

Hexagonal Order in Some Mesophases of Hexacyclen Derivatives

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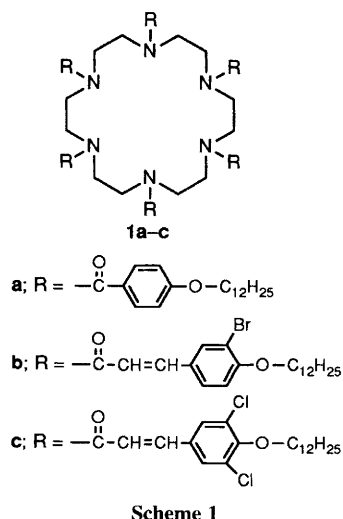
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High-resolution X-ray diffraction measurements on the hexacyclen derivatives **1a–c** have provided the first direct experimental evidence of hexagonal order in a hexacyclen mesophase.

The liquid-crystalline structure of hexacyclen derivatives has been previously studied by X-ray diffraction (XRD) using low resolution techniques.^{1,2} On the basis of these measurements, as well as optical microscopy, the structure of **1a** (Scheme 1) in its liquid-crystalline phase was suggested to be hexagonal-tubular.¹ However, higher-order characteristic hexagonal peaks have never been observed in any hexacyclen derivative, even in high resolution powder XRD experiments.³ More-

over, computer simulations³ revealed that the cores of the molecules tend to collapse and that they prefer to take on a rod-like conformation when in the gas phase. These results suggested a lamellar smectic phase, although a hexagonal columnar structure could not be ruled out.³ We now have conclusive evidence of hexagonal columnar order in two new hexacyclen derivatives.

We have performed high resolution powder XRD on two



new compounds: **1b** and **c** (Scheme 1), obtained by acylation of commercially available hexacyclen (Fluka) with the corresponding cinnamic acid chlorides,[†] as described for **1a**.¹⁻³ NMR, IR and elemental analysis data were in agreement with the assigned structures.⁴ The X-ray experiments were performed at the National Synchrotron Light Source beamline X9A using a sagittally focusing double silicon crystal monochromator and a flat germanium analyser to achieve a resolution of 0.0009 \AA^{-1} . The samples were loaded into 0.8 mm capillary tubes that were placed into an oven with better than 0.4°C temperature control. The samples were rotated at 140 rpm to ensure a good powder average. The samples were heated from room temperature directly to the mesophase and were moved every few hours to minimize the effects of radiation damage.

Results of molecular mechanics calculations on isolated molecules proved inconclusive. Three conformations of each molecule (**1a-c**) were modelled using the mechanics package POLYGRAF: one in which the tails are oriented radially, a second in which the tails pair together affording approximate threefold symmetry, and a third in which the tails group together in two arrays of three so that the resulting shape is approximately linear. These conformations were then subject to energy minimization using the conjugate gradient method in the Dreiding force field.⁵ It was found that for **1b** and **c**, the linear and threefold symmetric conformations had similar energies, unlike the previously studied³ **1a** which exhibited a preference for a linear conformation. This might indicate that **1b** and **c** would be more likely to form a hexagonal phase than **1a**.

The powder X-ray diffractograms are presented in Fig. 1. To ensure consistency, we repeated the measurements made on **1a**³ with this experimental setup. As can be seen from Fig. 1(a), for **1a** only the (100) diffraction peak at 0.1883 \AA^{-1} can be seen. Neither the (200) nor the (110) can be distinguished. The existence of the latter (*i.e.* a $\sqrt{3}:1$ ratio of the peak positions) is crucial for the identification of hexagonal order.

Fig. 1(b) shows the diffractogram for **1b**. A strong (100) peak is clearly evident at 0.190 \AA^{-1} ; a weaker (110) peak at

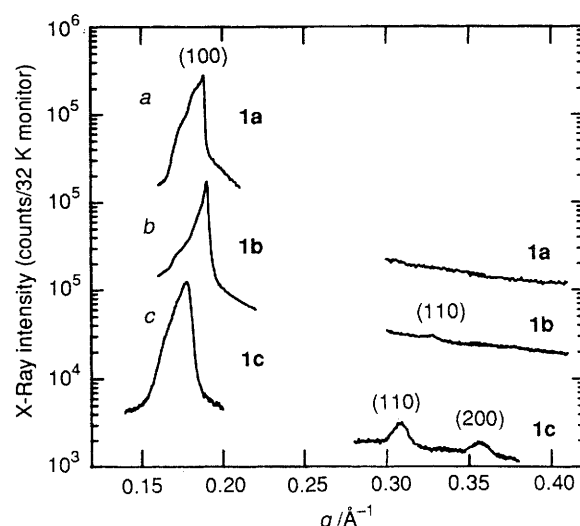


Fig. 1 High resolution X-ray diffractograms for **1a**, **b** and **c**. We employ the convention $q \equiv 2\pi/d = (4\pi/\lambda) \sin\theta$. The point spacing is 0.00005 \AA^{-1} and each point was counted for approximately 24 s. The asymmetric line shape visible in the (100) peaks is due to the focusing geometry of the diffractometer. The (110) peak in **1b** and the (110) and (200) peaks in **1c** are clearly visible.

0.328 \AA^{-1} is also visible, demonstrating the existence of hexagonal order. Even clearer results can be seen for **1c** in Fig. 1(c): strong (100), (110) and (200) peaks, at 0.178 \AA^{-1} , 0.3085 \AA^{-1} , and 0.3575 \AA^{-1} , respectively, are present.

These measurements demonstrate that **1b** and **c** form hexagonal columnar mesophases. This is the first conclusive experimental evidence of hexagonal columnar order in any hexacyclen mesophase. In our view, it is still an open question whether **1a** and other hexacyclen derivatives^{2,6} necessarily form columnar mesophases. It is possible that all such compounds form columnar mesophases, and that the differences in higher order XRD peak intensities represent quantitative differences in the extent of column undulation or intramolecular vibration.^{1,3} Alternatively, as seen in phasimide⁷ compounds, small differences in molecular structure may result in qualitative changes in mesophase symmetry, from hexagonal to lamellar.

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[†] Cinnamic acids were synthesized either by bromination of 4-dodecyloxybenzaldehyde and bromine in glacial acetic acid, or by chlorination of 4-dodecyloxybenzaldehyde in freshly distilled sulfurylchloride. 4-Dodecyloxybenzaldehyde was obtained by etherification of 4-hydroxybenzaldehyde with dodecylbromide in acetone in the presence of powdered potassium carbonate. The acids were then converted to the acid chlorides by means of oxalylchloride in dry benzene. A detailed description will be given elsewhere.