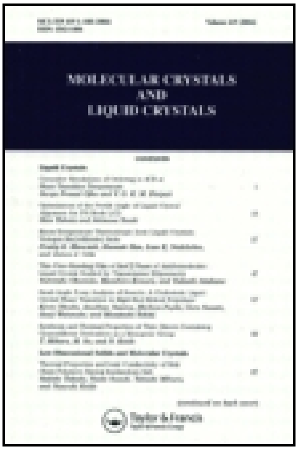

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A Hypothesis for the Molecular Organisation in the S_D and S_4 Phases

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A HYPOTHESIS FOR THE MOLECULAR ORGANISATION IN THE S_D AND S_4 PHASES

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Abstract: The structures of the S_D phase and of the birefringent phase formed at the S_AS_D or I S_D transition (provisionally called the S_4 phase) are discussed. It is suggested that the S_4 phase is discotic and that its basic structural unit is a more or less flat ring of dimeric molecules (this assembly being stabilised by interactions between the strong lateral dipoles of the molecules).

It is suggested that the S_4S_D transition entails the aggregation of these rings into cylindrical stacks with pointed ends. These units then form a complex jointed network with overall cubic symmetry. Such a structure is similar to a previously proposed model for the S_D phase but has lattice dimensions of twice the size.

Introduction

Following the earlier report by Gray *et al.* in 1957 of an interesting smectic polymorphism in $3'$-nitro-$4'$-n-hexadecyloxy-biphenyl-4-carboxylic acid (NHDBCA),[1] shown in Figure 1, and the analogous octadecyl compound (NODBCA), Demus *et al.* found that these compounds form an unusual type of thermotropic mesophase.[2] This mesophase they labelled the smectic D phase. It is unusual in that its only stable texture is a featureless isotropic state. The schemes of phase transitions

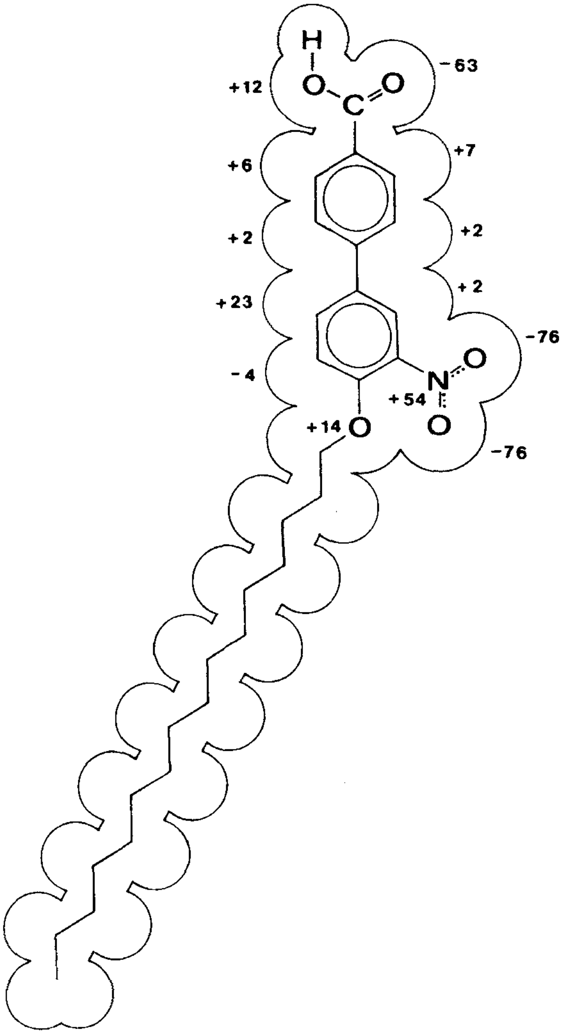

FIGURE 1: The molecule of NHDBCA. The van der Waals envelope of the molecule is shown. The numbers indicate the partial charges (as percentages of an electron) as calculated by a Hückel molecular orbital calculation using standard parameterisation (A Streitweiser Jr, Molecular Orbital Theory for Organic Chemists, John Wiley, 1961). This approach does not give any information about the charges on the atoms of the alkyl chain but these are expected to be small, ie, less than 5% of an electron.

for these two compounds are:

$$\text{NHDBCA}\quad \text{Solid} \xleftrightarrow{126.8} S_C \xleftrightarrow{171.0} S_D \xleftrightarrow{197.2} S_A \xleftrightarrow{201.9} \text{Isotropic}$$

$$\text{NODBCA}\quad \text{Solid II} \xleftrightarrow{85} \text{Solid I} \xleftrightarrow{124.6} S_C \xleftrightarrow{158.9} S_D \xleftrightarrow{195.0} \text{Isotropic}$$

The only other compounds which have subsequently been found to give S_D phases are analogues of NHDBCA and NODBCA in which the nitro-group is replaced by a cyano-group.[3]

Demus and Richter have described in detail the optical texture changes which occur at the S_CS_D and the S_AS_D transitions of NHDBCA.[4] When the S_D phase is formed by heating the S_C, it emerges as "characteristic rectangles, squares, hexagons and rhombs which coalesce without grain boundaries on further growing". The isotropic nature of this phase, together with the appearance of these polygons, suggests that there is long range structure and it would seem that the only explanation for the isotropic nature of the phase must lie in its having cubic symmetry. Since it is difficult to conceive of a pattern of individual molecules of NHDBCA with this symmetry which would also give a phase with liquid crystalline properties, Diele *et al.* proposed that there is "a cubic lattice of units of micellar dimensions".[5] A preliminary X-ray investigation carried out by these workers appeared to verify this. The diffraction pattern has two principal features - a diffuse ring at 4.5Å (characteristic of disordered alkyl chains) and a small number of sharp low angle reflections corresponding to repeat distances of the correct order for inter-micelle spacings. These were interpreted in terms of a body-centred cubic lattice of spherical assemblies (this structure being analogous to the earliest model proposed for the lyotropic cubic phases). The indexing of the first reflection as 110 gave a value for the unit cell parameter a = 61Å.

Following a more detailed re-examination of the X-ray diffraction pattern, Tardieu and Billard proposed a radically modified model.[6] They re-indexed the reflections (so that the first reflection now becomes 211) giving a new value for the unit cell dimension, a = 102Å, and they suggested that the molecular arrangement is analogous to an alternative model for the lyotropic cubic phase proposed by Luzzati and Spegt.[7] Part of this rather complex structure is shown in Figure 2. The molecules are aggregated in short cylinders (rather than spheres) and these cylinders are linked together to form two interwoven three-dimensional networks. Tardieu and Billard have pointed out that their observations are compatible with two alternative models; I, with the alkyl chains pointing inwards towards the centres of the cylinders and II, with the aromatic parts of the molecules packed in the centres of the cylinders and the alkyl chains radiating outwards.

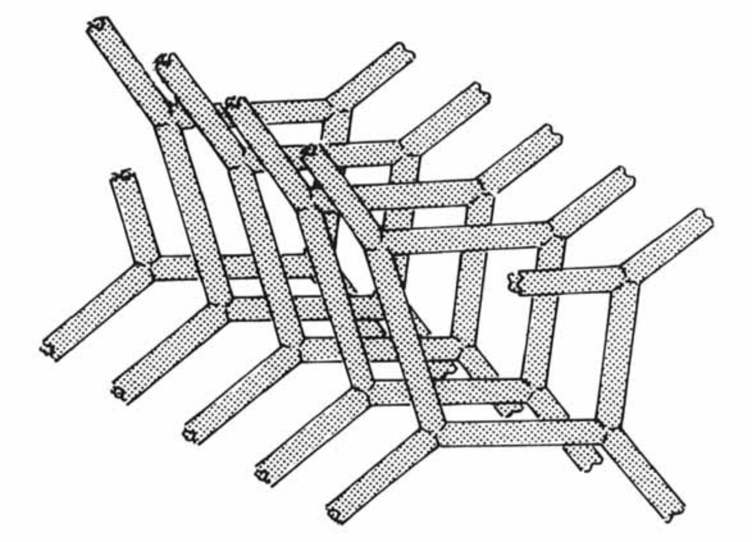

FIGURE 2: The Tardieu-Billard model for the S_D phase (after the model by Luzatti and Spegt for the lyotropic cubic phase). This diagram shows part of the structure. Helical units of this type are linked together to form two interwoven networks in such a manner that the overall structure has cubic symmetry.

The texture of the S_4 phase

As described by Demus and Richter,[4] when a sample of NHDBCA in the homeotropic S_A state is cooled, it does not pass directly into the isotropic texture of the S_D phase. It forms a highly birefringent state which has been provisionally termed the S_4 phase. The first texture which this phase adopts apparently consists of rod-like bâtonnets and this texture then develops into a pattern of mosaic grains. The S_4 mosaic texture then changes into the S_D isotropic texture.

The birefringent 'bâtonnet' texture is unlike any of the familiar textures adopted by smectic phases. Its appearance is, however, very similar to that of the mesophase of di*iso*butylsilanediol described by Eaborn and Hartshorne.[8] We have recently obtained evidence that this is a discotic phase[9] and it is tempting therefore to suggest that the S_4 phase of NHDBCA is discotic also.

Detailed optical examination of the silanediol mesophase showed that it does not consist of birefringent bâtonnets of mesophase separated by isotropic material. The whole sample is mesophase; the dark areas are homeotropic and the birefringent regions are disclination lines. A similar interpretation for the S_4 phase is suggested.

The isotropic texture (unique amongst thermotropic mesophases), the absence of paramorphosis and the pronounced supercooling at the S_AS_D transition, all imply that there is a fundamental distinction between the D phase and all other smectic phases. In fact, the only justification for calling this phase smectic appears to be that it occurs between two well-defined smectic phases. (Perhaps it is also unwise to judge mesophases solely by the company they keep!)

Molecular interactions in the S_D

In view of the rarity of the S_D phase, it would seem reasonable to assume that some particular feature or combination of features of the four molecular species known to adopt it is crucial. Let us therefore list the main features of these molecular structures and comment on their occurrence and influence in other smectogenic compounds.

1. *The overall shape of the molecule*: The aromatic and aliphatic parts are of almost equal length and are probably inclined to each other at an angle of approximately 40° at lower temperatures. This overall shape is shared by a large number of smectogenic molecules and it would not, on its own, be expected to lead to the formation of any novel mesophase. A segregation of the aliphatic and aromatic parts would seem probable at least for the lower temperature mesophases and the crystalline solids.

2. *The terminal carboxyl group*: This is also a feature shared by a large number of smectogenic compounds. It

would be expected to cause the molecules to pair together end-to-end by hydrogen bonding giving oblique z-shaped dimers in both the crystalline solid and the mesophases. Analogy with the alkoxybenzoic acids suggests that molecules of this shape will form a S_C phase.

3. *The nitro or cyano group*: As shown in Figure 1, the nitro group confers an appreciable lateral dipole on the molecules (and the cyano group is expected to behave very similarly). Smectogenic molecules with this feature are very rare and there is therefore the strong inference that side-by-side adhesion of the molecules due to electrostatic interactions may be the principal factor giving rise to the S_D and S_4 phases.

One arrangement of the molecules which is plausible and which takes account of all of the above factors is the flat ring shown in Figure 3. This would readily explain the formation of a discotic phase; the rings would 'see' each other as fairly rigid discs with circumferences consisting of flexible alkyl chains. As in other discotic phases, there is a tendency for the units to stack one above the other giving cylinders which then tend to arrange themselves in a hexagonal array. The increasing degree of organisation in this fashion with falling temperature will alter the elastic

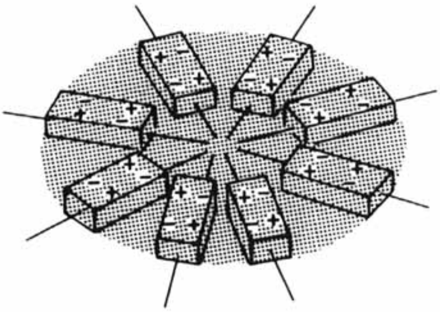

FIGURE 3: The aggregation of dimeric molecules into rings which it is suggested occurs in the S_4 phase. Because the rigid aromatic parts of the molecules are not tapered, they will not readily pack into a perfectly flat disc and the annulus of this ring which contains the aromatic parts of the molecules may therefore be slightly puckered.

constants of the phase and this is presumably reflected in the change from the 'bâtonnet texture' to a mosaic appearance with distinct grain boundaries.

When the cylinders have become sufficiently large and consolidated, they presumably re-arrange themselves to form a complex network of the Tardieu/Billard type. There are problems with the Tardieu/Billard model. Firstly, for either of the alternatives, I and II, there are awkward shaped volumes to be filled with the non-flexible aromatic parts of the molecules. Secondly, the structure does not incorporate the expected dimerisation of the molecules. Finally, the model looks too complicated to be credible and seems to lack a rationale. How do the rods "know" how long to grow and how do they manage to join together at exactly 120° when the joint regions must be amongst the more disordered parts of the structure? The relationship between the short range order and the long range order is not apparent.

If we adopt a dimer rather than a monomer as the structural unit, the first two of these problems are answered. We are however left with a lattice of twice the size of that described by Tardieu and Billard, and it might be thought that the X-ray diffraction data effectively rule out this possibility. However, it is to be expected that a structure of the type proposed will give a systematic pattern of strong and weak reflections and it is feasible that this causes an apparent halving of the lattice dimensions.

Concerning the final objections to the Tardieu/Billard model, there is a slightly modified viewpoint which makes a structure of this type look much more reasonable. It is likely that in the region of the central axis of the cylinders, the alkyl chains do not have sufficient space or fluidity to pack flat and they tend to protrude, giving the cylinders pointed ends (Figure 4). As the cylinders increase in length, the vertex angle decreases until it becomes 120°. It is *only* at this stage that the units can pack together giving an infinite lattice, and the relationship between the length of the cylinder and the vertex angle ensures that the cylinders are all of the same length when this happens. The structure should perhaps be regarded not as having regions of low order and other regions of high order - but rather in terms of a gradual distortion of the alkyl chain packing as we progress from the centres of the cylinders to the joint regions.

The above reasoning would appear to be valid for the lyotropic

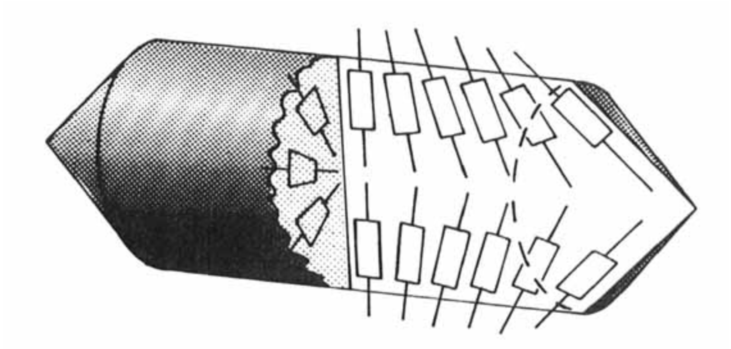

FIGURE 4: The molecular aggregation in the S_D phase. It is suggested that the rings shown in Figure 3 stack together to form cylinders and that the molecular congestion along the axes of these cylinders causes them to grow with pointed ends. As the cylinders increase in length, the vertex angle becomes smaller until it reaches 120°. It is only at this stage that the units can pack together forming an infinite lattice of the type shown in Figure 2.

cubic phases also and the general concept of "bevelled micelles" may be useful in a wider context in discussing the structures of some of the disputed lyotropic phases.

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