Molecular Crystals and Liquid Crystals

Static Dielectric Studies of Two Nematogenic Compounds

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Static dielectric constants of two nematogenic compounds viz., (i) 1-hexyl-4-(4-iso-thiocyanatophenyl) bicyclo [2,2,2] octane and (ii) 4'-(pentyloxy)-4-biphenyl carbonitrile, have been measured at different temperatures using a sensitive LCR bridge. Using these data the dipole moment associated with the molecules is estimated. The validity of this approach is discussed by comparing the order parameter S obtained from the refractive index data with the values of S computed from the predications of the mean-field theories. Boardewijk's theory is applied here with appropriate molecular parameters, to compute dipole-dipole correlation factors.

Keywords: dielectric constants; dipole moment

INTRODUCTION

Dielectric studies of nematogenic substances have played an important role in the development of electro-optical devices. The dielectric properties of nematic liquid crystals change drastically at the nematic-isotropic transition temperature. The dielectric

anisotropy, $\Delta\varepsilon[= \varepsilon_{\parallel} - \varepsilon_{\perp}]$ depends on the value and the direction of the dipole moment with respect to the long molecular axis. Here $\varepsilon_{\parallel}$ and $\varepsilon_{\perp}$ and are the dielectric constants parallel and perpendicular to the nematic director $\hat{n}$. In the isotropic phase $\varepsilon_{\mathrm{iso}}$, is comparable with the mean value $\bar{\varepsilon} = (\varepsilon_{\parallel} - 2\varepsilon_{\perp})/3$. The value of $\Delta\varepsilon$ in the case of a nematic system is determined by (i) the molecular polarizability and (ii) the permanent electric dipole moment. The magnitudes of these two factors determine the size and the value of the dielectric anisotropy. For rod like molecules, the polarizability along the long molecular axis is always greater than that in the perpendicular direction. Hence, in the absence of a permanent molecular dipole moment, the dielectric anisotropy is obtained by introducing strong dipoles respectively along the long axis of the molecule and perpendicular to it. Therefore, it is possible to obtain the nematic liquid crystals with any desired magnitude of $\Delta\varepsilon$, depending on the size of the dipole moment and the angle made by the dipole with the long axis of the molecule. In this paper, we report our investigations on the static dielectric constants of two nematogenic compounds namely viz.,

 (i) 1-hexyl-4-(4-isothiocyanatophenyl) bicyclo [2,2,2] octane, (HIPBO).
(ii) 4′-(pentyloxy)-4-biphenylcarbonitrile, (5OCB).

This study has been taken up to estimate the magnitude of dipole moment and the direction of the same with respect to the molecular axis.

EXPERIMENTAL

The nematic compounds 5OCB and HIPBO used in this investigation were supplied by M/s Aldrich Chemical Company (USA). Using Ortho plan Leitz polarizing microscope in conjunction with a hot stage the nematic–isotropic transition temperatures (T_C) of these two samples were determined and are respectively 68.5 and 86°C. These values are in good agreement with the standard values. The static dielectric constants $\varepsilon_{\parallel}$ and $\varepsilon_{\perp}$ were measured using a sensitive impedance analyser (Model 4194A, Hewlett-Packard, USA). A homogeneous alignment of the sample gave the dielectric component $\varepsilon_{\perp}$ when the applied electric field $\mathbf{E}$ as perpendicular to the nematic director $\hat{n}$, and the homeotropic alignment gave the other component $\varepsilon_{\parallel}$ when the applied field $\mathbf{E}$ was parallel to the director $\hat{n}$. Both these alignments were achieved by applying the magnetic field of about 2.4 T. The static dielectric constants ($\varepsilon_{\parallel}$, $\varepsilon_{\perp}$ and $\varepsilon_{\mathrm{iso}}$) were measured at various temperatures in the nematic and isotropic phases in the cooling mode, cooled from isotropic

melt. For dielectric measurements the samples were taken in a cell made up of two tin oxide coated glass plates. The thickness of the samples was lying between 12.5 to 50 μm. The frequency of the electric field was set at 10 KHz.

RESULTS AND DISCUSSION

Experimentally determined principal dielectric constants $\varepsilon_\parallel$, $\varepsilon_\perp$ and the isotropic dielectric constants ε_{iso} of 5OCB and HIPBO are shown graphically in Figures 1 and 2. The average values of the dielectric constants $\bar{\varepsilon} = (\varepsilon_\parallel - 2\varepsilon_\perp)/3$ determined from $\varepsilon_\parallel$ and $\varepsilon_\perp$ at different temperatures in the nematic phase are also shown in the same figures. Figure 3 shows the variation of dielectric anisotropy $\Delta\varepsilon$ as a function of temperature.
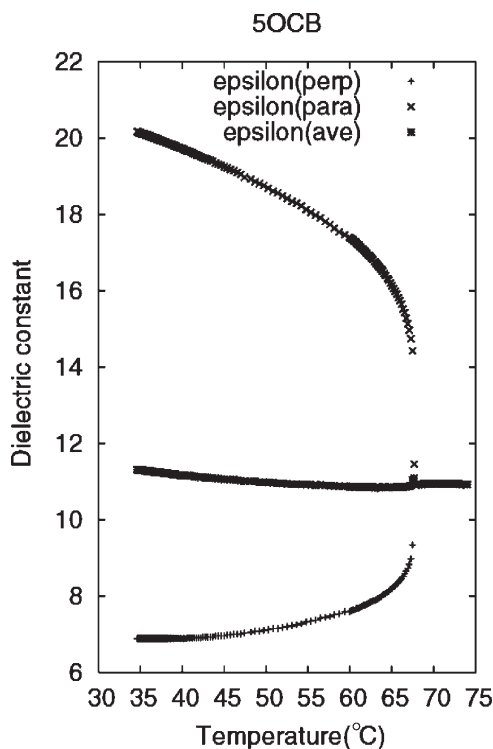
FIGURE 1 Variation of dielectric constants with temperature in the case of 5OCB.

D. Gopalakrishna et al.
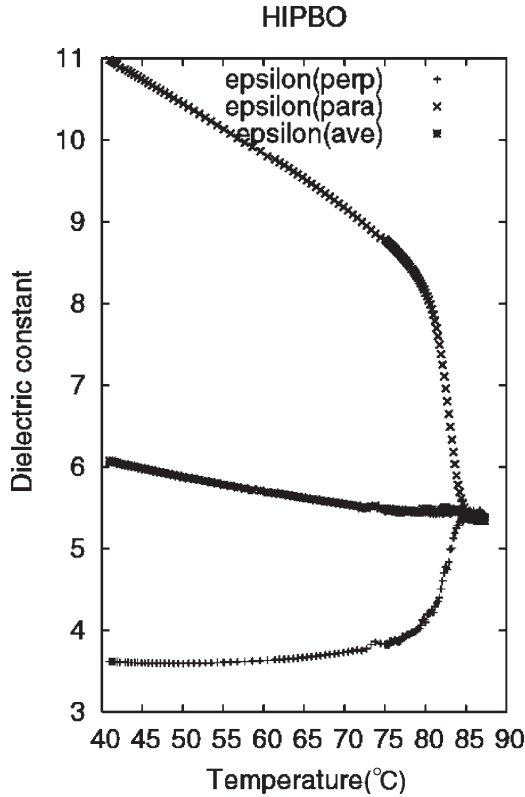
FIGURE 2 Variation of dielectric constants with temperature in the case of HIPBO.

As may be seen from Figures 1 and 2 that when the sample is cooled from the isotropic melt the principal dielectric constant $\varepsilon_\parallel$ increases whereas $\varepsilon_\perp$ decreases with decrease of temperature. Further the average value of the dielectric constant $\bar{\varepsilon}$ in the nematic phase near the transition in the case of 5OCB is lower than that of its extrapolated isotropic value but not so in the case of HIPBO. This is in accordance with the results reported by the earlier investigators for strongly polar and non-polar liquid crystalline materials respectively [1–10]. It is evident from the dipolar theory proposed by Madhusudana and Chadrasekhar [4] that in such cases the dipole moments associated with the molecules are arranged antiparallel to one another. Under these circumstances, using the measured values of the dielectric constants $(\varepsilon_\parallel, \varepsilon_\perp)$ and the refractive indices (n_e, n_o), the effective parallel and perpendicular components of dipole
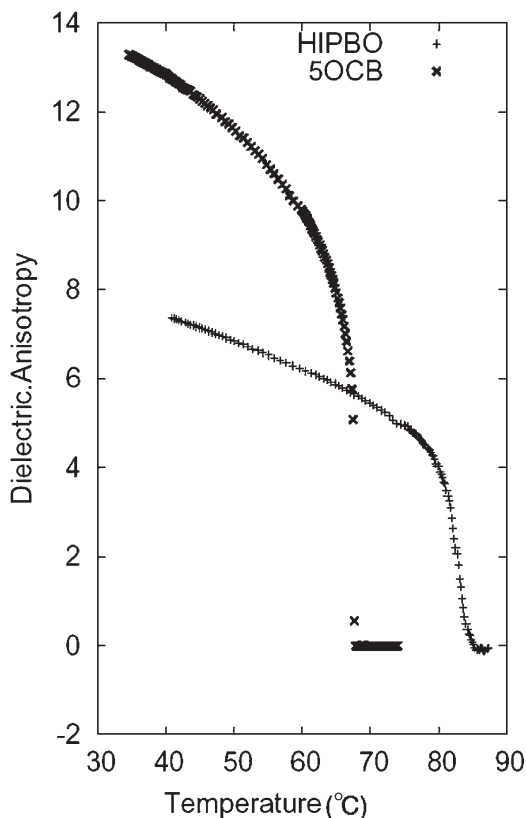
FIGURE 3 Variation of dielectric anisotropy in the case of HIPBO and 5OCB.

moment (μ_l and μ_t) of the molecules have been estimated from the following relations [11].

$$\mu_l^2 = \frac{9K_B T\{\varepsilon_\parallel - n_e^2(\infty)\}\{2\varepsilon_\parallel + n_e^2(\infty)\}}{4\pi N \varepsilon_\parallel \{n_e^2(\infty) + 2\}^2} \tag{1}$$

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

Here, N is the number of molecules per unit volume $n_e(\infty)$, and $n_o(\infty)$ are the refractive indices corresponding to $\lambda = \infty$ and are obtained by extrapolating the values of the refractive indices n_e n_o that are determined for various wavelengths in the visible region of the electromagnetic spectrum, to infinite wavelength. It is found

D. Gopalakrishna et al.

TABLE 1 Average Values of μ_l, μ_t and μ, of HIPBO and 5OCB

Compound	μ_l (D)	μ_t (D)	μ (D)
HIPBO	3.00	1.90	2.22
5OCB	4.00	2.65	3.10

$\mu, = (\mu_l + 2\mu_t)/3$.

that the components of dipole moment do not vary much with temperature. The average values of μ_l, μ_t and μ so obtained are given in Table 1. Here we have taken $n_e(\infty) = 1.725$; $n_o(\infty) = 1.520$; $N = 23.71 \times 10^{20}$ in the case of 5OCB and $n_e(\infty) = 1.616$; $n_o(\infty) = 1.526$; $N = 21.97 \times 10^{20}$ in the case of HIPBO. In both the compounds $\Delta\varepsilon$ (shown in Fig. 3) is large indicating that there is a strong dipole moment along the length of the molecule, which (μ) agrees broadly with our observation as given in Table 1. The results reported in Table 1 are also in conformity with earlier studies on the dielectric constants of nCB and nOCB [5,6,12–14].

   The orientational order parameter defined as $S = (3\cos^2\theta\text{-}1)$ is not influenced by the electric field and Sen *et al.* [15] and Urban *et al.* [2] have also reported this aspect. Maier and Meier [16] have obtained the equations for the principal dielectric constants and the dielectric anisotropy of the nematic phase interms of orientational order and they are given by

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

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

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

Here N is the number of molecules per unit volume, $h = 3\varepsilon/2\varepsilon + 1$ (cavity field factor), reactive field factor $F = 1/\alpha f$ with $f = 4N/3$ $[(\bar{\varepsilon} - 2)/(2\varepsilon + 1)]$; ($\mu$) is the dipole moment of free molecule; $\Delta\varepsilon =$ polarizability anisotropy; $\Delta\varepsilon =$ dielectric anisotropy and β is the angle that the permanent dipoles make with the long molecular axis. Using the values of (μ) and ε in these equations, we have obtained the order parameter S for an appropriate β value. The calculated and experimental order parameters [17,18] are given in Table 2. The value of the order parameters S calculated from experimental data of dielectric anisotropy; $\Delta\varepsilon$ and using equations (3–5) turns out to be much less than that obtained from optical and other methods. Similar results

TABLE 2 Comparison of Computed Values of S(calc) using Equation (3)–(5) with the Order Parameter S(exp) from Optical Method

	5OCB					HIPBO			
T(°C)	S(Exp) [17]ref	S(Cal)	β	μ in $\times 10^{-17}$ esu	T(°C)	S(exp) [18] ref	S(cal)	β	μ in $\times 10^{-17}$ esu
				•					10.
70	0.234	0.237	10.01	1.60	86	0.319	0.321	20.01	0.80
68	0.377	0.385	0.009	1.80	84	0.389	0.391	7.010	1.20
66	0.432	0.434	0.009	1.80	82	0.430	0.432	8.010	1.30
64	0.469	0.469	4.010	1.80	80	0.460	0.461	5.010	1.30
62	0.504	0.504	9.010	1.80	78	0.479	0.505	0.009	1.30
60	0.523	0.524	9.010	1.80	76	0.519	0.523	12.01	1.30
58	0.542	0.543	0.009	1.70	74	0.523	0.524	34.01	1.80
56	0.560	0.562	23.01	2.00	72	0.529	0.530	5.010	1.30
54	0.575	0.576	11.01	1.80	70	0.533	0.538	0.009	1.30
52	0.591	0.623	0.009	1.70	68	0.540	0.547	0.009	1.30
50	0.600	0.631	0.009	1.70	66	0.544	0.558	0.009	1.30
48	0.610	0.641	0.009	1.70	64	0.550	0.566	0.009	1.30
46	0.623	0.645	13.01	1.80	62	0.560	0.572	0.009	1.30
44	0.634	0.647	14.01	1.80	60	0.565	0.577	0.009	1.30
42	0.644	0.652	14.01	1.80	58	0.569	0.579	17.01	1.40
38	0.664	0.667	0.009	1.70	56	0.580	0.589	0.009	1.30

• Average $\mu = 1.77 \times 10^{-17}$ esu or (D) for 5OCB.
• Average $\mu = 1.30 \times 10^{-17}$ esu or (D) for HIPBO.

were also reported in earlier papers in the cases of nPCH by Sen *et al*. [2,15]. Table 2 shows the values of S determined and these are distinctly lower than the proper S values obtained from X-ray data [18]. Thus the results show that Maier and Meier,s theory for dielectric constants in anisotropic media of strongly polar molecules fails to give consistent results with the experimental values. This is due to the fact that only long range order was considered in Maier and Meier's theory, and the existence of short range order was completely ignored. Madhusudana and Chandrasekhar [4] in their theory have proposed the existence of antiparallel short-range order in the nematic phase of strongly polar molecules. Such short range antiparallel ordering in strongly polar nematic liquid crystals might cause a large decrease in $\varepsilon_\parallel$, resulting in decrease in dielectric anisotropy and thus a decrease in order parameter, nematic–isotropic transition temperature (T_c) and average values of μ_1, μ_t and μ, of HIPBO and 5OCB. The dipole moment of the molecules of HIPBO and 5OCB obtained from equations (1 and 2) turns out to be much higher than the values obtained from solution method. Here, for HIPBO and 5OCB the values of μ determined from Eq. (3–5) are found to be 13D and 18D which are very large. In fact such very large values were also reported by earlier investigators using the same equations.

THE DIPOLE-DIPOLE CORRELATION

The dipole-dipole correlations were considered in the theory developed by Frohlich [19] who generalized the former Kirkwood approach [20]. In this paper, Frohlich has defined the dipole-dipole correlations factor as

$$g = 1 +_i \Sigma_j < \mu_i\mu_j/\bar{\mu}^2 \tag{6}$$

where the summation is over all neighboring molecules. For the nematic phase we have seperate g- factors for the directions parallel and perpendicular to the director. Usually, the g-factors are calculated using

$$g_\parallel = (\mu_\parallel)^2/\mu_\parallel^2$$
$$g_\perp = (\mu_\perp)^2/\mu t^2 \tag{7}$$

$\mu_\parallel^2 = \mu^2[1 - (1 - 3\cos^2\beta)]S$ and $\mu_\perp^2 = \mu_\parallel = \mu^2[1 + (1 - 3\cos^2\beta)]S$, μ_l^2 and μ_t^2 are the longitudinal and transverse components of the dipole moment respectively. The factors $g_\parallel$ and $g_\perp$ are anisotropic Kirkwood dipole correlation factors defined with respect to the axes of the permittivity and are given in Table 3 for 5OCB and HIPBO. The results indicate

TABLE 3 Correlation Factors for 5OCb and HIPBO using Bordewijk's Theory

5OCB			HIPBO		
T(°C)	$g_\parallel$	$g_\perp$	T(°C)	$g_\parallel$	$g_\perp$
70	0.704	0.352	86	0.480	0.000
68	1.131	0.000	84	1.169	0.585
66	1.299	0.000	82	1.290	0.644
64	1.407	0.703	80	1.380	0.690
62	1.511	0.756	78	1.439	0.000
60	1.568	0.784	76	1.559	0.780
58	1.628	0.000	74	1.572	0.785
56	1.682	0.841	72	1.590	0.795
54	1.727	0.864	70	1.601	0.000
52	1.773	0.000	68	1.620	0.000
50	1.799	0.000	66	1.632	0.000
48	1.830	0.000	64	1.649	0.000
46	1.869	0.934	62	1.680	0.000
44	1.901	0.951	60	1.694	0.000
42	1.934	0.967	58	1.709	0.855
38	1.991	0.000	56	1.740	0.000

that there is considerable anti-parallel ordering of the molecular dipoles in the nematic phase [21]. The existence of angular correlations between molecules is responsible for mesophase formation, yet they are neglected in field theories. The Bordewijk theory of anisotropic dielectrics suggest interactions between molecular dipoles in the HIPBO and 5OCB as in the cases of alkyl-cyano-biphenyls and the correlations between the axes of the molecular polarizability tensor is even greater. Thus the correlation factors should be related to the actual order parameter. Dielectric studies of many strongly polar substances indicate that the dipole-dipole association plays an important role in determining the dielectric properties of substances in the nematic and isotropic phases [22]. The cyano-compounds, in particular, exhibit a considerable degree of the antiparallel associations leading to $g_\parallel < 1$ and with increasing temperature the g-factors go to unity, although the antiparallel correlations persist in the isotropic phase as well [23–25].

CONCLUSIONS

We have determined the static dielectric constants of two nematogenic compounds at different temperatures in their nematic and isotropic phases. These data were further used to compute the dipole moment

of the free molecule and hence the correlation factors to understand the anti-parallel arrangements in two systems.

BIBLIOGRAPHY

[1] Schadt & Helfrich, W. (1971). *App. Phys. Lett.*, *18*, 127.
[2] Urban, S., Gestblom, B., Brickert, T., & Wurflinger, A. Z. (1995). *Naturforsch*, *50a*, 984.
[3] Maier, W. & Meir, G. (1961). *Z. Naturforsch*, *16a*, 470.
[4] Madhusudhana, N. V. & Chandrasekhar, S. (1973). *Pramana*, *1*, 57.
[5] Ratna, B. R., Vijaya, M. S., Shashidhar, R., & Shdashiva, B. K. (1973) *Pramana*, *1*, 69.
[6] Ratna, B. R. & Shashidhar, R. (1977). *Mol. Cryst. Liq. Cryst.*, *42*, 185 and 1133.
[7] Bradshaw, M. J. & Raynes, E. P. (1983). *Mol Cryst Liq Cryst.*, *91*, 145.
[8] Chandrasekhar, S. (1985). *Mol. Cryst, Liq. Cryst.*, *124*, 1.
[9] Raszewski, Z. (1989). *Electron Technol.*, *20*, 37.
[10] Wu, S. T., Coates, D., & Bartmann. E. (1991). *Liquid Crystals*, *10*(5), 635.
[11] Bottcher, C. J. F. (1952). *Theory of Electric Polarization*, Elsevier Publishing Company: London, New York.
[12] Ratna, B. R. & Shashidhar, R. (1976). *Pramana*, *6*, 278.
[13] Ratna, B. R., Shashidhar, R., & Rao, K. V. (1980). Proceeding of International Liquid crystal conference, Chandrasekhar, S. (Ed.), Heyden, London, 135.
[14] KumaraSwamy, S. R., Somashekar, R., Madhava, M. S., & Revannasiddaiah, D. (1995). *Mol. Cryst. Liq Cryst.*, *26*, 51.
[15] Sen, S., Kali, S. K, Roy., & Roy, S. B. (1985). *Mol. Cryst. Liq. Cryst.*, *126*, 269
[16] Maier, W. & Meier, G. (1961). *Z. Naturforsch*, *16a*, 262 and 270.
[17] Mitra, M. (1994). *Mol Cryst. Liq. Cryst.*, *241*, 17.
[18] Divya, A. P., Somashekar, R., Revannasiddaiah, D., & Madhava, M. S. (1999). *Bull. Mat. Sci.*, *22*, 129.
[19] Frohlich, H. (1949). *Theory of Dielectrics*, Clarendon Press, Oxford.
[20] Kirkwood, J. G. (1939). *J. Chem. Phys.*, (USA), 7, 911.
[21] Dunmar, D. A., Manterfield, M. R., Miller, W. H., & Dunleavy, J. K. (1978). *Mol. Cryst. Liq. Cryst.*, *45*, 127.
[22] Urban, S. (1995). *Z.Naturforsch*, *50*, 826.
[23] Urban, S. & Wurflinger, A. (1997). *Adv. Chem. Phys.*, *98*, 147.
[24] Bradshaw, M. J. & Raynes, E. P. (1981) *Mol. Cryst. Liq. Cryst.*, (letters), bf 72, 73.
[25] Thoen, J. & Menu, G. (1983). *Mol. Cryst. Liq. Cryst.*, *97*, 163.