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B. S. Srikanta^a & N. V. Madhusudana^a

^a Raman Research Institute, Bangalore, 560 080, India

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Effect of Skewed Cybotactic Structure on the Dielectric Constants and Conductivities of Some Binary Mixtures Exhibiting the Nematic Phase†

B. S. SRIKANTA and N. V. MADHUSUDANA

Raman Research Institute, Bangalore 560 080, India

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2-cyano-4-heptylphenyl-4'-pentyl-4-biphenyl carboxylate (7P(2CN)5BC), a nematogen with a cyano group making a large angle ($\sim 60^\circ$) with the long axis of the molecule, has a moderately strong negative dielectric anisotropy ($\Delta\epsilon$). A mixture of 85 mole per cent of 7P(2CN)5BC with 15% of 4-*n*-heptyl-4'-cyanobiphenyl (7CB) exhibits a reversal of the dielectric anisotropy $\Delta\epsilon$ as the temperature is varied, becoming *negative* at higher temperatures. $\Delta\epsilon$ of mixtures with higher concentrations of 7CB is positive throughout the nematic range. The conductivity anisotropy $\Delta\sigma$ of these systems has been investigated for a range of frequencies from 300 Hz to 30 kHz. In 7P(2CN)5BC, $\Delta\sigma$ changes sign becoming negative at higher temperatures for all frequencies investigated. The results are discussed in terms of the temperature variation of the tilt angle of the skewed cybotactic structure of 7P(2CN)5BC.

INTRODUCTION

The dielectric and conductivity anisotropies of nematic liquid crystals have been investigated for a very large number of compounds. The effect of smectic-like short range order is known to have a direct influence on the conductivity anisotropy.¹ On the other hand, the effect of short range order on the low frequency dielectric constants is

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more difficult to delineate. This is because the values of the anisotropic dielectric constants depend on several factors, viz. (i) the principal polarizabilities of the molecules, (ii) the magnitude and mutual disposition of dipolar groups in the molecules, (iii) the orientational order, and (iv) the internal field, which is not easy to calculate for the highly anisotropic medium, and which also depends on the structure of the short range order.

We² recently found that the nematogenic compound 2-cyano-4-heptyl phenyl-4'-pentyl-4-biphenyl carboxylate (7P(2CN)5BC) has a skewed cybotactic (smectic-C type) short range order, whose tilt angle decreases appreciably with increase of temperature. Further, this had a noticeable influence on the temperature variation of the ordinary refractive index. Hence we undertook measurements on the dielectric and conductivity properties of this substance. The effect of the variation of the short range order on the thermal evolution of the conductivity anisotropy is quite obvious. But the dielectric constants do not have any unusual temperature dependence. However, the subtle effect of short range order on the dielectric constants is manifested when we mix 7P(2CN)5BC with 4'-*n*-heptyl-4-cyanobiphenyl (7CB) so as to get a very small dielectric anisotropy. After giving some experimental details in the next section, the results and discussion are covered in section 3.

EXPERIMENTAL

7P(2CN)5BC was obtained from E. Merck (Darmstadt) and used without further purification. 7CB was synthesized in our chemistry laboratory. The molecular structures of the two compounds are given

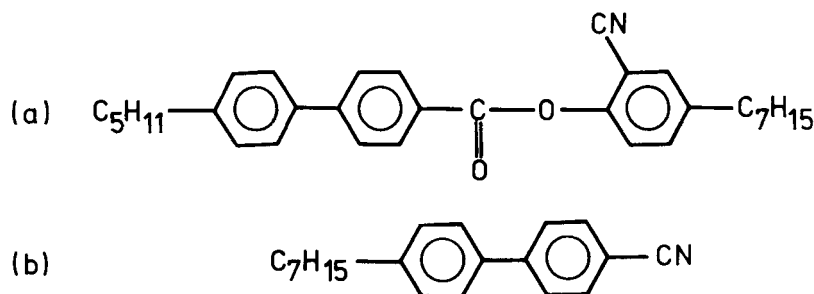


FIGURE 1 Structural formulae of (a) 2-cyano-4-heptyl phenyl-4'-pentyl-4-biphenyl carboxylate (7P(2CN)5BC) and (b) 4-heptyl-4'-cyanobiphenyl (7CB).

in Figure 1. The phase diagram of their mixtures³ is shown in Figure 2. The transition temperatures were determined using a Mettler hot stage (Model FP52) in conjunction with a polarizing microscope.

Dielectric and conductivity measurements were made on the following systems (percentages indicate mole per cent of the components):

- i) 7P(2CN)5BC
- ii) 85% 7P(2CN)5BC + 15% 7CB
- iii) 60% 7P(2CN)5BC + 40% 7CB
- iv) 39% 7P(2CN)5BC + 61% 7CB
- v) 20% 7P(2CN)5BC + 80% 7CB.

The principal dielectric constants ϵ_{\parallel} and ϵ_{\perp} were determined using samples of thickness of $\sim 125 \mu$ taken between two tin oxide coated plates. The measurements at 1592 Hz were made using a Wayne Kerr

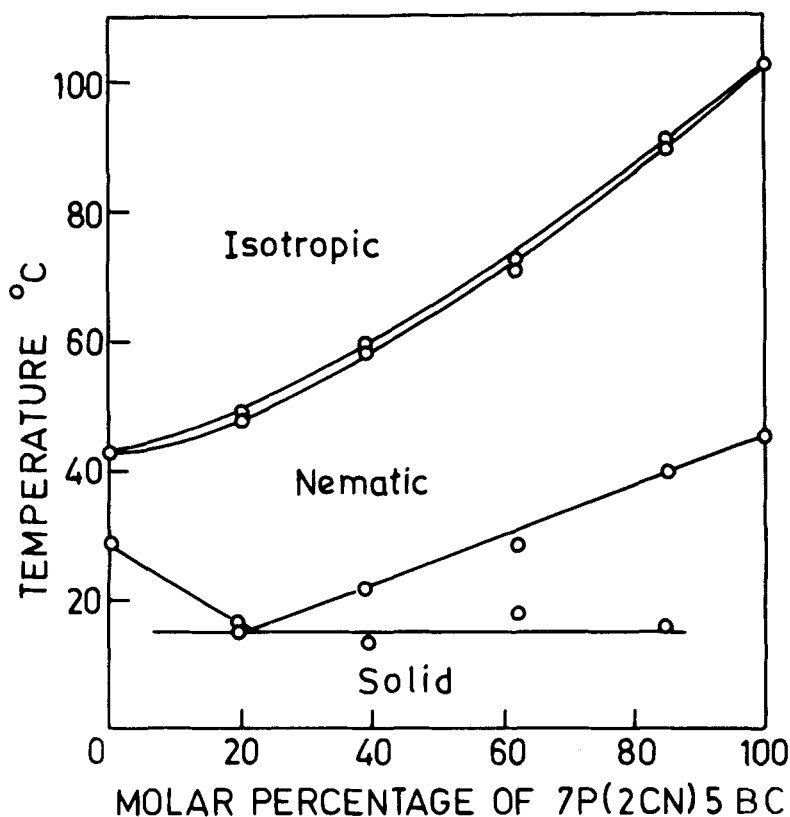


FIGURE 2 Phase diagram of mixtures of 7P(2CN)5BC and 7CB.

B642 bridge. A magnetic field of ~ 14 KG was used to align the samples. As we could rotate the cell through 90° about a vertical axis, both ϵ_{\parallel} and ϵ_{\perp} were measured on the same sample. The temperature was measured using a calibrated copper-constantan thermocouple and a Keithley 174 digital multimeter.

The principal conductivities σ_{\parallel} and σ_{\perp} were measured on the same samples over a range of frequencies from 300 Hz–30 kHz, using the Wayne Kerr bridge with an external source and detector (Lock-in-amplifier, Model PAR 186).

RESULTS AND DISCUSSION

The principal dielectric constants (ϵ_{\parallel} and ϵ_{\perp}) and the mean value $\bar{\epsilon} = (\epsilon_{\parallel} + 2\epsilon_{\perp})/3$ are shown for a few representative compositions in Figures 3–6, as functions of relative temperature ($T_{\text{NI}} - T$). The dielectric anisotropies ($\Delta\epsilon$) of all these systems have been plotted in Figure 7.

7P(2CN)5BC has a negative $\Delta\epsilon$ (Figure 3), because of a cyano group making an angle of $\sim 60^\circ$ with the long axis of the molecule (Figure 1). The $\bar{\epsilon}$ value decreases with temperature throughout the nematic range, but there is a sudden increase of $\sim 2\%$ in its value at T_{NI} . This may be partly caused by a decrease in the antiparallel correlation between the long axis components of the dipole moments of neighbouring molecules.^{4,5} It is interesting to note that ϵ_{\perp} decreases linearly as the temperature is increased without any striking change in its rate of variation near T_{NI} .

For mixtures with relatively high concentration of 7CB, $\Delta\epsilon$ is positive (Figure 7). In the mixture with 60% 7P(2CN)5BC (Figure 5), $\bar{\epsilon}$ decreases with temperature, the rate of variation being smaller than that in the pure compound. It also exhibits a positive jump of comparatively lower magnitude at T_{NI} . Further, ϵ_{\perp} shows a broad minimum. For mixtures with higher concentrations of 7CB, $\bar{\epsilon}$ increases with temperature (Figure 6). The latter result is caused by a reduction in the antiparallel correlation between neighbouring 7CB molecules with increase of temperature.⁴

In pure 7P(2CN)5BC and in mixtures with relatively high concentrations of 7P(2CN)5BC, ϵ_{is} decreases with temperature as in any other polar liquid. But in mixtures with high concentrations of 7CB (Figure 6), ϵ_{is} slightly increases as the temperature is increased above T_{NI} , and then decreases with temperature. This initial increase close to

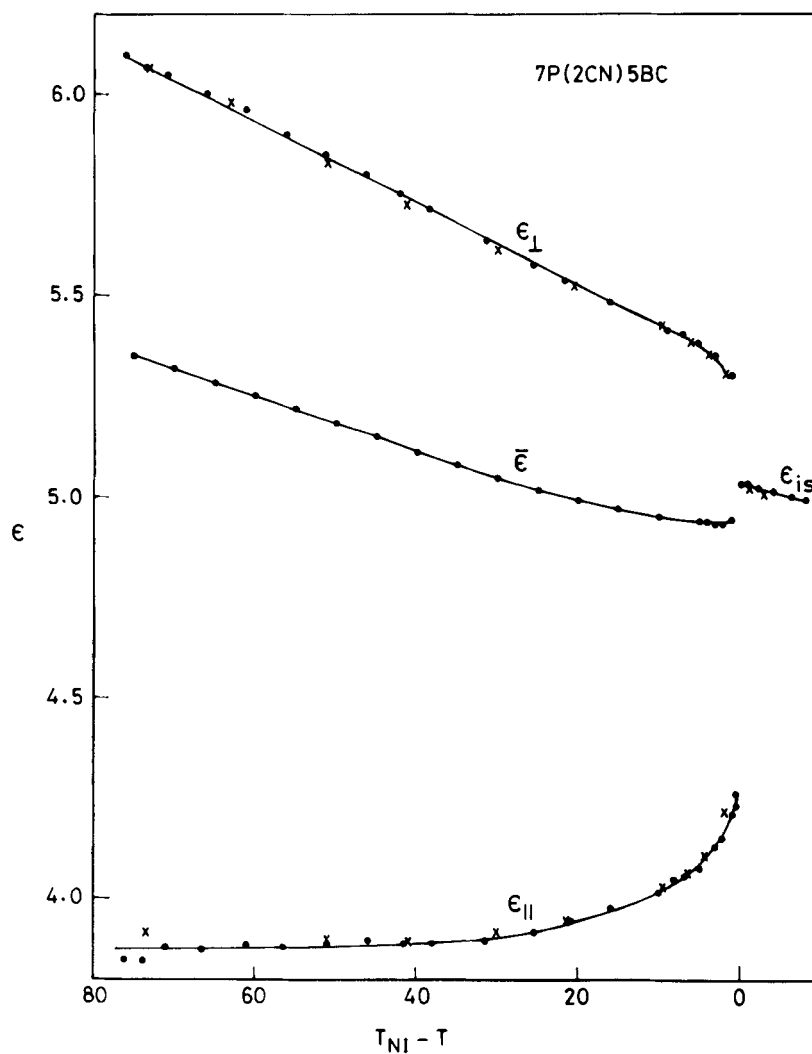


FIGURE 3 Dielectric constants of 7P(2CN)5BC as functions of relative temperature. Different symbols show the results of independent measurements.

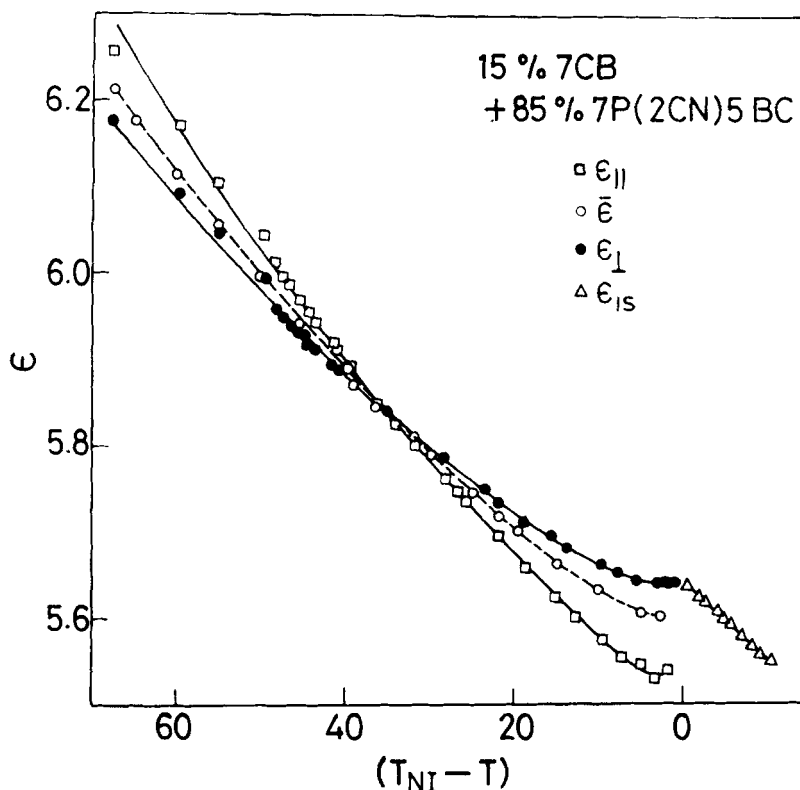


FIGURE 4 Dielectric constants of a mixture of 85 mole per cent 7P(2CN)5BC with 15 mole per cent 7CB as functions of relative temperature.

T_{NI} is again due to the reduction in the antiparallel short range order in the isotropic phase.

The mixture with 15% of 7CB exhibits very interesting features (Figure 4). Firstly, both $\epsilon_{||}$ and ϵ_{\perp} decrease with temperature in most of the nematic range, $\epsilon_{||}$ increasing only close to T_{NI} . $\Delta\epsilon$ is very small and changes sign as the temperature is varied. But rather unusually, the sign is *positive* at lower temperatures and *negative* at higher temperatures. We have confirmed this result by making measurements on a mixture with 15.2% 7CB. The results are similar to those given in Figure 4, except that the cross over occurs at a higher temperature.

This trend is opposite to the one expected on the basis of the theory of Maier and Meier,⁶ which predicts that

$$\epsilon_{||} = 1 + 4\pi N F h \left[\bar{\alpha} + \frac{2}{3} S \Delta\alpha + \frac{F\mu^2}{3kT} \{1 + (3\cos^2\beta - 1)S\} \right]$$

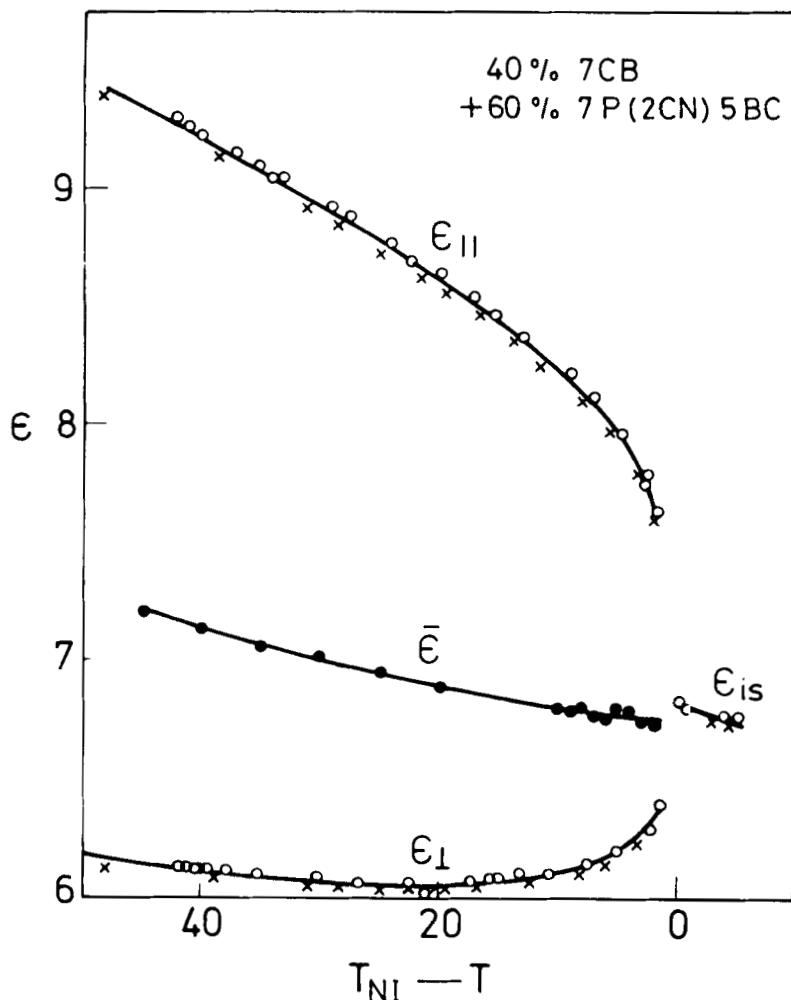


FIGURE 5 Dielectric constants of a mixture of 60 mole per cent of 7P(2CN)5BC with 40 mole per cent 7CB as functions of relative temperature.

and

$$\epsilon_{\perp} = 1 + 4\pi N F h \left[\bar{\alpha} - \frac{1}{3} S \Delta \alpha + \frac{F \mu^2}{3kT} \left(1 - \frac{1}{2} (3 \cos^2 \beta - 1) S \right) \right] \quad (1)$$

where $\Delta \alpha$ is the anisotropy of polarizability of a perfectly oriented medium, β is the angle made by the permanent dipole moment μ with the long axis of the molecule, $F = (1 - f\alpha)^{-1}$, f being the reaction

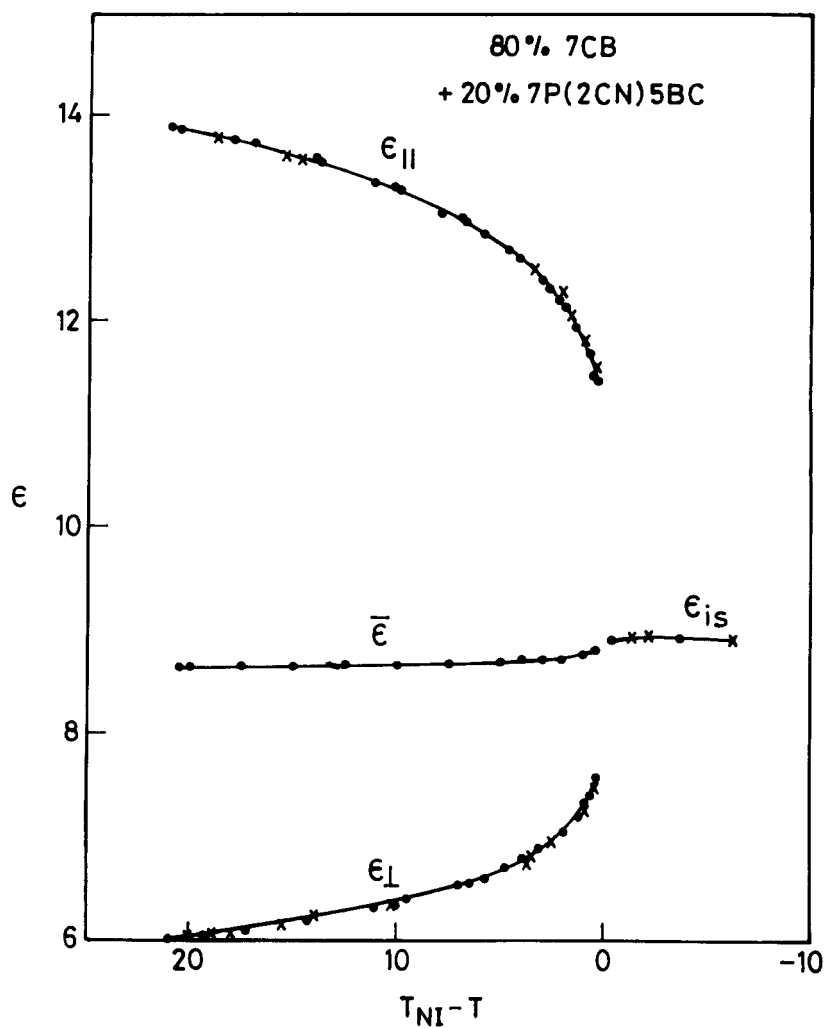


FIGURE 6 Dielectric constants of a mixture of 20 mole per cent of 7P(2CN)5BC with 80 mole per cent 7CB as functions of relative temperature.

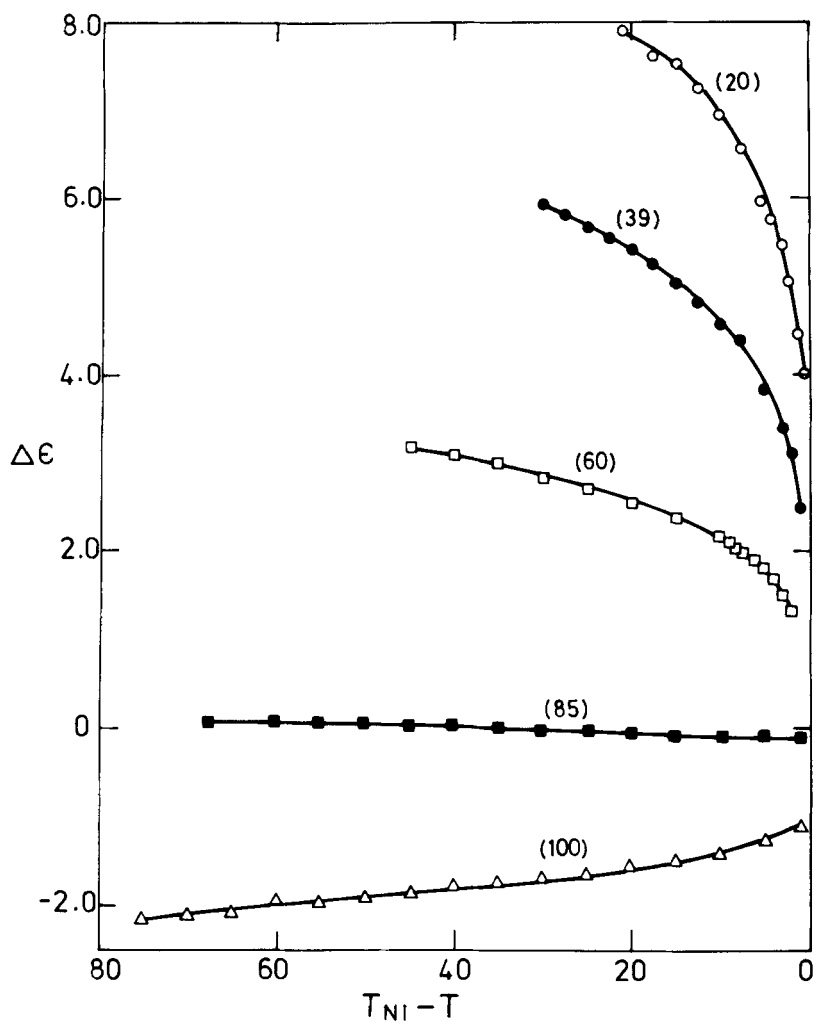


FIGURE 7 Dielectric anisotropies of various mixtures of 7P(2CN)5BC with 7CB as functions of relative temperature. The numbers in brackets indicate the mole percentage of 7P(2CN)5BC.

field factor, h is the cavity field factor, k the Boltzmann constant and S the degree of orientational order. If μ is sufficiently strong, it is clear that the last term in the square brackets in Eq. (1) predominates and then both ϵ_{\parallel} and ϵ_{\perp} can decrease with increase of temperature.

We get for the *anisotropy* of the dielectric constant

$$\Delta\epsilon = 4\pi NFh \left\{ \Delta\alpha - \frac{F\mu^2}{2kT} (1 - 3\cos^2\beta) \right\} S \quad (2)$$

If the two terms between the flower brackets in (2) are practically equal, it is clear that $\Delta\epsilon$ can change sign at some temperature T , and become *positive at higher temperatures*, as is indeed found in some systems.⁷

We believe that the reverse trend observed in our studies arise from the temperature variation of the skewed cybotactic type of short range order found in 7P(2CN)5BC. X-ray studies² reveal that the tilt angle of the skewed cybotactic structure (smectic C type short range order) decreases from $\sim 48^\circ$ at 25°C to $\sim 40^\circ$ at 87°C , the rate of decrease becoming stronger at higher temperatures. Indeed X-ray studies on the mixture with 15% 7CB also clearly reveal a skewed cybotactic structure, and just as in the case of 7P(2CN)5BC,² the ordinary index of this mixture also *decreases* with increase of temperature³ far away from T_{NI} . Benguigui⁸ has developed a theoretical model of the dielectric constants in the smectic C phase. A preliminary analysis based on this theory extended to a nematic liquid crystal with skewed cybotactic structure leads to the trend in $\Delta\epsilon$ observed experimentally. A detailed analysis is underway and will be published elsewhere.

The principal conductivities σ_{\parallel} and σ_{\perp} were measured on all systems over the frequency range 300 Hz–30 kHz. The conductivities for a typical case is shown in Figure 8. The important results are summarized below.

In all the systems, σ_{\parallel} and σ_{\perp} increase with frequency. In 7P(2CN)5BC (Figure 8) both of them vary in practically the same manner. This is in agreement with the expected trend,⁹ because in the frequency range covered the conductivity can be expressed as a quadratic function of ω : $\sigma(\omega) = \sigma(0) + \epsilon_0(\epsilon - 1)\tau\omega^2$.

In mixtures of 7P(2CN)5BC with 7CB, $\sigma_R (= \sigma_{\parallel}/\sigma_{\perp})$ is always > 1 . At low temperatures σ_{\parallel} increases with frequency more rapidly than in the case of σ_{\perp} , so that σ_R becomes large at high frequencies. As the temperature is increased, the frequency dependences of σ_{\parallel} and σ_{\perp} become similar (Figure 9). This result can be easily understood in terms of the contribution to the conductivity from the low frequency ϵ_{\parallel} relaxation of 7CB molecules.⁹

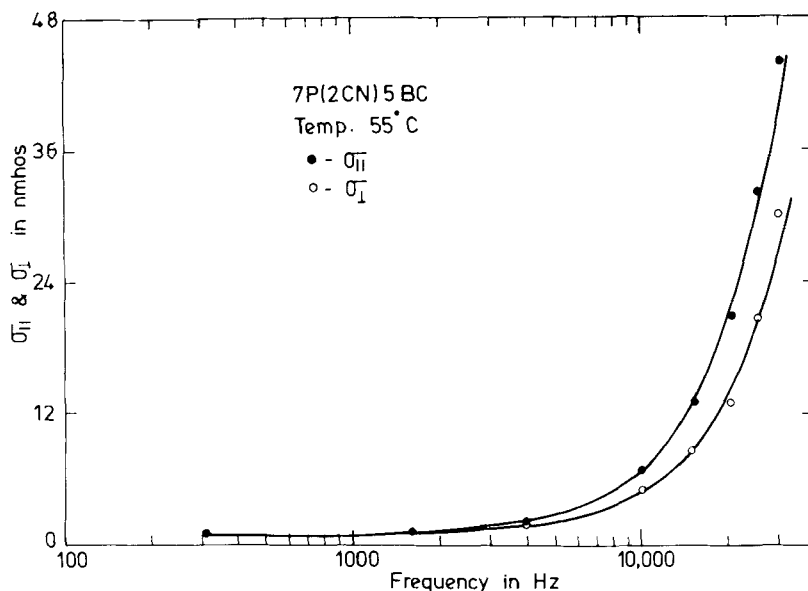


FIGURE 8 Frequency dependence of the principal conductivities of 7P(2CN)5BC at 55°C.

The temperature variations of the ratios of the principal conductivities σ_R at 1592 Hz are shown for all the systems studied in Figure 10. As we mentioned in the introduction, σ_R is a sensitive function of the short range order in the medium and also to some extent on the nature and concentration of the ionic species:^{10,11} σ_R generally increases with increasing conductivity of the medium. Our samples contained some unknown conducting impurities. We have indicated the average specific conductivity (at a common temperature = 42°C), $\bar{K} = (l/A)\bar{\sigma}$ where (l/A) is the geometric parameter of the measuring cell which is calculated by using the measured value of the capacitance of the empty cell. $\bar{\sigma}$ is the measured value of the conductivity if the sample is in the isotropic phase or $\bar{\sigma} = (\sigma_{||} + 2\sigma_{\perp})/3$ if the sample is in the nematic phase. It is clear that our 7CB sample has a much higher impurity content than the 7P(2CN)5BC sample, the mixtures having some intermediate values. In view of these differences in \bar{K} values of different systems, we can only discuss the temperature variations of σ_R values, rather than their absolute values. For a nematic liquid crystal without any cybotactic structure, σ_R depends only on the orientational order parameter S , and should monotonically decrease with temperature,^{10,11} the rate of decrease increasing as T_{NI} is approached.⁹ 7CB

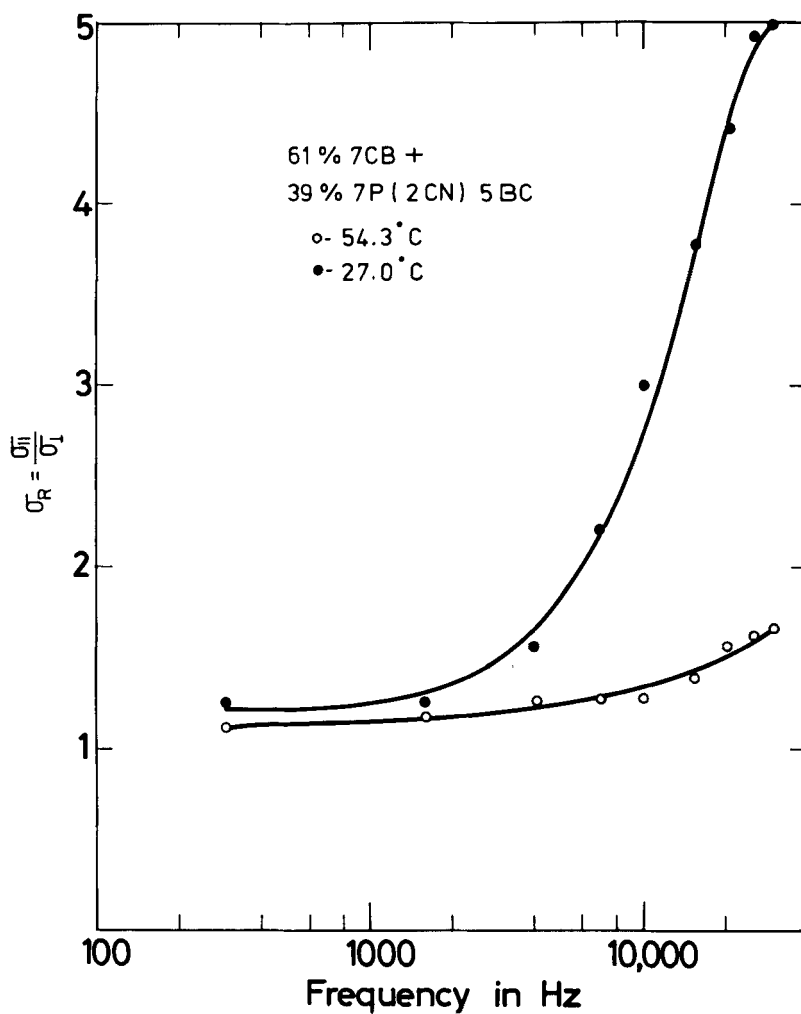


FIGURE 9 Frequency dependence of the ratio of the principal conductivities (σ_R) of a mixture of 39 mole per cent 7P(2CN)5BC with 61 mole per cent 7CB at two different temperatures.

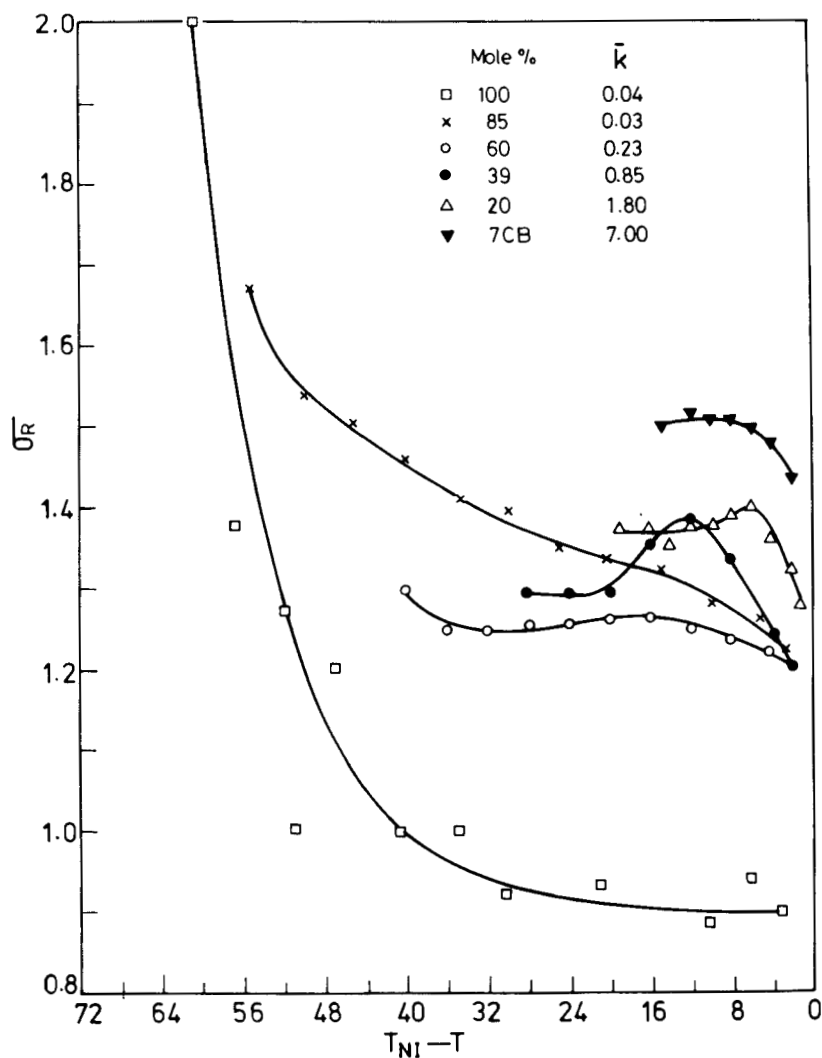


FIGURE 10 Temperature variations of the ratio of conductivities (at 1592 Hz) in the nematic phase of the systems studied. The numbers appearing immediately after the symbols are the mole percentages of 7P(2CN)5BC and the next number is the specific conductivity $\bar{k} \times 10^9 (\Omega \text{ cm})^{-1}$ at 42 °C.

has a cybotactic structure of the smectic A type, which is made up of bilayers¹² which arise due to the antiparallel correlations between the highly polar neighbouring molecule.^{4,5} The cybotactic order becomes somewhat stronger (i.e., its correlation length increases) with decrease of temperature, though 7CB does not exhibit the A phase.¹² As such σ_R of 7CB which is relatively high tends to level off and even decrease slightly at lower temperatures (Figure 10). On the other hand, as we have discussed earlier, 7P(2CN)5BC has a very strong skew cybotactic order whose strength as well as tilt angle decrease with increase of temperature.² Both of these parameters determine σ_R , assuming that the ions can flow more easily in the plane of the layers than in the perpendicular direction. At temperatures close to T_{NI} , the tilt angle is small, and $\sigma_R < 1$ (Figure 10). As the temperature is lowered, there is a very rapid increase of σ_R , the rate of increase becoming larger at lower temperatures, mainly because both the strength and tilt angle of the cybotactic groups increase. The lowering of the relaxation frequency of $\epsilon_{||}$ might also contribute to this increase in the σ_R values.⁹

Even for the mixture with 15% 7CB, as we discussed in connection with the dielectric properties, the structure should retain the skew cybotactic nature but its strength is probably reduced so that σ_R values go up compared to pure 7P(2CN)5BC. The temperature variation of σ_R is similar to that of the pure compound. With 40% of 7CB in the mixture, σ_R value shows a broad maximum and then a minimum before it starts to increase again. Close to T_{NI} , the strength of the cybotactic order should be so small that the temperature variation of σ_R is determined by that of the orientational order parameter. As the temperature is lowered, the cybotactic order starts building up and σ_R decreases. With further decrease of temperature, the increase in the tilt angle finally leads to an increasing trend of σ_R . With higher concentrations of 7CB, the peak in σ_R is shifted towards T_{NI} , probably because the cybotactic groups are more and more smectic A-like for these concentrations. In any case, the nematic range is also reduced and we see a general levelling off of σ_R at the lowest temperatures (Figure 10).

In conclusion, we have found that a temperature variation of the tilt angle of skewed cybotactic structure has an observable effect on both the dielectric constants and conductivities of the systems studied.

Acknowledgment

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