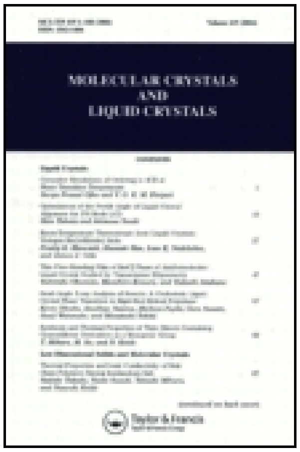

Molecular Crystals and Liquid Crystals
Publication details, including instructions for authors and subscription information:
http://www.tandfonline.com/loi/gmcl16

The Physical and Molecular Properties of Some Nematic Fluorobiphenylalkanes

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To cite this article: D. A. Dunmur , D. A. Hitchen & Hong Xi-jun (1986): The Physical and Molecular Properties of Some Nematic Fluorobiphenylalkanes, Molecular Crystals and Liquid Crystals, 140:2-4, 303-318

To link to this article: http://dx.doi.org/10.1080/00268948608080160

Mol. Cryst. Liq. Cryst., 1986, Vol. 140, pp. 303–318
0026-8941/86/1404-0303/$20.00/0

Printed in the United States of America

The Physical and Molecular Properties of Some Nematic Fluorobiphenylalkanes

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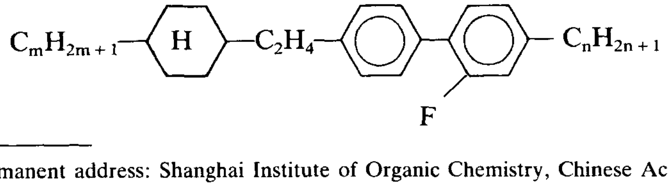
(*Received February 10, 1986*)

Measurements are reported of the electric permittivities, refractive indices and elastic constants for four members of the homologous series of alkyl-cyclohexyl alkyl-fluorobiphenyl ethanes. The results are analysed to give values for the order parameters of the nematogens, and in conjunction with dilute solution measurements on the mesogens yield values for the molecular properties of dipole moment and polarisability. The dielectric anisotropy of the materials is measured to be close to zero (~0.05), and changes sign from negative to positive with increasing temperature.

Keywords: nematic phases, fluorobiphenylalkanes

INTRODUCTION

The physical characterisation of new mesogens is an essential part of the development of liquid crystal materials for applications. Requirements for optimal operation of various devices are now established,[1] and further progress in their development relies on the preparation of materials with the necessary physical properties. A new class of mesogens that has attracted attention is the fluorinated cyclohexylbiphenylethanes[2,3] of general structure I_{mn}:



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Members of this homologous series have remarkably wide nematic ranges, between 0 and 100°C. They also have low viscosities, and so are of great potential use in preparing device mixtures. As well as enhancing the nematic properties of these molecules, the laterally substituted fluorine atom suppresses the tendency of the parent hydrocarbon to form smectic phases.[3] In view of the great utility of the I compounds as device materials, we have carried out an extensive study of the physical and molecular properties of four members of the series, I_{22}, I_{32}, I_{52} and I_{35}.

One characteristic of these compounds is their low mean permittivity and permittivity anisotropy. This is a result of the relatively small dipole moment of the C—F bond and the angle it makes with the principal inertial axis of the molecules. The small anisotropy in the permittivity (~0.05) is difficult to measure accurately, and as a consequence the determination of elastic constants from electric field-induced Freedericksz transitions is subject to error. Another complication of these materials, which will be discussed in more detail below, is the change in sign of the dielectric anisotropy with temperature.

EXPERIMENTAL

The electric permittivities were measured using a calibrated stainless steel cell, thermostatted to ± 0.1°C by a circulating fluid, and containing parallel plate electrodes of separation 1 mm. The liquid crystal was aligned parallel and perpendicular to the cell electrodes by an external magnetic field of 0.6 T. Complete alignment of the director was verified by measuring the capacitance of the cell as a function of magnetic field: saturation was usually achieved with field strengths of 0.3 T. Capacitance measurements were made at 1592 Hz using a Wayne Kerr B331 bridge.

At temperatures below 80°C, refractive indices were measured at 633 nm using an Abbé refractometer and homeotropic alignment of mesogenic samples was achieved by coating the prisms with a surfactant. For temperatures in excess of 80°C the refractometer could not be used, and refractive indices were measured by observing the refracted ordinary and extraordinary rays through a small thermostatted wedge-shaped cell placed between the poles of an electromagnet. The cell is illustrated in Figure 1. Results obtained with this cell were in good agreement with those obtained using the Abbé refractometer in an overlapping temperature range, and so we have

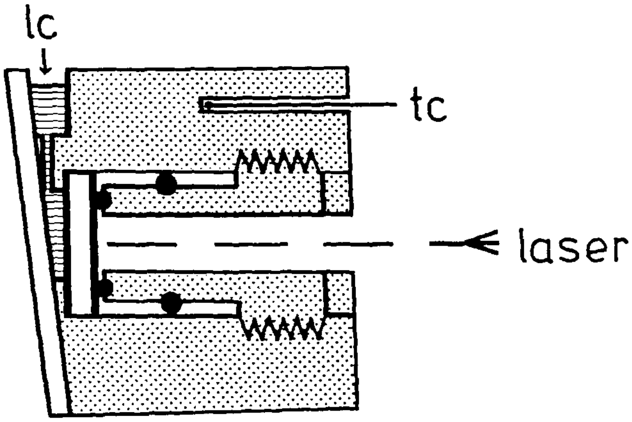

FIGURE 1 Demountable high temperature refractive index cell—*tc* = thermocouple; *lc* = liquid crystal.

been able to extend refractive index measurements to much higher temperatures.

Splay and bend elastic constants for the materials were derived from analysis of the capacitance/voltage curves for aligned cells subjected to a varying electric field. Because of the small electric permittivity anisotropy ($\Delta\epsilon$) of the I compounds, the threshold voltages for electric field-induced Freedericksz transitions are high (~10 V), and a further complication is the change in sign of $\Delta\epsilon$ with temperature. Our computer-controlled capacitance/voltage measurement system is described in detail elsewhere[4]: it enables the permittivity of a sample to be measured at a chosen frequency in the presence of a varying bias voltage at a different non-harmonic frequency. For the measurements reported in this paper, the varying bias voltage was at a frequency of 500 Hz, while the capacitance probe voltage was 200 mV at ~1000 Hz. Typical response curves for the materials studied are given in Figure 2. The small $\Delta\epsilon$ of these compounds limits the accuracy of the elastic constants, and analysis of the C/V curves is only reliable for the planar to homeotropic transition, which restricted measurements to temperatures for which $\Delta\epsilon$ was positive. Suitable cells for measurements of the planar to homeotropic Freedericksz transition were prepared in our laboratory using rubbed polyvinyl alcohol as the aligning surface: cells were typically, 27 μm thick. To obtain elastic constants for the I materials in regions of temperature where $\Delta\epsilon$ is negative, we have relied upon threshold voltage measurements. These were obtained for homeotropically aligned samples subjected to an electric field; values obtained from capacitance/

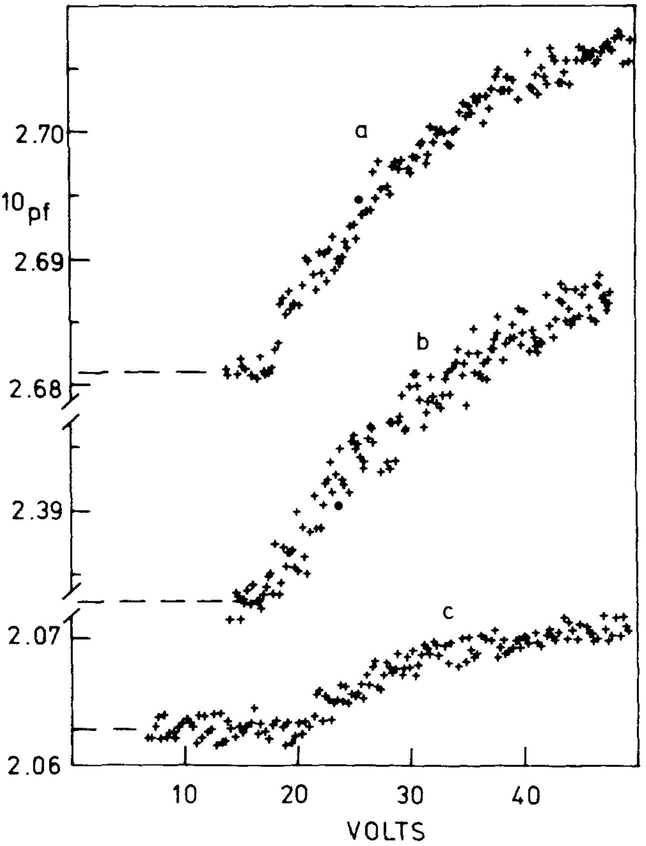

FIGURE 2 Response curves for the planar to homeotropic Freedericksz transition—(a) I35; (b) I52; (c) I32.

voltage curves were confirmed by determining the threshold for optical deformation from electric field-induced birefringence measurements.

Molecular properties for the I compounds reported in this paper were obtained from dilute solution measurements of densities, refractive indices and electric permittivities using methods described by us in earlier papers.[5,6] Densities were measured using an Anton Paar DMA 602 HT digital densimeter, while refractive indices and permittivities were obtained as described above. Cells for solution permittivity measurements were constructed from glass plates with a suitable electrode pattern deposited on them and separated by dispersed glass fibres of diameter 17 μm. All solution measurements were made at a temperature of 25.0 ± 0.1°C.

PHYSICAL PROPERTIES

The electric permittivities and refractive indices of I22, I32, I35 and I52 are presented in Figures 3–6. The most significant feature of the dielectric results is that the anisotropy changes from negative to positive with increasing temperature in the nematic phase. Of the compounds studied, those with shorter terminal alkyl chains have a cross-over temperature ($T_{\Delta\epsilon=0}$) at higher reduced temperatures than the homologues with longer chains. Because of the low values of the permittivities (~3.0), the absolute accuracy of the measurements reported is only ±3%, however we are confident of the precision of the measurements of anisotropy, particularly since the cross-over

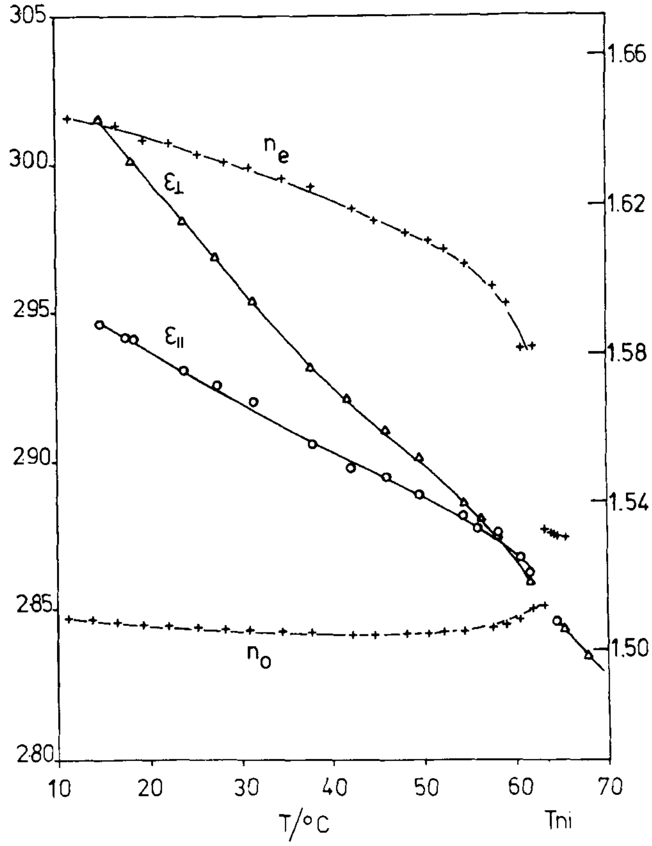

FIGURE 3 Electric permittivities (left-hand scale) and refractive indices (right-hand scale) of I22.

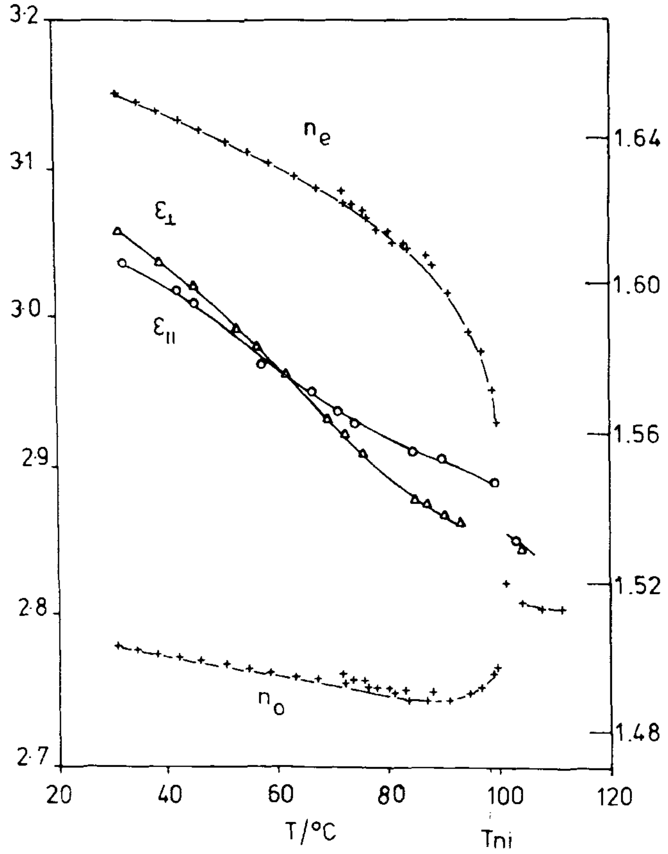

FIGURE 4 Electric permittivities (left-hand scale) and refractive indices (right-hand scale) of I32.

temperatures were largely confirmed by observations of Freedericksz transitions in homeotropic and homogeneous cells. Another interesting observation is the non-monotonic dependence of $\epsilon_\parallel$ on temperature in all the materials studied except I_{22}. The anomalous variation of $\epsilon_\parallel$ with temperature appears to be connected with the change in sign of $\Delta\epsilon$, and is masked for I_{22} by the proximity of $T_{\Delta\epsilon=0}$ to the nematic/isotropic transition temperature T_{NI}.

A feature of the I materials is their wide nematic ranges, within which the birefringence can vary from 0.2 to 0.1. Measurements of the refractive indices at high temperatures using a wedged-shaped cell matched well with low temperature results taken from an Abbe refractometer.

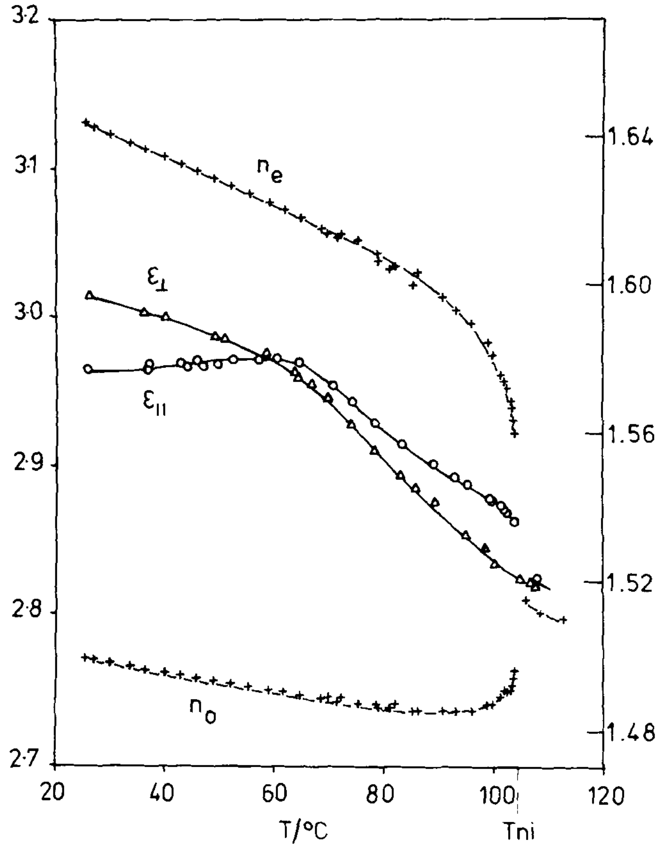

FIGURE 5 Electric permittivities (left-hand scale) and refractive indices (right-hand scale) of I52.

The simplest method of obtaining values for the elastic constants of nematic materials is to measure the threshold voltage for an electric field-induced Freedericksz transition[7]:

$$k_{ii} = V_i^2 \epsilon_0 \Delta\epsilon / \pi^2 \quad (i = 1, \text{ splay}; \ i = 3, \text{ bend}) \qquad (1)$$

V_1 is the threshold voltage for the transition planar to homeotropic, which can be observed in materials of positive dielectric anisotropy; V_3 is the threshold voltage for the homeotropic to planar transition observed for materials with $\Delta\epsilon$ negative. Threshold voltages V_1 and V_3 are plotted in Figure 7 as a function of temperature for I_{52}: these values were obtained by viewing under a polarising microscope cells

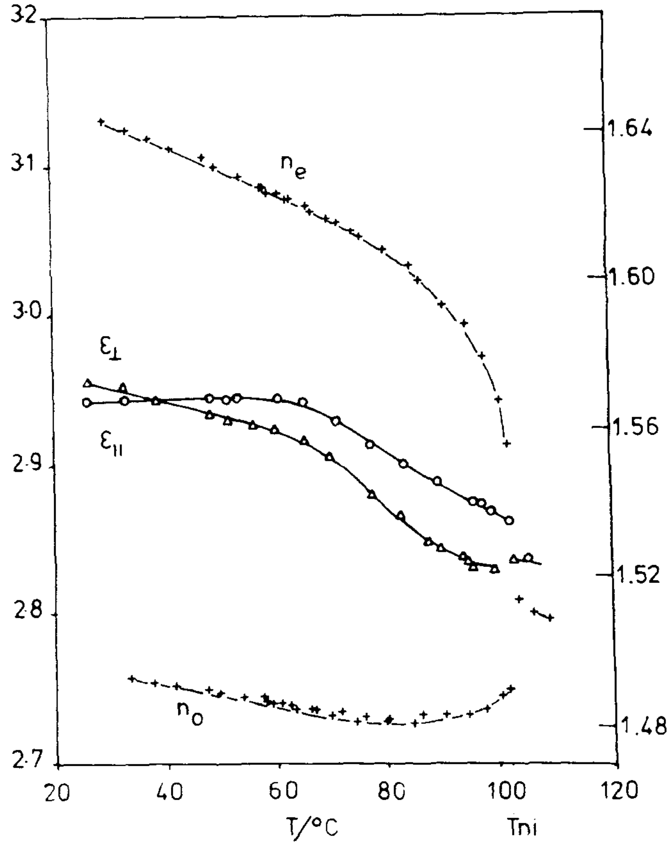

FIGURE 6 Electric permittivities (left-hand scale) and refractive indices (right-hand scale) of I35.

of different initial alignment subjected to a varying voltage. The curves V_1 and V_3 cross at a temperature which corresponds to $T_{\Delta\epsilon=0}$. Theoretically the voltage/temperature curves should be asymptotic to the line $T = T_{\Delta\epsilon=0}$, but the long relaxation time at the Freedericksz transition prevents this.

Measurements of k_{11} and k_{33} were obtained by fitting the capacitance/voltage data to the Euler-Lagrange equations for planar to homeotropic transitions, using essentially the method outlined by Deuling.[8] This procedure was only appropriate for I materials at temperatures such that $\Delta\epsilon$ is positive. Estimates of elastic constants for temperatures where $\Delta\epsilon < 0$ were obtained from threshold voltage measurements for the homeotropic to planar transition.

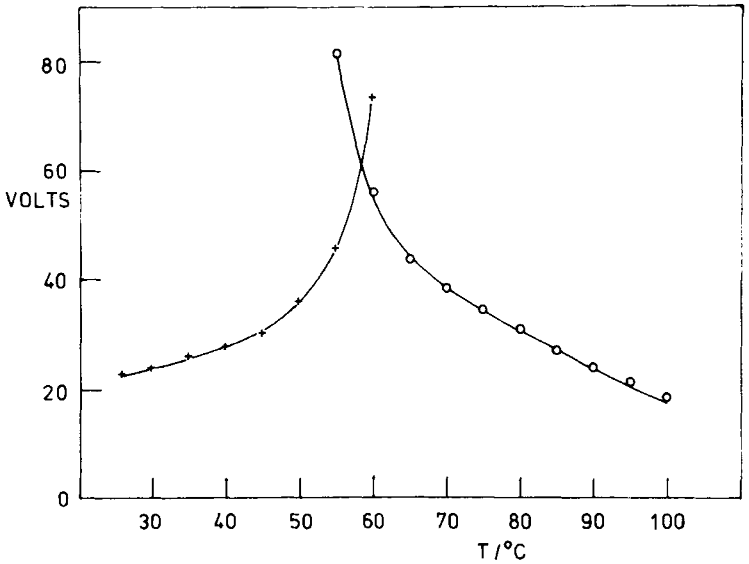

FIGURE 7 Threshold voltages measured by optical microscopy for homeotropic to planar (+ = V_3) and planar to homeotropic (○ = V_t) Freedericksz transitions in I52.

Results for the physical properties of the I materials studied are given in Table I. There is considerable error associated with the measurements of the dielectric anisotropy, especially close to $T_{\Delta\epsilon=0}$, and this contributes directly to the uncertainties in the measured elastic constants. We find that both k_{11} and k_{33} increase with increasing alkyl chain lengths. The low values for I_{32} must be viewed with caution since they are directly proportional to the low measured values of $\Delta\epsilon$ for this compound. Because of the very small $\Delta\epsilon$, our values for the elastic constants are subject to considerable error. However, threshold voltages should be accurate to ±1% and values of $\kappa = (k_{33} - k_{11})/k_{11}$ to 5%. The ratio k_{33}/k_{11} is considerably in excess

TABLE I

Physical properties[a] of I materials

Liquid crystal	T_{NI}(°C)	Density (25°C) (g cm^{-3})	$\epsilon_{\parallel}$	$\epsilon_{\perp}$	n_e	n_0	V_t	k_{11} (10^{-12} N)	k_{33} (10^{-12} N)	κ
I22	64	1.0163	2.89	2.91	1.6148	1.5037	—			
I32	99	1.0156	2.94	2.93	1.6108	1.4893	17.3	4.5	7.8	0.73
I52	103	1.003	2.91	2.87	1.6013	1.4824	18.4	9.4	16.3	0.66
I35	102	0.9975	2.92	2.89	1.6021	1.4851	18.9	10.8	18.9	0.75

[a] Measured at a reduced temperature $T/T_{NI} = 0.95$.

of one, which is in contrast to nematic mixtures doped with fluorine containing nematogens.

ORDER PARAMETERS

Before any correlation can be made between macroscopic and molecular properties in liquid crystals, it is necessary to know the orientational order parameter (S). Various techniques are available for measuring nematic order, of which the simplest is from refractive indices using the relation:

$$\frac{n_e^2 - n_0^2}{\overline{n}^2 - 1} = \frac{\Delta\alpha}{\alpha} S(T) \tag{2}$$

The effective polarisability α and the polarisability anisotropy $\Delta\alpha$ are usually obtained by an extrapolation procedure, which involves assuming a functional form for the temperature dependence of $S(T)$, and extrapolating the measured refractive indices to 0 K where $S = 1$. Haller's procedure[9] is based on the assumption that the dependence of order parameter on temperature can be represented by:

$$S(T) = \left(1 - \frac{T}{T_{\mathrm{NI}}}\right)^{\beta} \tag{3}$$

Recently Bradshaw and Tough[10] have described a method of obtaining order parameters from measured anisotropies by fitting results to a mean field function of temperature. They assume that the order parameter can be written as:

$$S = \frac{\int P_2(\cos\theta)\exp - (\gamma S P_2(\cos\theta)/T)\, d(\cos\theta)}{\int \exp - (\gamma S P_2(\cos\theta)/T)\, d(\cos\theta)} \tag{4}$$

The quantity γ is regarded as an adjustable parameter, and is not simply related to T_{NI} as required by the Maier–Saupe theory. A simple recursive method for obtaining solutions of Eq. (4) is described in Ref. 10, however we would like to correct a misprint in Eq. (A4) of Ref. 10, which is correctly given in the footnote.† Having determined

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† $$\overline{P}_{n-2}(\lambda) = \left[\frac{2n-1}{2n+3}\right]\left[\frac{n+2}{n-1}\right]\overline{P}_{n-2}(\lambda) + \frac{(2n+1)(2n-1)}{2\lambda(n-1)} \cdot \left[1 - \frac{2\lambda}{(2n-1)(2n+3)}\right]\overline{P}_n(\lambda)$$

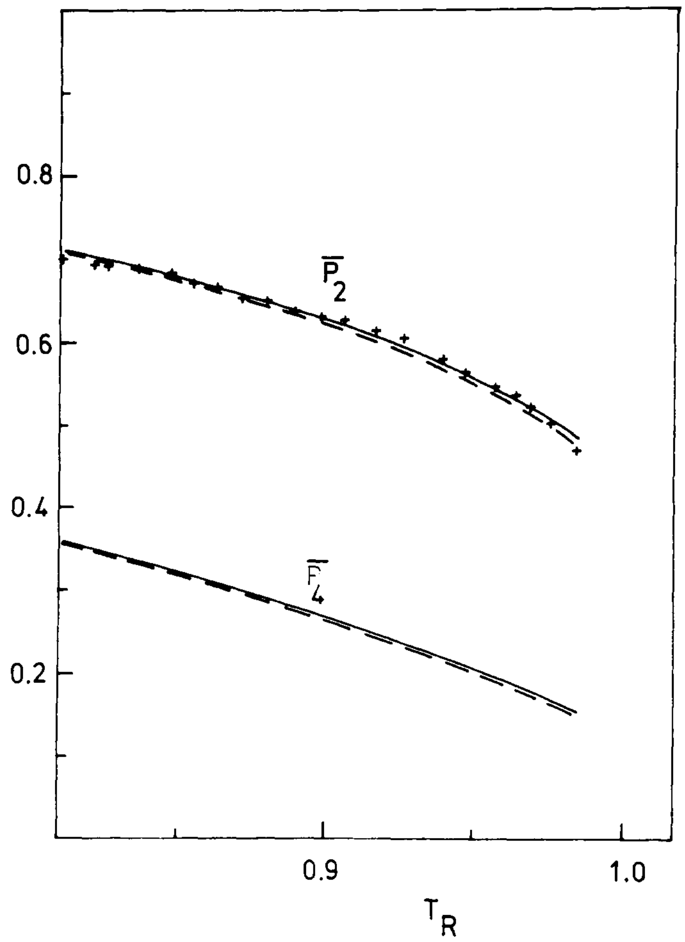

FIGURE 8 Order parameters against reduced temperature ($T_R = T/T_{NI}$) for I22.

a best fit value for γ it is simple to obtain higher order parameters such as $\overline{P_4(\cos\theta)}$:

$$\overline{P_4(\cos\theta)} = \frac{\int P_4(\cos\theta)\exp - (\gamma S P_2(\cos\theta)/T)\, d(\cos\theta)}{\int \exp - (\gamma S P_2(\cos\theta)/T)\, d(\cos\theta)} \tag{5}$$

Results for the order parameters obtained from our measurements of refractive indices for I_{22}, I_{32}, I_{52} and I_{35} using the Bradshaw–Tough method are given in Figures 8–11. In each of the graphs, the corresponding Maier–Saupe values, for which $\gamma = -4.5415\ T_{NI}$, are plotted as broken lines. It is clear that the mean field function Eq. (4)

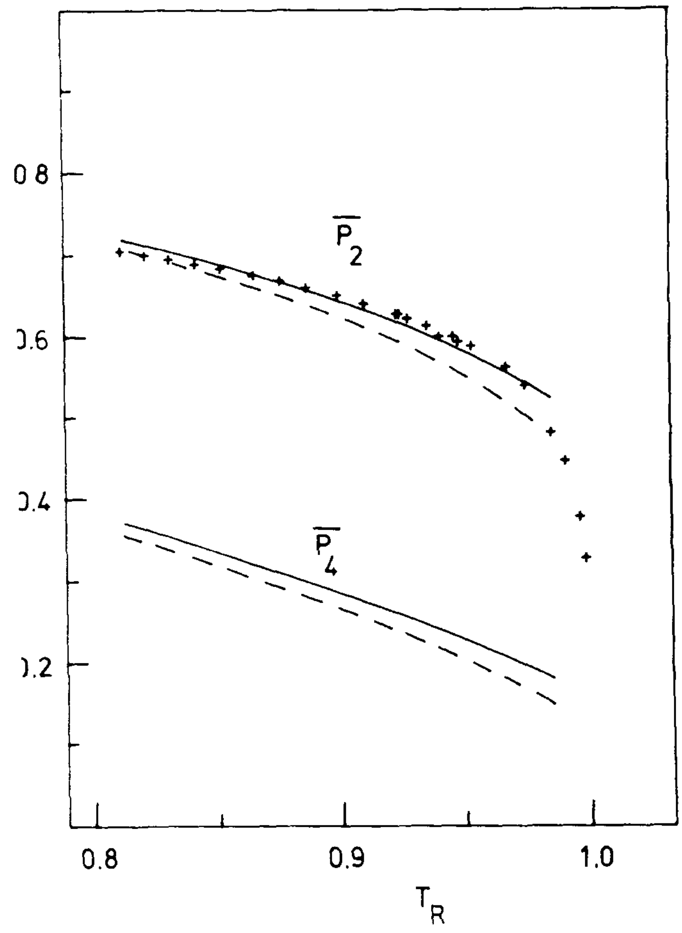

FIGURE 9 Order parameters against reduced temperature ($T_R = T/T_{NI}$) for I32.

is not accurate close to the nematic/isotropic transition, and in common with most materials the order parameter S of the I materials is lower than the mean field values close to this transition. In spite of this, the long nematic ranges of the I compounds studied here have allowed us to fit experimental results for the refractive indices over a range of temperature of at least 50°. The agreement between measured order parameters and Maier–Saupe values improves as the terminal alkyl chains get shorter, and for I_{22} is almost perfect. Close to T_{NI} there is a pretransitional reduction in S, which becomes more significant as the terminal alkyl chain length increases.

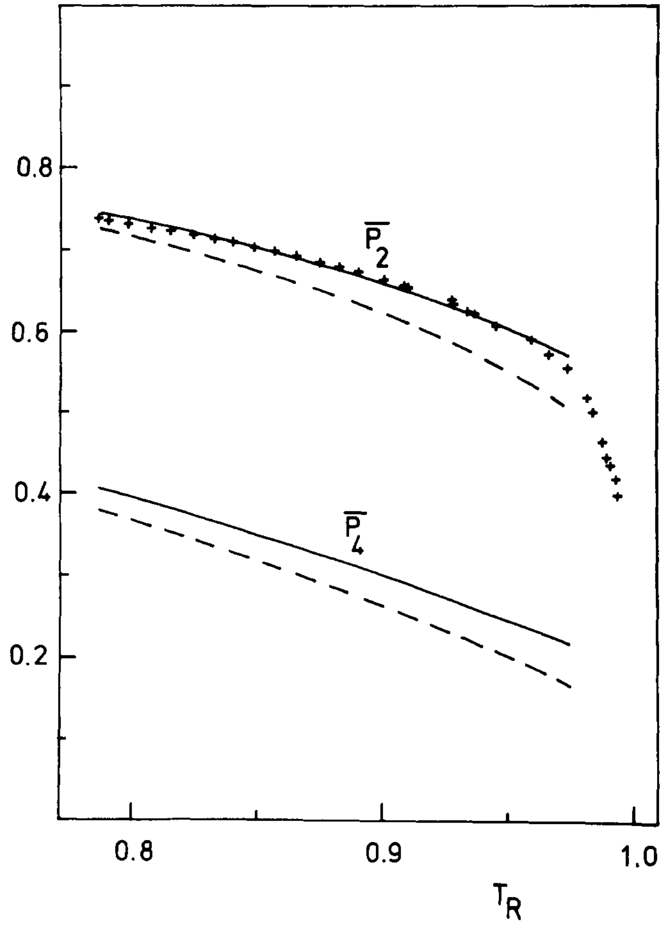

FIGURE 10 Order parameters against reduced temperature ($T_R = T/T_{NI}$) for I52.

MOLECULAR PROPERTIES

The molecular dipole moments and average polarisabilities were obtained from electric permittivity and refractive index measurements on dilute *p*-xylene solutions. The low values of the dipole moments meant that special care had to be taken in measuring the capacitance of the solutions, and it was necessary to use concentrations up to 20% by weight to obtain sufficient precision. Values for the polarisability anisotropy were obtained from fitting the bulk refractive indices to Eq. (2), and using α determined from solution refractive index measurements. The ratio $\Delta\alpha/\alpha$ was found using both the Haller

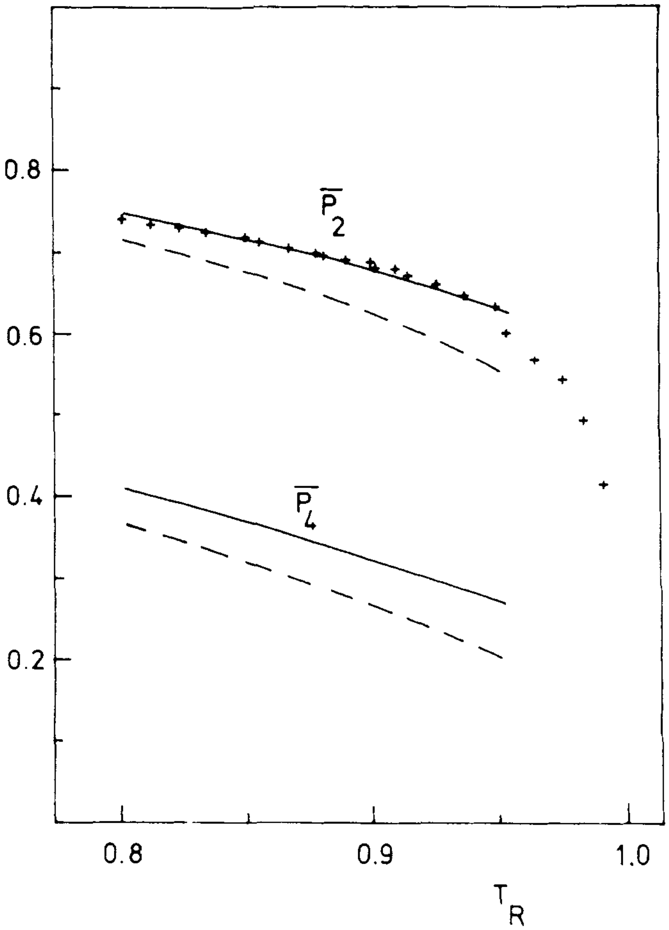

FIGURE 11 Order parameters against reduced temperature ($T_R = T/T_{NI}$) for I35.

extrapolation Eq. (3), and the Bradshaw-Tough procedure as described above. Both methods provide an effective polarisability anisotropy, related to the molecular axis which defines the order parameter. Results for the molecular properties of the I materials studied are collected in Table II. The magnitudes of all properties increase regularly with increasing chain length, although this is not reflected by the T_{NI}'s, which are approximately equal for three of the homologues studied. Dipole moments for the molecules are close to the value of 4.54×10^{-30} measured for 4-fluorobiphenyl. As has been remarked before,[6,11] there does not seem to be any simple relationship between molecular properties and the nematic to isotropic transition temperature.

TABLE II

Molecular properties of I materials

Molecule	Dipole moment (10^{-30} m)	β	Polarisability α	(10^{-40} J^{-1} C^{2}m^2) $\Delta\alpha$	Molar volume (10^{-6} m^3)
I22	4.6	80°	43.5	19.5	333.1
I32	5.0	71°	50.0	23.0	347.1
I52	4.9	72°	50.8	23.1	379.5
I35	5.1	72°	53.3	24.2	376.5

Members of the I series of liquid crystals are far from being axially symmetric, and there is a large transverse component of the molecular diole. We can obtain some estimate of the angle between the dipolar axis and the average molecular orientation by fitting measurements of the electric permittivities in the nematic phase to the Maier and Meier equations.[12] For weakly dipolar molecules it is probably reasonable to assume that the dipole correlation factors are close to unity, in which case the dielectric anisotropy can be written as:

$$\Delta\epsilon = \frac{NLFS}{\epsilon_0}\left[\Delta\alpha - \frac{F\,\mu^2}{2\,\mathrm{kT}}(1 - 3\cos^2\beta)\right] \tag{6}$$

L and F are internal cavity and reaction field factors,[5] assumed to be isotropic. The temperature at which $\Delta\epsilon$ becomes zero is determined by the equivalence of the polarisability and dipole moment contributions in Eq. (6). Using experimentally measured cross-over temperatures $T_{\Delta\epsilon=0}$ gives the dipole angles listed in Table II, and we conclude that the 'long' axes of I molecules are displaced from the biphenyl C_2 axis by about 15°. This interpretation of the change of sign of $\Delta\epsilon$ does not depend on the nematic properties of the material, although the effective molecular long axis must be determined by interactions with neighbouring molecules.

CONCLUSIONS

The formation of nematic phases stable over wide ranges of temperature by members of the I-homologous series provides yet another challenge to the theory of nematic stability. These materials have small off-axis dipoles, a modest polarisability anisotropy (comparable with 44'*n* pentylcyanobiphenyl) and a non-rigid structure, yet they have the widest low temperature ranges of any nematogens yet discovered. A key factor must be their flexibility, which depresses the crystallisation temperature and enhances the nematic ordering potential by allowing changes in the distribution of molecular conformers. Flexibility alone is not enough, and the anisotropically polarisable fluorobiphenyl core must be the source of angle-dependent forces which cause the nematic phase.

One remarkable feature of the I-materials is their small dielectric anisotropy, which changes sign with variation in temperature. We have attributed this change of sign to a competition between the contributions of anisotropic polarisability and dipole moment to the permittivity. This description of the phenomenon is not dependent on any nematic properties of the compounds, and so there should be a corresponding change in sign of the solution Kerr constant of the I materials; we are at present investigating this. Any differences between the solution and nematic behaviour can be ascribed to the nematic ordering potential, and the experiment might prove to be a sensitive probe of intermolecular forces in the nematic phase. It might be possible to exploit the change in sign of $\Delta\epsilon$ with temperature as a thermal switch, but in the pure I materials $(d\Delta\epsilon/dT)$ is rather small.

Acknowledgments

The authors wish to thank BDH Chemicals Ltd. for generously providing us with samples of the I materials. We are also grateful to the U.K. Science and Engineering Research Council for financial support, and the award of a research studentship to D.A.H. One of us (H. X-J) thanks the Royal Society and the Chinese Academy of Sciences for an exchange bursary. For assistance with some aspects of the experimental work we are grateful to Mrs. T. F. Waterworth (Postgraduate student) and Messrs M. Manterfield (Senior technician), W. A. Burrows and P. Spain (final year undergraduate students).

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