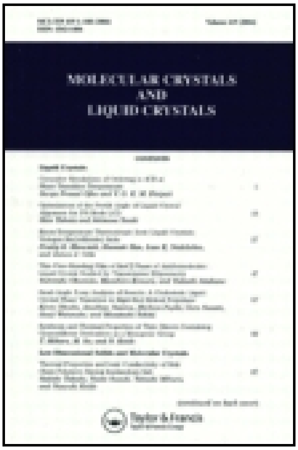

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The Temperature Dependence of Static Dielectric Permittivities and Dipole Moments of Two Mesogens and their Mixture

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The compounds *p*- pentylphenyl- 2-chloro- 4-(*p* -pentylbenzoyloxy)- benzoate and *p*-octylphenyl-2-chloro- 4-(*p*-heptylbenzoyloxy)- benzoate and their mixture (1:1 mole fraction) show nematic phases with supercooling effect below room temperature. Molecular dipole moments μ of the compounds have been determined by solution method. The static dielectric constants $\varepsilon_\parallel$ and $\varepsilon_\perp$ have been measured as functions of temperature at a frequency of 10 kHz. Mesogenic molecular dipole moments μ and their inclination angles β with the molecular long axis are determined following Maier and Meier equations. Short range antiferroelectric order is found to exist in the nematic phase. Kirkwood correlation factors have also been calculated.

Keywords: nematic phenyl benzoates; dielectric constants; dipole moments; dipole correlation factors

INTRODUCTION

Accurate measurement of the dielectric permittivities and refractive indices of liquid crystals is important from theoretical point of view as well as for tailoring and optimizing materials for electro-optical applications. Consequently there exists an interest in knowing the temperature dependence of these properties in liquid crystalline materials since the threshold voltage and other operational parameters of liquid crystal display depend on the anisotropy of the permittivity and the multiplexability of matrix displays may be limited by the temperature dependence of permittivity. Moreover, since

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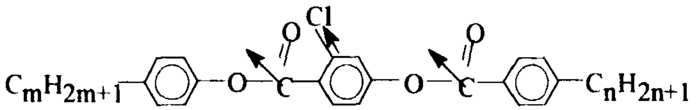
multicomponent mixtures are generally used in display devices dielectric and birefringence properties have also been studied for different types of mixtures.

In this paper we present some experimental measurements of dielectric properties of *p*-pentylphenyl -2-chloro-4 -(*p*-pentylbenzoyloxy) -benzoate [PCPB in short], *p*-octylphenyl-2-chloro-4-(*p*-heptylbenzoyloxy)-benzoate [OCHB in short] and a mixture of 1:1 molar concentration of the two compounds. X-ray, optical birefringence and density studies on the systems will be reported elsewhere. Free molecular dipole moments of PCPB and OCHB have also been determined from dielectric permittivity measurements in solution.

EXPERIMENTAL

The molecular formula and transition temperatures (°C) of the compounds obtained by texture studies are given below.



m=5, n=5	PCPB	K 39 (11.6) N 122 I
m=8, n=7	OCHB	K 38 (14.3) N 101 I
Mixture	(1:1 mole fraction)	K (<-4) N 109.3 I

Values within parentheses denote supercooled state and the arrows indicate the direction of group dipole moments. With increased chain lengths though T_{KN} decreases only by 1°C the T_{NI} drops drastically by 21°C. Moreover, the mixture is nematic even at room temperature though the individual components are not.

Molecular Dipole Moments

We have determined the molecular dipole moments of PCPB and OCHB by measuring the dielectric permittivity (ε) and refractive index (n) of solution of the compounds in a non-polar solvent viz. *p*-xylene. Dielectric permittivities were measured at 10 kHz using an LCR bridge and the refractive indices by thin prism method.[1] The effective dipole moment (μ) of a molecule in solution of concentration c (mole.cm^{-3}) at temperature T (°K) was calculated using the following relation[2]

$$\mu^2 = \frac{27kT}{4\pi N(\varepsilon_1+2)(n^2_1+2)} \; \frac{(\varepsilon_{12}-n^2_{12})-(\varepsilon_1-n^2_1)}{c}$$

where the suffixes 1 and 12 respectively refer to the solvent and solution parameters, N is the Avogadro number and k the Boltzmann constant. μ obtaned in esu-cm from above might be converted to Cm using the factor 3.3356×10^{-12}. We fitted the μ vs. weight percent (Wt%) curve to a polynomial and extrapolating the curve to infinite dilution the dipole moment of the isolated molecules was obtained.

Dielectric Parameters

Sample cells were made of ITO coated conducting glass plates separated by thin glass spacer. The sample was filled into a cell as isotropic liquid and cooled to the desired temperature at approximately 1°C/min in a magnetic field of 5KG to get aligned sample. Components of the dielectric permittivities $\varepsilon_{\parallel}$ and $\varepsilon_{\perp}$, parallel and perpendicular to the director of the nematic phase, were determined by measuring the sample capacitance at 10 kHz both parallel and perpendicular to the external magnetic field. The cells were calibrated with benzene and measured value of ε for p-xylene agreed within 2% of standard values. The cell temperature was maintained within ±0.5°C. The bridge voltage across the sample was too low (300 mV) to produce any electric-field-induced instabilities.

RESULTS AND DISCUSSIONS

Variations of dipole moments of the solutions of PCPB and OCHB with concentrations (Wt %) are shown in Fig. 1. Extrapolating the curve to infinite dilution molecular dipole moments of PCPB and OCHB are found to be 4.36D and 4.20D respectively. Thus both the molecules possess strong dipole moments although none has end polar group as in nCBs (cf., for

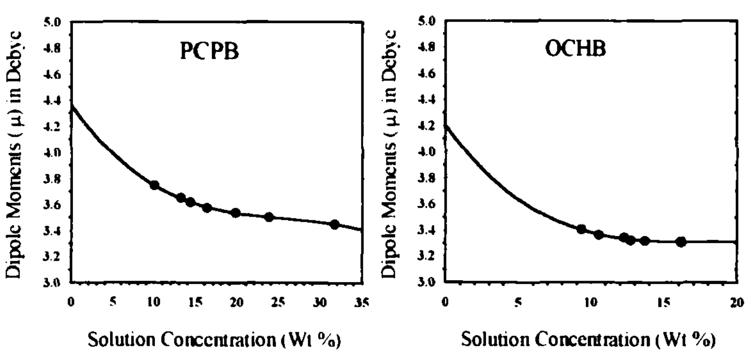


FIGURE 1 The dipole moments of PCPB and OCHB in p-xylene solution as a function of concentration.

example, $\mu \cong 5.0$D in 8CB). Also OCHB has slightly less dipole moment than PCPB, such behavior has been observed earlier in nCBs.[3]

Variations of dielectric parameters $\varepsilon_{\parallel}$, $\varepsilon_{\perp}$, $\bar{\varepsilon}$ and ε_{iso} with temperature are shown in Fig. 2 and that of $\Delta\varepsilon$ in Fig. 3. All the three systems show positive dielectric anisotropy. At low temperature $\Delta\varepsilon$ is considerably large in PCPB (~5.2) than in OCHB(~2.52) and mixture (~2.8) but near T_{NI} these are small and the differences are not large. However, these values are quite less compared to $\Delta\varepsilon$ values in compounds with strong polar end groups viz. nCBs (6.2 in 8CB) and alkoxy methyl cyanophenyl cinnamates (5.9 in 11OMCPC).[4] Average value of the dielectric constant $\bar{\varepsilon}$ is found to be about 4% less than extrapolated values of ε_{iso}. Similar difference has been observed in systems having strong axial moments.[4,5] In contrary non-polar molecules

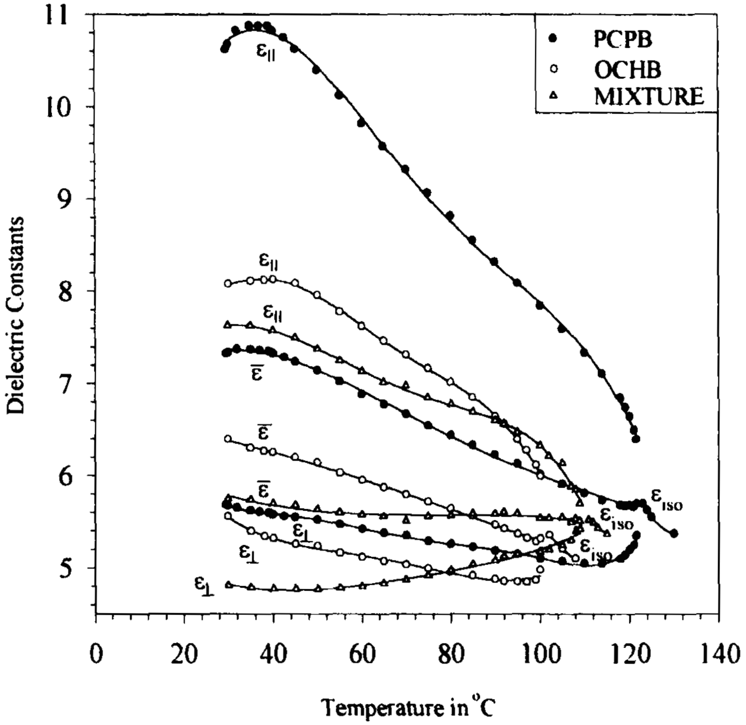


FIGURE 2 Variation of dielectric parameters with temperature.

like di-alkyl azobenzenes do not show such discontinuity.[6] This has been explained assuming the presence of short range antiferroelectric order in the nematic state.[7,8]

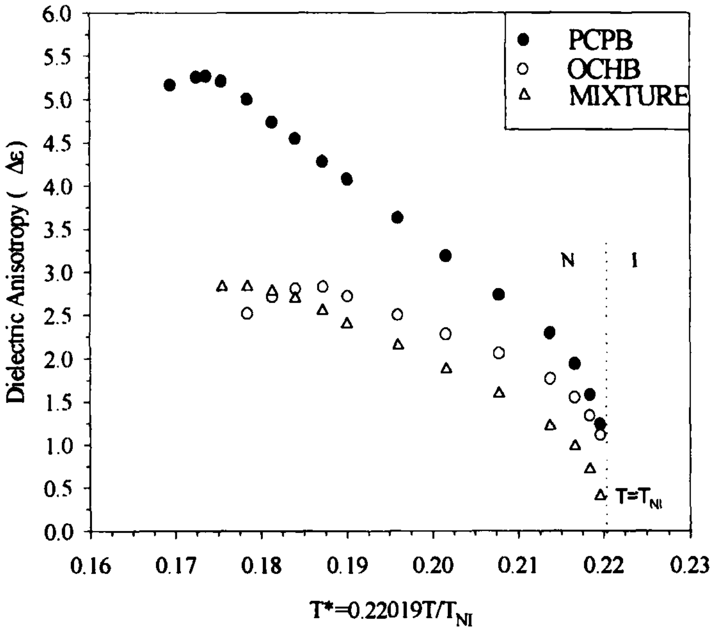
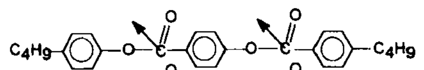
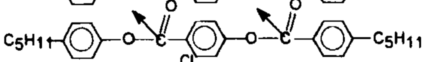
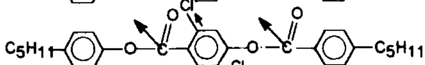
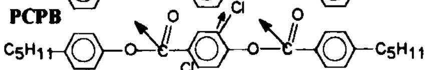
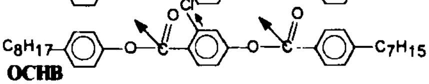


FIGURE 3 Variation of dielectric anisotropy with reduced temperature T*.

Influence of structural modification on the dielectric anisotropy of some phenyl benzoyloxy benzoates may be discussed here. Van Meter *et al.*[9] earlier reported Δε value only at $0.98T_{NI}$ (°K) for PCPB and few other benzoyloxy benzoates. Compiled data are shown in Table I. For PCPB our Δε value (2.06) is almost equal to the value (2.10) reported by Van Meter *et al.* We note that Δε increases when alkyl chain length is increased symmetrically from even number of C atoms to odd number (I and II), but it decreases on unsymmetrical increase of alkyl chain length from odd to even and odd number of C atoms (III and V). Dielectric anisotropy can be changed appreciably by adding a polar lateral substituent. Thus Δε increases from 1.2 to 2.06 when a 2-chloro group is attached (II and III) whereas it decreases to 0.4 on attachment of a 3-chloro group (II and IV). So parallel component of the dipole moment of 2-chloro group adds to those of the central ester linkages resulting in more +ve Δε whereas for 3-chloro substituent it acts in the reverse manner.

TABLE I **Dielectric anisotropy data for few phenyl benzoates**

	COMPOUNDS	Δε at $0.98T_{NI}$
I		1.0[10]
II		1.2[9]
III	 **PCPB**	2.06 2.10[9]
IV		0.40[9]
V	 **OCHB**	1.70

It is seen from the graphs that $\varepsilon_{\parallel}$ and Δε values decrease with increasing temperature as expected from simple Debye theory but both show a reverse trend within the supercooled region. In fact Bücher *et al.*[11] observed sign reversal of dielectric anisotropy in a 1:1 mixture by weight of PCPB and OCHB within 2.5-50 kHz frequency range at different temperatures, but at 50 Hz it was positive at all temperatures. Thus our observation is in conformity with the above and if we could have measured below 30°C, sign reversal of Δε might have been observed. Such behavior had also been observed in a pure compound very similar to PCPB (3-chloro substituent instead of 2-chloro) at 55°C at 10 kHz.[12] This has been assumed to be the result of dielectric loss in $\varepsilon_{\parallel}$ and occurs due to co-operative motion of the molecular long axis, not obviously due to free molecular reorientation.

It is also noted that in the mixture the values of $\varepsilon_{\parallel}$, $\varepsilon_{\perp}$, $\bar{\varepsilon}$ and Δε are considerably less than in the pure compounds but the values are close to those of OCHB. However, ε_{iso} values are found to lie between those of the pure compounds. These facts suggest that antiparallel correlation also exists in the mixture and its effect between OCHB molecules is predominant, however, in isotropic phase an average effect of both type of molecules occur.

Using the expressions for $\varepsilon_{\parallel}$ and $\varepsilon_{\perp}$ of Maier and Meier[13], obtained by extending Onsager's theory of isotropic liquid to nematics, we have calculated effective dipole moments μ and its angle β with the molecular long axis. These values at some selected temperatures are given in Table II. Order parameters from Maier-Saupe theoretical model, measured dielectric permittivities, density values and values of average molecular polarizability and polarizability anisotropy estimated from measured refractive indices were used in the calculation. It is observed that for both the compounds μ-values in the nematic phase are about 1 Debye less than the free molecular values again suggesting presence of antiparallel correlation between the neighbouring molecules.

TABLE II Mesogenic dipole moments and correlation factors

Sample	**Temp. (°C)**	**μ (Debye)**	**β (°)**	**$g_{\parallel}$**	**$g_{\perp}$**
	30	3.37	36.8	0.53	0.99
PCPB	60	3.45	35.7	0.58	0.92
	114.1*	3.39	38.3	0.57	0.99
	30	3.52	43.8	0.59	1.20
OCHB	60	3.56	40.8	0.66	1.14
	93.5*	3.54	41.1	0.67	1.06
	30	3.23	40.6	0.66	0.81
Mixture	60	3.35	41.0	0.72	0.88
	101.6*	3.62	46.4	0.80	1.08

* Temperature corresponds to 0.98T_{NI} (°K)

A quantitative measure of the correlation factor g is possible using Bordewijk[14] theory of anisotropic dielectrics which is an extension of Kirkwood-Fröhlich theory[15] where, unlike Maier-Meier theory, short-range dipole-dipole interaction was considered explicitly. Kirkwood correlation factor g takes into account the correlation between the neighbouring dipole moments only and is defined as

$$g_{\lambda} = \frac{< \sum_{i \neq j} (\mu_{\lambda})_i (\mu_{\lambda})_j >}{< \mu_{\lambda}^2 >}$$

where the subscript λ refers to axes || and ⊥ to the nematic director. The ensemble averages of the || and ⊥ components of the molecular dipole moments were calculated following the procedure of Bata and Buka.[16] These values are shown in Table II. Since $g_{\lambda} = 1$ signifies no correlation at all, we note that in all cases there is considerable antiparallel ordering of the molecular dipoles in the nematic phase and no significant correlation is observed perpendicular to the nematic director. It is also observed that $g_{\parallel}$

values in the supercooled region of both the compounds are significantly less than in other nematic region in conformity with the observation that $\varepsilon_{\parallel}$ reverses the trend of temperature dependence in the supercooled nematic phase.

Acknowledgements

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