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Transverse dipole association and negative dielectric anisotropy of nematic liquid crystals

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Measurements are reported of the dielectric properties of three laterally substituted dicyano compounds with large molecular dipole moments perpendicular to the long molecular axis. Results are given for the materials in solution, in the isotropic liquid state, and for one compound in the nematic state. There is evidence of a high degree of local ferroelectric order in all phases, and dipole correlation factors in excess of 3 were obtained. The significance of these observations for macroscopic ferroelectrically ordered and biaxial liquid-crystalline phases is considered.

1. Introduction

The dielectric properties of liquid crystals are important in many liquid crystal devices, since most such applications require the switching of a macroscopically aligned liquid crystal by an electric field. The switching occurs because of the intrinsic anisotropy of the permittivity tensor, which also provides valuable information about the molecular interactions and orientational order in the liquid-crystalline phase. There are two basic problems concerning the development of a theory of the dielectric properties of anisotropic fluids. One concerns the internal electric field, which we shall not address in this paper, and the other is how to take account of short-range dipole–dipole interactions in a fluid with partial orientational order. In this paper we shall consider the importance of local dipole–dipole interactions in determining the dielectric properties of nematics, and present some experimental results to show the existence of strong ferroelectric ordering in compounds with large transverse dipole moments.

It is convenient to divide liquid crystals into two groups on the basis of the sign of the permittivity anisotropy. For positive materials the maximum component of the permittivity is along the director axis, while for negative materials it is perpendicular to the director. For biaxial materials (some nematics and smectics) this division is less appropriate, but so far there are few dielectric measurements on biaxial liquid-crystalline phases. In some cases the dielectric anisotropy may change sign with frequency [1] or temperature [2], but this is well understood [32].

For positive materials with dipole moments along the major axis of the molecule there is strong evidence for local antiferroelectric order. This is thought to be responsible for the relatively weak temperature dependence of the mean permittivity in cyanobiphenyl liquid crystals [3], the reentrant phase behaviour in nematics and smectics formed by molecules with strongly polar end groups [4, 35, 36], and for the variety of S_A phases recently discovered [5]. We have proposed [6] that the largely apolar forces responsible for liquid-crystalline order should result in parallel as well

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as antiparallel dipole association, the balance being determined by relatively weak dipole–dipole interactions. However, evidence for the existence of local ferroelectric order has been rather inconclusive [7, 8].

Rod-like mesogens with negative permittivity anisotropies must have a dipole moment perpendicular to the molecular axis. These molecules are also likely to exhibit a preference for ferroelectric dipole ordering because of a favourable anisotropy in the radial distribution function. Indeed the existence of the ferroelectric polarization of chiral smectic C phases depends on the component of the dipole moment perpendicular to a plane containing the molecular long axis. An inescapable consequence of a transverse molecular dipole moment is local biaxiality. This may develop into macroscopic biaxiality as with S_C phases, or it may only be a local biaxiality, which none the less will contribute [9] to macroscopic properties. Recently the possibility of ferroelectric nematic phases has been considered [10, 11], and rod-like molecules with large transverse dipoles may be suitable candidates for forming such a phase.

In this paper we present some experimental measurements of the dielectric properties of molecules with large dipole moments perpendicular to their major axes. Measurements have been made in solution, in the pure liquid state and for one material in the nematic liquid-crystalline state. Our results show clear evidence for local ferroelectric order in these materials.

2. Theoretical background

If a rod-like molecule possesses a transverse dipole moment then it must be biaxial. It is therefore necessary to include biaxial order parameters in the description of the dielectric properties of liquid-crystalline phases of such compounds. For the general case it is convenient to write the traceless part of a second-rank tensor property in terms of two ordering matrices $Q_{\alpha\beta}$ and $T_{\alpha\beta}$:

$$\kappa_{\alpha\beta} = \tfrac{2}{3}[\kappa_1 Q_{\alpha\beta} + \tfrac{1}{2}\kappa_2 T_{\alpha\beta}]. \tag{1}$$

Here κ_1 and κ_2 are combinations of molecular components of the property tensor, $\kappa_1 = \kappa_{zz} - \frac{1}{2}(\kappa_{xx} + \kappa_{yy})$ and $\kappa_2 = \kappa_{xx} - \kappa_{yy}$, and the matrices $Q_{\alpha\beta}$ and $T_{\alpha\beta}$ are [12]

$$Q_{\alpha\beta} = \begin{bmatrix} -\frac{1}{2}(S-P) & & \\ & -\frac{1}{2}(S+P) & \\ & & S \end{bmatrix},$$

$$T_{\alpha\beta} = \begin{bmatrix} -\frac{1}{2}(D-C) & & \\ & -\frac{1}{2}(D+C) & \\ & & D \end{bmatrix}, \tag{2}$$

where

$$S = \langle\tfrac{1}{2}(3\cos^2\theta - 1)\rangle, \quad P = \langle\tfrac{3}{2}\sin^2\theta\cos 2\phi\rangle,$$

$$D = \langle\tfrac{3}{2}\sin^2\theta\cos 2\psi\rangle,$$

$$C = \langle\tfrac{3}{2}[(1+\cos^2\theta)\cos 2\phi\cos 2\psi - 2\cos\theta\sin 2\phi\sin 2\psi]\rangle;$$

θ, ϕ and ψ are the Euler angles relating the molecular axes x, y, z to the laboratory axis frame, and in a macroscopically uniaxial phase the order parameters P and C are identically zero.

Using the above notation for order parameters, it is possible to derive expressions for the principal permittivity components of a biaxial fluid phase as

$$\begin{aligned}\varepsilon_{\parallel} - 1 &= \varepsilon_0^{-1} NLF \Big\{ \bar{\alpha} + \tfrac{2}{3}\alpha_1 S + \tfrac{1}{3}\alpha_2 D \\ &\quad + \frac{F g_1^{(\parallel)}}{3kT} [\mu_z^2 (1 + 2S) + \mu_y^2 (1 - S - D) + \mu_x^2 (1 - S + D)] \Big\},\end{aligned} \tag{3}$$

$$\begin{aligned}\varepsilon'_{\perp} - 1 &= \varepsilon_0^{-1} NLF \Big\{ \bar{\alpha} - \tfrac{1}{3}\alpha_1 (S + P) - \tfrac{1}{6}\alpha_2 (D + C) \\ &\quad + \frac{F g_1^{(\perp')}}{6kT} [2\mu_z^2 (1 - S - P) + \mu_y^2 (2 + S + P + D + C) \\ &\quad + \mu_x^2 (2 + S + P - D - C)] \Big\},\end{aligned} \tag{4}$$

$$\begin{aligned}\varepsilon_{\perp} - 1 &= \varepsilon_0^{-1} NLF \Big\{ \bar{\alpha} - \tfrac{1}{3}\alpha_1 (S - P) - \tfrac{1}{6}\alpha_2 (D - C) \\ &\quad + \frac{F g_1^{(\perp)}}{6kT} [2\mu_z^2 (1 - S + P) + \mu_y^2 (2 + S - P + D - C) \\ &\quad + \mu_x^2 (2 + S - P - D + C)] \Big\}.\end{aligned} \tag{5}$$

In this equation we have assumed an isotropic internal field, and L and F are cavity and reaction field factors [13]. The molecular parameters are the dipole components (μ_x, μ_y, μ_z) along the principal axes of the polarizability tensor and the polarizabilities $\alpha_1 = \alpha_{zz} - \frac{1}{2}(\alpha_{xx} + \alpha_{yy})$ and $\alpha_2 = \alpha_{xx} - \alpha_{yy}$. $\bar{\alpha}$ is the mean polarizability and N is the molecular number density.

The Kirkwood correlation factors are defined by

$$g_1^{(i)} = 1 + V^{-1} \int G_1^{(i)} (\mathbf{r}) d\mathbf{r} \tag{6}$$

where $G_1^{(i)} (\mathbf{r})$ is the dipole correlation function for the dipole components along the laboratory axes (i) and V is the sample volume:

$$G_1^{(i)} (\mathbf{r}) = \frac{\langle \mu_i(0) \mu_i(\mathbf{r}) \rangle}{\langle \mu_i(0) \mu_i(0) \rangle}. \tag{7}$$

The angular brackets denote an ensemble average. g_1 may be calculated for various interaction models [11, 14], or expressed in terms of a generalized expansion of the spatial correlation function [15]. For local antiferroelectric order $g_1 < 1$, while for local ferroelectric order $g_1 > 1$. We have calculated [11] the dipole correlation factors for rod-like molecules with a dipole moment perpendicular to the molecular axis and have shown that this geometry results in $g_1 > 1$. Such molecules are therefore of interest with regard to the possibility of ferroelectrically ordered fluids. For uniaxial liquid crystals consisting of biaxial molecules only the order parameters S and D need to be included in equations (3)–(5) for the permittivity components. When dielectric data become available for biaxial phases, the full expression must be used.

In pure isotropic liquids the dipole correlation factor can be obtained from the measured permittivity, density and refractive index using [33]

$$g_1\mu^2 = \frac{9\varepsilon_0 kT}{N}\frac{(\varepsilon - n^2)(2\varepsilon + n^2)}{\varepsilon(n^2+2)^2}, \tag{8}$$

while for measurements on dilute solutions of a polar solute in a non-polar solvent the dipole correlation factor in solution is given by [34]

$$g_1 = \frac{9kT\,\varepsilon_0(2\varepsilon + n_2^2)^2}{\mu^2 N_A X_2(n_2^2+2)^2(2\varepsilon+1)}\left[\frac{\varepsilon-1}{\varepsilon}\frac{X_1M_1 + X_2M_2}{d} - \frac{3X_1M_1(\varepsilon_1 - 1)}{d_1(2\varepsilon+\varepsilon_1)} - \frac{3X_2M_2(n_2^2-1)}{d_2(2\varepsilon+n_2^2)}\right]. \tag{9}$$

Here ε, d and n are permittivities, densities and refractive indices respectively: subscript 1 refers to pure solvent, subscript 2 refers to pure solute, and unsubscripted quantities are for solutions. X_1 and X_2 are mole fractions, while M_1 and M_2 are the molecular weights of solvent and solute molecules. In equations (8) and (9) μ is the free-molecule dipole moment.

3. Experimental and results

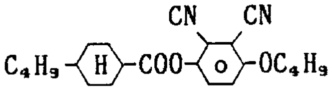
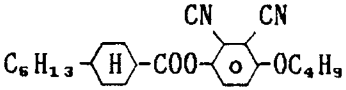
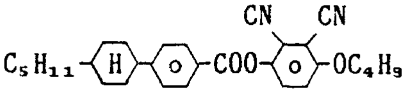
Our experimental technique for dielectric measurements in solution has been reported in earlier publications [2, 16]. For high-temperature measurements on the pure materials we used a stainless steel dielectric cell described in [17].

The materials studied together with a summary of their properties are given in table 1. Of these compounds, only 5HBENO4 has an enantiotropic nematic phase. We experienced some difficulty in making measurements in the nematic and isotropic phases of 5HBENO4 because of thermal decomposition, and these results are subject to significant uncertainty in the relative permittivity. Also, for this material we do not have refractive index or density data, so we relied on extrapolation from dilute solution measurements, which will contribute to uncertainty in the derived correlation factors for this material.

Our measurements of the permittivities of dilute solutions of the materials in *p*-xylene are given in figure 1, and a strong non-linear dependence on concentration is apparent. Correlation factors were obtained from these and measurements of solution densities and refractive indices, using equation (9). The derived values for g_1 are given in figure 2; these results refer to a temperature of 20°C. Measurements on the isotropic liquid state of the materials were made at elevated temperatures, but for 4HENO4 and 6HENO4 we were able to extrapolate to 20°C to obtain a value for g_1 corresponding to the pure state. These results fit well with the dilute solution measurements. The limited temperature range of measurements on 5HBENO4 together with experimental uncertainties prevented a similar extrapolation of g_1 for the pure material to 20°C. However, the value recorded at 150°C is not inconsistent with the dilute solution measurements. Derived values for the dipole correlation factors measured in the pure liquid state at different temperatures are recorded in table 2.

Nematic phase measurements for 5HBENO4 are given in figure 3. The material exhibited a strong negative permittivity anisotropy, and could be aligned satisfactorily with an external magnetic field of 0·6 T. Thermal decomposition limited the accuracy and reproducibility of the results. Measurements were made on three different

Table 1. Materials studied and summary of results.

Abbreviation	Structure	ε† (20°C)	K		S	N		I	Dipole moment/ Debye unit	g_1 (at transition point)
4HENO4		67	.	76°C	–	.	(55°C)	.	5·5	3·9 (K–I)
6HENO4		57	.	88°C	–	–		.	6·0	3·28 (K–I)
5HBENO4		–	.	143°C	–	.	150°C	.	6·4	1·84 (N–I)

† Extrapolated value.

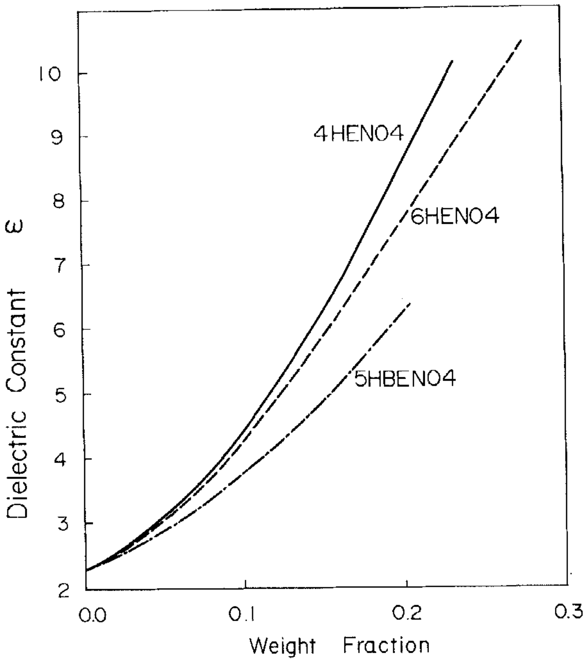


Figure 1. Permittivities of dilute solutions of 4HENO4, 6HENO4 and 5HBENO4 in *p*-xylene at 20°C.

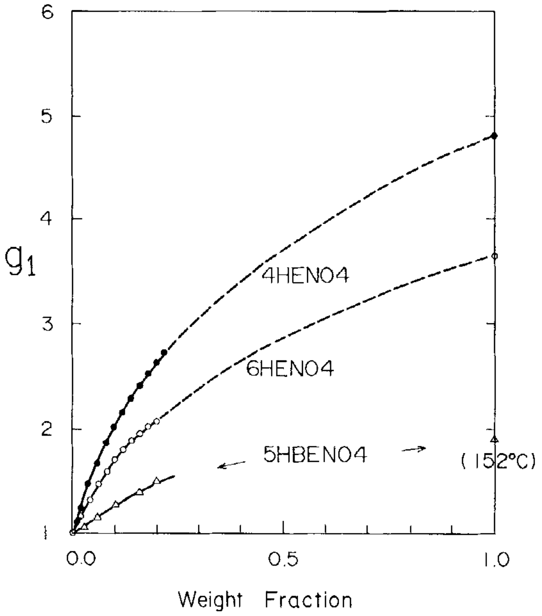


Figure 2. Dipole correlation factors g_1 as functions of weight fraction for *p*-xylene solution of dielectrically negative materials 4HENO4, 6HENO4 and 5HBENO4 at 20°C.

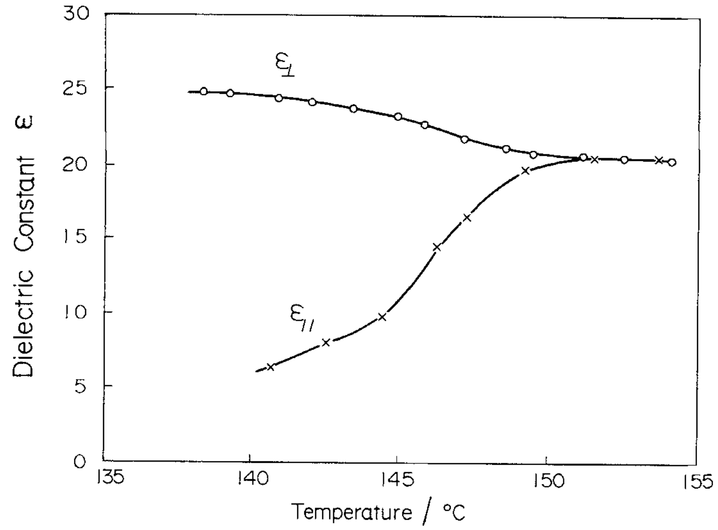


Figure 3. Permittivity of the dielectrically negative nematogen 5HBENO4.

Table 2. Kirkwood correlation factors g_l for pure materials 4HENO4, 6HENO4 and 5HBENO4.

4HENO4		6HENO4		5HBENO4	
T/K	g_l	*T*/K	g_l	*T*/K	g_l
368·6	3·72	371·2	3·21	151·1	1·86
370·4	3·70	373·6	3·20	151·2	1·93
371·9	3·68	375·3	3·19	151·6	1·92
373·8	3·66	377·2	3·18	152·5	1·86
375·8	3·64	379·3	3·17	153·8	1·93
377·3	3·63	380·8	3·16	154·1	1·86
379·2	3·62	382·0	3·15	154·2	1·93
381·2	3·60	383·7	3·14		
382·9	3·58	386·0	3·15		
384·9	3·56	387·9	3·13		
387·5	3·52	389·7	3·13		
388·9	3·50	391·4	3·12		
390·8	3·48	393·4	3·11		

samples, and in some cases it was possible to make repeat measurements on a single sample. A specimen set of results is given in figure 3, and we believe them to be reliable to ± 1 unit in the relative permittivity.

4. Discussion and conclusions

Molecules with large transverse dipole moments are of considerable interest in the context of liquid crystals from a number of standpoints. First, if the compounds form stable mesophases then they may have a negative dielectric anisotropy, and such materials can be used in positive-contrast guest–host displays [18] or in homeotropic-to-planar switched devices [19, 20]. Even if the compounds are not themselves mesogenic, they may be useful in formulating suitable liquid crystal mixtures. Two-frequency switched devices [1] often use mixtures of a relaxing component in a host of negative dielectric anisotropy to give the best switching characteristics. In this paper we have identified a new and important property of molecules with transverse dipole moments, which is their ability to order ferroelectrically. This results from an angle-dependent radial distribution function, which, coupled with the dipole–dipole tensor, favours parallel alignment of dipoles on interacting molecules. Such a result confirms our earlier proposal [6] that parallel dipole association should exist in liquid-crystalline systems.

It is only recently that compounds have been prepared with potential mesogenicity and moderate transverse dipole moments [20–30]. Although liquid-crystalline materials with very large positive dielectric anisotropies have been prepared (up to $+50$ [31]), it is apparently difficult to produce compounds with even moderate negative dielectric anisotropies. The work described in this paper has been concerned with the dielectric properties of some molecules with large transverse dipole moments. We have shown that these molecules associate in dilute solutions to give local ferroelectric order, and this persists into the pure liquid state. One of the materials studied, 5HBENO4, exhibited a nematic phase at high temperatures, and this has a large negative dielectric anisotropy ($\Delta\varepsilon \approx -10$). It is clear that local ferroelectric order is in part responsible for this high anisotropy, although we do not yet have sufficient data to be able to quantify the dipole correlation in the nematic phase. The discovery of materials with high negative dielectric anisotropy and strong local ferroelectric order will encourage continued research into new phase types and new applications for liquid crystals.

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