

Orientalional order parameters of nematogenic trans-4-propyl cyclohexyl-4 (trans-4-alkyl cyclohexyl) benzoates

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MS received 4 June 1982; revised 16 August 1982

Abstract. The refractive indices and densities of three members of trans-4-propyl cyclohexyl-4 (trans-4-alkyl cyclohexyl) benzoates are reported as functions of temperature in the nematic and isotropic phases. The principal molecular polarizabilities and order parameters (S) have been evaluated using the anisotropic internal field model (Neugebauer's approach). Also order parameters have been estimated by studying the dipole-dipole splittings in the wide line proton magnetic resonance (PMR) spectra. The results obtained are in close agreement with those obtained from refractive index measurements.

Keywords. Order parameter; refractive index; Nematic; proton magnetic resonance.

1. Introduction

It is very well established that the order parameter of liquid crystals governs most of its physical properties (de Gennes 1974; Chandrasekhar 1977). It is possible to describe the order parameter by any one of the tensorial properties. Presently, refractive index has been selected as a macroscopic property to represent the degree of ordering. Extensive studies have been made on refractive indices, birefringence and order parameters (de Jeu and Bordewijk 1978; Gasparoux *et al* 1979; Hanson and Shen 1976; Ibrahim and Haase 1979; Dabrowski *et al* 1980; Sarna *et al* 1979; Laurent and Journeaux 1976; Madhusudana *et al* 1971), but most of the compounds studied are those containing benzene groups in the central rigid core. In view of this we have carried out the refractive index and density measurements on the homologous series trans-4-propyl-cyclohexyl-4 (trans-4-alkyl cyclohexyl) benzoates containing cyclohexane groups in the central core. When more polarizable benzene rings are replaced by much less polarizable cyclohexane rings most of the physical properties differ considerably (Gray 1981; de Jeu 1981). It is likely that the liquid crystalline behaviour of the compounds is directly related to the occurrence of associated entities. We have evaluated the order parameter as a function of temperature for the homologous series using Neugebauer's anisotropic internal field model (Neugebauer 1950, 1954; Subramhanyam *et al* 1974).

We have employed the PMR technique to evaluate the order parameter. The doublet splitting δH arising from the dipole-dipole interaction of the adjacent ring protons was used to calculate the order parameter S by the equation (Spence *et al*

1953; Rowell *et al* 1965; Lee *et al* 1974; Shivaprakash and Shashidhara Prasad 1982).

$$\delta H = 4a (3/2 \cos^2 \phi - 1/2)S, \quad (1)$$

where a is an interaction parameter, ϕ is the angle between the para axis of the benzene ring and the long axis of the molecule. For proton dipole-dipole interaction $a = 3/2 \mu_H \Upsilon_{H-H}^{-3}$, where μ_H is the proton nuclear moment and Υ_{H-H} is the distance between the two interacting protons. The experimentally observed dipolar spectra show good agreement with the results calculated for dipole interaction of orthoprotons of the phenyl ring. The values of Υ_{H-H} and ϕ which have been estimated from molecular models (Maier and Saupe 1956) are taken to be 2.45 Å and 10° respectively. The order parameter as a function of the dipole-dipole splitting δH of the interacting protons turns out to be

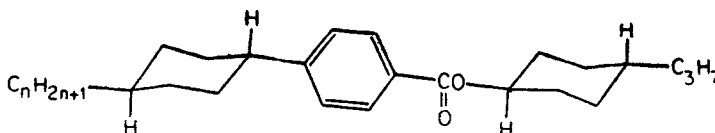
$$S = \delta H / 5.50. \quad (2)$$

The order parameters obtained by the wide line PMR studies are compared with those obtained by the optical studies.

2. Experimental

2.1 Optical studies

The samples of trans-4-propyl cyclohexyl-4 (trans-4-alkyl cyclohexyl) benzoates



with $n = 2, 3$ and 5 used in our studies are manufactured by E Merck, Darmstadt and were recrystallized before use. The phase transitions are given below

- (i) $n = 2$, trans-4-propyl cyclohexyl-4 (trans-4-ethyl cyclohexyl) benzoate (TPEB); Melting point 94°C; Clearing point 134°C
- (ii) $n = 3$, trans-4-propyl cyclohexyl-4 (trans-4-propyl cyclohexyl) benzoate (TPPB); Melting point 92°C; Clearing point 158°C
- (iii) $n = 5$, trans-4-propyl cyclohexyl-4 (trans-4-pentyl cyclohexyl) benzoate (TPPEB); Melting point 67°C; Clearing point 154°C.

2.1a. *Refractive indices measurement.* The refractive indices were measured by a prism technique by measuring the angles of minimum deviation and the angles of special hollow pyrex glass prisms with very small refracting angles (4–6°) with a precision coniometer spectrometer reading to 2'' of arc. The specimens were aligned along the axis of the prism by rubbing the surface of the prism. The aperture of the optical system was chosen to be very small to guarantee uniform

orientation. The temperature of the specimen was varied by an electrically controlled copper block of large thermal capacity which allowed steady temperatures to an accuracy of about 0.1°C. The refractive indices for the nematic and isotropic phases were measured for three wavelengths 4358, 5461 and 5893 Å to an accuracy of ± 0.002 .

2.1b. *Density measurements.* The densities of liquid crystalline and isotropic phases of the materials have been measured by studying the volume expansion of a known weight of the sample taken in a fine capillary and applying corrections for the volume expansion of a container (pyrex glass). The accuracy of the measurements was $\pm 0.005 \text{ g cm}^{-3}$.

2.2 PMR studies

Wide line PMR spectra were recorded at different temperatures using NMR spectrometer (Varian Associates V4200) at TIFR Bombay. The spectrometer consists of a water-cooled electromagnet with a pole diameter of 9 inches (22.5 cm) more and with a gap of 1.75 inches (4.5 cm), a current stabilizer, a model 5204 lock-in-analyser, a variable frequency oscillator-detector, a C1024 average computer and a strip chart recorder (Rigaku Denki) with necessary power supplies. The temperature of the sample was varied by immersing the probe in a bath of nitrogen gas which was electrically heated. Sample temperatures were measured by immersing a precalibrated copper-constantan thermocouple directly into the sample to an accuracy of 0.1°C. The accuracy in δH measurements is 0.2 gauss.

3. Results and discussion

The refractive index and density data for the nematic and isotropic phases are tabulated in tables 1 to 3. Figure 1 gives the temperature variation of birefringence. It was noticed that the birefringence values are much lower than those reported

Table 1. Refractive indices and densities in the nematic and isotropic phases of TPBB.

$T_c - T$ (°C)	Density (g/cc)	λ 4358		λ 5461		λ 5893	
		n_e	n_o	n_e	n_o	n_e	n_o
- 3 (liquid)	1.1405	1.509		1.497		1.496	
5	1.1543	1.560	1.505	1.543	1.487	1.540	1.484
9	1.1585	1.564	1.498	1.552	1.485	1.550	1.482
13	1.1624	1.568	1.495	1.555	1.483	1.553	1.479
17	1.1661	1.575	1.492	1.557	1.480	1.555	1.479
21	1.1696	1.577	1.491	1.558	1.480	1.556	1.477
25	1.1731	1.582	1.490	1.562	1.479	1.558	1.476
29	1.1764	1.583	1.489	1.563	1.478	1.559	1.475
33	1.1797	1.585	1.489	1.565	1.477	1.560	1.475
37	1.1829	1.586	1.488	1.565	1.477	1.565	1.475
40	1.1852	1.589	1.488	1.567	1.475	1.568	1.474

Table 2. Refractive indices and densities in the nematic and isotropic phases of TPPB.

$T_c - T$ (°C)	Density (g/cc)	λ 4358		λ 5461		λ 5893	
		n_e	n_o	n_e	n_o	n_e	n_o
- 2 (liquid)	1.0429	1.499		1.486		1.482	
3	1.0609	1.553	1.480	1.537	1.474	1.537	1.470
10	1.0685	1.566	1.478	1.548	1.470	1.542	1.468
14	1.0723	1.567	1.475	1.550	1.469	1.546	1.465
18	1.0759	1.570	1.475	1.553	1.467	1.548	1.462
22	1.0795	1.572	1.474	1.556	1.465	1.551	1.460
26	1.0829	1.575	1.474	1.557	1.465	1.553	1.460
30	1.0879	1.579	1.474	1.561	1.465	1.556	1.460
34	1.0895	1.582	1.473	1.565	1.465	1.558	1.460
38	1.0927	1.584	1.473	1.567	1.465	1.561	1.460
42	1.0958	1.589	1.472	1.570	1.465	1.565	1.460
46	1.0989	1.590	1.472	1.572	1.465	1.568	1.460
50	1.1019	1.592	1.470	1.575	1.465	1.570	1.460
54	1.1049	1.595	1.470	1.577	1.465	1.575	1.460
58	1.1079	1.599	1.470	1.580	1.465	1.578	1.460

Table 3. Refractive indices and densities in the nematic and isotropic phases of TPPEB.

$T_c - T$ (°C)	Density (g/cc)	λ 4358		λ 5461		λ 5893	
		n_e	n_o	n_e	n_o	n_e	n_o
- 5 (liquid)	1.0791	1.491		1.477		1.475	
5	1.0949	1.548	1.475	1.532	1.476	1.528	1.470
10	1.1001	1.559	1.472	1.542	1.475	1.536	1.468
15	1.1048	1.562	1.470	1.545	1.473	1.541	1.465
20	1.1093	1.566	1.470	1.548	1.470	1.544	1.465
25	1.1139	1.571	1.470	1.554	1.470	1.552	1.463
30	1.1195	1.576	1.470	1.559	1.470	1.555	1.462
35	1.1219	1.580	1.470	1.562	1.469	1.558	1.462
40	1.1259	1.582	1.470	1.563	1.468	1.559	1.462
45	1.1298	1.585	1.470	1.565	1.467	1.562	1.462
50	1.1365	1.588	1.470	1.568	1.465	1.565	1.462
55	1.1373	1.590	1.470	1.569	1.464	1.566	1.462
60	1.1410	1.592	1.470	1.572	1.463	1.568	1.462
65	1.1447	1.595	1.470	1.574	1.462	1.570	1.461
70	1.1482	1.598	1.470	1.576	1.462	1.571	1.461
75	1.1518	1.599	1.470	1.580	1.462	1.572	1.460
80	1.1553	1.600	1.470	1.582	1.461	1.573	1.460
85	1.1580	1.601	1.470	1.584	1.460	1.575	1.459
87	1.1602	1.602	1.470	1.585	1.460	1.576	1.458

earlier for materials comprising benzene groups (de Jeu and Bordewijk 1978; Gasparoux *et al* 1979; Hanson and Shen 1976; Ibrahim and Haase 1979; Dabrowski *et al* 1980; Sarna *et al* 1979; Laurent and Jourmeaux 1976; Madhusudana *et al* 1971) and also lower than those reported for trans-4-alkyl (4-cyano phenyl) cyclohexane series (Abdoh *et al* 1982).

The variation of order parameter (Neugebauer approach Haller plot (Haller *et al* 1973)) with temperature is shown in figure 2. Haller's extrapolation procedure used to get absolute values of S is known to yield values which are at best accurate to $\pm 10\%$. The S factor for the TPPEB compound is very high, possibly since this compound shows the liquid crystalline phase over a very wide range of temperature (87°C).

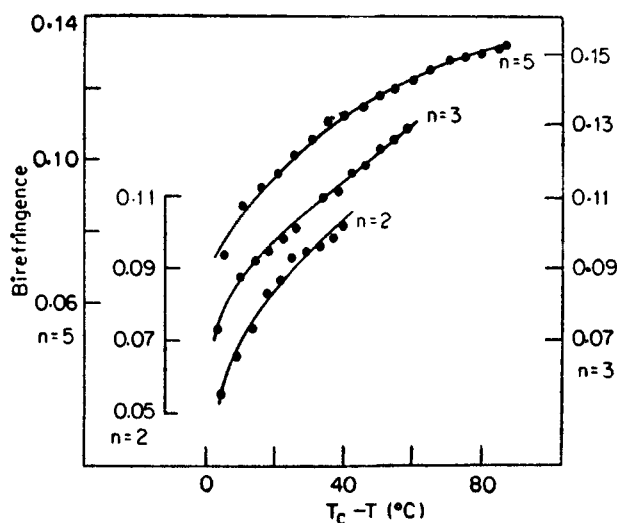


Figure 1. Temperature variation of birefringence for TPPEB ($n = 2$), TPPB ($n = 3$) and TPPEB ($n = 5$) for $\lambda 4358 \text{ \AA}$.

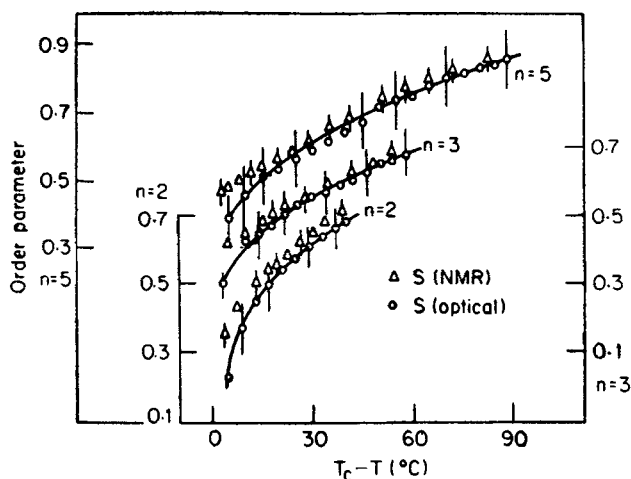


Figure 2. Temperature variation of S factor for TPPEB ($n = 2$), TPPB ($n = 3$) and TPPEB ($n = 5$) for $\lambda 4358 \text{ \AA}$.

The S values obtained by PMR measurements are also shown in figure 2. There is fairly good agreement between the two sets of values. The S values obtained by PMR data are slightly higher than those obtained from refractive index data. The discrepancy between the two sets of data increases with increasing temperature. This has been observed in other liquid crystalline materials also (Subramhanyam and Krishnamurti 1973; Subramhanyam *et al* 1974).

We had earlier observed that the discrepancy between the NMR and optical data decreases with increasing temperature (Abdoh *et al* 1982). The discrepancy also remained constant throughout the mesomorphic range (Shashidhara Prasad 1976; Subramhanyam and Shashidhara Prasad 1976; Shivaprakash 1981). This can be explained in terms of the increasing deviation of cylindrical symmetry of alkyl chain with respect to a position (Vaz *et al* 1981).

The compounds studied earlier (Abdoh *et al* 1982) have lower nematic-isotropic transition temperatures (thermal stabilities) whereas the compounds now studied have higher thermal stabilities. The various trends observed in the discrepancy between NMR and optical data can be understood in the light of interplay between the deviation from cylindrical symmetry influencing NMR data and decrease in optical anisotropy influencing refractive index data. For compounds of higher thermal stability (higher nematic isotropic transition) optical anisotropy effect plays a dominant role and overtakes the role played by cylindrical symmetry. As such the discrepancy increases with increasing temperature. In the same way the constancy and decreasing trend of discrepancy with increasing temperature can be understood. It is quite plausible that this discrepancy plays a significant role in the understanding of order-parameter fluctuations near liquid crystalline transitions.

We shall discuss the packing coefficient for this homologous series in the light of the order parameter studies (Shivaprakash and Shashidhara Prasad 1981). The packing coefficient defined to be the ratio of geometrical volume to the volume occupied per molecule in the crystal falls out separately for symmetric (TPPB = 0.757) and asymmetric (TPEB = 0.820, TPPEB = 0.794) end groups (Shivaprakash *et al* 1980). The higher values of the packing coefficients can be attributed to the higher densities of these compounds.

We observe that the packing coefficients and S values are quite high as compared with those of other nematogenic materials comprising of benzene moieties only. This can be attributed to the existence of the two cyclohexane groups on either side of the central benzene ring. These cyclohexane groups with their direction of polarization transverse to the length of the molecules and the polarization direction of benzene ring contribute to strong attractive interaction between neighbouring molecules to define an efficiently packed structure in the crystalline state which in turn explains the higher and wide range of ordering in nematic phase and change in physical properties.

Acknowledgements

The authors thank Professor A Bauer, West Germany, for the chemicals and Professor R Vijayaraghavan, TIFR, Bombay for providing experimental facilities. JSP would like to thank the University Grants Commission, India for a Career award. The award of research fellowships to Srinivasa and NCS by the University Grants

Commission, India is gratefully acknowledged. MMMA thanks Royal Jordan Government for a fellowship.

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