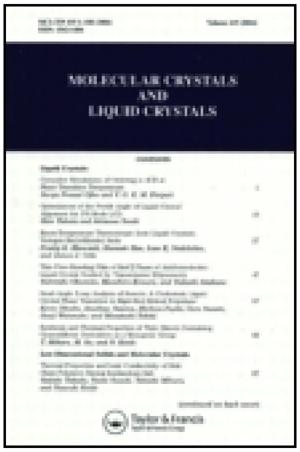

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S. K. Nataraju [a] & D. Krishnamurti [a]
[a] Department of Physics, University of Mysore, Mysore, 570 006, India

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Thermal Variation of the Optical Anisotropy of Some Homologues of Smectic Compounds

S. K. NATARAJU and D. KRISHNAMURTI
Department of Physics, University of Mysore, Mysore 570 006, India

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From the available birefringence data in the smectic–A phase of di-*n*-alkyl 4,4′-azoxy-α-methyl cinnamates the optical anisotropies of eleven members of the homologous series are calculated for different temperatures. It emerges that the optical anisotropy decreases with increase of temperature. From an analysis of the data, it is concluded that the net variation of the optical anisotropy with temperature is the sum total of the variations arising from the rotations of the methylenes of the end chains and the fluctuations in the orientation of the rigid portion of the molecules with respect to the normal to the smectic layers. The paper also presents results with regard to the coefficient of volume expansion in the smectic phase calculated from the thermal variation of the mean electric susceptibilities of the different homologues.

1. INTRODUCTION

It is well-known that in the smectic A and B mesophases the optically anisotropic molecules of the substance are arranged in layers with the long axis of the molecules normal to the layers. This kind of molecular ordering is responsible for the optically uniaxial positive character of the medium, the optic axis being normal to the layers. The layer spacing corresponds approximately to the molecular length. However, in cases where the end groups consist of alkyl chains, the molecules may not have their alkyl chains fully extended into a zig-zag confor-

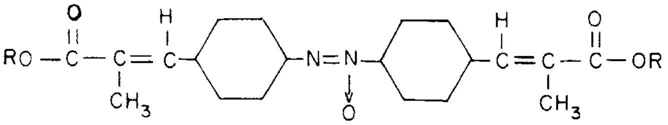

FIGURE 1 Structural formula of di-n-alkyl 4-4′-azoxy-α-methyl cinnamate.

mation. From our earlier studies,[1,2] it had emerged that it is necessary to take into account the anisotropic nature of the Lorentz field while calculating the principal polarizabilities of the molecules. With the aid of the Neugebauer and Born relations, the polarizabilities or the electric susceptibilities may be easily calculated. One of the important results of such a calculation is the fact that the optical anisotropy decreases with increasing temperature. This fact was emphasized in our earlier papers. It was possible from our calculations in the case of homologues of thallium soaps,[3] to explain the variation of the optical anisotropy with temperature as arising from the rotation of the methylenes about single C—C bonds. The case of thallium soaps was relatively simple in that the birefringence was low and further, except for the polar groups at the ends, the molecules consisted entirely of a chain of methylenes.

The present paper is concerned with the case of the homologous series, viz., di-n-alkyl-4-4′azoxy-α-methyl cinnamates. The structural formula for these homologues is shown in Figure 1. Here, the molecule may be considered as having a central rigid portion to which are attached the flexible end groups and in the different molecules, R corresponds to the different members of the alkyl series, viz., $CH_3(CH_2)_n$. The present paper discusses the variation of the optical anisotropy of the different homologues with temperature. The optical anisotropy associated with the central rigid portion is expected to be large, whereas the optical anisotropy due to the flexible end groups is small. The net variation with temperature is attributable to (i) the rotational motions associated with the methylenes of the end groups and (ii) the fluctuations in the orientation of the rigid portions of the molecules with respect to the normal to the smectic layers.

2. CALCULATION OF THE OPTICAL ANISOTROPY

The refractive index data for the homologous series of compounds of di-n-alkyl 4-4′-azoxy-α-methyl cinnamates in the smectic A phase and above the clearing point T_c also have been reported by Pelzl and

Sackmann.[4] The calculations of the electric susceptibilities χ_e, χ_o and $\bar{\chi}$ corresponding to the extraordinary ray, ordinary ray and the mean value viz., $\bar{\chi} = (\chi_e + 2\chi_0)/3$, are carried out by using the Neugebauer relations and the Born relation, following the same procedure as detailed in our earlier paper.[2] Density data are not available for the compounds mentioned above. Under the circumstances, we make use of the relation between the optical anisotropy $\Delta\alpha$ and $\Delta\chi$ viz.,

$$\Delta\alpha/\bar{\alpha} = \Delta\chi/\bar{\chi} \tag{1}$$

where $\Delta\alpha = (\alpha_e - \alpha_o)$, $\Delta\chi = (\chi_e - \chi_o)$, $\bar{\alpha} = (\alpha_e + 2\alpha_o)/3$ and $\bar{\chi} = (\chi_e + 2\chi_o)/3 = N\bar{\alpha}$. Here $\bar{\alpha}$ is the mean electronic polarizability of a molecule and N is the number of molecules per unit volume. If one can compute the value of $\bar{\alpha}$, it becomes immediately possible to calculate the value of $\Delta\alpha$ using Eq. (1). The mean polarizability associated with the central rigid portion is calculable from the fact of its being closely similar to the central rigid portion of *p*-azoxyanisole. Here, one has to make corrections for the fact that the benzene rings are attached to C—C groups, instead of the C—O groups in *p*-azoxyanisole. From bond polarizability data[5] correction can be made for this fact. With regard to the mean polarizability of the end groups shown in Figure 1, it is possible to calculate the same from the available refractive index in the case of ethyl ester of cinnamic acid and by using the bond polarizabilities to account for the differences in

TABLE I

di-alkyl ester	Clearing point (°C)	Mean molecular polarizability $\bar{\alpha}$	Coefficient of volume expansion $\times 10^4 (/ {}^\circ C)$
Ethyl	139.0	54.00	5.657
Propyl	130.0	57.59	5.598
Butyl	101.5	61.19	5.606
Amyl	99.7	64.78	5.596
Hexyl	90.0	68.38	5.640
Heptyl	90.0	71.97	5.965
Octyl	87.5	75.56	6.186
Nonyl	87.5	79.16	6.236
Decyl	87.5	82.75	6.050
Undecyl	87.9	86.35	6.910
Dodecyl	87.8	89.94	6.327

$\bar{\alpha}$ is in units of 10^{-24} cm^3. All the polarizability data refer to $\lambda = 5893$ Å.

the case of the different members of the homologous series. Table I gives the calculated values of the mean polarizabilities for eleven members of the homologous series. The mean polarizability of successive members of the series increases by a constant amount. Using Eq. (1) the optical anisotropy $\Delta\alpha$ at different temperatures may be calculated for each member of the series from the value of $\bar{\alpha}$, $\Delta\chi$ and $\bar{\chi}$. The calculations show that the optical anisotropy decreases with increase of temperature. The nature and origin of this decrease is discussed in the following section.

3. TEMPERATURE VARIATION OF THE OPTICAL ANISOTROPY

The variations of $\Delta\alpha$ with T_c/T for the different esters are shown in Figure 2. Table II presents the values of $\Delta\alpha$ at some selected values of T_c/T. It may be noted from Table II that at the highest temperatures of the smectic phase, i.e., close to T_c, the transition temperature to the isotropic phase, the values of $\Delta\alpha$ vary from 28×10^{-24} cm^3 for the di-ethyl ester to 32×10^{-24} cm^3 in the case of the di-undecyl ester. The above values (for $T_c/T \approx 1$) have a range of 4×10^{-24} cm^3. A comparison of the variation of $\Delta\alpha$ with the number of methylenes in the different esters reveals the following. For example, for a value of T_c/T equal to 1.08, the values of $\Delta\alpha$ are 30.8×10^{-24} cm^3 in the case of the di-ethyl ester and 35.6×10^{-24} cm^3 in the case of the di-nonyl ester. The net variation here is nearly 4.8×10^{-24} cm^3. The maximum contribution which each methylene group makes to the optical anisotropy was estimated by us in an earlier paper[3] to be about 0.35×10^{-24} cm^3. The maximum variation which one can expect here, say for fourteen methylenes, is 4.9×10^{-24} cm^3. The actual values of the variation for the two values of T_c/T referred to above are within the expected range of variation.

On the other hand, if one considers the temperature variation of $\Delta\alpha$, for example, in the case of the di-nonyl ester between 60 °C and 86 °C, the optical anisotropy decreases by about 4×10^{-24} cm^3. Surprisingly, in the case of the di-ethyl ester also, which has far fewer methylenes, there is a comparable decrease of 3.5×10^{-24} cm^3 over the range 90 °C to 134.2 °C. Therefore, it is clear that the entire decrease in $\Delta\alpha$ cannot be ascribed as solely due to the rotation of methylenes of the end chains and one is compelled to conclude that fluctuations should exist in the orientations of the rigid portion of the molecules with respect to the normal to the smectic layers. Hence, the

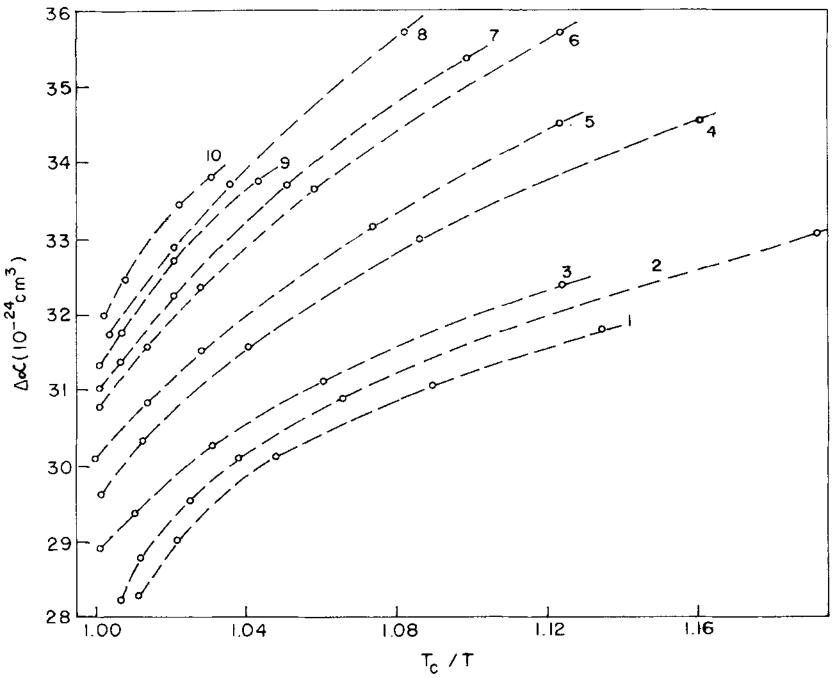

FIGURE 2 Variation of $\Delta\alpha$ with temperature in the case of the different di-alkyl esters. The serial numbers refer to the n in $(CH_2)_nCH_3$ at each end of the molecule.

TABLE II

Optical anisotropy $\Delta\alpha$ (10^{-24} cm^3) of the homologues at different T_c/T

di-alkyl ester	$(T_c/T) \approx 1$	$(T_c/T) = 1.02$	$(T_c/T) = 1.05$	$(T_c/T) = 1.08$	$(T_c/T) = 1.1$
Ethyl	28.30	28.81	30.09	30.80	31.35
Propyl	28.24	29.18	30.39	31.18	31.73
Butyl	28.93	29.73	30.78	31.53	32.10
Amyl	29.61	30.61	31.80	32.72	33.45
Hexyl	30.10	31.09	32.25	33.25	34.07
Heptyl	30.78	31.82	33.18	34.28	35.19
Octyl	31.01	32.10	33.53	34.65	—
Nonyl	31.74	32.73	34.25	35.60	—
Decyl	31.32	32.55	—	—	—
Undecyl	32.00	33.20	—	—	—
Dodecyl	31.64	—	—	—	—

All the polarizability data refer to λ = 5893 Å.

decrease in the optical anisotropy with increase in temperature has to be attributed not only to the rotation of the methylenes about C—C bonds, but also in a comparable measure to the fluctuations in the orientation of the central rigid portion of the molecules. The individual contributions of these two effects cannot be separated easily. Owing to the coexistence of both the effects referred to above, at the highest temperatures, in the smectic phase, the optical anisotropy of the different esters varies between 28×10^{-24} cm^3 to 32×10^{-24} cm^3.

Figure 3 exhibits the variation of $\Delta\alpha$ with the number of methylenes at any given T_c/T. From the curve for the highest temperatures ($T_c/T \approx 1$), it may be seen that with increase in the number of methylenes, the optical anisotropy exhibits an approximately linear increase in the range, $2n = 4$ to 12. However, for the higher members of the series, the optical anisotropy decreases, apparently because of the coiling of the chains which would give rise to a negative contribution to the anisotropy. In any case, on an average, the rate of increase of the optical anisotropy per methylene is of the same order of magnitude and less than the maximum value of 0.35×10^{-24} cm^3. The optical anisotropy associated with the central rigid portion is estimated to have a value around 31.8×10^{-24} cm^3.

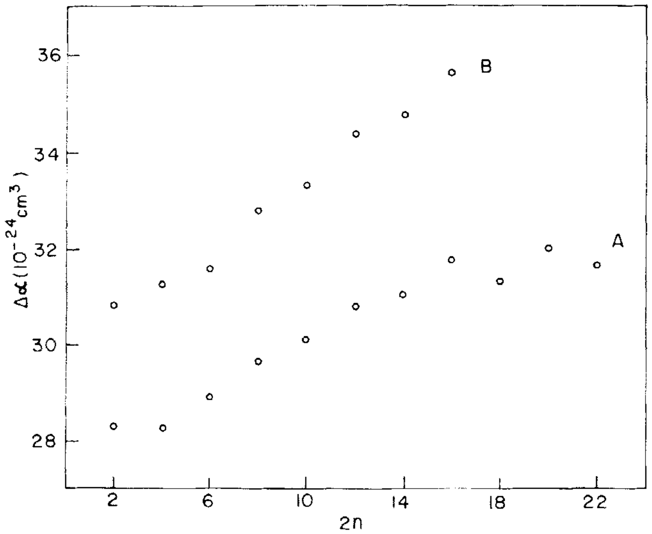

FIGURE 3 Variation of $\Delta\alpha$ with the total number of methylenes at both the ends of the molecule. (a) $T_c/T \approx 1$ and (b) $T_c/T = 1.08$.

TABLE III

Relative orientational order parameter for the di-ethyl ester

Temperature (°C)	90	105	120	130	134.2
Order parameter (S)	1	0.976	0.947	0.913	0.890

The characteristic alternation in the value of $\Delta\alpha$ of the successive members of the homologous series is significant at the lower temperatures, (e.g., $T_c/T = 1.08$), as may be seen in Figure 3.

Assuming that the value of $\Delta\alpha$ for the lowest temperatures corresponds to the maximum value of the optical anisotropy in the case of the di-ethyl ester having the least number of methylenes, it is possible to calculate the relative order parameters S at different temperatures by finding out the ratio of the value of $\Delta\alpha$ at any temperature with the maximum value of $\Delta\alpha$ ($= 31.8 \times 10^{-24}$ cm^3). The calculated values of S shown in Table III indicate that with increase of temperature, there are significant fluctuations in the orientation of the molecules. This result is again a surprising feature since one usually tacitly assumes that in the smectic A phase the molecules have their long axes normal to the smectic layers.

4. LORENTZ FIELD FACTORS AND OPTICAL ANISOTROPY

The Lorentz field factors, L_e and L_o are calculated from the relation

$$n_e^2 - 1 = 4\pi\chi_e(1 - 4\pi L_e\chi_e)^{-1} \tag{2}$$

and the corresponding similar relation for the ordinary refractive index.[2] The anisotropy of the Lorentz field factors, $L_o - L_e$ at each temperature is known to vary approximately linearly with the optical anisotropy.[6] The homologues under discussion here exhibit a similar variation as may be seen from Figure 4. The anisotropy of the Lorentz field factors which depends on the geometrical anisotropy of the molecular distribution evidently goes hand in hand with the corresponding effective optical anisotropy which also depends on the molecular distribution. An interesting feature with regard to Figure 4 is that a least square fit of the data for each homologue gives a straight

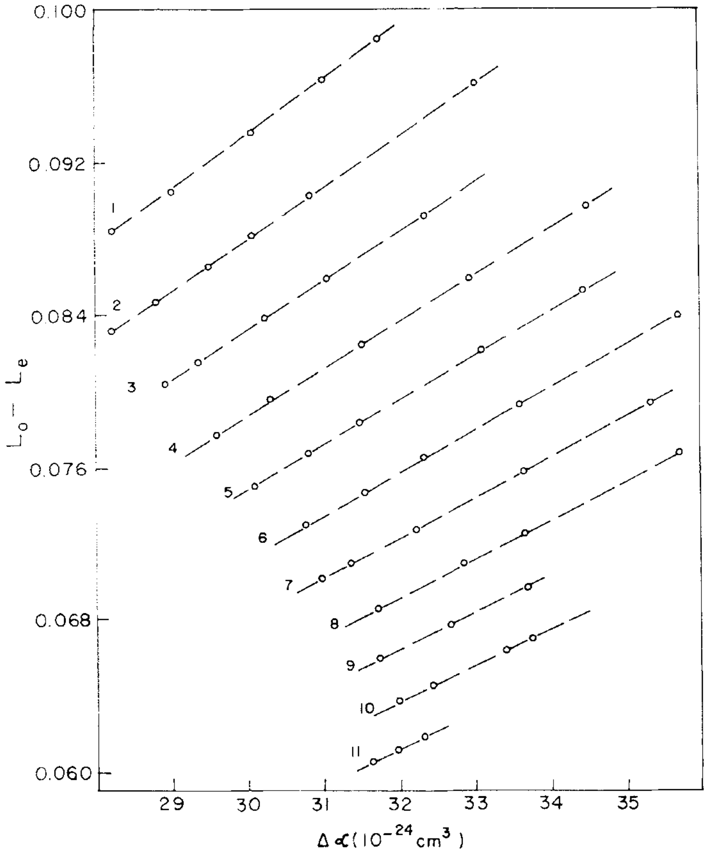

FIGURE 4 Variation of the anisotropy of the Lorentz field factors, $L_o - L_e$ with temperature, in the case of the different dialkyl esters. The serial numbers refer to the n in $(CH_2)_nCH_3$ at each end of the molecule.

line whose intercept turns out to be very small (≈ 0.003 to 0.005), consistent with the expectation that the geometrical anisotropy of the Lorentz field factors should vanish when the optical anisotropy vanishes. Further, if one calculates by interpolation the value of $L_o - L_e$ at the same T_c/T for the different esters, it is found that $L_o - L_e$ exhibits an approximately linear decrease with n, as shown in Figure 5. The methylene groups which are capable of rotation about single C—C bonds give rise to different conformations of the molecules and hence with increase in their number they reduce effectively the anisotropy of the Lorentz field.

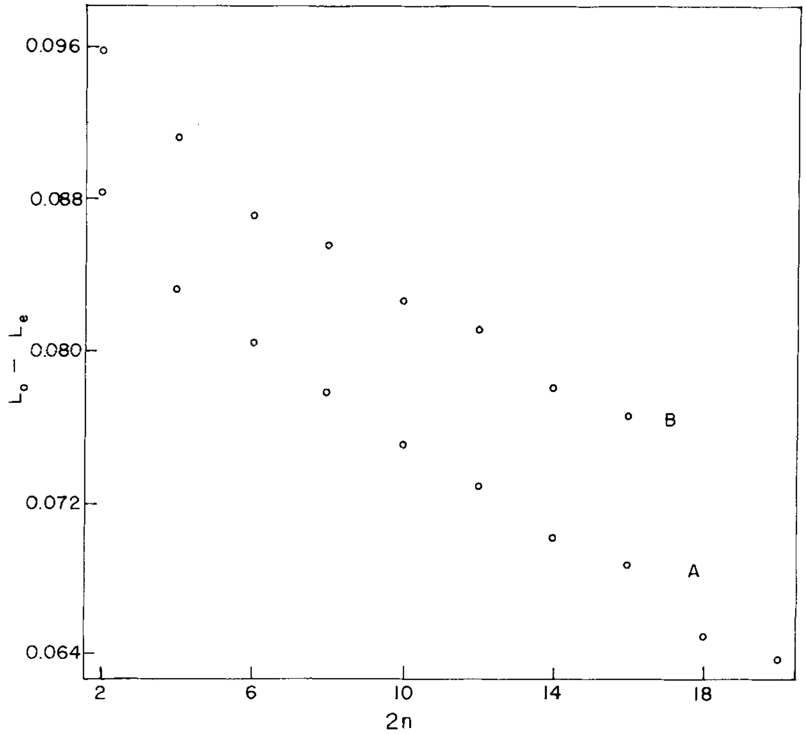

FIGURE 5 Variation of the anisotropy of the Lorentz field factors, $L_o - L_e$ with the total number of methylenes at both the ends of the molecule (a) $T_c/T \approx 1$ and (b) $T_c/T = 1.08$.

5. THERMAL EXPANSION

From the mean electric susceptibilities $\bar{\chi}$, calculable from the refractive index data at different temperatures, it is possible to calculate the volume coefficient of thermal expansion (γ) in the case of the different homologues. The mean polarizability $\bar{\alpha}$ should be a constant independent of temperature. It follows from the relation $\bar{\chi} = N\bar{\alpha}$ that,

$$\frac{d}{dT}(\log_e \bar{\chi}) = \frac{d}{dT}(\log_e N) = \frac{1}{N}\frac{dN}{dT} = -\frac{1}{V}\frac{dV}{dT} = -\gamma \qquad (3)$$

where V is the volume of the substance. Graphical plots of $-\log_e \bar{\chi}$ versus T for the different homologues are found to give straight lines for all the homologues and the lines have nearly the same slope as may

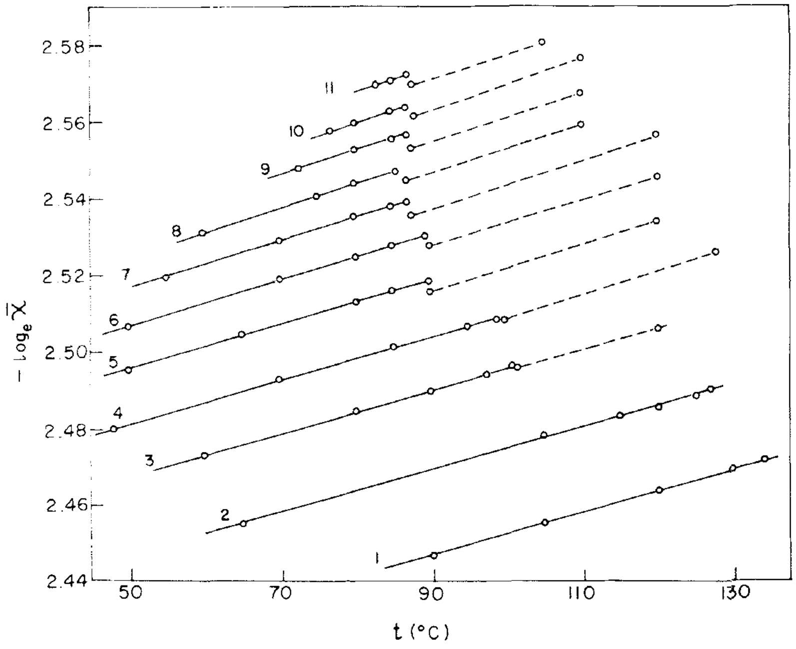

FIGURE 6 Variation of $-\log_e\bar{\chi}$ with temperature in the case of the different di-alkyl esters. The dotted line corresponds to the liquid phase. The serial numbers refer to the n in $(CH_2)_nCH_3$ at each end of the molecule.

be seen from Figure 6. The coefficient of volume expansion here, is somewhat smaller than for the case of the liquid. This may be expected because, here the condensed phase is an ordered phase with restricted freedom of motion. It is noteworthy that information about the coefficient of volume expansion is obtainable directly from optical data. An analysis of the available optical data for different mesomorphic substances is in progress in order to compare the values of the coefficients of volume expansion in them. The results will be reported separately.

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