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Polarization Field and Molecular Order in Smectic Liquid Crystals

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In the smectic A and B mesophases, the polarization field is anisotropic and the extraordinary and ordinary refractive indices n_e and n_0 are related to the effective polarizabilities α_e and α_0 and the internal field constants γ_e and γ_0 by the Neugebauer's relations. The Neugebauer relations lead to the Born relation which is valid to a high degree of accuracy particularly for the long wavelengths. The paper presents a method for calculating the anisotropic internal field constants and the ratio of α_e to α_0, even if density data are not available. The birefringence data reported by Pelzl and Sackmann for six cinnamates which exhibit both smectic A and B mesophases are discussed in terms of the theory and results are presented with regard to the internal field constants and the ratio of α_e to α_0 at different temperatures. Their variations are explained as due to mainly the rotational isomerism exhibited by the alkyl and alkoxy end-groups in the different compounds.

1 INTRODUCTION

In two recent papers[1,2] we have discussed the anisotropic nature of the polarization field in relation to the birefringence and the molecular order in nematic liquid crystals. Pelzl and Sackmann[3] have reported extensive and accurate data on the birefringence of many cinnamates which exhibit the nematic and smectic A or smectic A and smectic B mesophases. In their paper they have discussed their results qualitatively on the basis of the Lorenz–Lorentz formula. In the present paper, we make use of their data to calculate and discuss the anisotropic internal field constants and the optical anisotropy factor (α_e/α_0) in smectic A and B phases. For the above calculations we follow here a procedure somewhat different from the one adopted in our earlier paper owing to the non-availability of density data for all the compounds studied by Pelzl and Sackmann.

2 THEORETICAL CONSIDERATIONS

X-ray studies[4–6] reveal that in the smectic A phase the molecules are arranged parallel to one another in layers with their long axes normal to the layers and that the distribution of the molecules within each layer is irregular. In the uniaxial smectic B, the long axes of the molecules are normal to the layers and within each layer the molecules are probably in a hexagonally close-packed arrangement.

As in the case of the nematic phase previously discussed by us,[1] the refractive indices n_e and n_0 of the uniaxial smectic A and B modifications are related to the internal field constants γ_e and γ_0 and the effective polarizabilities α_e and α_0 by the Neugebauer relations. Also, $\gamma_e + 2\gamma_0 = 4\pi$. Since the density data for the compounds to be discussed here are not available, we introduce new parameters χ_e and χ_0, where $\chi_e = N\alpha_e$ and $\chi_0 = N\alpha_0$, N being the number of molecules per unit volume. The Neugebauer relations now take the following form.

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

$$(n_0^2 - 1) = 4\pi\chi_0(1 - \gamma_0\chi_0)^{-1}. \tag{2}$$

$$\frac{1}{\chi_e} + \frac{2}{\chi_0} = \frac{4\pi}{3}\left[\frac{n_e^2 + 2}{n_e^2 - 1} + \frac{2(n_0^2 + 2)}{(n_0^2 - 1)}\right]. \tag{3}$$

Also,

$$(\chi_e + 2\chi_0)/3 = \bar{\chi} = N\bar{\alpha} = N(\alpha_e + 2\alpha_0)/3. \tag{4}$$

The mean polarizability $\bar{\alpha}$ (for a given wavelength) is usually assumed to be constant in the different phases.

In order to calculate χ_e and χ_0 separately, we use a relation derived by Born[7] assuming a Lorentz field. This relation is more general and derivable from Eqs. (1) and (2) also. We define $\overline{n^2} = (n_e^2 + 2n_0^2)/3$. Let $n_e^2 = \overline{n^2} + 2u$, $\chi_e = \bar{\chi} + 2v$ and $\gamma_e = (4\pi/3) - 2w$. Here u, v, w are positive quantities. From the definitions of $\overline{n^2}$, $\bar{\chi}$ and the fact that $\gamma_e + 2\gamma_0 = 4\pi$, we have, $n_0^2 = \overline{n^2} - u$, $\chi_0 = \bar{\chi} - v$ and $\gamma_0 = (4\pi/3) + w$. It may easily be shown using Eqs. (1), (2) and (4) that

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

where q is given by the expression

$$q = -6uvw - 6uw\bar{\chi} + 8\pi uv - 6(\overline{n^2} - 1)vw. \tag{6}$$

In the Lorentz field approximation, all other terms in Eq. (6) except $8\pi uv$ would vanish because $\gamma_e = \gamma_0 = 4\pi/3$, i.e., $w = 0$. But in the case of the anisotropic internal field, the positive second order term $8\pi uv$ will be balanced roughly by the three negative second order terms so that the value of q will be very small. Neglecting the term involving q in Eq. (5) we have

$$\bar{\chi} = (\chi_e + 2\chi_0)/3 = \frac{3}{4\pi}\left(\frac{\bar{n}^2 - 1}{\bar{n}^2 + 2}\right). \tag{7}$$

Because of the constancy of $(\alpha_e + 2\alpha_0)/3$, Born expressed the above relation in the form

$$\frac{1}{\rho}\left(\frac{\bar{n}^2 - 1}{\bar{n}^2 + 2}\right) = \frac{4\pi}{3}\frac{L}{M}\bar{\alpha} = \text{constant}, \tag{8}$$

where ρ is the density, L is the Avagadro number, M the molecular weight of the substance and $\bar{\alpha}$ the mean polarizability.

With the available density and refractive index data for *p*-azoxyanisole we have confirmed that the values of $\bar{\alpha}$ calculated from the Lorenz–Lorentz relation for the liquid phase and the Born's relation for the nematic phase agree very well, particularly for the longer wavelengths. For the shorter wavelengths there is a small difference between the values obtained from the two approaches. Because u and v are smaller for longer wavelengths, it is evident that Eq. (7) is valid more accurately for the longer wavelengths than for shorter wavelengths. Therefore, at first we use Eqs. (3) and (7) and the available data for the longest wavelength ($\lambda 6440$) to calculate χ_e, χ_0 and $\bar{\chi}$. In the solution of Eqs. (3) and (7) the root corresponding to $\chi_e > \chi_0$ is chosen.

Using the values of χ_e and χ_0 obtained for $\lambda 6440$ in Eqs. (1) and (2), γ_e and γ_0 may be calculated. It was shown in our earlier papers[1,2] that γ_e and γ_0 are dependent only on the molecular distribution and hence are functions only of temperature and do not depend on the wavelength of light. Because Eq. (7) would be satisfied less accurately for the shorter wavelengths, one need not use Eq. (7) to calculate $\bar{\chi}$ for the shorter wavelengths. But, one can use the values of γ_e and γ_0 obtained from the data for $\lambda 6440$ at one temperature to calculate χ_e, χ_0 and $\bar{\chi}$ (at the same temperature) for shorter wavelengths from the corresponding index data with the aid of Eqs. (1), (2) and (4) only. For any other temperature also, the above procedure is followed in the same sequence as described, starting with the data for $\lambda 6440$.

3 RESULTS AND DISCUSSION

Pelzl and Sackmann[3] have reported the birefringence data for the following six compounds which exhibit the smectic A and B mesophases. The compounds are:

(1) ethyl *p*-(4-ethoxybenzylideneamino-)cinnamate
(2) ethyl *p*-(4-*n*-propyloxybenzylideneamino-)cinnamate
(3) *n*-propyl *p*-(4-*n*-butyloxybenzylideneamino-)cinnamate
(4) *n*-propyl *p*-(4-*n*-octyloxybenzylideneamino-)cinnamate
(5) *n*-amyl *p*-(4-*n*-octyloxybenzylideneamino-)cinnamate and
(6) *n*-butyl *p*-(4-phenylbenzylideneamino-)α-methylcinnamate.

The calculated data with regard to $f(=\chi_e/\chi_0 = \alpha_e/\alpha_0)$ and γ_e as a function of the reduced temperature $(t - t_{AB})$ are represented graphically in Figures 1 and 2 for the above compounds serially numbered (1 to 6). The numbers close to the curves correspond to the serial numbers of the compounds. t_{AB} corresponds to the temperature of the phase transition from smectic A to B. The quantities γ_0, χ_e, χ_0 and $\bar{\chi}$ may easily be obtained from the relevant relations given earlier. The values of f in Figure 1 are for λ6440. Our calculations show that the value of f at any temperature is greater for shorter wavelengths than for longer wavelengths. This is due to the greater dispersion of α_e than that of α_0, as is usually the case with long molecules.[1,2]

If in the smectic A and B phases the molecules in each layer were rigid and arranged perfectly parallel to one another, one should expect that $f(=\alpha_e/\alpha_0)$ should be constant at all temperatures (for a given wavelength). On the contrary, as may be seen from Figure 1, f decreases with increasing temperature.

First, we shall consider here the origin of the variation of f with temperature. The different compounds have at their ends alkyl and alkoxy groups of varying chain lengths. The X-ray studies[5] on some of these compounds and other similar compounds have revealed that the layer thicknesses in smectic A and B phases are significantly smaller than the molecular length corresponding to the most extended state of the chains of the end-groups and that the difference between the molecular length and layer thickness increases with increasing number of carbon atoms in the end groups. Besides, it was found that the layer thickness decreased with increasing temperature. These results are explained by Diele *et al*[5] as a consequence of rotational isomerism which may lead to the formation of buckled chains of the end groups. Infrared absorption studies[6,8,9] also indicate the existence of rotational isomerism in the smectic A and B phases.

Where the end-chains of a molecule are not fully extended, the different C—C bonds in the chain would on an average make larger angles with the molecular axis than in the case of fully extended zig-zag chains. Hence the ratio (α_e/α_0), for a molecule whose end groups are not fully extended, would be less than that for a fully extended case. Evidently, the probability of the occurrence of the conformations of buckled chains without hindrance by neighbours increases with increasing temperature and decreasing density.

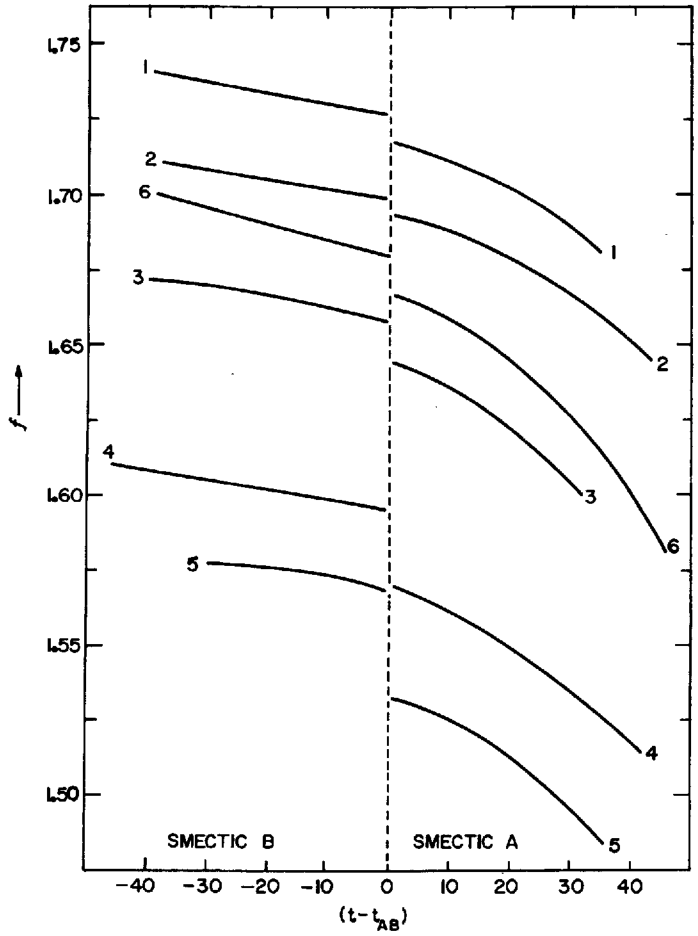

FIGURE 1 Variation of $f(=\alpha_e/\alpha_0)$ for λ6440 with the reduced temperature $(t - t_{AB})$.

Hence the value of f decreases faster with increasing temperature in the smectic A phase than in smectic B. Also, it is significant that the total change in f over the entire range of both smectic B and A is generally greater for molecules with larger number of carbon atoms in the end-groups (vide Figure 1, curves 1 to 5).

It may be noticed from Figure 1 (curves 1 to 5) that the values of f decrease with increasing number of carbon atoms in the end groups. The contribution of the central rigid portion of the molecule to the optical anisotropy $(\alpha_e - \alpha_0)$ may be expected to be the same in the different compounds (1 to 5). But the optical anisotropy arising from the end chains would in general be less and decrease with greater buckling. In other words, the contributions of the end chains to α_e and α_0 would become more or less equal. At the same time, the contributions of the end chains to both α_e and α_0 increase with increasing number of carbon atoms. As a net result the ratio (α_e/α_0) decreases with increasing number of carbon atoms.

For the different compounds (1 to 5) the values of γ_e exhibit an increase with increasing number of carbon atoms in the end groups. This progressive increase of γ_e is equivalent to a decrease in the anisotropy of the internal field caused probably by the increasing number of different rotational isomers possible with increasing number of methylene groups. Similarly, the more pronounced internal rotations which may be present in the smectic A phase may be responsible for the relatively greater variation of γ_e with temperature in that phase. Also, it is significant that the total change in γ_e over

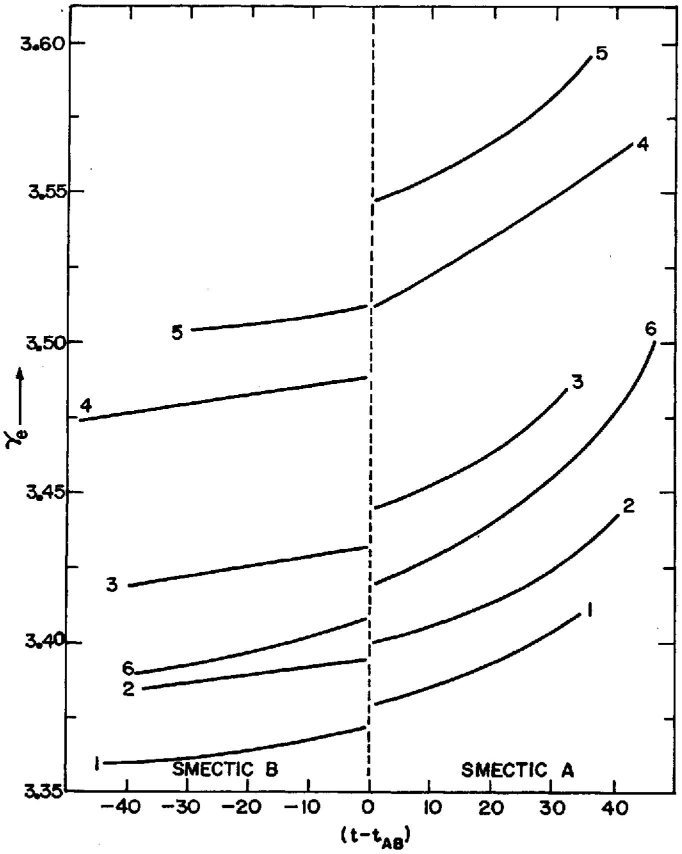

FIGURE 2 Variation of γ_e with the reduced temperature $(t - t_{AB})$.

the entire range of both smectic B and A is generally greater for molecules with larger number of carbon atoms in the end-groups (vide Figure 2, curves 1 to 5).

Apart from rotational isomerism, there may also be small fluctuations in the orientations of the molecules within each layer. The molecular lengths are of the order of 30Å. One cannot expect fluctuations of more than about 3° in the smectic B phase owing to the fact that the molecules are arranged in a close-packed structure. In the smectic A the fluctuations may be slightly larger. If one were to explain the decrease of (α_e/α_0) with increasing temperature as entirely due to fluctuations in orientation, one can estimate their order of magnitude. Increases in fluctuations of the order of 10° in smectic A and 5° in smectic B are required to explain the decrease of (α_e/α_0) with increasing temperature, and fluctuations of such magnitudes may be ruled out. It follows that the decrease of (α_e/α_0) is mainly due to rotational isomerism and to a lesser extent due to fluctuations in orientation.

Pelzl and Sackmann have also reported extensive birefringence data for a series of homologous compounds exhibiting the nematic, smectic A and cholesteric mesophases. These data may also be interpreted in terms of the anisotropic internal field and the results with regard to them will be reported separately.

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