



**HAL**  
open science

## ON THE STRUCTURE OF THE “ SMECTIC D MODIFICATION ”

A. Tardieu, J. Billard

► **To cite this version:**

A. Tardieu, J. Billard. ON THE STRUCTURE OF THE “ SMECTIC D MODIFICATION ”. Journal de Physique Colloques, 1976, 37 (C3), pp.C3-79-C3-81. 10.1051/jphyscol:1976313 . jpa-00216496

**HAL Id: jpa-00216496**

**<https://hal.science/jpa-00216496>**

Submitted on 4 Feb 2008

**HAL** is a multi-disciplinary open access archive for the deposit and dissemination of scientific research documents, whether they are published or not. The documents may come from teaching and research institutions in France or abroad, or from public or private research centers.

L'archive ouverte pluridisciplinaire **HAL**, est destinée au dépôt et à la diffusion de documents scientifiques de niveau recherche, publiés ou non, émanant des établissements d'enseignement et de recherche français ou étrangers, des laboratoires publics ou privés.

## ON THE STRUCTURE OF THE « SMECTIC D MODIFICATION »

A. TARDIEU

Centre de Génétique Moléculaire du C. N. R. S., 91190 Gif-sur-Yvette, France

J. BILLARD

Laboratoire de Physique de la Matière Condensée, Collège de France, 75231 Paris Cedex 05, France

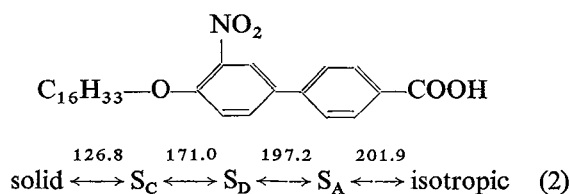
**Résumé.** — La structure de la phase *smectique de type D* a été réétudiée par diffraction des rayons X. Six ordres de réflexions ont été observés, qui correspondent à un réseau cubique centré, de groupe de symétrie Ia3d. Nous pensons qu'il s'agit de la même structure que celle d'une phase cubique observée avec les lipides.

**Abstract.** — The structure of the *smectic D modification* is reinvestigated by X-ray diffraction techniques. Six reflexions orders are observed which are in agreement with a body centered cubic lattice, space group Ia3d. We propose that the structure is similar to that of one cubic phase observed with lipids.

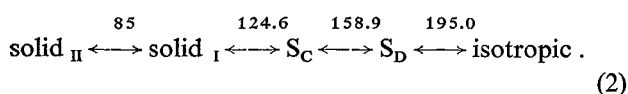
1. **Introduction.** — The *smectic D modification* was first observed and described by the Halle group in 1968 [1]. It has the particularity of being optically isotropic. This modification was latter on studied, also by the Halle group by X-Ray diffraction techniques, using a powder sample and a monodomain [2]. The powder diagram contained too many spots to be interpretable. However, on the basis of six reflexions organized in a pseudo hexagonal array observed with the monodomain, a cubic structure was proposed [2]. We report here a new series of X-Ray experiments, in which it has been possible to increase the number to visible reflexions. The cubic structure is confirmed and the symmetry group is determined.

2. **Experimental part.** — 2.1 SUBSTANCES. — Only two compounds are actually known to present the « smectic D modification » :

No. 1 : 4'-n-Hexadecyloxy-3'-nitrodiphenyl-4-carboxylic acid



No. 2 : 4'-n-Octadecyloxy-3'-nitrodiphenyl-4-carboxylic acid



The sample used, (hexadecyloxy-) was a gift from Pr. Sackmann.

2.2 X-RAY. — The pictures are Debye Scherrer diagrams, obtained with a Guinier type camera, with bent quartz monochromator, operating in vacuum. The radiation is Cu K $\alpha$  1 ( $\lambda = 1.54 \text{ \AA}$ ). The sample, about 0.7 mm thick, was held in a closed sample holder with mica windows. In order to avoid a spotted appearance for the X-Ray diagrams, the sample is rotated around its axis during the experiment. The sample seems damaged after repeated heating ; because of the small amount of sample available (a few mgs) only two pictures were taken, with and without rotation of the sample.

3. **Results.** — As observed by Diele *et al.* [2], the X-Ray diagrams show a diffuse reflexion, at high angles around  $s \simeq (4.5 \text{ \AA})^{-1}$  indicating that the hydrocarbon chains are in a *liquid* state. At low angles and without rotation, the diagram consists in a large series of spots, again similar to the results of Diele *et al.* ([2], Fig. 1).

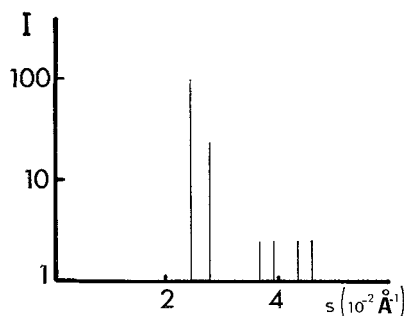


FIG. 1. — Schematic representation of the low angle part of the X-Ray diagram. The ordinate represents the intensity of each reflexion (estimated by eye), and the abscissa gives the diffraction angle, in the form of  $s = 2 \sin \theta / \lambda$ .

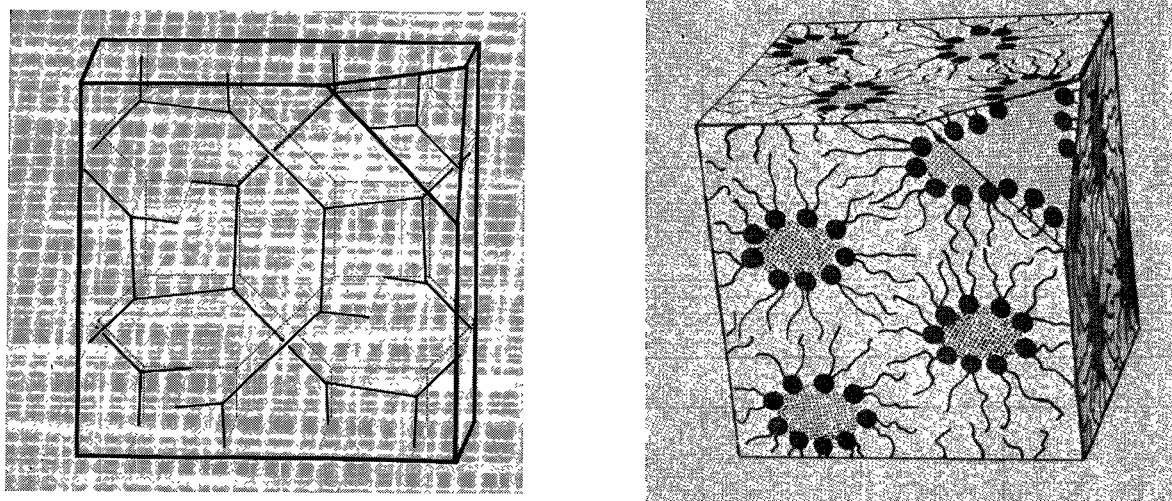


FIG. 2. — The cell is centred cubic space group Ia3d. The left frame represents a perspective view of one unit cell. The axis of the rods that sit on crystallographic two fold axis are represented by thin lines. The heavy lines show the limits of one unit cell. The right frame shows the distribution of water and lipids (the water regions are hatched, the polar groups of the lipids are represented by black dots and the hydrocarbon chains by curly lines, for a structure of type II (see text) as observed with egg lecithin.

When the sample is rotated, a series of six reflexion orders may be observed. The two first are very strong and the four others rather faint. Because of the difficulty of reproducing correctly the picture, it is just schematically drawn in figure 1. The spacing ratios of the six reflexions are :  $\sqrt{3}$ ,  $\sqrt{4}$ ,  $\sqrt{7}$ ,  $\sqrt{8}$ ,  $\sqrt{10}$ ,  $\sqrt{11}$ . Because of the presence of  $\sqrt{7}$ , the reflexions are only in agreement with a body centered cubic lattice, and have to be indexed (211), (220), (321), (400), (420) and (332). Thus the parameter of the unit cell is  $a = 102 \text{ \AA}$ . Assuming a density of  $0.89 \text{ g/cm}^3$ , this corresponds to about 1 150 molecules within the unit cell. Diele *et al.* [2] obtained a parameter  $a = 61 \text{ \AA}$  in indexing the first reflexion as  $\bar{1}10$ ; if it is now indexed 211, a becomes equal to  $105 \text{ \AA}$ , a value in very good agreement with our measurements when considering the size of the spots in figure 2 of reference [2].

If we assume that the high number of absent reflexions has to be explained by the symmetry group, the choice of the space group Ia3d (No. 230 of the International Tables [3]) is quite unambiguous in this case. This space group is the same as that of the cubic phase of lipid-water systems which is commonly observed between a lamellar phase and an hexagonal one. Although the number of observed reflexions is smaller here than is usually observed with lipids, the analogy of the intensity distribution [4] further suggests that in all the cases the structure is similar.

The structure of the cubic phase observed with lipids was solved by Luzzati and Spegt [5]. The structure consists in rods of finite length all identical and crystallographically equivalent, which lie along two-fold axes. These rods are linked three by three and define two infinite three dimensional networks, mutually interwoven and unconnected. The structure

is depicted in figure 2. For this class of structures in which a topological distinction can be made between the *inside* and the *outside* of the structure elements, it is proper to distinguish two types of distributions : type II if the head groups (with water if present) are localized along the rods, the paraffin chains filling the rest of the space, and type I if the paraffin chains are inside the rods and the water outside. Various examples are given in reference [4]. The choice between type I and type II in lipid-water systems can be guided by several considerations (see ref. [4]) such as by example the succession of the phases with increasing water content (type I if the succession is lamellar, cubic, hexagonal, type II if the succession is hexagonal, cubic, lamellar). An additional verification is provided by the comparison of observed and calculated intensities. Unfortunately, with the *smectic D modification* the small number of observed reflexions does not allow a precise crystallographic verification. Thus other experiments, using these and other compounds presenting this phase, would be needed in order to apply the criteria used with lipid systems to the *smectic D* system. One argument in favour of a type II structure would be that the *smectic D modification* is observed dry, condition in which with lipids type I structures are never observed; also a type II structure would allow the formation of dimers or polymers by the means of hydrogen bonding between the head groups.

Miscibility experiments with dry lipids (strontium soaps and lecithin) presenting this cubic phase have been attempted without success.

**4. Discussion.** — In this study we have been able to establish that the *smectic D modification* is a cubic phase, space group Ia3d. Because of the similarity

with a cubic phase observed with lipids, we have proposed the same structure with the ambiguity that it cannot be established if it is of type I or of type II. Other experiments, with powders or with monocrystals, using pure compounds or mixtures, will be needed to clarify this point. A precise study of the adjacent phases could also be helpful.

The *smectic D modification* is interesting in several respects. It is the first observation in Thermotropic Liquid Crystals of a phase presenting a well developed long range order in three dimensions, while remaining highly disordered at the atomic level (diffuse band at  $(4.5 \text{ \AA})^{-1}$ ); in this respect it is completely different from a plastic crystal. It is also the first observation in a compound which otherwise displays the classical

polymorphism of Thermotropic Liquid Crystals ( $S_C$ ,  $S_A$ ) of a phase typical of the polymorphism of Lyotropic Liquid Crystals. The reason for this peculiar behaviour can perhaps be related to the rough similarity of chemical structure of the compound studied and of lipids (a head group linked to a long hydrocarbon chain).

As already pointed out [2], the terminology adopted for this phase has to be reviewed as it does not fulfill the requirements [6] of a smectic phase.

**Acknowledgments.** — We thank Pr. Sackmann and Dr. Demus who kindly provided us with a sample of this precious compound.

#### References

- [1] DEMUS, D., KUNICKE, G., NEELSEN, J., SACKMANN, H., *Z. Naturforsch.* **23a** (1968) 84.
- [2] DIELE, S., BRAND, P., SACKMANN, H., *Mol. Cryst. Liq. Cryst.* **17** (1972) 163.
- [3] *International Tables for X-Ray Crystallography*, 1 (The Kynoch Press, Birmingham) 1952.
- [4] LUZZATI, V., TARDIEU, A., GULIK-KRZYWICKI, T., RIVAS, E., REISS-HUSSON, F., *Nature* **220** (1968) 485.
- [5] LUZZATI, V., SPEGT, P. A., *Nature* **215** (1967) 701.
- [6] FRIEDEL, G., *Ann. Phys. Chem.* **18** (1922) 273.