MOLECULAR PACKING OF SOME CHOLESTEROL DERIVATIVES

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A molecular packing study has been made using the geometrical analysis technique or "model" approach of Kitaigorodsky for cholesteryl methyl carbonate, cholesteryl ethyl carbonate and cholesteryl benzoate.

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It is known quite well that the molecular structure of mesogenic materials in the solid state prefigures the orientation of molecules in the liquid crystalline state. The molecular structural studies of liquid crystalline materials in the crystalline state provides a better understanding of the physical properties. An integrated study of the physical properties of liquid crystalline materials as related to the molecular structure provides a deeper understanding of the changes in physical properties with molecular structure variation, which enables us to synthesize liquid crystals to suit our applications. In particular the study of molecular structure and physical properties of cholesteric liquid crystals are of very great importance owing to the involvement of these compounds in a myriad of industrial and biological research areas such as thermography, display devices and the formation of artherosclerosis of arterial deposits containing cholesteryl esters.

An a priori determination of molecular packing has been made using the geometrical analysis technique or the model approach of Kitaigorodsky [1, 2] for cholesteryl methyl carbonate, cholesteryl ethyl carbonate and cholesteryl benzoate. The unit cell dimensions and space groups or these compounds which are required for molecular packing studies have been taken from the previous work [3–5] and are tabulated in Table I. Here it is assumed that the sterol nucleus remains invariant throughout the series. The molecular models were constructed using the intermolecular radii

$$R_{\text{carbon}} = 1.80 \text{ Å}, \quad R_{\text{oxygen}} = 1.52 \text{ Å}, \quad R_{\text{hydrogen}} = 1.17 \text{ Å}$$

and were arranged so that the distances between their centres corresponded to unit cell dimensions while taking care that the projection of one molecule falls into the hollows of

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TABLE I

Crystal data for cholesteryl methyl carbonate, cholesteryl ethyl carbonate and cholesteryl benzoate

		Cholesteryl methyl carbonate ($C_{29}H_{48}O_3$)	Cholesteryl ethyl carbonate ($C_{30}H_{50}O_3$)	Cholesteryl benzoate ($C_{34}H_{50}O_2$)
Unit cell dimensions	a	16.50 Å	17.89 Å	10.14 Å
	b	7.43 Å	11.34 Å	10.06 Å
	c	10.22 Å	13.11 Å	26.00 Å
	β	103.2°	105.2°	—
Space group		$P2_1$	$P2_1$	$P2_12_12_1$
Volume of the unit cell	V	1219.82 Å^3	2566.62 Å^3	2652.22 Å^3
Number of molecules per unit cell	Z	2	4	4
Calculated density	d_c	1.2102 gm/cc	1.187 gm/cc	1.228 gm/cc
Measured density	d_m	1.2091 gm/cc	1.143 gm/cc	1.231 gm/cc
Molecular weight	M	444.70	458.73	490.75

adjacent molecules with the closest possible packing. By means of the symmetry element of the particular space group, the initial orientation of the molecules were fixed by the angles φ_1, φ_2 and φ_3 as defined in Fig. 1. Subsequently geometrical calculations were

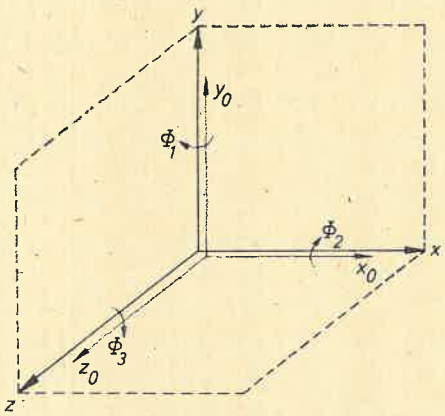

Fig. 1. The designation of the angles for molecular orientation

made with the contacts of molecules related by different symmetry conditions using the bond lengths and bond angles for the sterol molecule from the work of Craven and de Titta [6] and for the alkyl chains from Kennard and Watson [7]. Refined values of φ_1, φ_2 and φ_3 were estimated.

The sterol group can be considered to be a rectangular slab of 18 Å long, 7 Å wide and 4½ Å thick. The cholesterol part of the molecule is thick compared to the ester part. For all purposes we can consider the alkyl chain to be fully extended, as it is quite short

in the compounds under consideration. It is most probable that half of the cholesteryl ester molecules are arranged in the unit cell with their ester tails pointing up and half with their tails pointing down. Thus the arrangement of the molecules in the unit cell are interdigitated in an antiparallel array. The shape of the molecules of the cholesterol derivatives looks like flattened Indian clubs where the head is the sterol group and the ester chains handle is approximately 4 Å by 3½ Å in cross section. Thus for rigid elongated molecules of this kind it has been possible to arrange the molecules in the unit cell from the cell dimensions and space groups. By using these considerations Bernal et al. [8] have

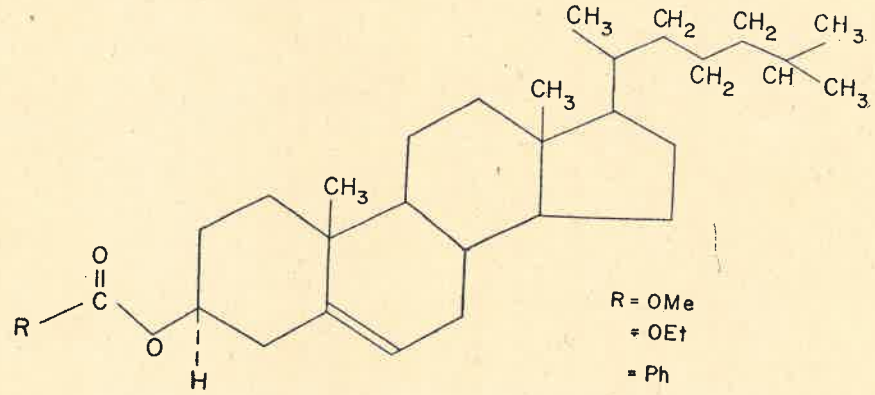

Fig. 2. Cholesteryl methyl carbonate, cholesteryl ethyl carbonate and cholesteryl benzoate molecules

deduced the molecular arrangements in the crystals of sterol derivatives. We have made a study of molecular arrangement in the crystalline phase for cholesteryl methyl carbonate, cholesteryl ethyl carbonate and cholesteryl benzoate (Fig. 2). The benzene

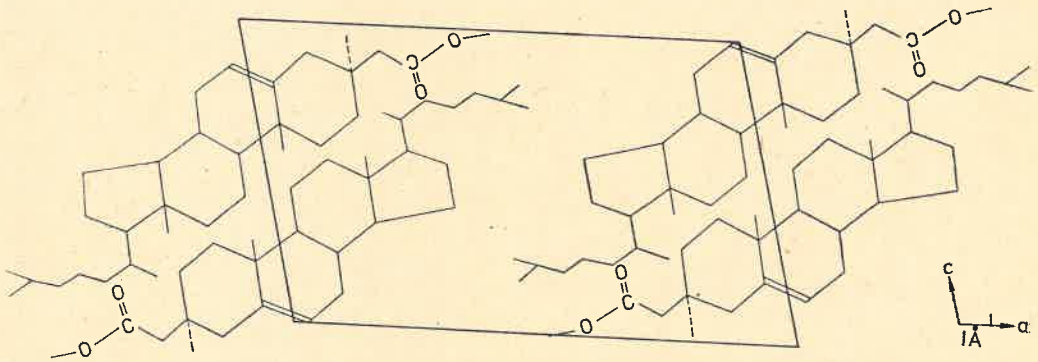

Fig. 3. Molecular packing of cholesteryl methyl carbonate about $\vec{b}$

ring which is in the side group of cholesteryl benzoate is taken to be planar and symmetrical.

The molecular packing about $\vec{b}$ (as obtained by the model approach) for cholesteryl methyl carbonate is shown in Fig. 3. The survey of the reflections obtained by the Weissen-

berg layer photographs about the $\vec{a}$ and $\vec{b}$ axes show that 020 and 102 reflections are the strongest in order. These reflections confirm the molecular orientations and packing, as obtained by the model approach.

Figure 4 shows the molecular packing of cholesteryl ethyl carbonate about $\vec{b}$. There are systematic similarities in major reflections of cholesteryl methyl carbonate and choles-

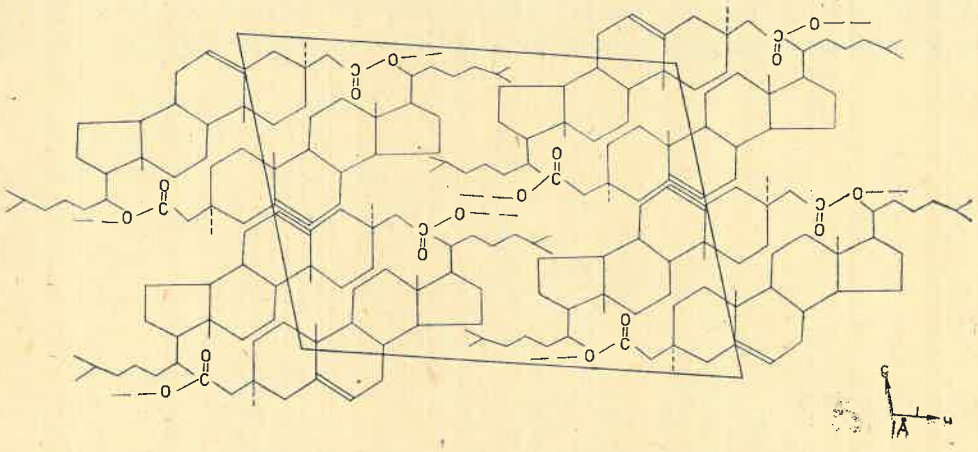

Fig. 4. Molecular packing of cholesteryl ethyl carbonate about $\vec{b}$

teryl ethyl carbonate, pointing out a similarity of packing of molecules. The Weissenberg layer photographs which are taken about the $\vec{b}$ and $\vec{c}$ axes, again give 020 and 102 as the strongest reflections in order.

Molecular packing of cholesteryl benzoate about $\vec{b}$ is shown in Fig. 5. The fact that there are 4 molecules per unit cell and the that c dimension is much greater than the long molecular axis suggests that the long molecular axis is nearly parallel to the $\vec{c}$ axis. Also

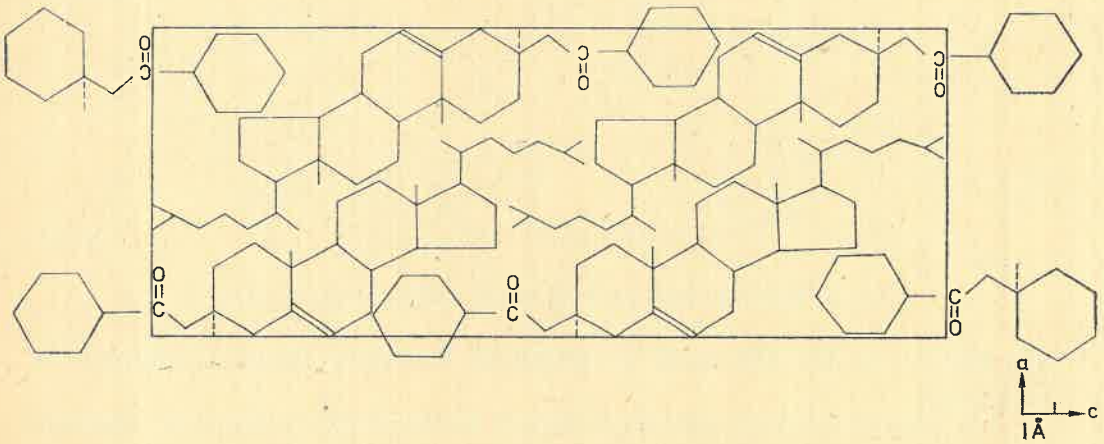

Fig. 5. Molecular packing of cholesteryl benzoate about b

since interactions between the carbonyl groups of esters on neighbouring molecules are expected to be strongest, and the *c* dimension is less than twice that of the long molecular axis, it is expected that in the unit cell half of the molecules have their esters moieties pointing up and half pointing down. Thus, there exists an antiparallel arrangement of the molecules in the unit cell. The strongest reflections observed confirm the molecular orientation obtained by geometrical analysis.

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