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## Optical anisotropy and local order parameter in a homologous series of cholesteryl esters of fatty acids

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The paper discusses estimates of local order parameters derived from refractive index data for a homologous series of cholesteryl esters of fatty acids. The local order parameter corresponds to the untwisted nematic structure in the cholesteric phase and, similar to nematogenic compounds, exhibits the well known even-odd alternation with increasing alkyl chain length. The calculated values of the optical anisotropy of the different homologues vary between 3.9 and  $6.5 \times 10^{-24} \text{ cm}^3$  indicating that the optical anisotropy arising from alkyl chain is significant when compared to the core contribution.

### 1. Introduction

In an earlier paper [1], the results of an experimental determination of the refractive index of cholesteryl oleyl carbonate (COC) in the cholesteric phase have been analysed to estimate the principal polarizabilities of COC. Using the same methodology, the temperature dependence of the local order parameter in the cholesteric phase, corresponding to the order in the untwisted nematic structure, is reported for homologous cholesteryl esters ( $n = 2$  to 15). The optical anisotropy of the mesogens in this homologous series has been estimated. We use the refractive index data of Pelzl and Sackmann [2] determined with an Abbe refractometer.

### 2. Methods

Pelzl and Sackmann use the notations  $n_1$  and  $n_2$  to denote the two refractive indices in the cholesteric phase ( $n_1 > n_2$ ). Here,  $n_1$  corresponds to the case when the electric vector lies in the plane of the specimen and  $n_2$  corresponds to the case when the electric vector lies along the cholesteric helical axis. Clearly  $n_2$  will involve  $\alpha_0$ , the polarizability transverse to the local nematic director, lying in a cholesteric layer. For the electric vector lying in a thin layer of cholesteric phase, the refractive index is a periodic function along the helical axis and it has been shown that  $n_1$  is approximately  $(n_e + n_0)/2$  where  $n_e$  is parallel and  $n_0$  is perpendicular to the local nematic director and  $n_2$  is  $n_0$  in a cholesteric phase [1, 3]. In fact a more exact expression,  $n_e = (2n_1^2 - n_2^2)^{1/2}$ , is given by Dreher *et al.* [47] and Muller and Stegemeyer [5] and it has been shown that both expressions are in agreement to within  $\pm 0.0002$  of  $n_e$ . Here, it should be emphasized that  $n_e$  and  $n_0$  correspond to the untwisted nematic structure in the cholesteric phase. For the purpose of calculating the local order parameter corresponding to the untwisted nematic structure, it is necessary to obtain the value of the anisotropy of molecular polarizabilities either from refractive index data from single crystals or from the polarizabilities computed by summing chemical

bond polarizabilities in the molecule. Ideally we would like to get the anisotropy of polarizability ( $\Delta\alpha_m = \alpha_{\parallel} - \alpha_{\perp}$ ) from the refractive index data for a phase in which  $S = 1$ , i.e. the molecules are aligned with their long axes exactly parallel, but are azimuthally randomly oriented. In the smectic A phase, exhibited by certain members of the homologous series of cholesteryl compounds discussed here, the molecules are better aligned with the long axes of the molecules normal to the layers. It may be expected that if one calculated the effective optical anisotropy ( $\Delta\alpha = \alpha_e - \alpha_0$ ) in the smectic phase at different temperatures, the value would correspond to the optical anisotropy of the molecule ( $\Delta\alpha_m = \alpha_{\parallel} - \alpha_{\perp}$ ) and remain almost a constant throughout the smectic A phase.

From refractive index data of the smectic phase of a number of cholesteryl compounds it was found by Subramanyam, Krishnamurti and Upkar Singh Hunjam [6, 7] that the anisotropy of the Lorentz field factors is very small. Under these circumstances, the Lorenz-Lorentz relation as given by [6, 7]

$$\chi_i = 3(n_i^2 - 1)/4\pi(n_i^2 + 2), \quad i = 1, 2 \quad (1)$$

(where  $\chi_1$  and  $\chi_2$  denote  $N\alpha_1$  and  $N\alpha_2$  respectively) is a reasonably good approximation for indices  $n_1$  and  $n_2$ . It has been shown that [8]

$$\chi_e + 2\chi_0 = \chi_2 + 2\chi_1 = 3\bar{\chi}$$

and

$$(\chi_e - \chi_0)/\bar{\chi} = (\alpha_e - \alpha_0)/\bar{\alpha}. \quad (2)$$

Using refractive index data and employing the above equations it was found that the values of  $(\chi_e - \chi_0)/\bar{\chi}$  are not quite constant with temperature. This suggests that in the smectic A phase, the molecules have flexibility associated with the alkyl chain conformational freedom. Under these circumstances, we assume that the maximum value of  $(\chi_e - \chi_0)/\bar{\chi}$  found at the lowest temperature of the smectic A phase to be the value corresponding to  $(\alpha_{\parallel} - \alpha_{\perp})/\bar{\alpha}$  of the molecule. In other words, we shall assume that at the lowest temperature of the smectic A phase (sm), the order parameter  $S_{sm} = 1.0$  to enable a meaningful comparison of the nematic  $S$  factors of the different members of the homologous series.

Hence, it follows that

$$\frac{((\chi_e - \chi_0)/\bar{\chi})_{ch}}{((\chi_e - \chi_0)/\bar{\chi})_{sm}} = \frac{(N_{ch}(\alpha_e - \alpha_0)/N_{ch})}{(N_{sm}(\alpha_{\parallel} - \alpha_{\perp})/N_{sm})} = \frac{\alpha_e - \alpha_0}{\alpha_{\parallel} - \alpha_{\perp}} = S. \quad (3)$$

Here  $N_{ch}$  and  $N_{sm}$  represent the number of molecules per unit volume in the cholesteric and smectic phases respectively. The mean polarizability  $\bar{\alpha}$  is assumed to be the same in all phases.

Pelzl and Sackmann have reported the refractive index data for three wavelengths ( $\lambda = 546, 589$  and  $644$  nm) at each temperature and there is very good agreement between the orientational order parameters derived from the cholesteric phase calculated using equation (3) and the data for the different wavelengths.

For compounds in the homologous series exhibiting a cholesteric phase only, the optical anisotropy of the corresponding molecule has been estimated using  $\Delta\alpha_m$  of the compounds exhibiting a smectic phase after correcting for the alkyl chain contribution. For  $n = 2$  to  $5$  and  $15$ ,  $\Delta\alpha_m$  has been estimated using bond polarizability data by considering the contribution to  $\alpha_{\parallel}$  and  $\alpha_{\perp}$  of methylene groups assuming they are in the transconformation. In the absence of crystalline refractive index data for  $n = 2$

to 5 and 15, this procedure helps in finding the extent and trends of the variation of the local order parameter  $S$  in the cholesteric phase. It also facilitates further comparisons with other members of the homologous series. The effective mean polarizability ( $\bar{\alpha}$ ) for all the members has been estimated as described in an earlier paper [3].

### 3. Determination of the angle $\langle\varphi\rangle$ between the helical axis and the plane containing the molecules

Let the direction of the long axis of the  $m$ th molecule be represented by unit vectors  $\mathbf{a}_m$  choosing a rectangular cartesian coordinate frame of reference with unit vectors  $\mathbf{i}, \mathbf{j}, \mathbf{k}$ . Assuming that the director is along  $\mathbf{k}$  and helical axis along  $\mathbf{j}$ , it is easily shown that (in cholesteric phases) [9]

$$\alpha_e = (\alpha_{\parallel} - \alpha_{\perp}) \overline{(\mathbf{a}_m \cdot \mathbf{k})^2} + \alpha_{\perp}, \quad (4)$$

$$\alpha_0 = (\alpha_{\parallel} - \alpha_{\perp}) \overline{(\mathbf{a}_m \cdot \mathbf{j})^2} + \alpha_{\perp}.$$

Here  $\alpha_e$  and  $\alpha_0$  are the polarizabilities along and transverse to the director of the untwisted nematic structure in the cholesteric phase, i.e.  $\alpha_0$  involves refractive index  $n_2$  in the cholesteric phase for the electric vector along the helical axis (and hence perpendicular to the plane containing the molecules). If this is so,  $\overline{(\mathbf{a}_m \cdot \mathbf{j})^2}$  should be zero. But from the refractive index  $n_2$  available in the cholesteric phase (which depends on  $\alpha_0$  and  $n_0$  in the lowest temperature smectic phase which in turn involves  $\alpha_{\perp}$  of the molecule), we find that  $\overline{(\mathbf{a}_m \cdot \mathbf{j})^2}$  or the angle between the plane containing the molecules and the helical axis estimated by the iteration procedure varies between 67 to 80 degrees with temperature in the cholesteric phase.

### 4. Results and discussion

Figure 1 shows the temperature variation of  $S$ , the local order parameter calculated from the refractive index data (averaged over values obtained with equation (3) for different wavelengths) for compounds exhibiting smectic and cholesteric phases. For compounds which show only the cholesteric phase, the temperature variations of  $S$  are given in figure 2. In fact these variations are quite similar to the temperature variation of orientational order parameters in nematic liquid crystals. The magnitude of the  $S$  factors obtained from birefringence data with the same methodology used in this paper are in reasonable agreement with  $S$  factors obtained from N.M.R. data in the case of substances exhibiting both nematic and smectic phases (see [8]). Such a comparison is not possible here due to the lack of N.M.R. data. Further, for compounds showing smectic A and nematic phases, the calculated values of the  $S$  factors are in the range (0.5–0.9) at reduced temperatures [8], which is also observed in these cholesteryl compounds.

Figure 3 shows the variation of the optical anisotropy ( $\Delta\alpha = \alpha_e - \alpha_0$ ) with the number of carbon atoms in the alkyl chain at  $T_c - T = 4^\circ\text{C}$  for the untwisted nematic structure defined with respect to the director lying in a thin cholesteric layer. An alternation is seen for the earlier members of the series. The trend of variations of the  $S$  factors with temperature is similar to that reported in the case of  $n$ -alkyl- $p$ -(4-ethoxy benzylidene amino) methyl cinnamates [8]. The optical anisotropy ( $\Delta\alpha_m = \alpha_{\parallel} - \alpha_{\perp}$ ) and effective mean polarizability ( $\bar{\alpha}$ ) for all the members of

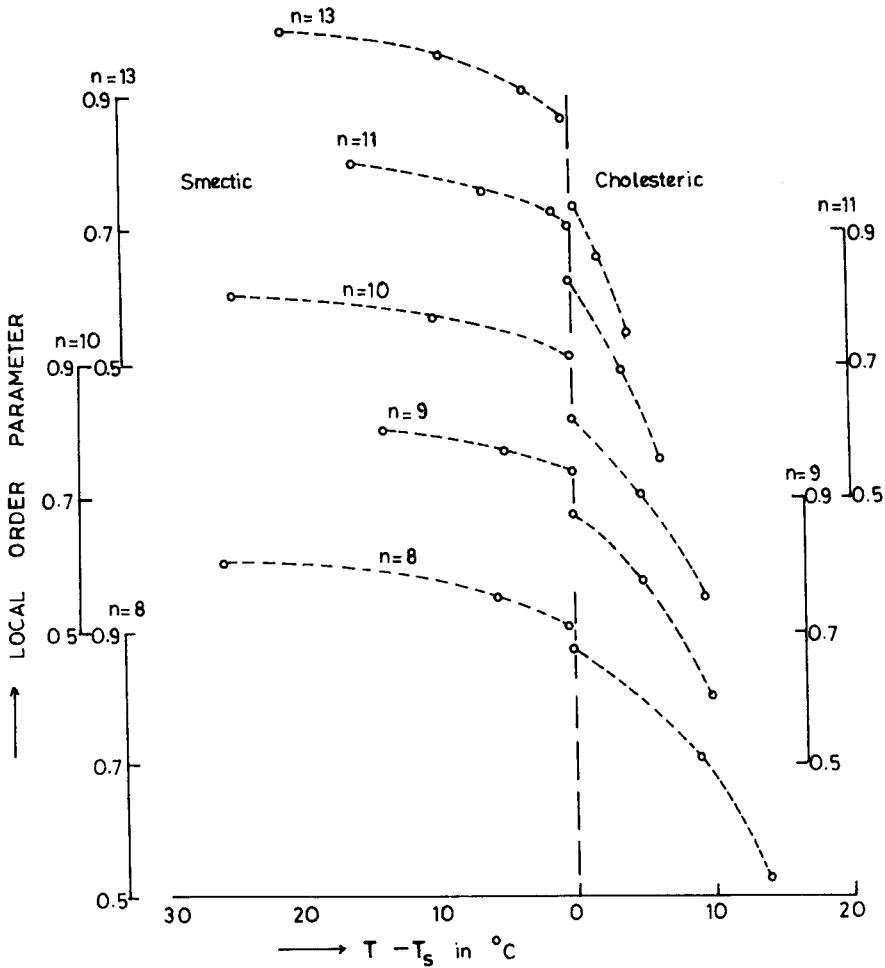


Figure 1. Variation of the local order parameter  $S$  with temperature for cholesteryl compounds showing both smectic and cholesteric phases.

Angle  $\langle\varphi\rangle$  (see text), effective polarizability ( $\times 10^{-24} \text{ cm}^3$ ) along the length of the molecule ( $\alpha_{\parallel}$ ), mean polarizability of the molecule ( $\bar{\alpha}$ ), the anisotropy of the molecule and the local order parameters at the reduced temperature  $T/T_c = 0.98$ .

	$n$									
	2	3	4	5	8	9	10	11	13	15
$\langle\varphi\rangle$ at $T_c - T = 4^\circ\text{C}$ (cholesteric)	71.0	70.0	68.0	69.0	69.0	71.0	72.0	71.0	71.0	72.0
$\alpha_{\parallel}$	53.3	55.3	57.3	59.3	65.2	67.1	69.1	71.0	75.0	79.5
$\bar{\alpha}$	50.7	52.5	54.4	56.2	61.8	63.2	65.5	67.3	71.0	76.7
$\Delta\alpha_m$	3.9	4.1	4.3	4.5	5.1	5.2	5.5	5.6	6.1	6.5
$S$	0.607	0.553	0.518	0.551	0.525	0.605	0.551	0.500	0.542	0.527

$$\Delta\alpha_m = \alpha_{\parallel} - \alpha_{\perp}.$$

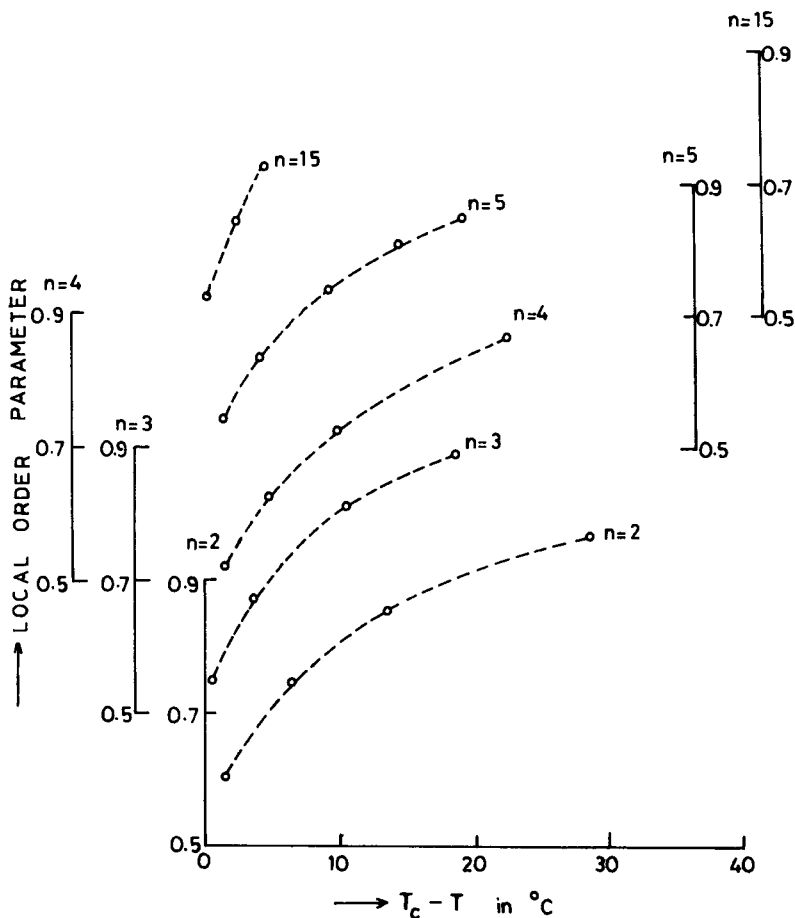


Figure 2. Variation of the local order parameter  $S$  with temperature for cholesteryl compounds showing only the cholesteric phase.

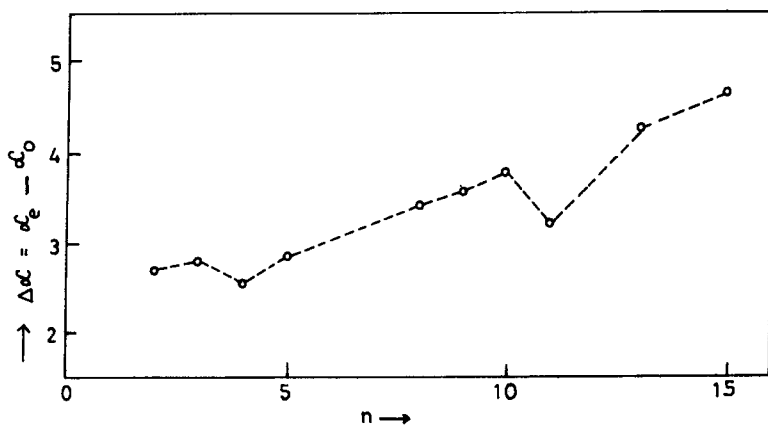


Figure 3. Variation of optical anisotropy  $\Delta\alpha$  ( $= \alpha_e - \alpha_o$ ) at  $T_c - T = 4^{\circ}C$  in the cholesteric phase with a number of carbon atoms  $n$  in the chain; calculated from refractive index data for  $\lambda = 5894 \text{ \AA}$ .

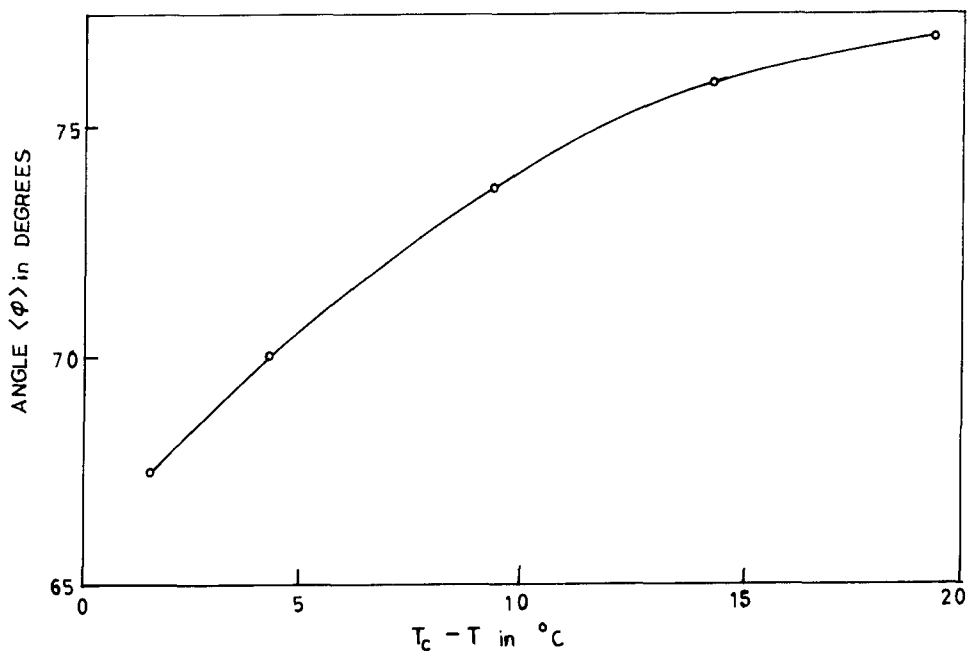


Figure 4. Variation of  $\langle \varphi \rangle$  with temperature in the cholesteric phase for  $n = 5$ .

homologous series corresponding to the molecule are given in the table. The optical anisotropy varies between  $3.9$  and  $6.5 \times 10^{-24} \text{ cm}^3$  for different esters, indicating that the contribution from the alkyl chain is significant. This is due to the fact that the contribution from the core to the total optical anisotropy in these cholesteric homologues is very small, whereas this is not so in the nematogenic compounds.

Apart from the above results, the following facts also emerge from our calculations:

- (1) At the same  $T_c - T$ , the angles  $\langle \varphi \rangle$  between the molecular axis and the helical axis obtained for the homologous series are given in the table; agreement among members of the series is within 5 per cent. This clearly indicates that the molecules are not perpendicular to the helical axis.
- (2) The temperature variation of  $\langle \varphi \rangle$  in the cholesteric phase is given in figure 4 for the  $n = 4$  homologue. The graph indicates a change in the helical arrangement with temperature.

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