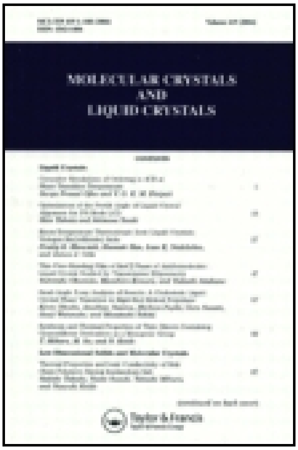

Molecular Crystals and Liquid Crystals Science and Technology. Section A. Molecular Crystals and Liquid Crystals

Small Angle X-Ray Diffraction Studies on the Homologous Series of Mesogenic 4-(trans-4′-n-Alkylcyclohexyl)Isothiocyanatoben

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Small Angle X-Ray Diffraction Studies on the Homologous Series of Mesogenic 4-(*trans*- 4'-n -Alkylcyclohexyl)Isothiocyanatobenzenes

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The compounds of the series (nCHBT in short, n=4–9) show only nematic phase with supercooling effect. 4CHBT and 5CHBT show monotropic transition. X-ray diffraction studies of magnetically oriented samples have been done in the entire nematic range which indicate that all the members possess ordinary nematic phase. The average intermolecular distance is found to be ~5.1Å for all of them. The apparent molecular length, l varies from 22.3Å for 4CHBT to 29.3Å for 9CHBT at $0.98T_{NI}$. Temperature dependence of these parameters has been discussed. Average values of apparent molecular lengths in their nematic range are found to be ~1.1 times of their respective molecular model lengths indicating the presence of bimolecular association. The orientational order parameters, $\langle P_2 \rangle$ were found to be slightly higher than Maier-Saupe theoretical values and lower than the values obtained from refractive index studies; whereas $\langle P_4 \rangle$ values were found to be comparable with Maier-Saupe values. The results have been discussed in relation to three other similar homologous series.

Keywords: nematic; X-ray diffraction; order parameters; molecular association

INTRODUCTION

J. W. Baran *et al.*[1] studied refractive index, density and dielectric constants of members of the homologous series 4- (*trans* -4' -n -alkylcyclohexyl)

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isothiocyanatobenzenes [nCHBT in short] with n=3-10. A. Nath *et al.*[2,3] have also measured several physical and molecular properties of 3CHBT from X-ray diffraction, refractive index, density and dielectric studies. N. K. Pradhan[4] has recently reported the results of X-ray diffraction studies and measurements of refractive index, magnetic susceptibility anisotropy, density and elastic constants for n=10 and 12. All the members of the series show only nematic phase. In this paper we present the results of our X-ray diffraction studies of the homologues with n=4-9 and discuss the effect of rigid core and end polar groups on their mesogenic properties.

EXPERIMENTAL

Phase transition temperatures were determined by texture studies. Small angle X-ray photographs were taken throughout the nematic range using Nickel filtered CuK_α radiation. The details of experimental arrangement have been given earlier.[5] The samples, taken in the glass capillary of about 1 mm diameter, were aligned by slow cooling from the isotropic phase to the desired temperature in presence of a magnetic field of 4 KG. All photographs were taken with X-rays perpendicular to the field direction. The temperatures were controlled within ±0.5°C by a temperature controller.

RESULTS AND DISCUSSIONS

The transition temperatures agree well with the reported values[6] within ±1°C, we also observed supercooling in most of the compounds. We found nematic marble textures in all cases and typical schlieren textures were observed near clearing points. The transition temperatures (in °C) are given below, monotropic temperatures in parentheses.

Transition temperatures	Crystallization temperatures
4CHBT K 34.5 (N 33.5) I	**~14.5**
5CHBT K 68.0 (N 51.8) I	**33**
6CHBT K 12.5 N 42.6 I	**~5**
7CHBT K 38.1 N 52.1 I	**18**
8CHBT K 27.8 N 45.4 I	**~16**
9CHBT K 39.1 N 53.4 I	**31.8**

It might be of interest to compare the phase sequence of nCHBT with three other related homologous series, whose molecular formulae are given below.

nCB : C_nH_{2n+1}-Ph-Ph-CN ; nBT : C_nH_{2n+1}-Ph-Ph-NCS
nPCH : C_nH_{2n+1}-Cy-Ph-CN ; nCHBT : C_nH_{2n+1}-Cy-Ph-NCS

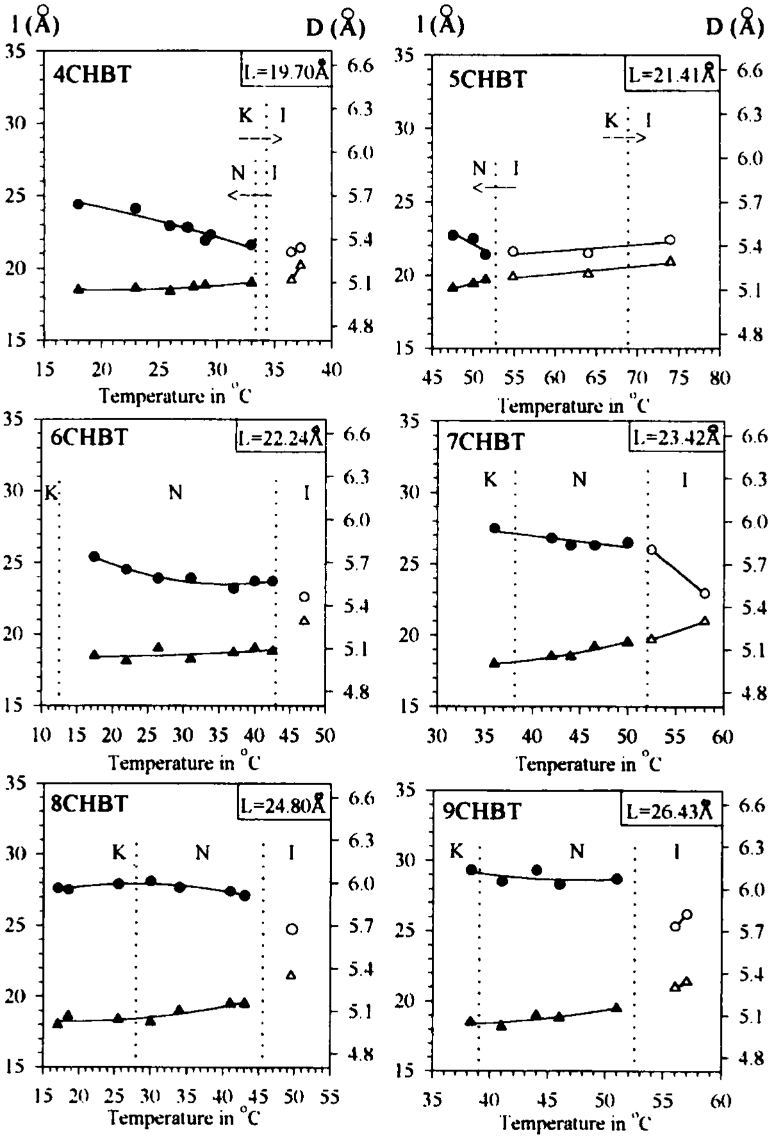

FIGURE 1 Variation of the average intermolecular distance (D: ▲△) and apparent molecular length(l: ●○) with temperature. L is the molecular model length.

While all members of nCHBT (n ≤ 12) show only nematic phase, the members of nCB with n ≥ 8 and nPCH series with n ≥ 10 show smectic A phase. Members of nBT series with n ≥ 4 show smectic E phase only. These differences may be the result of the differences in either central core or terminal group or both in the molecular structures.

Average intermolecular distances (D) were calculated locating the equatorial peak positions of the outer diffraction halo of the X-ray photographs, using the expression[7] $2D\sin\theta=1.117\lambda$. D values lie between 5.05 and 5.15 Å and no variation is found with alkyl chain length. With increasing temperature D values show slightly increasing trend as depicted in Figure 1. The average intermolecular spacing was found to be around 5.0 Å in nCB series.[8] This change in D may be the result of replacement of a planar benzene ring by a non-planar cyclohexyl ring.

Apparent molecular lengths (l), determined from the meridional diffraction peak using Bragg's relation, are found to be greater than the model lengths (L) of respective molecules obtained by HiperChem programme using MNDO method and atomic radii for r_H=1.6Å and r_S=2.015Å. Variation of l with temperature is shown in Figure 1. It is observed that l increases with chain length and decreases with temperature for all the homologues. The l/L ratio varies between 1.04 and 1.16. In 10CHBT and 12CHBT also the ratio was found to be about 1.15.[4] However, this ratio is smaller than the value (1.4) found in nCBs.[8] So some bimolecular association exists in nCHBT but the molecular overlap is certainly more than that in nCBs. Dielectric studies of 6CHBT in CCl_4 show the presence of both monomers and dimers[9a,b] but the association is weaker than that in the solution of 5CB in C_6H_6. Decrease of l with temperature, as noted above, may be due to the increased motion of alkyl chains, change in the molecular overlap or decrease of dimer concentration.

From the azimuthal intensity distribution of the outer diffraction halo we have calculated the orientational order parameters $\langle P_2\rangle$ and $\langle P_4\rangle$ after necessary background correction. The detailed procedure for calculation of these parameters has been reported earlier.[10] The errors in the calculation are estimated as ±0.02. Variations of $\langle P_2\rangle$ and $\langle P_4\rangle$ with temperature are shown in Figure 2, where we have also given Maier-Saupe (M-S) theoretical values. $\langle P_2\rangle$ values so determined are found to be higher than the M-S values as also previously observed in 3CHBT[2] and 10CHBT[4], whereas the $\langle P_4\rangle$ values are more or less consistent with the theoretical values. As it is known that the orientational behaviour of the nematic phase may be distinguished in two parts : a long range order and a short range one. Whereas the M-S model reflects long range ordering in the liquid crystal phases, a short-range local ordering due to intermolecular interactions also exists.[11] This short-range interaction causes an increase in $\langle P_2\rangle$ values. We have also calculated $\langle P_2\rangle$ values from the refractive index data of J. W. Baran *et al.*[1] following a

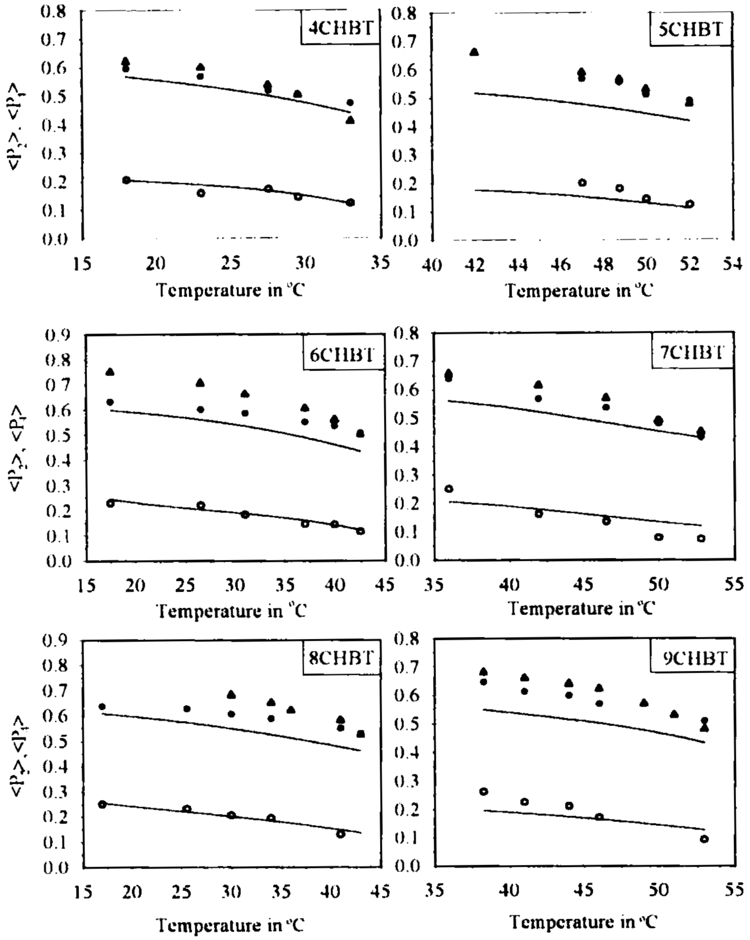

FIGURE 2 Variation of order parameters with temperature.

• X-ray $<P_2>$ data ○ X-ray $<P_4>$ data

▲ Refractive Index $<P_2>$ data — M-S values

procedure described by Zeminder *et al.*[12] These $<P_2>$ values are also shown in Figure 2. $<P_2>$ values obtained from two methods (X-ray and optical) differ considerably and such behaviour were reported in the previous papers.[13,14] This may be due to the differences in the techniques of alignment and difference in the averaging involved. Also there may be error in the estimation of ($\alpha_{||}$-$\alpha_{\perp}$) by Haller's extrapolation[15] method utilized in the determination of <P_2> from optical data.

The compounds in this series show a remarkable odd-even effect in the <P_2> values determined from both X-ray and refractive index studies and in polarizability anisotropy values. This effect was also observed previously in transition temperatures, dielectric and conductivity properties.[16] It will be discussed in details in a separate communication.

A comparison of the l/L (l, average value of apparent molecular length in the nematic phase) ratio, l-L difference and <P_2> values obtained from refractive index studies for the fifth member of nCB, nPCH, nBT and nCHBT series enables us to evaluate the changes of these quantities which are brought about by substitution of phenyl ring by a cyclohexyl ring or of a -CN by an -NCS or both. These data are collected in Table I. We find that replacement of a phenyl by a cyclohexyl group gives rise to nematic from SmE phase (5BT→5CHBT). Some bimolecular association exists in all cases, however strong intermolecular interaction between 5BT molecules in SmE layers cancels the probability of dimer formation. It is evident that overlap of the association increases when phenyl is replaced by cyclohexyl group or -CN is replaced by -NCS group and the effect is additive when both groups are changed simultaneously.

TABLE I Comparison of some properties of 5CB, 5PCH, 5BT and 5CHBT

Substitution	Example	l (A)	l-L(A)	l/L	<P_2>
-Ph-→-Cy-	(5CB→5PCH)	25.7[8]→24.9[17]	7.7→4.96	1.43→1.25	0.54[19] → 0.48[19]
&	(5BT→5CHBT)	20.0[18]→22.2	−1.9→0.79	0.92→1.04	~1* →0.62
-CN →-NCS	(5CB→5BT)	25.7 →20.0	7.7 →−1.9	1.43→0.92	0.54 → ~1
&	(5PCH→5CHBT)	24.9 →22.2	4.96→0.79	1.25→1.04	0.48 →0.62
Both	(5CB →5CHBT)	25.7 →22.2	7.7→0.79	1.43→1.04	0.54 →0.62

All <P_2>values from refractive index study are at $0.98T_{NI}$(°K). L_{5CB}=18[8] and L_{5PCH}=19.94, L_{5BT}=21.86, L_{5CHBT}= 21.41A from MNDO calculations. * SmE phase

We also note that replacement of a phenyl by cyclohexyl group decreases the <P_2> values whereas <P_2> increases when -CN is replaced by -NCS group. If both the groups are changed, then also <P_2> increases. These indicate that the effect of change of the groups on order parameter is additive but the effect of terminal group predominates.

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