Dipole moments and dielectric properties of fluorine substituted nematic liquid crystals

D. G. McDonnell[a]; E. P. Raynes[a]; R. A. Smith[a]

[a] The Royal Signals and Radar Establishment, Worcestershire, England

PLEASE SCROLL DOWN FOR ARTICLE

Dipole moments and dielectric properties of fluorine substituted nematic liquid crystals

by D. G. McDONNELL, E. P. RAYNES and R. A. SMITH

The Royal Signals and Radar Establishment, St Andrews Road, Malvern, Worcestershire, England

The effect of lateral fluorine substituents on the dielectric properties of a range of nematic liquid crystals is reported. Measurements of dipole moments and electric permittivities have been made and used to calculate Kirkwood correlation factors over a range of temperature. The results show that the extent and nature of dipole correlations are important considerations in determining the magnitude of the dielectric anisotropy in these materials. Correlation factors up to 1·4 are found, providing good evidence for the presence of parallel dipole associations.

1. Introduction

Over recent years the liquid crystal materials requirements for optimizing the performance of twisted nematic and other field effect displays have become increasingly complex. In many instances the desire for fast optical response at low temperatures and for high multiplexibility are mutually exclusive with low operating voltages, since the former properties degrade with increasing dielectric anisotropy. Some of the effects of replacing a polar cyano end group with a non-polar alkyl group may be summarized as:

Advantages
    Low Δn—wider angle of view
    Small K_{33}/K_{11} and $\Delta\varepsilon/\varepsilon_\perp$—increased multiplexibility
    Decreased viscosity—faster response times
Disadvantages
    e.g. lower $\Delta\varepsilon$—increased drive voltage

Therefore, to enable liquid crystal material scientists to arrive at some satisfactory compromise, mixtures based on non-polar (low $\Delta\varepsilon$, high voltage) materials are subsequently doped with strongly polar (large $\Delta\varepsilon$, low voltage) liquid crystals. Clearly in order to ensure the least degradation to the desirable properties of the low polar host, it is preferable to use low concentrations of very strongly polar dopants with very large dielectric anisotropies. These are compounds with large longitudinal dipoles usually provided by a cyano end group as in the 4-n-alkyl-4'-cyanobiphenyls. However short range dipole–dipole interactions in these materials have been shown [1] to result in a considerable antiparallel ordering of the molecular dipoles which significantly reduces their contribution to electric permittivities.

Previous studies of the effect of 2- and 2'-fluorine substitution on the properties of the 4-n-alkyl 4'-cyanobiphenyls have shown that the presence of the lateral fluorine reduces the extent of this anti-parallel dipole ordering [2] and similar conclusions have

also been found from studies [3, 4] on 2- and 3-fluoro-4-cyanophenyl esters. The work of Toriyama and Dunmur [3] also proposed the presence of both parallel and anti-parallel dipole–dipole associations. In order to examine the effect of lateral fluorines on this short range ordering more fully, we have extended our previous work to a much wider range of compounds. The extent and nature of the short range associations are shown to depend on the molecular structure and are given by the Kirkwood correlation factor g [5], which relates the actual dipole (μ) to the effective dipole (μ_{eff}) calculated from the dielectric permittivity in the isotropic phase. Thus

$$\mu_{\mathrm{eff}}^2 \;=\; \mu^2 g,$$

where

$$\mu_{\mathrm{eff}}^2 \;=\; \frac{(\varepsilon - n^2)(2\varepsilon + n^2)}{\varepsilon(n^2 + 2)^2} \times \frac{9\varepsilon_0 kT}{(\varrho/\mathrm{MWt})N_{\mathrm{A}}}$$

and ε_0 is the permittivity of a vacuum, ε is the material permittivity, n is the refractive index, ϱ is the density and MWt is the molecular weight.

2. Experimental

Transition temperatures were measured using a polarizing microscope fitted with a Mettler FP52 heating stage and FP5 control unit. Refractive indices were measured to an accuracy of 0·01 per cent at 589·6 nm (D1 sodium line) using an Abbé refractometer. The dielectric permittivities were determined to an absolute accuracy of 1 per cent from the capacitance of a thin (25 μm) parallel plate capacitor surrounded by a guard electrode measured both empty and full of liquid crystal [6]. The perpendicular permittivity, $\varepsilon_\perp$, was determined directly from low voltage data using electrodes coated with SiO, and the parallel permittivity, $\varepsilon_\parallel$, from extrapolation of the high voltage data [6]. Dielectric constants are reported for individual materials by extrapolation from measurements on 10 per cent by weight solutions in a ternary mixture of I compounds, [7] whose chemical formula and properties are
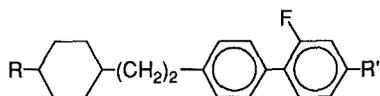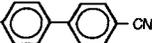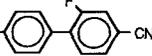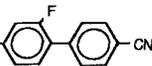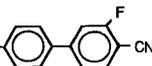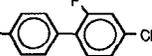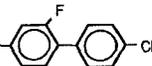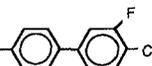

where $T_{\mathrm{NI}} = 100°\mathrm{C}$, $\varepsilon_\perp = 3·0$ and $\varepsilon_\parallel = 3·0$. Dipole moments were determined by extrapolation from refractive index and permittivity measurements on dilute (less than 10 per cent by weight) solutions in trans-1-*n*-propyl 4-(4'-ethylphenyl) cyclohexane (PCH32) using the method described by Raynes [8]. Densities were determined either by extrapolation from greater than 20 per cent by weight solutions in PCH32 or directly from measurements using an Anton Paar densiometer, model DMA 602HT. Kirkwood correlation factors [5] were computed from measurements of refractive indices and permittivities in the isotropic phase of the neat materials.

3. Results and discussion

As we have described, materials with a strong longitudinal dipole moment are essential components of mixtures for many field-effect liquid crystal displays, since they determine the magnitude of the dielectric anisotropy, and therefore the threshold voltage of the device. In order to develop further the highly successful

4-*n*-alkyl 4'-cyanobiphenyls for these applications, lateral fluorine substituents were added [9] in an attempt to increase the dielectric anisotropy by both increasing the longitudinal molecular dipole and reducing the extent of dipole–dipole anti-parallel associations. The dipole moments and extrapolated dielectric properties from 10 per cent by weight solutions of these 4-cyanobiphenyls in the low polarity I compound host are given in table 1. It should be noted that although the extrapolated dielectric anisotropies reported are compared at a fixed temperature (20°C), since this was well below the transition temperatures (> 90°C), order parameter effects were negligible.

Table 1. Lateral fluorinated cyanobiphenyls.

Material	Acronym	$T_{\rm NI}/°C$	Dipole moment μ/D	$\varepsilon_\perp$†	$\Delta\varepsilon$†
C_5H_{11}—⟨⟩—⟨⟩—CN	5CB	35	4·8	5·3	26·8
C_5H_{11}—⟨⟩—⟨F⟩—CN	2'F5CB	21	4·2	6·0	17·5
C_5H_{11}—⟨F⟩—⟨⟩—CN	2F5CB	0	5·2	7·3	29·6
C_5H_{11}—⟨⟩—⟨F⟩—CN	3'F5CB	−15	5·6	7·4	35·3
C_4H_9O—⟨⟩—⟨⟩—CN	4OCB	75	5·1	7·5	28·7
C_4H_9O—⟨⟩—⟨F⟩—CN	2'F4OCB	58	4·6	6·9	19·4
C_4H_9O—⟨F⟩—⟨⟩—CN	2F4OCB	35	5·7	7·9	33·0
C_4H_9O—⟨⟩—⟨F⟩—CN	3'F4OCB	18	5·9	8·0	38·4

† Extrapolated values from 10 wt % solutions in the I compounds at 20°C.

In general the extrapolated dielectric anisotropies scale with the square of the dipole moments, as predicted by the Maier–Maier equation, since at very low concentrations (less than 10 per cent by weight) in the low polarity solvent there should be little or no dipole–dipole associations (i.e. the Kirkwood *g* factor is effectively unity), and, when the transverse dipole moment is zero

$$\Delta\varepsilon = \Delta(n^2) + A\,\frac{\mu^2 S}{kT},$$

where μ is the longitudinal dipole and S is the order parameter. Therefore, although at low concentrations (< 10 per cent by weight) the effect of dipole–dipole correlations on dielectric anisotropies can be largely ignored, in practice the amount of polar dopants used in mixtures is normally greater than this and some regard must be given to both the extent and nature of these associations. Since not all of the dopants studied exhibited enantiotropic liquid-crystalline phases, in order to examine how fluorine substituents alter the degree of association, the Kirkwood correlation factors were calculated from the isotropic permittivities and these are plotted as a function of
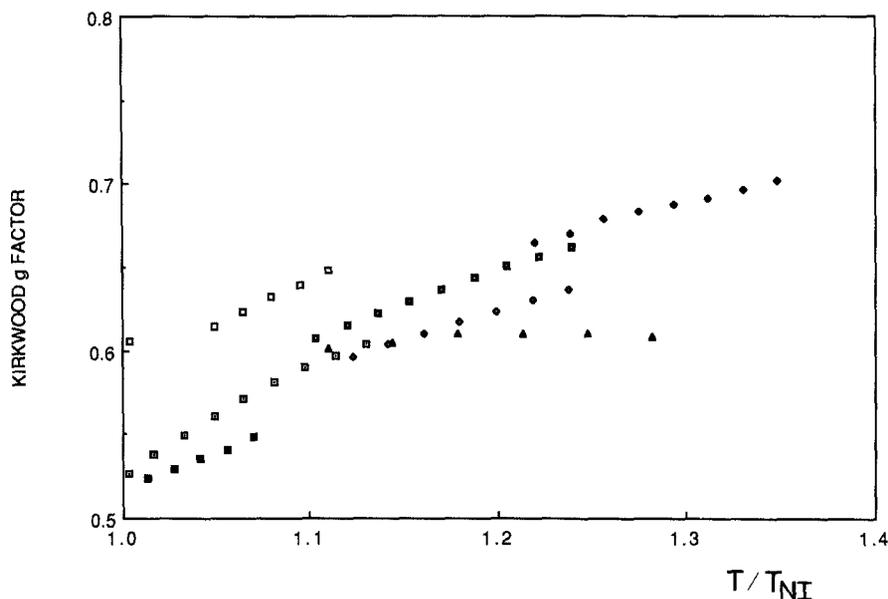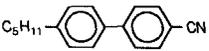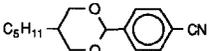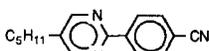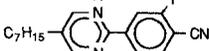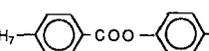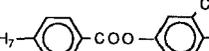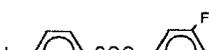
Figure 1.   Kirkwood correlation factors as a function of the reduced temperature for some of the biphenyl materials in table 1. □ = 5CB, ◆ = 2F5CB, ■ = 2′F5CB, ◇ = 3′F5CB, ■ = 4OCB, □ = 2′F4OCB, ▲ = 3′F4OCB.

reduced temperature in figure 1. For the alkyl homologues, g is increased by $\sim 0\cdot01$ whilst for the alkyloxy derivatives it is increased by $\sim 0\cdot1$.

In heterocyclic and ester materials, as shown in table 2, larger dipoles are obtained from the additional contribution of the hetero atoms or carbonyl groups and these are reflected in both the extrapolated perpendicular and parallel permittivity components and in the dielectric anisotropy. Once again, as expected, these results are

Table 2.   Heterocyclic and ester materials.

Material	Acronym	$T_{NI}/°C$	Dipole moment μ/D	$\varepsilon_{\perp}$†	$\Delta\varepsilon$†
C_5H_{11}—⬡—⬡—CN	5CB	35	4·8	5·3	26·8
C_5H_{11}—⬡—⬡—CN	5PDX	21	5·7	8·2	29·6
C_5H_{11}—⬡—⬡—CN	5PYR	0	6·0	7·6	43·5
C_7H_{15}—⬡—⬡—CN	3′F7PYR	24	6·9	8·3	48·3
C_3H_7—⬡—COO—⬡—CN	3CBE	51	5·8	7·4	35·1
C_3H_7—⬡—COO—⬡—CN	3′Cl3CBE	–	6·4	10·5	50·0
C_3H_7—⬡—COO—⬡—CN	3′F3CBE	16	6·3	9·8	51·9

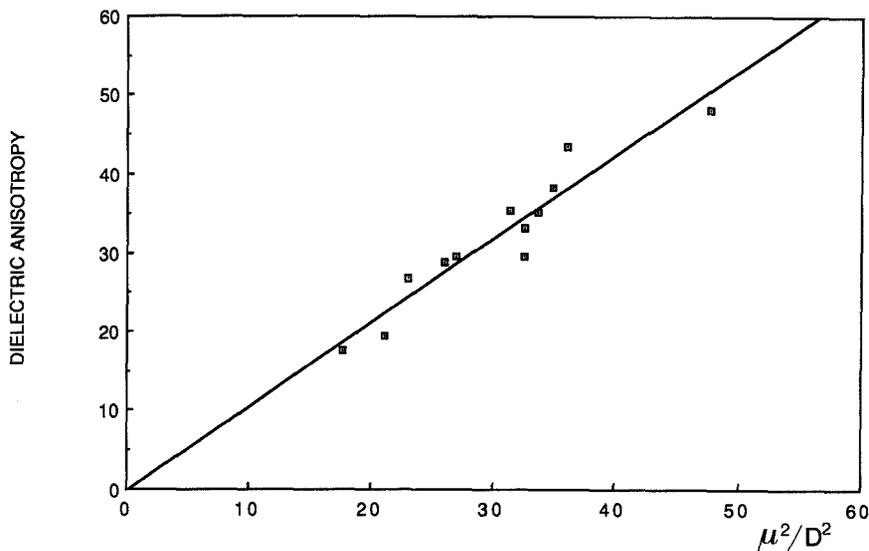† Extrapolated values from 10 wt % solutions in the I compounds at 20°C.

Figure 2. Plot of extrapolated dielectric anisotropies against dipole moment squared for the materials reported in tables 1 and 2. The interpolated line is the prediction from the Maier–Meir equation.

in good agreement with the Maier–Maier equation and $\Delta\varepsilon$ is proportional to μ^2 (see figure 2).

In the isotropic phase of the heterocyclic materials, the correlation factors (see figure 3) reflect a significant degree of anti-parallel associations, and fluorination in the case of the pyrimidine, actually decreases g slightly. However, exceptionally in the
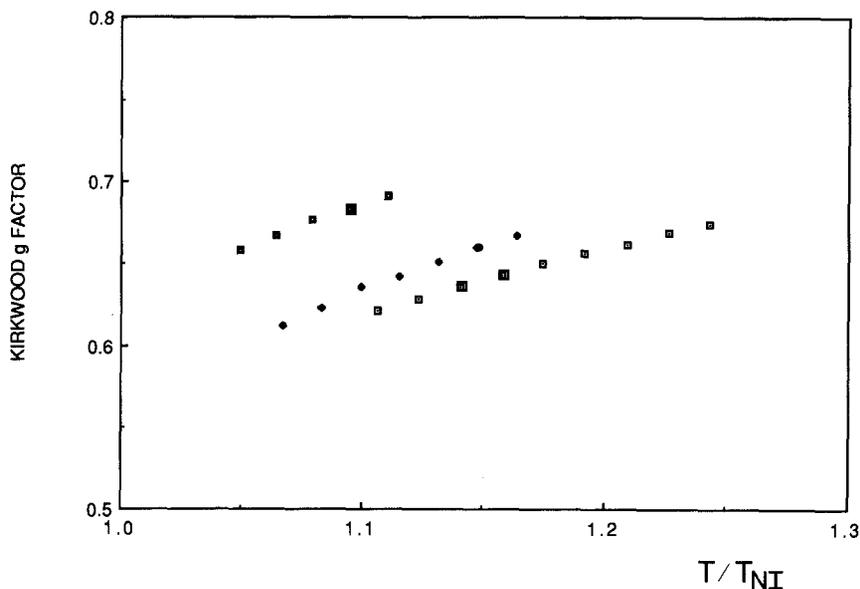
Figure 3. Kirkwood correlation factors plotted against the reduced temperature for some of the heterocyclic compounds reported in table 2. □ = 3′F7PYR, ◆ = 5PDX, ▣ = 5PYR.
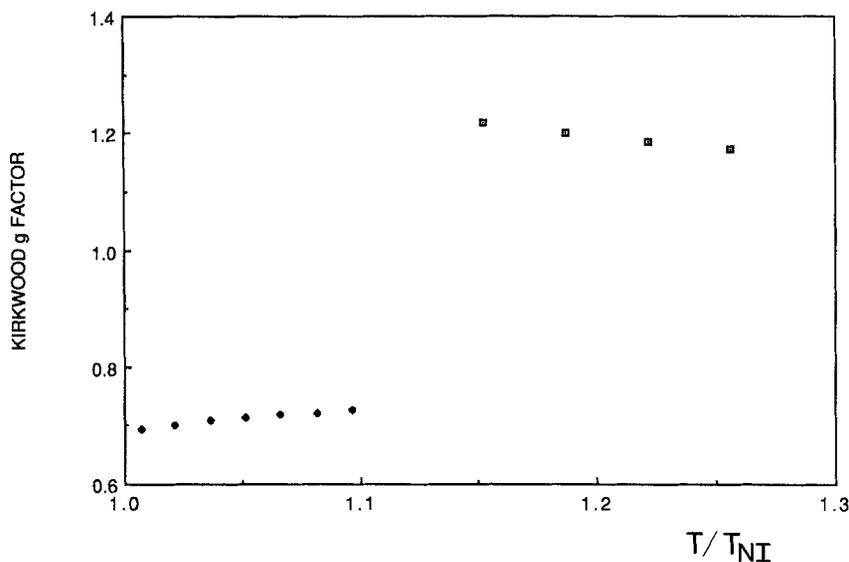
Figure 4. Kirkwood correlation factors as a function of the reduced temperature for two cyanobenzoate esters. □ = 3'F3CBE, ◆ = 5CBE.
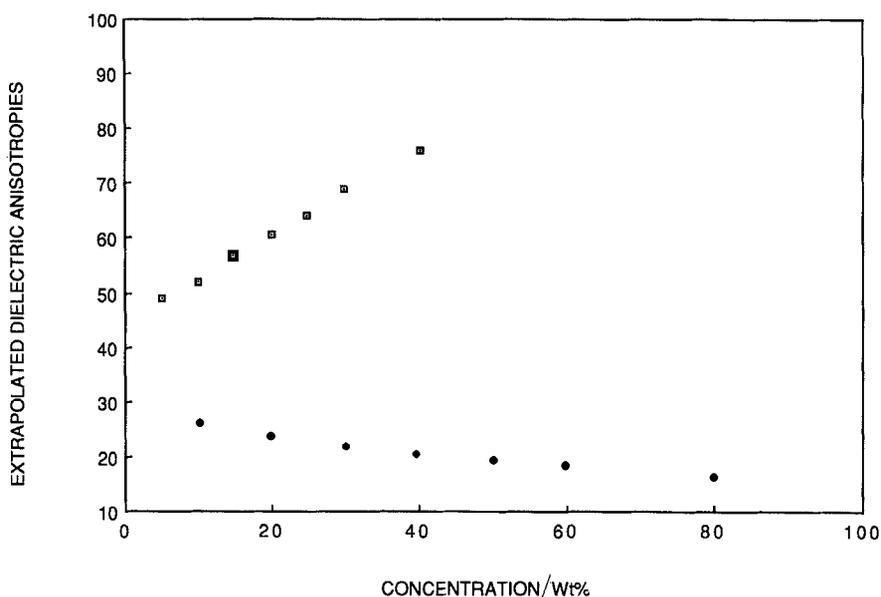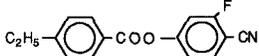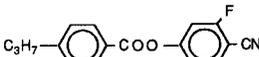
Figure 5. A comparison of the extrapolated dielectric anisotropies as a function of concentration for 3'F3CBE and 5CB. □ = 3'F3CBE, ◆ = 5CB.

case of the esters (see figure 4), the effect of the 3'-fluoro substituent produces a correlation factor g of greater than 1, and is direct evidence in support of the concept of parallel associations proposed by Toriyama and Dunmur [3]. This is further illustrated with reference to figure 5 in which the extrapolated dielectric anisotropies ($\Delta\varepsilon$) of 3' F3CBE and 5CB are plotted as a function of the concentration from which the values were obtained. All of the measurements were made at 20°C in the I

compound ternary mixture host. The negative slope for the 5CB curve is typical for a material with strong anti-parallel dipole–dipole associations which is reduced on dilution. On the other hand the steeply rising slope for the 3′-fluoro-substituted ester suggests the presence of parallel dipole–dipole associations which disappear, causing the extrapolated dielectric anisotropy to decrease on dilution.

To examine this unusual behaviour in the esters more fully we have also studied the other alkyl homologues of the 3′-fluoro-substituted esters as well as some multi-fluorinated analogues [10] (see table 3). Unfortunately the additional fluorines reduced the solubility in the low polarity host and prevented comparative measurements of the permittivities. The correlation factors for selected samples from table 3 are shown in figure 6 as a function of the reduced temperature.

Table 3. Lateral fluorinated benzoate esters.

Material	Acronym	$T_{NI}/°C$	Dipole moment μ/D	$\varepsilon_\perp$†	$\Delta\varepsilon$†
C_2H_5–◯–COO–◯–CN	3′F2CBE	0	6·6	–	–
C_3H_7–◯–COO–◯–CN	3′F3CBE	16·0	6·6	9·8	51·9
C_5H_{11}–◯–COO–◯–CN	3′F5CBE	24·0	6·6	9·3	41·6
C_7H_{15}–◯–COO–◯–CN	3′F7CBE	28	6·6	8·5	41·7
C_5H_{11}–◯–COO–◯–CN	2,6F5CBE	−7	6·8	–	–
C_5H_{11}–◯–COO–◯–CN	2,6,3′F5CBE	−13	7·4	19	40·0
C_4H_9O–◯–COO–◯–CN	2F4OCBE	61	6·9	7·5	42·6
C_4H_9O–◯–COO–◯–CN	2,3′F4OCBE	21·5	7·5	10·7	53·9
C_4H_9O–◯–COO–◯–CN	2,6,3′F4OCBE	27	7·9	9·9	54·2
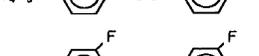
† Extrapolated values from 10 wt % solutions in the I compounds at 20°C.

The extent of parallel dipole–dipole associations for the 3′-fluoro 4′-cyanophenyl esters decreases with increasing alkyl chain length and the additional fluorines also tend to reduce rather than enhance parallel dipole–dipole associations. The extent of the parallel dipolar interactions of the 3′-fluoro esters, particularly for the ethyl homologue appears unique and gives rise to nematogens with very large dielectric anisotropies. This is seen very clearly in the variation of the permittivities with temperature of a binary mixture (50/50) of the pentyl and heptyl derivatives (T_{NI} of 24°C) measured at 1 kHz which has a dielectric anisotropy of 60 (see figure 7).
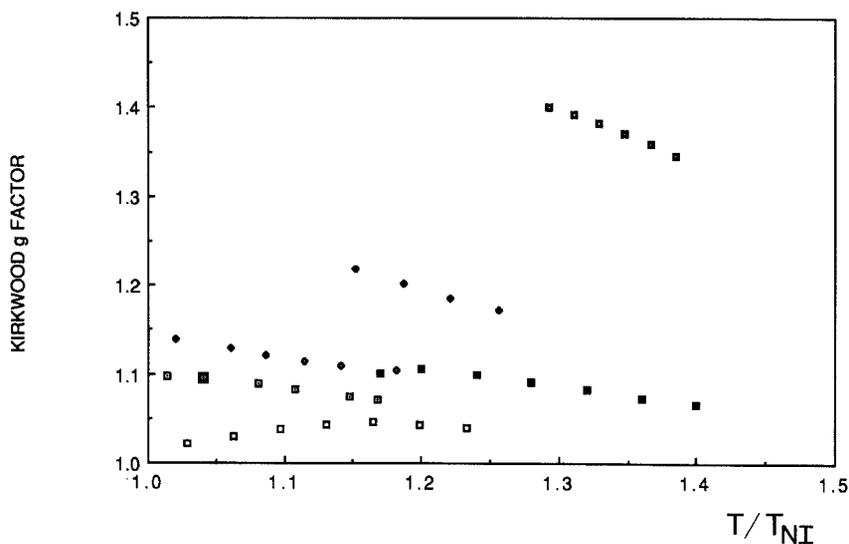
Figure 6. Kirkwood correlation factors plotted against the reduced temperature for some of the esters reported in table 3. □ = 3′F7CBE, ◆ = 3′F3CBE, ▣ = 3′F2CBE, ◆ = 3′F5CBE, ■ = 2,6,3′F5CBE, ☐ = 2,3′F4OCBE.
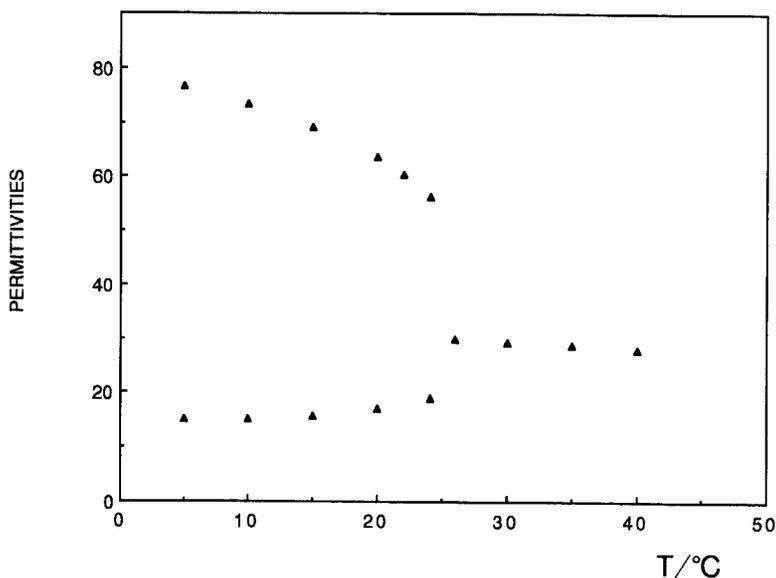

Figure 7. The permittivities as a function of temperature for a 50/50 binary mixture of 3′F5CBE and 3′F7CBE measured at 1 kHz.

4. Conclusions

The effects of lateral fluorine substituents on the dipolar and subsequent dielectric properties of a wide range of materials with large positive dielectric anisotropies have been studied. The increase in the molecular dipole is greatest ($\sim 0.8\,D$) when the fluorine is ortho to the cyano group. In dilute solutions (10 per cent by weight) in a low polarity host, when the Kirkwood correlation factor approximates to 1, the

increase in dipole moment is reflected in extrapolated values of $\Delta\varepsilon$. Fluorination has also been shown to alter the correlation factor of the undiluted materials in their isotropic phases. For the cyanobiphenyls, it is increased by ~ 0.01 for the alkyls and by ~ 0.1 for the alkyloxy derivatives. Exceptionally in cyano benzoate esters, the 3'-fluoro substituent produces *g* factors of up to 1.4, significantly higher than the value of 1 reported by Schad and Kelly [4] for the heptyl homologue. This large *g* factor provides evidence in support of the concept of parallel associations proposed by Toriyama and Dunmur [3].

References

[1] DUNMUR, D. A., MANTERFIELD, M. R., MILLER, W. H., and DUNLEAVY, J. K., 1978, *Molec. Crystals liq. Crystals*, **45**, 127.
[2] McDONNELL, D. G., RAYNES, E. P., and SMITH, R. A., 1985, *Molec. Crystals liq. Crystals*, **123**, 169.
[3] TORIYAMA, K., and DUNMUR, D. A., 1985, *Molec. Phys.*, **56**, 479.
[4] SCHAD, HP., and KELLY, S. M., 1985, *J. Phys., Paris*, **46**, 1395.
[5] KIRKWOOD, J. G., 1939, *J. chem. Phys.*, **7**, 911.
[6] CLARK, M. G., RAYNES, E. P., SMITH, R. A., and TOUGH, R. J. A., *J. Phys.* D, **13**, 2151.
[7] B.D.H. Ltd, Broom Road, Poole, Dorset.
[8] RAYNES, E. P., 1985, *Molec. Crystals liq. Crystals Lett*, (3–4) 69.
[9] GRAY, G. W., HIRD, M., IFILL, A., LACEY, D., and TOYNE, K. J. (unpublished results).
[10] GRAY, G. W., HIRD, M., LACEY, D., SCROWSTON, R. M., and TOYNE, K. J., 1988, Presented at the XII International Liquid Crystal Conference, Freiburg, paper SY03.