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THE STRUCTURE OF A NUMBER OF NEMATOGENS

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Résumé. — Nous avons effectué des mesures de diffraction des rayons X sur cinq composés nématogènes dans les phases nématique et liquide isotrope. L'interprétation des résultats permet d'obtenir des informations sur l'empilement des molécules.

Deux bases de Schiff $R_1 \longrightarrow CH = N \longrightarrow R_2$, MBBA ($R_1 = CH_3O$, $R_2 = nC_4H_9$) et EBBA ($R_1 = C_2H_5O$, $R_2 = nC_4H_9$) ont des structures très voisines, l'homologue de plus grand poids moléculaire étant de loin le plus ordonné. Dans une troisième base de Schiff, MBCA ($R_1 = CH_3O$, $R_2 = CN$), l'empilement semble être plus proche de celui d'un cristal car la distance de répétition le long de l'axe de la texture est inférieure de 3 Å à la longueur moléculaire.

Deux cyanobiphényles $R - \langle O \rangle - \langle O \rangle - CN : 5 CB (R = C_5H_{11})$ et 7 CB ($R = C_7H_{15}$) ont des structures très voisines avec un ordre local très prononcé. La manifestation la plus frappante de cet ordre local est l'existence d'une distance de répétition le long de l'axe de la texture, d'environ 1,4 fois la longueur moléculaire. L'interprétation que nous en donnons est celle-ci : les molécules sont disposées en pseudo-couches à une échelle locale et dans chaque couche il y a superposition des extrémités de deux molécules voisines. L'ordre s'étend sur 100 à 150 molécules et est plus prononcé pour l'homologue de plus grand poids moléculaire.

Dans tous les cas un ordre local très analogue à celui de la phase nématique subsiste dans le liquide isotrope.

Abstract. — X-ray diffraction measurements have been made on five nematogens in the nematic and isotropic liquid phases. The data have been interpreted to give information about the molecular packing.

Two Schiff's bases $R_1 - \langle O \rangle - CH = N - \langle O \rangle - R_2$: MBBA ($R_1 = CH_3O$, $R_2 = nC_4H_9$) and EBBA ($R_1 = C_2H_5O$, $R_2 = nC_4H_9$) have very similar structures, the higher homologue being much the more ordered. A third Schiff's base MBCA ($R_1 = CH_3O$, $R_2 = CN$) is thought to have a more crystal-like packing resulting in a repeat distance (« d » spacing) along the texture axis 3 Å shorter than the molecular length.

Two cyanobiphenyls $R - \langle O \rangle - CN : 5 CB$ ($R = C_5H_{11}$) and 7 CB ($R = C_7H_{15}$) have very similar structures, with pronounced local ordering. This is revealed most strikingly in a repeat distance along the texture axis of ~ 1.4 molecular lengths, which is interpreted as arising from an overlapping head to tail arrangement of molecules resulting in a quasi-layer (smectic A) structure on a local scale. The order extends over 100-150 molecules and is more pronounced for the higher homologue.

In all cases, local order very similar to that in the nematic phase persists in the isotropic liquids.

1. Introduction. — Although the general features of the molecular organisation in nematic liquid crystal phases are well-known, there is little experimental information on the various distribution functions describing these structures. This information is in principle obtainable from diffraction experiments but in practice the problem is complex and no such detailed work has yet been reported. Furthermore it has become clear over the past few years [1-3] that there are different kinds of nematic phase among which the local molecular organisation is qualitatively different. A prerequisite for any detailed investigation of particular nematogens is a broad knowledge of their structure in relation to that of other nematic phases. This paper contains a report of the first stages of an X-ray diffraction investigation of the structures of two room temperature nematics and closely related compounds. It is concerned with a semiquantitative interpretation of the experimental data to give some of the important features of the molecular arrangement in the nematic and isotropic liquid phases. The five materials studied are as follows : A) Three Schiff's base.

$$\begin{array}{c} R_1 \bigotimes C_{R_1}^H \bigotimes R_2 \\ R_1 & R_2 \end{array}$$

1. MeO	n-Đu	p-methoxybenzylidene p-n-butylaniline	MBBA
2. EtO	n-Bu	p-ethyoxybenzylidene p-n-butylaniline	EBBA
3. MeO	CN	p-methoxybenzylidene p-cyanoaniline	MBCA

B) Two cyanobiphenyls⁴

1.	4' n-pentyl-4-cyanobiphenyl	5 CB
2.	4' n-heptyl-4-cyanobiphenyl	7 CB

These materials have the following phase behaviour.

t/°C	MBBA	EBBA	MBCA	5 CB	7 CB
				<u> </u>	<u> </u>
Crystal \rightarrow Nematic	20.9	35.0	108.0	22.6	29.0
Nematic \rightarrow Isotropic Liquid	42.0	78.5	119.0	35.1	42.4

The Schiff's bases, particularly MBBA, are sensitive to atmospheric moisture, which lowers their N-I transition temperature. The values given above were measured on typical samples. More detailed structural work and an investigation of the molecular dynamics by neutron scattering are in progress on certain of these materials and will be reported elsewhere.

2. Experimental. — Samples as obtained commercially were used without further purification. Care was taken to minimise the exposure of the Schiff's bases to the atmosphere. Measurement of the transition temperatures showed that the samples used were of adequate purity.

For photographic work most specimens were sealed into thin walled (~ 0.05 mm) pyrex glass capillaries 1 to 2 mm in diameter. For some measurements, on specimens cooled below room temperature, a flat sample holder, 1 mm thick with thin beryllium windows, was used. In each case the specimen was mounted in a copper block whose temperature was controlled within about ± 1 °C and measured with a thermocouple located near the sample. Diffraction photographs were taken using a flat plate camera with roughly monochromatised radiation obtained by running a copper anode at a low voltage

and using a nickel filter. This eliminates most of the white background and gives results which are adequate for a first investigation. The films were monitored using a microdensitometer and in a few cases complete contour maps of the scattering intensity have been prepared.

Specimens in the nematic phase were aligned by means of a magnetic field, and fields of up to 7 kOe were obtained using permanent magnets. In all cases the degree of alignment produced was determined as a function of field and it was found that saturation alignment was produced in the Schiff's bases at fields less than 1 kOe while the biphenyls required 1-2 kOe. In all subsequent work fields greater than these saturation values were used to align the specimens. All the materials could be supercooled in the nematic phase to some extent and measurements have been made on all specimens near the crystal nematic transition temperature, particularly for EBBA as a function of temperature.

Unoriented specimens of all the materials except MBCA in the nematic and isotropic liquid phase were investigated using a powder diffractomer and scintillation counter. Adequate monochromatisation was achieved by using a Ni filter and a pulse height analyser. The liquids were contained in a flat, 1 mm thick holder with windows of Al foil or mylar, and were examined using transmission geometry. Temperatures were held constant within ± 1 or 2 °C. In these experiments, some difficulty was experienced with preferred orientation in the nematic sample, presumably due to surface or flow effects, and reproducibility after heating to the isotropic phase and between runs was taken to indicate the absence of preferred orientation.

3. Results and discussion. — 3.1 GENERAL. — The diffraction patterns of all the aligned specimens are characteristic of materials having a definite texture axis. Typical photographs are shown in plates 1 to 4 for MBBA, EBBA, MBCA and 7 CB. In all cases there are two equatorial arcs of scattering, symmetrical about the equatorial plane. For all the materials at all temperatures in the nematic phase these features are

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PLATE 1. — X-ray diffraction photographs of the orientated nematic phases of (a) MBBA at 18 °C, (b) EBBA at 24 °C, (c) MBCA at 109 °C, (d) 7 CB at 24 °C.

qualitative similar, but differ quantitatively mainly in the length of the arc. The scattering about the meridional direction (parallel to the director) differs qualitatively between the different types of materials, showing that the molecular packing in the nematic phase varies significantly with the type of molecule. The detailed derivation of the various molecular distribution functions from experimental data is very complicated because only in certain special cases when there is either complete, or no correlation, between molecular orientation and position can the inter and intra-molecular components of the scattering intensity be simply separated. We make no attempt to deduce any of these distribution functions here, for which in any case more accurate intensity data would be required, but rather derive more qualitative information about the molecular packing by consideration of the positions, widths and intensity profiles of the major diffraction features.

(c)

The integrated intensities of the main equatorial and meridional reflections are best compared between specimens and as a function of temperature and phase using the diffractometer measurements on unoriented specimens. These data are shown in figures 1 and 2.

(d)

3.2 THE EQUATORIAL (IE) REFLECTIONS. - The position of the equatorial arcs in the equatorial plane is closely similar in all the materials. This diffraction feature arises essentially from the intermolecular spacings perpendicular to the long axes of the molecules. We obtain average intermolecular spacings for the purposes of comparison between materials by the rather arbitrary use of the formula $d = 1.2 \lambda/2 \sin \theta$ based on arguments of cylindrical symmetry. In all cases the average intermolecular spacing is close to 5.0 Å and increases smoothly through the nematic range into the isotropic phase by a total of 0.1 to 0.2 Å. This spacing corresponds approximately to the average width of the molecules and is certainly smaller than the diameter of a freely rotating molecule (~ 6.5 Å). Thus, while it is not clear how much local correlation exists in the orientation of molecules about their long axes the rotation about these axes is certainly very restricted.



Fig. 1. — Diffraction patterns for EBBA (solid lines) and MBBA (dotted lines) taken with CuK α radiation ($\lambda = 1.54$ Å). Upper curves are for the unoriented nematics and lower curves for the isotropic liquids. Temperatures were : MBBA, 23.5° and 40 °C and EBBA, 41° and 85 °C. Intensities are in arbitrary units but have been normalized to the highest angle (1 E) peaks for the isotropic phase. The inset graph shows the peak height of the

first (1 M) peak for EBBA as a function of temperature.

The width of the peak along the equatorial plane is related to the extent of ordering in the molecular packing. We obtain an approximate value for this using Hosemann's paracrystalline model [4, 5] when

$$\Delta X \simeq \left(\frac{\Delta}{\bar{r}}\right)^2 \frac{\pi}{\bar{r}} \simeq \frac{\pi^2}{6.25 L_r} \tag{1}$$

where ΔX is the width in S ($S = 2 \sin \theta/\lambda$); Δ , the disorder parameter, is the rms deviation of near neighbour distances about the mean \bar{r} and L_r is the maximum distance over which significant order extends (the correlation length). In all cases, and virtually independent of temperature

$$L_r/\bar{r} \simeq 5$$

which means that the distribution of the projections of the molecular centres onto a plane perpendicular to the local director is random beyond about 5 molecular diameters.

The integrated intensity of the IE reflections as well as their widths in the equatorial plane are insensitive to temperature. This is shown in the plots of scattered intensity versus 2 θ for unoriented specimens in figures 1 and 2. The IE peak changes with temperature only



FIG. 2. — Diffraction patterns for 7 CB (solid lines and 5 CB (dotted lines)) taken with CuK α radiation ($\lambda = 1.54$ Å). Upper curves are for the unoriented nematics and lower curves for the isotropic liquids. Temperatures were : 5 CB, 23.5° and 38 °C and 7 CB, 27° and 46 °C. Intensities are in arbitrary units but have been normalized to the highest angle (1 E) peaks for the isotropic phase. The insert graph shows the peak height of the first (1 M) peak for 7 CB as a function of temperature.

very slightly in profile or intensity, even into the isotropic phase. What does change with temperature, and differs between samples, is the length of the equatorial arcs. The loci of the intensity maxima fall, within experimental error, on the arcs of circles centred at the origin of reciprocal space. These arcs arise from local fluctuations of the director and the molecular orientations must be approximately in phase over distances greater than the correlation length L_r . High frequency molecular fluctuations, on the other hand, will reduce the intensity of the diffraction peaks relative to the general background. If $f(\theta)$ is the distribution function for the local orientation of the director then the intensity at an angle ψ from the equatorial plane may be written

$$I(\psi) = \int_{\psi}^{\pi/2} f(\theta) g(\theta, \psi) d\theta$$
 (2)

where $g(\theta, \psi)$ is a geometrical function. This formulation ignores any intrinsic width of the equatorial reflection perpendicular to the equatorial plane but this must be a good approximation since the reflections are good arcs of circles centred on the origin. We shall discuss elsewhere the detailed application of eq. (2) but typical $I(\psi)$ data are shown in figure 3. It is clear that $f(\theta)$ gets broader with increasing temperature and depends on the material but that its form is similar in all cases.



FIG. 3. — The intensity of the equatorial arcs (in terms of peak height) as a function of angle (ψ) from the equatorial plane for EBBA at 24 °C (------); EBBA at 70 °C (-----); 5 CB at 17 °C (-----).

The fact that the IE peak hardly changes in going to the isotropic liquid phase shows that the lateral ordering of the molecules is almost unchanged through the nematic phase and into the isotropic phase, up to distances of at least the correlation length L_r . In the nematic phase the *orientational* correlation of the long molecular axes extends over very much greater distances but this is not directly revealed by diffraction experiments on unoriented specimens due to the liquid-like packing of the molecular centres. Hence, we have no information about how far beyond L_r the orientational correlation extends in the isotropic liquid.

3.3 THE MERIDIONAL REFLECTIONS. — The form of the scattering in and about the meridional direction z^* (s parallel to the director) depends markedly on the type of material, and three distinct types of patterns are observed. The positions of the reflections are given in table I, expressed as Bragg spacings (d) and these

TABLE I

Parameters derived from the meridional reflections of the oriented nematic phases

	T	d_1	d_2	1		
Substance	٥C	Å	Å	Å	d_1/l	L_z/d_1
				—		—
MBBA	18	21.3	8.4	20	~ 1	2
	29	20.5	8.2			$1\frac{1}{2}$
EBBA	23	21.5	9.3	21	~ 1	6
	70	20.0	8.9			3
MBCA	109	14.1	7.1	17	~ 0.85	5
5 CB	17	25.7	13.5	18	~ 1.4	$4\frac{1}{2}$
7 CB	24	29.0		21	~ 1.4	4 ½

are compared with the maximum molecular lengths (1) measured on molecular models. For MBBA and EBBA the Bragg spacings (or correlation wavelengths) are within a few percent of the molecular lengths whereas for MBCA they are significantly smaller, and for the biphenyls much bigger, than the molecular lengths. The extent of ordering along the texture (z)axis is related to the width of the reflections at their centre. The correlation lengths L_z obtained using the paracrystalline theory (eq. (1)) are also given in table I relative to the *d*-spacings. Thus for all materials except MBBA the correlation length at the lower nematic temperatures is near 5 wavelengths and decreases with temperature; MBBA is much less well-ordered along the texture direction. This is demonstrated also by the comparison of intensities of the unoriented nematics in figure 1, the 1 M intensity for MBBA is much weaker than that for EBBA.

The results for EBBA and MBBA may be interpreted most easily. Thus, at low temperatures, the 1 M reflection for EBBA broadens and becomes more diffuse with increasing distance from the z^* axis, the 2 M reflection is shorter and the ends of the reflection merge with the general background scatter at positions which fall to a good approximation on an ellipse. These features are all predicted by the paracrystalline model [4, 5], the equation of the ellipse being

$$X^2 \Delta_b^2 + Z^2 \Delta_z^2 \approx 0.1$$

where Z and X are respectively the components of $S(S = 2 \sin \theta / \lambda)$ along the texture axis and in a direction perpendicular to this, Δ_z is the disorder parameter along the texture axis (cf. eq. (1)) and Δ_b is the disorder parameter describing the rms displacement in a direction perpendicular to the texture axis of nearest neighbours along this axis. For MBBA and EBBA throughout the nematic range Δ_b/\bar{r} (\bar{r} is the mean distance between the long molecular axes) is around unity. This means that even when there is quite extensive correlation of the z coordinates of the molecules, as for EBBA at low temperatures, the arrangement of the molecules into independent files is rather poor. This must imply a tendency to the formation of layers, but this is very weak as a simple estimate of a correlation length from the length of the 1 M reflection suggests only about 2 molecular widths for the extent of a layer. A slight tendency to the development of arcs is evident in some of the meridional reflections, particular for higher temperatures and higher scattering vectors. Quantitative interpretation is difficult as the basic scattering feature is a bar (or a sheet in three dimensions) which is spread into a flattened arc by the local fluctuation of the director. The d-spacing clearly decreases with increasing temperature for both these materials which might imply increased angular fluctuations between neighbouring molecules or an effective shortening of the molecules due to increased motion of the butyl chains, perhaps also with a change in the molecular packing.

For MBCA the meridional reflections are relatively weak and the 2 M reflection is more intense than the 1 M : relative peak heights are 1 M/1 E = 0.11 and 2 M/1 E = 0.19. Furthermore the meridional reflections are very well-developed arcs of roughly the same angular extent as the equatorial arc. We considered the possibility that there was only very weak molecular correlation along the texture axis (a classical nematic) so that the observed meridional arcs could be ascribed essentially to the molecular form factor F(s). However a calculation of this form factor for the z^* direction showed this not to be so as the observed peaks fall near minima in F(s). This must mean that there is some well-defined local molecular packing which must also account for the d spacing being 3 Å smaller than the molecular length. The fact that the meridional reflections are only very slightly flattened arcs means that in a fully ordered specimen these reflections are more nearly spots than bars which supports the idea of some local quasi-crystalline ordering. We therefore believe that a better understanding of the molecular packing in this nematic may stem from a knowledge of the crystal structure and we propose to investigate this.

The diffraction patterns of the biphenyls are very similar to each other but differ markedly from those of the other materials investigated here. Indeed, they closely resemble those of smectic materials but with more diffuse reflections [6]. The 1 M peak for 7 CB is very strong, as is shown in the diffraction pattern for the unoriented nematic (Fig. 2). The 1 M peak for 5 CB is weaker but of approximately the same size and shape (cf. plate 1 and Table I). Both 1 M peaks are in the form of short bars which have been slightly spread into flattened arcs by the local director fluctuations. Interpretation of the lengths of these reflections in terms of the paracrystal model and a disorder parameter Δ_b is unsatisfactory as Δ_b is more than two molecular diameters (\bar{r}) which means that there is effectively no file-like correlation along the z axis. A simple interpretation of the length of the 1 M reflections in terms of a crystal correlation length L_c , defined by $L_c \simeq \Delta S^{-1}$, gives L_c/\bar{r} as 4 for 5 CB and 5 for 7 CB. These correlation lengths are in reasonable agreement with those derived from the width of the 1 E peaks (Table I), and suggest that the short range order has a pronounced layer character. It is interesting to note that despite the relatively high ordering in these materials higher order meridional peaks are very weak indeed, compared to the 1 M peaks. Perhaps the most striking feature of the biphenyls is that the repeat unit along the texture axis is about 1.4 molecular lengths. This must result from strong molecular association, due presumably to the high dipole moments of these materials, and a possible configuration is shown schematically in figure 4. This suggested configuration implies highly mobile alkyl chains and this is currently being investigated by quasi-elastic neutron scattering. Furthermore, it implies a tendency



FIG. 4. — Schematic diagram of suggested local structure in 5 CB (and 7 CB), resulting in a repeat distance along the texture axis of ~ 1.4 molecular lengths, with highly mobile alkyl chains and a tendency to local layer formation.

to layer formation which is in agreement with the above discussion of the meridional reflections. Thus the 1 M reflections are relatively sharp and, for 7 CB, intense. The derived correlation lengths parallel and perpendicular to the texture axis suggest ordered regions containing about $5^2 \times 4.5 (\times 1.4) \approx 150$ molecules for 7 CB, and perhaps \sim 100 for 5 CB. This suggests that both these materials, more particularly 7 CB, are normal cybotatic nematics as discussed by de Vries [1]. Certainly they have quasi-smectic A ordering on a local scale and this increases with alkyl chain length. Indeed the next member of the series (8 CB) has a smectic A phase in addition to the nematic [7]. We do not place too much emphasis on whether or not these materials indeed have normal cybotactic groups since the definition of these, particularly in the case of normal cybotactics, must be arbitrary. The extent of possible ordering must be continuously variable over a wide range.

The relative extent of the order in the different materials, together with its temperature dependence, is reflected in the 1 M diffraction peaks for the unoriented nematics, and for the isotropic phases shown in figures 1 and 2. For the nematic phase, at least, the peaks are broader than for the oriented patterns because of the bar-like shape of the peaks for the

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oriented case. The height of the 1 M peak decreases markedly with temperature (and its width increases, see Table I) but it is clearly stronger for the higher homologue in each case. There appear to be no marked changes in the integrated intensities at the N-I transition and, while we have not yet examined the transition region in detail, any jumps are certainly relatively small. However, the 1 M peak clearly persists into the isotropic phase which shows that significant local ordering similar to that in the nematic phase still exists in the isotropic liquid.

4. Conclusions. — A preliminary investigation has been made of the structures of five nematogens. Within a homologous series (MBBA and EBBA or 5 CB and 7 CB) the structures are qualitatively similar but the extent of short range ordering is greater for the higher homologue. The structures of the different types of compounds in the nematic phase differ appreciably. MBBA and EBBA appear to form rather simple structures with no very strong correlations in local order, MBCA probably has a quasi-crystalline local ordering but the details have not been established. 5 CB and 7 CB have pronounced local order of a quasi-smectic A nature which is stronger for the higher homologue. The repeat distance along the texture axis is about 1.4 molecular lengths in both cases implying strong molecular association which is suggested to be of an overlapping head to tail nature.

Considerable local order, very similar to that in the nematic phase, has been observed in the isotropic liquid phases of these materials.

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