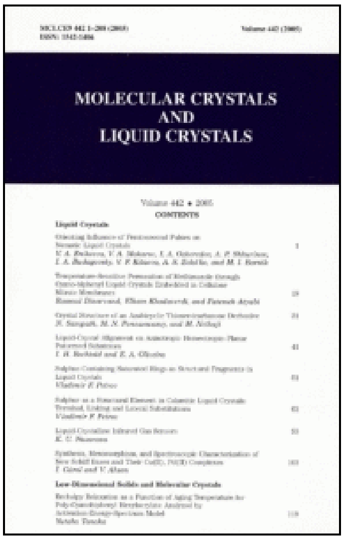

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Near Neighbour Correlations and the Dielectric Properties of Liquid Crystals

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NEAR NEIGHBOUR CORRELATIONS AND THE DIELECTRIC PROPERTIES OF LIQUID CRYSTALS

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Abstract

It is demonstrated experimentally that there can be a reversal of the sign of the dielectric anisotropy ($\Delta\varepsilon$) with decreasing temperature in a nematic. The results are explainable in terms of the Maier-Meier mean field theory and indicate that the occurrence of the smectic phase and the consequent dipole correlations within the smectic layers is not a necessary condition for the sign reversal of $\Delta\varepsilon$.

The idea of near neighbour antiparallel correlations (or antiferroelectric short range order) in nematic liquid crystals composed of polar molecules was first proposed in 1973 and its consequences were discussed on the basis of the Bethe-Peierls cluster approximation.[1] A prediction of the theory is that the mean dielectric constant $\bar{\varepsilon}=(\varepsilon_1+2\varepsilon_2)/3$, where ε_1 and ε_2 are the values along and perpendicular to the director, should show a discontinuous increase on going from the nematic to the isotropic phase. This has been found to be the case in a number of strongly positive materials,[2-4] the most striking confirmation being provided by the recent high precision measurements of Bradshaw and Raynes[4] on some cyano compounds which reveal even a pretransition effect in the antiparallel correlations. Negative dielectric anisotropy materials[5] also exhibit a discontinuous change in $\bar{\varepsilon}$ at T_{NI} evidently because of the antiparallel correlation of the longitudinal component (μ_ℓ) of the dipole moment. With non-polar materials,[6] on the other hand, there is no abrupt change in $\bar{\varepsilon}$ at T_{NI}.

A reversal of the sign of the dielectric anisotropy $\Delta\varepsilon(=\varepsilon_1-\varepsilon_2)$ with decrease of temperature has been observed in a few compounds[7,8], $\Delta\varepsilon$ changing from a relatively weak positive value near T_{NI} to a weak negative value at lower temperatures. As it happens, in these compounds this reversal is accompanied by the occurrence of a smectic A phase at lower temperatures. It has therefore been argued[7,8] that the smectic layer structure gives rise to a *parallel* correlation of μ_t, the transverse component of the dipole moment, in addition to the antiparallel correlation of the longitudinal component μ_ℓ, thus resulting in a crossover of ε_1 and ε_2. Now the smectic A layers are known to be *liquid-like*, and while it is true that the molecular distribution function in each layer cannot be strictly cylindrically symmetric as far as the near neighbours are concerned (since the molecules themselves are not cylindrically symmetric) the question arises as to whether the parallel correlations within each layer will be strong enough to bring about a reversal of the sign of $\Delta\varepsilon$.

Another possible explanation of this unusual temperature variation of the dielectric anisotropy follows directly from the theory of Maier and Meier.[5] According to this theory

$$\Delta\varepsilon = \varepsilon_1 - \varepsilon_2 = \frac{4\pi N_A \rho h F}{M}\left[\alpha_a - \frac{F\mu^2}{2k_B T}(1 - 3\cos^2\beta)\right]S \qquad (1)$$

where ρ is the density, h the cavity field factor, F the reaction field factor, M the molecular weight, α_a the polarizability anisotropy, β the angle which the net dipole moment (μ) makes with the long molecular axis and S the orientational order parameter. Consequently if the polarizability and permanent dipolar contributions in the square brackets on the right hand side of eqn.(1) are nearly balanced, there can be a reversal of $\Delta\varepsilon$ with temperature because of the factor T^{-1} in the second term. Indeed as was shown by us earlier[9] it is this T^{-1} factor which is responsible for the reversal of the sign of the Kerr constant of p-azoxyanisole (PAA) in the isotropic phase at $T_{NI} + 5^oK$. But if β of PAA had been slightly less than its actual value, the temperature at which $\Delta\varepsilon = 0$ would have occurred below T_{NI}. Theoretical curves illustrating this are shown in fig. 1; the parameters used in the curves are those for PAA with $\alpha_a = 21$ Å.[3]

We now demonstrate experimentally that this sign reversal of $\Delta\varepsilon$ can actually be observed in nematics. In order to do this, measurements were made on PAA mixed with small quantities of a positive nematogen, 4'-n-pentyl-4-cyanoterphenyl (5CT) or 4-n-methoxybenzylidene-4'-phenylazoaniline (MBPAA). The mixture

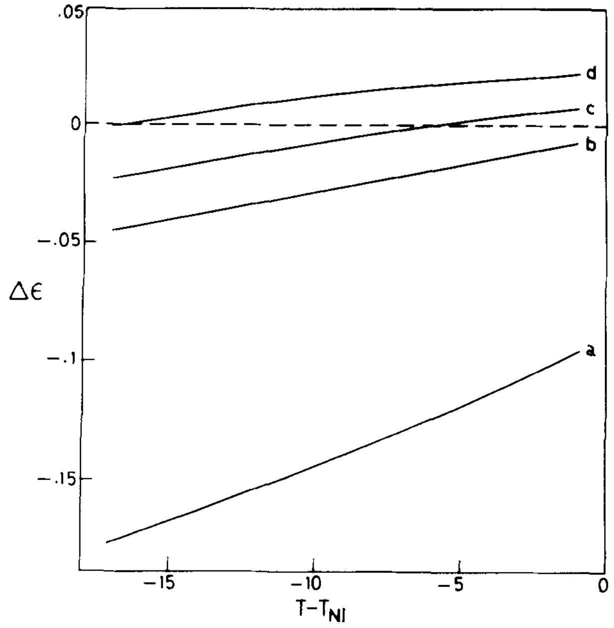
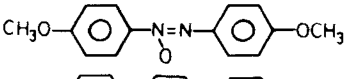
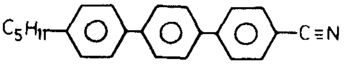
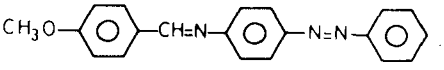


FIG. 1 Theoretical curves calculated from eqn.(1) for various values of β: (a) 64^o, (b) 62.5^o, (c) 62.25^o and (d) 62^o.

are also purely nematogenic and do not show a smectic phase. The purpose of adding 5CT or MBPAA was to reduce the effective β of PAA slightly and to increase T_{NI} by a few degrees.

The crystal-nematic (T_{CN}) and the nematic-isotropic (T_{NI}) transition temperatures of the pure components are given in Table I below.

Table I

Compound	Molecular structure	T_{CN}(^{o}C)	T_{NI}(^{o}C)
PAA		118	135.2
5CT		130	239
MBPAA		150	187.6

The principal dielectric constants were determined at 1592 Hz using a Wayne Kerr B642 bridge. Samples (125 μm thick) were aligned using a 15 kgauss magnetic field. $\varepsilon_1(H \parallel E)$ and $\varepsilon_2(H \perp E)$ were measured on the same sample by rotating the cell through 90° at each temperature. Other experimental details are as described in an earlier paper.[10] Measurements were first made on pure PAA and it was ascertained that the values are in agreement with the reported data for this compound.[5] Fig.2 shows the dielectric constants ε_1 and ε_2 for a 99.3 PAA/0.7 5CT (mole %) mixture and fig.3 the dielectric anisotropy $\Delta\varepsilon$ for mixtures of two different compositions.

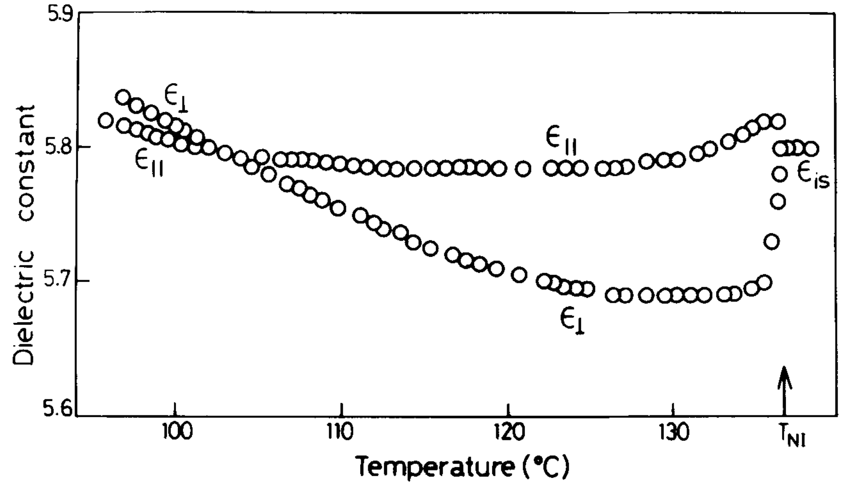


FIG.2 Principal dielectric constants of 99.3 PAA/0.7 5CT (mole %) mixture; T_{NI} = 136.6°C.

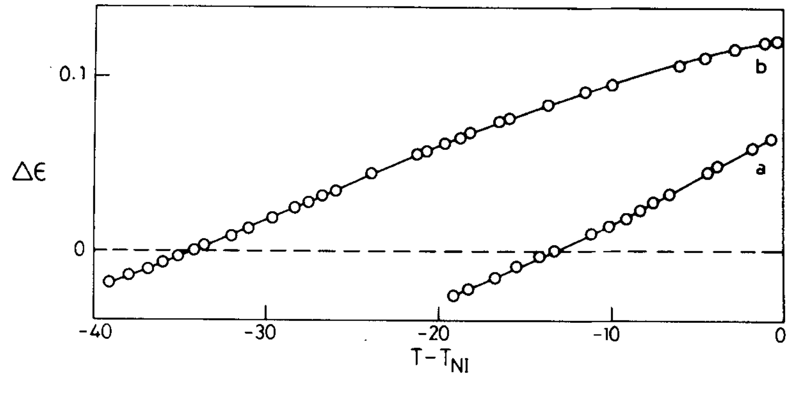


FIG.3 The dielectric anisotropy as a function of temperature for mixtures of PAA and 5CT. (a) 0.6 mole % 5CT; T_{NI} = 136.2°C, (b) 0.7 mole % 5CT; T_{NI} = 136.6°C.

The trends can be seen to be in qualitative accord with what is expected from the Maier-Meier theory - the crossover temperature decreasing with increasing proportion of the positive 5CT.

It was found that for concentrations greater than about 30 mole % of 5CT, the PAA/5CT mixture exhibits an induced smectic phase.[11] However it is extremely unlikely that this will affect the present conclusions which are based on measurements at very low concentrations of 5CT for which the mixture is purely nematogenic. Nevertheless to clinch the argument, measurements were also made on PAA/MBPAA mixtures. In this case the mixture shows only a nematic phase for all compositions (fig. 4). The temperature variation of $\Delta\varepsilon$ for mixtures of three different compositions are shown in fig.5 and again qualitatively the trend is as expected from the Maier-Meier theory. Thus it would seem reasonable to conclude that the parallel correlations within the smectic layers cannot be a dominant mechanism for the reversal of the sign of the dielectric anisotropy.

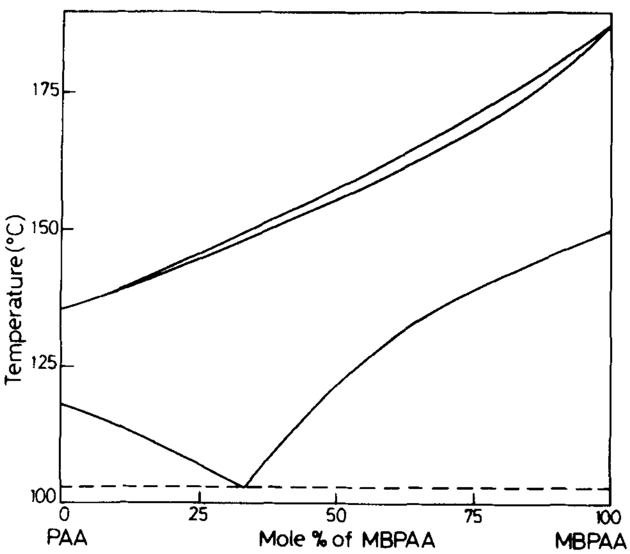


FIG.4 Phase diagram of mixtures of PAA and MBPAA.

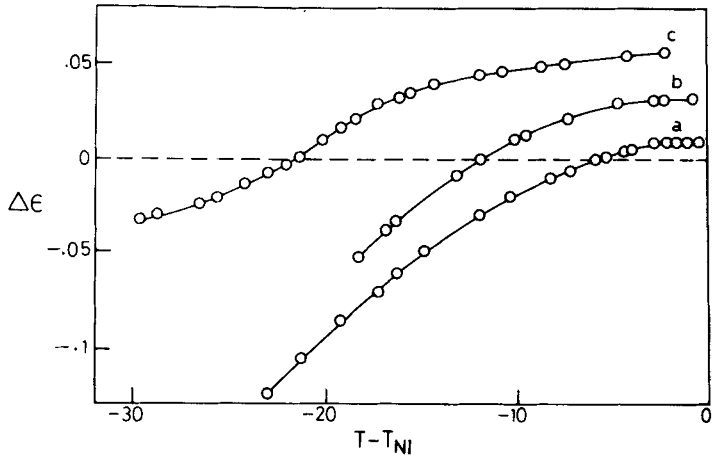


FIG.5 The dielectric anisotropy as a function of temperature for various concentrations of MBPAA in PAA: (a) 1.7 mole % MBPAA; T_{NI} = 135.6°C, (b) 3.0 mole % MBPAA; T_{NI} = 136.0°C and (c) 4.7 mole % MBPAA; T_{NI} = 136.6°C.

References

1 N.V.Madhusudana and S.Chandrasekhar, in 'Proceedings of the International Liquid Crystals Conference', Bangalore, December 1973, Pramana Supplement I, p.57; N.V.Madhusudana, K.L.Savithramma and S.Chandrasekhar, Pramana, 8, 22 (1977).

2 M.Schadt, J.Chem.Phys. 56, 1494 (1972).

3 B.R.Ratna and R.Shashidhar, Mol.Cryst.Liq.Cryst. 42, 113 (1977).

4 M.J.Bradshaw and E.P.Raynes, Mol.Cryst.Liq.Cryst.Letters, 72, 73 (1981)

5 W.Maier and G.Meier, Z.Naturforsch. 16a, 262 (1961).

6 W.H.de Jeu and Th.W.Lathouwers, Z.Naturforsch.29a, 905 (1974).

7 W.H.de Jeu, W.J.A.Goossens and P.Bordewijk, J.Chem.Phys. 61, 1985 (1974).

8 L.Benguigui, J.de Physique, 40, 705 (1979).

9 N.V.Madhusudana and S.Chandrasekhar, Liquid Crystals and Ordered Fluids, Vol.2, Eds. J.F.Johnson and R.S.Porter, p.657, Plenum (1974).

10 B.R.Ratna and R.Shashidhar, Pramana, 6, 278 (1976).

11 The complete phase diagram together with other studies of the PAA/5CT mixture will be reported separately.