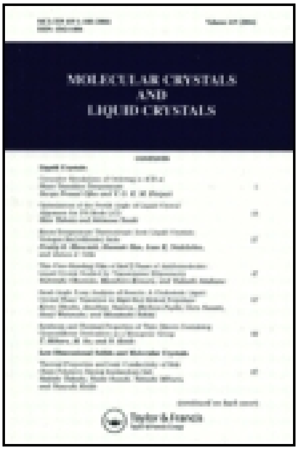

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Dipole-Dipole Association of Polar Molecules in a Non-Polar Liquid Crystal Solvent

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Dipole-Dipole Association of Polar Molecules in a Non-Polar Liquid Crystal Solvent

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Measurements are reported of the permittivity as a function of temperature and composition for strongly dipolar cyano-substituted molecules dissolved in a non-polar nematic liquid crystal solvent. Solute molecules with dipole moments perpendicular to the molecular alignment axes exhibited strong parallel association of their dipoles, even at low concentrations, and the measurements can be interpreted in terms of a ‘strong dimer’ model. Results for a solute molecule with a large dipole moment co-linear with the long molecular axis gave the major dipole correlation factor equal to 1, consistent with little or no preferred dipole-dipole correlation.

Keywords: dipole-dipole association, nematic, transverse dipole, dielectrics

INTRODUCTION

Understanding the dielectric properties of liquid crystals continues to provide a considerable research challenge. While the gross features of the dielectric behaviour of nematic and smectic A phases can be adequately described, many details remain to be explained. Mean field theories of liquid crystals neglect short-range interactions, and so provide a very limited model for interpreting physical properties. This is especially true of dielectric properties, where there is ample evidence to suggest that dipole-dipole interactions have an important influence on dielectric response. One manifestation of dipole-dipole forces can be molecular association, and this is best studied by measuring the dielectric properties of dilute solutions.[1–4] The existence of strong association in liquid crystals affects many of their properties. For example the appearance of reentrant phases in liquid crystal phase sequences has been explained[5–8] in term of the packing of monomers and dimers.

Molecular association will influence the free rotation of molecules, and molecular statistical models of the smectic C phase suggest[9,10] that restricted rotation of molecules about their long axes is a driving force for tilted layer structures. In optically active S_C^* phases the chirality of molecules breaks a reflection symmetry and restricted rotation results in ferro-electric ordering of transverse dipole components; it would seem likely that molecular interactions play some role in stabilizing the ferro-electric state.

In an earlier paper[4] we reported measurements of parallel dipole association in isotropic solutions of rod-like molecules having large components of the dipole moments across the molecular axis. The solute molecules studied had structures which might be expected to result in nematic phases, but our measurements were restricted to dilute isotropic solutions in a non-polar solvent (*p*-xylene). Our results indicated that even in the absence of a nematic ordering potential, the solute molecules tended to form dimers with parallel molecular axes and parallel dipole axes. Significant association was detectable at weight fractions of less than 0.1, and it seemed likely that in a nematic phase the association would be further enhanced. Some years ago we proposed[1] that apolar association of molecules in liquid crystal phases would result in parallel and anti-parallel dipole association, and it was the balance of these which determined the dielectric properties of the material. In order to investigate this further, we have measured the electric permittivity of dilute solutions of strongly dipolar solutes in a non-polar liquid crystal solvent. The solvent provides an orientationally ordered environment, and solution measurements enable the extent of association to be studied as a function of concentration and order parameter. Analysis of dielectric measurements on anisotropic solutions is complicated by the internal electric field, but we believe that a justifiably simple modification to the Onsager cavity and reaction field model gives a good description of the experimental system.

THEORY

Neglecting any local biaxial order, the principal permittivities ($\varepsilon_{\parallel}$, $\varepsilon_{\perp}$) for a uniaxial liquid crystal are given by Maier and Meier's equations:

$$\varepsilon_{\parallel} - 1 = \varepsilon_0^{-1} NLF\{\bar{\alpha} + \frac{2}{3}\Delta\alpha\, S + \frac{F g_1^{(\parallel)}}{3kT}[\mu_l^2(1 + 2S) + \mu_t^2(1 - S)]\} \tag{1}$$

$$\varepsilon_{\perp} - 1 = \varepsilon_0^{-1} NLF\{\bar{\alpha} - \frac{1}{3}\Delta\alpha\, S + \frac{F g_1^{(\perp)}}{6kT}[2\mu_l^2(1 - S) + \mu_t^2(2 + S)]\} \tag{2}$$

In these equations L and F are cavity field and reaction field factors, μ_l and μ_t are longitudinal and transverse molecular dipole components, N is the number density; $\bar{\alpha}$ and $\Delta\alpha$ are the mean molecular polarizability and polarizability anisotropy and S is the order parameter. The dipole correlation factors $g_1^{(i)}$ are defined by:

$$g_1^{(i)} = 1 + V^{-1}\int G_1^{(i)}(\mathbf{r})d(\mathbf{r})$$

$$G_1^{(i)}(\mathbf{r}) = \frac{<\mu_i(0)\mu_i(\mathbf{r})>}{<\mu_i(0)\mu_i(0)>} \tag{3}$$

They are a measure of the correlation of molecular dipole components projected onto the symmetry axes of the liquid crystal phase. For bound dimers the $g_1^{(i)}$'s will be related to the geometry of the dimer and should be independent of the degree of order, however for loose dimers in which there is some internal rotation of dipole components the g-factors may be complex functions of temperature.

The above equations apply to pure fluids, but the measurements described in this paper refer to polar solutes in anisotropic solutions. It is therefore necessary to formulate appropriate equations to enable the *g*-factors to be obtained for the solute molecules as a function of concentration. For isotropic solutions we have used the result given by Bottcher,[11] and using the approximation of isotropic cavity and reaction fields which is reasonable for non-polar liquid crystal solvents, it is straightforward to derive Equation (4) for polar solutes in anisotropic solutions:

$$[\mu_{eff}^{(i)}]^2 = \frac{9\varepsilon_0 kT(2\bar{\varepsilon} + \overline{n_2^2})^2}{N_A x_2(\overline{n_2^2} + 2)^2(2\bar{\varepsilon} + 1)}\left[\frac{(\varepsilon_i - 1)[x_1M_1 + x_2M_2]}{2\bar{\varepsilon}d} - \frac{3x_1M_1(\varepsilon_{1i} - 1)}{d_1(2\bar{\varepsilon} + \bar{\varepsilon}_1)} - \frac{3x_2M_2(n_{2i}^2 - 1)}{d_2(2\bar{\varepsilon} + \overline{n_2^2})}\right] \tag{4}$$

$\mu_{eff}^{(i)}$ is the root mean square effective dipole moment component along the principal directions of a uniaxial liquid crystal; the various other quantities are defined as follows, $\bar{\varepsilon} = 1/3(\varepsilon_{\parallel} + 2\varepsilon_{\perp})$ is the mean permittivity for the solution, and $\varepsilon_i = \varepsilon_{\parallel}$ or $\varepsilon_{\perp}$ are the measured components. The quantities subscripted with (1) refer to the solvent and those subscripted with (2) refer to solute, so that x_1, x_2, M_1, M_2 are the mole-fractions and molecular weights of solvent and solute. Mean values for the solute permittivity and refractive index (n_2) can be obtained by extrapolation.

Comparison of Equation (4) with Equations (1 and 2) gives that:

$$[\mu_{eff}^{(\parallel)}]^2 = g_1^{(\parallel)}[\mu_\ell^2(1 + 2S) + \mu_t^2(1 - S)]$$

$$[\mu_{eff}^{(\perp)}]^2 = g_1^{(\perp)}[\mu_\ell^2(1 - S) + \mu_t^2(1 + \tfrac{1}{2}S)] \tag{5}$$

where S is the order parameter of the solute. In our analysis of results we will assume that the solute order parameter equals the solvent order parameter. We believe that this is justified in view of the similarity of the structures of solute and solvent molecules. One possible problem with the analysis given below is the neglect of the local biaxial order, which could be significant for the solute molecules studied.

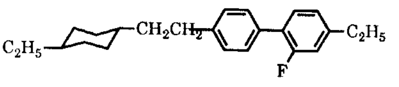
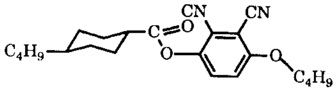
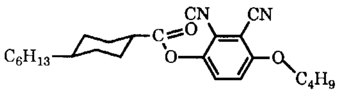
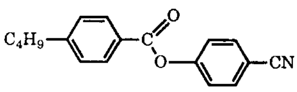
EXPERIMENTAL AND RESULTS

The materials studied in this work are listed in Table I. The compounds selected were dipolar mesogens that we have previously studied as dilute isotropic solutes, so that information was available on the free molecule dipole moments. A suitable nonpolar liquid crystal solvent is I22 (BDH Limited, Poole, UK), which has a nematic range of 13°C to 64°C, a mean permittivity of 3, and a zero dielectric anisotropy.[12]

Measurements of principal permittivities, refractive indices and densities of solutions of the mesogens in I22 were carried out as a function of temperature and composition using methods previously described.[2,4,12] Dielectric measurements were made on thin film samples aligned between indium/tin oxide coated glass electrodes. Planar alignment was achieved by depositing a layer of nylon on the surfaces of the glass electrodes and gently rubbing, while cells with perpendicular alignment were prepared by coating the glass electrodes with a surfactant. Refractive indices were obtained using an Abbé refractometer, the prisms of which had been treated

TABLE I

Materials studied

Structure and acronym	Transition temperatures							Dipole moment/Debye		
	K	T/°C	S_A	T/°C	N	T/°C	I	μ_0	μ_l	μ_t
I22 	*	13			*	64.0	*	1.38	0.8	1.36
4HENO4 	*	88	*			(52)	*	5.49	0.21	5.48
6HENO4 	*	86	*			(67)	*	6.0	0.23	5.99
C4CN 	*	68			*	(42)	*	5.77	5.47	1.81

1 Debye = 3.336×10^{-30} Cm

with a surfactant to give perpendicular (homeotropic) alignment, and densities were measured using an Anton Paar digital densimeter.

Results for the effective dipole moments calculated from Equation (4) are given in Figures 1–3 as a function of composition for different temperatures. For 4HENO4 and 6HENO4 the dielectric anisotropies of the solutions in I22 were negative, and this is clear from Figures 1 and 2 in which $(\mu_{eff}^2)_\perp > (\mu_{eff}^2)_\parallel$. Results for isotropic solutions in I22 at temperatures just above T_{NI} are also plotted, and the free solute molecule dipole moment μ_0 measured previously is marked on the ordinate axis. For weight fractions less than 0.1 the effective mean square dipole moments are almost independent of concentration, but for all the materials studied, there is evidence of a rapid variation at very low concentrations. It was possible to study solutions of 4HENO4 at concentrations up to 0.2 weight fraction, and the expected increase in μ_{eff}^2 was observed. Since the concentration dependence of μ_{eff}^2 was fairly weak we have analyzed the results by extrapolating to zero concentration.

The order parameters of the solutions were obtained by fitting refractive indices to a mean field expression using the Tough Bradshaw procedure detailed in Reference 12. In practice the derived order parameters were independent of concentration for equal reduced temperatures, indicating that the solute had little effect on the orientational order of the solvent.

Equation 5 indicates that there should be a linear dependence of μ_{eff}^2 on the order parameter, but this neglects the possible temperature dependence of $g_1^{(\parallel)}$ and $g_1^{(\perp)}$. Results for $[\mu_{eff}]^2$ normalised by μ_0^2 are given in Figure 4 for 4HENO4 and 6HENO4 and in Figure 5 for C4CN. For the materials studied $[\mu_{eff}]^2/\mu_0^2$ varies approximately linearly with order parameter; also plotted on the figures are theoretical results assuming that μ_l is zero for 4HENO4 and 6HENO4 and μ_t is zero for C4CN. In Figure 4 theoretical results are given for both $g_1 = 1$ and $g_1 = 2$. Further analysis is possible if the component dipole moments μ_l and μ_t can be estimated. The molecules were selected to have either a large transverse dipole moment and approximately zero longitudinal moment (4HENO4 and 6HENO4) or *v.v.* (C4CN), and the relative values of these, given in Table I, could be reliably estimated from bond dipole or group moment calculations.[13] Using these values for the dipole components and experimental results for the order parameter S, it is possible to obtain the dipole correlation factors $g_1^{(\parallel)}$ and $g_1^{(\perp)}$ from the derived mean square effective dipole moments using Equation (5). These results are recorded in Table II, and it can be noted that the g_1's are >1 for 4HENO4 and 6HENO4 indicating parallel dipole association, and for C4CN are <1 consistent with weak anti-parallel dipole association.

DISCUSSION AND CONCLUSIONS

An important observation from our results is that C4CN solutions in I22 have a markedly different behaviour from solutions of 4HENO4 and 6HENO4. The effective dipole moment measured in an isotropic solution of C4CN in I22 extrapolates at low concentrations to the value determined from dilute solutions in *p*-xylene. Nematic solutions of C4CN in I22 have a positive dielectric anisotropy, and there is evidence of a small amount of anti-parallel association as shown by an initial

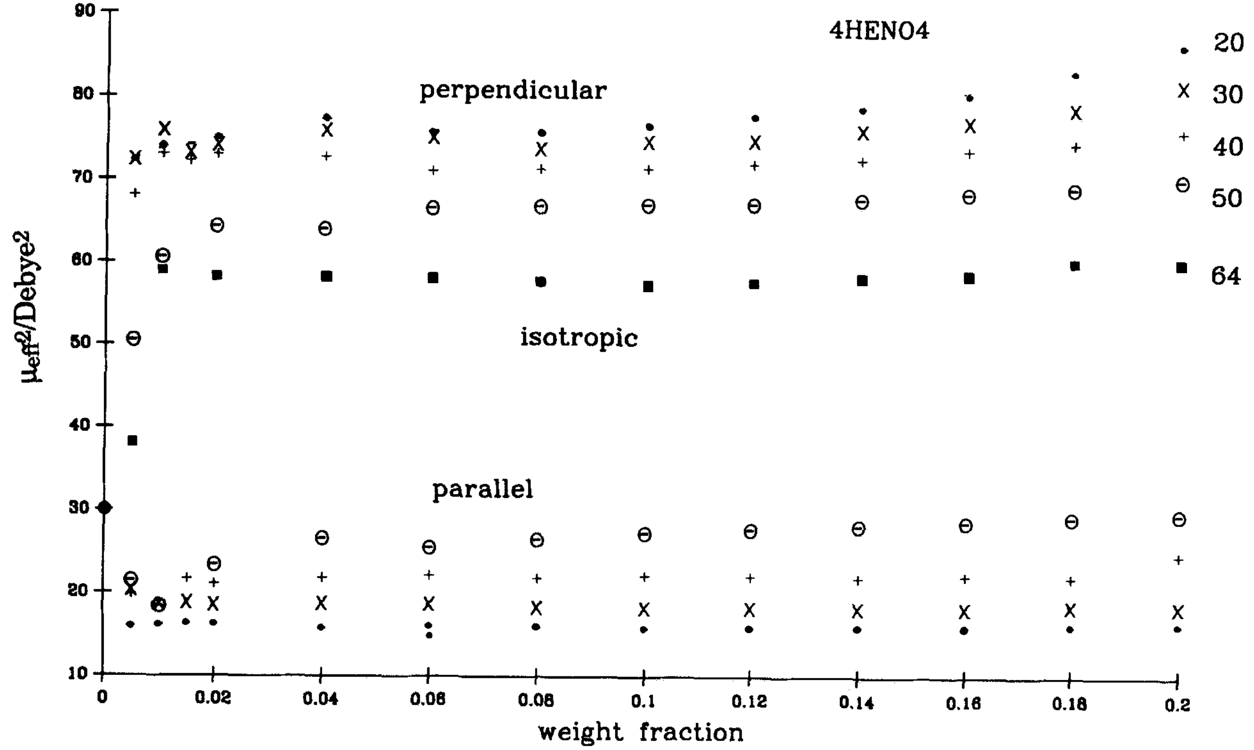


FIGURE 1 Mean square effective dipole moment of 4HENO4 as a function of weight fraction in I22 solutions of negative dielectric anisotropy. Nematic solutions-(●): 20°C, (×): 30°C, (+): 40°C, (⊖): 50°C; isotropic solution-(■): 64°C.

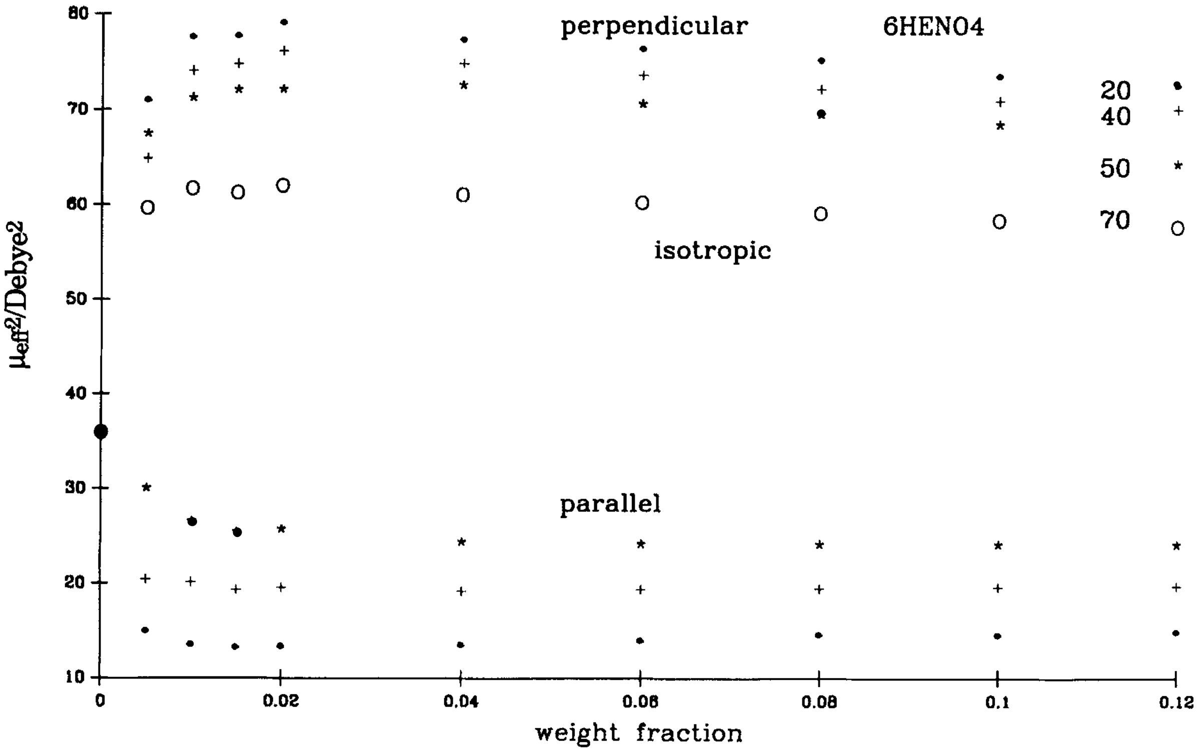


FIGURE 2 Mean square effective dipole moment of 6HENO4 as a function of weight fraction in I22 solutions of negative dielectric anisotropy. Nematic solutions-(●): 20°C, (+): 40°C, (*): 50°C; isotropic solution-(○): 70°C.

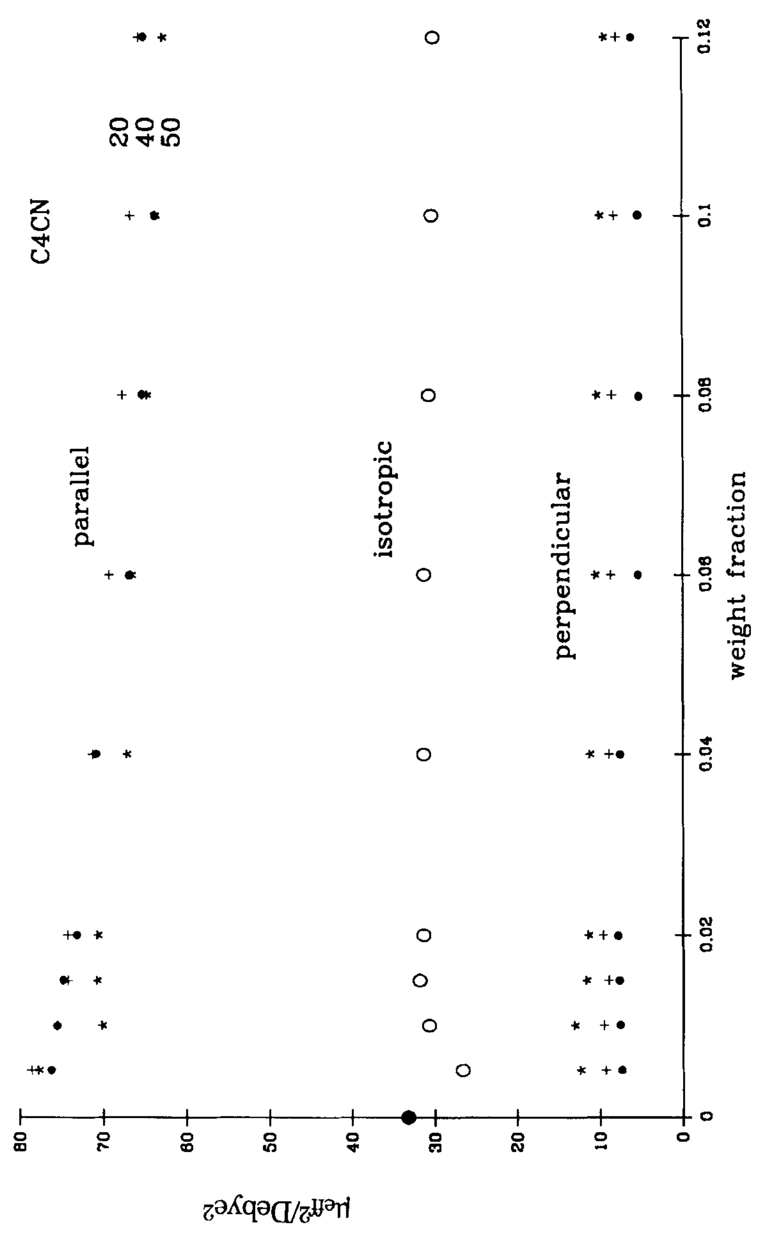


FIGURE 3 Mean square effective dipole moment of C4CN as a function of weight fraction in I22 solutions of positive dielectric anisotropy. Nematic solutions-(+): 20°C, (●): 40°C, (*): 50°C; isotropic solution-(○): 70°C.

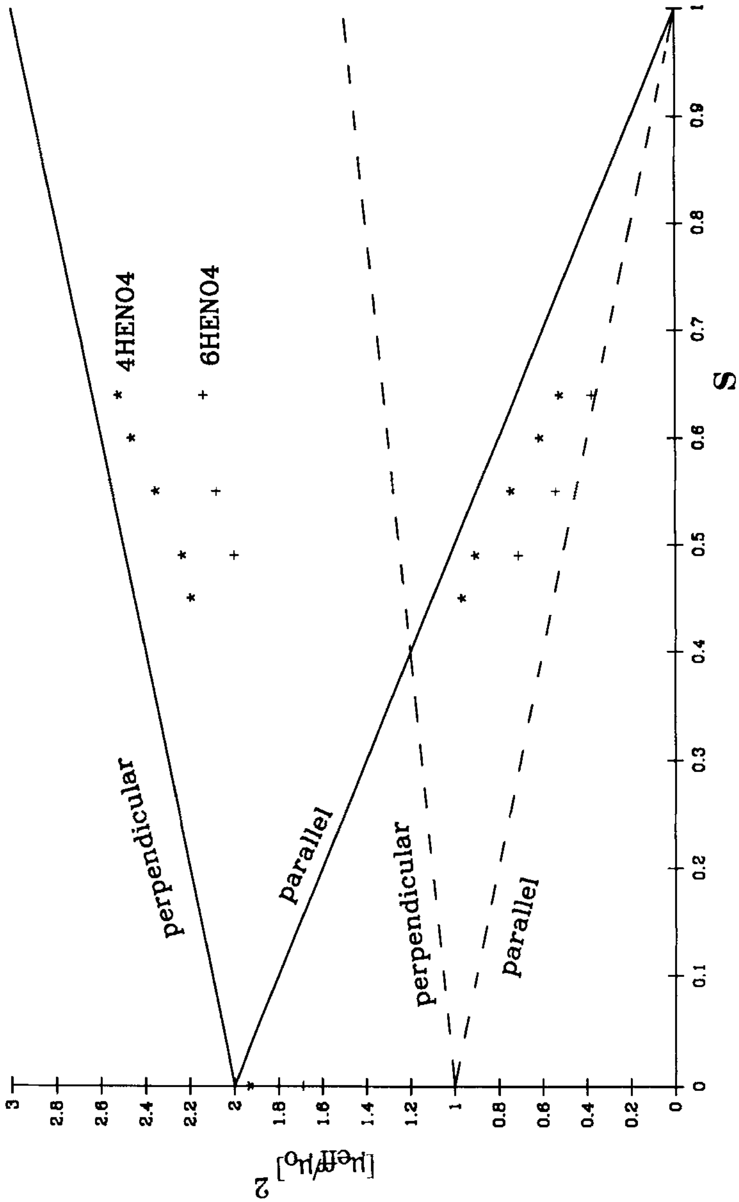


FIGURE 4 $[\mu_{eff}/\mu_0]^2$ as a function of order parameter S for 4HENO4 (*) and 6HENO4 (+). The full lines are those calculated from Equation (5) assuming $g_l = 2$, and $\mu_l = 0$, while the broken lines are for $g_l = 1$.

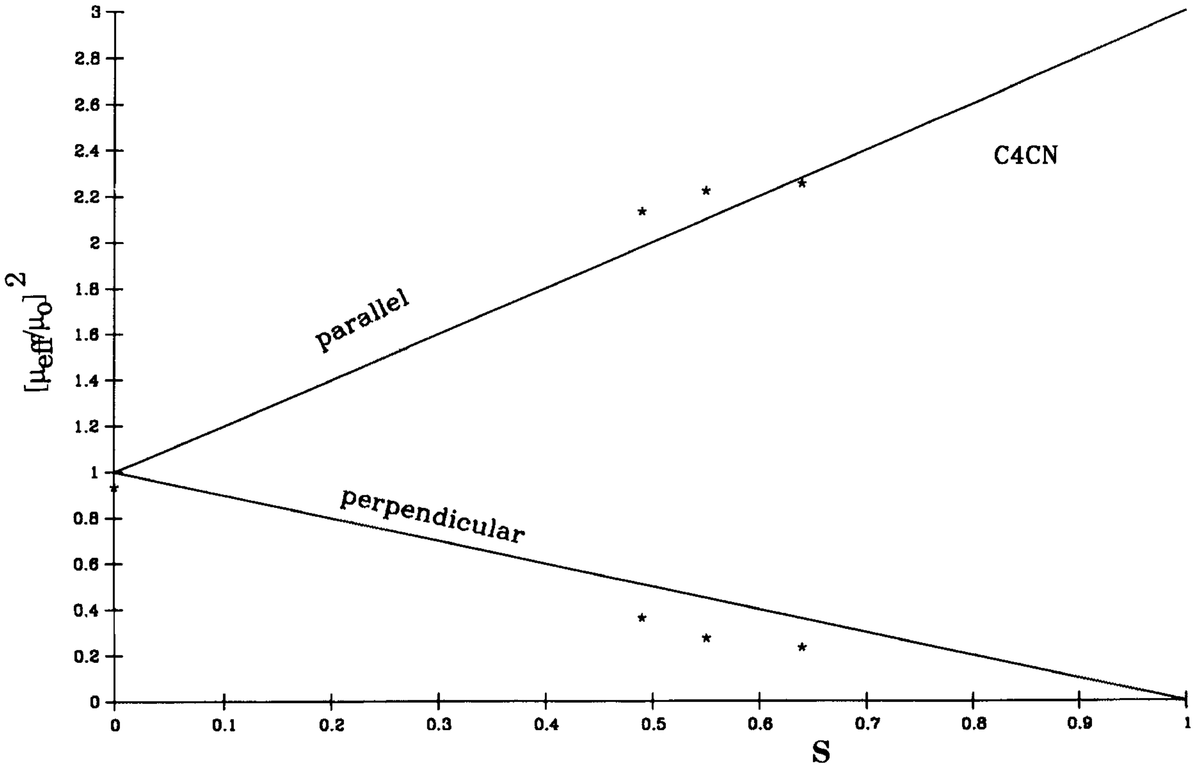


FIGURE 5 $[\mu_{eff}/\mu_0]^2$ as a function of order parameter S for C4CN; the full lines are those calculated from Equation (5) assuming $g_l = 1$, and $\mu_t = 0$.

TABLE II

Solution dipole correlation factors in I22

Solute mesogen		Temperature /°C						
		20	30	40	50	55	64*	70*
4HENO4	$g_1^{(\|\|)}$	1.4	1.5	1.6	1.7	1.7	1.9	
	$g_1^{(\perp)}$	1.9	1.9	1.8	1.8	1.8	1.9	
6HENO4	$g_1^{(\|\|)}$	1.0		1.2	1.4			1.7
	$g_1^{(\perp)}$	1.6		1.6	1.6			1.7
C4CN	$g_1^{(\|\|)}$	1.1		1.2	1.2			0.9
	$g_1^{(\perp)}$	0.5		0.5	0.6			0.9

* = isotropic solution in I22.

decrease in $[\mu_{eff}^{(||)}]^2$ with an increase in concentration; this is confirmed by calculated values of g_1's for C4CN. In terms of our model of apolar association[1] this would be interpreted as indicating a slight preference for anti-parallel over parallel dipole association. Our results for solutions of molecules with large transverse dipole moments were surprising, but are explicable in terms of a dimer model in which the dipoles are strongly coupled. The mean square effective dipole moment of 4HENO4 and 6HENO4 as measured in isotropic solutions of I22 extrapolates to a value approximately twice that obtained from measurements on dilute solutions in *p*-xylene. There is also evidence from our measurements of a rapid increase in $[\mu_{eff}^{(\perp)}]^2$ at low concentrations, and this is also apparent in the results from isotropic I22 solutions. The behaviour at low concentrations can be interpreted as the formation of dimers, and calculations of dipole correlation factors support this model. Experimental results plotted in Figure 4 are closer to the theoretical values for $g_1 = 2$ than for $g_1 = 1$. Our earlier measurements on 4HENO4 and 6HENO4 in dilute *p*-xylene solutions showed that there is a progressive parallel association of dipoles with increasing solute concentration, and even at a weight fraction of 0.05, the measured g_1's were about 1.5. The results reported in this paper suggest that in nematic solutions there is dimer formation at weight fractions between 0 and 0.01. We propose that the nematic ordering potential of the solvent promotes dimerisation, which persists even in the isotropic phase of I22, at least close to T_{NI}, because of local short range ordering. At higher concentrations around 0.2 weight fraction, there is evidence of a further increase in the effective dipole moment, which would be consistent with the formation of larger clusters of solute molecules with parallel transverse dipoles. The molecular interactions responsible for self-organization in liquid crystals will also cause the organization of solute molecules.

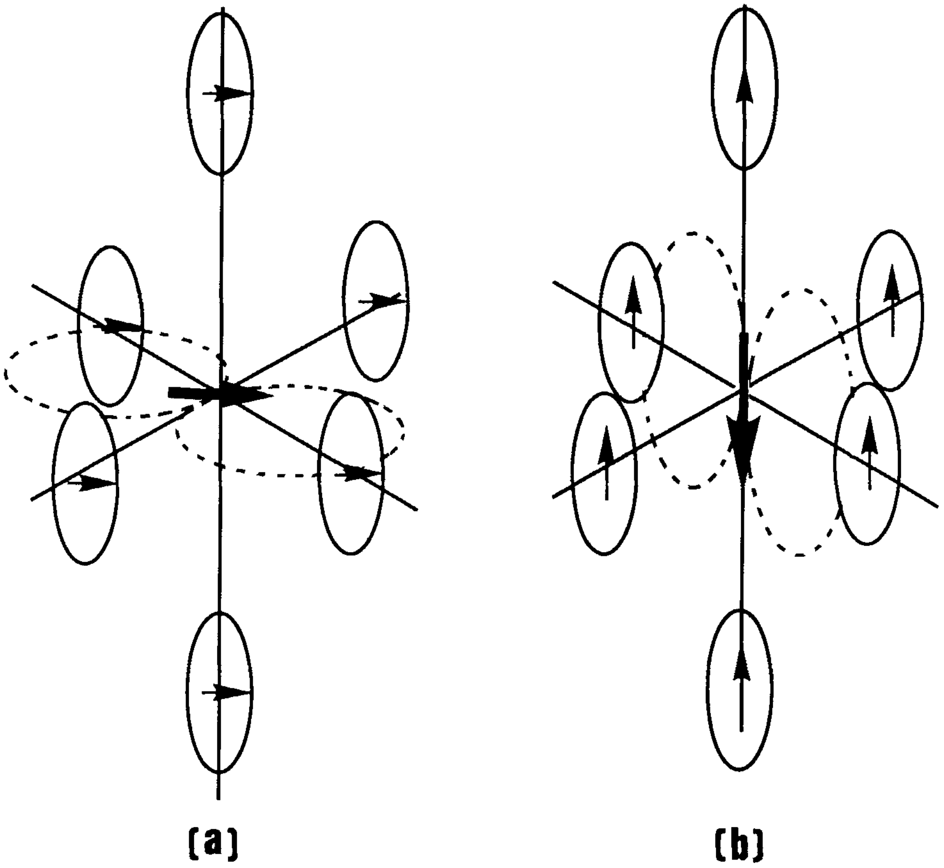


FIGURE 6 The depolarizing field at the centre of a prolate distribution of molecules with (a) transverse dipoles and (b) longitudinal dipoles. The electric field from dipoles is indicated by the broken lines.

We have proposed[1,2] that the apolar interactions responsible for liquid crystal phase formation will result in parallel and anti-parallel molecular association, and if the molecules are polar this will influence the dielectric properties. Where the parallel and antiparallel association is equal, then the measured low frequency dielectric response will be the same as if the molecules were unassociated. It is well-known that the dipole-dipole field at the centre of an isotropic array of parallel point dipoles is zero. As illustrated in Figure 6, prolate perturbation of the isotropic array in a direction parallel to the dipole directions results in a depolarizing field at the centre of the array; this will promote anti-parallel dipole association. On the other hand if the perturbation is perpendicular to the dipole direction, then parallel dipole association is preferred. Thus rod-like self-organizing molecules with large transverse dipole moments may be expected to exhibit parallel dipole association; we believe that the results given in this paper provide evidence for this. It will be interesting to investigate these effects in smectic A and smectic C phases to see if this local ferro-electric order can be further enhanced by other suitable phase structures. Choice of suitable molecular structures in which there is orthogonal dipolar and steric ordering may result in the formation of new biaxial ferroelectric phases which have been the subject of recent theoretical investigation.[14,15]

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