Dielectric Anisotropy and the Order Parameter of HXBBA

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Dielectric Anisotropy and the Order Parameter of HXBBA

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Measurements of dielectric anisotropy ($\Delta\epsilon$), refractive indices (n_e, n_o), birefringence (Δn) and density (ρ) have been made in the nematic and smectic phases of $N(-p$-hexyl-oxybenzylidene)-p-butylaniline (HXBBA). The results indicate that the various transitions are of the first order type except smectic B–smectic G, which may be a second order transition. The order parameter S has been determined using the isotropic internal field model (Vuks approach) and the anisotropic internal field model (Neugebauer's approach) and both the values agree fairly well. The dielectric anisotropy ($\Delta\epsilon$) increases strongly in the smectic phases while S increases only slowly. It is interpreted by an increase of dipole–dipole correlations.

INTRODUCTION

The dielectric anisotropy ($\Delta\epsilon$) in liquid crystals resulting from the angular correlations between the molecules not only throws light on the individual molecular structure but also on their ordering in the mesophase which is characterized by the order parameter.[1-3] The order parameter S is the single most important parameter of a liquid crystal which governs nearly all its physical properties.[1-3] The knowl-

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edge of $\Delta\epsilon$ and S and their temperature dependence are also important from technological point[1-3] and there has been several studies on their behaviour in the nematic phase of liquid crystals.[4] However, only few such studies on the smectic phases of liquid crystals are available in the literature.[5-11]

In this paper we report the results of our dielectric anisotropy ($\Delta\epsilon$) and the order parameter (S) measurements in the nematic and smectic phases of $N(-p$-hexyloxybenzylidene)-p-butylaniline HXBBA. The sample HXBBA,

$$C_6H_{13}O-\langle\bigcirc\rangle-CH=N-\langle\bigcirc\rangle-C_4H_9$$
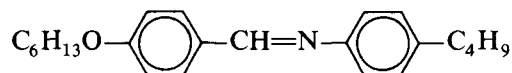
is a Shiff base possessing the following phase transitions:

$$K \rightarrow S_G \xrightarrow{56\,°C} S_B \xrightarrow{62\,°C} S_A \xrightarrow{72.5\,°C} N \xrightarrow{80\,°C} I$$
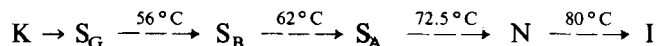
and S_G supercools. The study is expected to provide some important clues to the understanding of dielectric behaviour of smectic phase mesogens.

EXPERIMENTAL

The dielectric anisotropy ($\Delta\epsilon$) measurements of HXBBA were carried out in the temperature range: 45–82°C using a gold plated parallel plate capacitor (effective capacity 10.5 pF) having teflon spacer of thickness 0.03 cm. The sample in the isotropic phase was introduced into the cell through two fine holes drilled in the low potential terminal. The measurements of capacitance of the cell filled with the sample in nematic phase were made as a function of the magnetic field which indicated only a very little change in the value of capacitance beyond 1.5 KG. Hence a magnetic field of 3 KG was applied for aligning the sample. The magnetic field was provided by an electro-magnet (pole pieces 9 cm diameter). Measurements of dielectric per-mittivity were made at 2, 10 and 100 KHz using a Schering bridge (GR 716 C) with the magnetic field acting parallel to the a.c. field in one run and perpendicular in another run. To control the temperature, the cell was placed in a double walled glass jacket in which water from a regulated thermostat was circulated. The sample was cooled very slowly in the aligning field from the nematic to the smectic phases. The cell was kept at the required temperature for at least 40 minutes

before taking the measurements. It took about 8 hours to complete each run. The error in the measurement of dielectric permittivity was less than $\pm 1\%$.

The order parameter (S) has been determined using optical anisotropy measurements which yield fairly accurate values of S in comparison with that obtained using other bulk tensorial properties such as electric and magnetic susceptibilities, elastic constants, etc.[12,13] The experimental set up for the measurement of birefringence and density (ρ) was the same as described elsewhere.[13] The ordinary and isotropic refractive indices, n_o and n, respectively, were determined using Abbe refractometer. All the optical measurements were made at $\lambda = 5893\,°A$. The density (ρ) measurements were carried out with a U-shaped bicapillary dilatometer and travelling microscope. The dilatometer was calibrated using deionized water and the thermal expansion of the glass was also taken into account. The dilatometer was kept in a cylinder through which water was circulated from a thermostat. The temperature was regulated to an accuracy of $\pm 0.2\,°C$.

RESULTS AND DISCUSSION

Figure 1(a) shows the dielectric permittivity components: $\epsilon_{\parallel}$ (when the aligning magnetic field B was parallel to the a.c. electric field) and $\epsilon_{\perp}$ (when B was perpendicular to a.c. electric field) as functions of temperature at 2, 10 and 100 KHz. It is evident from the curves that $\epsilon_{\parallel}$ exhibits a clear dielectric dispersion while $\epsilon_{\perp}$ shows the absence of any such dispersion. The density (ρ), ordinary and extraordinary refractive indices n_o, n_e and their anisotropy Δn ($= n_e - n_o$) curves are drawn in Figures 2, 3(a) and 3(b), respectively.

The transitions are easily observed by the discontinuities in these curves which suggest that all these transitions are of first order type except smectic B–smectic G, which may be a second order transition as no sharp discontinuity at this transition is observed. The nature of such transition could be ascertained by specific heat measurements.[14] However, J. V. Rao et al.[15] reported these transitions to be of the first order using density and ultrasonic velocity measurements. Similar studies of density and refractive indices have been used by some workers[15,16] to identify the phase transitions in mesogens. From Figure 1(b) it is evident that dielectric anisotropy $\Delta\epsilon$ ($= \epsilon_{\parallel} - \epsilon_{\perp}$) is low in the nematic phase, but it increases strongly in the smectic phase.
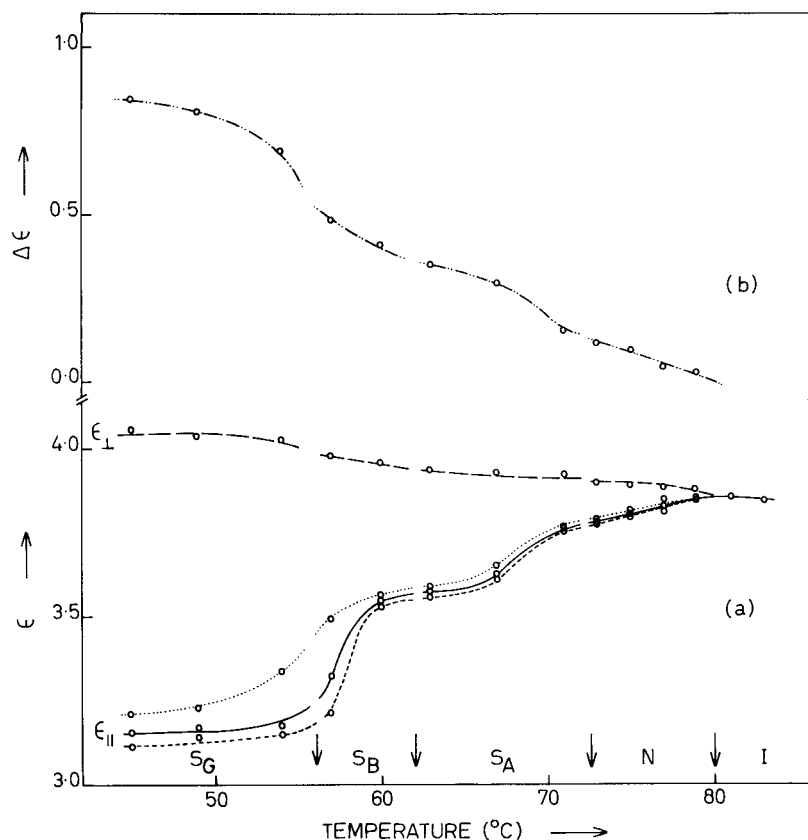
FIGURE 1 (a) Temperature dependence of $\epsilon_\parallel$ at 2 KHz ($\cdot\cdot$ O $\cdot\cdot$ O $\cdot\cdot$), 10 KHz (—O—O—) and 100 KHz (--O--O--) and $\epsilon_\perp$ at 2 KHz (—O—O—). (b) Temperature dependence of $\Delta\epsilon$ and 2 KHz (—O—O—).
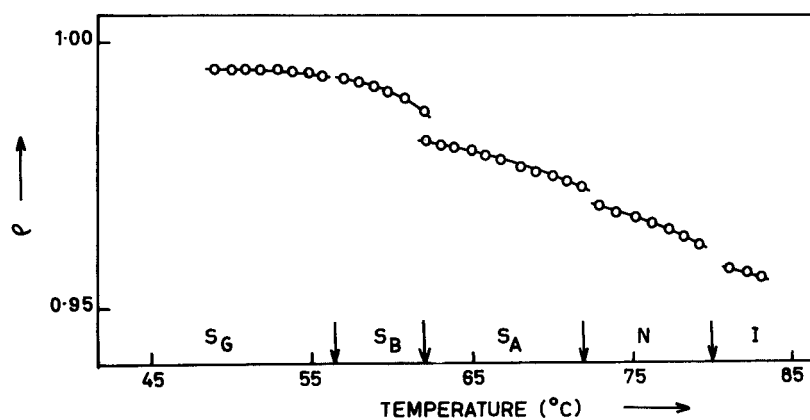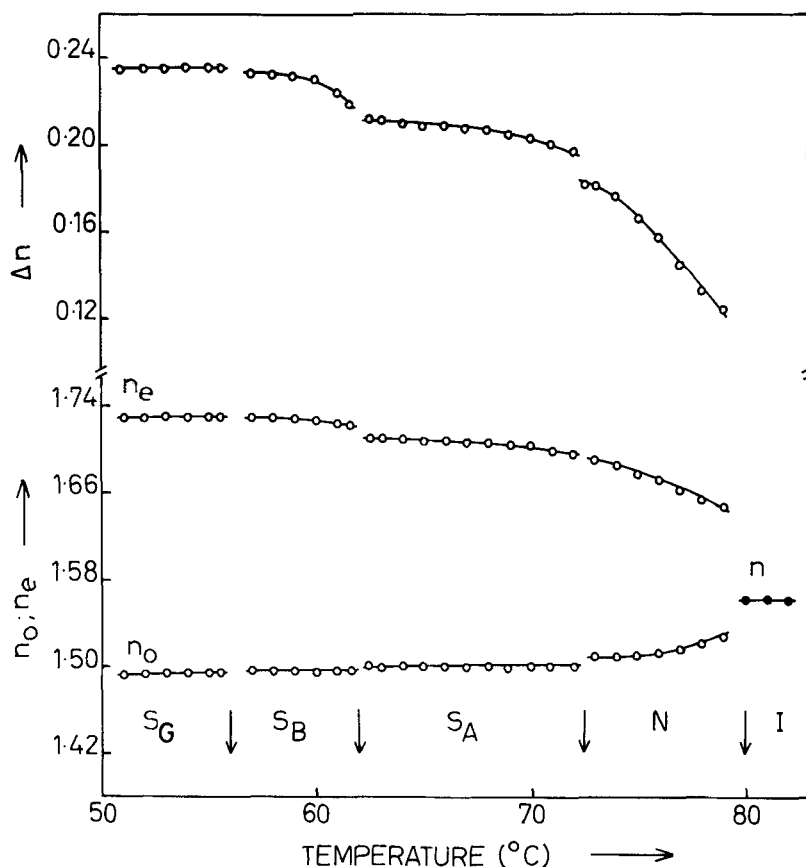

FIGURE 2 Temperature variation of density (ρ).

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FIGURE 3 (a) Temperature variation of refractive indices (n_o, n_e). (b) Birefringence (Δn) as a function of temperature.

The order parameter S in various smectic phases of the sample increases slowly when T decreases (Figure 4). The behaviour of $\Delta \epsilon$ in the nematic phase is in accordance with the theory proposed by Maier and Meier[17] for nematic liquid crystals. In the smectic phase of liquid crystals De Jeu et al.[6] suggested that the dipolar correlations should be considered, which had been completely neglected in Maier and Meier theory. They have shown that the ordering in layers increase considerably the short range dipole–dipole correlations.[4,6,7,19] In our case the increase of $\epsilon_\perp$ and decrease of $\epsilon_\parallel$ and hence an increase of $\Delta \epsilon$ suggests that when the smectic ordering appears, there is tendency for the parallel components of the molecular dipole to form antiparallel short range ordering and for the perpendicular components to form parallel

ordering. However, no attempt has been made to calculate the correlation factors as we do not have sufficient data to prove that our measurements of $\epsilon_\parallel$ at 2 KHz are not affected by dispersion. This compound is likely to give dispersions in the S_B phase in 1–10 KHz region like in 60.6 as reported by Kresse et al.[18] and in S_G phase, the dispersion is expected to be even below 1 KHz. The order parameter S has been determined using the relation

$$S = \frac{\alpha_e - \alpha_o}{\alpha_\parallel - \alpha_\perp}$$

where α_e and α_o are the principal polarizabilities in the mesomorphic phases and $\alpha_\parallel$ and $\alpha_\perp$ the principal molecular polarizabilities. As suggested by Haller et al.,[20] $(\alpha_\parallel - \alpha_\perp)$ is assumed to be the values of $(\alpha_e - \alpha_o)$ at absolute zero.

The principal polarizabilities α_e, α_o may be determined with the knowledge of the nature of the local field. Assuming the local field to be isotropic as in Vuks relations,[21] one obtains,

$$\alpha_{e,o} = \frac{3}{4\pi N} \frac{n_{e,o}^2 - 1}{\bar{n}^2 + 2}$$
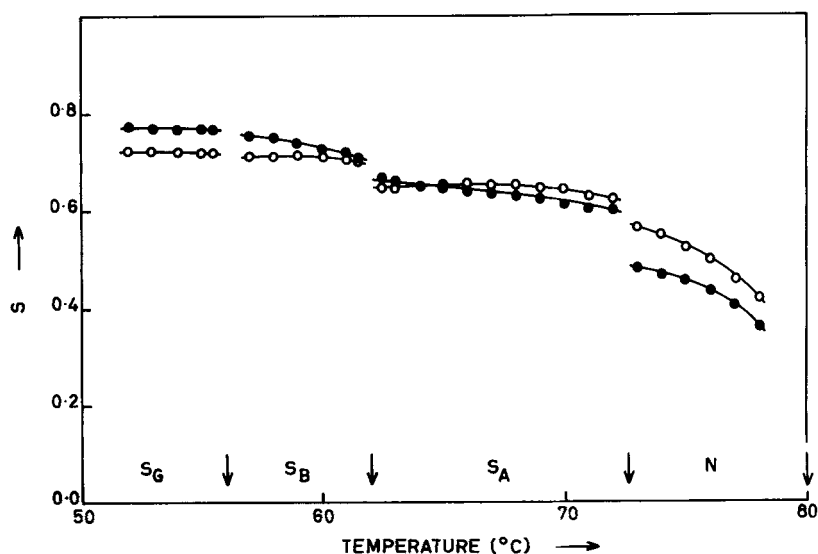

FIGURE 4   Temperature variation of the order parameter S (using Vuk's approach: O; using Neugebauer's approach: ●).

where $\bar{n}^2 = (n_e^2 + 2n_o^2)/3$ and N is the number of molecules per c.c. $= N_A \rho / M$ where N_A is the Avogadro's number, ρ is the density and M is the molecular weight, n_e, n_o are respectively the extraordinary and ordinary refractive indices. The value of $(\alpha_{||} - \alpha_{\perp})$ is obtained by extrapolating the linear portions of the curve $\log(\alpha_e - \alpha_o)$ vs. $\log(T - T_c)/T_c$ in the nematic phase to $T = 0\,^\circ K$.

If, however, the local field is anisotropic as indeed the case, one can use Neugebauer's relations[22] and obtain

$$\frac{1}{\alpha_e} + \frac{2}{\alpha_o} = \frac{4\pi N}{3}\left[\frac{n_e^2 + 2}{n_e^2 - 1} + \frac{2\left(n_o^2 + 2\right)}{n_o^2 - 1}\right]$$

and

$$\alpha_e + 2\alpha_o = \frac{9}{4\pi N_i}\left(\frac{n^2 - 1}{n^2 + 2}\right)$$

assuming that the mean polarizability $\bar{\alpha}$ remains the same in all the phases, n is the refractive index in the isotropic phase and N_i is the number of molecules per c.c. in the isotropic phase. As before, $\alpha_{||} - \alpha_{\perp}$ is determined by extrapolating $\log(\alpha_e/\alpha_o)$ vs. $\log(T - T_c)$ curve to $T = 0\,^\circ K$. Thus knowing the values of α_e, α_o and $\alpha_{||} - \alpha_{\perp}$ the value of S can be determined.

The order parameter S, computed using isotropic local field model (Vuks approach) and the anisotropic local field model (Neugebauer's approach) agree fairly well (Figure 4). It appears that although α_e and α_o vary with the model used, the ratio is not sensitive to the model.[23]

Acknowledgments

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