The triangular cylinder phase – a new mode of self assembly in liquid crystalline soft matter

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Supporting Information

1. DSC Investigations

![DSC heating and cooling curves](image)

**Fig. S1.** DSC heating (a) and cooling (b) curves (10 K/min; $T$ in °C).
2. Additional X-ray data

2.1 Aligned sample of 1

Figure S2. Diffraction pattern for an aligned sample of compound 1 with the columns parallel to the horizontal sample–air interface at 60 °C (2D detector HI-STAR, Siemens, using Ni-filtered CuK\textsubscript{α} radiation, X-ray beam parallel to the sample-air interface): a) full scattering range, b) small angle region of the pattern showing the hexagonal reciprocal lattices for the predominant orientation of the columns (green lines) and for a minor part of the sample (black lines), the 11 reflection observed in the powder patterns is too weak to be found in the 2D patterns.

2.2 Synchrotron X-ray diffraction and electron density reconstruction

High-resolution small-angle powder diffraction experiments were recorded at Station MPW6.2 of the synchrotron at Daresbury, U.K. Samples were held in evacuated 1 mm capillaries. A modified Linkam hot stage was used, with a hole for the capillary drilled through the silver heating block and with mica windows attached to it on each side. A quadrant RAPID2 detector for small angles, and a curved RAPID2 detector for wide angles were used. Q calibration and linearization were verified using several orders of layer reflections from a series of \textit{n}-alkanes. Diffraction intensities were Lorentz and multiplicity corrected. Fourier reconstruction of the electron density was carried out using the general formula:

\[ \rho(xyz) = \Sigma_{hkl} F(hkl) \exp[2\pi i(hx + ky + lz)] = \Sigma_{hkl} \sqrt{I(hkl)} \exp[2\pi i(hx + ky + lz) + i\phi(hkl)]. \]
Here $\phi(hkl)$ is the phase of the $(hkl)$ reflection and $I$ is the corrected intensity. For columnar phases (2-dimensional order) the relation

$$\rho(xy) = \sum_{hk} F(hk) \exp[2\pi i(hx+ky)] = \sum_{hk} \sqrt{I(hk)} \exp[2\pi i(hx+ky) + i\phi(hk)]$$

was used.

Table S1. Indices, $d$-spacings ($d_{\text{obs}}$: experimental; $d_{\text{calc}}$: calculated), intensities and phases of reflections used to reconstruct electron densities of the Col$_{\text{hex}}$ phase at $T = 60$ °C.

<table>
<thead>
<tr>
<th>$(hk)$</th>
<th>$d_{\text{obs.}}$ (Å)</th>
<th>$d_{\text{cal.}}$ (Å)</th>
<th>$I(hk)$</th>
<th>$\phi(hk)$</th>
</tr>
</thead>
<tbody>
<tr>
<td>(10)</td>
<td>41.5</td>
<td>41.5</td>
<td>100.0</td>
<td>$\pi$</td>
</tr>
<tr>
<td>(11)</td>
<td>24.1</td>
<td>24.0</td>
<td>0.1</td>
<td>0</td>
</tr>
<tr>
<td>(20)</td>
<td>20.9</td>
<td>20.8</td>
<td>3.0</td>
<td>$\pi$</td>
</tr>
</tbody>
</table>

$a = 47.9$ Å

3. Number of molecules per unit cell

a) Calculation based on density
- Unit cell volume obtained from the lattice parameter $a_{\text{hex}} = 47.9$ Å, and assuming a height of $c = 4.5$ Å corresponding to the average stacking distance along the columns derived from the maximum of the outer diffuse X-ray scattering: $V_{\text{cell}} = 8942$ Å$^3$.
- Molar mass $M = 820$ g/mol.
- Assumed density $\rho = 1.0$ g/ml.
- Number of molecules in a unit cell: $n_{\text{cell}} = (a^2 c \sqrt{3} N_A \rho) / 2M = 6.6$.

b) Calculation based on volume increments
- Molecular volume in the isotropic liquid: $V_{\text{mol,ls}} = 1491$ Å$^3$ (calculated using the ratio of the average packing coefficient in the crystal $k = 0.7$ and in the isotropic liquid $k = 0.55$ according to Kitaigorodski, A. I, “Molekülkristalle”, Akademieverlag Berlin, 1979).
- Number of molecules in a unit cell with crystal-like density: $n_{\text{cell,cr}} = V_{\text{cell}} / V_{\text{mol,cr}} = 7.6$; with liquid-like density: $n_{\text{cell,is}} = V_{\text{cell}} / V_{\text{mol,ls}} = 6.0$; in the LC phase estimated as the intermediate between that in the crystalline and the liquid phase: $n_{\text{cell,LC}} = 6.8$. 
c) **Average number**
Average value of both calculations: $n_{\text{cell,LC}} = (6.6 + 6.8) / 2 = 6.7$.

4. **Molecular dynamics simulation**

Annealing dynamics runs were carried out using the Universal Force Field (Material Studio, Accelrys). The structure in Figure 2e was obtained with six molecules in a rhombic prism box with the base equal to the 2-d unit cell with $a = 47.9\AA$ and a height of 0.45nm, with 3d periodic boundary conditions. 30 temperature cycles of NVT dynamics were run between 300 and 700 K, with a total annealing time of 30 ps.

5. **Analytical Data**

$^1$H NMR (CDCl$_3$, J/Hz, 400 MHz) $\delta = 7.54$-$7.45$ (m, 4 H, Ar-H), 7.33 (d, $^3\!J$(H,H) = 7.9, 1 H, Ar-H), 7.19 (dd, $^3\!J$(H,H) = 7.9, $^4\!J$(H,H) = 1.7, 1 H, Ar-H), 7.14 (d, $^4\!J$(H,H) = 1.7, 1 H, Ar-H), 6.99-6.85 (m, 4 H, Ar-H), 6.00 (bs, 1 H, OH), 4.17 (t, $^3\!J$(H,H) = 5.0, 2 H, CH$_2$), 4.08 (s, 2 H, CH$_2$), 4.00-3.96 (m, 4 H, CH$_2$), 3.80 (t, $^3\!J$(H,H) = 5.0, 2 H, CH$_2$), 3.68-3.57 (m, 12 H, CH$_2$), 1.83-1.76 (m, 4 H, CH$_2$), 1.49-1.42 (m, 4 H, CH$_2$), 1.40-1.20 (m, 24 H, CH$_2$), 0.96-0.85 (m, 6 H, CH$_3$).

$^{13}$C NMR (CDCl$_3$, 100 MHz) $\delta = 171.8$, 158.8, 158.1, 155.9, 140.9, 133.1, 130.7, 130.5, 130.4, 129.1, 127.9, 119.6, 114.8, 113.9, 111.6, 71.2, 70.9, 70.6, 70.5, 70.3, 70.2, 69.7, 69.0, 68.4, 68.1, 68.0, 31.9, 31.6, 29.7, 29.7, 29.6, 29.6, 29.5, 29.4, 29.3, 26.1, 25.8, 22.7, 22.6, 14.1, 14.1; calculated for C$_{50}$H$_{76}$O$_9$·H$_2$O C 71.56, H 9.37; found C 71.81, H 9.22 %.