Refractive Indices, Densities, Polarizabilities and Molecular Order in Cholesteric Liquid Crystals

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Version of record first published: 14 Oct 2011.

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The temperature variation of refractive indices (n_o, n_e), birefringence (Δn), density (ρ) and order parameter (S) of two cholesteric liquid crystals—cholesteryl benzoate and laurate are reported in the smectic, cholesteric and isotropic phases. The order parameters have been evaluated using Aver'yanov's relations. The S values determined are good agreement with NMR data.

The mean polarizabilities ($\bar{\alpha}$) of a few cholesteric liquid crystals have been evaluated using (i) the modified method of Lippincott-δ-function potential model and (ii) the additivity rule of bond polarizabilities. There is good agreement between the values of $\bar{\alpha}$ calculated by these methods and experimental values, thereby suggesting the general applicability of Lippincott-δ-function potential model to liquid crystals.

INTRODUCTION

One of the principal structural characteristics of cholesteric liquid crystals (CLC) is the degree of molecular order in quasi-nematic layers S = $1/2(3\cos^2\theta - 1)$ where θ is the angle between the long axes of the molecules and the direction of the axis of preferential orientation (the director) in the layer. The molecular ordering in a cholesteric mesophase has been investigated by optical circular dichroism, optical rotatory dispersion in UV, visible and IR regions of the spectrum and by ESR and NMR.[1-7]

The molecules of cholesteric mesogens consist of a rigid moiety and semi-flexible ends. To develop the theory of the mesophase we need information (i) on the degree of mobility of the end groups which depends on the length of the side chain and (ii) on the influence of the end groups on the orientation of the rigid core of the molecule. Recently, Aver'yanov *et al.* have shown that the refractometric data[8,9] can be used to obtain the orientational order parameter for cholesteric liquid crystals.

The molecular polarizabilities are intimately woven in the definition and evaluation of order parameter of liquid crystals using optical tensorial properties. The principal polarizabilities and the mean polarizability of molecules also provide useful information on conformal stereo chemical analyses and the estimation of helical content in liquid crystals. Experimental methods such as light scattering, Kerr-effect and molecular refractivity, and few theoretical methods are available in literature to evaluate polarizability coefficients. Recently, Murthy *et al.* [10] have successfully applied the Lippincott-δ-function potential model for the evaluation of polarizability of the two series of nematogenic liquid crystals.

We have evaluated the orientational order parameters for cholesteryl benzoate and laurate using Aver'yanov's relations. The mean polarizabilities $(\bar{\alpha})$ of a few cholesterogenic materials have been evaluated using (i) the additivity rule of bond polarizabilities and (ii) the modified method of Lippincott-δ-function potential model.
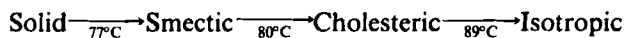
EXPERIMENTAL

The compounds for which the refractive index and density data are reported, in this communication, are listed below

(i) Cholesteryl benzoate

$$\text{Solid} \xrightarrow[148°C]{} \text{Cholesteric} \xrightarrow[176°C]{} \text{Isotropic}$$

(ii) Cholesteryl laurate

$$\text{Solid} \xrightarrow[77°C]{} \text{Smectic} \xrightarrow[80°C]{} \text{Cholesteric} \xrightarrow[89°C]{} \text{Isotropic}$$

The commercially available compounds (supplied by Eastman Organic Chemicals, USA) were purified by successive recrystallization. Oriented specimens were prepared inside special hollow glass prisms with very small refracting angles (4–5°). The glass plates which were used for the hollow prisms were optically flat and the two surfaces of the plates were perfectly parallel. The prism was precalibrated by measuring the refractive indices of distilled water, acetone, benzene and methyl iodide. The inside surfaces of the prism were rubbed vertically along the refracting edge and the liquid crystal sample was allowed to flow along the edge by melting a few crystals placed at the top. The combination of rubbing and flow produced a homogeneously oriented cholesteric specimen.

The prism was put inside an electrically controlled aluminum block. The temperature was measured by using thermocouples which were precalibrated against the melting point of pure benzoic acid and salicylic acid. The relative temperatures were obtained to an accuracy of ±0.01°C and could be main-

TABLE I

Refractive indices and densities in the cholesteric and isotropic phases—Cholesteryl benzoate

Temperature (°C)	λ5461 Å		λ5893 Å		Density (gm/cc)
	n_e	n_o	n_e	n_o	
150.0	1.4803	1.5808	1.4798	1.5802	1.1605
152.5	1.4806	1.5769	1.4803	1.5763	1.1585
155.0	1.4811	1.5725	1.4806	1.5721	1.1570
157.5	1.4815	1.5705	1.4810	1.5701	1.1548
160.0	1.4819	1.5662	1.4813	1.5656	1.1534
162.5	1.4823	1.5635	1.4817	1.5629	1.1513
165.0	1.4827	1.5616	1.4820	1.5606	1.1496
167.5	1.4831	1.5553	1.4824	1.5546	1.1478
170.0	1.4836	1.5524	1.4829	1.5516	1.1455
172.0	1.4839	1.5459	1.4833	1.5453	1.1442
175.0	1.4844	1.5368	1.4837	1.5362	1.1410
180.0 (liquid)	1.4987		1.4963		

tained constant to within the same limits during different sets of observations. The angles of minimum deviation and the angle of the prism were measured with a precision Goniometer Spectrometer (Freiberger Prazisionsmechanik, East Germany), which could measure angles to an accuracy of 2″ of arc. The refractive indices are estimated to be accurate to ±0.001. The values are presented in Tables I and II.

The densities in the liquid crystalline phase were determined by studying the volume expansion of a known weight of the material in a capillary tube with

TABLE II

Refractive indices and densities in the cholesteric and isotropic phases—Cholesteryl laurate

Temperature (°C)	λ5461 Å		λ5893 Å		Density (gm/cc)
	n_e	n_o	n_e	n_o	
77.0	1.4929	1.5658	1.4904	1.5646	0.9430
78.0	1.4932	1.5637	1.4906	1.5624	0.9420
79.0	1.4934	1.5620	1.4908	1.5607	0.9413
80.0	1.4936	1.5598	1.4910	1.5585	0.9405
81.0	1.4939	1.5565	1.4913	1.5551	0.9370
82.0	1.4942	1.5538	1.4917	1.5527	0.9358
83.0	1.4943	1.5502	1.4921	1.5493	0.9346
84.0	1.4950	1.5472	1.4925	1.5460	0.9340
85.0	1.4953	1.5446	1.4929	1.5436	0.9325
86.0	1.4958	1.5421	1.4933	1.5409	0.9318
87.0	1.4963	1.5401	1.4939	1.5389	0.9295
92.0 (liquid)	1.5098		1.5074		

uniform cross section and are corrected for the thermal expansion of glass. The density data are given in Tables I and II.

THEORETICAL EVALUATION OF MOLECULAR POLARIZABILITIES

(I) Additivity rule of bond polarizability

Denbigh[11] has shown that an empirical additive scheme of bond polarizabilities can give the mean polarizability of a compound. We have employed this scheme to determine the molecular polarizabilities of few cholesterogenic materials. The bond polarizability data have been taken from Denbigh,[11] Le Fevre,[12] Rao *et al.*,[13] Le Fevre *et al.*[14] and Vogel *et al.*[15] Parallel and perpendicular components of the polarizabilities are evaluated using the crystalline structures.[16-23]

For directional properties in anisotropic crystals it is necessary to use, not an average polarizability for each bond, but an ellipsoid of polarizability. The polarizability contribution in a principal direction k of the polarizability ellipsoid of a polyatomic molecule is given by

$$\alpha_k = \Sigma\ \alpha_1 \cos^2 \theta + \Sigma\ \alpha_t \sin^2 \theta \qquad (1)$$

(summed over all the bonds), where θ is the angle between a bond and the direction k. α_1 and α_t are the polarizabilities along and across the bond, respectively. In the case of benzene molecule, the contribution along a direction k is given by

$$\alpha_k = \alpha_{11} \cos^2 \theta_1 + \alpha_{22} \cos^2 \theta_2 + \alpha_{33} \cos^2 \theta_3 \qquad (2)$$

θ_1, θ_2 and θ_3 are the angles between α_{11}, α_{22} and α_{33} and the direction in question, respectively.

The polarizability anisotropy $\Delta\alpha$ can be calculated from the bond polarizability data. The molecular axis is taken to be along the line joining the para positions of the benzene rings with molecule itself being rigid. An estimation of the transverse polarizability $\alpha_\perp$ and anisotropy of polarizability $\Delta\alpha$ is made by using $\alpha_\parallel + 2\alpha_\perp = 3\bar{\alpha}$ and $\Delta\alpha = \alpha_\parallel - \alpha_\perp$ respectively. The results are tabulated in Tables III and IV.

(II) Lippincott-δ-function potential model

The one dimensional δ-function potential model developed by Frost[24-26] and improved by Lippincott[27] is one of the most useful methods suggested in studying the spectroscopic parameters like vibrational frequencies and anharmonicities. It is also useful in considering polarizability as an effective criterion in judging the proximity of wave function to real situations. According to this

TABLE III

Molecular polarizabilities of homologous cholesteryl alkanoates (10^{-24} cm^3)

Compounds	$\alpha_{\parallel}$	$\alpha_{\perp}$	$\bar{\alpha}$	$\Delta\alpha$	$\Delta\alpha/\bar{\alpha}$
Cholesteryl methanoate	78.151	44.496	55.714	33.655	0.604
Cholesteryl ethanoate	80.127	45.139	56.802	34.987	0.615
Cholesteryl propionate	82.104	45.784	57.891	36.320	0.627
Cholesteryl butanoate	84.081	46.427	58.979	37.653	0.638
Cholesteryl pentanoate	86.058	47.072	60.068	38.986	0.649
Cholesteryl hexanoate	88.034	47.715	61.156	40.319	0.659
Cholesteryl heptanoate	90.012	48.359	62.245	41.651	0.669
Cholesteryl octanoate	91.987	49.003	63.333	42.984	0.678
Cholesteryl nonanoate	93.964	49.647	64.422	44.317	0.687
Cholesteryl decanoate	95.941	50.291	65.510	45.650	0.696
Cholesteryl undecanoate	97.918	50.935	66.598	46.983	0.705
Cholesteryl dodecanoate	99.895	51.579	67.686	48.316	0.714

model the potential energy of an n-electron system is the sum of the single electron δ-function potentials. The space integral of this function is definite and is known as "δ-function strength" or "Reduced electronegativity (REN)." The linear combination of all these delta function atomic orbitals forms the molecular orbit.

The semi-empirical model was used by Lippincott and Stutman[28] and others[29-33] for the calculation of the molecular polarizabilities of few molecular systems. Rao et al.[34] and Murthy et al.[35,36] have used this model for the calculation of polarizability of biopolymers.

The mean polarizability is given by the expression

$$\bar{\alpha} = \tfrac{1}{3}(\Sigma \, \alpha_{\parallel p} + \Sigma \, \alpha_{\parallel n} + \Sigma \, 2\alpha_{\perp}) \qquad (3)$$

TABLE IV

Molecular polarizabilities of cholesterol derivatives (10^{-24} cm^3)

Compounds	$\alpha_{\parallel}$	$\alpha_{\perp}$	$\bar{\alpha}$	$\Delta\alpha$	$\Delta\alpha/\bar{\alpha}$
Cholesteryl methyl carbonate	78.489	44.066	55.541	34.423	0.610
Cholesteryl ethyl carbonate	80.466	44.710	56.628	35.756	0.604
Cholesteryl chloride	74.906	44.278	54.487	30.628	0.562
Cholesteryl bromide	76.276	45.078	55.482	31.198	0.562
Cholesteryl benzoate	89.282	40.759	56.934	48.523	0.852
Cholesteryl cinnamate	92.298	44.429	60.385	47.869	0.792

where $\Sigma\,\alpha_{\|p}$ is the parallel bond component, $\Sigma\,\alpha_{\|n}$ parallel non-bonded region electron contribution, $\Sigma\,2\alpha_\perp$ perpendicular bond contribution.

The bond region electron contribution to parallel polarizability is calculated using the linear combination of atomic δ-function wave function and is given by

$$\alpha_{\|p} = \frac{4nA}{a_o}\left(\frac{R^2}{4} + \frac{1}{2C_R^2}\right)^2 \exp\left[-\frac{(x_1 - x_2)^2}{4}\right] \qquad (4)$$

where n is the bond order, a_o the Bohr radius, A the reduced electronegativity or δ-function strength, R the internuclear distance, x_1 and x_2 Pauling's electronegativities of atoms A and B in the bond A—B, C_R a constant. The nonbond region electron contribution is given by

$$\Sigma\,\alpha_{\|n} = \Sigma f_j \alpha_j \qquad (5)$$

where f_j is the fraction of the non-bonded region electrons of jth atom and α_j is its atomic polarizability. The bond perpendicular component is given by

$$\Sigma\,2\alpha_\perp = n_{df}\left[\frac{\Sigma\,x_j^2\,\alpha_j}{\Sigma\,x_j^2}\right] \qquad (6)$$

where $n_{df} = 3N - n_b$ is the number of degrees of freedom, N the number of atoms and n_b the number of bonds.

The bond lengths are taken from the detailed crystal structure analyses.[16-23] The calculated values of parallel, perpendicular and mean polarizabilities are presented in Tables V and VI.

The mean polarizabilities obtained by Lippincott model are agreeing with those of method (i), but the parallel and perpendicular components of the polarizabilities differ considerably. In the evaluation of parallel and perpendicular components of polarizabilities by method (i), we assume a molecular axis about which the bond polarizability components are resolved from which in turn the mean polarizability is extrapolated and it is these values which are compared with the experimental values.

Assuming that there is a random distribution of individual bonds comprised by molecule about a molecular axis we can take the mean angle formed by the individual bonds with the molecular axis to be 45°. Then the component parallel to the axis is given by the component of the total $(\alpha_{\|p} + \alpha_{\|n})$ value along the axis. With this value of $\alpha_\|$, we can calculate the perpendicular component $\alpha_\perp$ by

$$3\bar{\alpha} = \alpha_\| + 2\alpha_\perp \qquad (7)$$

The theoretical values of polarizability and anisotropy of polarizabilities obtained by this method agree with those obtained from method (i) as can be seen from the Tables III to VI. Agreement between the values of $\bar{\alpha}$ obtained by

TABLE V

Molecular polarizabilities of homologous cholesteryl alkanoates (10^{-24} cm^3)

Compounds	$(\alpha_{\|p} + \alpha_{\|n})$	$\alpha_\perp$	$\bar{\alpha}$	About the molecular axis		
				$\alpha_\|$	$\alpha_\perp$	$\Delta\alpha$
Cholesteryl methanoate	112.936	27.629	56.065	79.858	44.169	35.088
Cholesteryl ethanoate	116.861	28.755	58.122	82.633	45.269	36.733
Cholesteryl propionate	120.785	29.651	60.029	85.408	47.339	38.068
Cholesteryl butanoate	124.708	30.540	61.932	88.182	48.807	39.375
Cholesteryl pentanoate	128.631	31.432	63.832	90.956	50.267	40.685
Cholesteryl hexanoate	132.555	31.870	65.432	93.731	51.727	41.995
Cholesteryl heptanoate	136.473	32.761	67.332	96.501	53.187	43.305
Cholesteryl octanoate	140.401	33.647	69.232	99.279	54.647	44.615
Cholesteryl nonanoate	144.246	34.536	71.132	102.052	36.107	45.925
Cholesteryl decanoate	148.246	35.425	73.032	104.826	57.567	47.235
Cholesteryl undecanoate	152.169	38.275	74.932	107.600	59.027	48.573
Cholesteryl dodecanoate	156.092	41.125	76.832	110.374	60.487	49.887

these two methods suggest the general applicability of the Lippincott-δ-function potential model to liquid crystals.

RESULTS AND DISCUSSION

We observe from the tabulated data (Table III) of polarizabilities that the mean polarizability of the molecule increases linearly with the number of CH$_2$ groups in the alkyl chain of the esters. The increment in the mean polarizability $\delta(\bar{\alpha})$ per CH$_2$ group is 1.088×10^{-24} cm^3. The anisotropy of polarizability $\Delta\alpha$, and $\Delta\alpha/\bar{\alpha}$ also increase linearly. The increment in anisotropy of polarizability per CH$_2$ group, $\delta(\Delta\alpha)$ is 1.332×10^{-24} cm^3. It is clear from the Figure 1 that the rate of increase of anisotropy of polarizability with chain length is

TABLE VI

Molecular polarizabilities of cholesterol derivatives (10^{-24} cm^3)

| Compounds	$(\alpha_{\|p} + \delta_{\|n})$	$\alpha_\perp$	$\bar{\alpha}$	About the molecular axis		
				$\alpha_\|$	$\alpha_\perp$	$\Delta\alpha$
Cholesteryl methyl carbonate	115.409	27.834	57.026	81.605	44.736	36.869
Cholesteryl ethyl carbonate	116.989	28.960	58.303	82.724	46.092	36.631
Cholesteryl chloride	109.227	26.179	53.862	77.235	42.176	35.059
Cholesteryl bromide	110.901	26.504	54.636	78.419	42.745	35.673
Cholesteryl benzoate	131.179	26.128	61.145	92.757	45.339	47.418
Cholesteryl cinnamate	136.544	27.743	64.010	96.551	47.738	48.819
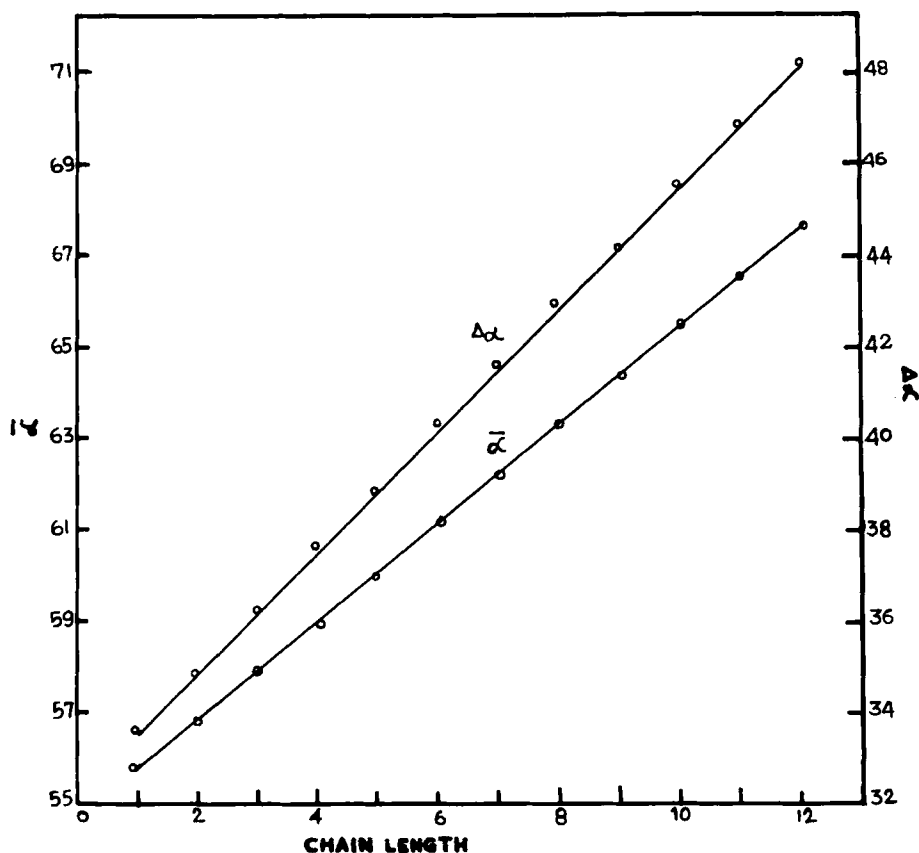
FIGURE 1   Variation of $\Delta\alpha$ and $\bar{\alpha}$ with the number of carbon atoms.

comparatively higher than that of mean polarizability. It is found that the values of $\Delta\alpha$ calculated from cholesteryl benzoate and cholesteryl laurate from refractive index data agree with those of bond polarizability data.

Figure 2 shows that $\Delta\alpha/\bar{\alpha}$ decreases linearly with the number of carbon atoms in the alkyl chain for nematic liquid crystals (NLC)[37] whereas in the case of cholesteric liquid crystals $\Delta\alpha/\bar{\alpha}$ increases linearly with the number of carbon atoms in the alkyl chain. Also, for nematic liquid crystals the rate of decrease is more in symmetric molecules (4,4'-di-*n*-alkyloxyazoxy benzene) than that in asymmetric molecules (*p*-(*p*-ethoxyphenylazo)phenyl alkanoates). These features can be explained as follows. The central rigid core is altogether different in cholesteric and nematic liquid crystals. The polarizability anisotropy $\Delta\alpha$ arises mainly from the core. The alkyl chain contributes more to the mean polarizability than to the anisotropy. Also, we have observed that the mean polarizability increases more rapidly than anisotropy of polarizabil-
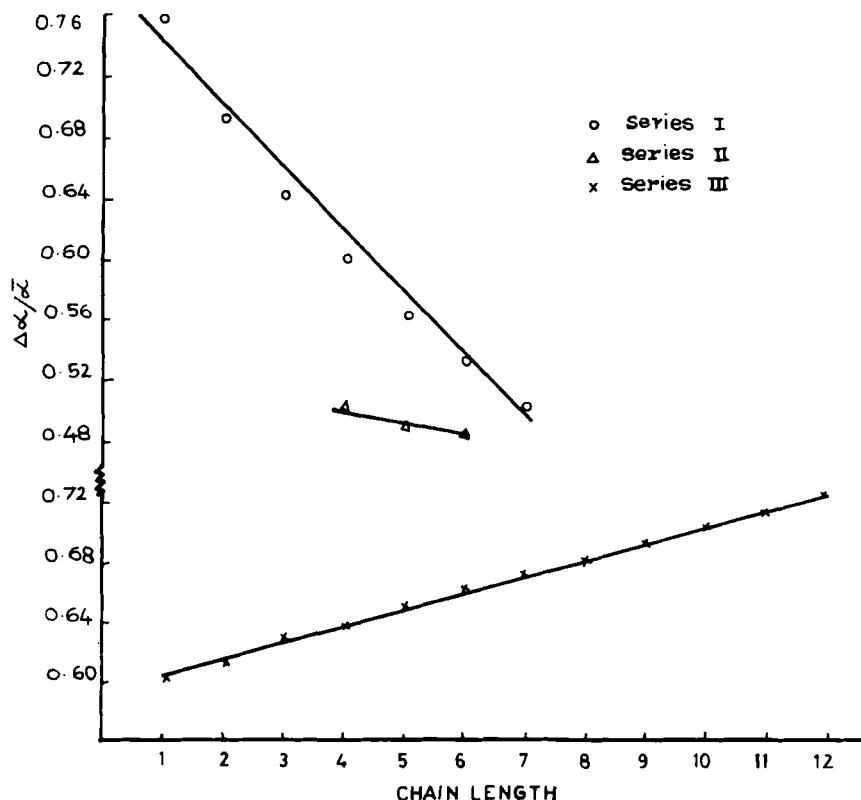
FIGURE 2   Variation of $\Delta\alpha/\bar{\alpha}$ with the number of carbon atoms for the homologous series 4,4'-di-*n*-alkyloxyazoxy benzene (I), *p*-(*p*-ethoxyphenylazo)phenyl-alkanoates (II) and cholesteryl alkanoates (III).

ity for nematic liquid crystals, whereas anisotropy of polarizability increases more rapidly than the mean polarizability for cholesteric liquid crystals. In the case of cholesteric liquid crystals, the central moiety is large as compared to nematic liquid crystals, thereby the contribution to anisotropy is more. Also, the side chain is extended on only side of the central moiety. As such the ratio $\Delta\alpha/\bar{\alpha}$ is an increasing function of chain length in cholesteric liquid crystals. In the case of nematic liquid crystals (symmetric) the side chain is extended on either side of the central core, as such the alkyl chain contribute more to the mean polarizability which in turn makes $\Delta\alpha/\bar{\alpha}$ a decreasing function of chain length. The rate of decrease is more in symmetric (NLC) molecules than that of asymmetric (NLC) molecules. This is due to the fact that the side chain is extended on only one side of the central moiety in the case of asymmetric molecules.
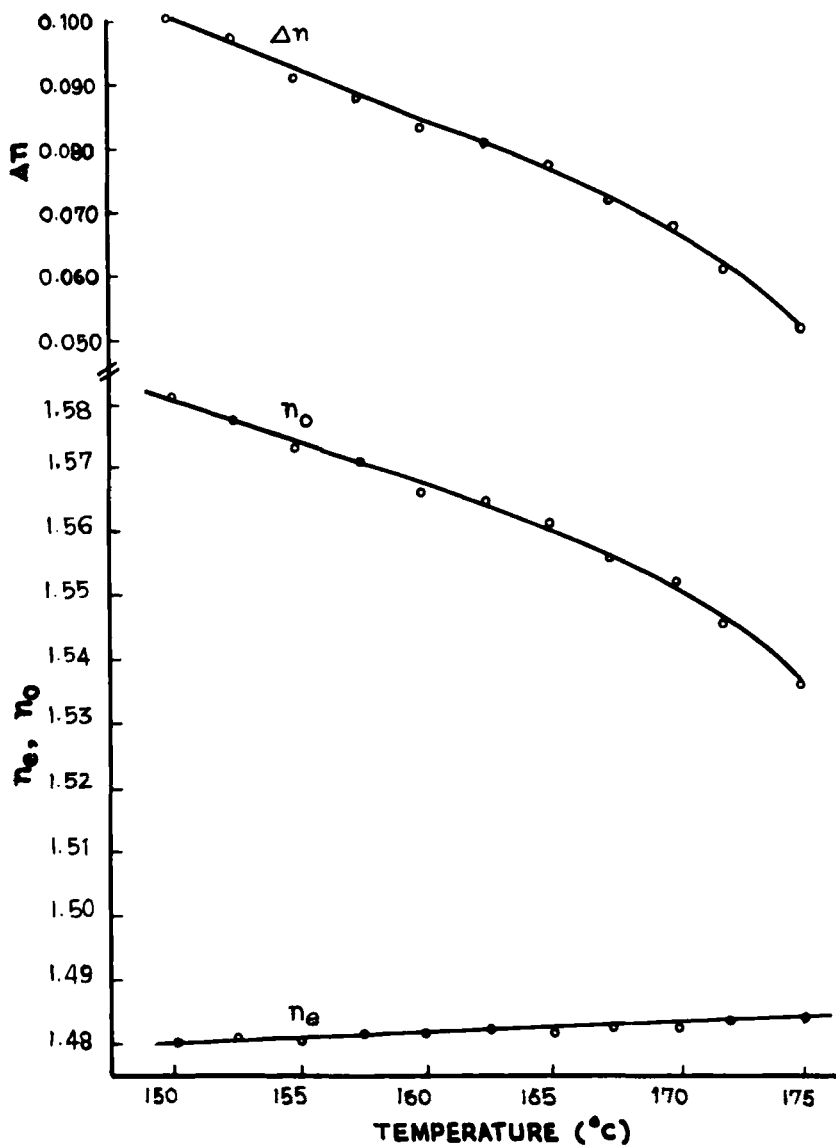
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FIGURE 3 Variation of the refractive indices (n_e, n_o) and birefringence (Δn) with the temperature for cholesteryl benzoate.

The characteristic temperature dependence of n_e and n_o, and the temperature variation of double refraction in the liquid crystalline materials can be explained by the structure and the degree of order. The temperature variation of the ordinary and the extraordinary refractive indices (n_o, n_e), and the birefringence (Δn) of cholesteryl benzoate and laurate are shown in Figures 3 and 4 respectively.

An increase in temperature involves a larger average fluctuation of the parallel-oriented molecules around the preferred direction of the orientation indicating a decrease of $\bar{\alpha}_\parallel$ and an increase of $\bar{\alpha}_\perp$. Since the density also decreases with increasing temperature, the double refraction generally diminishes with
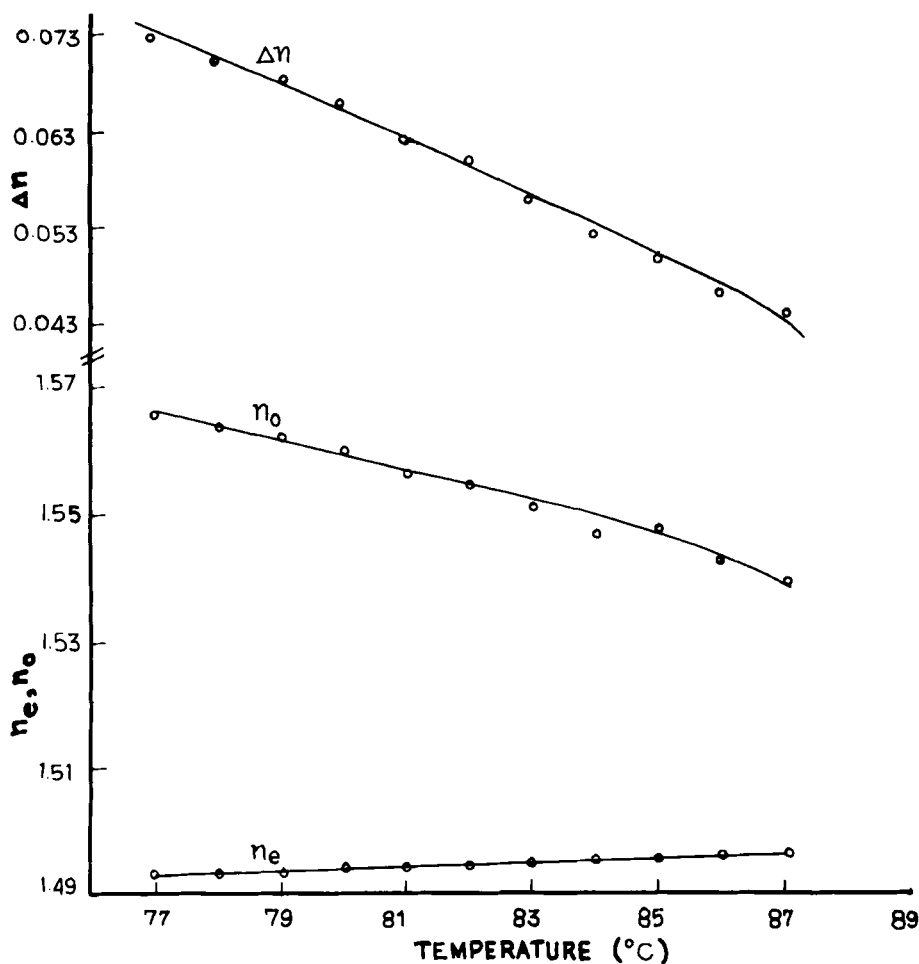

FIGURE 4   Variation of the refractive indices (n_e, n_o) and birefringence (Δn) with the temperature for cholesteryl laurate.

increasing temperature. In the cholesteric phase (cholesteryl benzoate and laurate) n_o decreases with temperature. Also the effect of temperature on $\bar{\alpha}_\perp$ is more pronounced than on density.

The value of the refractive index in an oriented liquid crystal is determined by the density and the average polarizabilities $\bar{\alpha}_\parallel$ and $\bar{\alpha}_\perp$. The average polarizabilities on the other hand, are determined by the degree of order and the principal polarizabilities of molecules α_1 and α_t (α_1-longitudinal polarizability, α_t transverse polarizability). Therefore the temperature variation of $\bar{\alpha}_\parallel$ and $\bar{\alpha}_\perp$, and hence the shape of (n, temperature) curves also depends on α_1 and α_t.

The variation of order paramater S with temperature for cholesteryl benzoate and laurate are shown in Figures 5 and 6. We have also given the S-factor curves determined by the wide line NMR spectra[7] for comparison. There is good agreement between the two sets of values. But the value of S obtained by birefringence data are somewhat smaller than those obtained from NMR data. This has been observed in nematogenic materials also.[37,38] This feature may be explained as follows. If the molecules were rigid, then the conformation of the molecules and hence their anisotropies in the two phases would be identical. But, in most of the cases, motions of parts of the molecule, e.g., free rotation about the single bonds (as in the case of the CH_2 and CH_3 groups at
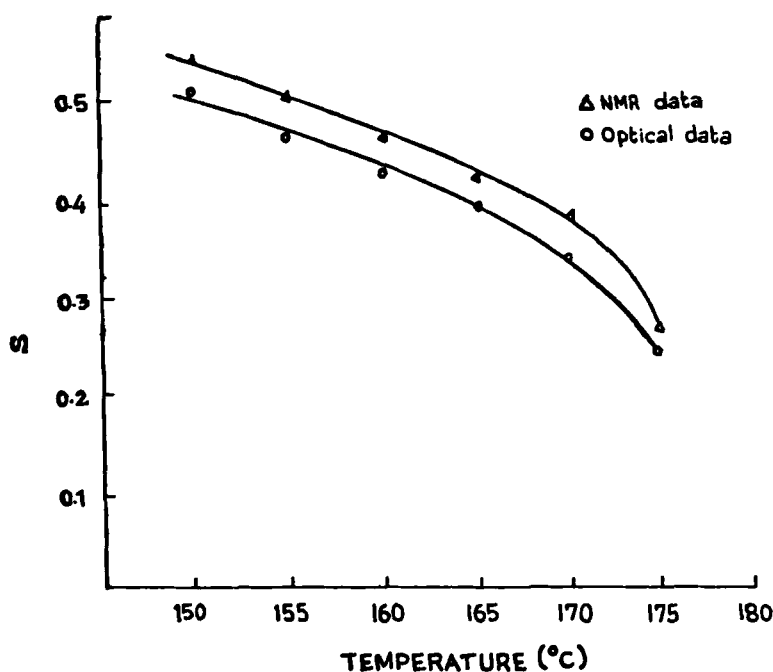

FIGURE 5   Variation of the order parameter with the temperature for cholesteryl benzoate.
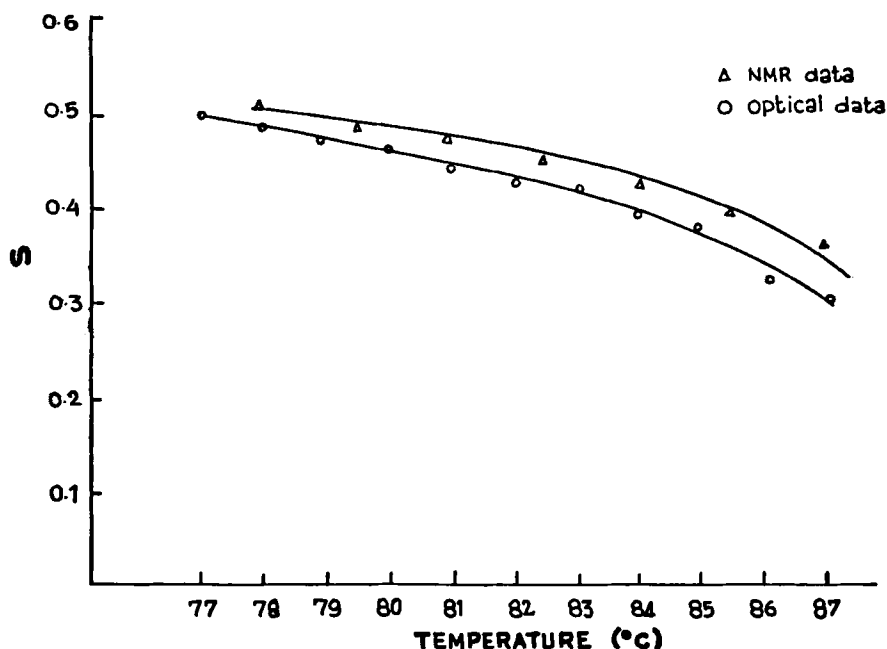
FIGURE 6 Variation of the order parameter with the temperature for cholesteryl laurate.

the end of the molecule), are always possible in the liquid crystalline phase. The fractional number of molecules in which such motions take place and the amplitudes of such motions increase with increasing temperature. As a result there should be a small but systematic decrease in the optical anisotropy with increasing temperature. Clearly, when one uses the optical anisotropy from the refractive index in the crystalline phase for calculating the order parameter S, it would be smaller than the true value.

CONCLUSION

The present investigation indicates that the δ-function potential model is useful in estimating molecular polarizabilities of liquid crystalline materials. This method, besides lending a satisfactory support to the usual refractometric method, serves as an alternative for estimating the molecular polarizabilities and hence molecular anisotropy. Agreement between the values of $\bar{\alpha}$ obtained by the two theoretical methods lends a satisfactory support to the reliability and suggests the general applicability of the Lippincott-δ-function potential model to liquid crystals.

  Since this δ-function model gives explicit equations showing the R-dependence of the parallel component of the polarizability and the R-independ-

ent form of the perpendicular component, application of these relationships to other problems should be possible. For example Raman intensities are proportional to $(\partial\alpha/\partial q)^2$, the square of the polarizability derivative for a given mode of vibration. Thus it should be possible to obtain some results concerning Raman intensities from the proposed model.

The long side chain in the cholesterogenic materials is purported to play a major role in the structural conformation and stabilization of the cholesteric phase, confirming the results of earlier studies of the X-ray diffraction.

Acknowledgment

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