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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) phasmidiques 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 ø, the initial of the Greek root Φάσμινδικ) 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'-triheptyloxybenzoate)]-aniline 7a and terephthal-bis-[4-(3', 4', 5'-tridodecyloxybenzoate)]-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 (H₂, 5 % Pd-C, EtOAc)
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.

Compounds 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): 1730, 1620, 1590, 1500, 1340, 1225, 1205, 1180, 1130, 1120 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 (°).

<table>
<thead>
<tr>
<th></th>
<th>K</th>
<th>Φob</th>
<th>Φh</th>
<th>I</th>
</tr>
</thead>
<tbody>
<tr>
<td>7a</td>
<td>●</td>
<td>80</td>
<td>82</td>
<td>—</td>
</tr>
<tr>
<td>7b</td>
<td>●</td>
<td>70</td>
<td>81.5</td>
<td>92</td>
</tr>
</tbody>
</table>

(*) K: crystal; Φob: phasmidic phase with an oblique 2D lattice; Φh: 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→Φob: 15.6 kcal.mol⁻¹; ΔH_Φob→Φh: 0.06 kcal.mol⁻¹; ΔH_Φh→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 $\Phi_{ob}$ phase and those of the $\Phi_h$ 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 $\frac{2 \sin \theta}{\lambda} = \frac{1}{4.5} \text{ Å}^{-1}$ where $2 \theta$ 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>
<thead>
<tr>
<th>Symmetry and lattice constants</th>
<th>Indices</th>
<th>Observed lattice spacings (Å)</th>
<th>Calculated lattice spacings (Å)</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>7a</strong> $T = 81^\circ C$</td>
<td>10</td>
<td>33.94</td>
<td>33.94</td>
</tr>
<tr>
<td>$a = 34.06$ Å</td>
<td>01</td>
<td>22.34</td>
<td>22.34</td>
</tr>
<tr>
<td>$b = 22.42$ Å</td>
<td>11</td>
<td>18.29</td>
<td>17.99</td>
</tr>
<tr>
<td>$\beta = 94.7^\circ$ Oblique</td>
<td>20</td>
<td>16.97</td>
<td>16.97</td>
</tr>
<tr>
<td></td>
<td>21</td>
<td>12.79</td>
<td>13.01</td>
</tr>
<tr>
<td><strong>7b</strong> $T = 75^\circ C$</td>
<td>10</td>
<td>39.22</td>
<td>39.22</td>
</tr>
<tr>
<td>$a = 39.22$</td>
<td>01</td>
<td>22.34</td>
<td>22.34</td>
</tr>
<tr>
<td>$b = 23.00$</td>
<td>11</td>
<td>19.61</td>
<td>19.61</td>
</tr>
<tr>
<td>Oblique ?</td>
<td>20</td>
<td></td>
<td></td>
</tr>
<tr>
<td><strong>7b</strong> $T = 85^\circ C$</td>
<td>10</td>
<td>39.22</td>
<td>39.22</td>
</tr>
<tr>
<td>$a = 46.00$</td>
<td>11</td>
<td>23.07</td>
<td>23.00</td>
</tr>
<tr>
<td>Hexagonal</td>
<td>20</td>
<td>19.61</td>
<td>19.61</td>
</tr>
</tbody>
</table>
Fig. 1. — (a) Optical texture of the $\Phi_{ob}$ phase of $7a$ (25 °C on cooling); (b) Optical texture of the $\Phi_b$ phase of $7b$ (89 °C on cooling); (c) Optical texture of the $\Phi_{ob}$ 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 \( \approx 0.9 \, \text{Å} \). 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 \( \approx 23 \, \text{Å} \) 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 Å\(^2\) for 7b and 28 Å\(^2\) for 7a while it reaches 37.5 Å\(^2\) in the case of the charge transfer complex (the minimum value in a crystalline paraffine is \( \approx 20 \, \text{Å}^2 \)).

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 Å 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 \( \Phi_h \) phase in which the aromatic cores are surrounded by the paraffinic chains will imply three cores per 5 Å 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) \( \Phi_{ob} \); (b) \( \Phi_h \). : 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'-trialkoxycarbonyloxy) phenyl esters). They too display such a mesomorphism and their study is in progress.

Acknowledgments.

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References

    b) DESTRADE, C., FOUCHER, P., GASPAROUX, H., NGUYEN HUU TINH, LEVELUT, A. M., MALTHÈTE, J.,
      L-499.