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PHYSICAL AND MOLECULAR PROPERTIES OF THREE MESOGENIC PHENYL CYCLOHEXYL COMPOUNDS.

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Abstract Experimentally determined values of density, optical birefringence (Δn) and moleculer parameters obtained from X-ray diffraction analysis of three mesomorphic compounds, two having non-polar phenyl cyclohexane and one alkyl phenyl cyclohexane with a polar terminal group are reported here. Orientational order parameters at different temperatures were calculated both from birefringence and X-ray diffraction of aligned compounds.

INTRODUCTION

It has been shown by Schadt et al[1-2] that the introduction of a double bond at specific side chain positions markedly affect the physical properties of calamitic liquid crystals. It is also well known that the structures of the rigid core of liquid crystal molecules strongly influence the material properties of mesogens.

In continuation of our study of mesogenic alkenyl compounds[3] with bicyclohexanes, we have undertaken the investigation of the mesomorphic behaviour of two alkenyl non-polar phenyl cyclohexane compounds and one alkyl phenyl cyclohexane compound with a polar terminal group. The molecular structures of the compounds and their phase behaviour as determined by texture studies under polarizing microscope are given below. Here Cy represents cyclohexane ring and the temperatures are in °C. Supercooling temperatures are given in parentheses.

1.	3CPOd(3)1	C3H7-Cy-Ph-O-CH2-CH=CH-CH3	C 43(25.5) N 58 I
2.	5CPOd(3)1	C5H11-Cy-Ph-O-CH2-CH=CH-CH3	C 32(22.8) N 67 I
3.	3CPS	C3H7-Cy-Ph-NCS	C 39(34) N 42 I

Results of X-ray diffraction and optical studies have been reported here. Schadt et al[1] reported the refractive indices and elastic constants of 3CPOd(3)1.

EXPERIMENTAL

X-ray diffraction study

Small angle X-ray photographs were taken throughout the mesomorphic range using a high temperature camera[4] and a temperature controller Indotherm 401D. The samples were aligned by slowly cooling from the isotropic phase to the desired temperature in the presence of magnetic field of 1 Kgauss. All photographs were taken with X-rays perpendicular to the magnetic field direction. In order to determine the various parameters, the photographs were scanned both linearly and circularly by an optical microdensitometer (Carl Zeiss, Jena, Model MD100).

Optical study

The ordinary and extra-ordinary refractive indices (n_o, n_e) for the three wavelengths (λ=6907, 5780 and 5461 Å) were measured within ± 0.001 by a thin prism of refracting angle less than 2^o following the procedure described earlier[5]. The densities of the sample were determined by a dilatometer of capillary type, experimental uncertainity was estimated to be 1%.

From the values of the refractive indices the molecular polarizabilities (α_o, α_e) and orientational order parameters $\langle P_2 \rangle$ where calculated by the method of Zemindar et al[5]. Polarizabilities of the molecules were also calculated using the additive rule of bond polarizability proposed by Le Febre[6].

RESULTS AND DISCUSSIONS

Since α_o and α_e values at different wavelengths are quite close we have shown in Table I the values of mean polarizability α and polarizability anisotropy $\Delta\alpha$ only for λ=5780 Å. We find that for the first two compounds the calculated and experimental values of α agree quite well, the experimental values of $\Delta\alpha$ agree better with values obtained from Vuks' model rather than Neugebauer's model for all the compounds. The Δn values near the melting points for 3CPOd(3)1, 5CPOd(3)1 and 3CPS are 0.068, 0.097 and 0.143 respectively. We find that for 3CPS the Δn value is much larger than with the compounds having double bond in the side chain. This low anisotropy may be due to the influence of the Π-electrons of -C=C- double bond in the alkenyl side chain which are in the even positions making angle with the long axis of the molecule. It will be interesting to study the optical anisotropy of the compounds having double bond in the odd positions.

For the compound 3CPOd(3)1 and 5CPOd(3)1, beyond the temperatures 45 and 52°C respectively, birefringence could not be measured because the ordinary rays were not visible. The orientational order parameter $\langle P_2 \rangle$ at these temperatures drops to a very low value. Most probably alignment is destroyed at this temperature due to thermal fluctuations.

TABLE - I

Compound	α		$\Delta\alpha$		
				Experimental	
	Calculated	Expt.	Calculated	Vuks	Neug.
3CPOd(3)1	33.92	33.10	14.02	11.47	9.68
5CPOd(3)1	37.50	39.71	14.74	15.18	12.68
3CPS	32.29	38.35	17.24	14.15	10.91

α and $\Delta\alpha$ are in 10^{-24} cm^3 unit.

<u>Parameters from x-ray diffraction study</u>

Aligned diffraction photographs for the three compounds at different temperatures are given in figures 1 (a),(b), (c). X-ray intensity data from linear scanning of outerhalos were fitted to a Gaussian form[7] with a background varying linearly with the scattering vector q. The best fitted value of q_o gives the value of intermolecular distances D from the relation $D = 2\pi(1.117/q_o)$. The D values are found to be temparature independent for all the compounds. From the best fitted values of Δq we calculated the correlation lengths and it has been found that the local director is random beyond five moleculer diameters which is normally found in most nematic liquid crystals.

Apparent molecular lengths (l) for the three compounds obtained from meridional diffraction peaks using Bragg's relation, are 16.8, 19.1 and about 26 Å. respectively.They do not vary significantly with temperature. Lengths (L) measured from the stereo-model unit are found to be 17.1 Å, 19.0 Å and 15.1 Å . Thus the non-polar molecules are in fully extended form in the liquid crystalline phase and there is no dimer formation. Van der Waals type of interactions are responsible for the stability of mesophases of these two compounds. The dipole moment of the polar compound has been determined by us and is found to have large value of 4.2 Debye[8]. This compound in the liquid crystalline phase forms dimer due to dipole - dipole interactions resulting in a large value of apparent molecular length.

Temperature variation of order parameters $\langle P_2\rangle$ and $\langle P_4\rangle$ calculated from x-ray and optical data are shown in figures 2 (a),(b),(c). The experimental uncertainity in both $\langle P_2\rangle$ and $\langle P_4\rangle$ are estimated to be ±0.02. The detailed procedure for calculation of $\langle P_2\rangle$ and $\langle P_4\rangle$ has been discussed earlier[4]. These values are compared with theoretical values based on the Maier-Saupe model. $\langle P_2\rangle$ values determined from x-ray data are higher than the Maier-Saupe values. It is well known that the orientational behaviour of the nematic phase may be distinguished in

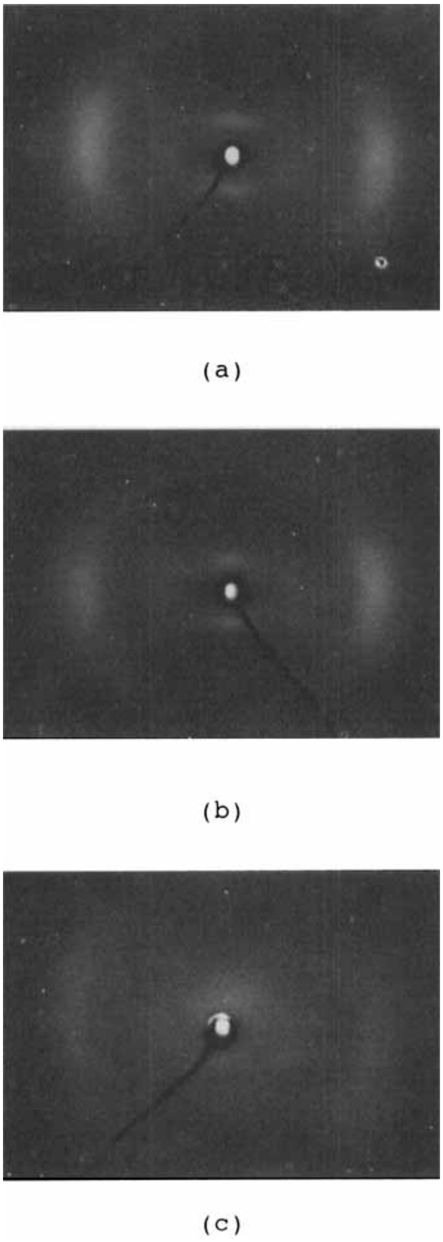

FIGURE 1 X-ray diffraction photograph of aligned samples (a) 3CPOd(3) at 41°C ,(b) 5CPOd(3) at 45°C, (c) 3CPS at 39°C.

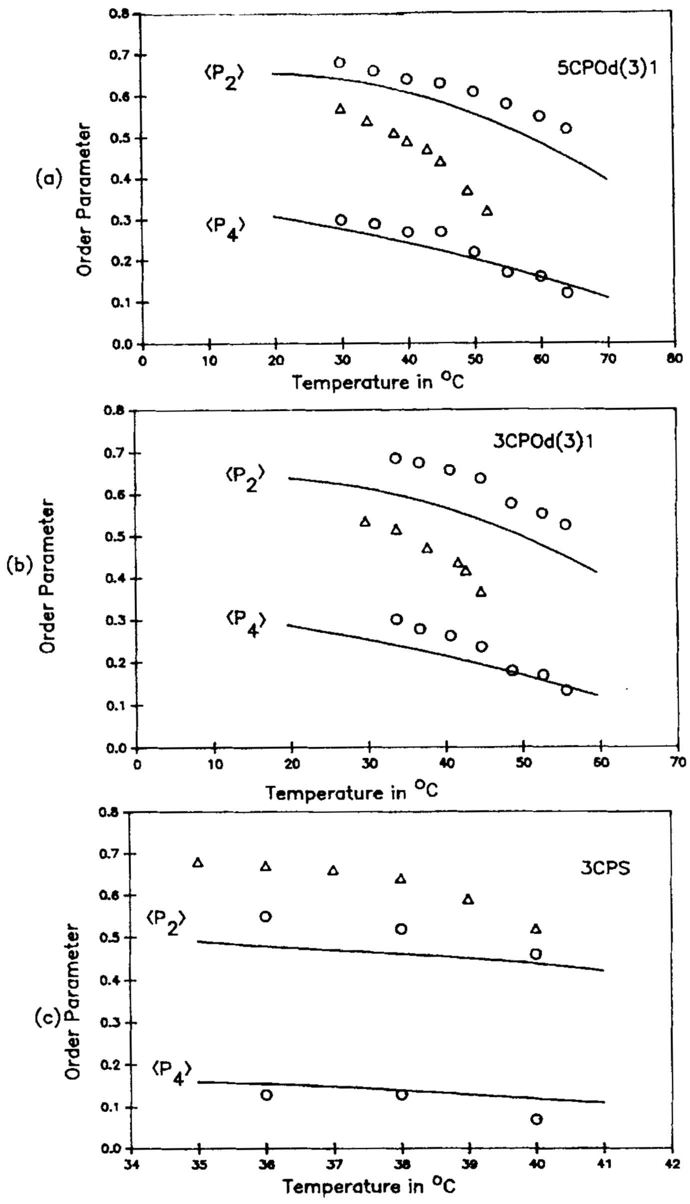

FIGURE 2 Variation of order parameters with temperature.
Δ - optical data, o - x-ray data, —— MS theoretical values.

two parts : a long range order and a short range order. Whereas the Maier-Saupe model reflects long range ordering in the liquid crystalline phase, a short range local ordering due to intermolecular interactions also exists[9]. This short range interaction causes an increase in the orientational order parameter $\langle P_2 \rangle$ of the compounds. $\langle P_2 \rangle$ values obtained from two methods differs considerably and such behaviours were reported in our previous papers[10,11]. This may be due to the difference in the technique of alignment and difference in the averaging involved. Also there is approximation in the estimation of the solid phase data of $(\alpha_{\parallel}-\alpha_{\perp})$ by Haller's[12] method. Surface treatment produced highly ordered orientated molecules for the polar compound resulting in high values of order parameters determined by optical studies.

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