74	152·93	
	61·71	147·98	76·24	
	41·08	57·98	67·17	
Equivalent angle set	117·07	90·26	27·07	2nd
	118·29	32·02	103·76	molecule
	41·08	57·98	67·17	

Start angles	90·00	90·00	90·00
Step angles	30·00	30·00	30·00
Weighting factors	0·02	1·00	1·00
F	0·085		
Δ	−0·000		
R2 R3 R1	76·400	59·802	44·398
R2/R1 R3/R1 R2/R3	1·7208	1·3470	1·2775
Optimized angle set	117·19	90·02	27·19
	61·85	147·98	75·99
	138·94	122·02	112·80
Equivalent angle set	117·19	90·02	27·19	2nd
	118·15	32·02	104·01	molecule
	41·06	57·98	67·20	

Start angles	92·00	92·00	92·00
Step angles	30·00	30·00	30·00
Weighting factors	0·02	1·00	1·00
F	0·084		
Δ	−0·000		
R2 R3 R1	76·400	59·841	44·359
R2/R1 R3/R1 R2/R3	1·7223	1·3490	1·2767
Optimized angle set	117·20	90·00	27·20	1st
	118·08	148·05	104·00	molecule
	41·01	121·95	67·18	

Start angles	179·00	88·00	88·00
Step angles	30·00	30·00	30·00
Weighting factors	0·02	1·00	1·00
F	0·088		
Δ	−0·003		
R2 R3 R1	76·338	59·837	44·424
R2/R1 R3/R1 R2/R3	1·7184	1·3470	1·2758
Optimized angle set	240·53	85·20	29·94	
	64·66	147·51	71·06	
	139·30	122·04	112·28	
Equivalent angle set	119·47	85·20	29·94	2nd
	115·34	32·49	108·94	molecule
	40·70	57·96	67·72	

anthracene molecules in the unit cell differ by less than 10°. The optimized angle sets with $F \le 0.088$ appear to represent reasonable results. For most start-

Table 2 (*cont.*)

Start angles	87·00	87·00	87·00
Step angles	30·00	30·00	30·00
Weighting factors	0·02	1·00	1·00
F	0·084		
Δ	0·000		
R2 R3 R1	76·400	59·841	44·359
R2/R1 R3/R1 R2/R3	1·7223	1·3490	1·2767
Optimized angle set	117·20	90·01	27·20	1st
	118·08	148·05	104·00	molecule
	41·00	121·95	67·18	

Start angles	30·00	60·00	90·00
Step angles	30·00	30·00	30·00
Weighting factors	0·02	1·00	1·00
F	0·084		
Δ	0·000		
R2 R3 R1	76·400	59·841	44·359
R2/R1 R3/R1 R2/R3	1·7223	1·3490	1·2767
Optimized angle set	62·80	90·00	152·80	
	118·08	148·05	104·00	
	139·00	58·05	112·82	
Equivalent angle set	117·18	90·00	27·20	1st
	118·08	148·05	104·00	molecule
	41·00	121·95	67·18	

Start angle	22·00	76·00	88·00
Step angle	30·00	30·00	30·00
Weighting factors	0·02	1·00	1·00
F	0·085		
Δ	0·000		
R2 R3 R1	76·400	59·802	44·398
R2/R1 R3/R2 R2/R3	1·7208	1·3470	1·2775
Optimized angle set	62·80	90·00	152·80	
	61·86	147·98	75·97	
	41·06	57·98	67·20	
Equivalent angle set	117·20	90·00	27·20	2nd
	118·14	32·02	104·03	molecule
	41·06	57·98	67·20	

ing sets chosen, initial step angles of 30° were found to be suitable for optimization.

This method can be used for other monoclinic molecular crystals. It should also be possible to apply this optimization method of molecular orientation to other crystal systems with the exception of the cubic system with isotropic molecular properties. It may also be useful in studies of optical properties of liquid crystals.

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