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Orientational Order of Some Nematogenic Compounds

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Orientational Order of Some Nematogenic Compounds

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The paper discusses the results of the calculation of the orientational order parameters in the case of five nematogenic compounds. The order parameters are compared with the Maier–Saupe theoretical curve. The calculated values of characteristic absorption wavelength in each case corresponds to the conjugated bridge of the molecule.

1. INTRODUCTION

A number of earlier investigators have made NMR[1,2], Diamagnetic anisotropy[3], and birefringence[4–10] studies for the calculation of orientational order parameter (S-factor) in nematic phase of nematogenic compounds. Here we present the orientational order for the compounds listed below

(i) 4-*N*-Hexyloxy 4′-*N*-amyl-α-cyanobenzyl
($C_6H_{13}OC_6H_4C(CN):CHC_6H_4C_5H_{11}$)

(ii) 4-*N*-amyl 4′-hexyloxy-α-cyanobenzyl
($C_5H_{11}C_6H_4C(CN):CHC_6H_4C_6H_{13}O$)

(iii) 4-cyanophenyl derivative of (4-*N*-amyloxy benzoic acid)
($C_5H_9OC_6H_4CO:OC_6H_4CN$)

(iv) 4-*n* hexyl benzyl derivative of 4-δ-cyanobutoxy phenyl
($C_7H_{15}C_6H_4CO:OC_6H_4OC_4H_8CN$)

(v) 4-*N*-octyloxy 4′-cyano bi phenyl
($C_8H_{17}OC_6H_4C_6H_4CN$)

using birefringence and density data reported by Rumtsef *et al.*[11]

Although there are different approaches for the calculation of orientational order from refractive index data[12-16], it should be mentioned here that the different approaches, give reasonably consistent results and there is a broad agreement with the values obtained from other studies. Madhusudana[17] has discussed the relative merits of these approaches. In the present study Neugebauer relations have been employed since it accounts, to some extent, for the effect of the polarization field in the nematic phase. For the calculation of S-factors, it is necessary to obtain the value of anisotropic polarizability $(\alpha_{\parallel} - \alpha_{\perp})$ for the case wherein the molecules are perfectly parallel to each other and oriented along the preferred direction. This can be obtained using the refractive index data in the crystalline phase or using the bond polarizability data.

2. CALCULATION OF POLARIZABILITIES

The polarizabilities α_e, α_0 and $\bar{\alpha}$ in nematic and isotropic phases are calculated using Neugebauer and Lorenz-Lorentz relations respectively.[10] These values are tabulated in Table I.

3. CALCULATION OF ANISOTROPIC POLARIZABILITY $\Delta\alpha = \alpha_{\parallel} - \alpha_{\perp}$

Subramhanyam *et al.*[18] have discussed in detail regarding the estimation of anisotropic polarizability of the molecule using bond polariza-

TABLE I

Calculated polarizabilities from refractive index data and bond polarizability data in units of 10^{-24} cm^3 for the five compounds

Temp. $(T_c - T)$ in °C	1		2		3		4		5	
	α_e	α_0	α_e	α_0	α_e	α_0	α_e	α_0	α_e	α_0
0.5	58.7	46.7	58.2	47.2	40.8	33.6	51.6	45.8	43.9	37.3
1.0	59.1	46.5	58.7	46.9	40.9	33.5	52.5	45.4	44.7	36.9
5.0	61.6	45.3	60.7	45.9	41.5	33.2	52.7	45.2	46.0	36.2
10.0	62.4	44.8	61.7	45.4	42.9	33.0	—	—	46.7	35.9
20.0	63.4	44.4	63.2	44.7	44.0[a]	31.9[a]	—	—	47.5	35.5
$\bar{\alpha}_{iso}$	50.7		50.8		36.0		47.8		39.5	
$\bar{\alpha}_{Bond}$	51.0		51.0		36.4		49.8		39.5	
$\alpha_{\parallel Bond}$	69.3		69.3		47.9		57.1		51.2	
$\Delta\alpha_{Bond}$	27.4		27.4		17.9		13.9		17.6	
$L_o - L_e$ at $T_c - T = 5$	0.080		0.052		0.038		0.020		0.043	

[a] $T_c - T = 30$

bility data. In the calculation of $\Delta\alpha$ we take the molecular axis to be along the line joining the centres of the two benzene rings and assume molecules to be rigid. The calculated values of $\alpha_{\parallel}$, $\bar{\alpha}$ and $\Delta\alpha$ are given in Table I.

4. CALCULATION OF ORDER PARAMETER(S)

The orientational order parameters at different temperatures are calculated using the values of α_e, α_0 and $\Delta\alpha$ given in Table I for the five compounds. In Figure 1, the order parameters S for the five compounds are compared with those of Maier–Saupe theoretical curve.[19,20] The values of S for the compound 1 are consistently higher than those of compound 2, wherein compound 2 is similar to compound 1 except for the fact that the end chains on either side of central rigid portion of the molecule are interchanged. This clearly indicates that the pseudo-potential and hence the anisotropic pair potential for compound 1 is steeper than that for compound 2. In fact, the anisotropy $(L_0 - L_e)$ of the Lorentz field factor calculated at the same $T_c - T$ (Table I) for compound 2 is less than that of compound 1 indicating that as a consequence of numerous conformations possible

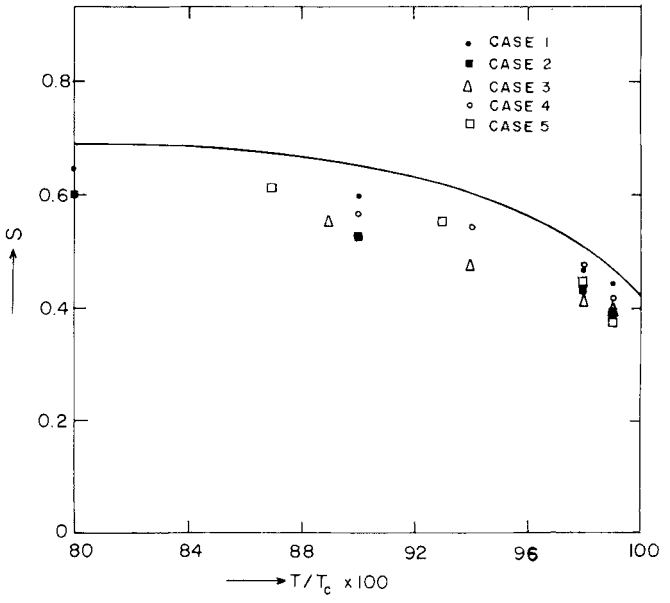

FIGURE 1 Orientational order parameter versus reduced temperature for the five nematogenic compounds. The curve predicted by the Maier–Saupe theory.

TABLE II

Characteristic absorption wavelength for some nematic compounds calculated using dispersion relation for mean polarizability

Compounds	λ_0 in Å	Standard value C. N. R. Rao *et al.*	
PAA	2474	3380	N=N
PAP	2403	3380	N=N
Anisaldazine	2240	2350 3380	C=N N=N
MBBA	2010	2350	C=N
Case 1	2260	1710	C=C
Case 2	2470	1710	C=C
Case 3	1470	1600	C=O
Case 4	2170	1600	C=O
Case 5	1690	1710	C=C

for the end chains, there is a reduction in the anisotropy of polarization field. In all the five cases, the *S*-factor curves are almost parallel to the Maier-Saupe theoretical curve and lie slightly below the theoretical curve. Thus Maier-Saupe theory gives a general trend of variation of order parameter with temperature for the above nematogenic compounds.

In Table II are given the values of λ_0, the characteristic absorption wavelength calculated, using dispersion relation for the polarizability for the above five compounds along with the compounds like PAA, PAP, anisaldazine and MBBA which have been studied extensively. The characteristic wavelength λ_0 in each case corresponds approximately to the conjugated bridge of the molecule.

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