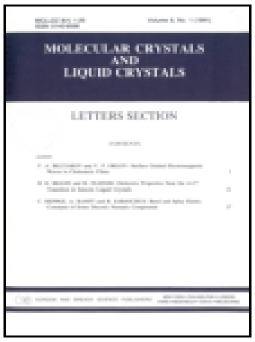

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Macroscopic properties and their temperature dependence of the mesogen 4 cyano-4/-n-nonyl biphenyl as a function of temperature

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ABSTRACT

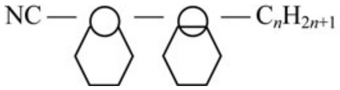
The thermal dependence of optical and dielectric properties of one member namely 4 cyano-4/-n-nonyl biphenyl (code name 9CB) of the mesogenic homologous series of 4 cyano-4/-n-alkyl biphenyl (nCBs) is reported. The variation of orientational order parameter with temperature is determined and comparison made with theoretical Maier–Saupe values as well as the order parameter values of the other member of the series. The effect of temperature on the effective molecular dipole moment μ and the angle of inclination β of the dipole axis with the preferred direction are investigated.

KEYWORDS

Birefringence; dielectric permittivity; dipole moment; mesogen; order parameter

Introduction

As a part of our investigation on the mesogenic properties of the series 4 cyano-4/-n-alkyl biphenyl (nCBs), optical and dielectric studies have been conducted on one member of the series, namely 4 cyano-4/-n-nonyl biphenyl (code name 9CB) having the structural formula



with $n= 9$

and molecular formula C_{23} H_{27} N. The compound 9CB is known to undergo the following phase transitions (Merck Ltd.).

$$\text{Solid} \xrightarrow{42^\circ C} \text{SmecticA} \xrightarrow{48^\circ C} \text{Nematic} \xrightarrow{50^\circ C} \text{Isotropic}$$

Studies made so far cover the following aspects of the cyanobiphenyls: (i) permittivities and refractive indices of some members [1] with the results analyzed in terms of the Maier and Meier theory [2]; (ii) estimation of the free molecular dipole moment and polarizability from Kerr effect measurements on dilute solution of 5CB [1]; (iii) pretransitional effects in nematics with cyano end groups including some *n*CBs [3] and the discontinuity in the mean permittivities at T_{NI} has been attributed to pretransitional change in the antiparallel ordering; (iv) dielectric properties of some members focusing on the phase transitional region [4]; (v) permittivity of some members of the cyanobiphenyls in solution with different solvents

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[5,6]; (vi) calorimetric estimation of the heat capacity and enthalpy near phase transition in alkyl cyanobiphenyls to assess the order of the phase transition [7]; (vii) dynamic Kerr effect behavior and transient molecular reorientation in the nematic phase of some of the *n*CBs [8]; (viii) dielectric properties of 5CB under high pressure [9]; (ix) dielectric relaxation in 8CB at low frequency [10]; (x) the effect of mixing 8CB with other compounds [11,12]; (xi) surface properties such as wetting of 8CB [13].

It may be noted that these studies do not encompass a systematic experimental study of the variation with temperature of the polarizability anisotropy and that of the orientational order parameter from optical studies for all *n*CBs. The Kerr effect measurements [1], performed to obtain the free molecular dipole moment of 5CB, do not cover the thermal variations of the effective mesogenic molecular dipole moment, nor the angle of inclination of the molecular dipole moment with the preferred direction for 9CB or for any other member of the series. Experimental estimate of the correlation factor, which is important for the understanding of the nature of association of molecules in the liquid crystalline phase, has also not been obtained for all members of *n*CBs.

The present article reports some of these studies on 9CB. The results are compared with the theoretical Maier–Saupe [14] values as also with those calculated using Maier and Meier theory [2]. This is supplemented with a systematic study of the variation of the effective dipole moment μ in the mesophase and the angle of inclination β of the molecular dipole moment with the preferred direction, computed using the results from optical study together with the data collected by us from dielectric studies. Furthermore, in order to obtain an estimate of the correlation factor "g," the dipole moment of the molecule in solution has been determined at various concentrations and the results extrapolated to infinite dilution to get the free molecular dipole moment μ_{iso}.

Experimental methods

Texture studies

Texture studies were performed using a polarizing microscrope (Leitz) having a hot stage (Mettler FP 82 HT) to confirm the different phases and also for phase transition temperatures. The powdered sample was heated beyond the isotropic temperature and placed as a thin film on a glass slide and a cover slip was placed on it. Observations were performed under crossed polarizer with a magnification 150×. One and two temperature cycles were performed at a rate of 1°C/min. Then photographs of the sample were taken at different temperatures.

Optical studies

Optical studies were performed using Chatelien Wedge principle. The powdered sample was placed on 1°–2° glass prism and the prism angle was determined by the reflected beams from two side of it. Details of the experimental arrangement are given in ref. 15. The inner surfaces of the prism were treated by polyvinyl alcohol for alignment of the sample. Then the prism with the sample was placed in a sample holder (fabricated in house) whose temperature may be regulated up to ± 1°C with the help of a temperature controller. The sample holder with sample was then placed in a magnetic field of strength ∼ 8 kg for alignment. A He Ne laser beam ($\lambda = 633$ nm) passed through the sample by a hole on the sample holder. The refracted beams (extra ordinary and ordinary) emerge out and projected on a screen ∼ 4 m away. By measuring the distances and applying simple geometry the angular deviations and corresponding refractive indices n_e and n_o were determined.

The density of the sample was determined at various temperatures. In melted form the sample was introduced in a dilatometer, which was placed in a heat bath. The sample height was measured by traveling microscope. From birefringence studies and density measurements the polarizabilities could be determined as a function of temperature.

Dielectric studies

A pair of indium tin oxide (ITO) coated conducting glass plates separated by thin cover slips by its three sides was used to form the sample cell (capacitor). The cell was calibrated by standard liquids benzene and p-xylene with the help of a LCR meter (6471 Forbes Tinsley). The sample was introduced into the cell as isotropic liquid and the open end sealed. Then it is placed in a sample holder (designed and fabricated in house) which is connected to a temperature controller so that the temperature of the sample can be regulated (± 1°C). The sample was taken through a number of temperature cycles at the rate of 1°C/min. in the presence of a magnetic field of $\sim$ 8 kg to get an aligned monodomain sample. Readings for the parallel and perpendicular components of capacitance were taken at various temperatures during cooling at frequencies of 1, 10, and 100 kHz. The values of the parallel and perpendicular components of the dielectric constant $\varepsilon_{||}$ and $\varepsilon_{\perp}$ were obtained from the capacitance values by standard procedure. The bridge voltage across the sample was maintained low enough ($\sim$ 0.3 V) so as not to produce any electric field induced instabilities.

Molecular dipole moment measurement

Solutions of the sample at different concentrations (by % wt.) were made in a nonpolar solvent viz. p-xylene. The solution was introduced into a fresh sample cell prepared and standardized as before and the dielectric permittivities ε of the solution were determined at 1 kHz for each of the concentrations of the solution at a fixed temperature (34°C) using the LCR bridge (6471 Forbes Tinsley). The refractive indices n of the solution were obtained for each concentrations using a He Ne laser beam and the Chatelain Wedge method described in detail in ref. 15. The dipole moment μ of the molecule in a solution of concentration c (mole/cc) at a fixed temperature (°K) was calculated using the following relation [16]:

$$\mu^2 = \frac{27\,kT(\varepsilon_{12} - n_{12}^2) - (\varepsilon_1 - n_1^2)}{4\pi N(\varepsilon_1 + 2)(n_1^2 + 2)\,c}, \tag{1}$$

where the suffixes 1 and 12 refer to the solvent and solution parameters, respectively, N is the Avogadro number, and k is the Boltzman constant. The variation of the dipole moment μ with solution concentration (in % wt.) was fitted to a polynomial and the curve extrapolated to infinite dilution to obtain the dipole moment μ_{iso} of the isolated molecule. The values of esu.cm. obtained from the above might be converted to cm using the factor 3.3356×10^{-12}.

Results and discussion

Texture studies

The transition temperatures as observed from texture studies are as follows:

$$\text{Solid} \xrightarrow{42^\circ C} \text{SmecticA} \underset{47.3^\circ C}{\overset{47.6^\circ C}{\rightleftarrows}} \text{Nematic} \underset{49.2^\circ C}{\overset{49.6^\circ C}{\rightleftarrows}} \text{Isotropic}$$

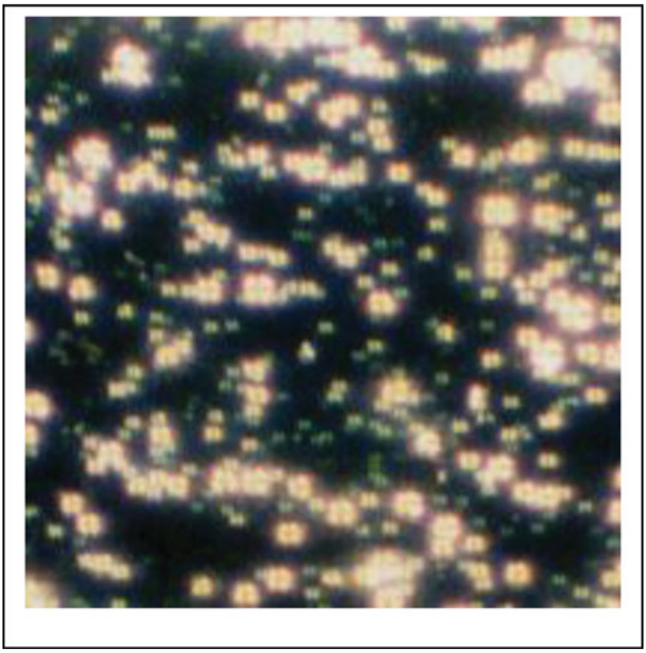

Figure 1. Smectic A phase of 9CB at 44°C.

The phase transition temperatures from smectic A to nematic and nematic to isotropic are in excellent agreement with the quoted values supplied by Merck Ltd. Representative texture photographs of the nematic and smectic A phases of each of the compounds are depicted in Figs. 1 and 2 show a focal conic texture of the smectic A phase.

Optical studies

Figures 3 and 4 show the variation of refractive indices n_e, n_o and polarizability α_e, α_o with temperature for 9CB. Discontinuities in the refractive indices and polarizabilities are observed at the phase transitions from smectic A to nematic and nematic to isotropic phases for the

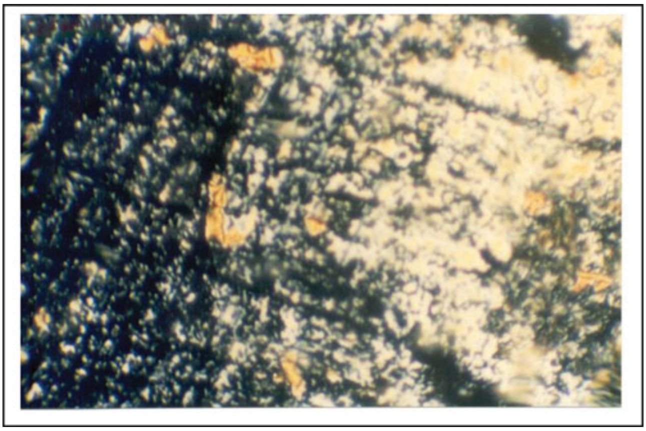

Figure 2. Nematic phase of 9CB at 48°C.

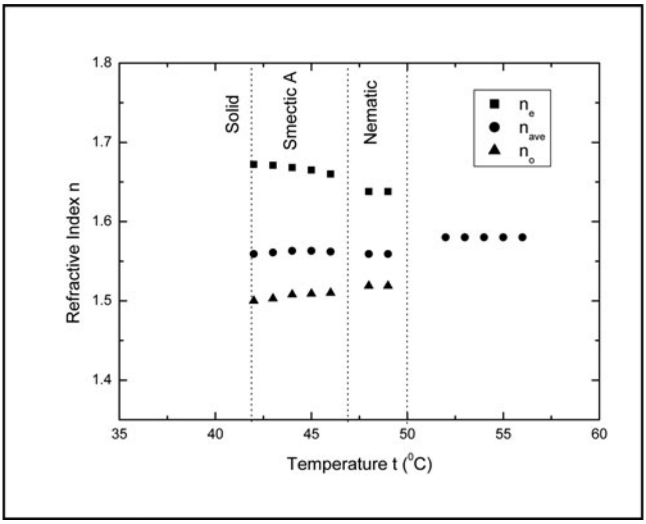

Figure 3. Variation of refractive indices with temperature of 9CB.

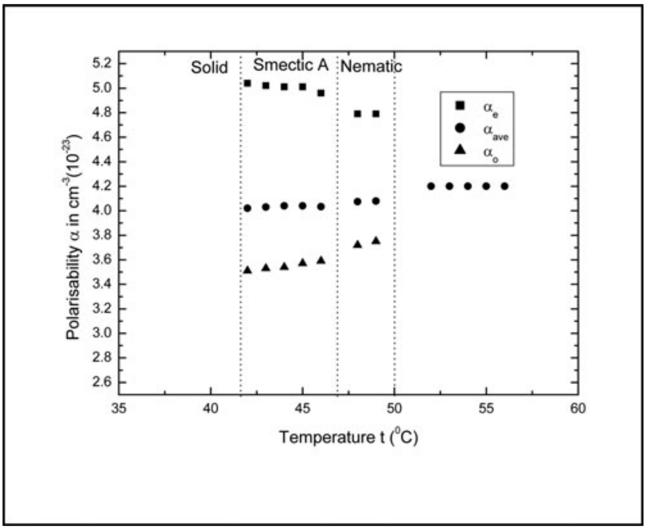

Figure 4. Variation of polarizability with temperature of 9CB.

compound. It has been suggested [17] that the discrepancy between n_{ave} and n_{iso} at nematic-isotropic transition is exhibited by molecules of high molecular dipole moments (4–5 D). The value of the free molecular dipole moment of 4.8 D (9CB) supports this observation. n_{iso} is greater than n_{ave} at nematic-isotropic transition for the compound.

For 9CB, optical anisotropy Δn is found to be 0.165 (44°C) and 0.113 (49°C), the quoted values being 0.160 and 0.119 at the above bracketed temperatures. The values of $n_{||}$ and $n_{\perp}$ obtained by Dunmur et al. [1] for 9CB are 1.669 and 1.510 at 45°C and compare well with the values of 1.670 and 1.509 at the same temperature.

The polarizability curves show a discontinuity at smectic A-nematic transition as already stated, however, the nature of discontinuity are not same for the compound as evident from earlier figures. At smectic A-nematic transition, for 9CB Δn decreases closing in the gap between α_e and α_o. High-precision density measurements (with a precision of $\pm\ 5 \times 10^{-5}$

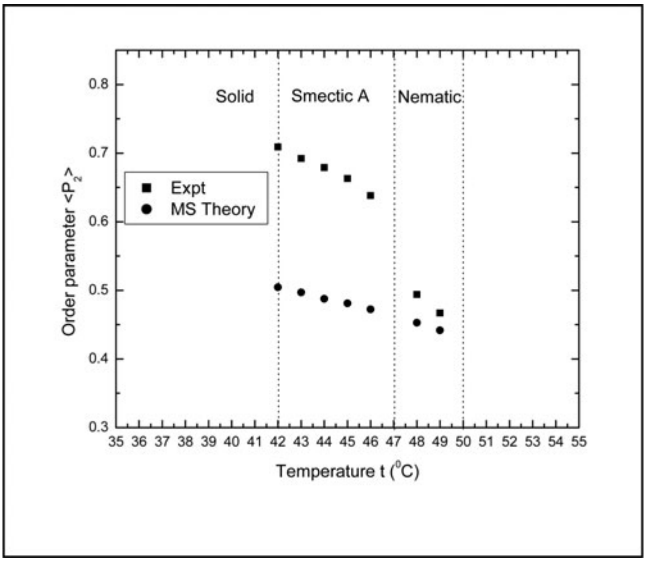

Figure 5. Variation of order parameter with temperature of 9CB.

g cm^{-3}) was carried out at smectic A to nematic transition of a mixture of 9CB and 10CB [17] showing that the transition crosses from second to first order as the temperature range of the nematic phase decreases with change in concentration of the two components of the mixtures.

The orientational order parameter $<P_2>_{expt}$ in both the smectic A and nematic phases were calculated from our experimental polarizability values using the relation $<P_2> = (\alpha_e\text{-}\alpha_o)/(\alpha_{||}\text{-}\alpha_\perp)$ [18], where $\alpha_{||}$ and $\alpha_\perp$ are the polarizabilities parallel and perpendicular to the long axis corresponding to the solid phase and have been obtained using Haller's [19] extrapolation procedure. Variation of $<P_2>_{expt}$ with temperature determined as above together with the theoretical Maier–Saupe values $<P_2>_{MS}$ has been depicted in Fig. 5 for 9CB. The experimental values though slightly greater than the theoretically predicted Maier–Saupe values are in close agreement in the nematic phase. The difference between $<P_2>_{expt}$ and $<P_2>_{MS}$ in the smectic A region is understandable as Maier–Saupe values are pertainable to the nematic region only.

Based on dielectric studies the orientational order parameter has been determined using an empirical expression for a correction factor [4] for the *n*CBs. The values of order parameter calculated on the basis of this approach for 9CB is in good agreement with our experimental values obtained from birefringence. The values of order parameter derived [1] using Maier and Meier theory are on the other hand much less than the Maier–Saupe theoretical values. As already discussed [1], this illustrates the inadequacy of the Maier and Meier theory which apparently over-emphasizes the role of molecular anisotropy at the expense of local order. $<P_2>$ and $<P_4>$ have been determined for 9CB from Raman scattering experiments [20]. The values of $<P_2>_{expt}$ for 9CB agree well with these values.

Dielectric studies and dipole moment

The variations of dielectric constant with temperature at three different frequencies of 1, 10, and 100 kHz are depicted in Figs. 6–8.

In case of 9CB, ε_{ave} has values of 7.67, 7.22, and 6.46 at 1, 10, and 100 kHz, respectively, at a temperature of 44°C, i.e., the dielectric permittivity decreases by about 6% and 16% (44°C) for increase in operating frequency from 1 kHz to 10 kHz and 1 kHz to 100 kHz, respectively.

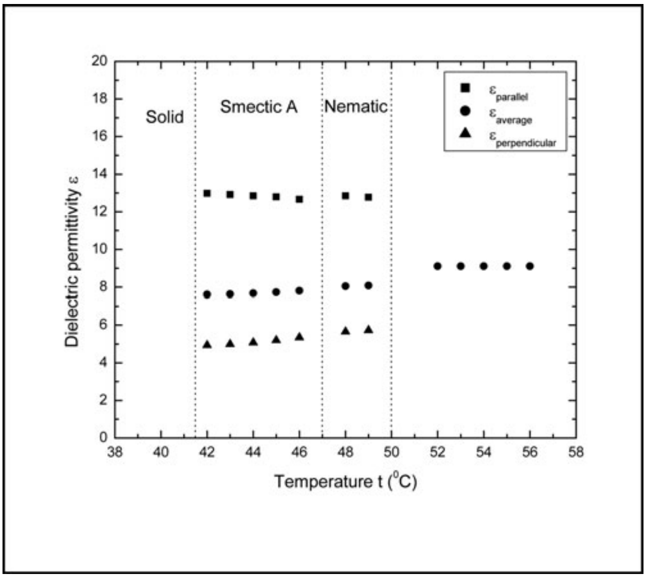

Figure 6. Variation of dielectric permittivity with temperature of 9CB at 1 kHz.

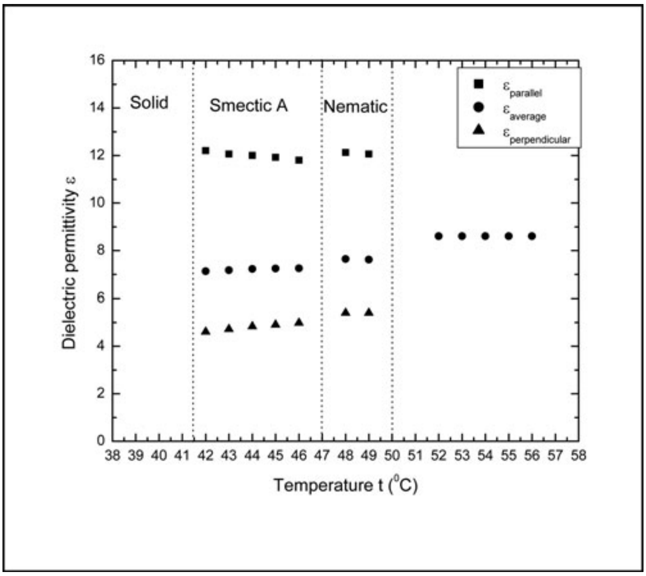

Figure 7. Variation of dielectric permittivity with temperature of 9CB at 10 kHz.

If we make a comparison with the other member 8CB of the series, ε_{ave} values are higher for 8CB than 9CB [21]. Dielectric permittivity values reported by Dunmur et al.[1] at a frequency of 1592 Hz is, in general, consistent with these values.

It has been observed that dielectric data are affected by ionic conductance below 1 kHz [22] and in some cases even up to 100 kHz [10,23]. In these, observations at 1, 10, and 100 kHz have been standardized separately at each of these operating frequencies using both p-xylene and benzene and it is expected that the effect of any such parasitic phenomenon would be cancelled out in the process of standardization. Also the presence of significant amount of impurities is ruled out since this would be specially reflected in the phase transition temperatures observed

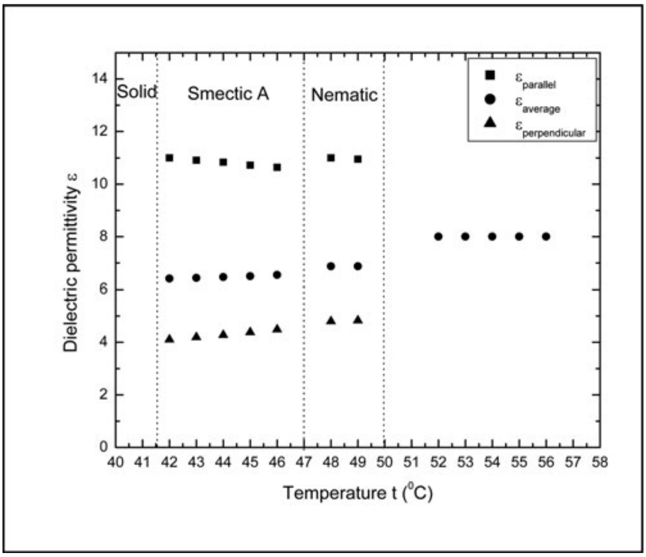

Figure 8. Variation of dielectric permittivity with temperature of 9CB at 100 kHz.

by us during texture studies, which is not the case. It is thus natural to conclude that the decrease in ε is mainly dictated by dielectric loss. It has been observed for 8CB [10] that the reason for the loss at low frequencies is ionic conductance rather than any other phenomenon such as molecular rotation. Our values are, in general, accordance with those obtained in ref. 1, though the parallel components in the nematic range are consistently slightly lower, whereas the perpendicular components are slightly higher than those reported therein. However, ε_{ave} agrees extremely well with the average ε values of ref. 1. $\Delta\varepsilon$ at 37°C and 1 kHz is ~ 7 which is slightly less than the quoted value of 7.7 at the same temperature (frequency not specified). For 9CB, $\Delta\varepsilon$ at 44°C at 1 kHz is ~ 7.77 which is slightly greater than the quoted value of 7.4 at the same temperature (frequency not specified). Discontinuity is observed at smectic to nematic transition for all the three frequencies of dielectric curves for 9CB. The discontinuity of ε_{ave} at T_{NI} has been well studied [3] for different cyano nematics and has been attributed to pretransitional changes in antiparallel ordering. The decrease in ε_{ave} observed in the nematic phase as compared to the ε_{iso} value as T_{NI} is approached from the isotropic phase may be attributed to an increase in the antiparallel correlation which reduces the molecular dipole contribution.

The variations of μ and β with temperature are depicted in Figs. 9 and 10, respectively. With increase in frequency the effective molecular dipole moment decreases; its values being 3.17, 3.04, and 2.81 D for 9CB at 44°C for frequencies of 1, 10, and 100 kHz, an effect which is also reflected in the dielectric permittivity. A discontinuity is observed in the μ values for all the frequencies at the smectic A-nematic transition. This feature is also observed in the discontinuity of the dielectric permittivity at the smectic A-nematic transition and is attributed to long range antiferroelectric dipole ordering [4]. For 9CB, the μ values increase at smectic A to nematic transition at each of the frequencies.

Within smectic A region, β remains fairly constant around 25° but falls sharply to about 10° in the nematic region as the isotropic temperature is approached. The angle between the mechanical axis and the optic axis has been determined for various cyanobiphenyls by a population distribution model and it is found that the angle gradually increases with the length of the alkyl chain [21].

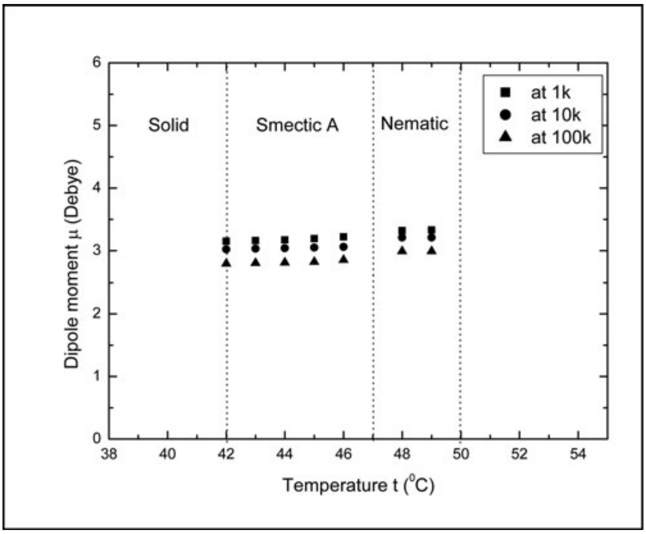

Figure 9. Variation of dipole moment with temperature of 9CB.

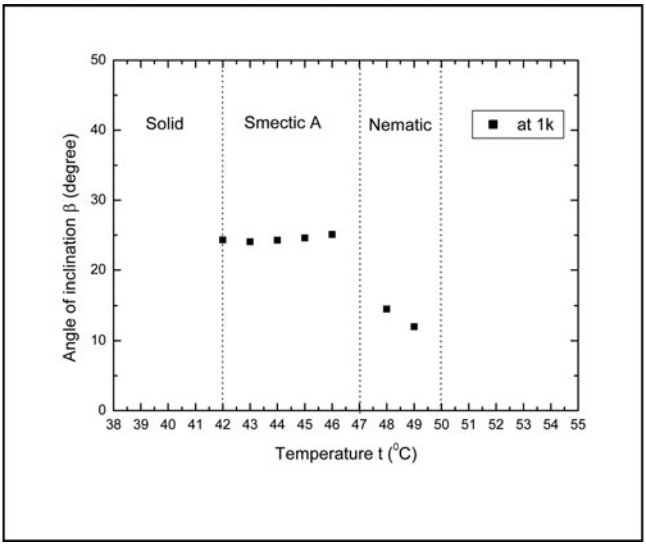

Figure 10. Variation of angle of inclination with temperature of 9CB at 1 kHz.

The dipole moment in solution at 1 kHz at a fixed temperature (44°C for 9CB) and at various concentrations (% wt.) have been depicted in Fig. 11. Extrapolating the curve to zero concentration, i.e., infinite dilution the dipole moment of the molecule in isolation, i.e., free dipole moment is found to be 4.8 D.

The correlation factor g estimated using the expression $g = \mu^2/{\mu_{iso}}^2$ is found. In case of 9CB, the effective and free molecular dipole moments (44°C, 1 kHz) are 3.17 and 4.8 D, respectively, yielding $g = 0.44$. Since $g = 1$ for no association between molecules and deviation of g from unity is indicative of molecular association, the molecular-molecular correlation in case of both 8CB and 9CB appear to be strong. Positive deviation of g from unity, i.e., $g > 1$ results from parallel orientation of dipoles of neighboring molecules while g 3c; 1, results from antiparallel orientation, indicating strong antiparallel correlation between molecules in case of 9CB.

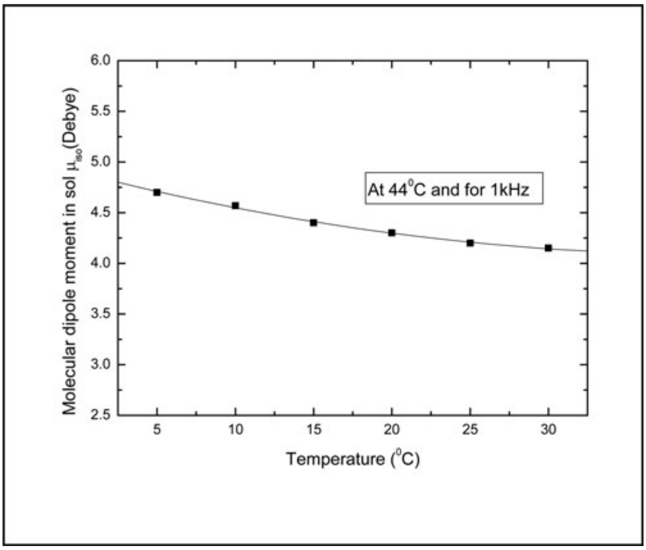

Figure 11. Variation of μ_{sol} with concentration of 9CB.

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