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CHAIN ORDERING IN THE NEMATIC PHASE OF 4OBA

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ABSTRACT From the intensity profile of the X-ray diffraction pattern in the nematic phase of 4OBA it is inferred that the alkoxy chains have an orientational order.

Introduction It is known that chains have orientational order in the smectic C phase of some compounds. This order manifests itself by giving asymmetric outer diffuse maxima in the X-ray diffraction pattern recorded in a conventional way[1]. However, in the nematic phase, since these maxima are symmetric, the chain alignment is not obvious. In this communication we present evidence for chain ordering in the nematic phase of p-n Butoxy Benzoic Acid (4OBA) from the subtle features in the X-ray pattern. The orientational order parameter, S_{Ch}, for the chains is also estimated.

Experimental X-ray diffraction patterns of 4OBA were recorded using a Laue camera and Ni filtered CuKα radiation. Monodomain samples were obtained by slow cooling from the isotropic phase in a magnetic field of 0.16T. Temperature stability was about ± 0.5°C during the exposure time varying from 30 to 90 minutes. The angular intensity distribution [I(θ)] of the outer diffuse maxima was measured as a function of angle θ along the equatorial arc using a microdensitometer. Intensities were normalised to one hundred at the peak and to zero at the background.

Method Of Calculation Leadbetter and Norris[2] have shown that I(θ) is related to the orientational distribution function f(β) of the molecules by-

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

They have also shown that the calculated $f(\beta)$ fits well with Maier-Saupe type distribution function $f(\beta) = \exp(a \cos^2 \beta)$, where a is the variational parameter. Assuming this form of $f(\beta)$, $I(\theta)$ can be shown to be[3]

$$I(\theta) = C \exp(a \cos^2 \theta) \operatorname{erf}(\sqrt{a} \cos \theta) / \sqrt{a} \cos \theta \qquad (2)$$

This expression was used in all our calculations in view of its computational ease. The constant of proportionality C was chosen so that $I_{cal}(\theta)$ matches with $I_{obs}(\theta)$ at $\theta = 0^0$.

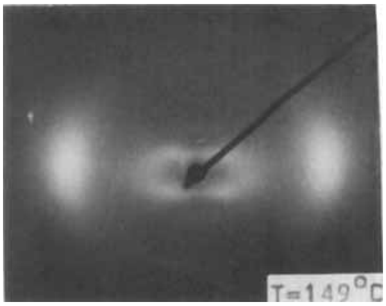

PLATE 1

<u>Results and Discussion</u>

4OBA has a cybotactic nematic phase(147C<T<160C) The director [that is the packing direction for a molecule] aligns along the magnetic field direction with the planar normal [in the cybotactic groups] distributed on a cone around the field direction [plate 1].

$I_{obs}(\theta)$ vs θ (at $T \approx 149^0C$) for 4OBA has a broad distribution with a flat maximum. A fit obtained for $I_{obs}(\theta)$ by assuming a single Maier - Saupe molecular distribution function [fig.1a] is very poor and gives a value of $S = 0.5 (a=3.46)$ for the orientational order parameter which is too low compared to its value(0.76) obtained by refractive index (RI) measurements[4]. The flatness of the distribution suggests that the <u>para</u>-axes of the benzene rings in the dimer molecule may not be colinear[5]. For non-colinear <u>para</u>-axes $I_{cal}(\theta)$ can be written as

$$I_{cal}(\theta) = I_{R_1}(\theta + \theta_0) + I_{R_2}(\theta - \theta_0) \qquad (3)$$

where θ_0 is the angle between the <u>para</u>-axes and the molecular axis [fig.2b]. I_{R_1} and I_{R_2} were calculated using eq.2 with the same value of a for both. The best fit was obtained with $a=6.2 (S=0.72)$ and $\theta_0 = 14.5^0$. Though $I_{cal}(\theta)$ fits reasonably well with $I_{obs}(\theta)$ [fig.1a] the value of θ_0 does not reflect the reality of the system indicating the superfluous nature of the fit. This is so, because in 4OBA the para-axes of the two benzene rings of the dimer molecule are expected to be colinear(one of the reasons for choosing this sample). A deliberate geometrical distortion in the O-H-O bond of the hydrogen bonded ring of the dimer has brought about a non-colinearity of < 7^0 [fig.2b].

H^2NMR[6] and refractive index measurements on the Alkoxy Benzoic Acids(mOBA) give an orientational order parameter of ≈ 0.75 to 0.80. Hence a narrow distribution of I(θ) vs θ is expected in 4OBA contrary to the observed results [fig.1]. Accepting the S_R value of 0.76 from RI measurements, the intensiy distribution for the rigid portions [$I_R(\theta)$] was generated using eq.2 . The difference distribution $I_{obs}(\theta)- I_R(\theta)$ shown in fig.1b exhibits well defined peaks at $\theta_c \approx \pm 23$. It is our contention that this difference arises out of contributions ($I_{Ch}(\theta)$) from the ordered chains. The justification for this procedure can be given as follows.The value of S obtained by RI measurements depends upon the anisotropy in the molecular polarizability ($\Delta\alpha$) which is relatively less sensitive to chain contributions[7]. So is the case with the order parameter obtained by H^2NMR of the O-H^2-O bonded linkage, since these deuterons are along the axis of the molecule. On the other hand, the I(θ) distribution in X-ray diffraction depends upon the order of all the parts of the molecules.

The difference distribution, though symmetric about the equator, is asymmetric about θ_c. This is because of the non-zero chain contributions at $\theta=0^0$. θ_c ($\approx 23^0 \pm 3^0$), which is supposed to correspond to the angle between the chain axis and the axis of the rigid portion [fig.2a], is relatively insensitive to the choice of S_R.

Assuming (1) $S_R=0.76$, (2) the chain distribution to be symmetric about the director and about θ_c and (3) the distributions of the chains and of the rigid portions to be independent of each other, a fit was obtained for $I_{obs}(\theta)$ using equation

$$I_{cal}(\theta) = I_R(\theta) + I_{Ch_1}(\theta+\theta_c) + I_{Ch_2}(\theta-\theta_c) \qquad (4)$$

where I_R, I_{Ch_1} and I_{Ch_2} were calculated using eq.2. The parameters obtained from this fit [fig.1c] are $\theta_c = \pm 22.24$ and $S_{Ch} = 0.8$ ($a_{Ch} = 8.23$). The apparently large value of

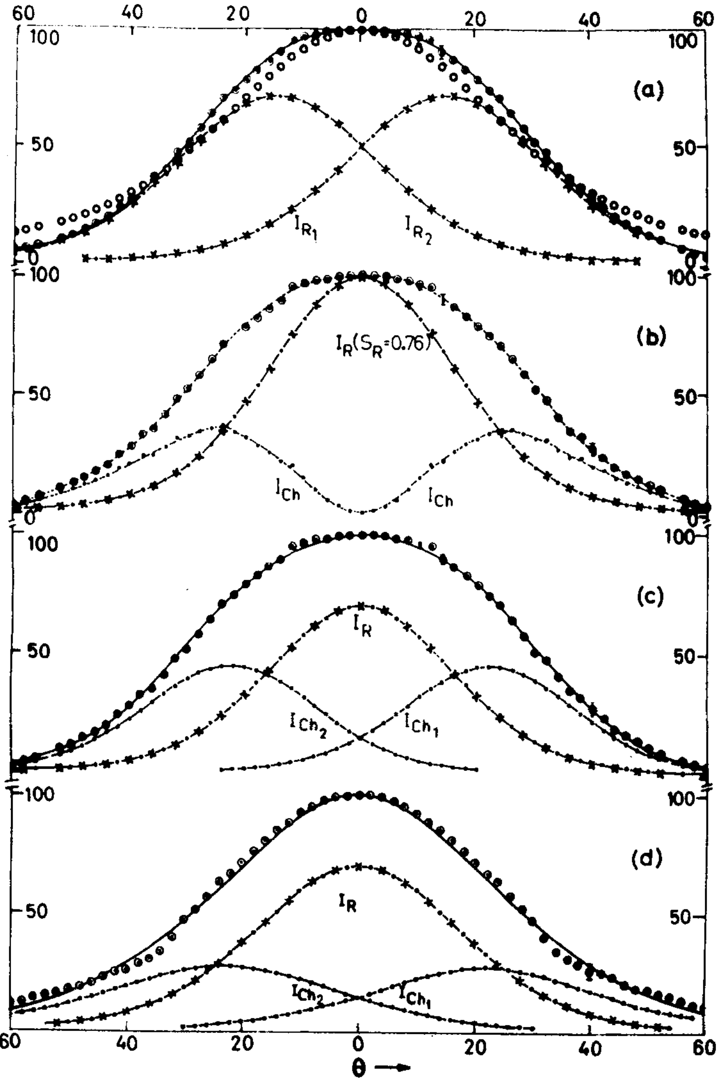

FIGURE 1 I(θ) VS θ IN THE NEMATIC PHASE OF 4OBA
(⊙) EXPERIMENTAL, (—) $I_{cal}(\theta)$, (X-·-X) $I_R(\theta)$, (-·-) $I_{Ch}(\theta)$.
(o) SINGLE MAIER-SAUPE FIT., (---) GUIDE TO EYE.
(a) $I_{cal}(\theta) = I_{R_1}(\theta+\theta_0) + I_{R_2}(\theta-\theta_0)$
(b) $I_{Ch}(\theta) = I_{obs}(\theta) - I_R(\theta)$ calculated for $S_R = 0.76$
(c) $I_{cal}(\theta) = I_R(\theta) + I_{Ch_1}(\theta+\theta_C) + I_{Ch_2}(\theta-\theta_C)$ [$T \approx 149^0$ C, $S_R = .76$]
(d) $I_{cal}(\theta) = I_R(\theta) + I_{Ch_1}(\theta+\theta_C) + I_{Ch_2}(\theta-\theta_C)$ [$T \approx 158^0$ C, $S_R = .70$]

S_{Ch} compared to S_R is reasonable in view of a similar observation in 3OBA from the H^2NMR measurements[8]. Taking the bond angles and bond lengths of the crystalline 4OBA reported by Bryan and Fallon[9], θ_c was estimated to be $23^0 \pm 3^0$ [fig.2a] which is in good agreement with that deduced above giving credibility to the present fit. The assumption that the chain and the rigid portion distributions are independent of each other may have an effect on the absolute values of S_R and S_{Ch}.

The broadening in $I(\theta)$ can also arise due to pretransitional effects, since the temperature of our observation is close to T_{CN}[2]. In order to clarify this point, the diffraction pattern obtained at $T \approx T_{CN} + 10^0$ was also analysed (fig.1d). This gives the same θ_c value but with different S_R and S_{Ch} values due to enhanced broadening at elevated temperature as expected. Further, in this system, the tilt angle θ_t in the cybotactic groups is very large, $>50^0$ (plate 1), compared to the calculated peak separations(fig.1). If the observed broadening was due to S_c

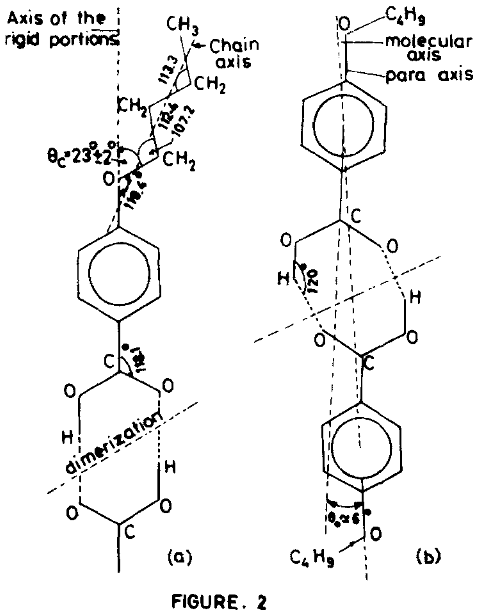

FIGURE. 2
a) 4OBA MOLECULE (b) 4OBA MOLECULE WITH O—H··O BOND DISTORTED

type fluctuations, (1) the anticipated $I(\theta)$ distribution would also be broad to that extent with maxima 100^0 apart, which is contrary to the observation (fig.1) and (2) the meridionial reflections would not have shown four clearly split maxima [plate 1].

The presence of two peaks at $\pm\ \theta_c$ suggests that the chains are not parallel to each other all through the sample but are distributed on a cone of apex angle θ_c around the director.

Conclusions The observed intensity distribution in the X-ray pattern of nematic 4OBA can be explained as a sum of two contributions , one from the rigid portions and other from the chains. This approach gives a value of $\approx 22^0$ for the angle between the axes of the two portions of the molecule which finds justification on geometrical grounds. The chains are distributed over a cone of angle $\approx 22^0$ around the director. Our results suggest that it is important to consider chain contributions to the scattered intensity while analysing X-ray data, especially when these are expected to be comparable to the contributions due to the rigid portions [for higher homologues], so that the results can be compared with those of other experiments.

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