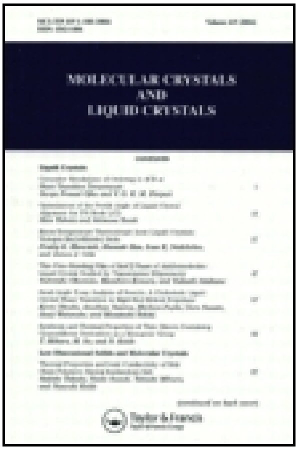

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B. M. Craven [a] , Patricia Sawzik [a] & N. G. Guerina [a]

[a] Department of Crystallography, University of Pittsburgh, Pittsburgh, Pennsylvania, 15260, USA

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BIREFRINGENCE AND THE MOLECULAR ARRANGEMENT IN CRYSTALS OF CHOLESTERYL LAURATE

B.M.CRAVEN, PATRICIA SAWZIK and N.G.GUERINA*
Department of Crystallography, University of
Pittsburgh, Pittsburgh, Pennsylvania 15260 USA

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ABSTRACT: Refractive indices for crystals of cholesteryl laurate are X = 1.505, Y = 1.515, Z = 1.580 with estimated errors of 0.003. The Z-axis of the optic indicatrix makes angles of about 15° with the molecular long axes and 1° with the average direction of all bonded atom C-C and C-O vectors in the crystal.

In considering the optical properties of mesogens, the maximum refractive index is expected to be observed when light travels with the electric vector close to the preferred direction for the molecular long axes.[1] In the smectic and cholesteric phases of the cholesteryl n-alkanoate esters, the validity of this assumption is difficult to gauge because of uncertainty in the details of the molecular arrangement.[2] We report optical properties for crystals of cholesteryl laurate where the x-ray structure has been determined[3,4] and found to have some features which may also occur in the mesophases. Thus the molecules are in an almost fully extended conformation (Figure 1) and are in approximately parallel or antiparallel array. The crystal structure is monoclinic with space group $P2_1$ and has two molecules which are not related by crystal symmetry (A and B; see Figure 1). Their cholesteryl ring systems are nearly perpendicular to each other. Thus the local environment of a particular molecule at a given

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*Present address: Department of Anatomy, Harvard University Medical School, Cambridge, Massachusetts 02138.

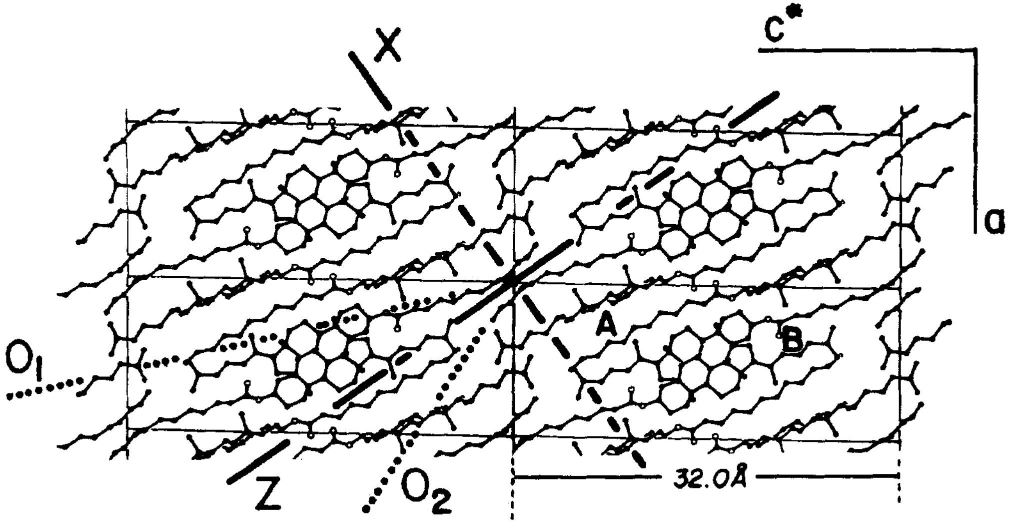

FIGURE 1 The crystal structure of cholesteryl laurate at 298 K in projection down the b-axis. Molecules A and B, having ring systems which are almost normal to each other, are not related by crystallographic symmetry. Principal axes of the optical indicatrix Z, X are shown as heavy lines and the optic axes O_1, O_2 are shown dotted.

instant might be similar in the mesophases and in this complex crystal structure.

Crystals of cholesteryl laurate were obtained as flat plates which showed well developed (001) faces and were elongated along the b-direction. A crystal was cut in the form of an orthogonal block 1.0 x 1.5 x 0.4 mm along a, b and c, respectively. The orientation of the crystal axes was established by x-ray precession photography of this crystal, which was then transferred to an improvised two-circle stage on a polarizing microscope. In the view down the b-axis, the extinction direction for polarized light was 34.5° from the crystal c* and 55.5° from a (Figure 1). The principal refractive indices, Z = 1.505, Y = 1.515, Z = 1.580 with estimated errors of 0.003, were measured by observation of the Becke line when the crystal was immersed in a series of standardized aqueous solutions of potassium mercuri-iodide. The optic indicatrix has Y along the crystal b-axis and Z at 34.5° from c*. The optic axial angle is 2V = 44° and the birefringence is positive. One of the optic axes is close (12°) to the c*-direction which is the normal to the plane of the molecular layers in the crystal structure.

As shown in Table 1, the long axis of the optic indicatrix (Z) is about 15° from the directions of the molecular long axes for molecules A and B when these axes are defined as the best least squares lines through all the carbon and oxygen atoms of the molecule. In the calculations, all atoms were assigned equal weight. However, such a geometrical definition of the molecular long axis is not necessarily the most appropriate for making correlations with the optical properties. As discussed by Hartshorne,[1] the charge polarization induced by light is most effective at short range. The strongest contributions come from the interactions between pairs of covalently bonded atoms. In an effort to take this into account, the best least squares line was calculated for the array of interatomic vectors between all pairs of bonded C-C and C-O atoms in the crystal structure. There are 44 bond vectors per molecule or 176 per unit cell. These calculations were based on the atomic coordinates of Sawzik and Craven,[3] assuming all bond vectors to have equal weight. The result could have been obtained less readily by calculating the directions

TABLE 1 Relationship between optic indicatrix and the molecular arrangement.

(a) Direction cosines, γ

These are given with respect to the orthogonal crystal axes a, b, c*. The directions are designated as follows:

Z : direction of the long axis of the optic indicatrix.

M_A, M_B : best least squares line through all 41 carbon and oxygen atoms of molecules A or B.

R_A, R_B : best least squares line through the tetracyclic ring systems, atoms C(1) through C(19) of molecules A or B.

T_A, T_B : best least squares line through the molecular tail substituents consisting of atoms C(20) through C(27) of molecules A or B.

L_A, L_B : best least squares line through the laurate chain, consisting of atoms C(28) through C(39) and the two oxygen atoms of molecules A or B.

V_A, V_B : best least squares line through the array of all interatomic vectors between covalently bonded C-C and C-O atoms. Subscripts refer to the two symmetry related molecules of the type either A or B respectively.

V : best least squares line through the array of all vectors in the crystal structure between bonded C-C and C-O atoms.

Table 1 (cont.)

	$\gamma(\underline{a})$	$\gamma(\underline{b})$	$\gamma(\underline{c}^*)$		$\gamma(\underline{a})$	$\gamma(\underline{b})$	$\gamma(\underline{c}^*)$
Z	0.56641	0	0.82413	V	0.58356	0	0.81207
M_A	0.35536	0.09897	0.92947	M_B	0.31627	-0.10139	0.94324
R_A	0.36513	0.17112	0.91510	R_B	0.43394	-0.02911	0.90047
T_A	0.44899	0.00341	0.89353	T_B	0.46589	0.18779	0.86469
L_A	0.43889	-0.09761	0.89322	L_B	0.40345	-0.22038	0.88807
V_A	0.58290	0	0.81254	V_B	0.58455	0	0.81136

(b) Angles (°) between selected pairs of directions

$Z-\underline{c}^*$	34.5	R_A-L_A	16.0	$Z-M_A$	14.7	$Z-V$	1.2
$M_A-\underline{c}^*$	21.6	R_B-L_B	11.1	$Z-M_B$	17.0	V_A-V_B	0.2
$M_B-\underline{c}^*$	19.4	$M_A-\underline{b}$	84.3	$Z-V_A$	1.1		
M_A-M_B	11.7	$M_B-\underline{b}$	95.8	$Z-V_B$	1.3		

of the principle moments of inertia for the vector density within 2 Å of the origin in the Patterson function of cholesteryl laurate. It was found that the direction of the best least squares line through the bond vector array made an angle of only 1.2° with the direction of the longest axis of the optic indicatrix. This angle is believed to be similar to the error in the optical measurements. Although the agreement is within experimental error, this may be fortuitous. Thus the C-H bond vectors (68/molecule) have been neglected.

We conclude only that qualitative statements regarding relationships between the orientation of the optic indicatrix and the "molecular long axes" for cholesteryl esters may be subject to errors which are at least 15°.

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