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Orientational Order Parameter in 1-Hexyl-4-(4-Isothiocyanatophenyl) Bicyclo [2, 2, 2] Octane using X-Rays

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1-Hexyl-4-(4-isothiocyanatophenyl)bicyclo[2,2,2]octane (HIPBO), a nematic liquid crystal which shows nematic phase in the temperature range 52.8 to 90.2°C, has been used along with imaging plate system to record X-ray Laue type diffraction pattern at different temperatures. For this purpose oriented sample was used. Orientational order parameter was obtained using Fourier method, recently reported by us, and has been compared with that of other existing methods.

Keywords: Orientational order; Nematic; X-rays

Introduction

A quantitative description of a nematic phase is always expressed interms of order parameter, which is non-zero and vanishes in isotropic phase [1]. The applicability of a nematic liquid crystal in electro-optical devices is determined by its orientational order parameter and hence there is a continued interest in these parameters computed using various methods [2-6]. Among the different approaches, X-ray method is now emerging as a .powerful tool to compute the temperature variation of these orientational order parameters [7–15]. In this article we have computed the second and fourth moments of the distribution function determined using the X-rays arc intensity of a Laue type pattern obtained with an oriented sample of 1-Hexy-4-(4-isothiocyanatophenyl) bicyclo [2, 2, 2] octane (HIPBO).

Experimental

The compound HIPBO was obtained from M/s Aldrich Chemical Company, (U.S.A). Its crystal to nematic and nematic to isotropic transition temperatures were determined using a polarizing microscope in conjunction with a specially constructed hot stage, and also from DSC recordings. The observed transition temperatures are respectively 52.8 and 90.2°C. The enthalpy of transition ΔH at these temperatures were also calculated and are respectively found to be equal to 41.18 and 2.01 J/g. For X-ray intensity recordings the sample was taken in a sealed Lindemann capillary tube and oriented in a magnetic field of strength 6 Kilogauss. The X-ray intensity data from the sample were collected using rotating anode X-ray generator (Rigaku Ultra X18, Japan) at different temperatures in the nematic phase, the temperature being controlled to an accuracy of ±0.1°C. An image plate with a plate diameter of 18 cm was used as the detector (Marresearch, Germany) to collect the intensity data. The distance between the detector and the sample was set at 201.1 mm. Using the supplied X-ray software the X-ray intensity data were sorted as a function of the arc angle The wavelength of the X-rays used was 1.5418Å (Cu Kα). A flat graphite crystal monochromator (Huber, Germany) was used during recordings. The intensity versus arc angle data were obtained by integrating the diffused reflections over an annular ring centered on these reflections. The intensity data were measured in steps of approximately 10 minutes (arc angle). The intensity recordings for a few temperatures are shown in Figure 1.

Computation of order parameter

Arc intensity of a diffraction ring observed in a nematic phase is related to distribution function of the molecular axis via [12]

$$I(\phi) = \int_{\phi}^{\pi/2} f(\beta)\, \sec^2(\phi)\, \sin\beta\, d\beta/(\tan^2\beta - \tan^2\phi)^{1/2} \quad (1)$$

recently we have shown that the above equation can be inverted using a Fourier transform technique [15] by identifying

$$K(\phi,\beta) = \sin\beta/\cos^2\phi\, (\tan^2\beta - \tan^2\phi)^{1/2} \quad (2)$$

and thus taking the Fourier transform of eq. (2), we find the ratio of the corresponding Fourier coefficients of the given intensity arc profile and hence to obtain the distribution function f (β) which are used to find second (P_2) and fourth (P_4) moments.

Results and Discussion

The temperature variation of P_2 for HIPBO is given in Figure 2. Also, in Figure 2 we have plotted the values of P_2 determined using Deutsch method. It is evident from Figure 2, that there is a very good agreement indicating that the present approach is quite reliable. In fact, a comparison of experimental and redetermined intensity from eq. (1) in the present method show that the agreement is less than 1% of the mean value. In Figure 3, we have P_4 versus P_2 along with the results of Maier-Saupe, Hamphries-James-Luckhurst (HJL) and the limit which arises from Schwartz inequality [Ref.1, p 56],

$$P_4 \geq (35\,P_2^2 - 10\,P_2 - 7)/18.$$

The experimental values are in agreement with Hamphries-James-Luckhurst model which suggests that the pair correlations are quite important in these systems and they can have a profound influence on the interpretation of data based on a one-particle approximation. The fact that P_4 is smaller than predicted by Maier-Saupe theory suggests that ϕ fluctuations are not large as expected from the theory.

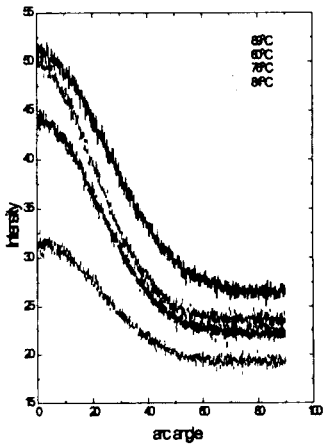

FIGURE 1. X-ray profiles for 1-Hexyl-4-(4-isothiocynatophenyl) bicyclo[2,2,2] octane (HIPBO) at various temperatures.

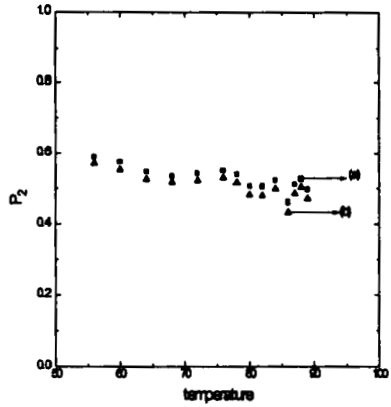

FIGURE 2: Variation of orientational order parameter P_2 with temperature in the case of HIPBO:
(a) Present method and (b) Deutsch method.

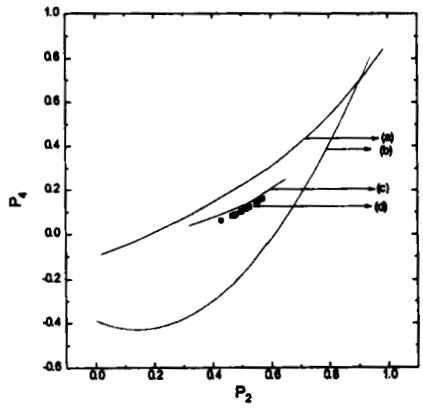

FIGURE 3: The variation of P_4 with respect to P_2
(a) Maier-Saupe Model
(b) $P_4 \geq (35\ P_2^2\text{-}10\ P_2\text{-}7)/18$
(c) Hamphries-James-Luckhurst Model
(d) Present method.

Conclusion

Using X-ray data, we have determined the orientational distribution function using Fourier technique and hence second (P_2) and fourth (P_4) moments. There is a good agreement with the values obtained by Deutsch analytical solutions. Also, X-ray method gives a better agreement with model Hamphries-James-Luckhurst for the plot of P_4 versus P_2, indicating that pair correlations are quite important.

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