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STRUCTURE OF THE NEMATIC PHASE OF PBABA

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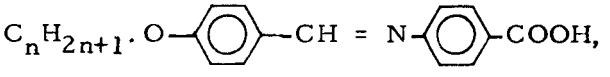
ABSTRACT : X-ray diffraction investigations of the nematic phase (191°C - 276°C) of p-n-propyl-oxybenzylidene-p-amino benzoic acid have shown that this phase is a skewed cybotactic nematic phase. The diffraction patterns, obtained with aligned samples, reveal an additional surprising structural feature, - the presence of one dimensional molecular correlation in a direction parallel to the nematic director. At 192°C, it is found that the molecular unit, thus correlated, is about 37 Å in length (dimer length) and the correlation range extends up to about seven such units. This 1-d correlation persists up to the N-I transition.

The nematic phases of all the higher members (n = 7, 8, 9) of the compounds,



studied by us (n = 1, 3, 6, 7, 8, 9) by X-ray diffraction[1] have been found to be typical skewed cybotactic nematic[2] (N_{SC}) phases with S_c type short-range-order.

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However in the case of PBABA (n = 3) and HxBABA (n = 6), the diffraction pattern of the nematic phase is not that of a simple N_{SC} phase, but reveals additional diffraction lines perpendicular to the nematic director, $\underset{\sim}{n}$, indicating the presence of molecular correlation along $\underset{\sim}{n}$. This feature is quite pronounced in the case of PBABA, where the S_c type short-range-order is found to be quite weak. In order to understand the structure of PBABA in the N_{SC} phase, X-ray diffraction studies have been carried out with aligned samples of this compound.

Ni-filtered Cu radiation and a Laue camera were used in these experiments. Pure samples of PBABA, obtained by repeated recrystallisation from ethyl alcohol, were contained in quartz capillaries of 0.5 mm diameter, kept perpendicular to the incident X-ray beam. Aligned samples were obtained by slowly recycling the sample through the C-N_{SC} transition, where C is thought to be a crystalline phase with some disorder. The temperature stability in these experiments was about $\pm$ 0.25°C.

The diffraction photographs taken at different temperatures, spanning the temperature domain of the N_{SC} phase of PBABA show similar features. A typical diffraction pattern obtained at 192°C (just above the C-N_{SC} transition) is shown in Fig. 1. The following features are observed in these patterns : (a) At small scattering angles ($2\theta \approx 2^{\circ}$) a diffraction ring and four faint and very diffuse spots are seen and at larger angles ($2\theta \approx 20^{\circ}$), two outer diffuse arcs (along the equator, $\perp \underset{\sim}{n}$), typical of a well-aligned nematic, are observed. The spots and the arcs are characteristic of the diffraction pattern of an N_{SC} phase. (b) A number of diffraction lines, all $\perp \underset{\sim}{n}$, are seen along the meridian ($// \underset{\sim}{n}$). These seem to be due to planes or layers of diffraction, caused by one-dimensional molecular correlation along $\underset{\sim}{n}$, a surprising feature, hitherto not observed in nematics. However, this type of correlation has been observed in the highly ordered

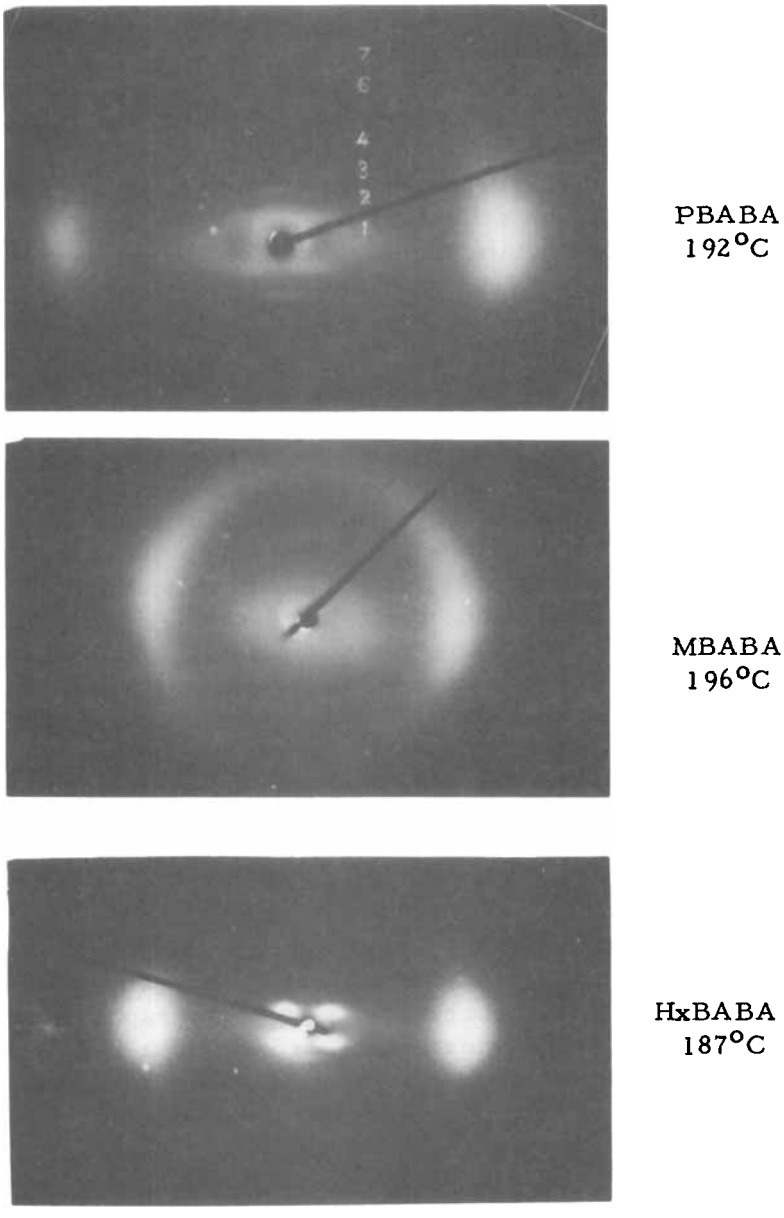

FIGURE 1 Diffraction patterns of PBABA, MBABA and HxBABA.

S_H phase of TBBA and other compounds[3, *]. With increasing temperature, the inner spots become more diffuse, the outer arcs spread out more and the intensity of the diffraction lines decreases.

The diffraction pattern obtained at 192°C has been analysed (with the help of a densitometer) to obtain the lattice spacings, d_{ls}, corresponding to equatorial ($\perp \underset{\sim}{n}$) and meridional ($// \underset{\sim}{n}$) reflections. The Bragg condition was used to calculate these spacings, except in the case of D, the intermolecular distance $\perp \underset{\sim}{n}$, where De Vries relation[2] was used. The values of d_{ls} are given in Table I.

We do not know what the ring (d_{ls} = 35.0 Å) corresponds to. The (meridional) diffraction lines do indeed correspond to layers of diffraction of various orders, resulting from the 1-d correlation of molecular units of length 37.1 Å, along $\underset{\sim}{n}$. This length is very close to the dimer length of 37.6 Å, indicating that the dimers are correlated along their long axes ($// \underset{\sim}{n}$). Indeed, these layer reflections are comparable to those obtained with fibres[4] having crystallographic repeats, whose spacings are of dimeric length. From the width of the layer lines, the correlation length has been estimated to be 6.5 times the dimer length. The molecular tilt angle has been estimated to be $55^\circ \pm 10^\circ$ from the inclination of the diffuse diffraction spots with respect to $\underset{\sim}{n}$.

The diffraction patterns obtained with MBABA (n = 1) and HxBABA (n = 6), in the nematic phase are also shown in Fig. 1, for comparison. The photographs show that neither an S_C-type short-range-order nor a 1-d molecular correlation $// \underset{\sim}{n}$ exists in MBABA, whereas both are present in HxBABA, the short-range-order being quite strong, as is evident from the intense,

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* We are very thankful to Dr. A. De Vries for pointing this out to us.

TABLE I

Equatorial ($\perp \underset{\sim}{n}$)		Meridional ($// \underset{\sim}{n}$)		
Reflection Type	d_{1s}(Å)	Layer Order(m)	d_{1s}(Å)+	Relative Intensity
Ring	35.0	1	38.4	Strong
Arc	5.2(=D)	2	18.2	Strong
		3	12.4	Medium
		4	8.9	Medium
		6	6.5	Weak
		7	5.3	Medium

+ These values of d_{1s} are not very accurate due to the large sloping background on which the meridional reflections are superposed. The inaccuracy in the case of orders 1 and 6 is quite large ($\approx$ 3 to 5 per cent).

sharp diffraction spots. This seems to indicate that the hydrocarbon chain length plays a dominant role in the formation of chains of molecules correlated along their long axes. However, this correlation is broken, when the chain becomes sufficiently long ($n > 6$) to stabilize the S_c phase.

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