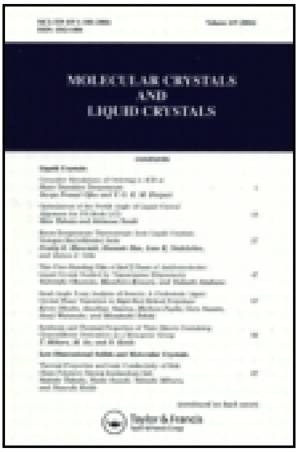

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Static Dielectric Studies in the Nematic Phase of a Nematogenic Compound

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Static Dielectric Studies in the Nematic Phase of a Nematogenic Compound

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Static dielectric permittivity in the nematic phase of a Nematogenic compound 4-4′ Dipentylazoxy benzene had been measured at various temperatures using a sensitive LCR meter. Using these data, the dipole moment associated with the molecule is calculated. The validity of this approach is discussed by comparing the order parameter 'S' obtained from the Refractive index with the values of 'S' computed from the predictions of the mean field theories. Boardwijk's theory is applied here with appropriate molecular parameters to compute dipole–dipole correlation factor.

Keywords Dipole–dipole correlations; dipole moments; static dielectric properties

1. Introduction

Nematic liquid crystals exhibit anisotropy property of solids as well as fluidity of isotropic liquid and are made up of calamitic molecules. The rod like shaped molecules can be obtained by joining two or more phenyl rings or cyclohexyl rings in a relatively rigid manner group and attached with flexible aliphatic end chains. When self-assembled into molecular organized structures with long range orientational order it shows anisotropy as well as fluidity as a function of temperature and they are called liquid crystals [1,2].

Strongly polar Liquid crystal substances are attractive soft materials both from the view points of fundamental research and their application to electro-optic devices. Consequently studies in operational characteristics of liquid crystal devices depend on their anisotropic dielectric and optical properties. Studies of dielectric properties of liquid crystal are therefore vital to their applications and in addition provide very useful information about their molecular structure and intermolecular forces. The permittivity tensor components $\varepsilon_{\parallel}$ and $\varepsilon_{\perp}$ as a function of temperature and frequency, the dielectric anisotropy $\Delta\varepsilon = [\varepsilon_{\parallel} - \varepsilon_{\perp}]$, were studied. From electric dipole moment molecular polarizability anisotropy were evaluated the size and the value of dielectric anisotropy. The dielectric anisotropy is low and positive in the absence of a dipole moment [3–10]. The present paper discusses the dipole structure of 4-4′ Dipentylazoxy benzene and their dielectric properties.

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2. Experimental

The experimental works were carried out at the centre for Liquid Crystal Research, Bangalore. The nematic sample used in this investigation was obtained from M/s. Aldrich Chemical Company (USA), the nematic-isotropic transition temperature T_c was estimated with the help of transmitting light polarizing microscope and a specially constructed hot stage and thermal central unit. The observed value of T_c was found to be 68.5°c and is in good agreement with the reported value. The static dielectric permittivity measurements were carried out by planar and homeotropic alignments of the molecules. The static dielectric measurements work were carried out on the sample using two Indium Tin Oxide coated plates with a pre-treatment of silane. A combination of this coating and a 2.4 Tesla Magnetic field was used to obtain homeotropically aligned mesophases by slowly cooling the sample from the isotropic phase. The static dielectric permittivity component tensors $\varepsilon_{\|}$ and $\varepsilon_{\perp}$ were measured by a sensitive impedance analyser (Model 4194A, Hewlett Packard, USA). A homogenous alignment of the sample gave the dielectric component $\varepsilon_{\perp}$ when the applied electric field **E** was perpendicular to **B** and the homeotropic alignment gave the other component $\varepsilon_{\|}$ when the applied field **E** was parallel to **B**. The thickness of the sample was 12.52 to 5.1 μm. All the measurements were carried out at different temperatures in the liquid crystal phases. The frequency of the electric field was set at 10 kHz. Figure 1 shows the structural formula of 4-4′ Dipentylazoxy benzene.

3. Results and Discussion

Figure 2 show the variation of dielectric permittivity tensor components $\varepsilon_{\|}$, $\varepsilon_{\perp}$, and the dielectric permittivity of the isotropic phase ε_{iso} as a function of temperature in the nematic phase. The average value of dielectric permittivity $\bar{\varepsilon} = [\varepsilon_{\|} - 2\varepsilon_{\perp}/3]$ was estimated from the value of permittivity tensor components $\varepsilon_{\|}$ and $\varepsilon_{\perp}$ in the nematic region.

Figure 3 Shows that the dielectric anisotropy $\Delta\varepsilon$ decreases with increase of temperature. Our observations show that (Fig. 2) when the compound is cooled from the isotropic phase the values of the principal dielectric permittivity tensor components $\varepsilon_{\|}$ increases whereas $\varepsilon_{\perp}$ decreases up to a certain temperature. Average values of the dielectric constants $\bar{\varepsilon}$ in the nematic phase is lower than that of extrapolated isotropic value.

From the dipolar theory suggested by Madhusudhana and Chandrasekhar [5] strongly polar molecules are arranged antiparallel to one another. The refractive index measurements were made using Goniometer and small angled prisms (3–5^0) at different temperatures in the nematic and isotropic phases for λ 589.3 nm. $n_e(\infty)$ and $n_o(\infty)$ which are the refractive indices corresponding to $\lambda = \infty$ are obtained by extrapolating the values of the refractive indices n_e, n_o that are estimated

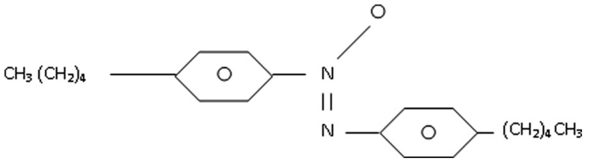

Figure 1. Chemical structure of 4-4′ di-pentylazoxy benzene.

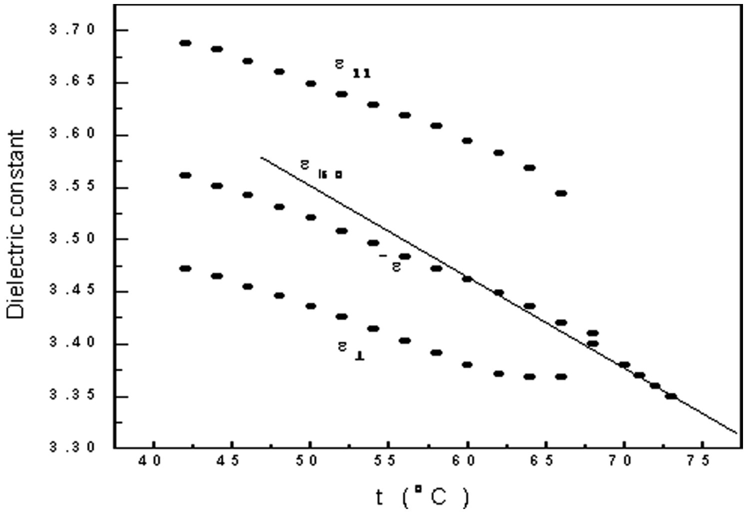

Figure 2. The variation of dielectric permittivity with temperature.

for different wavelengths of the light we have taken $n_e = 1.687$ n_o 1.518 N is the number of molecules/unit volume $N = 17.68 \times 1020$. From the measured values of dielectric permittivity tensor components ($\varepsilon_{||}$, $\varepsilon_{\perp}$) and the experimental values of the refractive indices (n_e, n_o), we have evaluated the effective parallel and perpendicular of dipole moments (μ_l and μ_t) of the molecules using the following equation [11].

$$\mu_l^2 = \frac{9K_BT\{\varepsilon_{||} - n_e^2(\infty)\}\{2\varepsilon_{||} + n_e^2(\infty)\}}{4\pi N\varepsilon_{||}\{n_e^2(\infty) + 2)\}^2} \qquad (1)$$

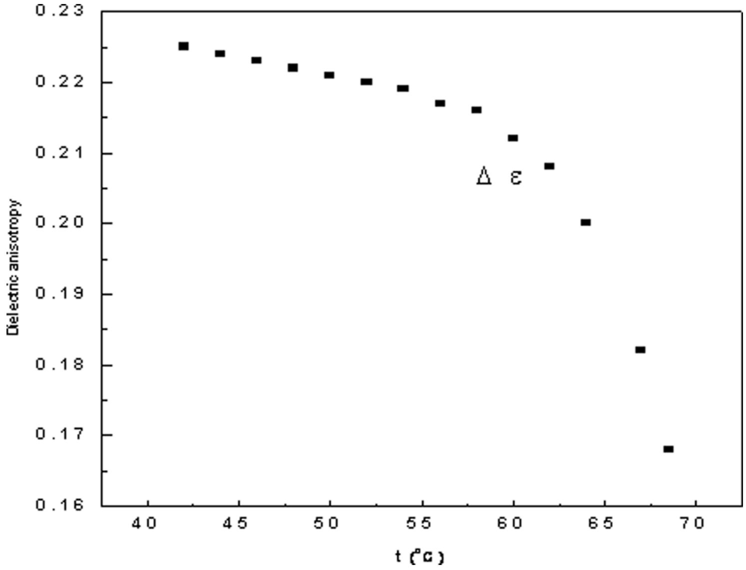

Figure 3. The variation of dielectric anisotropy with temperature.

$$\mu_t^2 = \frac{9K_BT\{\varepsilon_\perp - n_o^2(\infty)\}\{2\varepsilon_\perp + n_o^2(\infty)\}}{4\pi N\varepsilon_\perp\{n_o^2(\infty)+2)\}^2} \tag{2}$$

It is found that the components of dipole moment do not vary much with temperature. For the calculation of dipole moments of average values of μ_l, μ_t and $\bar{\mu}$ are reported in Table 1. $\Delta\varepsilon$ (Fig 3) is large and strong dipole moment along the length of the molecule and broadly in with our observation as agreement with μ as far our calculations (as shown in Table 1). In the present investigation dielectric permittivity and the dielectric anisotropy were analyzed using Maier and Meier equation [6]

$$\varepsilon_{||} = 1 + 4\pi NhF\left[\bar{\alpha} + \frac{2}{3}\Delta\alpha S + \frac{F\mu^2}{3K_BT}\{1-(1-3\cos^2\ \beta)\}S\right] \tag{3}$$

$$\varepsilon_{||} = 1 + 4\pi NhF\left[\bar{\alpha} + \frac{1}{3}\Delta\alpha S + \frac{F\mu^2}{3K_BT}\left\{1-\frac{1}{2}(1-3\cos^2\ \beta)\right\}S\right] \tag{4}$$

$$\Delta\varepsilon = 4\pi NhF\left[\Delta\bar{\alpha} - \frac{F\mu^2}{2K_BT}(1-3\cos^2\ \beta)\right]S \tag{5}$$

β = angle between the dipole moment 'μ' and the long axis. N is the number of molecules/unit cc, $h = \frac{3\varepsilon}{2\varepsilon+1}$ (Cavity field factor) reactive field factor $F = \frac{1}{\alpha f}$, with $F = \frac{4N}{3}\left[\frac{(\bar{\varepsilon}-2)}{(2\varepsilon+1)}\right]$, μ is the dipole moment of the free molecules, $\Delta\varepsilon$ – dielectric anisotropy, and $\Delta\alpha$ – polarizability anisotropy.

The orientational order parameter (S) values have been obtained from our optical studies (as shown in Fig. 4) and used with the present data dielectric measurements to compute β values, (Eq. 3–5). The order parameter (S) calculated is slightly greater than the experimental value. Figure 5 the variation of the angle of inclination β with temperature. It is found to decrease with temperature initially and then show a sharp increase as the isotropic transition temperature is approached. However as the isotropic temperature is approached this trend is disturbed β values shown significant flucation and to increase. This behavior may explain the rapid vibration of the molecules as the nematic – isotropic phase. We have obtained the order parameter 'S' for an appropriate β value. The results showed that Maier Meier theory for dielectric permittivity gives consistent agreement with the experimental values. The average values of μ_l, μ_t and $\bar{\mu}$ values of the dipole moment of the molecules to be much higher than the values obtained from solution method.

3.1. *The Dipole–Dipole Correlation*

Dipole Correlation in anisotropic fluids can be conveniently determined in terms of Kirkwood g factors derived for different principal axes of the permittivity tensor by

Table 1. Average values of μ_l, μ_t and μ $[\mu_{l+2}\mu_t]/3]$

Compound	μ_l (D)	μ_t (D)	μ (D)
DPAB	2.16	1.61	1.79

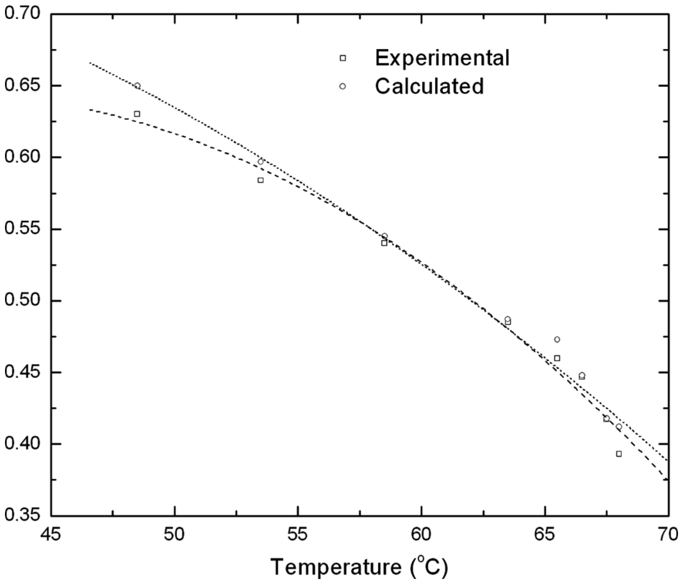

Figure 4. Variation of order parameter with temperature.

the following expression [12,13]:

$$g_{IK} = 1 + \frac{1}{\left\langle \mu_K^{(i)2} \right\rangle} \sum_{j \neq i}^{N} \left\langle \mu_K^{(i)} \mu_K^{(j)} \right\rangle, \tag{6}$$

where, k indicates a particular axis in the fluid and μ_k is the projection of the molecular dipole moment on to the k-axis. The values of the Kirkwood factors $g_{\|}$

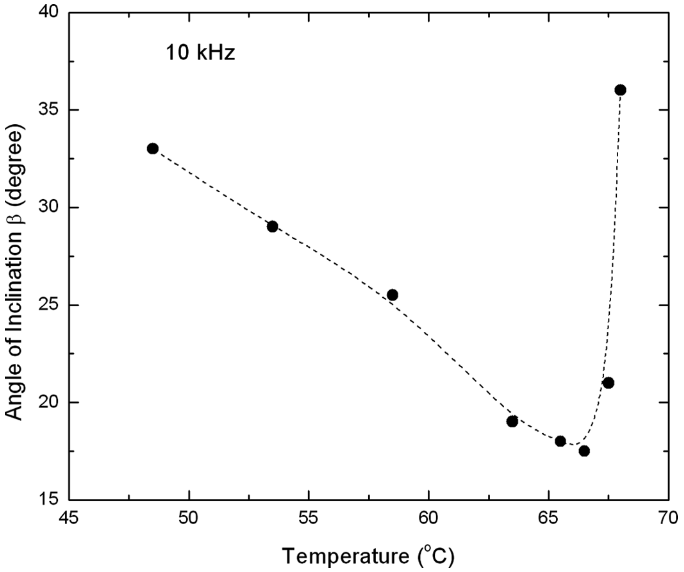

Figure 5. Variation of angle of inclination 'β' with temperatures.

Table 2. Dipole moment μ at different temperatures in the case of DPAB

t (°C)	μ (D)
68	2.00
67.5	3.00
66.5	3.00
65.5	3.00
63.5	5.00
58.5	3.00
53.5	3.00
48.5	3.00

Table 3. Correlation factors in the case of DPAB

t (°C)	68	67.5	66.5	65.5	63.5	58.5	53.5	48.5	38.5
$g_{\parallel}$	2.942	3.172	3.475	3.671	3.825	4.410	5.230	6.219	7.836
$g_{\perp}$	0.507	0.479	0.447	0.428	0.415	0.369	0.321	0.277	0.226

and $g_{\perp}$ computed using Eq. (6) are reported in Table 3. These results signify that there is a considerable ordering of the molecular diploes in the nematic phase [14]. The existence of angular correlation between the molecules is responsible for mesophase formation; these are neglected in field theories. The Bordewijk's theory [15] of anisotropic dielectrics suggests interaction between the molecular dipoles in the DPAB as in the cases of alkyl-cyano-biphenyls and the correlation between axes of the molecular polarizability tensor even larger. Studies of dielectric properties of many strongly polar substances indicate that the dipole–dipole association plays an important role in estimating the dielectric properties of materials in the nematic and isotropic phases [16].

4. Conclusions

On the basis of summary of the static dielectric permittivity (constant) in the nematic phase of a nematogenic sample was measured at different temperatures in their nematic and isotropic phases. These data were used to compute the dipole moment of the free molecules. Hence the correlations factors help to understand the antiparallel arrangements in the system. We have also quantified the behavior of dielectric in the nematic phase in terms of g factors.

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