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Résumé. — Les épaisseurs (d) des couches smectiques déterminées jusqu'à maintenant pour un certain nombre de dérivés cyano présentent une valeur anormale du rapport $d/l \sim 1{,}4$ où l est la longueur moléculaire. Nous avons montré que la quantité ($d - l$) est directement reliée à la longueur de la chaîne alkyl ou alkoxy de la molécule mais que cette quantité n'a pas de rapport simple avec la longueur du cœur aromatique. Ceci est en accord avec une structure en couches bimoléculaires qui présentent en leur centre des recouvrements de cœurs moléculaires. En utilisant un ensemble de mesures de l'intensité de diffusion des couches par rayons X et diffraction de neutrons sur plusieurs formes substituées d'une façon isotopique, nous avons pu confirmer et quantifier ce modèle pour un composé (4-cyano-4'-n-octylbiphényl, 8CB).

Abstract. — The smectic layer spacings (d) have been determined for a number of cyano derivatives which have an anomalous d/l ratio of ~ 1.4, where l is the molecular length. It is shown that the quantity ($d - l$) is directly related to the length of the alkyl or alkoxy tail of the molecule but is not simply related to the length of the aromatic core. This is consistent with a bimolecular layer structure having overlapping molecular cores at the layer centre. Using a combination of X-ray and neutron diffraction measurements of the intensity of the layer reflections on several isotopically substituted forms we have positively confirmed and quantified this model for one compound (4-cyano-4'-n-octylbiphenyl, 8CB).

1. **Introduction.** — It has been known for some time that certain cyano derivatives have smectic A phases in which the layer spacing (d) as measured by X-ray or neutron diffraction is considerably greater than the molecular length (l). Thus, for 4-cyano-4'-n-octylbiphenyl (8CB) and 4-cyano-4'-n-octyloxybiphenyl (8OCB) [1], and also for 4-cyano benzylidene-4'-n-octyloxyaniline (CBOOA) [2], d/l was found to be ~ 1.4. Furthermore, the wavelength d of the smectic-like fluctuations in the nematic phases of 4-cyano-4'-n-pentylbiphenyl (5CB) and 4-cyano-4'-n-heptyl-biphenyl (7CB) [3] was also found to be about 1.4 times the molecular lengths. Lydon and Coakley [1] considered various possible molecular packings which might give rise to such behaviour but recognizing that the origin of the effect must lie in the strong CN dipole, Leadbetter *et al.* [3] suggested a structure in which the molecular cores overlap, in a head-to-tail arrangement. This model was subsequently refined somewhat following density measurements [4] and at the same time Cladis *et al.* [5] suggested a similar packing configuration on the basis of their work on re-entrant nematic phases. In fact this semibilayer structure was suggested as being essential for the appearance of re-entrant nematic behaviour.

The object of this work was threefold :

(i) to investigate whether other cyano compounds show the same behaviour ;

(ii) to test the general features of the structural model described above by investigating a variety of substances with different tail and core dimensions ;

(iii) to determine as much structural detail as possible about one of these smectic A phases (that of (8CB)) by a combination of X-ray diffraction and neutron diffraction using selectively deuteriated specimens.

2. **Experimental.** — The list of substances studied and their transition temperatures is given in table I.

Data for CBOOA were taken from the literature [6]. All other materials were prepared and their phases characterized by methods described elsewhere [7-12].

Table I

Code	Formula	Transition Temperatures	References
8CB	C_8H_{17}—C_6H_4—C_6H_4—CN	C $\underset{21}{-}$ SA $\underset{33.6}{-}$ N $\underset{40.6}{-}$ I	[7]
8CB-d$_{17}$	C_8D_{17}—C_6H_4—C_6H_4—CN	C $\underset{21}{-}$ SA $\underset{33.0}{-}$ N $\underset{39.7}{-}$ I	[8]
8CB-d$_8$	C_8H_{17}—C_6D_4—C_6D_4—CN	C $\underset{21}{-}$ SA $\underset{34.7}{-}$ N $\underset{41.5}{-}$ I	[8]
8CB-d$_{26}$	C_8D_{17}—C_6D_4—C_6D_4—CN	C $\underset{21}{-}$ SA $\underset{33.0}{-}$ N $\underset{39.1}{-}$ I	[8]
8OCB	C_8H_{17}O—C_6H_4—C_6H_4—CN	C $\underset{54.5}{-}$ SA $\underset{67}{-}$ N $\underset{80}{-}$ I	[7]
10CB	$C_{10}H_{21}$—C_6H_4—C_6H_4—CN	C $\underset{44.0}{-}$ SA $\underset{51.6}{-}$ I	[9]
10OCB	$C_{10}H_{21}$—O—C_6H_4—C_6H_4—CN	C $\underset{60.5}{-}$ SA $\underset{84.2}{-}$ I	[10]
12CB	$C_{12}H_{25}$—C_6H_4—C_6H_4—CN	C $\underset{43.5}{-}$ SA $\underset{58}{-}$ I	[11]
12OCB	$C_{12}H_{25}$O—C_6H_4—C_6H_4—CN	C $\underset{69}{-}$ SA $\underset{89}{-}$ I	[11]
11CDP	$C_{11}H_{23}$—C_6H_4—C≡C—C_6H_4—CN	C —N $\underset{\downarrow 61.4}{}$ I ; SA	[12]
CBOOA	C_8H_{17}O—C_6H_4—N=CH—C_6H_4—CN	C $\underset{73}{-}$ SA $\underset{82.6}{-}$ N $\underset{108}{-}$ I	[6]

The layer spacings were measured by X-ray diffraction usually on powder specimens but sometimes using aligned samples, contained in 0.5-1.0 mm Lindemann glass tubes. Graphite monochromated CuKα radiation was used with a simple flat plate camera ; usually only first order (001) reflections were observed. Measurements on 8CB and 8OCB showed that the layer spacings in the S_A phases vary only very slightly with temperature. so we consider here for all compounds values near the middle of the smectic range.

The intensity measurements on 8CB were made on specimens aligned by cooling from the isotropic phase in a magnetic field of 0.2 T. The samples were contained in flat aluminium-walled containers of thickness between 0.5 mm and 1.0 mm. The effective sample areas were ~ 1 mm^2 for the X-ray measurements and ~ 1 cm^2 for the neutron experiments. The X-ray measurements were made using a diffractometer with a bent LiF monochromator in the diffracted beam, a scintillation counter and pulse height analyser, and also using a photographic technique which enabled the (001) and (002) reflections to be measured simultaneously. The neutron measurements were made using the guide tube diffractometer at AERE Harwell with a wavelength of 4.79 Å.

The 001 diffraction spots are intrinsically very sharp : any broadening being less than the instrumental resolution, and small samples are very well aligned as illustrated in the diffraction photograph in plate 1. For the larger samples used in the neutron experiments the alignment was less perfect and rocking curves on the 001 reflections indicated a distribution of orientations with half-width of $\gtrsim 10°$. Furthermore, the larger neutron samples and especially
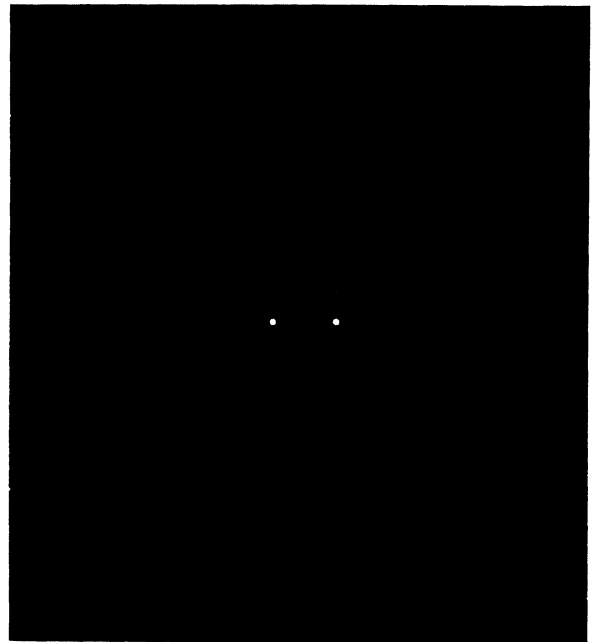

Plate 1. — An X-ray diffraction photograph of a magnetically aligned sample of the S_A phase of 8CB. The field direction is along [00*l*].

8CB, showed a tendency to flow and has to be handled very carefully. This possible misalignment of samples constitutes the major source of error in the intensity measurements and is especially important when comparing intensities for different specimens.

3. **Results and discussion.** — 3.1 LAYER SPACINGS. — The results for the layer spacings (*d*) in the various samples are given in table II. Also included are values

for the molecular lengths (l) which were calculated assuming standard bond lengths, angles and Van der Waals radii. These values were checked using CPK molecular models. The value of l is defined as the length of the molecule in its most extended conformation projected on the axis of minimum moment of inertia, (m). It is clear that in all cases $d/l \sim 1.4$ so that some form of bilayer structure must occur for all these substances.

Table II. — *Layer spacings* (d) *and molecular lengths* (l) *for various cyano compounds in their* S_A *phases* (*uncertainty in* $d \leqslant \pm 0.4$ Å).

Substance	d/Å	l/Å
8CB	31.6	22.1
8OCB	32.0	23.4
1OCB	35.5	24.5
10OCB	35.4	25.7
12CB	39.6	26.9
12OCB	41.6	28.2
11CDP	39.3	28.9
CBOOA	35.0	25.6

These results in fact provide strong support for the general type of model for this bilayer structure suggested earlier [4]. In figure 1 are shown plots of $d - l$ against a and b ; a is the length projected along m, of the molecular core, defined as the distance from the N-end of the molecule to the first atom in the chain, oxygen atoms being taken as part of the chain, and b is the length along m of the remainder of the tail. These definitions are to some extent arbitrary but the use of different measures of core and tail lengths. such as using the last carbon in the phenyl group to define the
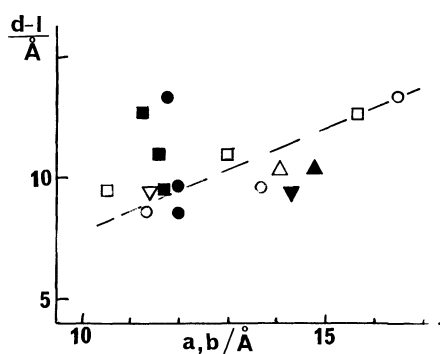

Fig. 1. — Plot of ($d - l$) against core length (a) or tail length (b) of the molecules

	a	b
NCB	●	○
NOCB	■	□
11CDP	▲	△
CBOOA	▼	▽

The line shows the approximately linear relation between $d - l$ and b.

boundary between core and tail, or projecting the lengths onto somewhat different axes in no way changes the qualitative behaviour shown in figure 1. This is that $d - l$ increases regularly with length of molecular tail : indeed, to within about $\pm$ 1 Å, $d - l$ is directly proportional to b although there are significant differences between alkyl and alkoxy compounds for the C_8 and C_{10} molecules. On the other hand there is no simple correlation with length of molecular core. This implies a structure in which the cores overlap in the middle of the layers in a head-to-tail manner with the tails extending outwards in both directions to the layer boundaries [4]. Such a structure should have a d spacing which is related to ($a + 2 b$) and this is examined in figure 2 which shows an approximately linear relation between the two. with $a + 2 b$ greater than d by about 7-8 %. It is not possible to make any more detailed inferences about the molecular packing from these correlations alone as d must depend on tail conformation. degree of overlap of the head-to-tail molecules and the angular distribution function $f(\beta)$ of the long axes, which results in m for the average molecule being at some angle $\langle \beta \rangle$ relative to the layer normal, even for a classical S_A in which $f(\beta)$ is peaked at $\beta = 0$. Nevertheless, the proposed head-to-tail packing with overlapping molecular cores does provide a simple explanation for all the above results.
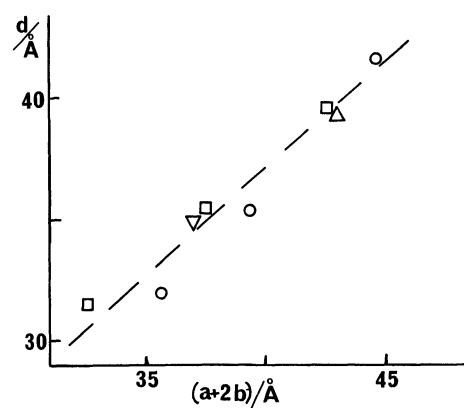

Fig. 2. — Plot of d against $a + 2 b$. ○, NCB ; □, NOCB ; △, 11CDP ; ▽, CBOOA. The line indicates the linear relation between d and ($a + 2 b$).

3.2 INTENSITY MEASUREMENTS ON 8CB. — The results of X-ray and neutron intensity measurements on the layer reflections of 8CB, after appropriate corrections for Lorentz and polarization factors are given in table III. The neutron intensities for the different isotopic compositions have also been normalized relative to each other. The second order reflections are either very weak or unobservable and no higher order reflections were observed. The existence of sharp 001 reflections implies the presence of long range order and hence of an average repeated structural unit within each layer.

Table III

Compound	Radiation	Relative neutron intensity ($l = 1, l = 2$)	$R(x)$
$^8_3$CB-d$_{25}$	Neutrons	1.0, Not observed	—
8CB-d$_8$	Neutrons	560, 1.3	450 ± 100
8CB-h$_{25}$	Neutrons	180, Not observed	—
8CB-h$_{25}$	X-rays	— —	$1\,300 \pm 200$

The intensity of the 001 reflections may then be written quite generally as

$$I(00l) = \alpha\delta\left(Q - \frac{2\pi l}{d}\right) \langle F(00l) \rangle^2 \qquad (1)$$

where α is a normalization constant.

$$\langle F(00l) \rangle = \left\langle \sum_n a_n \exp 2\pi i l Z_n/d \right\rangle \qquad (2)$$

in which a represents a generalized scattering amplitude ($a \simeq b$ for neutrons and $f(Q)$ for X-rays), the summation is over the atoms in the bimolecular *unit cell* and the average is over the possible unit cell configurations in the system. We now put

$$Z_n = Z_c + Z_{cn} \qquad (3)$$

where Z_c is the coordinate of the centre of the bimolecular unit (the centre of the layer for a perfect crystal) and Z_{cn} is the coordinate of atom n relative to Z_c. In order to proceed further with so little data we now assume that Z_{cn} is independent of Z_c when. for our centrosymmetric structure, we have

$$\langle F(00l) \rangle = \left\langle \sum_n a_n \cos 2\pi l Z_{cn}/d \right\rangle \langle \cos 2\pi l Z_c/d \rangle$$

$$= F^p(00l)\,\tau_l . \qquad (4)$$

The evaluation of $F^p(00l)$, the structure factor relative to the centre of the bimolecular unit. requires a model for this unit, while τ_l the smectic order parameter requires a knowledge of the distribution function for the molecular centres $P(Z)$. If this is assumed to be Gaussian then

$$\tau_l = \exp - 2\left(\frac{\pi l}{d}\right)^2 \langle Z^2 \rangle \qquad (5)$$

and with such limited data some such assumption is required to determine τ_l. However, as a first step in the analysis τ_l may be eliminated as follows. Let x and y refer to two different experiments on the same substance under identical conditions but in which the values of the scattering amplitudes a_n are different. This is achieved either by using X-rays and neutrons or by doing two neutron experiments with different isotopic compositions.

Then,

$$\frac{I_x(001)}{I_x(002)} = \frac{\alpha_x}{\alpha_x}\left[\frac{F_x^p(001)\,\tau_1}{F_x^p(002)\,\tau_2}\right]^2 = R_x \qquad (6)$$

and

$$R_x/R_y = \left[\frac{F_x^p(001)\,F_y^p(002)}{F_x^p(002)\,F_y^p(001)}\right]^2 = R(x, y) \qquad (7)$$

and

$$\frac{I_x(001)}{I_y(001)} = \left[\frac{\alpha_x}{\alpha_y}\frac{F_x^p(001)}{F_y^p(001)}\right]^2 = P(x, y) . \qquad (8)$$

For any given model the structure factor and intensity ratios of equations (7) and (8) may readily be calculated and compared with experiment. Once a model has been shown to be consistent with experiment the value of τ_1/τ_2 and hence $\langle Z^2 \rangle^{1/2}$ may be obtained using equations (5) and (6). The lack of higher order reflections ($l \geqslant 3$) shows that τ_l is a rapidly decreasing function of Q and that τ_1/τ_2 is the dominant influence on R_x. τ_l has no effect on $P(x, y)$ and were it not for the difficulties in determining absolute values of α_x and α_y and especially the possible large errors due to the differences in the alignment of the samples the $P(x, y)$ values would provide a more sensitive test of a model than the $R(x, y)$ values. Small differences in alignment have practically no effect on $R(x, y)$ and consequently the values of $R(x, y)$ are much more reliable than those of $P(x, y)$. The repeated structural unit was assumed to be a bimolecular group and our object is to determine first the gross configuration of this group and second any detail possible about its structure. Note that this assumption does not necessarily imply the existence of molecular dimers, it is simply the smallest repeat unit which will allow the head-to-tail arrangement of molecules required to prevent the material
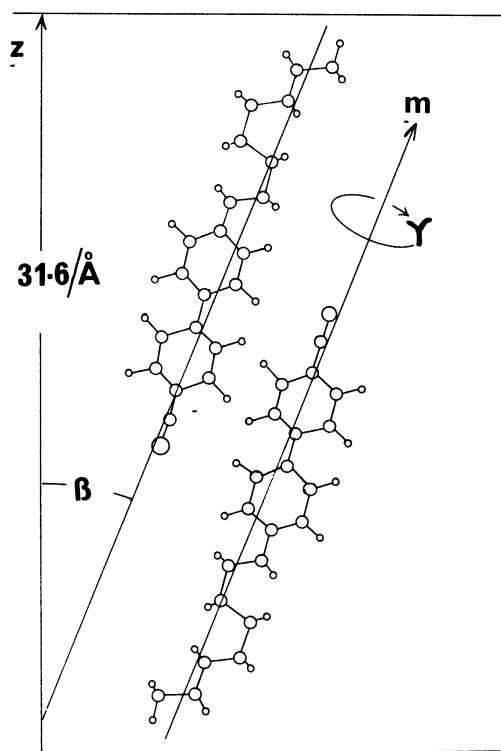

Fig. 3. — Diagram of the bimolecular unit cell with the molecules having a *kinked* alkyl chain conformation.

being ferroelectric. Ferroelectric properties have never been found in liquid crystals through alignment of the long axis direction.

The following model was used to calculate the $F^P(00l)$ values for the bimolecular unit cell (see Fig. 3).

Taking the mid-point of the layer as $Z = 0$ a molecule is placed in the layer so that the coordinate of its outermost atom is

$$|Z| = d/2 - V$$

where V is the appropriate Van der Waals radius. The internal conformation of the molecule is chosen to be either a kinked or extended alkyl chain. The axis of minimum moment of inertia of the molecule (m) is set at an angle β to the Z axis with the molecule having an orientation γ about this axis. The coordinates of the second molecule are generated from those of the first by a two-fold axis normal to the paper at $Z = 0$. The value of $F^P(00l)$ is calculated and averaged over all values of γ to take account of the assumed random orientation of the molecule about m. There will clearly be some distribution of β, but the data are insufficient to attempt to determine more than an effective average value $\langle \beta \rangle$. A more complicated model requiring much more computer time was constructed in which the average over γ was done independently for each molecule and in which an arbitrary distribution of the extent of molecular overlap was incorporated. For all values of β this model gave similar results to the simpler one above.

Using $F^P(00l)$ values derived from this model with $\beta = 0$ (model B, overlapping cores) and $\beta = 180°$ (model A, overlapping tails) values of $R(x. y)$ were calculated and are shown below. Here x refers to an X-ray experiment on 8CB-h_{25} and y refers to a neutron experiment on 8CB-d_8.

	$R(x, y)$		
	Extended chain	Kinked chain	Experiment
Model A...	160	320	$3 \pm {}^{2}_{1}$
Model B ...	3	5	

This is convincing evidence for model B while (as might be expected) the conformation of the alkyl chain makes little difference to the result. Comparison of the $P(x, y)$ values also favours model B although the agreement is less good, and we believe this to be due to the experimental difficulties, discussed earlier, of obtaining and keeping a well aligned monodomain specimen (or a good powder specimen).

			$P(x, y)$	
x	y	Model A (extended, kinked)	Model B (extended, kinked)	Experiment
8CB-d_8	8CB-h_{25}	0.3, 0.3	0.8, 0.8	~ 2
8CB-d_8	8CB-d_{25}	1.0, 0.5	13, 26	~ 550
8CB-h_{25}	8CB-d_{25}	3, 2	17, 35	~ 180

Qualitatively the lack of observed second order reflections for 8CB-d_{25} and 8CB-h_{25} is consistent with the small *structure factors* $[F(002)]$ for these reflections in both models A and B.

The comparisons shown in figure 4 demonstrate that model B gives a good fit to experiment for $\langle \beta \rangle$ in the range 0 to 35° while model A could be acceptable if $\langle \beta \rangle \approx 35°$. For a typical S_A phase the distribution of molecular long axis orientations $f(\beta)$ is expected to be such that generally $\langle P_2 \rangle \gtrsim 0.7$ which means that $\langle \beta \rangle \lesssim 25°$ which again suggests that model B is more likely. More importantly however we have recently determined $f(\beta)$ directly from X-ray diffraction measurements [13] and find a normal Maier-Saupe distribution centred at $\beta = 0$ and with $\langle P_2 \rangle \sim 0.7$ which provides positive confirmation of the model with overlapping cores in the layer-centre and with a normal distribution of long axes orientations.
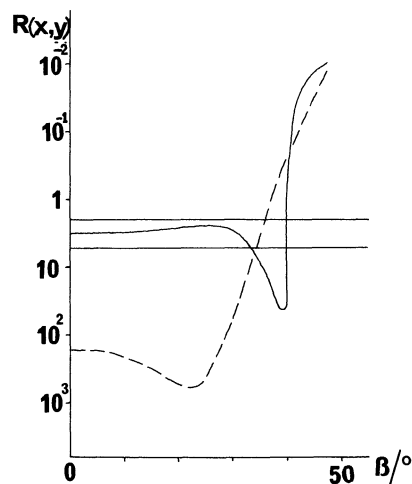
Having established that model B is a good repre-

Fig. 4. — Plot of $R(x, y)$ on a logarithmic scale against β for model A (dashed line) and model B (full line) for the extended alkyl chain molecular conformation. The *kinked* chain conformation gives similar results. The two horizontal lines indicate the upper and lower limits on the experimentally determined $R(x, y)$.

sentation of the average structure of the layers then, using the Gaussian approximation gives (eqs. (5) and (6))

$$\langle Z^2 \rangle^{1/2} = 6.5 \text{ Å}.$$

It is worth emphasizing that this is about 20 % of the layer spacing so that high spatial disorder normal to the layers is an intrinsic and important part of the description of the S_A structure. Indeed the simple crystal-like representation of the average structure (Fig. 3) cannot fill space to give the correct density

without the addition of a degree of disorder of this magnitude. As discussed elsewhere [4] it seems likely that both this disorder and the angle between core and extended tail are important in determining the molecular packing.

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