

Effect of a rigid nonpolar solute on the splay, bend elastic constants, and on rotational viscosity coefficient of 4,4'-n-octyl-cyanobiphenyl

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The effect of a rigid nonpolar nonmesogenic solute ‘‘biphenyl,’’ that is, $C_6H_5-C_6H_5$ on the splay and bend elastic constants and on the rotational viscosity coefficient of 4,4'-n-octyl-cyanobiphenyl is reported. The experiments involve the measurement of the voltage dependence of the capacitance of a cell filled with the mixture. Anomalous behavior of both K_{11} and $\Delta\epsilon$ near the $N-S_A$ transition have been observed.

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I. INTRODUCTION

It is well known that, with few exceptions, the presence of nonmesomorphic solutes in nematics depress the normal nematic-isotropic transition temperature (T_{NI}) [1]. Moreover, experiments [2,3] over the last few decades have confirmed that the presence of such impurities leads to the formation of a two-phase region. This is consistent with the laws of thermodynamics and the first-order nature of the $N-I$ transition. Two types of models have proved to be generally useful for investigating $N-I$ transitions in dilute solutions. The first is a lattice model [4,5] that takes into account the role of intermolecular repulsion or the steric effect. The other [6] is the mean-field theory of the Maier-Saupe type that takes into account the anisotropic intermolecular attraction or the dispersion forces. More recently Mukherjee [7] has explained the behavior of the two-phase region using the phenomenological Landau de Gennes theory.

The role of nonmesogenic impurities on a mesogen, which exhibits a smectic phase as well, has not received a great deal of attention from either experimentalists or theorists. Here too, in favorable circumstances, remains a possibility of the existence of a two-phase region near the smectic transition [8].

In this paper we report the results of measurements carried out on a mixture of biphenyl and 4,4'-n-octyl-cyanobiphenyl (8CB). The latter which has a strong polar group and a long alkyl chain, has received considerable attention from experimentalists over the last few decades [9–12] and is known to exhibit a first order S_A-N transition. The biphenyl-8CB system to the best of our knowledge, has not been studied before and is a natural and interesting choice in its own merit since the solute, which is chemically $C_6H_5-C_6H_5$, is a nonmesogenic, nonpolar rigid molecule and is nothing but 8CB deprived of its cyano group and the flexible alkyl chain. We have observed that biphenyl is easily miscible with 8CB and lowers both T_{AN} and T_{NI} by an amount that depends on the impurity concentration. The range of the nematic phase, i.e., $(T_{NI}-T_{AN})$ however, is not significantly altered. The effect of this rodlike nonpolar impurity on the dielectric anisotropy, on the Frank elastic constants (splay and bend), and on the effective rotational viscosity coefficient of pure 8CB has been reported here. To the best of our knowledge, no measurement has yet been re-

ported on the effect of impurities on the elastic constants and the viscosity coefficient of a nematic. The experiments we have carried out involve an electric-field-induced Fréedericksz transition and consist of two parts. The dielectric anisotropy and the Frank elastic constants are extracted from a set of measurements of the voltage dependence of the capacitance of a sample cell filled with the 8CB and biphenyl mixture. For the determination of the rotational viscosity coefficient a method based on dynamic Fréedericksz transition is used. Interesting features have emerged from these measurements and the splay elastic constant is seen to exhibit anomalous behavior in the vicinity of the S_A-N transitions for the impurity concentration exceeding a certain value.

II. PRINCIPLE OF THE METHOD

The splay elastic constant K_{11} is related to the Fréedericksz threshold voltage V_{th} by the relation

$$K_{11} = \epsilon_0 \Delta\epsilon / \pi^2 V_{th}^2, \quad (1)$$

where ϵ_0 is the permittivity of free space and $\Delta\epsilon = \epsilon_{||} - \epsilon_{\perp}$, the dielectric anisotropy of the sample. The method of determination of $\Delta\epsilon$ is described below.

The exact relationship between the cell capacitance C and the voltage V applied across the cell was obtained by Gruler *et al.* [13],

$$\frac{V}{V_{th}} = \frac{2}{\pi} (1 + \gamma \sin^2 \phi_m)^{1/2} \times \int_0^{\phi_m} \left[\frac{(1 + \kappa \sin^2 \phi)}{(1 + \gamma \sin^2 \phi)(\sin^2 \phi_m - \sin^2 \phi)} \right]^{1/2} d\phi \quad (2)$$

and

$$\frac{C}{C_{\perp}} = \frac{\int_0^{\phi_m} \left[\frac{(1 + \kappa \sin^2 \phi)(1 + \gamma \sin^2 \phi)}{(\sin^2 \phi_m - \sin^2 \phi)} \right]^{1/2} d\phi}{\int_0^{\phi_m} \left[\frac{(1 + \kappa \sin^2 \phi)}{(1 + \gamma \sin^2 \phi)(\sin^2 \phi_m - \sin^2 \phi)} \right]^{1/2} d\phi}, \quad (3)$$

where $\kappa = K_{33}/K_{11} - 1$ (K_{33} being the bend elastic constant), $\gamma = \epsilon_{||}/\epsilon_{\perp} - 1$, ϕ is the tilt angle made by the director with a direction parallel to the cell walls, ϕ_m is the tilt angle at the

center of the cell, and C_{\perp} is the capacitance of the cell when the liquid crystal molecules are homogeneously aligned, that is, before the onset of Fréedericksz transition when the voltage applied is lower than the threshold voltage. These equations can be combined to yield

$$\frac{C - C_{\perp}}{C_{\perp}} = \gamma - \frac{2\gamma}{\pi} (1 + \gamma \sin^2 \phi_m)^{1/2} \frac{V_{th}}{V} \times \int_0^{\sin \phi_m} \left[\frac{(1 + \kappa x^2)(1 - x^2)}{(1 + \gamma x^2)(\sin^2 \phi_m - x^2)} \right]^{1/2} dx \quad (4)$$

When the applied voltage is much higher than the threshold voltage, the director at the center of the cell becomes perpendicular to the cell walls and $\phi_m = \pi/2$. Then the above equation reduces to

$$\frac{C - C_{\perp}}{C_{\perp}} = \gamma - \frac{2\gamma}{\pi} (1 + \gamma)^{1/2} \frac{V_{th}}{V} \int_0^1 \left[\frac{(1 + \kappa x^2)}{(1 + \gamma x^2)} \right]^{1/2} dx \quad (5)$$

or dividing by γ ,

$$\frac{C - C_{\perp}}{C_{\parallel} - C_{\perp}} = C_R = 1 - \frac{2}{\pi} (1 + \gamma)^{1/2} \frac{V_{th}}{V} \int_0^1 \left[\frac{(1 + \kappa x^2)}{(1 + \gamma x^2)} \right]^{1/2} dx, \quad (6)$$

where C_R may be called the reduced capacitance. C_{\parallel} is the capacitance of the cell when the nematic is homeotropically oriented, i.e., the value of C in the limit $1/V \rightarrow 0$. ϵ_{\parallel} and ϵ_{\perp} may be obtained by dividing C_{\parallel} and C_{\perp} by the empty cell capacitance C_0 , respectively. In the above equation use has been made of the relation $\gamma = (C_{\parallel} - C_{\perp})/C_{\perp}$.

Thus Eq. (5) predicts that a plot of $(C - C_{\perp})/C_{\perp}$ against $1/V$ for $V \gg V_{th}$ should be linear and the extrapolated value of the ordinate for $1/V \rightarrow 0$ should directly provide the value of $\gamma = \Delta\epsilon/\epsilon_{\perp}$. This procedure for obtaining γ was first suggested by Meyerhofer [14].

The variation of capacitance with applied voltage was fitted against Eqs. (2) and (3) to obtain V_{th} and κ . We then used Eq. (1) to calculate K_{11} and hence K_{33} . This method for obtaining V_{th} and κ was suggested by Morris *et al.* [11].

The viscous behavior of a nematic can be obtained by studying the response to a sudden change in an applied magnetic or electric field that is normally stronger than the Fréedericksz-threshold value. In case of deformations involving a pure twist there is no hydrodynamic flow. The molecules merely rotate without any translational motion and the analysis is rather simple [15]. The situation is far more complicated in case of a splay geometry, which we have studied, since the director reorientation is now accompanied by a hydrodynamic flow. The gradient of the angular velocity of the director produces a backflow motion, first demonstrated by Pieranski *et al.* [16], giving rise to a frictional torque. The sudden removal of an external field in this case would result in a director relaxation time

$$\tau = \gamma_1^* d^2 / (\pi^2 K_{11}), \quad (7)$$

where γ_1^* is the effective rotational viscosity coefficient, d is the cell thickness, and K_{11} is the splay elastic constant. In practice γ_1^* is about 10% less than the rotational viscosity coefficient γ_1 .

We have determined the relaxation time τ by measuring the decay of the capacitance in a nematic cell. The details are given in the next section.

III. DETAILS OF THE EXPERIMENTAL METHOD

We have used a Hewlett-Packard LCR meter HP 4274A to measure the capacitance of the sample cell. The instrument employs the so-called ‘‘autobalancing bridge method’’ to measure both the real and complex parts of impedance simultaneously. The voltage was varied from 0.1 V to 5 V at a frequency of 1 KHz. The sample cells, which were of very high precision, were obtained from Displaytech, USA. The cells, consisting of two indium tin oxide (ITO)-coated glass plates with a spacing of 4 μm and an active area of 0.26 cm^2 , underwent brushed polyimide treatment to ensure planar orientation. They also had a guard ring incorporated in them to minimize fringe electric fields. The temperature of the cells was controlled to remain within ± 0.1 K by placing the cells within a Mettler hot stage FP 82. The texture of the samples was viewed through a Leitz polarizing microscope and photographs were taken with the help of Photoautomat. Both 8CB and biphenyl were obtained from Merck and were used without further purification.

The samples that we have used were mixtures of various concentrations of biphenyl, ranging from 0.4% to 6.4%, in pure 8CB. The smectic-to-nematic transition temperature, T_{AN} and the nematic-to-isotropic transition temperature T_{NI} were determined from texture studies of the samples. Various photographs were taken at different stages of the transition. In the capacitance measurement experiments the probe voltage of the LCR meter HP 4274A provided the aligning ac electric field. The voltage was varied from 0.1 V to 5 V at a frequency of 1 KHz in the C_p - G mode of the instrument. In the neighborhood of the Fréedericksz transition, readings were taken at intervals of 10 mV. The samples were filled in the cells and the C - V variation was recorded at a large number of temperatures ranging from the smectic-to-nematic transition temperature T_{AN} to a few degrees beyond the nematic-to-isotropic transition temperature T_{NI} . It must be noted that all measurements were carried out as the temperatures of the sample were increased, gradually starting from $T < T_{AN}$ and none of the measurements were taken during cooling. Figure 1 shows a few capacitance-voltage variations of the mixture with biphenyl concentration 4.59% at temperatures near the two transitions S_A - N and N - I and at an intermediate temperature. There is always need to have a refinement in the value of V_{th} as the C - V curves obtained in a polyamide cell usually do not exhibit a very sharp threshold of the Fréedericksz transition so as to yield a precise value of V_{th} from the data directly. From the C - V data ϵ_{\perp} and ϵ_{\parallel} were calculated and subsequently V_{th} and κ were determined as described below. ϵ_{\perp} was determined directly from the value of the capacitance at voltages lower than the threshold voltage (before the onset of the Fréedericksz tran-

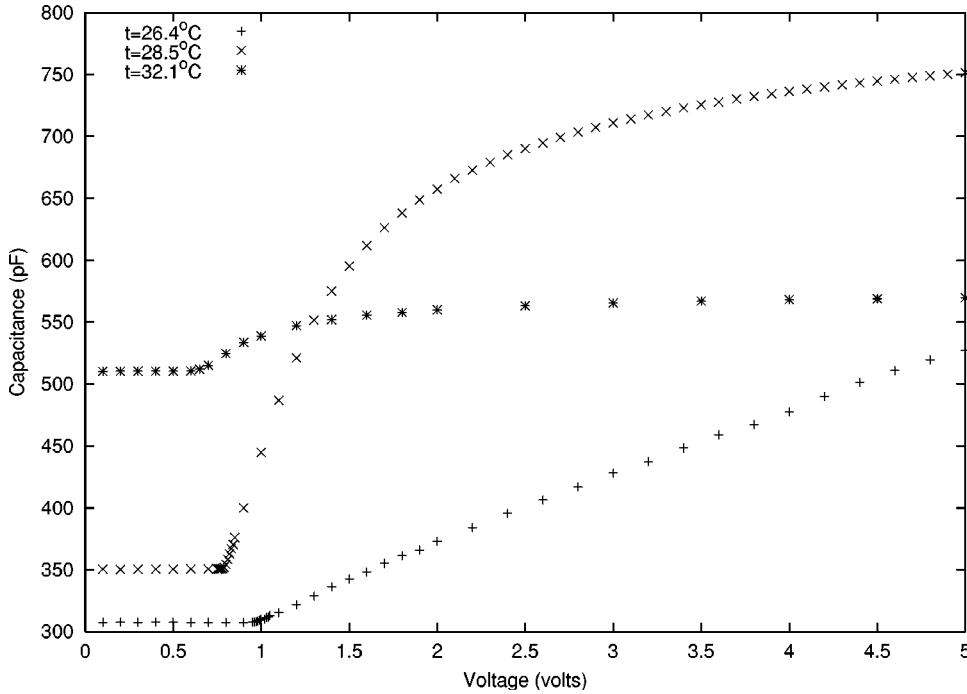


FIG. 1. Variation of capacitance C with voltage V for different temperatures t for a 4.59% mixture of biphenyl in 8CB.

sition), by dividing the capacitance C_{\perp} by the empty cell capacitance C_0 . ϵ_{\parallel} was obtained by plotting C against $1/V$ for the higher voltage range (4.0–5.0 V). The extrapolated value of capacitance in the limit $1/V \rightarrow 0$ gives C_{\parallel} , which when divided by C_0 gives ϵ_{\parallel} .

A direct measurement of C_{\parallel} was also carried out to check the reliability of the value of γ obtained by the above method. A homeotropic alignment was obtained in the ITO-coated glass cells using CTAB (cetyl trimethyl ammonium bromide) and the capacitance of the cell was measured while a 10 KG magnetic field was applied across the cell. The values of γ thus obtained never differed from the γ 's obtained from the $(1/V)$ -extrapolation method by more than 0.1%.

A two-parameter nonlinear least square fit for finding V_{th} and κ worked in the following manner. Starting values of V_{th} and γ were taken directly from the experiment. Equation (2) was then used to obtain the ϕ_m 's for all values of V for which measurements of capacitance were carried out. The ϕ_m 's thus obtained were used in Eq. (3) to obtain C . The error that was minimized in the least square program is $\sum_{i=1}^n (C_i^{expt} - C_i)^2$ where C_i^{expt} is the measured value of the capacitance at $V=V_i$ and C_i is the value of capacitance obtained by solving Eq. (3), n being the number of data points for a particular temperature. The final values of V_{th} never differed a great deal from the input values.

For the rotational viscosity coefficient measurements, we have used a Hewlett-Packard impedance gain-phase analyzer HP 4194A in the programmable mode to record the decay of capacitance with time. An integration time of 500 μ s was chosen that resulted in an interval of 5 ms between successive readings at the operating frequency that was fixed at 10 KHz. With our instrument, a delay time in multiples of 1 ms, could be introduced between the readings but in this case we did not introduce any delay since the decay of the capaci-

tance was found to be pretty fast. The ac probe voltage across the sample cell was held fixed at 0.3 V. A low-frequency ac voltage about 2 V peak to peak was applied across the cell for about 30 s. It was switched off and the transient (decaying) capacitance of the cell was captured as a function of time by the HP 4194A. A plot of this decay of capacitance with time, which was always found to be exponential, was then dumped into a HP 7475A plotter that was connected to the impedance analyzer over a HPIB bus. From the plots thus obtained for different concentrations of biphenyl mixtures at different temperatures, the time constant τ was calculated and using the values of K_{11} obtained from the static capacitance measurements, the effective rotational viscosity coefficient γ_1^* was evaluated.

IV. RESULTS AND DISCUSSION

The transition temperatures T_{NI} (upper), T_{NI} (lower), and T_{AN} were determined from optical texture studies and the

TABLE I. Variation of phase transition temperatures T_{AN} and T_{NI} with concentration of biphenyl in 8CB.

Concentration (%)	T_{AN}	T_{NI} (lower)	T_{NI} (upper)
0.00	33.2	40.1	40.2
0.40	32.8	39.8	39.9
0.90	31.0	38.1	38.4
1.58	29.9	37.2	37.6
2.00	29.6	36.5	37.1
3.30	27.1	34.3	35.0
4.00	25.5	33.1	33.9
4.59	24.9	32.2	33.2
6.40	-	28.2	29.8

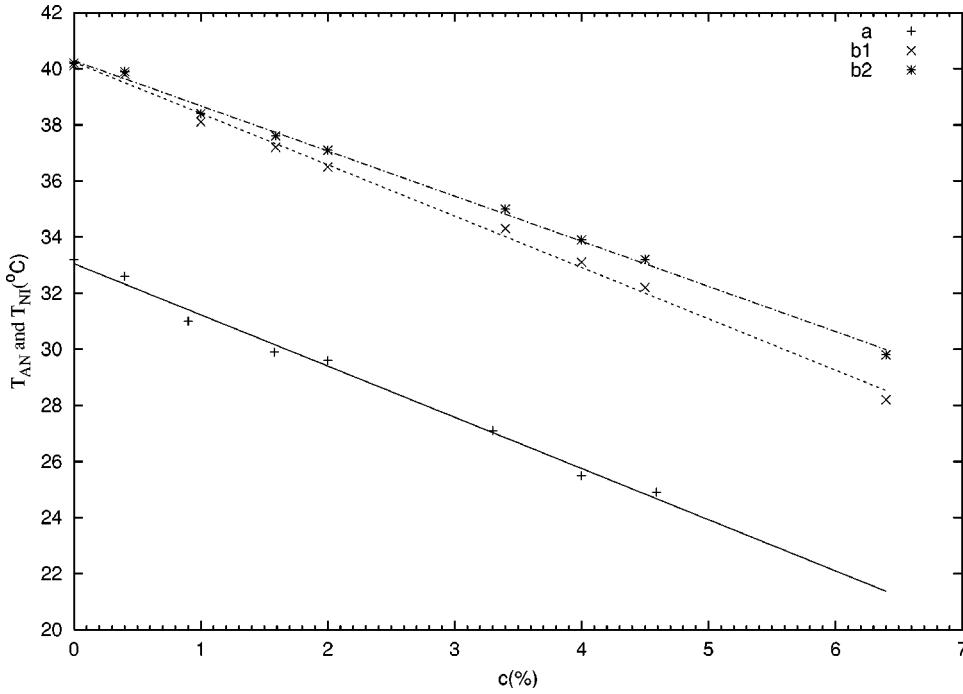


FIG. 2. Variation of T_{NI} and T_{AN} with concentration of biphenyl, c . [$a=T_{AN}$, $b1=T_{NI}$ (lower), $b2=T_{NI}$ (upper)].

results are presented in Table I and Fig. 2. T_{NI} (upper) is the temperature at which the field of view of the polarizing microscope (with crossed polarizer and analyzer) becomes completely dark. All real nematics contain impurities and Rosenblatt [17] has observed in 8CB a two-phase ($N+I$) region of temperature of width 13 mK in the absence of an electric field. Needless to say, with our temperature resolution of 0.1 K, we were unable to confirm this. The width of the two-phase region was seen to increase with the concentration of biphenyl and for the maximum concentration of 6.4% this was 1.6 K. We were unable to work with higher

impurity concentrations because of nonavailability of an experimental arrangement for producing subambient temperatures. All the transition temperatures reported in Table I were determined without the presence of any external field. However, we confirmed that with the highest electric field we applied across the sample cells, namely, 1.25×10^4 V/cm, there was no noticeable change in any of the transition temperatures.

The temperature dependence of the dielectric anisotropy for the concentration c of biphenyl ranging from 0% to 4.59% is shown in Fig. 3. In pure 8CB and for all mixtures

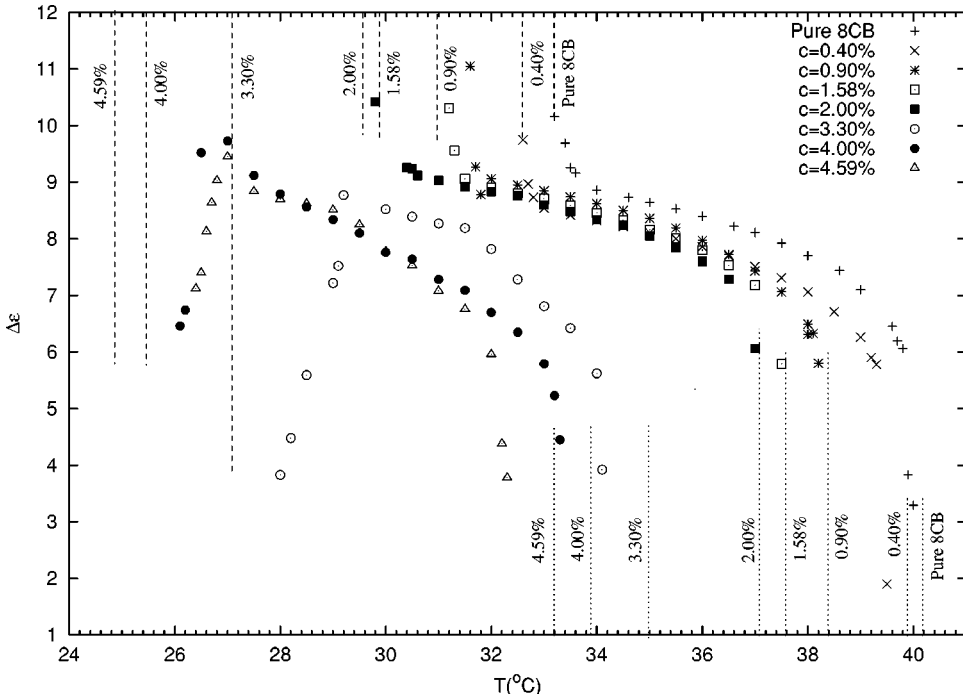


FIG. 3. Variation of $\Delta\epsilon$ with T for different concentrations of biphenyl in 8CB. The vertical lines denote the transition temperatures T_{AN} and T_{NI} for different concentrations of biphenyl in 8CB as shown in Table I.

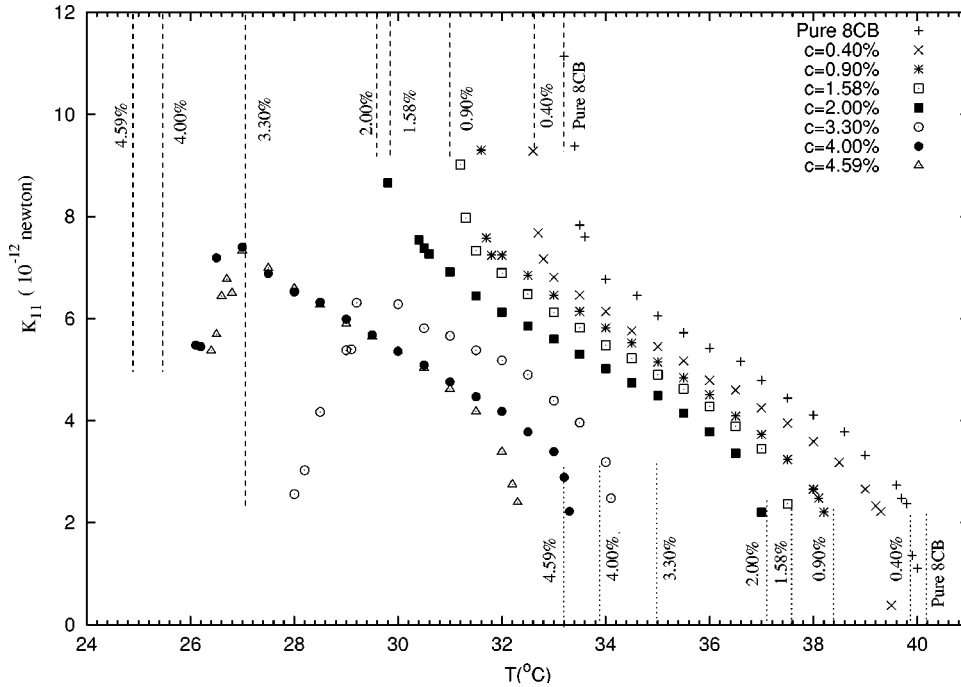


FIG. 4. Variation of K_{11} with T for different concentrations of biphenyl in 8CB. The vertical lines denote the transition temperatures T_{AN} and T_{NI} for different concentrations of biphenyl in 8CB as shown in Table I.

that we have studied, $\Delta\epsilon$ in the neighborhood of T_{NI} shows the same feature, in that it disappears at T_{NI} (upper). At this particular temperature the field of view in the microscope with crossed polars is completely dark and hence the phase is isotropic. Values of the dielectric constant ϵ_{iso} obtained well within the isotropic phase show a gradual increase with temperature for pure 8CB as well as for all mixtures we have studied.

Focusing on the behavior of $\Delta\epsilon$ as T_{AN} is approached from the higher temperature side, we find that for biphenyl concentration c up to 2.00%, $\Delta\epsilon$ in mixtures behaves in the same way as that in pure 8CB, namely, it shows a sharp increase. However, for impurity concentrations of 3.30% and higher, $\Delta\epsilon$ goes down sharply while always remaining positive (at least in the temperature range we have explored). We have noted that the decrease in $\Delta\epsilon$ results from a reduction of ϵ_{\parallel} (ϵ_{\perp} remaining fairly constant) as T_{AN} is approached. A similar decrease in ϵ_{\parallel} as T_{AN} is approached has been observed in pure p,p' -diheptylazoxybenzene where the N - S_A transition is almost second order. This has been attributed to the presence of pretransitional effects within the nematic phase [18].

The temperature and concentration dependence of the splay elastic constant K_{11} is shown in Fig. 4. The ratio κ was seen to approach the value 0 and stay around that value at and around transition but then it was seen to increase again with increase in temperature. The plot of bend elastic constant K_{33} with T is shown in Fig. 5.

The bend elastic constant K_{33} is seen to diverge as the smectic phase is approached from the nematic side. The behavior was of the type $\Delta K_{33} \propto t^{\nu}$, where ΔK_{33} is the difference [11] between K_{33} and its nematic part, $t = (T/T_{AN}^* - 1)$, and ν is the critical exponent. We found that for all the samples studied ν is 1.0 ± 0.1 , which is in agreement with the exponent obtained by Morris *et al.* [11] in pure 8CB. It

must be recalled, however, that anisotropic scaling laws predict that ΔK_{33} should vary as the correlation length ξ_{\parallel} both above and below T_{AN} and this should result in an exponent ν_{\parallel} , which from x-ray scattering experiments in many samples turn out to be $\approx 0.57-0.75$ [8]. But the temperature T_{AN}^* at which K_{33} diverges is slightly higher (~ 1 K) than T_{AN} for the mixtures and, for ease of the eye, is indicated by vertical lines in Fig. 5. We are, however, unable to say if the weak first-order S_A - N transition in pure 8CB approaches a second-order transition in the mixtures and this needs more detailed studies.

On plotting K_{11} against γ we find that the variations for all the concentrations lie nearly on a universal curve, as shown in Fig. 6. The deviations that are seen in the figure are mainly the points for the higher concentration mixtures that lie in the vicinity of the two transitions.

The abrupt decrease in ϵ_{\parallel} as the smectic phase is approached seems to occur at relatively higher concentrations of biphenyl and is totally absent in pure 8CB and in the mixtures of low impurity concentration. The optical texture studies we have performed fail to reveal the existence of any smectic phase other than smectic A in the mixtures at low temperatures. It may however be conjectured that the increase in the proportion of biphenyl in the mixture, though small, is leading to a type of ordering, cybotactic or otherwise, of the 8CB molecules where the contribution of the permanent dipole moment of the $-CN$ group to ϵ_{\parallel} is greatly reduced.

The decrease in ϵ_{\parallel} , which suggests the existence of pretransitional smectic effects within the nematic phase, occurs only for biphenyl concentrations greater than a limiting value. It may be noted that the ratio T_{AN}/T_{NI} changes from 0.9779 in pure 8CB to 0.9735 in the 4.59% biphenyl-8CB mixture. It may be pointed out that the decrease in this ratio,

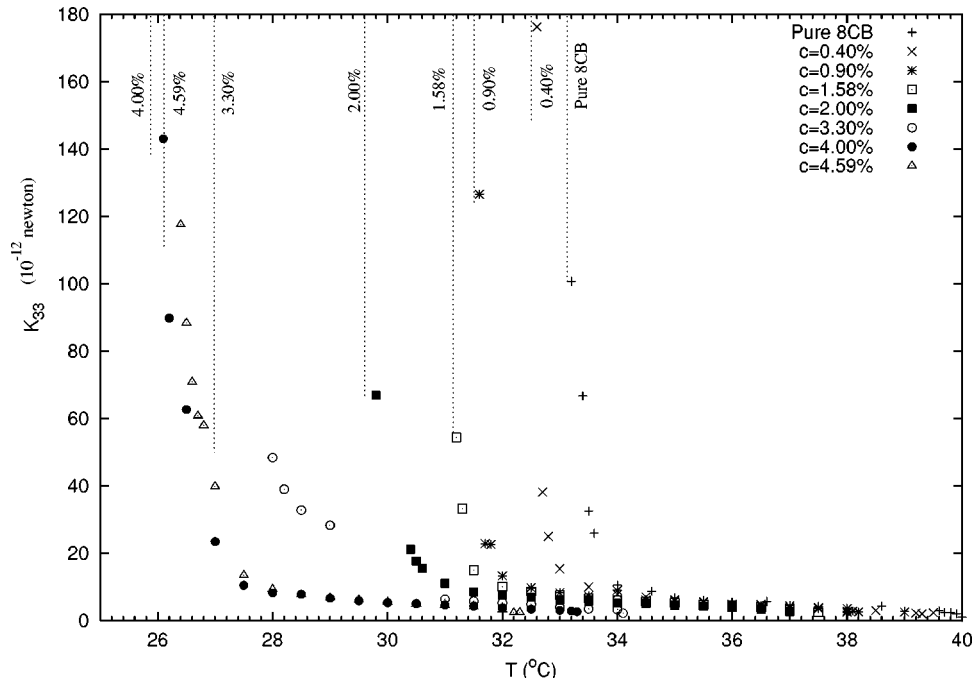


FIG. 5. Variation of K_{33} with T for different concentrations of biphenyl in 8CB.

though marginal, is believed to favor a second order S_A-N transition.

The temperature dependence of the rotational viscosity coefficient for the concentration of biphenyl ranging from 0% to 4.59% is shown in Fig. 7. T_{NI} (upper) is the temperature at which the field of view of the polarizing microscope (with crossed polarizer and analyzer) becomes completely dark. In pure 8CB and for all the mixtures γ_1^* in the neighborhood of T_{NI} , it shows the same feature in that it disappears at or before T_{NI} (upper). However, as we approach T_{AN} from the higher temperature side we find that for impurity

concentrations up to 2.00%, γ_1^* shows a sharp increase as in pure 8CB while for impurity concentration of and higher than 3.30%, γ_1^* is seen to decrease sharply. We are not aware of any systematic study involving the effect of non-mesogenic solutes on the rotational viscosity coefficient of nematics in the neighborhood of the nematic-smectic transition. The Miesowicz viscosities of a mixture of 8OCB and 4TPB (exhibiting the nematic-smectic transition) were recently investigated by Janik *et al.* [19] using a Miesowicz viscometer.

Figure 8 shows the plot of $1/T$ vs $\ln(\gamma_1^*/\Delta\epsilon)$. The dielec-

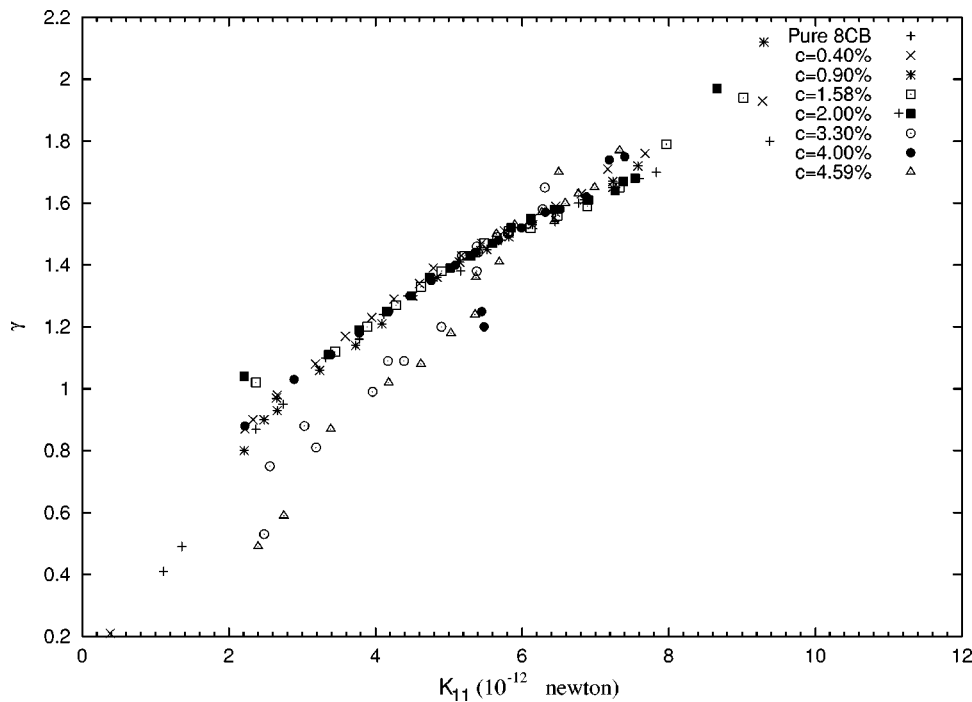


FIG. 6. Variation of K_{11} with γ for different concentrations of biphenyl in 8CB.

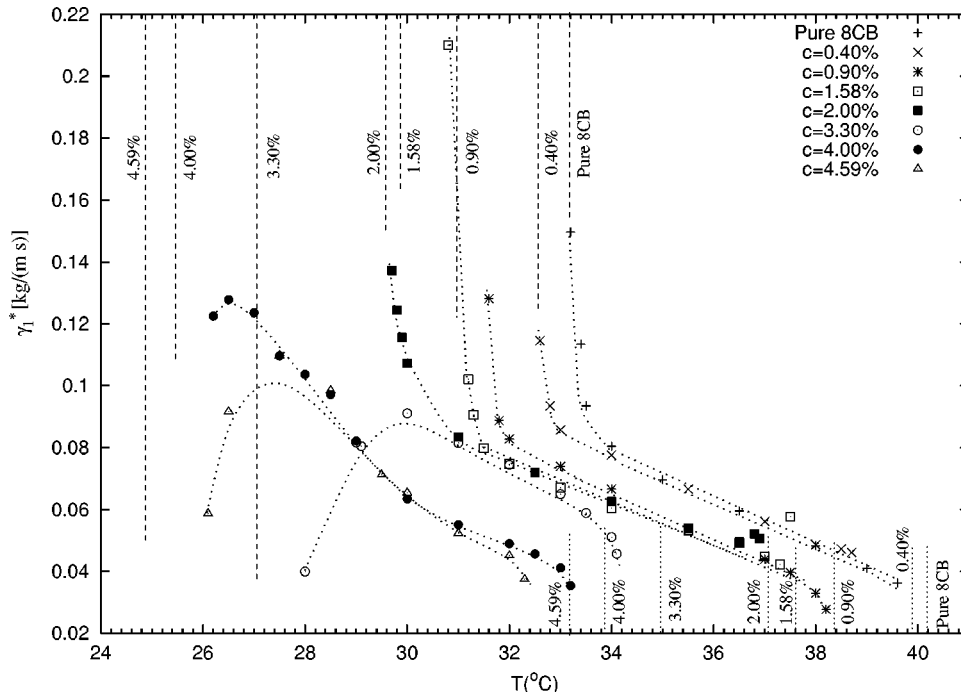


FIG. 7. Variation of γ_1^* with T for different concentrations of biphenyl in 8CB. The vertical lines denote the transition temperatures T_{AN} and T_{NI} .

tric anisotropy $\Delta\epsilon$ is roughly proportional to the long-range nematic order parameter. For pure as well as all mixtures the plot of $1/T$ vs $\ln(\gamma_1^*/\Delta\epsilon)$ gives a straight line. The same sort of dependence has been obtained by Gasparoux and Prost [20], Heppke and Schneider [21] for *n*-(*p*-methoxybenzylidene)-*p'*-butylaniline (MBBA), and Prost *et al.* [22] for a mixture of two isomers of *p*-methoxy-*p'*-butylazoxybenzene. Close to T_{NI} and T_{AN} there are deviations and those points have not been shown in the figure. From the slope of these plots the activation energy for diffusion [15] was calculated and has been shown in Table II.

V. CONCLUSIONS

To summarize, it can be stated that the presence of the rigid, nonpolar and nonmesogenic solute biphenyl in 8CB results in a change in the dielectric anisotropy $\Delta\epsilon$, the splay elastic constant K_{11} , and the effective rotational viscosity coefficient γ_1^* . In the neighborhood of the nematic-smectic A transition for the concentration of biphenyl $\geq 3.3\%$ the changes in these quantities have been found to be anomalous in that, instead of the usual rapid increase observed on cooling, $\Delta\epsilon$, K_{11} , and γ_1^* sharply decrease. This may perhaps be attributed to the presence of pretransitional effects within the

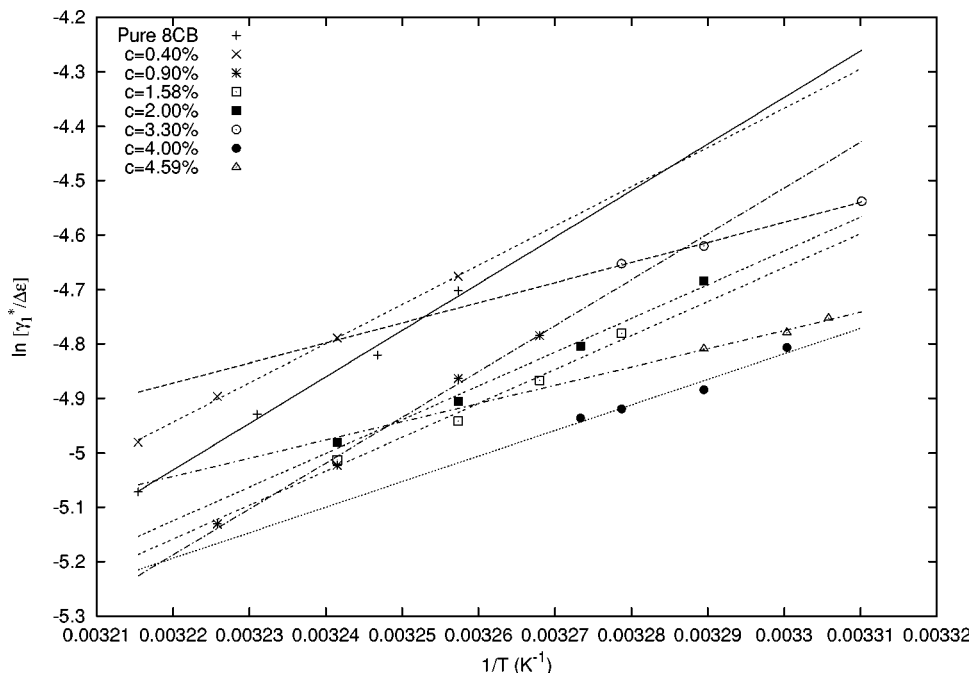


FIG. 8. Variation of $\ln(\gamma_1^*/\Delta\epsilon)$ vs $1/T$ for different concentrations of biphenyl in 8CB.

TABLE II. Variation of activation energies with concentration of biphenyl in 8CB.

Concentration (%)	Activation energy (eV)
0.00	0.74
0.40	0.62
0.90	0.73
1.58	0.54
2.00	0.53
3.30	0.32
4.00	0.40
4.59	0.29

nematic phase. From optical texture studies we could not identify any new smectic phase in the mixtures other than what is found in 8CB. The bend elastic constant K_{33} in all

the mixtures was found to diverge as the smectic phase was approached and the critical exponent was found to be the same as that observed for pure 8CB, although the temperatures at which the divergences occur were slightly higher than the respective values of T_{AN} . More elaborate studies involving differential scanning calorimetry, x-ray diffraction, and refractive index measurements (to obtain the long-range nematic order parameter) may perhaps reveal more about what is actually happening in the mixtures near the nematic-smectic-A transition particularly for those containing relatively higher biphenyl concentration.

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- [1] D. E. Martire *et al.*, J. Chem. Phys. **64**, 1456 (1976).
 [2] H. Peterson and D. E. Martire, Mol. Cryst. Liq. Cryst. **25**, 89 (1974).
 [3] B. Kroberg, D. Gilson, and D. Patterson, J. Chem. Soc., Faraday Trans. 2 **72**, 1673 (1976).
 [4] M. Cotter and D. E. Martire, Mol. Cryst. Liq. Cryst. **7**, 295 (1969).
 [5] M. Cotter, Mol. Cryst. Liq. Cryst. **35**, 33 (1976).
 [6] W. Maier and A. Saupe, Z. Naturforsch. **14A**, 882 (1959).
 [7] P. K. Mukherjee, Liq. Cryst. **22**, 239 (1997).
 [8] P. G. de Gennes and J. Prost, *The Physics of Liquid Crystals* (Clarendon Press, Oxford, 1993).
 [9] P. P. Karat and N. V. Madhusudana, Mol. Cryst. Liq. Cryst. **40**, 239 (1977).
 [10] M. Bradshaw, E. Raynes, J. Bunning, and T. E. Faber, J. Phys. (France) **46**, 1513 (1985).
 [11] S. W. Morris, P. Palffy-Muhoray, and D. Balzarini, Mol. Cryst. Liq. Cryst. **139**, 263 (1986).
 [12] P. Chattopadhyay and S. K. Roy, Mol. Cryst. Liq. Cryst. **89**, 257 (1994).
 [13] H. Gruler, T. J. Scheffer, and G. Meier, Z. Naturforsch. **27A**, 966 (1972).
 [14] D. Meyerhofer, J. Appl. Phys. **46**, 5084 (1975).
 [15] W. H. de Jeu, in *Physical Properties of Liquid Crystalline Materials*, edited by G. Gray (Gordon and Breach, New York, 1980), Vol. 1.
 [16] P. Pieranski, F. Brochard, and E. Guyon, J. Phys. A **34**, 35 (1973).
 [17] C. Rosenblatt, Phys. Rev. A **25**, 1239 (1982).
 [18] W. H. de Jeu, W. J. A. Goosens, and P. Bordewijk, J. Chem. Phys. **61**, 1985 (1974).
 [19] J. Janik, J. K. Moscicki, K. Czuprynski, and R. Dabrowski, Phys. Rev. E **58**, 3251 (1998).
 [20] H. Gasparoux and J. Prost, J. Phys. (Paris) **32**, 953 (1971).
 [21] G. Heppke and F. Schneider, Z. Naturforsch. **27A**, 976 (1972).
 [22] J. Prost, G. Sigand, and B. Regaya, J. Phys. (France) Lett. **37**, L341 (1976).