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ORIENTATIONAL ORDER PARAMETERS IN THE SMECTIC C AND NEMATIC PHASE OF HEPTYLOXYAZOXYBENZENE (HAB).

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Abstract Orientational order parameters (OOP) in the smectic C and nematic phases of heptyloxyazoxybenzene (HAB) have been determined from x-ray diffraction and refractive index studies. Order parameters determined from x-ray studies have been corrected for the random orientation of the director in a cone in the smectic C phase of HAB. The causes of discrepancy between the experimental and theoretical OOP values have been discussed.

INTRODUCTION

Quantitative knowledge of orientational order parameters (OOP) is necessary to test either the different theories of liquid crystalline mesophases or the applicability of the liquid crystal in a display device. The compound heptyloxyazoxybenzene (HAB), which has a smectic C and a nematic phase, has been a subject of much interest and has been widely studied by different workers[1-6]. OOP of HAB in the nematic phase were determined by Leadbetter et al from x-ray measurements[1]. Chistyakov et al has estimated the tilt angle in the smectic C and nematic phase[2]. A.de Vries had earlier reported the presence of skewed cybotactic nematic phase in this compound[3]. McMillan has measured the anisotropic liquid structure factor in the nematic phase[4].

From x-ray critical scattering Terauchi et al has investigated the nature of the smectic C to nematic phase transition[5]. The ordinary refractive index and birefringence of HAB in the nematic phase have been reported by others[6,7]. In this paper we report the density, refractive indices (n_o,n_e), birefringence and OOP values of this compound both in the smectic C and nematic phases from x-ray diffraction and optical studies. We have explained the anomaly in experimental orientational order parameter values in the smectic C phase, as obtained from x-ray scattering intensities, using a model of random tilt. This model has been succesfully applied to the smectic C phase of a commercial liquid crystal mixture having smectic A phase as well[8], but to our knowledge no such attempt has been made on compounds having smectic C phase without smectic A phase. OOP's determined from x-ray diffraction and refractive index studies are found to differ significantly in the smectic C phase, reason for which has been discussed. We have also compared our experimental results with those of other workers.

EXPERIMENTAL

Transition temperatures of this compound were determined using a Mettler FP82 Thermosystem, and were found to agree with literature values. The measured values are the following:

$$\text{Crystal} \xleftrightarrow{74^{o}C} \text{Smectic C} \xleftrightarrow{93^{o}C} \text{Nematic} \xleftrightarrow{124^{o}C} \text{Isotropic}$$

The experimental set up and the procedure for order parameter determination from x-ray diffraction[9] and refractive index and density[10] studies have been described in detail in our earlier publications. Samples were aligned using a magnetic field of about 6 Kilogauss for x-ray

diffraction experiment. Refractive indices were measured by a thin hollow prism method, sample being surface aligned by rubbing.

RESULTS AND DISCUSSIONS

(a) X-ray diffraction studies

The x-ray diffraction photographs of the oriented sample in the nematic phase shows the presence of skewed cybotactic groups, with the inner ring split up into four spots of strong intensity. Tilt angle in the nematic phase has been measured to be 29.5 degree at 97°C, the value changing to 29.2 degree at 93°C (the nematic to smectic C transition point), which are in agreement with those reported by Leadbetter et al[1] but deviate from those given by Chistyakov and Chaikowsky by 3-4 degree[2].

The x-ray diffraction photographs of the smectic C phase of HAB were similar to those obtained from monodomain smectic A samples, indicating that in our sample the director is randomly oriented in a cone about the layer normal of the smectic C phase, which is the laboratory fixed magnetic field direction. The possible smectic C configuration in this case is of azimuthal disorder (Figure 2b in Reference 1). Tilt angle, θ_t, in this phase has thus been determined indirectly from the layer thickness, l, using the relation $\theta_t = \cos^{-1}(d/l)$, where l is the length of the molecule in all-trans configuration and d is the smectic layer spacing. The molecular model length of the HAB molecule in all- trans configuration is 30.55Å. The tilt angles so determined vary from 40 to 42 degree. However, Leadbetter et al from direct measurements[1], have shown that in the smectic C phase of HAB the tilt angle is (32± 2) degree. This seems to conform to the view[1] that the effective molecular lengths are shorter than the most extended configuration by about 3Å, implying considerable

disorder in the alkyl chains. Thus the tilt angles in the smectic C phase has been calculated using l= 27.55Å in the present paper. Temperature variation of the tilt angle is small, varying from 29.2 degree at 93°C to 32.7 degree at 75°C. Experimentally obtained layer spacing d = 24.38Å ± 0.22, which is in agreement with the previously reported values of Leadbetter et al[1].

The orientational distribution function $f(\theta)$ and hence the orientational order parameters $\langle P_2 \rangle$ and $\langle P_4 \rangle$ have been determined from x-ray intensity data using the method described previously[9]. The temperature variation of $\langle P_2 \rangle$ and $\langle P_4 \rangle$ are shown in figure 1. The $\langle P_2 \rangle$ and $\langle P_4 \rangle$ values reported by Leadbetter et al in the nematic phase of HAB is also shown in the figure. Experimental $\langle P_2 \rangle$ and $\langle P_4 \rangle$ values in the nematic phase agree quite well with those of Leadbetter et al[1] and also with those calculated from Maier-Saupe mean field theory. We have also calculated the orientational order parameters using McMillan's potential[11] for smectic A phase:

$$\varepsilon(\cos\theta,z)=-\varepsilon_0\left[\delta\alpha\tau\cos(2\pi z/d)+\left\{\eta+\alpha\sigma\cos(2\pi z/d)\right\}P_2(\cos\theta)\right]$$

where α and δ are two adjustable parameters, z is the displacement along the layer normal, d is the layer thickness, $\eta = \langle P_2(\cos\theta)\rangle$, the orientational order parameter, while $\tau = \langle\cos(2\pi z/d)\rangle$ is the translational order parameter and $\sigma = \langle P_2(\cos\theta)\cos(2\pi z/d)\rangle$ is the mixed translational and orientational order parameter. Using this potential, the values of $\delta = .6$, $\alpha = .39$, the experimental nematic to isotropic and smectic C to nematic transition temperatures are reproduced and a reasonably good fit to the measured orientational order parameters in the nematic phase is obtained. However, the agreement between the experimental and calculated $\langle P_2 \rangle$ and $\langle P_4 \rangle$ in the smectic C phase is poor, the experimental order parameters decreasing with decreasing temperature. This is due to the fact that

the molecular tilt at lower temperatures causes the observed orientational distribution function with respect to the layer normal to become broader at lower temperatures. Since the layer normal is parallel to the applied magnetic field direction and normal to the x-ray

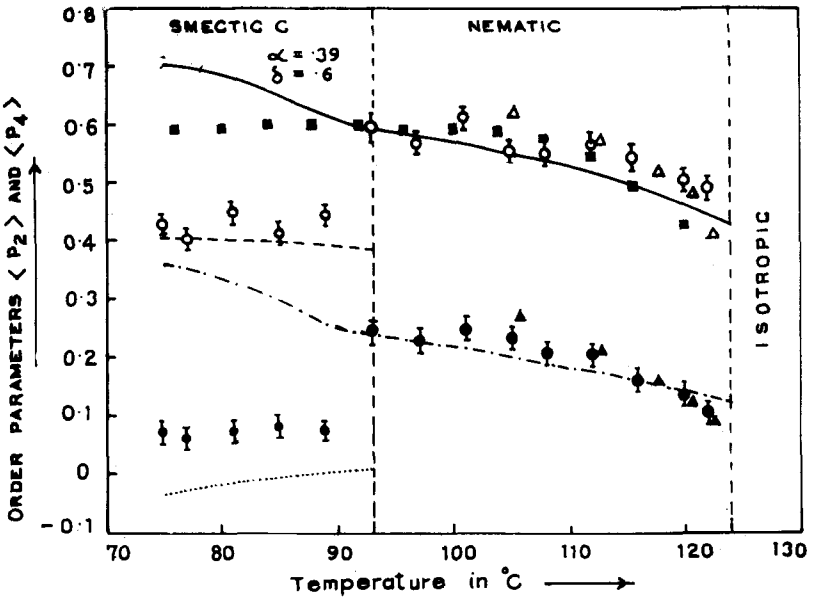

FIGURE 1 The orientational order parameters for HAB; o, x-ray data for $\langle P_2 \rangle$; ●, x-ray data for $\langle P_4 \rangle$; ■, refractive index data for $\langle P_2 \rangle$; solid line is theoretical $\langle P_2 \rangle$ from McMillan's potential; dashed line is theoretical $\langle P_4 \rangle$ from McMillan's potential. In smectic C phase the experimental points o and ● correspond to apparent values of order parameters determined with respect to the layer normal. Theoretical apparent order parameters for the smectic C phase including allowance for the tilt angle are represented as follows : – – – – – –, apparent $\langle P_2 \rangle$; ..... apparent $\langle P_4 \rangle$; ▲, x-ray data for $\langle P_2 \rangle$ from Leadbetter et al; ▲ , x-ray data for $\langle P_4 \rangle$ from Leadbetter et al (reference 1). Vertical bars show estimated errors.

beam, the diffraction pattern is caused by the apparent orientational distribution function about the layer normal[8]. Following the procedure given in reference 8, we have calculated the apparent orientational order parameter values in the smectic C phase. The agreement between the experimental and calculated values is fairly good (see figure 1).

(b) Refractive index and density studies

Figure 2 shows the temperature dependences of refractive

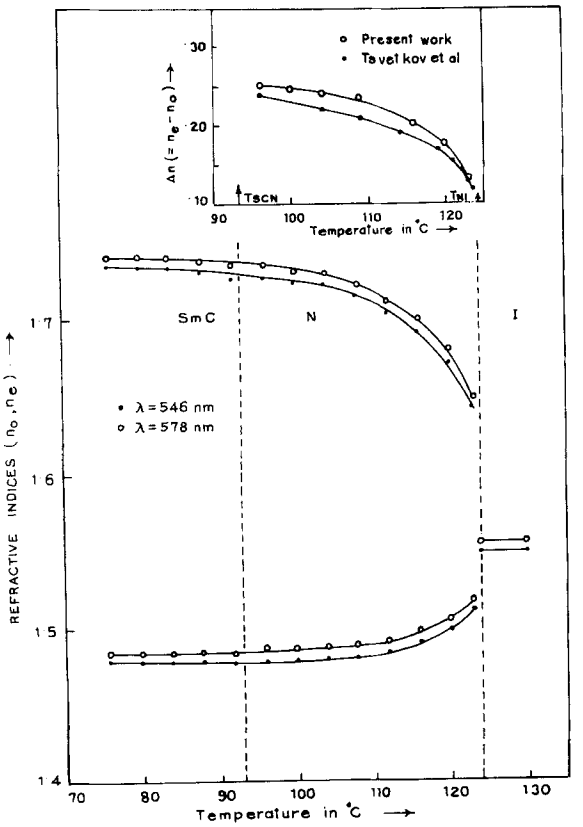

FIGURE 2 Temperature dependence of the ordinary (n_o) and extraordinary (n_e) refractive indices of HAB. Inset shows birefringence values in the nematic phase as compared with Tsvetkov et al (reference 7).

indices, n_o,n_e at two different wavelengths λ=578nm and 546nm. On comparing our Δn (= $n_e - n_o$) values, as shown in inset of figure 2, with those obtained by Tsvetkov et al[7] at λ=546nm, in nematic phase, a reasonable agreement is found.

The density variation of HAB in the temperature range 70°C to 130°C is shown in figure 3. From the figures 2 and 3 it appears that there is a continuous change in the refractive index and density values in going from smectic C

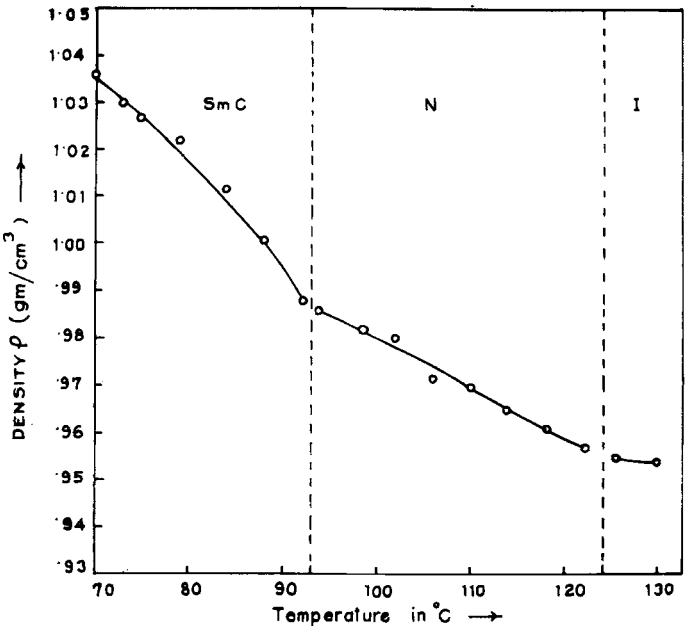

FIGURE 3 The density of HAB as a function of temperature. Solid line is guide to the eye only.

to nematic phase, implying second order phase transition.

Orientational order parameter values obtained on analysing the refractive index and density data, as a function of temperature, using Vuks procedure, are also shown in Figure 1. Although there is good agreement between the OOP's determined from different methods in the nematic phase, there is a large discrepancy in the order parameters

in the smectic C phase. This is due to the fact that in the refractive index determination experiment, the director, in both the nematic and smectic C phases, is pinned along the direction of the surface alignment, whereas, in the x-ray diffraction studies we have seen that the director in the smectic C phase is randomly oriented on a cone about the layer normal. Hence the anisotropy and OOP, which depends on anisotropy, are greater in case of surface aligned samples of HAB than the magnetically aligned samples. However, the OOP values from refractive index measurements in the smectic C phase are still lower than the theoretical values, which may be due to the observed disordering in the alkyl chain[1] part of the HAB molecules in the smectic C phase, causing anisotropy of the system to be reduced.

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