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# **Tubular Mesophases: a Structural Analysis**

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The hitherto doubtful tubular mesomorphism of **1a** has been confirmed by X-ray diffraction experiments on a mixture of the mesophase of **1a** with the mesophase of its Br-substituted analogue **1b**.

Thermotropic mesogenic materials are interesting because of their anisotropic physical properties. In order to obtain mesogens for specific use such as one-dimensional arrays of metal atoms or ions embedded in a disordered organic matrix, attention has recently been focused on ionic and non-ionic columnar metallomesogens.<sup>1</sup> A few years ago, we contemplated the possibility of building up molecular channels in a columnar mesomorphic form.<sup>2.3</sup> At the time, the existence of a hexagonal tubular mesophase for a benzoyl-substituted aza macrocycle such as **1a** was proposed but not unambiguously established: the X-ray diffraction patterns showed only one sharp ring in such a way that the possibility of lamellar order was not completely ruled out. Nevertheless, it has recently been reported that macrocycles, such as cinnamoyl-substi-



tuted aza crown derivatives, can form columnar aggregates by photocycloaddition in a poor solvent.<sup>4</sup> On the other hand, a columnar mesomorphic order can be induced by complexation of transition metal ions with non-mesogenic aza macrocycles.<sup>5,6</sup>

More recently, Idziack et al.7 have suggested, from energyminimization calculations, that an isolated molecule of mesogenic hexacyclen derivative 1a had an elongated shape rather than a disc-like one, and consequently that a smectic, rather than a columnar model, was slightly preferred. The same authors have examined similar mesogenic macrocycles bearing one bromine, 2a or two chlorine, 2b atoms, that show a clearly identified hexagonal columnar mesophase.8 In these novel systems, six halogenated 4-(dodecyloxy)cinnamoyl groups are grafted onto the aza crown instead of the six 4-(dodecyloxy)benzoyl groups in **1a**, and energy minimization calculations led to similar energies for the conformation in which the hydrocarbon tails are paired affording a plane ring with threefold symmetry and the conformation in which the tails are arranged in two bundles of three giving an almost rod-like molecule. However, some points are still to be clarified about this kind of hexagonal columnar order.

The shape of a mesogen is not always clearly connected with the symmetry of the corresponding mesophase. For example, linear molecules such as phasmids<sup>9–11</sup> can present both smectic and columnar mesophases with the same rod-like polycyclic core, depending on the number, length and position of grafted chains. Consequently, the mesogenic macrocycle **1a** could gather in a columnar phase in spite of a preferred elongated conformation.<sup>7</sup> On the other hand, the fact that macrocycles **2a** and **2b** exhibit columnar mesomorphism does not entail inevitably that molecules of compound **1a**, which have benzoyl tails, are organized in a columnar order, even if they adopt the same type of conformation.

A second point of interest is the role of heavy atoms on the diffraction patterns since they can act as a label but can also modify the molecular motions.

We have now synthesized the 3-bromobenzoyl derivative of **1a**, **1b**, characterized its mesomorphism and studied X-ray patterns of a mixture **1a/b**. The macrocyclic polyamide **1b** was prepared as previously described<sup>2.3</sup> by reaction of hexacyclen (Fluka AG) with 6 equiv. of 3-bromo-4-(dodecyloxy)benzoyl chloride in dry dimethylacetamide in the presence of 6 equiv. of *p*-dimethylamino-pyridine. 3-Bromo-4-(dodecyloxy)benzoyl acid was obtained according to Kelly<sup>12</sup> (m.p. 107.5 °C. lit.<sup>12</sup> 108 °C). The crude brominated macrocyclic polyamide **1b** was purified by TLC (silica gel, eluent: CH<sub>2</sub>Cl<sub>2</sub>–10% methanol) and recrystallized from methanol–diethyl ether (40% yield; m.p. 164.5 °C, monotropic mesophase above 133 °C).†

Based upon a comparison with the results obtained on **1a**, **2a** and **2b**, we were able to derive the position of the halogens in each system and to estimate the influence of the substitution of heavy atoms upon the thermal motion in the mesophase.



**Fig. 1** Contribution of the molecular form factor F in electron units versus the scattering vector  $q = (4\pi \sin \theta)/\lambda$  (Å<sup>-1</sup>) ( $\lambda$ : X-ray wavelength; q: Bragg angle). Empty circles: contribution of a core without halogen; full circles: contribution of halogen atoms. Curve (a) corresponds to 1a and 1b, curve (b) to 2a and 2b.<sup>8</sup> The positions of successive diffraction rings are indicated by vertical bars sitting above the horizontal axis for (a) and below for (b).

X-Ray diffraction experiments were done on aligned samples with a monochromatic Cu-K $\alpha$  X-ray beam. Patterns are recorded on photographic films; the sample is aligned by stretching on the wall of a Lindeman glass tube. The temperature of the sample is maintained within  $\pm 0.25$  K.

Two mixtures have been prepared by dissolving **1a** and **1b** in CH<sub>2</sub>Cl<sub>2</sub>. After evaporation to dryness, a mesophase was observed, respectively above 137 °C for 74.9% **1a**, 25.1% **1b** (I) and 136.5 °C for 57.8% **1a**, 42.2% **1b** (II). Mixture I was stable enough to be studied by X-ray diffraction; the patterns show one intense sharp ring corresponding to a lattice spacing  $d_0$ : 32 Å and three very weak rings corresponding to lattice spacings  $d_0/2$ ,  $d_0/\sqrt{7}$  and  $d_0/3$ . The intensity of the first ring is several orders of magnitude higher than that of the three other rings. With mixture II, recrystallization occurred during the investigation.

Because of their entire miscibility, the mesophases of both **1a** and **1b** have the same hexagonal columnar structure. The absence of 110 lines  $(d_o/\sqrt{3})$  in the X-ray pattern can be easily explained by looking at the form factor of a molecule. In Fig. 1 the diffracted amplitudes coming from the core of the molecule (*i.e.* the aza macrocycle with the six benzoyl groups) and from the bromines are calculated assuming a cyclindrical repartition of the electronic density and using the molecular measurements reported in ref. 3. It appears that for the scattering vector corresponding to 110, the diffracted amplitude issued from the bromine atom is cancelled by that of the core, while the two terms have the same sign in the vicinity of 210, 300 peaks. Conversely, the bromine labelling enhanced the 110 and 200 peaks when grafted onto **2a**. Another

<sup>&</sup>lt;sup>†</sup> The thermal and optical properties of **1b** and of the mixtures **1a/b** have been studied by differential microcalorimetry and with a polarizing microscope equipped with a variable temperature stage. <sup>1</sup>H NMR [(CDCl<sub>3</sub>), 200 MHz, 293 K]; δ 0.86 (18H, t, CH<sub>3</sub>), 1.25 (108H, m, CH<sub>2</sub>), 1.81 (12H, m, CH<sub>2</sub>-CH<sub>2</sub>O), 3.68 (24H, broad m, CH<sub>2</sub>-N), 4.02 (12H, t, CH<sub>2</sub>O), 6.82 (6H, d, ArH), 7.33 (12H, broad m, ArH).

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important point is the Debye-Waller damping. It is clear from Fig. 1 that the core contribution to the 110 line would rise to a measurable intensity for the mesophase of 1a, unless the thermal motions are of large amplitude. Since the high order 200 and 210 peaks are detected when brominated mesogen is added, we can assert that the thermal motions are less important in the brominated mixture than in pure 1a. Moreover, looking at results of ref. 8, it appears that 2a (with one Br) and 2b (with two Cl) present the same form factor, but the diffracted intensity of 110 and 200 lines is higher for the latter, which confirms that the heavy atoms hindered thermal molecular motions.

In conclusion, we have shown that the substitution of one hydrogen of the benzoyl groups of **1a** by a halogen atom offers a good labelling method for X-ray diffraction structural studies of the mesomorphic order. The disc-like shape of the molecules is asserted and the size of the molecule fits with that estimated from models. Moreover, the introduction of heavy atoms on the cyclic molecules enhanced the stiffness of the column, which is especially low for simple organic tubular mesophases.

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