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Phasmids : a new class of liquid crystals

J. Malthête

Laboratoire de Chimie des Interactions Moléculaires, Collège de France, 75231 Paris Cedex, France

A. M. Levelut

Laboratoire de Physique des Solides, associé au CNRS, Bâtiment 510, 91405 Orsay Cedex, France

and Nguyen Huu Tinh

Centre de Recherche Paul-Pascal, Domaine Universitaire, 33405 Talence Cedex, France

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Résumé. — On décrit deux dérivés hexa alcoxy de la téréphtal-bis-[benzoyloxy-4-aniline] *7a* et *7b*. Ils présentent deux nouveaux types de mésophases pour lesquelles le qualificatif (phases) *phasmidi-ques* est proposé. L'une de ces mésophases possède un réseau bidimensionnel hexagonal, l'autre un réseau bidimensionnel oblique.

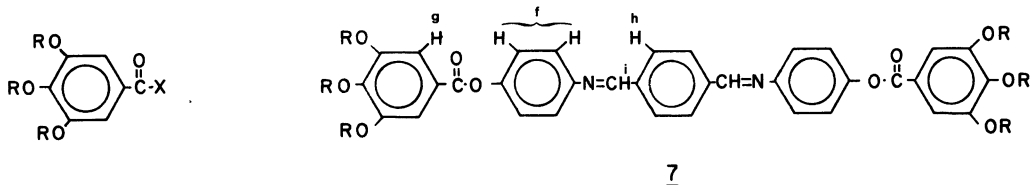
Abstract. — Two hexa-alkoxy derivatives (*7a* and *7b*) of terephthal-bis-[4-benzoyloxyaniline] are described. They exhibit two new types of mesophase for which the term *phasmidic* is proposed : one has an hexagonal 2D lattice and the second an oblique 2D lattice.

1. Introduction.

Besides the classical liquid crystals observed with rod-like molecules, thermotropic mesophases consisting of two-dimensional aromatic flat molecules have been known for a few years [1]. More recently mesogenic cone-shaped molecular structures have been described [2]. So, it was interesting to examine the possible mesomorphic properties of molecules with a rod-like rigid core ending in two half-disk-shaped moieties as, for example, the three benzene ring structure *7* with two trialkoxybenzoate groups at its extremities. We propose the term *phasmids* (from the name of six-legged stick-like insects) and *phasmidic* phases (denoted Φ , the initial of the Greek root $\Phi\acute{\alpha}\sigma\mu\alpha$ -) for distinguishing respectively this new type of mesogenic molecule and the observed mesophases that we present here.

2. Preparation.

The synthesis of terephthal-bis-[4-(3', 4', 5'-triheptyloxybenzoyloxy)-aniline] *7a* and terephthal-bis-[4-(3', 4', 5'-tridodecyloxybenzoyloxy)-aniline] *7b* was carried out by reaction of two equivalents of the corresponding amine *6a* or *6b* with terephthaldehyde in absolute ethanol (one drop of AcOH as catalyst, 30 min reflux) and recrystallized from an ethanol-ether mixture (60-65 % yield). Aminoesters *6* were prepared by catalytic reduction (H_2 , 5 % Pd-C, EtOAc)



1 X = OCH₃, R = H

2 X = OCH₃

3 X = OH

4 X = Cl

5 X = O-

6 X = O-

a R = n-C₇H₁₅-

b R = n-C₁₂H₂₅-

a R = n-C₇H₁₅-

b R = CH₃^a-(CH₂)₆^b-CH₂^c-CH₂^d-CH₂^e

of nitroesters **5**, obtained in four steps from methyl gallate. Reaction of **1** with three equivalents of the corresponding *n*-alkyl bromide (respectively *n*-C₇H₁₅Br and *n*-C₁₂H₂₅Br for **2a** and **2b**) in acetone with an excess of K₂CO₃ (20 h reflux) and saponification of the resulting triether **3** (KOH, 80 % ethanol, 1 h reflux) afforded acids **3a** (m.p. 41 °C, ethanol) and **3b** (m.p. 58 °C, ethanol). *p*-nitrophenol was then esterified in anhydrous pyridine with the acid chloride **4**, obtained by reaction of **3** with SOCl₂ (1 h reflux), to give **6**.

Compound **7a** (pale yellow crystals). Found : C, 75.3; H, 8.9. Calc. for C₇₆H₁₀₈N₂O₁₀ : C, 75.5; H, 9.0 %. Compound **7b** (pale yellow crystals). Found : C, 78.2; H, 10.4. Calc. for C₁₀₆H₁₆₈N₂O₁₀ : C, 78.1; H, 10.4. ¹H N.m.r. (CDCl₃, 200 MHz), δ (Me₄Si) 0.88 (18 H, *t*, a-CH₃), 1.27 (96 H, *m*, b-CH₂), 1.49 (12H, *m*, c-CH₂), 1.81 (12H, *m*, d-CH₂), 4.06 (12H, *t*, e-CH₂; both triplets corresponding to the equivalent *meta* e-CH₂ (8H) and *para* e-CH₂ (4H) separated by addition of some C₆D₆), 7.24, 7.33 (8H, 2 × *d*, f-ArH), 7.42 (4H, *s*, g-ArH), 8.03 (4H, *s*, h-ArH), 8.56 (2H, *s*, i-CH=N). I.r. (Nujol) : 1 730, 1 620, 1 590, 1 500, 1 340, 1 225, 1 205, 1 180, 1 130, 1 120 and 715 cm⁻¹.

3. Results.

Both phasmids **7a** and **7b** are mesogenic. Transition temperatures (Table I) were determined by calorimetry using a DSC2 (Perkin-Elmer). The textures were observed with a polarizing microscope equipped with a heating and cooling stage (Mettler FP5).

Table I. — Transition temperatures of phasmids **7a** and **7b** (°).

	K	Φ _{ob}	Φ _h	I
7a	● 80	● 82	—	●
7b (°)	● 70	● 81.5	● 92	●

(°) K : crystal; Φ_{ob} : phasmidic phase with an *oblique* 2D lattice; Φ_h : phasmidic phase with an *hexagonal* 2D lattice; I : isotropic liquid; ● : the phase exists; — : the phase does not exist.

(°) Crystal-crystal transition at 28 °C (ΔH = 0.9 kcal.mol⁻¹); ΔH_{K→Φ_{ob}} : 15.6 kcal.mol⁻¹; ΔH_{Φ_{ob}→Φ_h} : 0.06 kcal.mol⁻¹; ΔH_{Φ_h→I} : 1.4 kcal.mol⁻¹.

All the mesophases have fan-shaped textures (Figs. 1a, 1b and 1c) and are not mutually miscible. Concerning the phasmid *7b* we did not observe any obvious difference between the textures of the Φ_{ob} phase and those of the Φ_h phase (Figs. 1b and 1c).

4. X-ray diffraction experiments.

The structural information is derived mainly from diffraction patterns obtained from powder samples with a classical Guinier camera. The diffraction pattern can be divided into two zones : the small angle area contains several sharp diffraction rings corresponding to a 2D regular lattice, while a unique broad diffuse band is seen at large angle. This band approximately corresponds to a scattering vector $\frac{2 \sin \theta}{\lambda} = \frac{1}{4.5} \text{ \AA}^{-1}$ where 2θ is the angle of the diffracted X rays with the incident beam. This ring is therefore characteristic of the melted state of the paraffinic moieties of the molecules. Complementary information is given by diffraction patterns obtained with aligned samples. Our samples were poorly aligned ; nevertheless we have obtained confirmation that the mesophases are columnar phases in which the columns are parallel to the alignment direction and form a 2D crystalline lattice, since all the Bragg spots lie in a reciprocal plane perpendicular to the column axis. The diffuse ring corresponding to the paraffinic chains remains nearly isotropic for aligned samples, this fact reflects the high degree of orientational disorder of the paraffinic chains.

A final point must be emphasized : whereas we observe generally some diffraction bands characteristic of the stacking of the aromatic moieties in a column for disk-like liquid crystals (3), such bands are not seen in this case. We can conclude that the diffraction due to interferences between neighbouring cores takes place at the same place as interferences coming from the paraffinic chains leading to a situation similar to that of a smectic A or C phase.

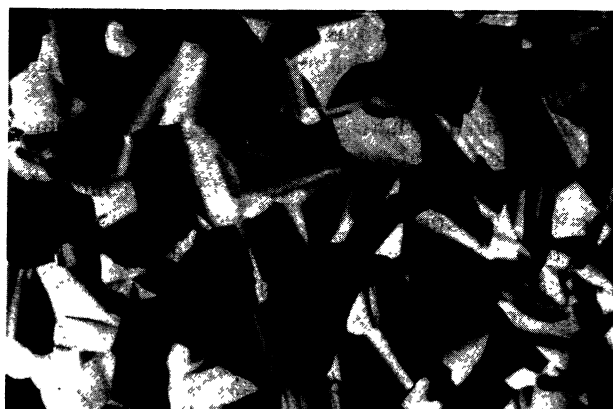
In order to have a more precise idea of the structure of a column, we can compare the lattices of the 2D ordering in the three mesophases.

Table II. — *Assignment of the observed lattice spacing for the three mesophases.*

Symmetry and lattice constants	Indices	Observed lattice spacings (Å)	Calculated lattice spacings (Å)
<i>7a</i> $T = 81 \text{ }^\circ\text{C}$ $a = 34.06 \text{ \AA}$ $b = 22.42 \text{ \AA}$ $\beta = 94.7^\circ$ Oblique	10	33.94	33.94
	01	22.34	22.34
	$1\bar{1}$	—	19.41
	11	18.29	17.99
	20	16.97	16.97
	$2\bar{1}$	—	14.09
	21	12.79	13.01
<i>7b</i> $T = 75 \text{ }^\circ\text{C}$ $a = 39.22$ $b = 23.00$ Oblique ?	10	39.22	39.22
	01	22.34	22.34
	11	—	19.84
	20	19.61	19.61
<i>7b</i> $T = 85 \text{ }^\circ\text{C}$ $a = 46.00$ Hexagonal	10	39.22	39.22
	11	23.07	23.00
	20	19.61	19.61



a)



b)



c)

Fig. 1. — (a) Optical texture of the Φ_{ob} phase of 7a (25 °C on cooling); (b) Optical texture of the Φ_h phase of 7b (89 °C on cooling); (c) Optical texture of the Φ_{ob} phase of 7b (50 °C on cooling).

The three observed rings in the low temperature mesophase of *7b* do not allow an unambiguous assignment of the lattice and the isomorphism of this phase with that of *7a* cannot be excluded. If we compare the lattice constants of the two compounds we remark that *a* increases with the number of carbon atoms of the aliphatic chains while *b* remains nearly constant. The increment of *a* per methylene is $\approx 0.9 \text{ \AA}$. Therefore it is reasonable to suppose that this mesophase has a lamellar structure with *a* equal to the thickness of the lamellae. In each lamella molecules form columns which are equally spaced by $\approx 23 \text{ \AA}$ in an oblique 2D lattice. This structure has some similarity to that of the mesophase observed with a charge transfer compound [4], but in this last case the mean distance between two columns is not as well defined as in the phasmidic phase.

In order to explain such a difference in the behaviour of the two mesogenic species, we can argue that the distance between two columns is not determined by the same interactions : in the case of the charge transfer complex, the width of a column takes into account the size of the two cores forming the complex i.e. 2, 6, 2', 6'-tetra-aryl 4,4'-bis-thiapyranylidene (DIPS) + TCNQ, while in the phasmids the six chains which are in threes at each end of the molecule have a kind of splay configuration near the core (Fig. 2a), becoming parallel at the paraffinic interface. This configuration determines the distance between two columns. Therefore we understand that the cores are more or less disordered, whereas they are regularly stacked, at least for DIPS, in the charge transfer complex.

Assuming a specific gravity of 1 g/cm^3 we can estimate the mean area per paraffinic chain : it is 26 \AA^2 for *7b* and 28 \AA^2 for *7a* while it reaches 37.5 \AA^2 in the case of the charge transfer complex (the minimum value in a crystalline paraffine is $\approx 20 \text{ \AA}^2$).

The hexagonal symmetry of the high temperature mesophase in *7b* is rather unexpected. We should note that a specific gravity of 1 g/cm^3 and a mean core-to-core distance of 4.5 \AA would imply three molecules per unit-cell which consequently must be put on a two-fold axis. Figure 2b gives only a mean image of the high temperature phasmidic phase of *7b*. In fact we can assume an organization similar to the normal hexagonal phases observed in lyotropic systems while the thermotropic columnar D phases are similar to the inverted hexagonal phases. The first lyotropic phases correspond to cylinders with a paraffinic core surrounded by water, whereas in the second type the core of each cylinder contains water surrounded by the amphiphilic molecules [5]. A model of Φ_h phase in which the aromatic cores are surrounded by the paraffinic chains will imply three cores per 5 \AA column length ; such an organization seems unlikely, unless phasmids form clusters of three molecules.

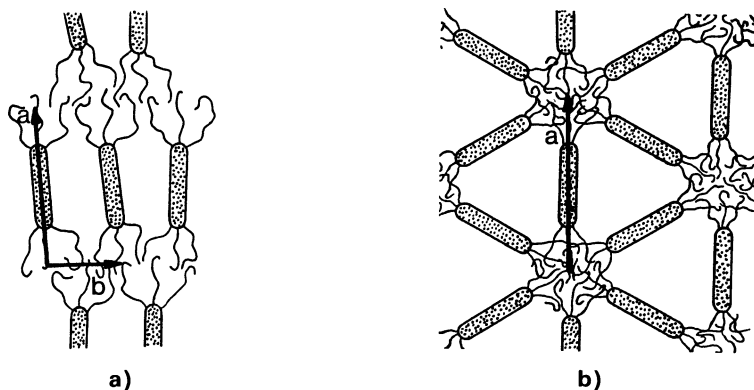


Fig. 2. — Schematic representation of a section perpendicular to the column axis in the two phasmidic phases : (a) Φ_{ob} ; (b) Φ_h . : a phasmid.

Anyway, whatever the model should be, the values of the lattice constants in the two phasmidic phases imply necessarily a huge positional and orientational disorder of the cores. Therefore the discrimination between the two kinds of hexagonal phasmidic phase — analogous to the normal and inverted hexagonal lyotropic phases — is not obvious in the present state of our knowledge, and further investigations must be made to test our model.

5. Conclusion.

Some rod-like (6) and lath-shaped (7) mesogens with more than two end chains were previously known, but their mesophases were those of classical liquid crystals, i.e. smectic and nematic phases. In phasmids, the rod-like core and half-disk ends give mesophases structurally different from those consisting of disk-like or rod-like molecules, such an intermediate state between columnar and lamellar phases has been proposed by Billard [8].

The presence of an hexagonal high temperature phase suggests a similarity with lyotropic mesophases. The number of paraffinic chains for a given core size plays here a role similar to that of the mean area per polar head in a lyotropic system.

Moreover, although no nematogenic phasmid has been yet obtained, this new class of liquid crystal consisting of hybrid rod-like and half-disk-like molecules, seems to be a good candidate for the search for a thermotropic biaxial nematic [9]. Other phasmids are derivatives of 1,4-benzene dicarboxylic and *trans*-1,4-cyclohexanedicarboxylic acids (symmetrical 4-(3', 4', 5'-trialkoxybenzoyloxy) phenyl esters). They too display such a mesomorphism and their study is in progress.

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