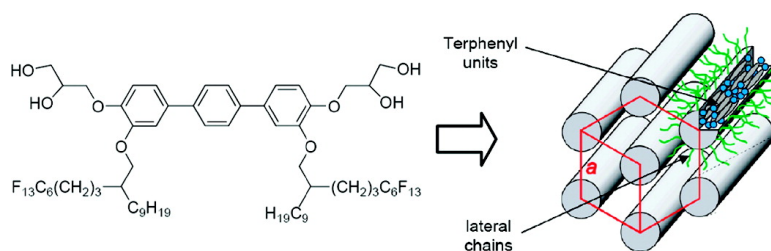


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2D and 3D Ordered Columnar Liquid Crystal Phases by Bundles of Bolaamphiphiles with Swallow-Tail Side Chains

Marko Prehm,[†] Feng Liu,[‡] Xiangbing Zeng,[‡] Goran Ungar,^{*,‡} and Carsten Tschierske^{*,†}

Martin-Luther-University Halle-Wittenberg, Institute of Chemistry, Organic Chemistry, Kurt-Mothes Str. 2, D-06120 Halle, Germany, and Department of Engineering Materials, University of Sheffield, Mappin Street, Sheffield S1 3JD, U.K.

Received July 23, 2008; E-mail: g.ungar@sheffield.ac.uk; carsten.tschierske@chemie.uni-halle.de

Liquid crystalline (LC) self-assembled superstructures combine order and mobility, the features indispensable for their technological applications, as well as being at the basis of life.¹ The discovery that disk-like molecules can organize into LC phases in which the molecules stack up in columns² initiated intense activity in the field of columnar LC phases.³ Especially the overlapping π -systems of aromatic disk-like molecules within the self-assembled columns lead to interesting charge carrier properties which stimulated much research in this field.⁴ Like disk-like molecules, rod-like (calamitic) molecules can also form columnar LC phases if two or three alkyl chains are attached to each end of a rod-like unit.^{5,6} In the columnar LC phases of these polycatenar compounds⁵ and related dumbbell molecules,⁷ the layers of smectic phases are disrupted into stripes which adopt a periodic 2D organization. In these columns the rod-like cores are on average perpendicular or highly tilted to the column long axis (Figure 1b–d). Hence, in none of the known low-molar-mass columnar LC phases is the mesogen long axis parallel to the column axis (however for polymers, see below). MC/MD simulations by Frenkel et al. using hard spherocylinders are ambiguous about the existence of such a phase, the large system favoring a 3D “crystal”.⁸

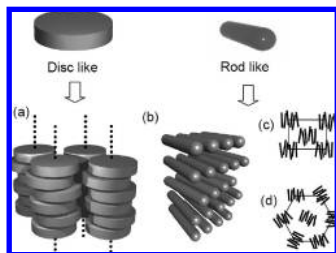


Figure 1. Columnar LC phases formed by molecules incorporating anisometric units: (a) disk-like molecules and (b–d) polycatenar rod-like molecules; in (c) and (d) the view is along the columns.

Here we report two new modes of organization in columnar LC phases where rod-like mesogenic units do lie parallel to the column axis. This is achieved by lateral attachment of two branched (swallow-tail) chains to a rigid *p*-terphenyl unit. Each of the swallow-tail groups has a semiperfluorinated and an alkyl branch. Glycerol groups are attached to both ends of the rod-like units, providing end-to-end linking by hydrogen bonding (compound **1**; see Figure 2a). At reduced temperature long-range periodicity gradually develops in addition to the 2D periodic spacing of columns, giving rise to a 3D phase.

Compound **1**⁹ shows an enantiotropic (stable) liquid crystalline phase between 81 and 154 °C with a phase transition at 130 °C

(see below). The observed texture is characteristic for columnar phases (Figure 2b). In the whole temperature range the X-ray diffraction pattern (Figure 2d) is characterized by diffuse wide angle scattering (maximum at $d = 0.50$ nm), confirming the LC nature, i.e. lack of preferred molecular position, in both mesophases. The small angle diffraction pattern of a surface aligned sample (Figure 2d) indicates a 2D lattice with hexagonal symmetry. This is confirmed by the 1:1/ $\sqrt{3}$:1/2 ratio of d -values of small angle powder reflections (see Figure 3a, $a_{\text{hex}} = 3.11$ nm).

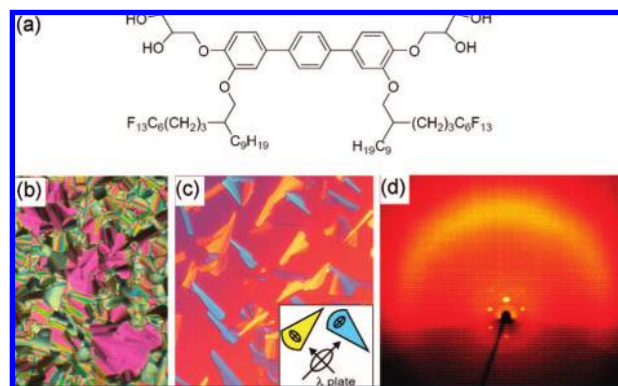


Figure 2. Compound **1**: (a) Molecular structure; phase transitions (second DSC heating scan, 10 K min⁻¹): Cr 81 °C [21.3 kJ·mol⁻¹], 3D 130 °C [-], Col_{hex} 154 °C [7.8 kJ·mol⁻¹], Iso; Cr = crystalline solid, Iso = isotropic liquid, Col_{hex} = hexagonal columnar phase, 3D = correlated Col_{hex} phase. (b) Texture between crossed polarizers at 140 °C. (c) Texture with a λ -plate retarder, the indicatrix orientation in the compensator, and in the two types of fans is shown in the inset. (d) X-ray diffraction pattern of a surface aligned sample at $T = 129$ °C (X-ray beam parallel to the surface).

The electron density map reconstructed from the small angle diffraction pattern in the Col_{hex} phase at 140 °C is shown in Figure 3c (see Supporting Information for details). Each column has a central circular density minimum (red) and six maxima at the periphery (purple). Due to dynamic averaging the minimum contains the aromatic cores, glycerol units, and much of the alkyl parts of the side chains, while the peripheral maxima are dominated by the electron-rich perfluorinated segments. From these data it is concluded that in this Col_{hex} phase the bolaamphiphilic cores (terphenyls + glycerol groups) form the column cores which are surrounded by the fluid continuum of the lateral chains. That the bolaamphiphilic cores are oriented parallel to the column axis is shown by the color of the fans in the optical micrograph (Figure 2c) taken with a λ -plate. The yellow and blue colors define the orientation of the high-index axis as tangential rather than radial. Since the columns are also tangential in the fans,¹⁰ and the high-index axis is known to be parallel to the terphenyl long axis, it follows that the terphenyls are coaxial with the columns.

[†] Martin-Luther-University Halle-Wittenberg.

[‡] University of Sheffield.

At ca. 130 °C an additional weak diffraction peak, corresponding to $d = 2.03$ nm, appears in the X-ray diffraction pattern (see Figure 3b), which upon further cooling continuously increases in intensity. At the same time $hk0$ reflections show virtually no change. This seems to indicate a second-order phase transition, and accordingly, no peak can be found in the DSC traces (see Figure S1). Also the optical texture does not change; only a continuous increase in birefringence with decreasing temperature is seen. The width of this additional peak is resolution limited, and its spacing corresponds to the length of the bolaamphiphilic core ($L = 2.0$ – 2.1 nm in a conformation with compact glycerol groups). Therefore, it is assigned to the establishment of long-range order (correlation length at least 120 nm) along the column axis arising from the segregation of the aromatic cores from the polar glycerol groups (Figure 3d). In this mesophase adjacent columns must be in register, leading to a mesophase with a 3D lattice based on a hexagonal arrangement of columns. The intensification of the additional reflection suggests that intercolumnar order increases with decreasing temperature.

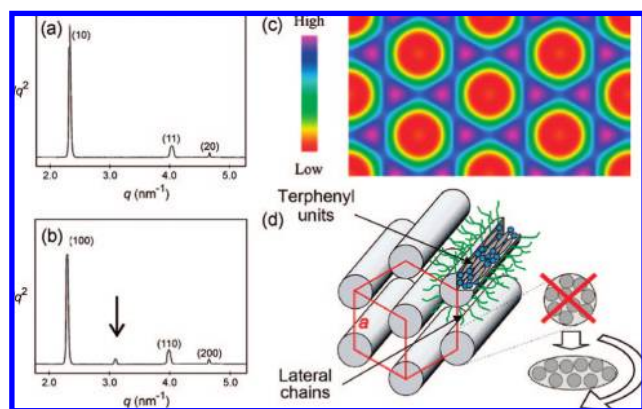


Figure 3. Compound 1: Powder diffraction pattern (a) at $T = 140$ °C (Col_{hex}) and (b) at 120 °C (3D) obtained with synchrotron source. (c) Reconstructed electron density map of the Col_{hex} phase at $T = 140$ °C, with view down the column axis. (d) Model of the organization in the mesophases with hexagonal symmetry.

Dividing the unit cell volume (estimated from a_{hex} and L) by molecular volume gives approximately nine molecules per cell (see Table S2). Thus approximately nine terphenyl units are arranged side-by-side in a bundle forming the aromatic column core in both phases. For the side chains on all molecules to have access to the column periphery, the local cross section of the aromatic column core is likely to be elliptical (ribbon-like), rather than circular (Figure 3d); orientational averaging over space and time then gives rise to hexagonal symmetry and the circular core in the density map (Figure 3c).¹¹

Regarding the nature of the low-temperature phase, although there is 3D long-range order in density fluctuations, we still regard it as liquid crystalline, since there is no preferred position for individual molecules in the x,y -plane (hence the diffuse wide-angle X-ray scattering).¹²

In summary, two new modes of LC organization are reported, with the aromatic rods grouped in bundles: (a) a 2D columnar phase, where rod-like units are aligned parallel to the column axis and not across it as in polycatenar compounds and other rod-like mesogens with bulky end chains,¹³ and (b) a 3D mesophase, with disordered bundles of mesogens and a fluid continuum surrounding these bundles.¹⁴ The 2D-to-3D transition observed here, along with the fact that it appears to be second order, is important from a theoretical point of view, and parallels can be drawn with the nematic–smectic-A transition. The mesophases reported here are

in some respect related to columnar mesophases of hairy rod main chain polymers,¹⁵ as the systems can be viewed as hydrogen-bonded supramolecular polymers with the lateral chains as hairy side groups. However, in contrast to these polymers the molecules reported here are organized in bundles. Even some flexible and semiflexible polymers without lateral chains exhibit a main-chain columnar LC phase, but there again each chain forms a column of its own.^{16,17} The hairy rod polymers represent an important class of semiconducting organic electronic materials for potential use in OLEDs, organic transistors, and photovoltaic devices.¹⁸ Hence, investigation of the low molecular weight molecules reported herein can provide clues concerning the controlled organization of important functional materials by directed design of molecular tectons.

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Supporting Information Available: DSC, X-ray data, synthesis and analytical data. This material is available free of charge via Internet at <http://pubs.acs.org>.

References

- (1) Demus, D.; Goodby, J.; Gray, G. W.; Spiess, H.-W.; Vill, V. *Handbook of Liquid Crystals* Wiley-VCH: Weinheim, Germany, 1998. Tschierske, C. *Annu. Rep. Prog. Chem. Sect. C Phys. Chem.* **2001**, *97*, 191–267.
- (2) Chandrasekhar, S.; Sadashiva, B. K.; Suresh, K. A. *Pramana* **1977**, *9*, 471–480.
- (3) Laschat, S.; Baro, A.; Steinke, N.; Giesselmann, F.; Hägele, C.; Scalia, G.; Judele, R.; Kapatsina, E.; Sauer, S.; Schreivogel, A.; Tosoni, M. *Angew. Chem., Int. Ed.* **2007**, *46*, 4832–4887.
- (4) Sergeev, S.; Pisulab, W.; Geerts, Y. H. *Chem. Soc. Rev.* **2007**, *36*, 1902–1929.
- (5) Malthete, J.; Levelut, A. M.; Tinh, N. H. *J. Phys. Lett.* **1985**, *46*, L875–L880. Gharbia, M.; Gharbi, A.; Nguyen, H. T.; Malthete, J. *Curr. Opin. Colloid Interface Sci.* **2002**, *7*, 312–325. Donnio, B.; Heinrich, B.; Allouchi, H.; Kain, J.; Diele, S.; Guillon, D.; Bruce, D. W. *J. Am. Chem. Soc.* **2004**, *126*, 15258–15268.
- (6) Bruce, D. W. *Acc. Chem. Res.* **2000**, *33*, 831–840.
- (7) Ryu, J.-H.; Cho, B.-K.; Lee, M. *Bull. Korean Chem. Soc.* **2006**, *27*, 1270–1282. Nishikawa, E.; Samulski, E. T. *Liq. Cryst.* **2000**, *27*, 1457–1463. Lose, D.; Diele, S.; Pelzl, G.; Dietzmann, E.; Weissflog, W. *Liq. Cryst.* **1998**, *24*, 707–717.
- (8) Veerman, J. A. C.; Frenkel, D. *Phys. Rev. A* **1991**, *43*, 4334–4343.
- (9) Due to the presence of the stereogenic centers in the glycerol groups, the investigated systems represent mixtures of four distinct stereoisomers.
- (10) Oswald, P.; Kleman, M. *J. Phys. (Paris)* **1981**, *42*, 1461–1472.
- (11) The fact that there is no distinct central maximum in the electron density profile of a column corresponding to the aromatic core, surrounded by a low-density ring from the alkyl region, is in line with rotational averaging of ribbon-like cores.
- (12) Pershan, P. S. *Structure of Liquid Crystal Phases*; World Scientific: Singapore, 1988.
- (13) This is similar to the Lam_N and Lam_{Sm} phases of bolaamphiphiles with a linear lateral chain where rod-like units are parallel to the layer planes and not perpendicular as in SmA phases or tilted as in SmC phases: Prehm, M.; Cheng, X. H.; Diele, S.; Das, M. K.; Tschierske, C. *J. Am. Chem. Soc.* **2002**, *124*, 12072–12073. Prehm, M.; Diele, S.; Das, M. K.; Tschierske, C. *J. Am. Chem. Soc.* **2003**, *125*, 614–615. Patel, N. M.; Syed, I. M.; Rosenblatt, C.; Prehm, M.; Tschierske, C. *Liq. Cryst.* **2005**, *32*, 55–61. Tschierske, C. *Chem. Soc. Rev.* **2007**, *36*, 1930–1970.
- (14) Hexagonal mesophases with an inverse structure, where fluid chains form the column core surrounded by rod-like mesogens arranged with or without register parallel to the columns, were reported recently: Chen, B.; Baumeister, U.; Pelzl, G.; Das, M. K.; Zeng, X. B.; Ungar, G.; Tschierske, C. *J. Am. Chem. Soc.* **2005**, *127*, 16578–16591.
- (15) Fu, K.; Sekine, N.; Sone, M.; Tokita, M.; Watanabe, J. *Polym. J.* **2002**, *34*, 291–297. Carbonnier, B.; Andreopoulou, A. K.; Pakula, T.; Kallitis, J. K. *Macromol. Chem. Phys.* **2005**, *206*, 66–76. Riala, P.; Andreopoulou, A.; Kallitis, J.; Gitsas, A.; Floudas, G. *Polymer* **2006**, *47*, 7241–7250.
- (16) Ungar, G. *Polymer* **1993**, *34*, 2050–2059.
- (17) In this case the lock-in of longitudinal interchain register leads to a Col_{hex} -to-crystal B transition which is first order: Ungar, G.; Feijoo, J. L.; Percec, V.; Yourd, R. *Macromolecules* **1991**, *24*, 953–957.
- (18) Anthony, J. E. *Chem. Rev.* **2006**, *106*, 5028–5048.

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