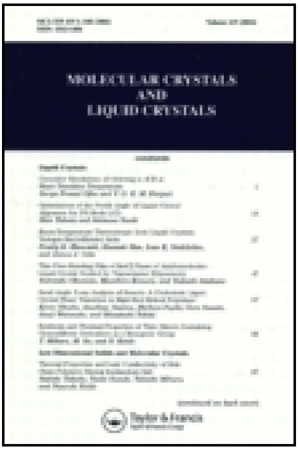

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Orientational Order in *n*-alkyl-*p*-(4-ethoxy benzylidene amino)-α-methyl cinnamates

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The paper discusses the results of the calculation of the orientational order parameters and the Lorentz field factors from birefringence data in the case of the homologous series of compounds, *n*-alkyl-*p*-(4-ethoxy benzylidene amino)-α-methyl cinnamates. The order parameters are found to exhibit the well known zig-zag alternation with increase in the number of carbon atoms of the alkyl chain. The anisotropy (L_o-L_e), of the Lorentz field factors also decreases with increasing number of carbon atoms indicating that as a consequence of the numerous conformations possible for the alkyl group, there is a reduction in the anisotropy of the polarization field. 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

The calculation of the orientational order parameter in nematic compounds from refractive index data had been the subject matter of a number of earlier investigations.[1-6] The present authors had used the Neugebauer relations[7,8] which incorporate the anisotropic nature of the Lorentz field factors. For purposes of calculation of the order parameter S, it is necessary to obtain the value of the anisotropy of polarizabilities, either from the refractive index data of the crystalline phase or from the anisotropy of the polarizabilities of the several chemical bonds in the molecule. However, it would be ideal to calculate the anisotropy of polarizabilities ($\alpha_{\parallel} - \alpha_{\perp}$) from the refractive index data for a phase in which $S = 1$, i.e., molecules are aligned with their long axes exactly parallel to one another. As is well-known, in the smectic A phase the molecules are all aligned parallel to one another in layers, with the long axes of the molecules normal to the layers, but without any positional order in the individual layers. In the smectic A phase also, the Neugebauer relations are valid (see for example, Billard,[10] and Krishnamurti and Subramhanyam[11]). It may be expected that if one calculates the values of the effective optical anisotropy in the smectic phase at different temperatures, the values would correspond to the optical anisotropy ($\alpha_{\parallel} - \alpha_{\perp}$) and remain constant throughout the smectic A phase. The birefringence studies carried out by Pelzl and Sackmann[9] in the case of a series of homologous compounds, namely, *n*-alkyl-*p*-(4-ethoxy benzylidene amino)-α-methyl cinnamates, provide the necessary data for our calculations. These compounds exhibit the smectic A and nematic phases. Our calculations have led to some interesting results which are discussed in the following.

DETAILS OF THE CALCULATION OF THE ORDER PARAMETER

The homologous compounds under discussion have the chemical formula $C_2H_5O(C_6H_4)CH{:}N(C_6H_4)\ CH{:}C(CH_3)(COOR)$ where R is alkyl group $CH_3(CH_2)_n$, with $n = 1$ to 8. Pelzl and Sackmann have not reported density data for the above compounds. The procedure adopted for our calculations here is similar to that described in detail in an earlier paper.[11] The following is a brief outline. Here, α_e and α_o refer to the effective polarizabilities for the extraordinary and ordinary vibrations, $\alpha_{\parallel}$ and $\alpha_{\perp}$ are the polarizabilities for vibrations parallel and perpendicular to the long axis of the molecule and $\bar{\alpha}$ is the mean polarizability. N is the number of molecules per unit volume, N being a function of temperature. We denote $N\alpha_e$, $N\alpha_o$, $N\bar{\alpha}$, $N\alpha_{\parallel}$ and $N\alpha_{\perp}$ by χ_e, χ_o, $\bar{\chi}$, $\chi_{\parallel}$ and $\chi_{\perp}$ respectively. The Neugebauer relations now take the following form:[11]

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

$$n_o^2 - 1 = 4\pi\chi_o(1 - 4\pi L_o\chi_o)^{-1}. \tag{2}$$

Here, L_e and L_o are the Lorentz field factors for the extraordinary and ordinary vibrations. Using the fact that,

$$L_e + 2L_o = 1, \tag{3}$$

and combining Eqs. (1) and (2)

$$\frac{1}{\chi_e} + \frac{2}{\chi_o} = \frac{4\pi}{3}\left[\frac{n_e^2+2}{n_e^2-1} + \frac{2(n_o^2+2)}{n_o^2-1}\right]. \tag{4}$$

Further, the Born relation[11,12] given below is valid.

$$(\chi_e + 2\chi_o)/3 = \bar{\chi} = \frac{3}{4\pi}\left[\frac{\overline{n^2} - 1}{\overline{n^2} + 2}\right], \tag{5}$$

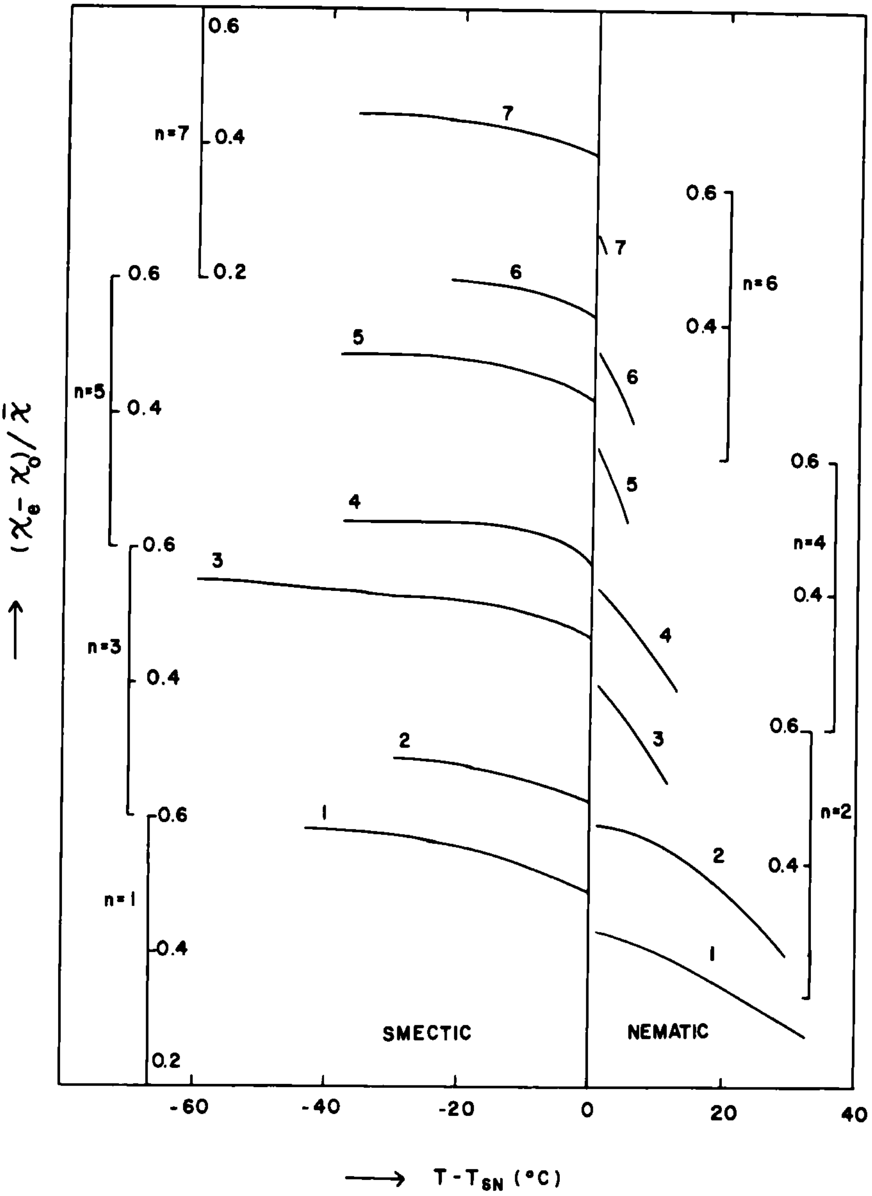

FIGURE 1 Variation of $(\chi_e - \chi_o)/\bar{\chi}$ with temperature in the case of the different homologues, calculated from index data for λ 5893 Å.

where $\bar{n}^2 = (n_e^2 + 2n_o^2)/3$. Also it may be noted that,

$$(\chi_e - \chi_o)/\bar{\chi} = N(\alpha_e - \alpha_o)/N\bar{\alpha} = (\alpha_e - \alpha_o)/\bar{\alpha}. \tag{6}$$

Using Eqs. (4) and (5) χ_e and χ_o are calculated at each temperature. From these calculations it is found that the values of $(\chi_e - \chi_o)/\bar{\chi}$ which, prima facie, may be expected to remain constant in the smectic A phase, are not quite constant especially in the case of the lower members of the homologous series, (vide Figure 1). This indicates that in the smectic A phase, the molecules have some flexibility associated with the alkyl chain at the end of each molecule, owing to the different conformations which may be assumed by the chain. In the case of the higher members of the series, the values of $(\chi_e - \chi_o)/\bar{\chi}$ at the lower temperatures in the smectic A phase do not vary so drastically, apparently because of the fact that the numerous possible conformations of the end chain lead to roughly the same contribution to optical anisotropy at different temperatures. Under these circumstances, we find that it is best to assume that the maximum value of $(\alpha_e - \alpha_o)$ found at the lowest temperature of the smectic A phase as the value corresponding to $(\alpha_{\parallel} - \alpha_{\perp})$ of the molecule. In other words, we shall assume that at the lowest temperature of the smectic A phase, the order parameter S has a value normalized to unity to enable meaningful

TABLE I

Calculated values of the order parameters of *n*-alkyl-*p*-(4-ethoxy benzylidene amino)-α-methyl cinnamates from index data for λ 5983 Å

Ethyl ester:	$T_{SN} = 94°C$			$T_{NI} = 123.0°C$		
$T_{NI} - T$	3	5.5	8	18	33	48
S	0.478	0.541	0.562	0.694	0.801	0.874
Propyl ester:	$T_{SN} = 90.9°C$			$T_{NI} = 121.8°C$		
$T_{NI} - T$	1.8	4.3	11.8	21.8	41	—
S	0.461	0.548	0.666	0.759	0.889	—
Butyl ester:	$T_{SN} = 86.0°C$			$T_{NI} = 100.6°C$		
$T_{NI} - T$	3.1	5.6	10.6	15.6	—	—
S	0.439	0.530	0.648	0.727	—	—
Amyl ester:	$T_{SN} = 84.2°C$			$T_{NI} = 100.5°C$		
$T_{NI} - T$	3	5.5	10.5	16.5		
S	0.512	0.587	0.696	0.800		
Hexyl ester:	$T_{SN} = 83.0°C$			$T_{NI} = 91.2°C$		
$T_{NI} - T$	3.2	6.2	8.7	—	—	—
S	0.474	0.620	0.725	—	—	—
Heptyl ester:	$T_{SN} = 82.3°C$			$T_{NI} = 90.2°C$		
$T_{NI} - T$	2.2	5.2	8.0	—	—	—
S	0.547	0.686	0.780	—	—	—
Octyl ester:	$T_{SN} = 81.8°C$			$T_{NI} = 85.3°C$		
$T_{NI} - T$	2.8	3.9	—	—	—	—
S	0.545	0.631	—	—	—	—
Nonyl ester:	$T_{SN} = 82.4°C$			$T_{NI} = 85°C$		
$T_{NI} - T$	2.1	2.9	—	—	—	—
S	0.630	0.680	—	—	—	—

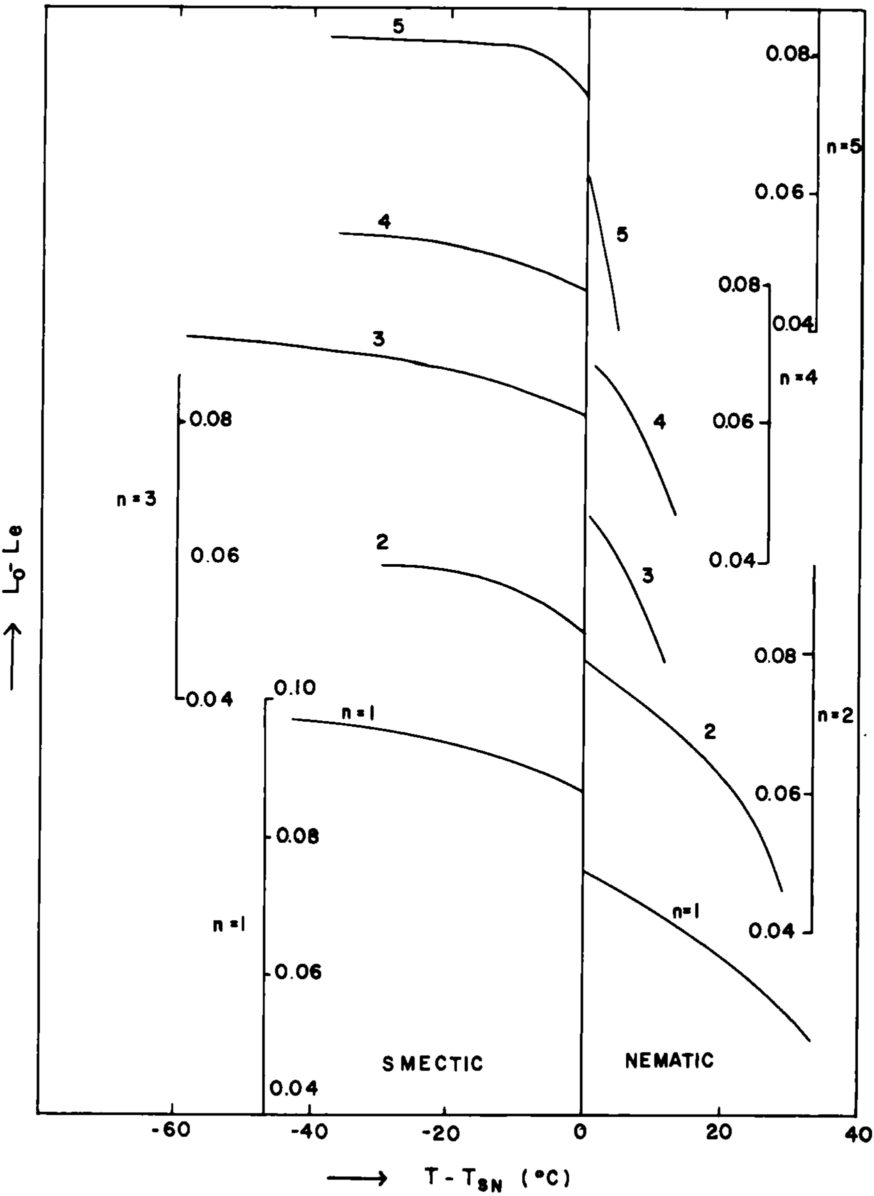

FIGURE 2 Variation of $L_o - L_e$ with temperature in the case of the different homologues, calculated from index data for λ 5893 Å.

comparison of the S factors of the different members of the homologous series.

According to our assumptions here, at the lowest temperature of the smectic phase,

$$[(\chi_e - \chi_o)/\bar{\chi}]_{\mathrm{sm.L.T}} = (\chi_{\parallel} - \chi_{\perp})/\bar{\chi} = (\alpha_{\parallel} - \alpha_{\perp})/\bar{\alpha}. \tag{7}$$

Hence, it follows that

$$\frac{[(\chi_e - \chi_o)/\bar{\chi}]_{\mathrm{nematic}}}{[(\chi_e - \chi_o)/\bar{\chi}]_{\mathrm{sm.L.T}}} = \frac{[N_n(\alpha_e - \alpha_o)/N_n\bar{\alpha}]}{[N_{\mathrm{sm}}(\alpha_{\parallel} - \alpha_{\perp})/N_{\mathrm{sm}}\bar{\alpha}]} = \frac{\alpha_e - \alpha_o}{\alpha_{\parallel} - \alpha_{\perp}} = S \tag{8}$$

Here, N_n and N_{sm} represent the number of molecules per unit volume of the nematic and smectic phases respectively. The mean polarizability $\bar{\alpha}$ is assumed to be the same in all phases. The effects of the variation of the χ's with temperature cancel out in the ratios of the form $(\chi_e - \chi_o)/\bar{\chi}$ which are involved here.

Pelzl and Sackmann have reported the index data for three wavelengths (546,589 and 644 nm) at each temperature and there is agreement between the orientational order parameters calculated using the data for the different wavelengths. However, for the sake of brevity, the values of S calculated from the index data for λ 5893Å alone are given in Table I.

The Lorentz field factors L_e and L_o (corresponding to the incident light being plane polarized with its vibration direction along the optic axis and perpendicular to the optic axis respectively) are calculable using Eqs. (1) and (3). The values of $L_o - L_e$ are graphically represented in Figure 2.

DISCUSSION

The molecules of the homologous series here possess a central rigid portion similar to the molecule of MBBA. The mean polarizability $\bar{\alpha}$ of the molecule of MBBA had been calculated earlier[6] from the refractive index for the isotropic phase of MBBA. By applying corrections to the existence of different end groups in the case of the different molecules, the mean polarizabilities of the different molecules discussed here are calculated and the values are shown in Table II. The corrections are made using the isotropic bond polarizabilities given by Le Fevre and Le Fevre.[13] Now it is possible to evaluate the optical anisotropy $\Delta\alpha(= \alpha_{\parallel} - \alpha_{\perp})$, using Eq. (7). The calculated values of the optical anisotropy are shown in Table II. It may be remarked here that the values of the optical anisotropy for the various compounds are nearly equal. The origin of this feature may be traced to the fact that a major portion of the optical anisotropy arises from the central rigid portion common to all the molecules and that the optical anisotropy arising from the end groups is relatively small owing to their assuming numerous conformations. The following other facts also emerge from our calculations.

TABLE II

Mean polarizabilities and optical anisotropy of *n*-alkyl-*p*-(4-ethoxy benzylidene amino)-α-methyl cinnamates

R	$\bar{\alpha} \times 10^{24}$ cm^3	$(\alpha_\parallel - \alpha_\perp)$† $\times 10^{24}$ cm^3
Ethyl	43.0	25.0
Propyl	44.9	25.1
Butyl	46.7	25.8
Amyl	48.6	25.1
Hexyl	50.4	24.6
Heptyl	52.3	24.1
Octyl	54.1	24.3
Nonyl	55.9	24.2

† Values in column 3 refer to the lowest temperature of smectic A phase (abbreviated sm.L.T).

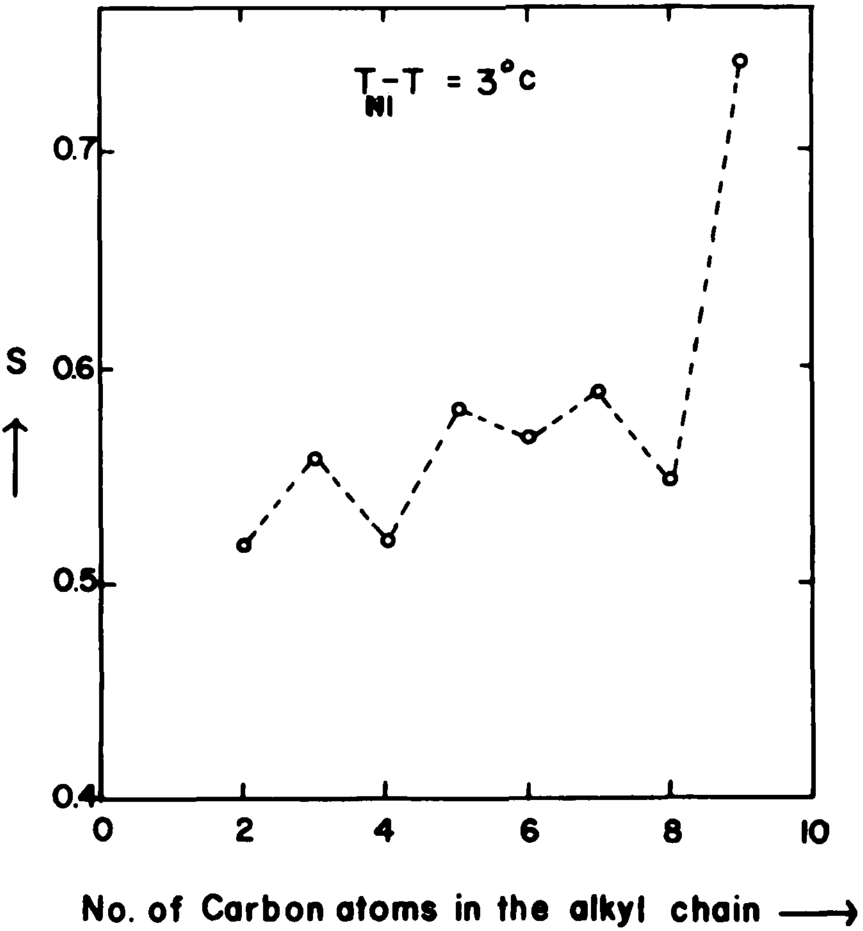

FIGURE 3 Variation of the order parameter (at the same reduced temperature) in the case of different homologues, calculated from index data for λ 5893 Å.

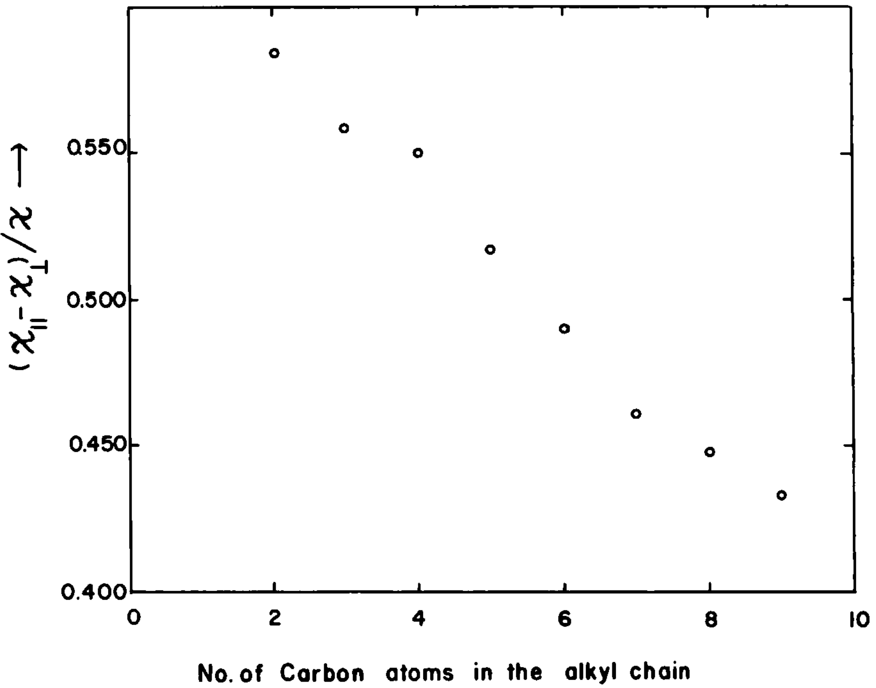

FIGURE 4 Variation of $(\chi_\parallel - \chi_\perp)/\bar{\chi}$ with number of carbon atoms in the alkyl chain, calculated from index data for λ 5893 Å.

(i) There is a general alternation in the values of the order parameters of the homologous series as has been reported in the case of the other homologous series.[14,15] Figure 3 shows the values of S at $(T_{NI} - T)$ corresponding to 3°, for the different members of the series.

(ii) Figure 4 shows the variation of $(\chi_\parallel - \chi_\perp)/\bar{\chi}$, i.e., $(\alpha_\parallel - \alpha_\perp)/\bar{\alpha}$, with the number of carbon atoms in the alkyl chain. An alternation is seen for the earlier members of the series. However, with increasing numbers of methylenes in the alkyl chain, the general trend is for $(\alpha_\parallel - \alpha_\perp)/\bar{\alpha}$ to decrease with further increase in the number of carbon atoms. This is due to (a) the values of $\bar{\alpha}$ increasing monotonically and (b) the values of $(\alpha_\parallel - \alpha_\perp)$ decreasing slightly with increasing number of carbon atoms, (vide Table II). It may be pointed out here that essentially similar features have been observed by Hanson and Shen[16] in their studies with homologous of *p*,*p*′-di-*n*-alkoxy-azoxybenzenes.

(iii) From the values of $(L_o - L_e)$ at the lowest temperature of the smectic A phase, (vide Figure 5) it is clear that the anisotropy of the Lorentz field factors $(L_o - L_e)$ decreases with increase in the number of carbon atoms in the alkyl end groups. The tendency for the end chain of the molecule to be fully

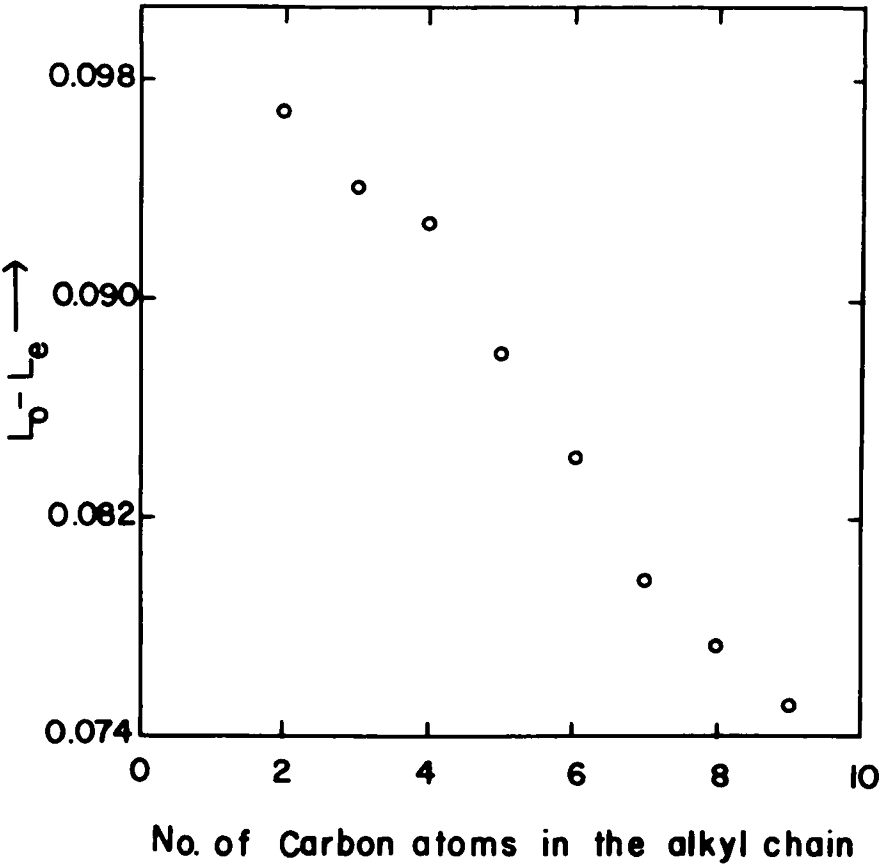

FIGURE 5 Variation of the value of ($L_o - L_e$), at the lowest temperature of the smectic A phase, with the number of carbon atoms in the alkyl chain, calculated from index data for λ 5893Å.

extended is less for the higher members of the series and there is a decrease in the anisotropy of the Lorentz field factors. It may also be noted that the values of ($L_o - L_e$) in Figure 2 decrease significantly in the nematic phase with increase of temperature, consistent with the expectation that the positional distribution of the molecules tend to be less anisotropic at the higher temperatures.

(iv) For the homologous series under discussion, there is approximately a linear variation of ($L_o - L_e$) with S indicating that with increase of temperature there is a systematic decrease in the anisotropy of molecular distribution and the orientational order.

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