Formation of thermotropic and lyotropic smectic and columnar liquid crystalline phases by a novel type of rigid rod-like amphiphilic molecule

Marius Kölbel,[a] Carsten Tschierske*[a]† and Siegmar Diele[b]

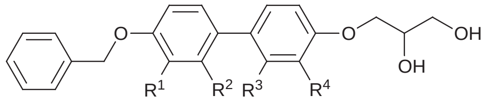
[a] *Institut für Organische Chemie der Martin-Luther-Universität Halle-Wittenberg, D-06120 Halle, Kurt-Mothes-Str. 2, Germany*
[b] *Institut für Physikalische Chemie der Martin-Luther-Universität Halle-Wittenberg, D-06108 Halle, Mühlpforte 1, Germany*

4-Benzyloxy-4′-(2,3-dihydroxypropyloxy)biphenyls with lateral methyl substituents are a novel class of amphiphilic mesogens displaying thermotropic and lyotropic smectic and columnar mesophases due to microsegregation of hydrophilic regions from all-aromatic segments in the absence of a flexible alkyl chain.

The liquid crystalline state which combines order and mobility on a molecular level is of great interest for material science as well as for life science and is found in different classes of compounds. Most are anisometric (rod-shaped or disc-like) molecules and amphiphilic molecules. These molecules consist of an anisometric or a polar basic unit to which one or more flexible chains are grafted. Usually these are alkyl chains and provide the mobility whereas the order is provided by the packing of the anisometric groups or by the attractive forces between the polar groups. Liquid crystalline materials without flexible chains are rare. Examples are *p*-oligophenylenes[1] and high molecular mass condensed polyaromatic compounds (carbonaceous materials).[2] More recently columnar liquid crystalline properties have been found for some polyhalogenated small aromatic compounds such as indene derivatives and pseudoazulenes[3] and for salts of 3-phenyloxyphenyl-2-propionic acid, important non-steroidal antiinflammatory drugs (fenoprofens).[4] Also molecules consisting of aromatic systems with polar groups around their peripheries such as, for example, some drugs, dyes, nucleic acids and antibiotics, can form lyotropic mesophases with protic solvents. In these chromonic liquid crystals[5] the solvent provides the mobility.

Here, we report on a novel type of amphiphiles without flexible alkyl chains, consisting only of a hydrophilic *rac*-2,3-dihydroxypropyl group and a linear array of three *p*-substituted benzene rings providing a rather rigid lipophilic unit.[6] Both the attractive interactions between the rigid aromatic units and the hydrogen bonding provided by the 1,2-diol[7] unit give rise to the very high melting point of **1**. In order to diminish the attractive interactions between the aromatic units a single methyl group was grafted at different positions laterally to the biphenyl unit of **1**. Indeed, a dramatic decrease in the melting temperature was possible and liquid crystalline properties can be observed for all methyl-substituted compounds **2**–**5**.‡ The influence of the position of the lateral substituent on the thermotropic properties is shown in Table 1.

Table 1 Phase transition temperatures of **1**–**5** as determined by polarising microscopy. Abbreviations: K = crystalline solid, S_A = smectic A phase, Col = columnar phase, Cub? = optically isotropic, probably cubic mesophase, Iso = isotropic liquid



	R^1	R^2	R^3	R^4	*T*/°C (pure compounds)	*T*/°C (glycerol saturated samples)
1	H	H	H	H	K 230 Iso	—
2	H	H	H	Me	K 147 (S_A 130) Iso	S_A 140 Iso
3	H	H	Me	H	K 103 (Cub? 70 S_C 73) Iso	Col 96 Iso
4	H	Me	H	H	K 95 (S_A 62) Iso	S_A 70 Col 79 Iso
5	Me	H	H	H	K 128 Col_{ob} 151 Iso	Col 125 S_A 143 Iso

Compounds **2** and **4** show a monotropic phase easily identified as a smectic layer structure (S_A phase) by its typical fan like texture and regions with homeotropic orientation and oily streaks, observed by microscopy between crossed polarisers. For compound **3** one observes a monotropic tilted smectic phase (S_C phase), identified by its typical *schlieren* texture, which on further cooling turns into a highly viscous and optically isotropic (probably cubic) phase. Owing to the monotropic nature of these mesophases, a more detailed investigation by X-ray scattering was however not possible.

An enantiotropic mesophase was found for **5** between 128 and 151 °C. It is characterised by regions with spherulitic as well as broken fan shaped texture (Fig. 1). No homeotropic orientation can be obtained by shearing the sample. Therefore an S_A phase can be ruled out. X-Ray studies provide a diffuse scattering in the wide angle region and three non-equidistant reflections in the small angle region (d_1 = 3.55, d_2 = 1.93, d_3 = 1.27 nm), excluding a smectic layer structure. As there are no references to a hexagonal or a rectangular 2D lattice, we evaluated the pattern under the assumption of a two-dimensional oblique cell, assigning the observed reflections to (10), (01) and (11) with increasing ϕ-values and obtained lattice parameters a = 9.95, c = 5.41 nm and β = 159.1°. In the light of the fact that the aromatic unit should provide a rod-like molecular shape and that the mesophases of **2**–**4** represent layer structures, it seems likely that the columnar phase results from the collapse of smectic layers into band-like segments (ribbons). The collapse can be caused either by an incompatibility of two incommensurate length scales or by a different space filling of microsegregated regions. The first case is found at the transition between smectic bilayer and monolayer structures ($S_{\tilde{C}}$, $S_{\tilde{A}}$ phases).[8] The second type is known from the thermotropic mesophases of pure soaps[9] and has been proposed for columnar mesophases of polycatenar compounds,[10] and several types of calamitic amphiphiles containing oligo(oxyethylene) units.[11,12]

In the crystalline state of **5** in the small angle region three equidistant reflections are observed with a period of d = 3.55

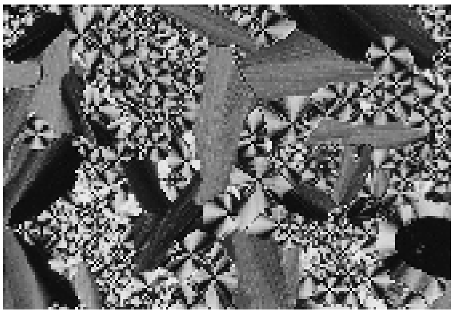


Fig. 1 Polarised optical micrograph of the columnar phase of **5** at 150 °C

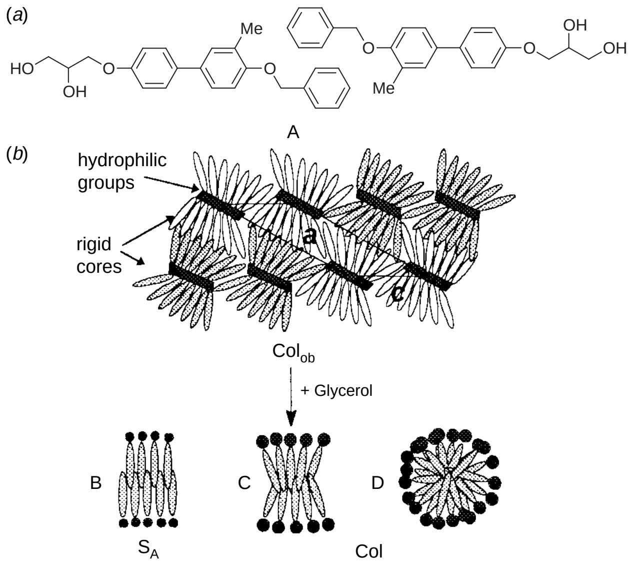


Fig. 2 Schematic presentation of the proposed arrangement of the molecules of **5** in its mesophases. (*a*) Intercalation of two molecules, (*b*) cross-section through a possible thermotropic Col_{ob} phase (A) and through aggregates of possible lyotropic mesophases, formed on addition of glycerol: layer of an S_A-phase (B), ribbon (C) and cylindrical aggregate (D).

nm. The corresponding scattering vector remains on heating the sample whereas the higher orders are significantly shifted at the transition to the liquid crystalline state. Therefore, we assume that the thickness of the ribbons is *ca.* 3.5 nm. The molecular length L obtained from CPK models is 2.3 nm. Thus we can conclude on a bilayer arrangement with strongly tilted molecules and/or with a high degree of intercalation. Intercalation of the terminal benzyl groups seems to be likely because the methyl groups provide a partial tapering of the molecules which should facilitate their intercalation [Fig. 2(*a*)]. The shape of the molecules and the intercalation increase the diameter of the aromatic regions with respect to the polar regions of the head groups. Thus, the frustration of the bilayer structure can be explained by the different space filling of the segregated regions of the polar and the aromatic molecular parts.

A possible model which is in accord with the obtained lattice parameter is shown in Fig. 2(*b*), arrangement A. According to this model the oblique lattice results from the organisation of pairs of ribbons (grey and white) consisting of partly intercalated and tilted molecules. Each pair differs from the neighbouring pairs by the average tilt direction of the molecules. The individual ribbons should have a lateral diameter of *ca.* 5 nm and *ca.* ten molecules are arranged side by side an average.

Being amphiphilic, the liquid crystalline properties of **2**–**5** should be influenced by solvents. Their behaviour in the solvent saturated state and in the contact region with the protic solvent glycerol§ was investigated by polarising microscopy. In the contact region between **5** and glycerol the columnar mesophase is destabilised and the formation of an S_A phase with a maximum clearing temperature of 143 °C is observed. In a medium concentration range no columnar mesophase can be found. However, on further increasing the glycerol content a second columnar mesophase appears. This observation confirms the proposed model of the organisation of **5** in the columnar mesophase. The solvent molecules are built in between the polar head groups and increase the diameter of these regions. At a certain solvent content an equivalent space filling of the aromatic and the polar regions is reached, the ribbons fuse and a stable layer structure is found (S_A phase). On further increased solvent content the size of the polar regions could exceed that of the aromatic regions and again the layers break up with formation of a columnar phase. Thus, with respect to the space filling of the different regions the two columnar phases should be inverted to each other. The second columnar phase could again represent a ribbon phase [Fig. 2(*b*), arrangement C], but a columnar phase consisting of cylindrical aggregates [Fig. 2(*b*), arrangement D], cannot be excluded. Columnar phases can also be induced on addition of glycerol to **3** and **4** (Table 1). These induced columnar phases have the same optical texture as that induced in the system **5**–glycerol and should be related to it.

In summary, it was found that rigid all-aromatic amphiphiles represent novel amphotropic liquid crystals.[13] They show the same diversity of different mesophases as thermotropic and lyotropic systems of classical flexible amphiphiles. However, the hydrophobic interactions between flexible alkyl chains are replaced by interactions of rigid aromatic units and therefore ribbon structures are formed. Moreover, a tilted S_C phase was detected which has never been found in the mesophase sequence of conventional flexible amphiphiles and also its appearance is related to the rigid molecular structure.

This work was supported by the Deutsche Forschungsgemeinschaft and the Fonds der Chemischen Industrie.

Notes and References

† E-mail: coqfx@mlucom6.urz.uni-halle.de

‡ All analytical data of the investigated compounds are in accord with the proposed structures, *e.g.* **5**: $C_{23}H_{24}O_4$ requires (found): C, 75.80 (75.54); H, 6.64 (6.38%). ^1H NMR [$(CD_3)_2SO$, 200 MHz], δ 7.56–7.31 (9 H, m, Ar-H), 7.09–6.97 (3 H, m, Ar-H), 5.18 (2 H, s, $ArCH_2O$), 4.95 (1 H, d, J 4.9 Hz, sec. OH), 4.67 (1 H, t, J 5.7 Hz, prim. OH), 4.08–3.81 (3 H, m, $ArOCH_2CHOH$), 3.48 (2 H, dd, J 5.6 Hz, CH_2OH), 2.28 (3 H, s, CH_3).

§ Glycerol was chosen because of its high boiling point and because it represents the basic unit of the hydrophilic groups of compounds **1**–**5**.

1 G. W. Smith, *Mol. Cryst. Liq. Cryst.*, 1979, **49**, 207; I. C. Lewis and J. B. Barr, *Mol. Cryst. Liq. Cryst.*, 1981, **72**, 65.
2 H. Honda, *Carbon*, 1988, **26**, 139.
3 J. Barbera, O. A. Rakitin, M. B. Ros and T. Torroba, *Angew. Chem.*, 1998, **110**, 308.
4 T. Rades and C. C. Müller-Goymann, *Eur. J. Pharm. Biopharm.*, 1994, **40**, 277.
5 T. K. Attwood and J. E. Lydon, *Mol. Cryst. Liq. Cryst.*, 1984, **108**, 349.
6 Spiro-tensides and -phospholipids have recently been investigated as non-aromatic rigid amphiphiles: F. M. Menger and J. Ding, *Angew. Chem.*, 1996, **108**, 2266.
7 A. S. C. Lawrence, *Mol. Cryst. Liq. Cryst.*, 1969, **7**, 1; C. Tschierske, G. Brezesinski, F. Kuschel and H. Zaschke, *Mol. Cryst. Liq. Cryst., Lett.*, 1989, **6**, 139.
8 F. Hardouin, A. M. Levelut, M. F. Achard and G. Sigaud, *J. Chim. Phys.*, 1983, **80**, 53.
9 A. Skoulios and V. Luzzati, *Nature*, 1959, **183**, 1310.
10 H. T. Nguyen, C. Destrade and J. Malthete, *Adv. Mater.*, 1997, **9**, 375.
11 J. A. Schröter, C. Tschierske, M. Wittenberg and J. H. Wendorff, *Angew. Chem.*, 1997, **109**, 1160; *Angew. Chem., Int. Ed. Engl.*, 1997, **36**, 1119; F. Hildebrandt, J. A. Schröter, C. Tschierske, R. Festag, M. Wittenberg and J. H. Wendorff, *Adv. Mater.*, 1997, **9**, 564; B. Neumann, C. Sauer, S. Diele and C. Tschierske, *J. Mater. Chem.*, 1996, **6**, 1087.
12 M. Lee, N.-K. Oh and W.-C. Zin, *Chem. Commun.*, 1996, 1787; M. Lee, N.-K. Oh, H. K. Lee and W.-C. Zin, *Macromolecules*, 1996, **29**, 5567.
13 C. Tschierske, *Prog. Polym. Sci.*, 1996, **21**, 775.

Received in Bath, UK, 27th March 1998; 8/02540A