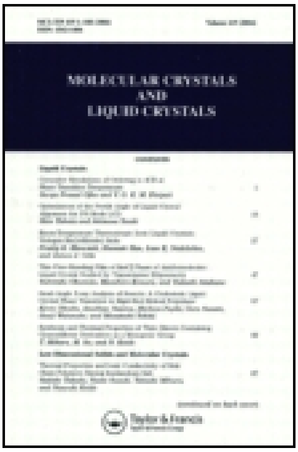

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MOLECULAR ORIENTATIONAL ORDERING OF A LONG CHAIN MESOGENIC COMPOUND.

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Abstract In this communication we present the order parameter values of the chain part of the compound 5- (trans -4- heptylcyclohexyl) -2- (4- cyanophenyl) pyrimidine (HCCPP) in the nematic phase, from the subtle features in the X-ray diffraction pattern and its refractive index anisotropy data.

INTRODUCTION

Liquid crystal molecules, usually elongated and relatively flat, exhibit long range orientational order in the mesomorphic phases. Various experimental methods have been used to measure orientational ordering of mesogenic molecules in uniaxial liquid crystals. But in reality, typical mesogenic compounds are neither rigid nor highly symmetric, flexible hydrocarbon 'tails' are attached to either one or both ends of a central core. The tail part often has low symmetry and more internal degrees of freedom and as a result, it can take different conformations.

In our laboratory orientational order parameter values have been estimated from X-ray diffraction and optical methods etc. for different mesogenic compounds which have flexible hydrocarbon chain. It has been found that orientational order parameter values for this type of mesogens as determined from X-ray diffraction technique are much less than those from refractive index measurements[1]. The discrepancy between the results obtained from these two methods is due to the contribution of the long hydrocarbon chain whose axis is tilted with respect to the axis of the core. Thus it is important to consider the chain contribution to the scatterred intensity separately while analysing X-ray data and comparing it to the contribution due to the rigid part[2].

In this paper we estimated orientational order parameter of the chain part of a mesogenic compound in the nematic phase. This compound has been studied by X-ray diffraction and optical methods[1] and it has the following structure and transition temperatures:

$$C_7H_{15}—C_6H_{10}—C_4N_2H—C_6H_4—CN$$

$$C \underset{75^\circ C}{\overset{82^\circ C}{\rightleftarrows}} SmA \xrightarrow{158^\circ C} N \xrightarrow{223^\circ} I$$

CALCULATIONS AND RESULTS

Leadbetter and Norries[3] have shown that X-ray intensity distribution along the equatorial arc $I(\theta)$, keeping the Bragg angle constant, is related to the orientational distribution function $f(\beta)$ of the molecules by

$$I(\theta) = C \int f(\beta) \sec^2\theta \,(\tan^2\beta - \tan^2\theta)^{-1/2} \sin\beta d\beta \qquad (1)$$

θ value at $I(\theta)$ maximum is taken to be equal to zero. Equation (1) can be solved to determine $f(\beta)$ from experimental $I(\theta)$ values. The orientational order parameter (OOP) can be calculated from the distribution function $f(\beta)$ readily[3]. They have also shown that the calculated $f(\beta)$ fits well with the Maier-Saupe type distribution function

$$f(\beta)=\exp(\alpha \cos^2\beta) \qquad (2)$$

where `α' is the variational parameter. Assuming this form of $f(\beta)$, $I(\theta)$ can be written as

$$I(\theta) = \frac{C \exp(\alpha \cos^2\theta) \operatorname{erf}(\alpha \cos\theta)}{\alpha \cos\theta} \qquad (3)$$

where $\alpha = \frac{6.8123\ S}{\tau}$, $\tau = T/T_{NI}$, S being the orientational order parameter.

The crystal structure of this compound HCCPP had been solved by us[4]. From the crystallographic data we calculated the angle θ_c between the mean axis of the chain part and the axis of the rigid portion which was found to be 27.89°. The equation (2) was used to calculate chain part contributions and rigid part contributions separately and then added together to give the total x-ray intensity distribution, which can be written as

$$I_{cal}(\theta) = C_1 I_R(\theta) + C_2[I_{ch}(\theta+\theta_c) + I_{ch}(\theta-\theta_c)] \qquad (4)$$

where $I_R(\theta)$ is due to the rigid part and $I_{ch}(\theta+\theta_c)$, $I_{ch}(\theta-\theta_c)$ include chain part contribution having two symmectric orientations of the chain $\pm\theta_c$ with respect to the rigid core. θ ranges from 0° to 90°. $I_R(\theta)$, $I_{ch}(\theta+\theta_c)$ and $I_{ch}(\theta-\theta_c)$ were calculated using the relation (2) but with different values of the order parameter. In the calculation of `α' for the rigid part of the molecule, S was taken as determined from refractive index measurement.[1] This is justified since rigid part of the molecule containing cyanophenyl and pyrimidine groups, being highly polarizable, contribute to the refractive indices of the molecule much more than the chain part. For the chain part we varied the value of α and hence its order parameter, so that the experimentally determined X-ray intensity distribution $I_{obs}(\theta)$ fits the value calculated from equation (4). The constants of proportionality C_1 and C_2 were chosen on the basis of the number of non hydrogen atoms included in rigid and chain parts separately. For the compound HCCPP, their ratio is approximately 3 : 1,hence we took $C_1/C_2=3$. Figure 1 shows the fitting of the experimental and the calculated X-ray intensity distribution values for the nematic phase (158°C) of the compound. $I_{cal}(\theta)$ matches with $I_{obs}(\theta)$ for the value of S= 0.52 for the chain part of the molecule. Following this procedure, we estimated the chain order parameter values

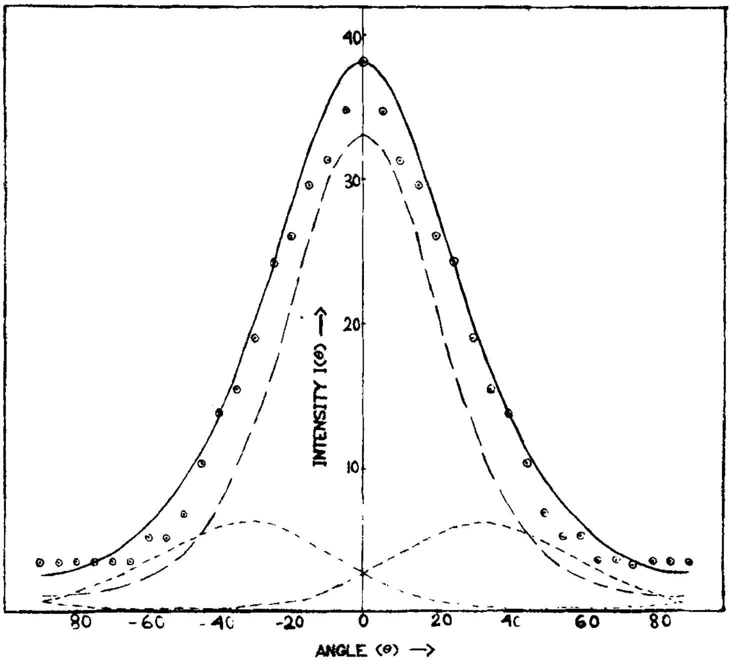

FIGURE 1 I(θ) vs θ at 158°C

———————— $I_{cal}(\theta)$ calculated

—— —— —— (Long dash) $I_R(\theta)$ calculated

-------------- (Short dash) $I_{chain}(\theta)$

O I(θ) experimental (x-ray)

over the whole range of nematic phase of the compound HCCPP. The results are given in Table I.

TABLE - I

Temp(°C)	OOP (X-ray)	OOP(optical)	OOP(Chain)
158	0.47	0.62	0.52
162	0.42	0.61	0.50
177	0.41	0.57	0.47
200	0.39	0.54	0.44

We find that the chain order parameter values are intermediate between the OOP values obtained for this compound from X-ray and refractive index measurements. This is not surprising, since as mentioned before, the refractive indices depend strongly on the rigid part which has understandably large OOP values. On the other hand X-ray diffraction studies provide a weighted mean (depending on the number of non hydrogen atoms) order parameter of the rigid part and the chain part, which not only has a lower value of order parameter but also has a tilt with respect to the rigid part axis. This tilting broadens the observed X-ray intensity distribution and thus lowers the OOP value determined from it.

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