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Optical Anisotropy and Relative Order in Cholesteryl-n-Alkyl Carbonates

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Optical Anisotropy and Relative Order in Cholesteryl-*n*-Alkyl Carbonates

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The paper discusses the results of the calculation of the relative order parameters and the optical anisotropies from birefringence data in the case of the homologous series of compounds, Cholesteryl-*n*-alkyl carbonates. The relative order parameters are found to exhibit the well known zig-zag alternation with increase in the number of atoms of the alkyl chain. The calculated values of the optical anisotropy of the different molecules are approximately equal, indicating that the optical anisotropy arises mainly from the central rigid portion of the molecule and that the contribution of the alkyl chain to the optical anisotropy is not significant.

INTRODUCTION

In an earlier paper,[1] it has been discussed that the results of the experimental determination of refractive index of cholesteryl oleyl carbonate (COC) in cholesteric phase using Abbe refractometer and the data have been analysed to correlate principal polarizabilities of COC. Using the same prescription, the dependence of relative order parameter on temperature and also on number of carbon atoms for a series of homologous cholesteryl *n*-alkyl carbonates in cholesteric phase are reported in this paper. The refractive index data determined using Abbe refractometer for the above compounds are available from the studies of R. Rettig *et al.*[2]

DETAILS OF THE CALCULATION

R. Rettig, G. Pelzl and D. Demus use the notations n_1 and n_2 to denote the two refractive indices in the cholesteric phase ($n_1 > n_2$) measured using Abbe refractometer. Here, n_1 corresponds to the case when electric vector lies in the plane of the specimen and n_2 corresponds to the case when electric vector lies along the helical axis. Clearly n_2 will involve $\alpha_\perp (= \alpha_0)$, the polarizability transverse to the long axes of the molecules. For electric vector lying in the thin layer, the refractive index is a periodic function along the helical axis and it has been shown that n_1 is approximately $(n_e + n_0)/2$ (see Ref. 1) and n_2 is n_0 in cholesteric phase. In fact, a more exact expression is $n_e = (2n_1^2 - n_2^2)^{1/2}$ as given by Dreher *et al.*[3] and Müller *et al.*[4] The values of n_e, evaluated for the cholesteryl compounds at $(T_c - T) = 3°C$ using both expressions are tabulated in Table I and as seen the agreement is within ± 0.0002. Here, it should be emphasized that n_e and n_0 (α_e and α_0) correspond to the untwisted nematic structure of the cholesteric compounds. From the index data of the smectic phase[5] of a number of cholesteryl compounds, it was found by Subramhanyam and Krishnamurti[6] that the anisotropy of Lorentz field factors in the case of cholesteryl compounds is very small. Under these circumstances, it was found by them that the Lorenz-Lorentz relation given below, is a reasonable good approximation for indices n_1 and n_2

$$\chi_i = \frac{3}{4\pi}\left(\frac{n_i^2 - 1}{n_i^2 + 2}\right) \qquad i = 1, 2 \tag{1}$$

TABLE I

Estimated mean polarizability $\bar{\alpha}$ and calculated optical anisotropy ($\Delta\alpha$) at $T_c - T = 3°C$ of cholesteryl-*n*-alkyl carbonates, in units of 10^{-24} cm^3

n	n_e[a] at $T_c - t = 3°C$	n_e[b] at $T_c - t = 3°C$	$(\alpha_e - \alpha_0)$ at $T_c - T = 3°C$	$\bar{\alpha}$
2	1.5018	1.5019	3.60	50.6
3	1.5031	1.5033	3.50	52.4
4	1.5058	1.5060	3.00	54.2
7	1.5042	1.5043	2.80	59.6
8	1.5050	1.5051	3.00	61.4
9	1.5058	1.5060	3.05	63.2
10	1.5033	1.5034	3.35	64.9
11	1.5034	1.5035	3.30	66.8

[a] $n_e = (2n_1^2 - n_2^2)^{1/2}$ (see Ref. 3 and 4)
[b] $n_e = (2n_1 - n_2)$

where $N\alpha_1$ and $N\alpha_2$ are denoted by χ_1 and χ_2 respectively. It is easily shown that[1]

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

and also

$$\frac{\chi_e - \chi_0}{\bar{\chi}} = \frac{\alpha_e - \alpha_0}{\bar{\alpha}} = \frac{\Delta\alpha S}{\bar{\alpha}} \tag{2}$$

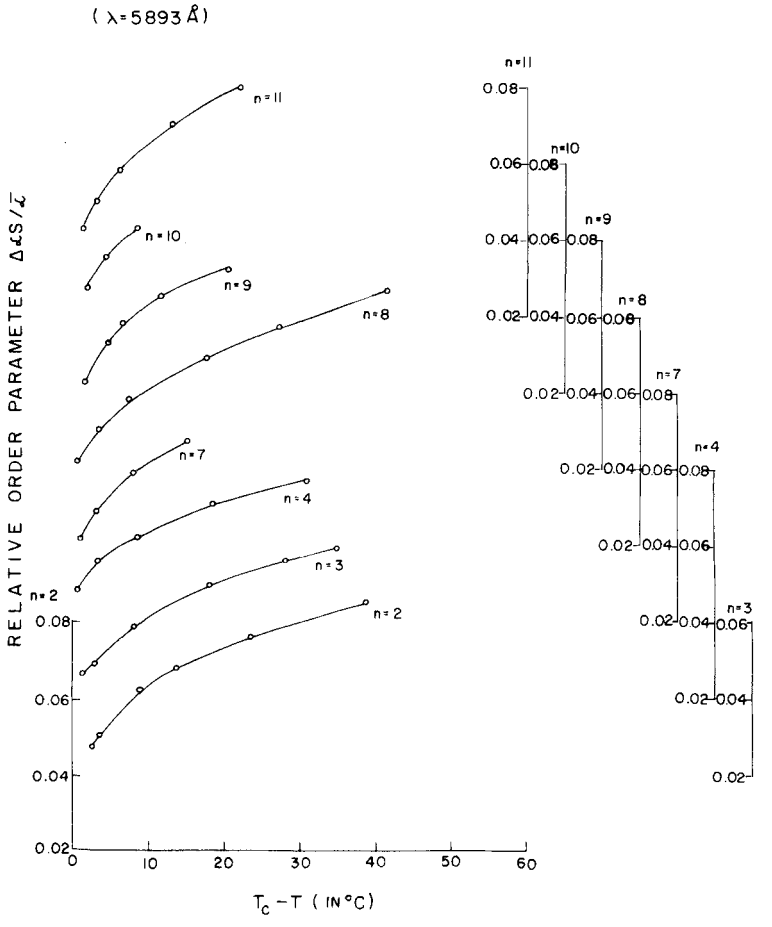

FIGURE 1 Variation of relative order parameter ($\Delta\alpha S/\bar{\alpha}$) with temperature in the case of the different homologous, calculated from index data for λ5893 Å.

where $\bar{\alpha}$ is the mean polarizability of the molecule, $\Delta\alpha S/\bar{\alpha}$ is the relative order[7] and $\Delta\alpha = (\alpha_{\parallel} - \alpha_{\perp})$ is the optical anisotropy of the molecule.

RESULTS AND DISCUSSION

Using relations (1) and (2), χ_e, χ_0 and then $(\chi_e - \chi_0)/\bar{\chi}$ are calculated for different compounds for the wavelength 5893 Å. Figure 1 shows the temperature variation of the relative order for the homologous series, cholesteryl-*n*-alkyl carbonates and in fact it is quite similar to the temperature variation of orientational order parameter of nematic liquid crystals.[8] Figure 2 shows the variation of the relative order with the number of carbon atoms. An alternation is seen for the earlier members of the series. However with increase in numbers of carbon atoms, the value of $\Delta\alpha S/\bar{\alpha}$ varies between 0.045 to 0.06. A similar feature has been observed in the case of *n*-alkyl-*p*-(4-ethoxy benzylidene amino)methyl cinnamates.[8] Since the mean polarizability of cholesterol is known (Ref. 6) and the mean polarizability of cholesteryl-*n*-alkyl carbonates are determined by making end corrections using bond polarizability data and are given in Table I along with calculated optical anisotropy $(\alpha_e - \alpha_0)$ at $T_c - T = 3°C$. The value of $(\alpha_e - \alpha_0)$ varies between 3.0 to 4.0×10^{-24} cm^3 for the different esters indicating that a major portion of the optical anisotropy arises from the cholesteryl group. $(\alpha_e - \alpha_0)$ decreases with increase of temperature, because of increase in thermal fluctuation in the orientation of the molecules.

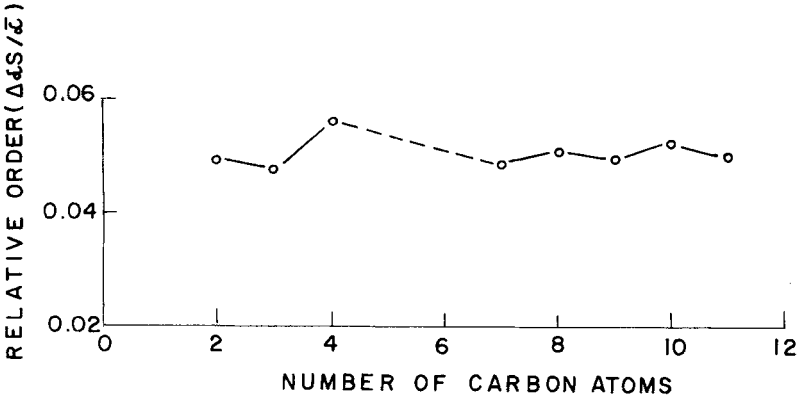

FIGURE 2 Variation of relative order parameter with number of carbon atoms in the alkyl chain, calculated from index data for λ5893 Å (at $T_c - T = 3°C$).

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