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# Molecular Packing in Nematics

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# MOLECULAR PACKING IN NEMATICS

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Abstract: In this communication it is demonstrated that among the different possible molecular packing directions in liquid crystals with molecules containing more than one aromatic ring, x-ray diffraction techniques can be used to pick out the correct one. Our x-ray diffraction measurements on mBABA indicate the packing to be parallel to the *para*-axes of the benzene rings.

Introduction In a liquid crystalline phase, the director can be defined as the average direction of molecular packing. It is necessary to define then an axis of the molecule parallel to which the molecules pack. In aromatic compounds with more than one benzene ring, the *para*-axes of the benzene rings are not always colinear. The packing direction in such a case can either be (i) along the line joining the centres of the extreme benzene rings (aa') as in Fig. 1a, or (ii) parallel to the *para*-axes. However, in all such compounds, a rod like structure of the molecule is assumed, making the differentiation between the above mentioned two kinds of packing direction redundant. It is the aim of this communication to show that indeed the two directions can be experimentally differentiated using x-ray diffraction techniques. Based on the results of our experiments on the *p*-n-Alkoxybenzylidene-*p*-Aminobenzoic Acids (mBABA) it is shown that the molecular packing appears to be parallel to the *para*-axes.

Experimental X-ray diffraction measurements were carried out on a Laue Camera using Ni-filtered CuKα radiation. Pure samples enclosed in capillaries of 0.7 mm to 1mm diameter were placed in a furnace fixed between the pole shoes of a magnet (H=0.16T).[1] All the patterns were recorded at a temperature 1°C above the nematic phase transition while heating. The temperature stability was better than ± 0.5°C during the exposure time of 30 min. to 90 min.

Effect of Packing on the Intensity Distribution of Outer Maxima In the X-ray diffraction pattern of an aligned sample the outer diffuse maxima due to the rigid portions of the molecules are in a direction perpendicular to the axis of electron density distribution[2] (approximately

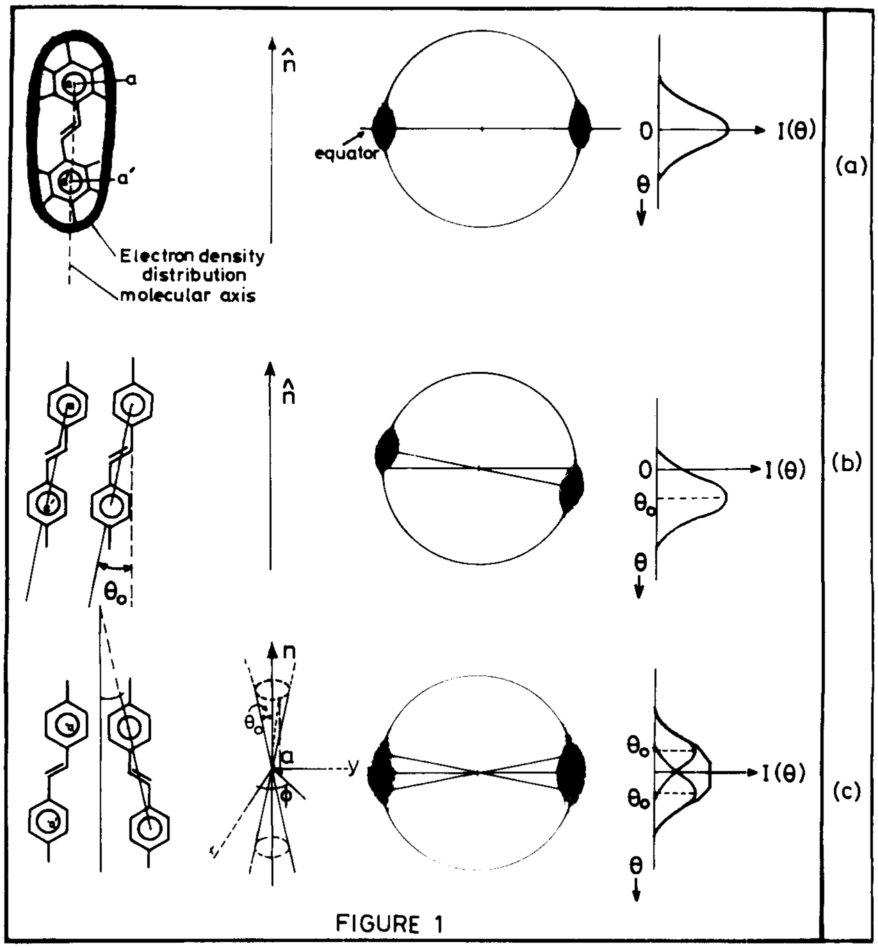

FIGURE 1

Molecular packing Direction -AND- The Corresponding X-ray Diffraction pattern

a) Parallel to aa'

b) Parallel to the para axis, ϕ locked in space

c) Parallel to the para axis, ϕ free in space taken as aa' in Fig. 1. Depending upon the molecular packing direction, the angular intensity distribution (I(Θ)) of these maxima is expected to show subtle differences at small angles around the equator. This feature can be used to assign the correct packing direction as follows: (1) For packing parallel to aa' (Fig. 1a) there will be a pair maxima located at the equator and broadened due to finite orientational disorder of the molecules. (2) Alternatively if the molecular packing is along the *para*-axes of the benzene rings (Fig. 1b, and 1c), two types of diffraction pattern could be observed: (i) a single pair of maxima shifted from the equator by an angle equal to the angle between aa' and the *para*-axes($\Theta_0$) (Fig. 1b) or (ii) two pairs of maxima equally spaced on either side of the equator at $\pm\ \Theta_0$ (Fig. 1c). This is possible if aa' lies on a cone with semi-vertex angle $\Theta_0$. However, these two peaks will not be resolved because each is broadened due to orientational disorder of the molecules and $\Theta_0$ is

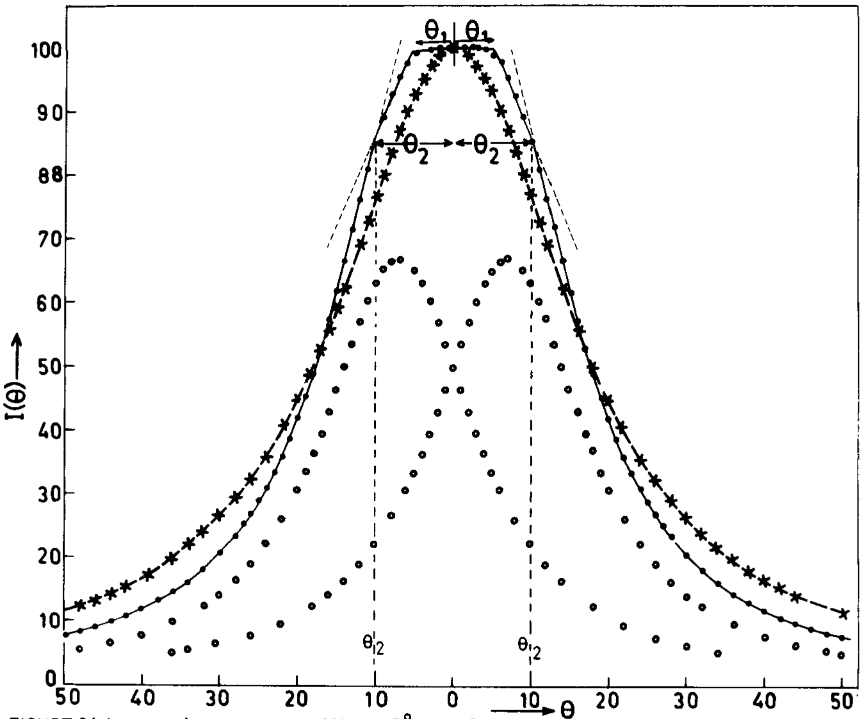

FIGURE 2(○) Lorentzians centred at (θ) = ± 7°, (-•-) Sum of above two Lorentzians (-*-) A Single Lorentzian with the same half width as that of the two put together small. When the orientational order parameter(S) is large, it should be possible to observe an intensity distribution with a maxima flat over $\Theta = \pm\Theta_1$, and a change of slope at $\Theta = \pm\Theta_2$. The values of $\Theta_1$ and $\Theta_2$ will depend upon the shape of the individual distribution and upon $\Theta_0$. Fig. 2 shows such a distribution with two Lorentzians centred at $\Theta = \pm 7°$, along with a single Lorentzian (centred at $\Theta=0°$ with the same half width as that due to the two Lorentzians put together.

Results and Discussions The angular intensity distribution of the outer diffuse maxima ($I(\Theta)$) for the members of the series mBABA was measured on a microdensitometer. For each value of $\Theta$, the peak position is located by radial scanning. The intensities are normalized to zero at the background and to one hundred at the peak position. The measurements were repeated on samples from different batches and with different exposure times and the results are reproducible. The observed behaviour for the members of the series mBABA (Fig. 3b) is similar to that depicted in Fig. 1c and Fig. 2.

A typical representation of $I(\Theta)$ at low values of $\Theta$ for 1BABA and 3BABA is shown in Fig. 3b. The error on these measurements is less than 0.5% for $\Theta < 15°$ and less than 2.5% for higher values of $\Theta$. Lower members of the series are chosen in order to avoid chain contributions.[3] The distributions are flat over $\Theta = \pm 4°$ and there is a distinct change of slope at $\Theta = \pm 11°$ to $\pm 12°$. A fit is obtained for 1BABA assuming two Lorentzians centred at $\pm \Theta_0$ just to illustrate the presence of two peaks (Fig. 3b), though the intensities may not have a perfect Lorentzian distribution. Such a fit gives $\Theta_0 = 8.5°$. This compares well with the geometrically obtained value of $\Theta_0$ for mBABA. ($\Theta_0 \approx 10°$ for a monomer, and $\approx 7°$ for a dimer as shown in Fig. 3a). The discrepancy between the observed and the expected value of $\Theta_0$ could be attributed to the fact that the axis of the electron density distribution need not coincide with aa'.

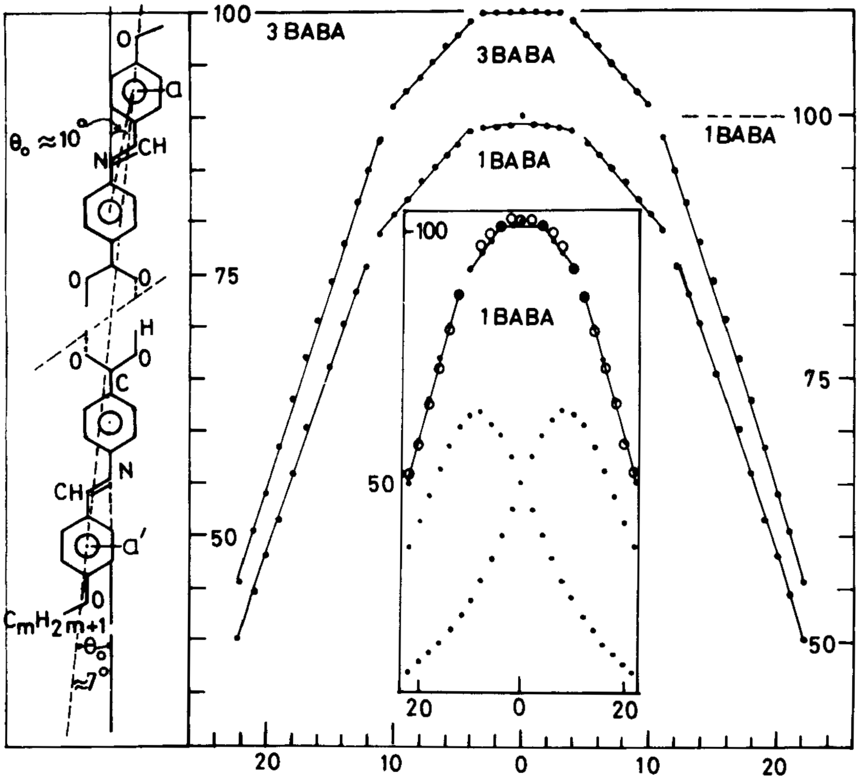

FIGURE 3(a)
mBABA
DIMER

(b)(•) Experimental values of I(θ) at small θ for 1BABA and 3BABA
(·) Two Lorentzians giving best fit for 1BABA
(o) Sum of two Lorentzians
(–) Solid line is just a guide to eye

Conclusions We have demonstrated the possibility of identifying the packing direction in a molecule using x-ray diffraction technique. Our results clearly indicate that (1) in the nematic phase of mBABA, packing is parallel to the *para*-axes of the benzene rings and not parallel to aa' and (2) aa' is distributed on a cone of angle 8.5° around the director, which could be due to either static or dynamic disorder of the benzene rings of a molecule. Such a diffraction pattern is expected for all other nematic phases (of aromatic molecules) with $\Theta_0 \neq 0$.

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