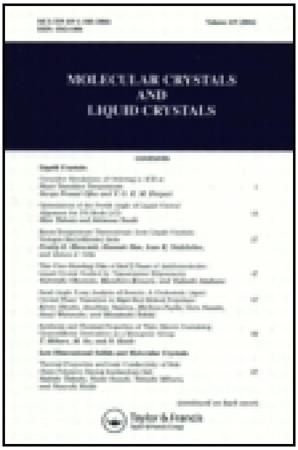

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The Dielectric and Optical Properties of the Homologous Series of Cyano-Alkyl-Biphenyl Liquid Crystals

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The Dielectric and Optical Properties of the Homologous Series of Cyano-Alkyl-Biphenyl Liquid Crystals

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The electric permittivities, refractive indices and densities of the homologous series of alkyl-cyano-biphenyls ($C_nH_{2n+1}\cdot\phi\cdot\phi\cdot CN$) have been measured as a function of temperature in the nematic phases for $n = 5$ to 9, and in the smectic phases for $n = 8$ and 9. The results have been analysed in terms of the Maier and Meier theory to yield values for the molecular dipole moments and polarizabilities. Kerr effect measurements on dilute solutions of 44′-*n*-pentyl-cyano-biphenyl at different temperatures are reported, and in conjunction with similar dielectric and optical measurements have provided results for the free molecule dipole moment and polarizabilites; values for the higher homologues are predicted using a bond additivity model. Bordewijk's theory is applied to the permittivity measurements, and using appropriate molecular parameters, dipole–dipole correlation factors are calculated.

INTRODUCTION

The fundamental feature of liquid crystals is their anisotropy. This anisotropy results from angular correlations between molecules and may be characterised by a local order parameter S which can be measured by various spectroscopic techniques. When a liquid crystal is subjected to certain external perturbations such as electric or magnetic fields, surface forces or shear stress, a macroscopic anisotropy may be induced. If the macroscopic alignment is complete it is possible to obtain information on the local order parameter from measurements on anisotropic bulk properties such as electric permittivity, refractive index and diamagnetic susceptibility.[1] To obtain values for S from such measurements requires a prior knowledge of the effective molecular electrical or magnetic properties in the liquid crystalline phase and a description of the internal field. In the case of magnetic properties the internal field effects are small and the local order parameter can be reliably obtained from magnetic susceptibility measurements, however for electrical permittivity and refractive index measurements the problem of the internal electric field remains.

The major stimulus to liquid crystal research in recent years has been the development of visual display devices based on various electro-optic effects.[2] The operational characteristics of these devices depend on the anisotropic dielectric and optical properties of the mesogens, and measurements of the components of the electric permittivity tensor and principal refractive indices are important in the characterisation and development of new materials. Of many compounds that have been used in display devices, the alkyl-cyano-biphenyls ($C_nH_{2n+1}\cdot\phi\cdot\phi\cdot CN$) discovered by Gray[3] have many desirable features, such as low temperature nematic ranges and photochemical inertness. Mesogenic behaviour is shown by members of the homologous series from $n = 5$ to $n = 10$, with the higher members ($n = 8$ to 10) having smectic phases. Studies of the properties of homologous series of mesogens are particularly useful since relatively small changes in molecular structure are accompanied by significant changes in macroscopic properties. The values of these properties can then be interpreted in terms of molecular parameters using appropriate statistical theories.

Measurements of electric permittivities and refractive indices of liquid crystals can provide valuable tests of the theories of the dielectric properties of anisotropic fluids, and perhaps stimulate the further development of such theories. Most attention has been directed towards the theoretical description of the anisotropic dielectric properties of the nematic phase, although measurements have been made[4] of the electric permittivities of materials showing a number of mesophases.

In this paper we report a series of measurements of the dielectric and optical properties of the homologous series of alkyl-cyano-biphenyls from $n = 5$ to $n = 9$. Accurate measurements of densities have also been made to enable our results to be analysed in terms of the theory of Maier and Meier.[5] The more rigorous theory of anisotropic fluid dielectrics developed by Bordewijk[6] takes specific account of long-range dipole-dipole interactions; using values for molecular polarizability and dipole moments derived from dilute solution measurements of the Kerr constant, electric permittivity and refractive index, we have obtained values for the dipole-dipole correlation coefficients (Kirkwood g-factors) in the mesophases. Refractive indices[7] and electric permittivities[8] of some members of the series have already been reported by other workers. Our measurements are in substantial agreement, but there are some differences which may be due to either differing sample purities or different experimental conditions. These differences are commented upon in the discussion.

EXPERIMENTAL

Electric permittivity measurements

The components of the electric permittivity tensor were measured by placing the material in a cell containing parallel stainless steel electrodes which was thermostatted to $\pm 0.1°C$. The separation of the electrodes could be varied between 0.1 and 5 mms, and measurements were typically made with a separation of 1 mm. Measurements of capacitance were made using a Wayne Kerr Autobalance bridge (type B331) operating at a frequency of 1592 Hz. The cell was calibrated at a given electrode separation by measuring the capacitance of standard dielectric liquids whose relative permittivities spanned the range $2 \rightarrow 13$. In all cases the permittivities of the standard liquids were measured in our laboratory and values differed by less than 2% from literature values.

In order to obtain values for the permittivity components of the aligned liquid crystals, the cell was placed between the pole pieces of an electromagnet, such that the electrodes of the cell were either parallel or perpendicular to the magnetic field direction. To ensure that the samples were fully aligned, capacitance measurements were made on each material at a single temperature as a function of magnetic field strength, and subsequent measurements were made at field strengths corresponding to the fully aligned state. The effect of the measuring electric field of the capacitance bridge was also investigated by making measurements at different bridge voltages, and choosing a bridge voltage that did not disturb the magnetic alignment of the liquid crystal. It is well-known that smectic phases are not easily aligned by magnetic fields, and for measurements on these phases the alignment was produced by cooling from the nematic phase in the presence of a saturating magnetic field.

Refractive index measurements

Refractive indices were measured by a number of different techniques. For measurements in the nematic phase surface treatment of the prism of an Abbé or Pulfrich refractometer enable values to be readily obtained for the perpendicular (ordinary) refractive index. It is also possible in some circumstances to obtain the parallel (extraordinary) index, depending on the degree of macroscopic alignment that can be induced at the prism surface. In most cases it is preferable to obtain the parallel index by measuring the birefringence using the wedge technique described by Haller *et al.*[9] Neither of these methods is suitable for the measurement of the refractive indices in the smectic phase since it is not possible to induce alignment by surface forces. To obtain values for smectic phase refractive indices we constructed a thin glass wedge, which was filled with the liquid crystal. The mesogen was then aligned by cooling from the nematic phase in the presence of a magnetic field, when it became doubly refracting. A beam of plane-polarised light from a helium-neon laser was then directed through the wedge, and the divergence of the ordinary and extraordinary rays was measured. To achieve a separation of these rays with the narrow wedge used (0.02 radians) it was necessary to use an optical path length of about 10 m; a knowledge of the wedge angle, path length and beam displacements gives the refractive indices directly.

Density measurements

The densities of the materials were measured over the complete mesogenic range using an Anton Paar Digital Densimeter (Model No. DMA 02C).

Kerr constant measurements

In order to analyse our dielectric and optical measurements on mesophases in terms of the Bordewijk theory, values for the free molecule polarizabilities were necessary. These were obtained from measurements of the Kerr constant of dilute solutions over a range of concentrations and temperature. Measurements were made at a wavelength of 632.8 nm using a sensitive modulation technique that has already been described.[10]

RESULTS AND DISCUSSION

I) *Pure mesogens* Our results for the electric permittivities, refractive indices and densities of the homologous series of alkyl-cyano-biphenyls are summarised in Table I. More detailed results are given in the following sections, except for the measurements of densities which will be the subject of a forthcoming publication.[11] The materials were supplied by BDH Chemicals Limited and used without further purification: observed transition temperatures were mostly in agreement with those reported[12] by other workers.

Electric permittivities

The components of the permittivity tensor measured parallel and perpendicular to the director are given in Figures 1–5. The results represent measurements taken on a number of different samples using different cell configurations. In any single run the precision of the measurements was better than 1 %, but successive runs with different samples often gave systematic differences in the derived permittivities of up to 7 %. The reason for these

TABLE I

Physical properties of alkyl-cyano-biphenyls R $\cdot \phi \cdot \phi \cdot$ CN

Liquid crystal (R)	Transition[a] temperatures °C			Temperature °C	Density ρ gm/cc	Relative permittivities		Refractive indices	
	t_k	t_s	t_c			$\varepsilon_{\parallel}$	$\varepsilon_{\perp}$	$n_{\parallel}$	$n_{\perp}$
C_5H_{11}(5CB)	22.5		35.2	29.0	1.019	17.1	7.2	1.702	1.539
C_6H_{13}(6CB)	14.5		29.4	22.0	1.015	16.7	6.9	1.701	1.538
C_7H_{15}(7CB)	28.5		42.5	36.0	0.995	15.7	6.0	1.682	1.522
C_8H_{17}(8CB)	21.0	33.5	40.2	27.0	0.996	13.6	5.1	1.673	1.516
				37.0	0.985	13.7	6.0	1.661	1.524
C_9H_{19}(9CB)	40.5	47.8	49.7	44.0	0.978	12.5	5.1	1.668	1.508
				49.0	0.970	13.1	5.7	1.638	1.519

[a] t_k = crystal → smectic A or nematic
t_s = smectic A → nematic
t_c = nematic → isotropic

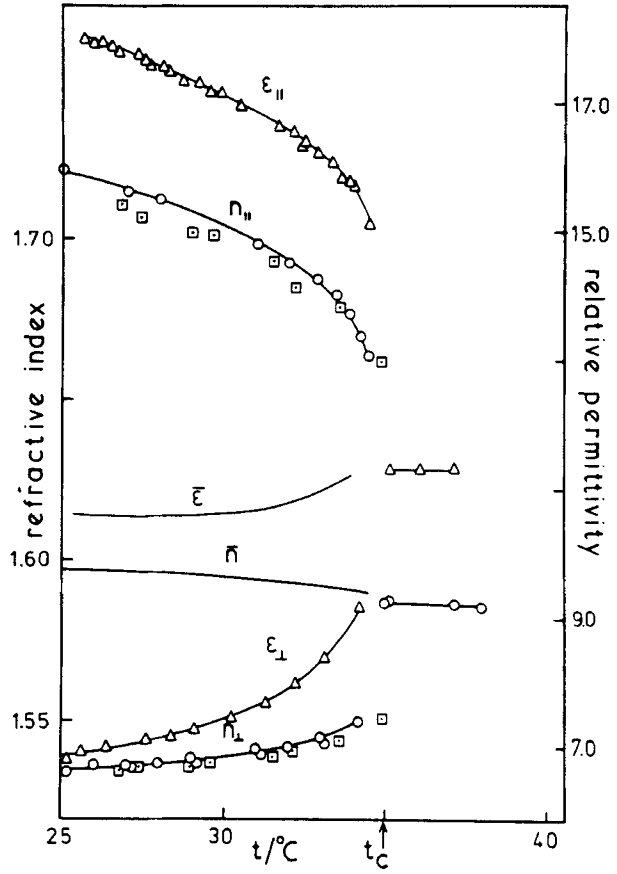

FIGURE 1 Electric permittivity and refractive index of 5CB; in Figures 1–5. (△) = permittivities (this work); (○) = refractive indices (this work); (□) = refractive indices (Ref. 7).

differences is not clear to us and certainly does not correspond to obvious deterioration of the liquid crystals, since transition temperatures were constant within ±0.2°C for different samples of the same mesogen.

Our results for 5CB and 7CB are in agreement with values already in the literature.[13,14] Ratra and Shashidhar[8] have reported measurements of the electric permittivity components of 5CB to 8CB in their nematic ranges which are in general accord with ours. However we find that their isotropic permittivities and parallel components are consistently lower than those reported here. These authors relied on surface forces acting across thin samples to produce the homeotropic alignment necessary for the measurement of the parallel component of the permittivity. An incomplete alignment would result in an apparent lowering of this component and may explain the

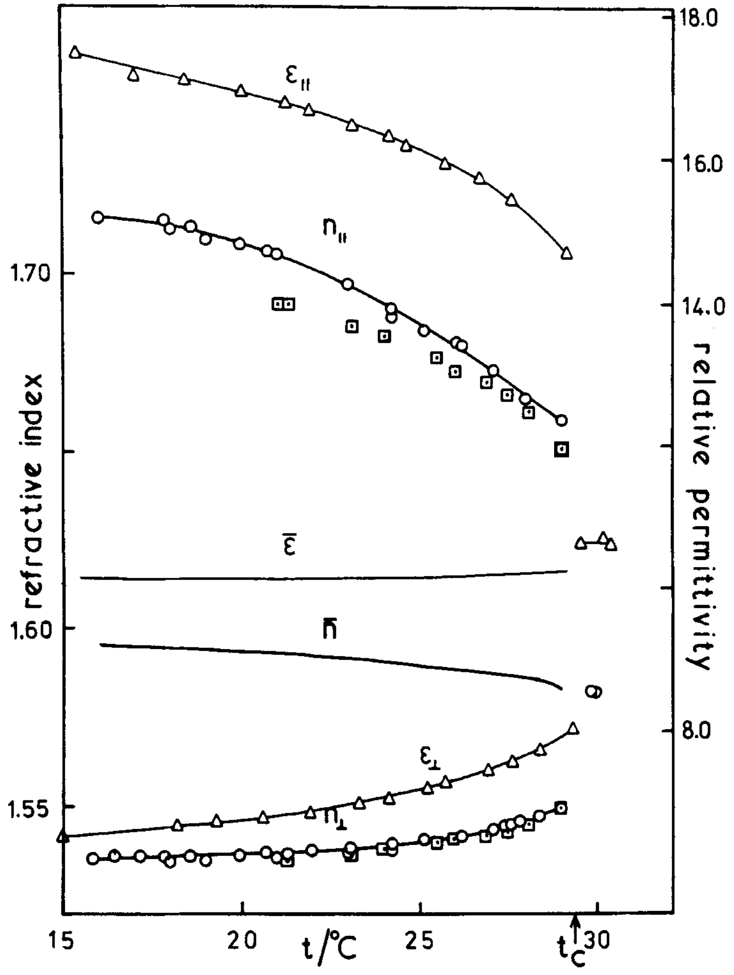

FIGURE 2 Electric permittivity and refractive index of 6CB.

differences in the recorded values. Such an explanation would not be applicable to the discrepancies noted between our isotropic values. All the permittivities reported in this paper were obtained in the presence of orientating magnetic fields of 0.5 Tesla with sample thicknesses greater than 500 μm. The effect of sample thickness on measured dielectric properties has not been fully investigated and may be responsible for the apparent differences in measured permittivities.

For those materials having smectic phases a slight discontinuity in the temperature gradient of the electric permittivity is noticeable, with the

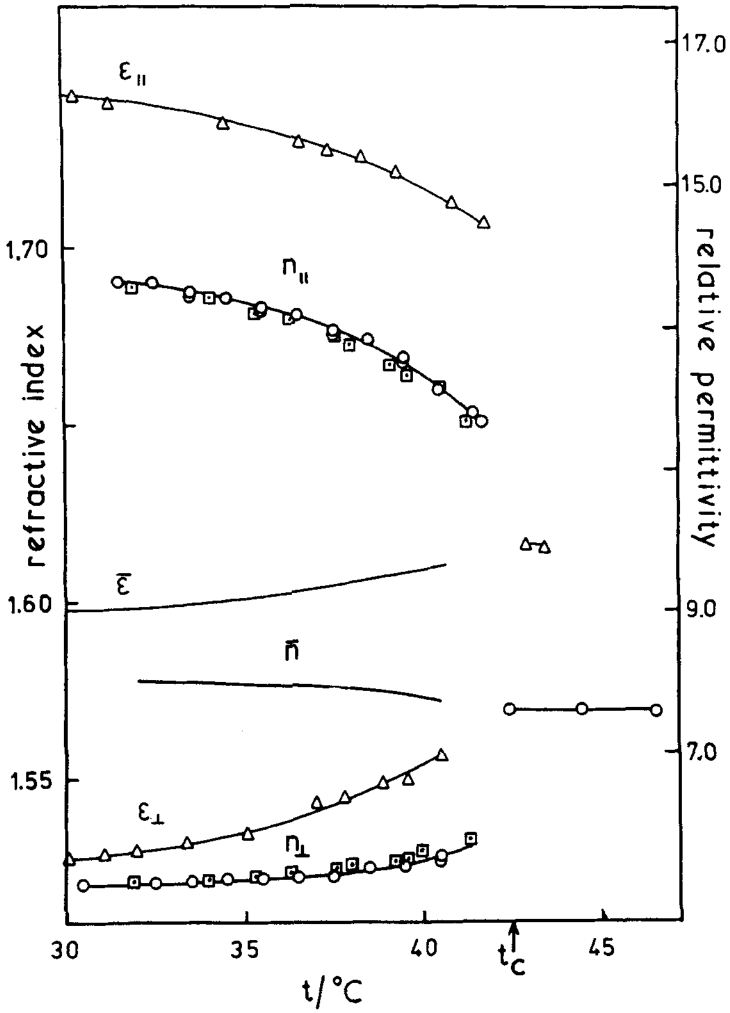

FIGURE 3 Electric permittivity and refractive index of 7CB.

permittivity anisotropy being less in the smectic phase than in the nematic phase. Such a lowering in $\Delta\varepsilon$ at the nematic to isotropic transition has been explained qualitatively[15] in terms of enhanced dipole-dipole correlation in smectic layers. In making measurements on 9CB we observed strong fluctuations of the measured capacitance up to 1.5°C above the observed transition temperature. We have not observed such behaviour with other mesogens, and it suggests that pretransitional effects may be particularly strong in 9CB.

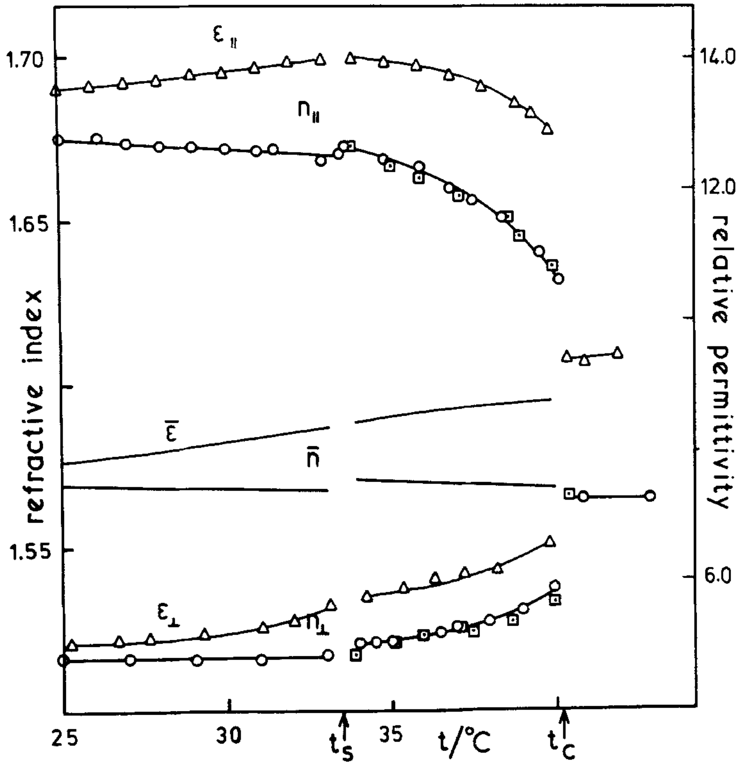

FIGURE 4 Electric permittivity and refractive index of 8CB.

Refractive indices

Refractive index measurements for the materials studied are presented in Figures 1 to 5. The lines represent a best fit through the experimental measurements obtained from different runs, and the corresponding refractive indices are believed to be accurate to ±0.1 %. The most accurate method for obtaining refractive indices is from samples aligned on the prism of a refractometer. For those materials that could be aligned in this way the refractive indices were measured at a wavelength of 589 nm. It was not possible to use this technique for 8CB and 9CB, which possess smectic phases, and measurements were made at a wavelength of 633 nm using the method described in the previous section. They have been corrected to correspond to a wavelength of 589 nm using an empirical dispersion formula of the form, $n_i(\lambda) = n_i(0) + \delta_i \lambda^{-1}$, with $\delta_\parallel = 60$ nm and $\delta_\perp = 30$ nm.

Our values for the refractive indices of the nematic phases of 5CB to 8CB agree with those obtained by Karat and Madhusudana.[7] Their measurements

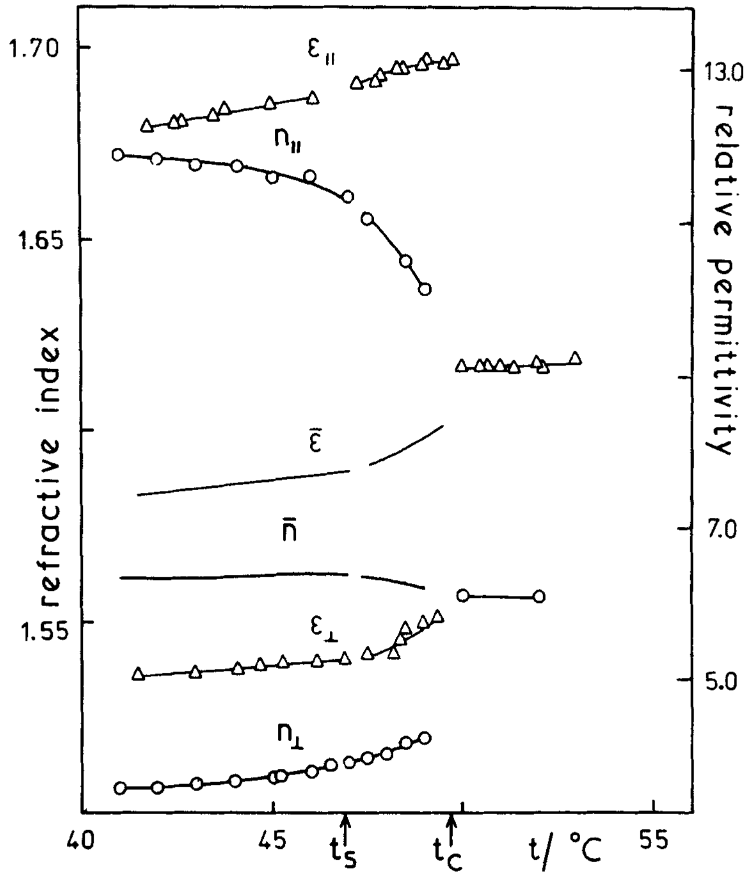

FIGURE 5 Electric permittivity and refractive index of 9CB.

were made at three wavelengths, and the empirical dispersion formula above adequately describes the observed dispersion between 589 nm and 633 nm.

II) *Dilute solutions of 5CB in benzene* Measurements of the permittivity, Kerr constant, density and refractive index were made on dilute solutions of 5CB in benzene at a series of temperatures in the range 10°C to 50°C. Solutions of various concentrations were studied and the results fitted to a linear function of weight fraction w_2 of the solute (5CB) by equations of the form:

$$X_{12} = X_1(1 + Y(X)w_2) \tag{1}$$

TABLE II

Permittivities, refractive indices, densities and Kerr constants of dilute solutions of 5CB in benzene[a]

Temperature °C	Relative permittivity		Refractive index		Density gm cm^{-3}		Kerr constant (10^{-15} Volts^{-2} m)	
	ε	α	n_1^2	β	ρ_1	γ	B_1	δ
11.7	2.269	4.7	2.282	0.103	0.8878	0.127	4.60	255
14.7	2.263	4.6	2.276	0.101	0.8845	0.129	4.56	250
24.9	2.256	4.6	2.259	0.106	0.8737	0.138	4.44	234
35.0	2.228	4.2	2.240	0.113	0.8628	0.150	4.33	216
45.6	2.198	4.4	2.221	0.159	0.8503	0.153	4.22	200

[a] The parameters in the table are defined by the following equations for solution permittivity (ε_{12}), refractive index (n_{12}), density (ρ_{12}) and Kerr constant (B_{12}): $\varepsilon_{12} = \varepsilon_1(1 + \alpha w_2)$, $n_{12}^2 = n_1^2(1 + \beta w_2)$, $\rho_{12} = \rho_1(1 + \gamma w_2)$, $B_{12} = B_1(1 + \delta w_2)$. w_2 is the weight fraction of 5CB.

X_{12} is the measured value of the appropriate property for the solution, while X_1 is the value of the property for the pure solvent (benzene) at the same temperature. Values for X_{12}, X_1 and $Y(X)$ are listed in Table II for the various properties measured. The analysis of these results in terms of molecular parameters will be given in the next section.

ANALYSIS

Molecular dipole moments and polarizability components

Measurements of the permittivities, refractive indices and densities of solutions of 5CB in benzene over a range of temperature yield a value for the molecular dipole moment of $15.9 \pm 0.2 \times 10^{-30}$ Cm (4.76 ± 0.05 D), and for the mean polarizability a value of $37.5 \pm 0.3 \times 10^{-40}$ J^{-1} C^{2}m^2 (33.7 ± 0.3 Å^3).

The molar Kerr constants at infinite dilution for 5CB listed in Table III were obtained by the method described by Le Fèvre and Le Fèvre[16] using the results listed in Table II. The molar Kerr constant is related to molecular parameters by the equation:[17]

$$_mK = \frac{N}{81\varepsilon_0}\left[\gamma + \frac{1}{kT}\left(\frac{2\mu\beta}{3} + \frac{9\alpha^{(0)}}{5}\alpha\kappa^2\right) + \frac{3\mu^2}{10k^2T^2}(\alpha_{33} - \alpha)\right], \qquad (2)$$

in which the notation of Ref. 17 has been used. The parameters β and γ are related to the components of the first and second hyperpolarizability tensors, $\alpha^{(0)}$ and α are the mean static and optical polarizabilities, α_{33} is the component of polarizability along the direction of the dipole moment (μ), and κ is related

TABLE III

Molar Kerr constants for 5CB extrapolated to infinite dilution

Temperature °C	${}_mK(10^{-24}\ C^2m^5\ J^{-2})$ expt.	calc.
11.7	5.56	5.53
14.7	5.39	5.41
24.9	5.03	5.06
35.0	4.71	4.74
45.6	4.35	4.43

to the anisotropy in the polarizability by:

$$\kappa^2 = \frac{\alpha_{\alpha\beta}\alpha_{\alpha\beta} - 3\alpha^2}{6\alpha^2} \tag{3}$$

If axial symmetry is assumed for the molecule then

$$\kappa = \frac{\alpha_{33} - \alpha_{22}}{3\alpha} = \frac{\Delta\alpha}{3\alpha} \tag{4}$$

In principle it is possible to analyse the temperature dependence of ${}_mK$ to yield values for the dipole moment, polarizability and hyperpolarizabilities, but in practice the precision of the measurements is rarely sufficiently high to allow such an analysis, and contributions from the hyperpolarizabilities in Eq. (2) are often neglected. Studies[17,18] of the temperature dependence of the Kerr effect in gases have shown that the hyperpolarizability contributions may amount to 30% of the measured ${}_mK$, but for highly anisotropic dipolar molecules such as 5CB their contribution is probably less than 10%.

A least-squares analysis of the temperature dependence of ${}_mK$ for 5CB, using the molecular dipole moment given above, yields a value for $\Delta\alpha$ of $19.6 \pm 0.9 \times 10^{-40}J^{-1}C^2m^2$ (17.6 ± 0.8 Å^3) if hyperpolarizability contributions are neglected. The corresponding calculated values for ${}_mK$ are listed in Table III. If a temperature independent term is included in the expression for ${}_mK$ we obtain a value for $\Delta\alpha$ of $21.1 \times 10^{-40}J^{-1}C^2m^2$ (19.0 Å^3).

Bond additivity models are often used to predict dipole moments and polarizabilities of complex molecules, and in Table IV we compare the predicted molecular parameters for 5CB with our measured values. A more accurate prediction of the molecular properties of the higher homologues of the alkyl-cyano-biphenyls can be obtained by adding the appropriate bond contribution for the methylene groups to our measured values for 5CB. Such results are also listed in Table IV and are compared with other literature values where possible.

TABLE IV

Molecular properties of alkyl-cyano-biphenyls R·ϕ·ϕ·CN

	Dipole moment (10^{-30} Cm)		Polarizability (10^{-40} J^{-1} C^{2}m^2)		Polarizability anisotropy (10^{-40} J^{-1} C^{2}m^2)	
Molecule	expt.	calc.[c]	expt.	calc.	expt.	calc.
5CB	15.9 ± 0.2	16.1	37.5 ± 0.3	37.3[d]	19.6 ± 0.9	20.6[d]
6CB		16.2		40.1[e]		18.9[e]
7CB	16.4[a] 14.5[b]	16.4		42.4[e]		17.6[e]
8CB		16.6		44.8[e]		16.4[e]
9CB		16.7		47.2[e]		15.0[e]

[a] D. Lippens, Thesis, University of Lille, 1976.

[b] Ref. 14.

[c] Based on a dipole moment of 14.1 × 10^{-30} Cm for cyano-biphenyl and a dipole moment of 1.3 × 10^{-30} Cm for toluene (J. Smith, Electric Dipole Moments (Butterworths, London 1955) p. 221). A methylene group moment of 0.17 was derived from the dipole moments of the homologous series of alkyl nitriles (C. P. Smyth, Dielectric Behaviour and Structure (McGraw Hill, New York 1955) p. 282.).

[d] Calculated from bond polarizabilities quoted in Ref. 16, and assuming a dihedral angle between the planes of the benzene rings of 20° (H. Suzuki, Electronic Absorption Spectra of Organic Molecules (Academic Press, New York 1967)).

[e] Derived from our measured polarizability for 5CB and C—H and C—C bond polarizabilities quoted in Ref. 16.

Mesogenic permittivities and refractive indices

The task of statistical dielectric theories of ordered mesophases is to interpret the measured permittivity components in terms of the local order parameter and molecular properties such as polarizabilities and dipole moments. Maier and Meier[5] extended Onsager's theory of isotropic dielectrics to the nematic phase, and for molecules assumed to have axial symmetry, their equations for the principal permittivity components are:

$$\varepsilon_{\parallel} = 1 + NLF\varepsilon_0^{-1}\left\{\bar{\alpha} + \frac{2\Delta\alpha S}{3} + \frac{F\mu^2}{3kT}(1 + 2S)\right\} \tag{5}$$

$$\varepsilon_{\perp} = 1 + NLF\varepsilon_0^{-1}\left\{\bar{\alpha} - \frac{\Delta\alpha S}{3} + \frac{F\mu^2}{3kT}(1 - S)\right\} \tag{6}$$

L and *F* are cavity field and reaction field factors for a spherical cavity in an isotropic continuum. It is possible to modify these expressions for anisotropic cavities in anisotropic dielectrics, but the problem arises of specifying the shape of the microscopic cavity. The cavity field[6] and reaction field[19,20] factors for a spherical cavity of radius a in an anisotropic dielectric are:

$$L_i = \frac{\varepsilon_i}{\varepsilon_i - \Omega_i(\varepsilon_i - 1)} \tag{7}$$

$$F_i = (1 - \bar{\alpha}f_i)^{-1} \quad \text{with} \quad f_i = (4\pi a^3\varepsilon_0)^{-1}\left[\frac{\varepsilon_i(1-\Omega_i) - 2\Omega_i}{\varepsilon_i(1-\Omega_i) + \Omega_i}\right] \tag{8}$$

where Ω_i is defined by:

$$\Omega_i = a^3(2\varepsilon_\parallel^{1/2}\varepsilon_\perp)^{-1}\int_0^\infty \left[\left(s + \frac{a^2}{\varepsilon_i}\right)R\right]^{-1} \mathrm{d}s \tag{9}$$

with

$$R^2 = \left(s + \frac{a^2}{\varepsilon_\parallel}\right)\left(s + \frac{a^2}{\varepsilon_\perp}\right)^2 \tag{10}$$

Strictly $\bar{\alpha}$ and f_i in Eq. (8) should be tensors, but we have assumed that the principal axes of f coincide with the permittivity axes, and that the polarizability α can be replaced by its isotropic part in calculating the reaction field. Analogous expressions to Eqs. (5) and (6) exist relating the refractive indices to the molecular polarizabilities.

Using our measured permittivities, refractive indices and densities we have solved Eqs. (5) and (6) to give values for $\bar{\alpha}$, $\Delta\alpha$, μ and S at various temperatures. The results are listed in Table V using both the isotropic and anisotropic internal field factors discussed above. The molecular parameters vary slightly with temperature over the mesogenic range, and the extent of this variation is indicated by the quoted uncertainties. Comparing the results in

TABLE V

Molecular parameters for alkyl-cyano-biphenyl liquid crystals

	Dipole moment (10^{-30} Cm)		Polarizability anisotropy (10^{-40} J^{-1} C^{2}m^2)		Polarizability (10^{-40} J^{-1} C^{2}m^2)	
Liquid crystal	(i)	(ii)	(i)	(ii)	(i)	(ii)
5CB	11.0 ± 0.5	10.6 ± 0.8	33 ± 9	39 ± 9	36.7	36.6
6CB	10.7 ± 0.3	10.4 ± 0.4	31 ± 1	36 ± 1	38.7	38.6
7CB	11.0 ± 0.6	10.6 ± 0.8	32 ± 6	36 ± 6	40.7	40.6
8CB (smectic)	10.2 ± 0.3	9.8 ± 0.3	28 ± 2	32 ± 2	42.3	42.2
8CB (nematic)	10.8 ± 0.2	10.5 ± 0.3	30 ± 3	34 ± 3	42.8	42.7
9CB (smectic)	10.4 ± 0.3	10.1 ± 0.3	33 ± 2	38 ± 2	44.9	44.6
9CB (nematic)	10.9 ± 0.2	10.5 ± 0.2	29 ± 2	33 ± 2	44.8	44.8

(i) isotropic internal field
(ii) anisotropic internal field

Table V with those in Table IV shows that although the mean polarizability of molecules in the liquid crystalline phase is close to that of the free molecule, there are substantial differences between the values for dipole moments and polarizability anisotropies. These differences can be attributed to the simplifications implicit in the Maier and Meier theory, which additionally fails to account for the discontinuity in the mean permittivity at the nematic to isotropic transition.

It is interesting to compare the order parameter obtained from Eqs. (5) and (6) with the universal curve obtained from the mean field theory of nematics.[21] In Figure 6 are plotted *S* values for the homologous series as a

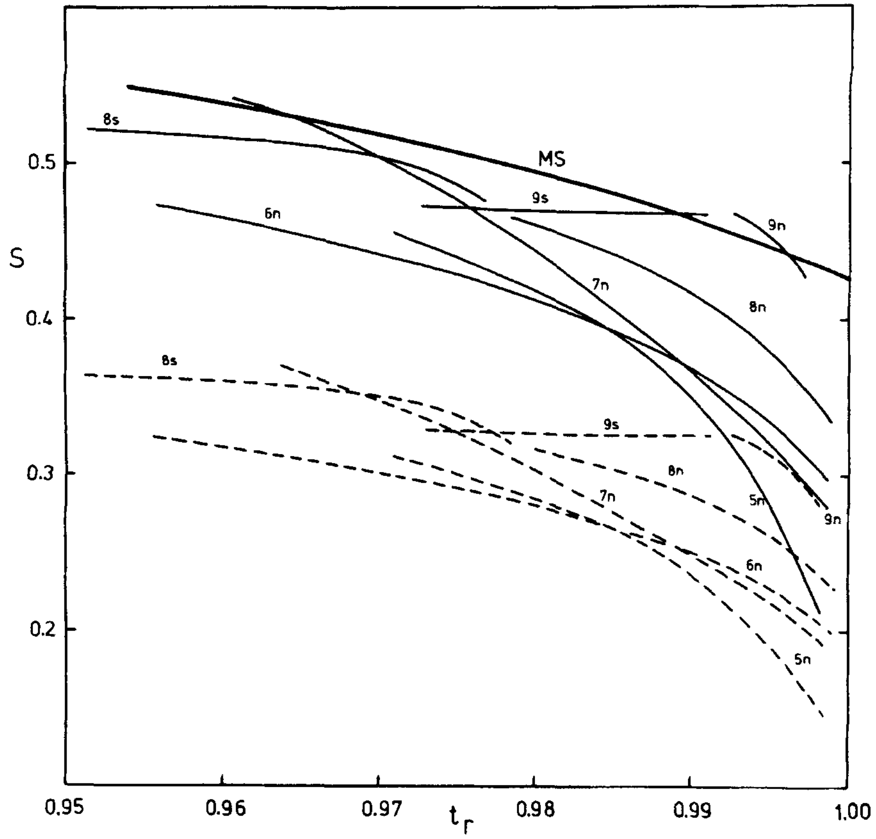

FIGURE 6 Order parameter as a function of reduced temperature for alkyl-cyano-biphenyl liquid crystals. The thick line (MS) represents the Maier–Saupe curve, while the thin lines are from the Maier and Meier theory using an isotropic internal field, and the broken lines are from the Maier and Meier theory using an anisotropic internal field. *n* = nematic, *s* = smectic.

function of reduced temperature, and it is clear that the derived order parameters are much smaller than the predictions of mean field theory, which are largely confirmed by experiment. This again illustrates the inadequacy of the Maier and Meier theory which apparently over-emphasises the role of molecular anisotropy at the expense of the local order parameter.

A more ambitious approach to the molecular interpretation of the dielectric properties of anisotropic dielectrics has been developed by Bordewijk[6] using the Kirkwood–Fröhlich theory for isotropic dielectrics as a basis. This theory includes dipole-dipole correlations between molecules, although its original application required rather restrictive assumptions to be made about either the local order parameter or the molecular polarizability anisotropy. The expressions relating the permittivity components to the molecular dipole moment are given below:

$$\frac{(\varepsilon_{\parallel} - n_{\parallel}^2)[\varepsilon_{\parallel} + (n_{\parallel}^2 - \varepsilon_{\parallel})\Omega_{\parallel}]}{\varepsilon_{\parallel}(n_{\parallel}^2 - 1)^2} = \frac{\varepsilon_0 g_{\parallel} \mu_{\parallel}^2}{N\alpha_{\parallel}^2 kT} \tag{11}$$

and

$$\frac{(\varepsilon_{\perp} - n_{\perp}^2)[\varepsilon_{\perp} + (n_{\perp}^2 - \varepsilon_{\perp})\Omega_{\perp}]}{\varepsilon_{\perp}(n_{\perp}^2 - 1)^2} = \frac{\varepsilon_0 g_{\perp} \mu_{\perp}^2}{2N\alpha_{\perp}^2 kT} \tag{12}$$

where

$$\mu_{\parallel}^2 = \tfrac{1}{3}\mu^2(1 + 2S), \qquad \mu_{\perp}^2 = \tfrac{2}{3}\mu^2(1 - S)$$

$$\alpha_{\parallel} = \bar{\alpha} + \tfrac{2}{3}\Delta\alpha S, \quad \text{and} \quad \alpha_{\perp} = \bar{\alpha} - \tfrac{1}{3}\Delta\alpha S$$

Equations (11) and (12) reduce to those given by Bordewijk for the two cases of ideal order $S = 1$, or isotropic polarizability $\Delta\alpha = 0$. The factors $g_{\parallel}$ and $g_{\perp}$ are anisotropic Kirkwood dipole correlation factors defined with respect to the axes of the permittivity. Using the values quoted in Table IV for the molecular parameters $\bar{\alpha}$, μ, and $\Delta\alpha$ together with values for S taken from the

TABLE VI

Dipole correlation factors for alkyl-cyano-biphenyl liquid crystals

Liquid crystal	Temperature °C	$g_{\parallel}$	$g_{\perp}$
5CB	29.0	0.2713	0.5628
6CB	22.0	0.2673	0.5529
7CB	36.0	0.2759	0.5552
8CB	27.0	0.2346	0.4690
	37.0	0.2714	0.5206
9CB	44.0	0.2343	0.4874
	49.0	0.3072	0.5252

Maier and Saupe mean field theory we obtain the correlation factors given in Table VI. The results indicate that there is considerable anti-parallel ordering of the molecular dipoles in the nematic phase.

CONCLUSIONS

The dielectric and optical properties of the homologous series of alkyl-cyano-biphenyl mesogens provide useful data to correlate with molecular properties. It has been found that the dielectric anisotropy and birefringence decrease with increasing chain length, a fact which is reflected in the polarizability anisotropies derived from the Maier and Meier equations, and which is in accord with the predictions of a bond additivity model for the polarizabilities. There remains a substantial difference, however, between the free molecule polarizability anisotropies and those derived from measurements on the mesophase. The Maier and Meier theory apparently places too much emphasis on the molecular anisotropy and not enough on the local order. This comment is also applicable to the mean field theories of nematic liquid crystals which predict molecular pseudo-potentials to be much more anisotropic than is physically reasonable.[22] An important omission in the Maier and Meier theory is the lack of an explicit dependence of the internal field factors on the local order parameter. Introducing such a dependence would presumably reduce the derived molecular anisotropies.

The existence of angular correlations between molecules is responsible for mesophase formation, yet they are neglected in mean field theories. The Bordewijk theory of anisotropic dielectrics suggests that there is substantial anti-parallel correlation between molecular dipoles in the alkyl-cyano-biphenyls: it is likely that the correlation between axes of the molecular polarizability tensor is even greater, although dielectric measurements do not provide a direct measure of its importance. Measurements of depolarized light scattering[23] and the Kerr effect[24] of liquid crystals provide information on the angular correlation of polarizability axes, and it is hoped that such studies together with the dielectric measurements will provide a complete picture of angular correlation in liquid crystals.

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