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The Structure of Cholesteryl Propionate in Mesomorphic State

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X-ray diffraction studies on cholesteryl propionate is reported in this paper. Apparent molecular length (*l*) and average distance between the long axes of the neighbouring molecules have been calculated at different temperature. The molecular length has been found to increase as the temperature increases.

X-ray diffraction studies on cholesteryl propionate at different temperature is reported in this paper. This is a part of our programme for the evaluation of the structure of various mesophases, determination of order parameters of samples aligned by magnetic and electric field. X-ray diffraction studies of various cholesteryl esters have been reported by Wendorff *et al.*[1]

No X-ray diffraction work for the propionate has been reported so far.

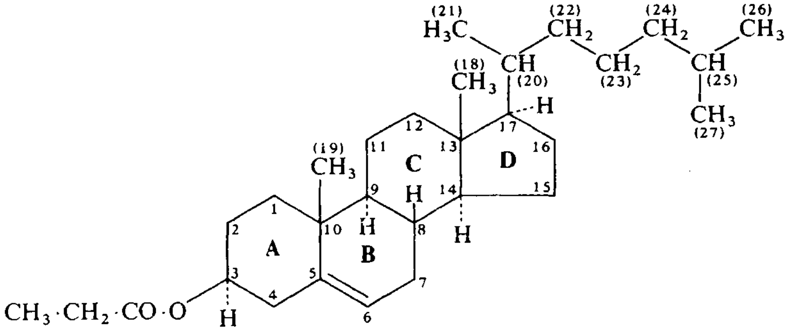

FIGURE 1

The structure and configuration of cholesteryl propionate is shown in Figure 1.[2] Rings A, B, C and D, a hydrogenated 1,2-cyclopentenophenan, methyl groups at C_{10} and C_{13}, and an eight-carbon side chain at C_{17}. The rings are not aromatic and the structure is not planar.[3] The ring system is rigid while the saturated chain and the radical (C_2H_5) behave like two somewhat more flexible tails attached to the rigid part.[4]

Cholesteryl propionate forms a mesophase on heating as well as on cooling.

Precise scanning calorimetry demonstrated the existence of two solid phases with different melting points. The following recrystallisation path was suggested.[5]

$$\begin{tikzcd}
\text{Solid I} \arrow[r, shift left, "95.2^\circ"] & \text{Cholesteric Mesophase} \arrow[l, shift left, "82.4^\circ"] \arrow[r, shift left, "111.8^\circ"] \arrow[d, shift right, "88^\circ"'] & \text{Isotropic liquid} \arrow[l, shift left, "109.6^\circ"] \\
& \text{Solid II} \arrow[u, shift right, "98.0^\circ"'] &
\end{tikzcd}$$

Sample of cholesteryl propionate was obtained from Kundan and Company, India. This was purified by recrystallizing from acetone and also from chloroform-methanol. The sample was then dried in a vacuum desiccator. The transition temperature from the solid to the cholesteric phase has been found to be $\approx 94^\circ$, and from cholesteric to isotropic $\approx 110^\circ$; but super cooling brought down the temperature to 82°C.

X-ray diffraction patterns were recorded on a Laue camera with high temperature attachments and a modified collimating system. The temperatures were measured and regulated with the help of thermocouples inserted in the block. The sample in the form of a bead was kept in the central hole on a stainless steel disc. Diffraction halos from glass produced some difficulties, so samples could not be taken in a glass capillary.

The data were analysed in terms of the angular position of the diffraction maxima which has been accurately determined by scanning with the help of an optical densitometer model No. DM 803 (Electronics Corporation of India Ltd.). Sample to film distance was measured accurately by calibrating with 111 reflection of aluminium. Apparent molecular length (l) and average distance (d) between the long axes of the neighbouring molecules can be determined from the diffraction maxima on the X-ray photographs. The theory of the relationship between the molecular parameters and the diffraction maxima has been given by de Vries.[6,7] θ's for inner and outer maxima, l^* and d values are given in Table I, Inner maxima give us l^* and outer maxima give us d. All the spacings were calculated using the formula

$$2 \times \sin\theta = K\lambda \tag{1}$$

TABLE I

Molecular parameters at different temperatures of the mesomorphic phase

Ester	T°C	Inner ring	l	K	Outer ring	d
Cholesterol Propionate	84°	2.58°	18.49	1.15	8.14°	6.07 Å
	89°	2.30°	19.20	1.11	8.1°	6.10 Å
	94°	2.24°	19.74	1.08	7.88°	6.28 Å
	98°	2.20°	20.05	1.06	8.00°	6.18 Å
	108°	2.15°	20.56	1.04	8.5°	6.14 Å

where K is a constant depending on the arrangement and shape of the molecules and on the particular spacing we are concerned with.

de Vries has discussed the equation in detail. The "d" values were calculated using $K = 1.117$. The l^* values were calculated from Bragg's law. The quantity l^* is of course, not the actual long spacing l. It is used merely as a convienient way of expressing the data obtained. However, a calculation of K values at different temperatures are given in Column five of Table I. With the help of stereomodel units (W. Bochi Glasapparate fabrik 920-Flawil) we measured the molecular length L in their completely extended form and found the value to be 21.28 Å.

The K value was calculated from l^* and L values at different temperatures. In our laboratory we have fabricated a high temperature attachment for taking the photograph in a magnetic field.[8] We tried to align cholesteric propionate with the help of a magnetic field of 10 K gauss, but no change was observed. d values are not very consistent with temperature and l^* is found to be increasing with temperature. Photographs have been taken from the solid phase temperature to 108°C .The dependence of l^* on temperature has not been explained properly as yet. We do not know the appropriate value or values of K to use in Eq. 1. We followed the approach of Wendorff *et al.*[1] to calculate K. But K decreases with increasing temperature. This is not consistent with the theory given by de Vries.[6,7]

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References

1. S. H. Wendorff and P. F. Price, *Mol. Cryst. Liq. Cryst.*, **24**, 129 (1973).
2. *Steroids*, L. F. Fieser and M. Fieser, Reinhold Publishing Corporation, 1961, p. 1-2.
3. G. W. Gray and P. A. Winson, *Liquid Crystals and Plastic Crystals*, Vol. 1, John Wiley and Sons Inc., New York (1974).

4. P. G. de Gennes, *The Physics of Liquid Crystals*, Clarendon Press, Oxford.
5. F. J. Johnson and R. S. Porter, *Liquid Crystals and Ordered Fluid*, Plenum Press, New York (1970).
6. A. de Vries, *Mol. Cryst. Liq. Cryst.*, **10**, 219 (1970).
7. A. de Vries, *Mol. Cryst. Liq. Cryst.*, **11**, 361 (1970).
8. B. Jha and R. Paul, *Proc. Nucl. Phys. Solid State Phys. Symp.*, **19C**, 491 (1976).