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Liquid Crystals Based on Shape-Persistent Macrocyclic Mesogens[†]

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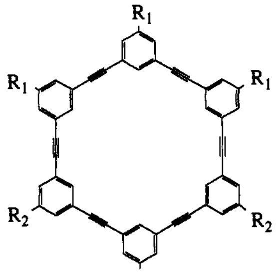
Since first reported more than a decade ago,[1] discotic liquid crystals have attracted considerable attention. A variety of organic compounds have been shown to exhibit discotic phases.[2] Among these are derivatives of benzene, triphenylene, truxene, cyclohexane, porphyrins, phthalocyanines, calixarenes, and hexacyclen. Columnar mesophases based on macrocyclic compounds[3,4] are particularly interesting because of their potential to self-organize into supramolecular channels that could be processed into macroscopically aligned nanotubules. This possibility prompted us to search for discotic liquid crystals based on phenylacetylene macrocycles (PAMs) such as **1**–**4**. The relative rigidity and large internal diameter (the hydrogen to hydrogen distance across the ring interior is ca. 8 Å) of PAMs makes them candidates for mesogens of tubular liquid crystal phases. Unlike hexacyclen derivatives in which the macrocycle can collapse due to its inherent flexibility,[5] columnar phases based on PAMs should produce materials with well-defined and noncollapsible internal channels. Moreover, the possibility of adding functionalization to the *endo* positions of the PAM ring might allow the channel's internal environment to be modified easily. Consequently, it may be possible to tailor the transport properties of oriented thin films of such materials over a broad spectrum.



1 a: $R_1 = R_2 = COO^nC_4H_9$
b: $R_1 = R_2 = COO^nC_7H_{15}$
c: $R_1 = R_2 = COO^nC_8H_{17}$
d: $R_1 = R_2 = COO^nC_{16}H_{33}$
2 a: $R_1 = R_2 = O^nC_4H_9$
b: $R_1 = R_2 = O^nC_6H_{13}$
c: $R_1 = R_2 = O^nC_7H_{15}$
3 a: $R_1 = R_2 = OCO^nC_4H_9$
b: $R_1 = R_2 = OCO^nC_7H_{15}$
4: $R_1 = COO^nC_6H_{13}$,
$R_2 = O^nC_6H_{13}$

Table 1.[a] Phase Transition Temperatures and Heats of Transition for PAMs **2c**, **3b**, and **4** on Cooling from the Isotopic Melt

PAM	decreasing temperature $\longrightarrow$
2 c	isotropic $\xrightarrow[192]{-0.32}$ D_n $\xrightarrow[168]{-56.8}$ crystalline I $\xrightarrow[144]{-11.2}$ crystalline II
3 b	isotropic $\xrightarrow[241]{-0.51}$ D_n $\xrightarrow[121]{-13.3}$ crystalline I $\xrightarrow[104]{-0.71}$ crystalline II
4	isotropic $\xrightarrow[202]{-0.14}$ D_n $\xrightarrow[130]{-2.4}$ D_{hd} $\xrightarrow[103]{-5.2}$ crystalline

[a] The enthalpy change (kJ/mol) is shown above the arrow, and the transition temperature (°C) is shown below the arrow.

We have demonstrated the ability to synthesize PAMs that are site-specifically functionalized and geometrically controlled,[6] and we have shown that these molecules can self-associate in nonpolar organic solvents, apparently driven by π-stacking interactions.[7] It was found that PAMs with ester functionalities like **1a** have the strongest association constant (K_{assoc} = 60 M^{-1} at 20 °C in $CDCl_3$) and PAMs with segregated ester and ether functionalities like **4** show weaker self-association (K_{assoc} = 26 M^{-1} at 20 °C in $CDCl_3$), while **2a** and **3a**, which had ether and alkanoate functionalities, respectively, did not show any evidence of self-association under the same conditions.[8] Therefore, it is natural to anticipate that PAMs with ester functional groups might be the best choice for discotic mesogens because of their strong π-stacking tendencies. Although DSC and optical microscopy (OM) showed evidence of ordered fluid phases, there was no clearing point up to 300 °C for **1b** or **1c**. Even when the number of carbons in the side chain increased to 16 (**1d**), no clearing point was observed. We presume that the attractive π-stacking forces are so strong in the absence of solvent that the molecules cannot disorder into isotropic liquid, even at elevated temperatures. The highly viscous nature of these phases make them difficult to study.

In contrast to **1a-d**, PAMs **2c** and **3b** exhibit both ordered fluid and isotropic phases. When these compounds are subjected to DSC analyses, each shows three reversible phase transitions. These transitions display considerable temperature hysteresis, presumably due to their high melt viscosities. On cooling the isotropic melts, each compound first undergoes a transition with a small enthalpy change (Table 1). Below the temperature of this first transition, these compounds are visibly flowing, birefringent fluids that exhibit *schlieren* textures. Powder X-ray diffraction (XRD, Cu K$_\alpha$ radiation) scans recorded in this phase show only broad and diffuse peaks. Thus, both **2c** and **3b** self-organize into the discotic nematic phase, D$_n$, upon cooling from the isotropic melt. The wide temperature range (>100 °C) over which the D$_n$ phase is stable for **3b** is striking (Table 1).

On further cooling, each of **2c** and **3b** undergoes a second phase transition (Table 1). Below this transition, neither compound is easily deformed when sheared, characteristic of a crystalline solid or highly viscous LC phase. When viewed between crossed polarizers, **2c** shows a birefringent, needle-like morphology, while **3b** gives a birefringent fan-like texture. Powder XRD scans on **2c** in this phase reveal several relatively sharp Bragg reflections between $2\theta = 5°$ and $2\theta = 25°$ characteristic of a high

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degree of order. Therefore, we believe that **2c** crystallizes directly from the nematic state. The large enthalpy associated with this transition is consistent with this assignment. In contrast, XRD of **3b** just below the nematic phase shows Bragg reflections in the 2θ range 3–10°, with diffuse scattering at higher angles on which a few broad and weak reflections are superimposed. The exact nature of this phase is not known at this time although it is probably best characterized as crystalline. On further cooling, each of **2c** and **3b** undergoes a third phase transition (Table 1). The transition is rather sharp for **2c** and is probably associated with a second crystalline phase. In the case of **3b**, however, the transition is broad and is accompanied by a slight sharpening of the high-angle peaks in the powder XRD scan. The nature of this phase has not yet been determined.

The DSC profile of **2b** is very similar to that of **2c**. Three phase transitions were observed. On cooling, the first phase transition occurs at 233 °C with $\Delta H = -0.18$ kJ/mol, the second at 216 °C with $\Delta H = -48.9$ kJ/mol, and the third at 183 °C with $\Delta H = -13.7$ kJ/mol. The high temperatures associated with these phase transitions preclude detailed microscopic or X-ray studies because of decomposition.

PAM **4** exhibits monotropic behavior. On heating, the DSC trace of **4** is complex regardless of the sample's history. However, on cooling from the isotropic liquid state, it showed three well-defined and reproducible phase transitions. The first phase transition occurs at 202 °C and has an enthalpy change of −0.14 kJ/mol. As with **2c** and **3b**, PAM **4** displays a *schlieren* texture below this transition (see Figure 1) and the XRD scan of this phase contains only diffuse peaks, thus indicating the D_n phase. Upon further cooling to 130 °C, a second phase transition is observed with an enthalpy change of −2.43 kJ/mol. Slow cooling from the nematic phase results in the growth of a pattern with finger-like contours (see Figure 1). Similar patterns have been seen in other columnar LC phases.[9] Powder XRD scans at 120 °C show one diffuse peak having d spacing of ca. 5 Å and three sharper peaks with d spacings of 24.0, 13.8, and 11.9 Å. The ratios for these d spacings are 1:0.575:0.496, in good agreement with that expected for the hexagonal lattice (i.e., 1:0.577:0.5). A lattice constant of $a = 27.7$ Å is obtained, consistent with the molecular dimension of **4**.[10] The absence of sharp Bragg reflections in the range 3.5–4.6 Å indicates periodic ordering in only two dimensions, suggesting that the phase is hexagonal with liquid-like fluctuations along the column direction (D_{hd}). It should be noted, however, that the (110) and (200) peaks have relative intensities that are larger than those of typical D_{hd} phases. This behavior might be a consequence of the unusual packing in tubular mesophases and is consistent with preliminary structure factor calculations on a simple model.[10] At 103 °C, **4** experiences another phase transition with a corresponding enthalpy change of −5.2 kJ/mol. The OM texture shows little change through this transition. However, a very prominent peak at 3.8 Å appears in the XRD scan. This observation suggests that, below this transition, the mesogens stack periodically along the columnar axis as in a D_0 phase.

These findings raise intriguing questions about the apparent accommodation of a high fraction of free volume in these phases.[11] In light of the idea of tubular mesophases, it is of interest to understand the spatial distribution of this free volume and to determine the factors which lead to stabilization of ordered phases with large fractions of free volume. Further investigations along these lines are in progress.

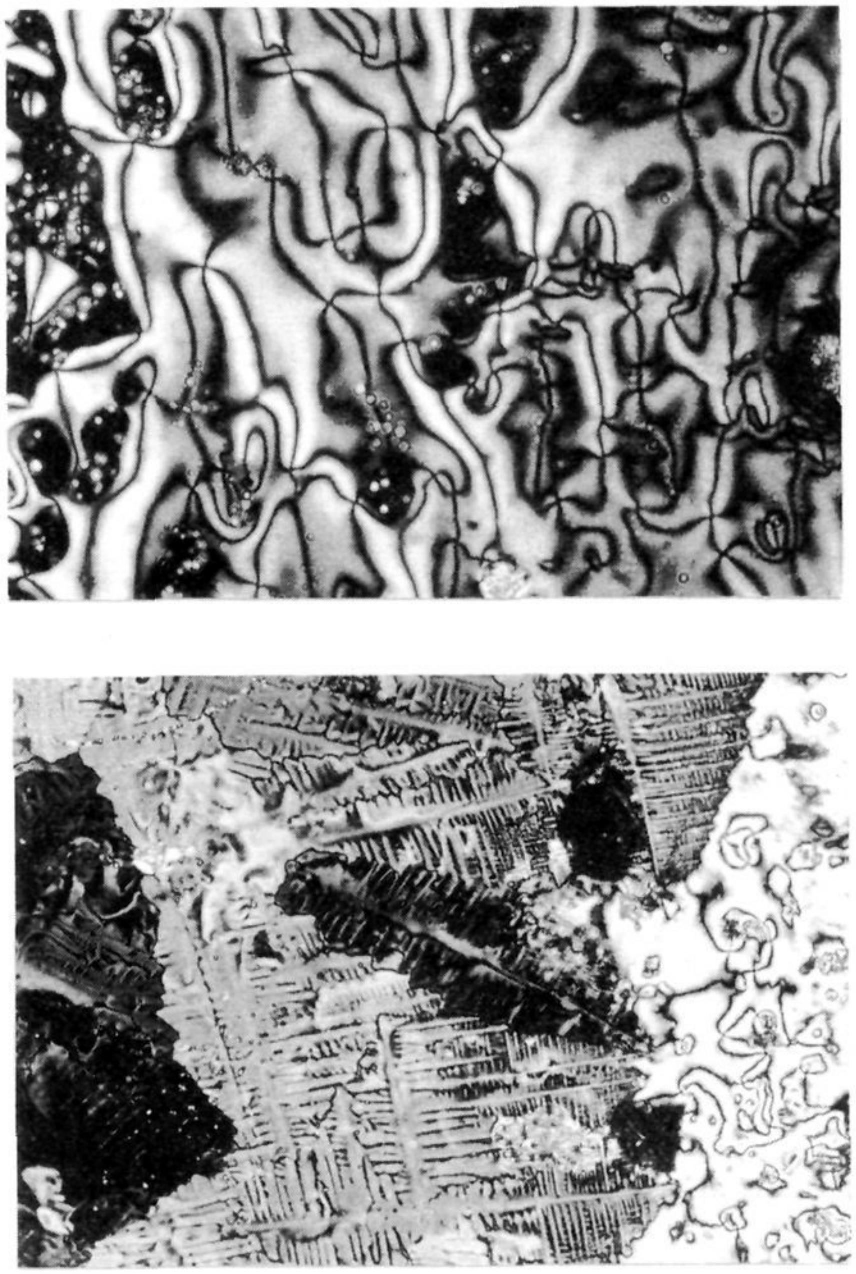

Figure 1. Optical micrographs between crossed polarizers of PAM **4**. The top micrograph was taken at 170 °C in the nematic phase. The bottom micrograph shows the growth of the columnar phase from the nematic melt (120 °C).

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Supplementary Material Available: Spectroscopic and analytical data for compounds **1–4**, DSC traces of **2b,c**, **3b**, and **4**, X-ray diffraction data of **2c**, **3b**, and **4**, and molecular model of **4** (9 pages). This material is contained in many libraries on microfiche, immediately follows this article in the microfilm version of the journal, and can be ordered from the ACS; see any current masthead page for ordering information.

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(11) Although it is conceivable that the void space of the macrocycles is occupied by small molecules (e.g., residual solvent), we have not obtained any analytical data to support this notion.