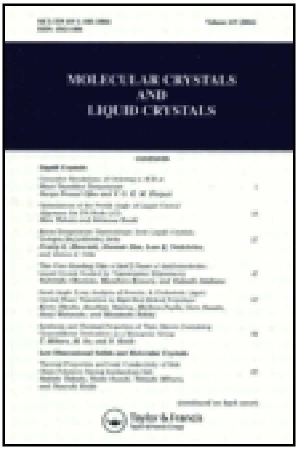

Molecular Crystals and Liquid Crystals
Publication details, including instructions for authors and subscription information:
http://www.tandfonline.com/loi/gmcl16

Structural Features from Reflection Spectra: Orientation of 1, 3,-bis-(Dimethylamino) trimethinium Perchlorate Molecules in the Crystal

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Version of record first published: 21 Mar 2007.

To cite this article: Bruce B. Johnson , Paolo Gramaccioni & William T. Simpson (1974): Structural Features from Reflection Spectra: Orientation of 1, 3,-bis-(Dimethylamino) trimethinium Perchlorate Molecules in the Crystal, Molecular Crystals and Liquid Crystals, 28:1-2, 99-115

To link to this article: http://dx.doi.org/10.1080/15421407408083155

Mol. Cryst. Liq. Cryst., Vol. 28, pp. 99-115
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Printed in Dordrecht, Holland

Structural Features from Reflection Spectra: Orientation of 1, 3,-bis-(Dimethylamino) trimethinium Perchlorate Molecules in the Crystal

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(*Received October 18, 1973*)

If the orientation of a molecular electronic transition moment with respect to the molecular framework is known, reflection spectra of crystalline samples on various faces may be used to locate the molecules in question. This can be done through projection of the transition moment on the faces, or through use of the optical indicatrix. The two methods are briefly compared, and the preferred indicatrix method is applied to crystals of the dye 1,3-*bis*-(dimethylamino)trimethinium perchlorate. Along each principal axis of the indicatrix, best fit values for reasonant frequency, plasma frequency, and damping constant are obtained in the frequency range of the first singlet. Parameters of the crystal structure having to do with the orientation of the dye molecules are then deduced from this information.

Reflection spectroscopy can be used to find the orientations of transition moments with respect to a crystal frame (or morphology). Usually, knowledge of the molecular orientation relative to the same frame is combined with this information to determine the directions of the transition moments with respect to the molecular frame. In spite of the fact that there are pitfalls, such determinations may be considered almost standard.[1, 2, 3] In cases where the crystal structure is not known, and in which the relation of the transition moment direction to the molecular geometry is known, the process can in principle be turned around:

reflection spectroscopy can be used to determine crucial structural features perhaps even paving the way towards the determination of crystal structures themselves. Before the advent of large computers optical data were often used to help elucidate crystal structures.[4, 5] These efforts were in a sense rudimentary owing to a lack of experimental and quantum theoretical understanding of molecular electronic transitions, particularly the relation of transition-moment directions to molecular geometry. Today, though much more is known, it must be admitted that the availability of large computers has decreased the need to bring in such adjuncts as the use of optical data.

In any event, in this paper we consider the interpretation of reflection spectra in relation to molecular structure and crystal structure with the aim of obtaining structural features from reflections. First a general expository description of the particular method to be used will be set out, after which the method will be illustrated through the prediction of several main structural features of 1,3-*bis*-(dimethylamino)trimethinium perchlorate (BDTP) crystals. Our interest in this topic was heightened when it was found that rough estimates of structural features of BDTP made on the basis of the reflection spectra were not only trivially easy but surprisingly accurate.

Anex and Fratini[6] used a simple but powerful method to find the orientation of the auramine anions in crystals of auramine perchlorate. Auramine is triclinic, with only one molecule per unit cell. Since all the molecules are parallel, qualitative considerations involving the principal directions alone lead to a prediction of the orientation with respect to the crystal morphology. Fratini, Karle and Karle[7] later determined the structure using X-ray methods, and found that the orientations predicted by the two methods were the same within a few degrees. In the method to be illustrated here we shall likewise make use of qualitative considerations involving principal directions, but because of the higher symmetry of BDTP compared with auramine perchlorate shall have the opportunity to bring in some additional considerations.

THEORETICAL CONSIDERATIONS

The basic equation used in interpreting reflection spectra is the Fresnel formula, which relates the reflection coefficient R to the complex index of refraction $\hat{n} = n + ik$. For normal incidence

$$R = \frac{|\hat{n} - 1|^2}{|\hat{n} + 1|^2} = \frac{n^2 + k^2 - 2n + 1}{n^2 + k^2 + 2n + 1} \quad . \tag{1}$$

Two methods have then been used to go beyond the complex index of refraction: Krönig-Kramers analysis and classical dispersion theory.[1] The Krönig-

Kramers analysis involves using the dispersion relations of Krönig and Kramers to relate the real and imaginary parts of the index of refraction after which the imaginary part can in turn be related to the projection of the transition moment on a given face. If the orientation of the transition moment in a molecule-fixed frame is independently known, structural parameters can be found.

Classical dispersion theory involves the use of a suitable classical dispersion equation (such as the Sellmeier formula, (2)) to simulate the $\hat{n}$ and hence the observed reflection spectra. In the simplest way, for any face, one assumes

$$\hat{n} - 1 = \sum_j \frac{\omega_{pj}^2}{\omega_j^2 - \omega^2 - i\gamma_j\omega} \tag{2}$$

where ω is the circular frequency of the light
ω_j is the resonant frequency of the j^{th} transition
γ_j is the damping constant of the j^{th} transition
ω_{pj} is the plasma frequency ($\omega_{pj}{}^2 = 8\pi N\omega_j e^2 q_j{}^2/\hbar$)
N is the number of molecules per cc
q_j is the transition moment length of the j^{th} transition projected on the face (later, on a principal axis)
e is the fundamental charge.

The apparent single molecule parameters ω_j, γ_j and ω_{pj} are varied until a good fit to the observed reflection spectra is obtained. Because the Sellmeier equation involves a sum over all electronic transitions, practically speaking an effective transition or transitions must be introduced at the blue end to simulate the background contributions (something similar has to be done with a Krönig-Kramers analysis). After a best fit is obtained a total molecular transition moment length may be related to the projection of the transition moment as it appears in ω_{pj}, and thus features of the crystal structure adduced.

Common to the two methods briefly outlined above is the idea of attributing the reflection observed on a face to the projection of the transition moment on the face. With qualifications (the incident beam must be polarized along principal directions) this idea has been used for some time (e.g. Albrecht and Simpson[8]). However, the reflection coefficient depends on the index of refraction, and the index of refraction is not a vector and cannot be expected to project. This is our point of departure.

Classically the optical properties of a homogeneous anisotropic solid are described by a geometrical construct known as the optical indicatrix.[5,9,10] Although the indicatrix is usually used to explain optical phenomena in the transparent region it can also be used in absorptive regions, though not without complications. In the discussion of the use of the indicatrix given below these complications will at first be ignored. The treatment draws heavily from the useful acount given by Ramachandran and Ramaseshan.[10]

The first step is to bring in Maxwell's macroscopic equations. If it is assumed that magnetic effects may be neglected and if plane-wave solutions for **E**, **D**, **H** and **B** exist, Maxwell's equations imply

$$\underset{\sim}{D} = n^2 (\underset{\sim}{E} - (\underset{\sim}{E} \cdot \underset{\sim}{s}) \underset{\sim}{s}) \tag{3}$$

where s is the propagation vector. Taking the dot product of both sides with **D**, this becomes

$$\underset{\sim}{D} \cdot \underset{\sim}{D} = n^2 (\underset{\sim}{D} \cdot \underset{\sim}{E} - (\underset{\sim}{E} \cdot \underset{\sim}{s})(\underset{\sim}{D} \cdot \underset{\sim}{s}))$$

or, since **D**·s = 0,

$$\frac{1}{n^2} = \frac{\underset{\sim}{D} \cdot \underset{\sim}{E}}{D^2} \tag{4}$$

Usually the relation between **D** and **E** is described by the dielectric tensor ϵ or, equivalently,

$$\underset{\sim}{E} = \underset{\sim}{aD} \quad \text{where} \quad \underset{\sim}{a} = \underset{\sim}{\epsilon}^{-1} \tag{5}$$

Both ϵ and **a** are symmetric tensors of the second rank, (and can, in general, be complex).

Now a tensor surface may be defined with respect to a such that in any direction the reciprocal of r^2 is equal to the "magnitude of the tensor property"[†] in that direction (r is the length of a vector from the origin to the surface). The equation of the surface is:

$$\frac{1}{r^2} = \underset{\sim}{d} \cdot \underset{\sim}{a} \cdot \underset{\sim}{d} = \frac{\underset{\sim}{D} \cdot \underset{\sim}{a} \cdot \underset{\sim}{D}}{D^2} = \frac{\underset{\sim}{D} \cdot \underset{\sim}{E}}{D^2} \tag{6}$$

where $\mathbf{d} = \frac{\mathbf{D}}{|\mathbf{D}|}$ is a unit vector. If the **d** vectors are expressed in terms of the appropriate direction cosines (l_1, l_2, l_3) of any orthonormal coordinate system, 6 becomes

$$\frac{1}{r^2} = \sum_{i=1}^{3} \sum_{j=1}^{3} a_{ij} l_i l_j ,$$

a relation which may be rewritten in the standard form for an ellipsoid

$$1 = \sum_{i=1}^{3} \sum_{j=1}^{3} a_{ij} x_i x_j . \tag{7}$$

Comparing Eqs. 4 and 6 it can be seen that the radius of the ellipsoid in any direction would be the index of refraction for any admissible plane-wave solution with a **D** vector in that direction. In a charge-free region, Maxwell's equations require that **D**, **E** and s must be coplanar, and **D** must be perpendicular to s.

[†] Invariant matrix triple product

(For our subsequent work, as proven in Appendix A, it can further be shown that the Fresnel formula (1) is valid if **D**, **E**, s are coplanar.) Ramachandran and Ramaseshan[10] give a simple geometric argument showing, for the transparent case, that because of these restrictions there are essentially only two plane-wave solutions for light propagating in an anisotropic crystal. We are interested in those solutions corresponding to waves excited by polarized light impinging at normal incidence on an arbitrary face. The solutions correspond to the principal directions for the face, with **D** polarized along the major and minor axes of the ellipse that results from taking a slice of the ellipsoid normal to the propagation direction. Since we shall need to make use of this result, in Appendix B a matrix algebraic formalism which can be used to slice the ellipsoid, and which was used later in this paper, is set out.

In the absorptive case, the solutions to Maxwell's equation are assumed to be plane damped waves. The index of refraction in Eq. 4 is complex $\hat{n} = n + ik$, and the tensor surface has both real and imaginary parts

$$\frac{\underset{\sim}{D} \cdot \underset{\sim}{\hat{a}} \cdot \underset{\sim}{D}}{D^2} = \frac{\underset{\sim}{D} \cdot \underset{\sim}{a} \cdot \underset{\sim}{D}}{D^2} + i\,\frac{\underset{\sim}{D} \cdot \underset{\sim}{b} \cdot \underset{\sim}{D}}{D^2} \tag{8}$$

where $\underset{\sim}{\hat{a}} = \underset{\sim}{\hat{\epsilon}}^{-1} = a + ib$ and $\underset{\sim}{\hat{\epsilon}} + i\underset{\sim}{\eta}$. The expressions for both the real and imaginary parts are in the form of ellipsoids, but caution must be exercised in the interpretation.

At this point we introduce the assumption that effective principal directions may, as an approximation, be taken along the extrema of the ellipse α resulting from slicing the ellipsoid representing the *real* part of $\hat{a}$.‡ The coefficients of the equation for the real ellipse when it is in its normal form are denoted α_I and α_{II}. The *diagonal* coefficients of the imaginary ellipse in the coordinate system that diagonalizes the real ellipse are denoted β_I and β_{II}, and the indices of refractions, $\hat{n}_I$ and $\hat{n}_{II}$. Our assumption about the effective principal directions then takes on the following form

$$\frac{1}{\hat{n}_I^2} = \alpha_I + i\beta_I \quad \text{and} \quad \frac{1}{\hat{n}_{II}^2} = \alpha_{II} + i\beta_{II} \tag{9}$$

Solving for $\hat{n}^2$ along the first principal direction, say,

$$\hat{n}_I^2 = \frac{\alpha_I}{\alpha_I^2 + \beta_I^2} - \frac{i\beta_I}{\alpha_I^2 + \beta_I^2} \tag{10}$$

---

‡ This assumption goes over into the correct procedure as one, so to speak, enters and leaves an absorptive region, frequency-wise. In our reflection experiments on arbitrary faces for BDTP the polarization directions were held constant through such regions at the value found to be correct entering the region from the low-frequency side, and did not differ by more than a few degrees from the value found upon leaving the region from the high-frequency side.

A reflectivity can now be calculated by taking the complex square root and applying Fresnel's equation (1). In general, if not practical terms, one tries all ellipsoids in all orientations until calculated reflectivities best match observation, preferably for a sufficient number of faces so as to introduce some redundancy.

To conclude, our viewpoint is that on the face of it the indicatrix method is to be preferred over the method of projecting moments (whether dispersion theory or Krönig-Kramers procedures are used for fitting). To be sure we have not been able to handle the dispersion in the principal directions in a rigorous fashion. For this and similar reasons we do not feel that any empirical success, or the lack of it, obtained here in connection with this one example should be considered either as "proving" or "disproving " the indicatrix approach.

Some simple calculations contrasting the results of the two methods may help to clarify the point. As a model the "crystal" was taken to be an array of parallel dipoles on a cubic lattice. The ellipsoids are uniaxial (two principal radii are equal) with the transition of interest along the unique axis. The dielectric constant for this axis was obtained essentially from Eq. 2. The calculations were done as outlined above for faces making various angles with the common direction of the dipoles.

The projection calculations were carried out by projecting the transition moment length on the various faces and using Eq. 2. The principal directions were assumed to be parallel and perpendicular to the projected transition moment length (these coincide with the principal directions found using the indicatrix method).

Calculated reflection spectra are shown in Figure 1 for faces whose normals make angles of 90°, 60° and 30° with the dipoles. The transition length is 2 Å. In comparing the results of the two methods of calculation, one is immediately

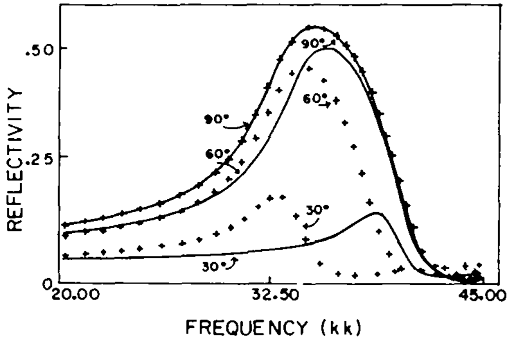


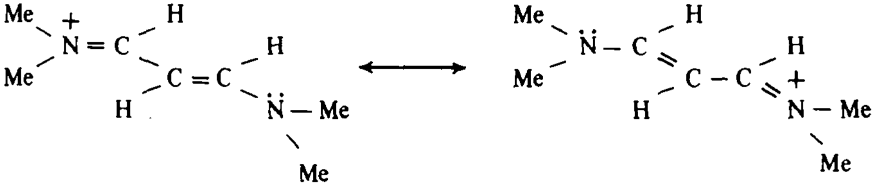
FIGURE 1. Reflectivities Calculated for a Cubic Array of Parallel Dipoles. Transition-moment projection procedure-crosses; Optical indicatrix method-solid line. Angle face normal makes with common direction of dipoles is shown. Parameters used in Sellmeier formula were $q = 2A$, $\gamma = 3$ kk, and $\omega_0 = 32.5$ kk.

struck by the blue shift of the reflection peak obtained by the indicatrix calculations relative to that found by the projection method. In detail, the indicatrix calculations show the energy of the red edge of the reflection band shifting toward the blue, while the energy of the blue edge remains constant as angle is changed. The blue shift probably represents the attempt, so to speak, on the part of the Maxwell-Lorentz theory to bring in the increasing participation of longitudinal modes as the angle decreases. That is (when $\omega_p{}^2/2\omega_0 > \gamma$) the peak shifts from ω_- towards $\omega_+ = \omega_0 + \omega_p{}^2/2\omega_0$. Also to be noted: the value of the peak reflectivity is by no means the same between the two methods for angles greater than 0°. (Not surprisingly, when the dipoles lie in the face, the calculated spectra along the principal axis for both methods are identical.) Not shown is the fact that as the transition moments decrease these differences become less pronounced.

In the present research the preferred, indicatrix method was used as outlined above to solve specifically for structural parameters of the compound BDTP.

DESCRIPTION AND PRELIMINARY ANALYSIS OF EXPERIMENT

In order to get structural information from reflection spectroscopy, one needs to be considering a crystal the molecules of which are understood – in that the direction of a transition moment at a definite frequency is known. The dye BDTP is such a molecule. The positive ion of BDTP has two principal resonating structures:



The first singlet-singlet transition is relatively intense and has a transition moment parallel to the N-N vector. It has an energy of 32.4 kk and a one-dimensional oscillator strength of 2.7 (q=1.6 Å).

BDTP was synthesized by refluxing a mixture of 1,3,3-tri-methoxypropene (0.076 moles), 33% aqueous dimethylamine (0.15 moles) and dimethylammonium perchlorate (0.076 moles) for four hours. After reaction the mixture was cooled (to *ca* 10° C) and the white precipitate which formed was collected by filtration. Several recrystallizations from absolute ethanol gave a product with a melting point of 118.5-119.5°. The density of BDTP was found to be 1.33 ± .02 g/cc as determined by weighing a known volume of a mixture of benzene and bromobenzene in which BDTP crystals were floated.

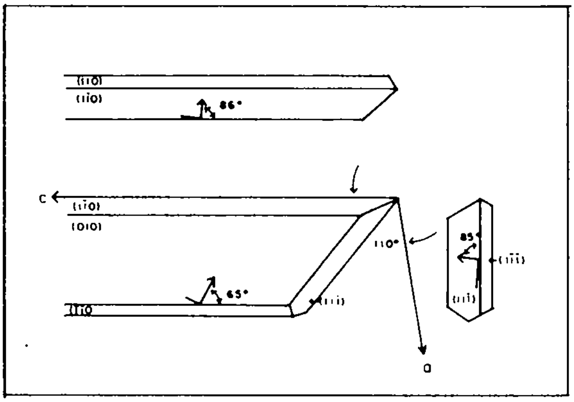


FIGURE 2. Crystal morphology of BDTP. Face labelled with Miller indices.[11] Principal directions indicated by lines and arrows (arrow denotes R_{max}).

Crystals with large clear faces suitable for reflection studies were obtained from acetic anhydride by cooling from 45°C at a rate of 0.5-1.0° per hour. Figure 2 shows the external habit, the principal directions, the crystallographic axes, and the Miller indices for the faces under study. A Nonius optical two-circle goniometer was used to determine the interfacial angles. Morphological considerations led to the identification of the crystal as monoclinic and to the labeling of the (010) face. The other Miller indices were assigned with the help of B. Matthews.[11]

On each face a co-ordinate system was envisaged with the z axis normal to the face, the y axis parallel to R_{max}, and the x axis parallel to R_{min}. The interfacial angles were used to determine Eulerian angles as defined in Goldstein[12] for rotation from the coordinate system on the (010) to the coordinate system on the other two faces. A consistent scheme of Eulerian angles is given in Table I.

TABLE I

	φ	θ	ψ
(010) → (11$\bar{1}$)	78°	72°	175°
(010) → (1$\bar{1}$0)	205°	68°	356°

The reflection spectrometer has been described before.[13] The orientations of the principal directions were determined with the crystal mounted in the reflection spectrometer using monochromatic light at 380 nm. Difficulties in obtaining reproducibility of these measurements suggest that the uncertainty may be as much as ± 5°. On the (11$\bar{1}$) face, from about 360 to 290 nm, a dispersion of the principal directions was noticed, though the direction stabilized on the short wavelength side at almost the same value as that on the long wavelength side. The spectra reported here for the $(11\bar{1})$ face were in any case taken along the principal directions determined at 380 nm.

Polarized reflection measurements were made on a number of crystal specimens, for both principal directions on three faces (the (010), $(11\bar{1})$, $(1\bar{1}0)$). Representative spectra are shown in Figure 3. (The reflection coefficient between different crystals is accurate to within 5%.) Even a casual inspection of the spectra shows two important features. For one thing the first transition is split, and for another, the reflectivities are higher and wider than normal.

Crystals of the monoclinic class have either a mirror plane or a two-fold axis of rotation. By convention the unique axis is taken to be the *b* axis. Since physical properties must exhibit the same symmetry as the crystal, the components of a split transition must be parallel to the unique axis (the *b* axis), or perpendicular to this axis (the *ac* plane).

The (010) face shows the *ac*-polarized transition. It is moderately strong and polarized along the direction of $R_{\max}$. Ideally one would like to be able to find a face containing the *b* axis in order to permit examination of the *b*-polarized transition. Since BDTP does not have such a naturally occurring face, we must accomodate by looking at faces that give us information about this transition.§ Both the $(11\bar{1})$ and the $(1\bar{1}0)$ show evidence of two transitions with what must be the *b*-polarized transition on the high energy side. In Section 3 of this paper we shall see how the calculational ideas developed in Section 1 that utilize the optical indicatrix can be used to analyze the data from the $(11\bar{1})$ and $(1\bar{1}0)$ faces (neither of which contains the *b* axis) and provide information about the *b* axis transition. However first we shall go into the qualitative considerations that by themselves lead to details of the crystal structure which are surprisingly accurate.

For the qualitative analysis it was assumed that the magnitude of highest reflectivity along a principal direction is proportional to the square of the projection of the transition moment along that direction. A simple model of the crystal structure in which symmetrically arranged pairs of molecules are featured shows how the molecules must be oriented relative to each other-Figure 4. Since there is no reflection (other than background) along the $R_{\min}$ direction of the (010) face, the transition moments must lie in the plane determined by the *b* axis and the $R_{\max}$ direction of the (010) face. In this plane the molecules (thin arrows in the Figure) have an angular relation that is characterized by the acute angle θ between the transition moments and the *b* axis.

The first, and easiest, structural feature to find is the orientation of the plane in which all the transition moments lie. This is shown by the orientation of the

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§ Another approach that has been used to obtain information when the desired face does not naturally occur is to cut an artificial face at the same angle as the desired face.[3]

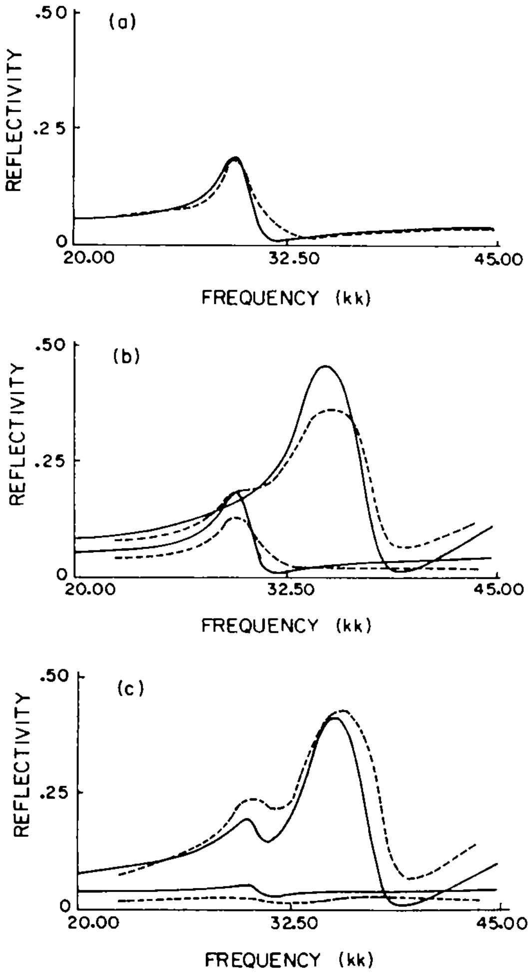

FIGURE 3. Experimental (dashed line) and calculated (solid line) spectra. (a) Spectrum on R_{max} of (010). (Since spectrum on R_{min} direction is featureless, it is not shown.); (b) Spectra for R_{max} and R_{min} of $(11\bar{1})$; (c) spectra for R_{max} and R_{min} of $(1\bar{1}0)$.

R_{max} direction of the (010) face. The plane is found to make an angle of 65° with the *c* axis.

The acute angle made by the molecules with the *b* axis is more difficult to find. The cotangent of this angle would be the ratio of intensity along the *b* axis to that along the R_{max} direction in the *ac* plane. Qualitatively we may approximate the *b*-axis intensity by using the information on the $(1\bar{1}0)$ and $(11\bar{1})$ faces – that is, by projecting the reflectivities on the *b* axis. Projected reflectivities from the separate faces can be compared to the maximum reflectivity found on the (010) face to give a range for cot θ.

The angle to be used for the projection ψ_{lmn} is found by subtracting 90° from the interfacial angles. For the $(11\bar{1})$ face this angle is 18°, and the highest reflectivity seen is 0.36. For the $(1\bar{1}0)$ face this angle is 22° and the maximum reflection coefficient is 0.43. The highest reflectivity on the (010) face is 0.18. Specifically, the relation used was

$$\cot^2\theta = \frac{q_b^2}{q_{ac}^2} \approx \frac{R_b^{max}}{R_{ac}^{max}}$$

where

$$R_b^{max} = R_{(lmn)}^{max} / \cos\psi_{lmn} \ .$$

Then from the $(11\bar{1})$ face it is found that $\theta = 34°$ whereas from the $(1\bar{1}0)$ face, $\theta = 32°$. Thus, roughly, the angle between the molecules and the *b* axis would be in the range of 30°-36°. This is the angle referred to by Matthews, *et. al.*,[14] for comparison with the angle they determined using X-ray diffraction, namely 28.5°.

The interesting feature of the qualitative determination is its simplicity. The quantitative determination set forth in the next section would be preferred not only because of its greater objectivity but also it is felt that the problem of extracting information from crystal faces not related to any symmetry elements is unusual and important. For the quantitative determination we have basically to find the location and characteristics of the complex optical indicatrix.

QUANTITATIVE RESULTS AND DISCUSSION

In this section we shall see how to deal with some of the complications inherent in the problem in a particular way for a particular example. First, a few general comments.

The real and imaginary ellipsoids of the indicatrix do not have to be congruent (diagonal in the same coordinate system) and the orientations of the principal axes can show dispersion. However each ellipsoid must exhibit all the symmetry operations of the crystal.

Crystals belonging to the triclinic class have no symmetry feature that restricts either the directions of or the directional dispersion of the principal axes of the ellipsoids. In cases involving intensely absorbing triclinic crystals (as in Anex and Fratini's work[6]) the orientation of transition moments (which are all parallel) can be found easily by consideration of the principal directions on several faces. As noted above, monoclinic crystals have either a mirror plane or a two-fold axis of rotation. In terms of an ellipsoid both symmetry features amount to a unique axis (either perpendicular to the mirror plane or parallel to the two-fold axis). Therefore the **a** and **b** ellipsoids (8) will have a common axis (by convention it will be along the *b* crystallographic axis) which cannot show directional dispersion. The other axes have no constraints other than that they must be perpendicular to the unique axes. Orthorhombic crystals have many more symmetry features than monoclinic crystals. The principal axes of the ellipsoids must be parallel to the crystallographic axes and cannot show any directional dispersion.

If by symmetry or, approximately, by accident, one can assume that the real and imaginary parts of the dielectric tensor are congruent, (crystals must be effectively orthorhombic) then the real and imaginary parts of $\hat{\epsilon}(=\epsilon + i\eta)$ can be simultaneously diagonalized, and the inverse

$$\underset{\sim}{\hat{\epsilon}}^{-1} = \underset{\sim}{a} + i\underset{\sim}{b}$$

can be simply characterized. In the normal forms

$$a_{ij} = \frac{\epsilon_{ij}}{\epsilon_{ij}^2 + \eta_{ij}^2}\,\delta_{ij} \qquad b_{ij} = \frac{-\eta_{ij}}{\epsilon_{ij}^2 + \eta_{ij}^2}\,\delta_{ij}\ . \tag{11}$$

If the real and imaginary parts of the dielectric tensor are not congruent, the characterization of the multiplicative inverse can be effected through use of matrix-algebraic approximation methods. It is assumed at the outset that for BDTP in the frequency range of interest there is no dispersion of the effective principal axes, and that the **a** and **b** ellipsoids are congruent. These assumptions seem reasonably good on two accounts: there is no apparent dispersion of the $R_{\max}$ direction on the (010) face (the *ac* plane), and the major contribution to the polarizability should be parallel to the long molecular axis. (Optically the crystal would be orthorhombic if all the transitions were polarized parallel to the N-N axis.) We shall, then, be using relations 11.

A simple and, it is felt, promising method of obtaining trial values characterizing the ellipsoids is to assume that along each principal axis a Sellmeier dispersion formula holds. The calculational method applied in this paper makes use of this idea. The calculation was begun by doing a classical dispersion theory fit using the Sellmeier formula (2) for each principal direction of the (010) face. (It was mentioned in Section 1 that for analysis of reflection data along principal axes of the indicatrix, the projection method and the indicatrix method are identical.) This gave Sellmeier terms for the two axes of the ellipsoid that lie in the *ac* plane. The Sellmeier terms for the *b*-axis polarized transition were then approximated using an oscillator strength which would exhaust the potential for absorption inherent in the single-molecule absorptions. These values (along with the appropriate ω_0, γ) were then used to characterize a trial ellipsoid, and the trigonometric calculation undertaken.

A computer program was written (for use on the University of Oregon

PDP-10 computer) that slices the ellipsoids and calculates the reflectivity along arbitrary principal directions. The calculated curves for the (11$\bar{1}$) and (1$\bar{1}$0) faces were compared subjectively to the experimental spectra, and the parameters varied to a best fit. Computer plotting[15] was used (as it was also for the prior work on the (010)) and all in all some fifty reflections were generated for comparison with the observed ones. The final parameters for the Sellmeier equation (2) used along each principal axis of the indicatrix are listed in Table II.

TABLE II

		b axis	ac plane	
			R_{max}	R_{min}
transition parameters	q	1.65 ± .05 A°	.77 ± .05 A°	---
	ω_c	32.5 A°	29.3 kk	---
	γ	2.25 kk	1.7 kk	---
background parameters	q	2 A°	3.3 A°	3.3 A°
	ω_c	50 kk	100 kk	100 kk
	γ*	3 kk	3 kk	3 kk

* Nominal value used for convenience

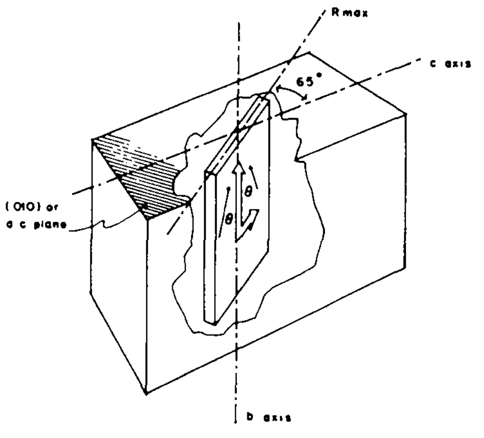

FIGURE 4. Schematic of molecular orientation. Since there is only background reflectivity along R_{min} of (010), transition moments must lie in the plane defined by the b axis and R_{max}, shown by the slab in the figure. Heavy arrows in the slab indicate the two crystal transition moments – one along the b axis and one in the ac plane. Thin arrows indicate transition moments of molecules themselves oriented so as to produce the observed dichroic ratio. The acute angle θ between the b axis and the transition moment of a molecule is featured in the text as an important structural parameter.

The curves of best fit are shown in Figure 3 along with the experimental reflections. The error estimates are again subjective and rather severe in that outside the error limits the fit is qualitatively in disagreement with experiment. Looking at Figure 3b and 3c one might not think that the fit is as good as it could be. The calculated reflectivity fits the experiment well on the $R_{\max}$ direction of the $(1\bar{1}0)$ face, while it is too high on the $(11\bar{1})$ face. Our attempts to correct this invariably led to serious alterations in the shape of the $R_{\max}$ spectra for the $(1\bar{1}0)$ face. We tried to keep the criteria for best-fit broad. These included positions of the peaks, shapes of the curves, and the absolute magnitudes and widths of the reflectivities.

Two different pieces of structural information are available from the results. These structural parameters are described in Section 2. and in Figure 4. The angle of the plane containing the molecules was given as 65°. The determination of this angle is comparable to the structural determination of Anex and Fratini.[6] The angle θ, between the long molecular axis and the *b* axis is equal to the arccotangent of the dichroic ratio (1.65/0.77 from Table II). It is $\theta = 25 \pm 2°$. Just as in the case of the value found qualitatively in the previous section (some 30°-36°) this is to be compared with the value of 28.5° ± 0.5° obtained by Matthews, *et. al.*, [14].[‖]

Not only are structural results obtainable from a study of this type, but also parameters describing spectral characteristics for the particular crystal. The spectral results obtained for BDTP are listed in Table III.

TABLE III

ac polarized transition	b polarized transition	solution
q = .77 ± .05 A° f = .6 ± .1 ω_c = 29.3 kk	q = 1.65 ± .05 A° f = 2.9 ± .2 ω_o = 32.5 kk	q = 1.6 A° f = 2.7 ω_o = 32.4 kk
	f_{xtal} = 3.5 ± .3	

The oscillator strengths, f, for the crystal data were calculated from the transition moments using

$$f = \frac{2m\omega q^2}{\hbar}$$

[‖] Anomalous dichroic ratios have been observed before, (3, 16, 17) and attributed to the mixing-in of higher energy (in our case, short-axis polarized) transitions. For at least this reason, one does not know whether the small discrepancy between the optical and X-ray methods is due to errors in the optical method, or to the mixing-in of higher energy transitions.

where m = mass of electron
ω = frequency of the transition
q = transition moment length.

The two components of the split band are reasonably well delineated and show a splitting of 3.2 kk. In addition to this considerable splitting, a marked degree of hyperchromism ($f_{\text{xtal}} > f_{\text{soln}}$) is seen. Because of the high intensity of the single-molecule transition, neither of these results is especially surprising.

APPENDIX A

We are to consider reflection by an anisotropic medium where the transmitted beam has been excited by plane polarized light impinging on an arbitrary face at normal incidence. Ramachandran and Ramaseshan[10] show that for such a transmitted beam with a polarization parallel to either principal direction of the face, **D**, **E** and s, the propagation vector, will be coplanar. In this Appendix we shall affirm that Fresnel's equation (1) for normal incidence holds in this case.

The electric fields of the incident, reflected, and transmitted waves respectively may be taken as:

$$\underset{\sim}{E}_I = E_{Io}\, e^{i\omega(t - \frac{n_1}{c} z)}\, \underset{\sim}{i}$$

$$\underset{\sim}{E}_R = E_{Ro}\, e^{i\omega(t + \frac{n_1}{c} z)}\, \underset{\sim}{i}$$

$$\underset{\sim}{E}_T = E_{To}\, e^{i\omega(t - \frac{n_2}{c} z)} (\cos\alpha\, \underset{\sim}{i} + \sin\alpha\, \underset{\sim}{k}).$$

Because of the coplanarity of **D**, **E**, and s together with the fact that **D**, **H**, and s form an orthogonal triplet we may also write

$$\underset{\sim}{H}_I = n_1 E_{Io}\, e^{i\omega(t - \frac{n_1}{c} z)}\, \underset{\sim}{j}$$

$$\underset{\sim}{H}_R = -\, n_1 E_{Ro}\, e^{i\omega(t + \frac{n_1}{c} z)}\, \underset{\sim}{j}$$

$$\underset{\sim}{H}_T = n_2 E_{To} \cos\alpha\, e^{i\omega(t - \frac{n_2}{c} z)}\, \underset{\sim}{j}\,.$$

We now apply the usual boundary conditions (at $z = 0$ the tangetial components of **E** and **H** must be equal) to obtain

$$E_{Io} + E_{Ro} = E_{To} \cos\alpha$$

$$n_1 E_{Io} - n_1 E_{Ro} = n_2 E_{To} \cos\alpha\ .$$

With $n_1 = 1$ and $n_2 = n$, this leads to

$$\frac{E_{Ro}}{E_{Io}} = -\frac{n - 1}{n + 1}$$

so that the reflection coefficient

$$R = \frac{\underset{\sim}{E}_R \times \underset{\sim}{H}^{\bullet}_{R}|_{z}}{\underset{\sim}{E}_I \times \underset{\sim}{H}^{\bullet}_{R}|_{z}}$$

becomes

$$\frac{|n-1|^2}{|n+1|^2}\,.$$

Thus Fresnel's equation for normal incidence is seen to hold provided that the polarization of the incident beam is lined up with one of the principal directions.

APPENDIX B

The object here is to show how the ellipses that result from slicing the indicatrix parallel to an arbitrary face were generated. The ellipses resulting from the **a** and **b** ellipsoids (where $\epsilon^{-1} = \mathbf{a} + i\mathbf{b}$) were handled in the same manner, so in this Appendix we shall use just the **a** ellipse. The equation of an ellipsoid in the coordinate system in which it is diagonal may be written

$$(x_p\ y_p\ z_p)\begin{pmatrix} a_{11} & 0 & 0 \\ 0 & a_{22} & 0 \\ 0 & 0 & a_{33} \end{pmatrix}\begin{pmatrix} x_p \\ y_p \\ z_p \end{pmatrix} = 1 \qquad \text{(B-1)}$$

or

$$\underset{\sim}{x}^{\bullet}_p\ \underset{\sim}{a}_p\ \underset{\sim}{x}_p = 1$$

where the subscript p stands for "principal" co-ordinate system.

On each face of interest a coordinate system was defined with the z axis normal to the face. Suppose the $(l\ m\ n)$ face is used as a practical reference face. Then for any face $(r\ s\ t)$

$$\underset{\sim}{x}_{(r\,s\,t)} = \underset{\sim}{T}_{(l\,m\,n)\to(r\,s\,t)}\ \underset{\sim}{x}_{(l\,m\,n)} \qquad \text{(B-2)}$$

where **T** depends on the Eulerian angles relating the reference face to the arbitrary face (to be sure, after the establishment of suitable conventions). Again with suitable conventions, there must be a transformation locating the ellipsoid with respect to the reference system. If we call this transformation $\mathbf{T}_{p\to(l\,m\,n)}$, then any vector with components x_p has components

$$\underset{\sim}{x}_{(l\,m\,n)} = \underset{\sim}{T}_{p\to(l\,m\,n)}\ \underset{\sim}{x}_p\ . \qquad \text{(B-3)}$$

From (B-3) we may find $\mathbf{T}_{p\to(r\,s\,t)}$ by observing that

$$\underset{\sim}{x}_{(r\,s\,t)} = \underset{\sim}{T}_{(l\,m\,n)\to(r\,s\,t)}\ \underset{\sim}{T}_{p\to(l\,m\,n)}\ \underset{\sim}{x}_p\ .$$

that is

$$\underset{\sim}{T}_{p\to(r\,s\,t)} = \underset{\sim}{T}_{(l\,m\,n)\to(r\,s\,t)}\,\underset{\sim}{T}_{p\to(l\,m\,n)}\ \cdot \qquad \text{(B-4)}$$

Returning to (B-1), written as involving $T_{p\to(r\,s\,t)}$ and its inverse

$$\underset{\sim}{x}^{+}_{p}\,[\underset{\sim}{T}_{p\to(r\,s\,t)}]^{-1}\,\underset{\sim}{T}_{p\to(r\,s\,t)}\,\underset{\sim}{a}_{p}\,[\underset{\sim}{T}_{p\to(r\,s\,t)}]^{-1}\,\underset{\sim}{T}_{p\to(r\,s\,t)}\,\underset{\sim}{x}_{p} = 1$$

we find

$$\underset{\sim}{x}^{+}_{(r\,s\,t)}\,\underset{\sim}{a}_{(r\,s\,t)}\,\underset{\sim}{x}_{(r\,s\,t)} = 1 \qquad \text{(B-5)}$$

where

$$\underset{\sim}{a}_{(r\,s\,t)} = \underset{\sim}{T}_{p\to(r\,s\,t)}\,\underset{\sim}{a}_{p}\,[\underset{\sim}{T}_{p\to(r\,s\,t)}]^{-1}\ \cdot$$

Thus for any face, the equation of the ellipse traced on the face is B-5 with $z = 0$.

In practise, in the most general terms, we guess (or deduce)[¶] a $\mathbf{T}_{p\to(l\,m\,n)}$ to furnish a trial location of the indicatrix. We then compute the various $\mathbf{T}_{p\to(r\,s\,t)}$ for the faces being studied using B-4. With any one such, we use B-5 to give trial values of $R_{\max}$ and $R_{\min}$ for that face (but using also **b** as explained in the text).

Acknowledgment

The authors would like to thank Professor Brian Matthews for his interest and generous advice.

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[¶] In the specific example presented in the text, symmetry arguments and other physical arguments helped us locate the indicatrix.