[12] The corresponding vinyl bromide resulting from hydrobromination of the triple bond was isolated as a side product.

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Design of New Mesogenic Block Molecules: Formation of Columnar Mesophases by Calamitic Bolaamphiphiles with Lateral Lipophilic Substituents**

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Carsten Tschierske,* Jens Kain, and Siegmar Diele

The investigation of the driving forces of molecular self-organization is a present topic of chemical research. During the last decades the formation of supramolecular structures based on the microphase separation of incompatible subunits which are covalently linked within macromolecules (block copolymers) has been studied intensively.[1] Such segregation effects are not limited to polymers, but also play an important role in biological systems as well as in the self-organization of low molecular weight materials, especially for the formation of positionally ordered (smectic, columnar, and cubic) liquid crystalline phases.[2] Here, the ordered assemblies often result from the combined action of rigidity and microsegregation. In most cases these two driving forces act in the same direction, enhancing each other. If, however, microsegregation and rigidity compete with each other, novel low molecular weight block molecules should result which could be able to form new supramolecular structures.

Recently we reported on the liquid crystalline compound **1**, which can be regarded as a block molecule containing three incompatible portions: a rigid, rodlike terphenyl unit; two flexible, lipophilic chains; and a lateral hydrophilic group (Figure 1).[3] The large lateral substituent disturbs the parallel alignment of the rigid cores, and in this way makes the formation of smectic layer structures difficult. However, it did not completely suppress the formation of mesophases, but gave rise to a rectangular columnar mesophase (Col_r). The formation of this columnar phase was explained by the microsegregation of the lateral polar chains from the rigid terphenyl cores into cylindrical domains with a locally enhanced concentration of the flexible and polar polyether chains. This leads to a fragmentation of the smectic layer structure into ribbonlike segments, which organize into the rectangular two-dimensional lattice of the columnar mesophase.[3]

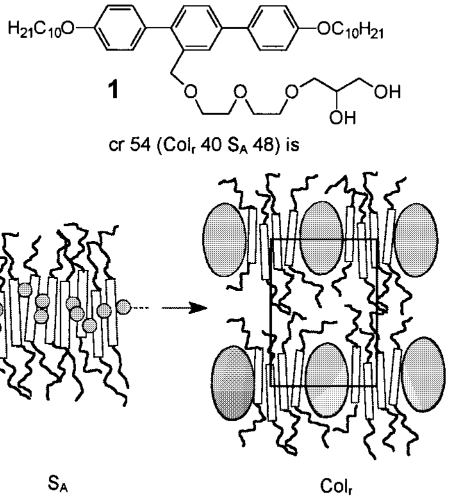
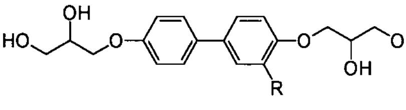


Figure 1. Structure of compound **1** and models of its organization in the mesophases (abbreviations: cr = crystalline phase, S_A = smectic A phase, Col_r = rectangular columnar phase, is = isotropic liquid).

In an attempt to generalize the conclusions made for the self-organization of **1**, we have now synthesized the novel low molecular weight triblock molecules **3**–**6**. The topology of the incompatible moieties is the reverse of that in **1** (Table 1).[4] Whereas in **1** the lipophilic chains are grafted in terminal positions and the hydrophilic group is attached in a lateral



2–6

Table 1. Transition temperatures for **2**–**6**, as determined by polarized light microscopy.[a]

Compd	R	T [°C]
2	H	cr 245 S_A 294 is[7c]
3	CH_3	cr 104 S_A 231 is
4	n-C_3H_7	cr ?[b] S_A 149 is
5	n-C_9H_{19}	cr 67 Col 98 is
6	n-$C_{11}H_{23}$	cr 84 Col_r 116 is

[a] Abbreviations are explained in the legend to Figure 1. [b] No crystalline phase has been obtained yet.

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position at the rigid terphenyl unit, compounds **3**–**6** contain hydrophilic terminal groups and a lipophilic lateral group connected with a biphenyl unit. Bearing hydrophilic groups at both ends of a hydrophobic molecular part, these molecules belong to the class of bolaamphiphiles.[5]

Bolaamphiphiles are of great interest, because such lipids form stable monolayer membranes and represent a main constituent of the cell membranes of archae bacteria. Many bolaamphiphiles can also form highly stable smectic liquid crystalline phases.[6–8] These mesophases can be further stabilized if rigid calamitic segments, such as biphenyl units, are introduced into the hydrophobic central part of the molecules (**2**, Table 1).[7c] The presence of small lateral groups at the biphenyl core of such calamitic bolaamphiphilic tetraols (**3** and **4**) leads to a drastic lowering of the melting temperatures. Also the stability of the liquid crystalline phases is reduced considerably, but **5** and **6** still exhibit enantiotropic mesomorphism despite their very long lateral alkyl groups. The liquid crystalline phases of **3** and **4** with small lateral substituents are S_A monolayer structures (S_{A1}), as expected. For the S_{A1} phase of **3** a layer thickness of 1.8 nm (0.86 molecular lengths) was determined by X-ray diffraction.

However, the mesophases formed by the long-chain compounds **5** and **6** are different from those of **3** and **4**. This was first indicated by polarized light optical microscopy between crossed polarizers. On cooling of **5** and **6** from their isotropic liquid states, the formation of fernlike dendritic textures can be observed at 98 °C and 116 °C, respectively; these coalesce to mosaiclike textures with spherulitic domains (Figure 2). Remarkably, the mesophase of **6**, with the longer lateral chain, is more stable than that of **5**. This is in contrast to the observations usually made on elongation of lateral chains of nonamphiphilic calamitic liquid crystals.

To clarify the structures of these phases, X-ray diffraction investigations were carried out with well-developed monodomains of the mesophase of **6**. The outer diffuse scattering, which excludes a crystalline phase or a highly ordered smectic low-temperature mesophase, forms a closed ring, indicating strong deviations of the molecular long axes from a preferred direction. The small-angle region exhibits a lot of spotlike reflections, confirming a rectangular columnar 2D lattice. The lattice parameters are $a = 5.4$ nm and $b = 5.8$ nm (Figure 3 and Table 2). The length of the molecules **6** in their most extended conformation from head group to head group is only 2.1 nm (CPK models). Thus, both lattice parameters are significantly larger than twice the molecular dimensions. To deduce a suitable model for the arrangement of the molecules in this columnar mesophase, we have to take into account the following considerations:

- The large lateral alkyl groups should disturb the parallel organization of the rigid cores. However, the strong attractive interactions provided by hydrogen bonding at both ends of the bolaamphiphilic molecules[7] should inhibit the complete collapse of the smectic layers.
- Because of the position of the alkyl chains close to one of the diol head groups, the two head groups become nonequivalent. The ability to form intermolecular hydrogen bonds should be reduced for the diol groups neighboring the alkyl chains in comparison with the other diol groups.
- The lipophilic and flexible alkyl chains are incompatible with both the polar diol groups and the rigid biphenyl units, and have a tendency to segregate and to form distinct regions with a locally enhanced concentration of lipophilic chains.

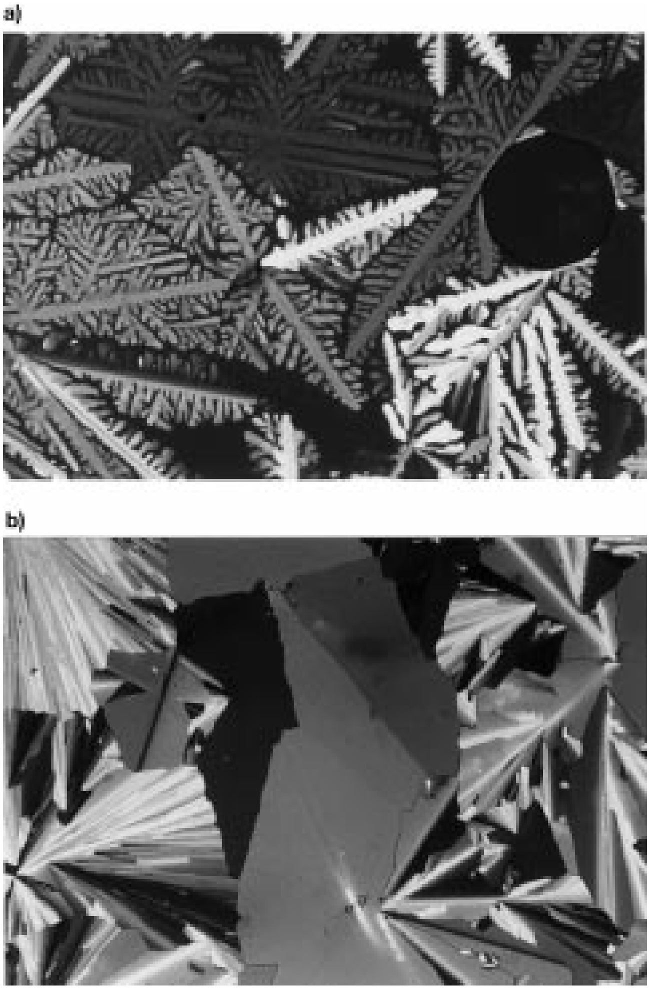

Figure 2. Polarized light optical micrographs of the mesophase of **6**; a) fernlike dendritic texture at 116 °C; b) mosaiclike texture with spherulitic domains at 115.5 °C.

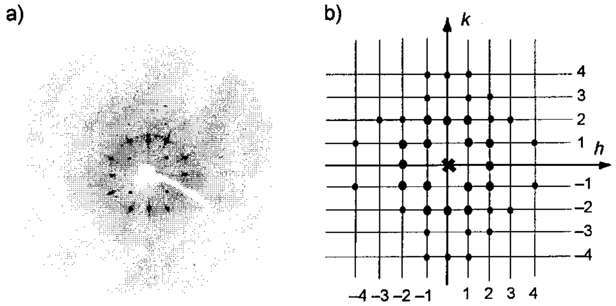

Figure 3. a) Small-angle X-ray diffraction pattern of an aligned sample of **6** at 113 °C (2D detector); b) sketch of the diffraction pattern.

Based on these considerations a tentative model for the columnar mesophase of **6** can be deduced: Accordingly, the molecules should organize in such a way that their lipophilic chains can concentrate with formation of separate regions. This could be achieved if the molecules in neighboring layers

Table 2. Bragg reflections and Miller indices for the mesophase of **6** at $T = 113\,^{\circ}C$.

hk	$\Theta_{obs.}$ [°]	Θ_{calcd} [°]
11	1.14	1.12
02	1.52	1.52
20	1.63	1.63
12	1.82	1.73
21	1.85	1.80
13	2.42	2.42
23	2.76	2.80
32	2.88	2.88
14	3.13	3.15
41	3.34	3.35

align on average antiparallel, whereas molecules in the same layer arrange parallel as shown in Figure 4b. Since the hydrogen-bonding ability of the diol groups next to the alkyl chains is reduced for steric reasons, their intermolecular hydrogen-bonding networks should preferably collapse, whereas those of the diol groups at the opposite end of the molecules largely remain intact.

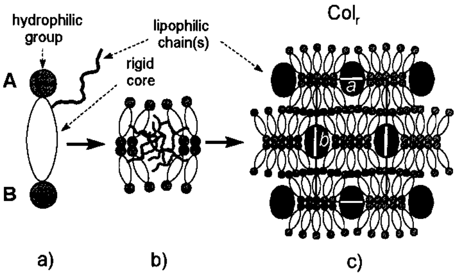

Figure 4. Arrangement suggested for the molecules of **6** in the rectangular columnar mesophase.

The lipophilic regions formed by microsegregation of the alkyl chains should therefore interrupt the hydrogen-bonding networks of the diol groups neighboring the alkyl chains (A in Figure 4), whereas the others should remain. This could lead to the coexistence of two different types of hydrogen-bonding networks in the system. One type, formed by the head groups neighboring the alkyl chains, is continuous in only one dimension; that is, this network is located within the ribbons. The second type is formed by the diol groups at the opposite termini of the biphenyl cores (B in Figure 4) and should be continuous in two dimensions; that is, this network represents undulated layers connecting the ribbons. In other words, every second hydrogen-bonding network is disrupted by the cylindrical domains of the alkyl chains. Thus, less space is available for the diol groups within the ribbons than for those in the layers, and therefore the degree of interdigitation should be different in these two regions. An optimum space filling could be ensured by a nonintercalated head-to-head arrangement of the polar head groups in the ribbons, whereas the head groups in the layers should be strongly intercalated (Figure 4c).

On the basis of these assumptions one of the lattice parameters should correspond to twice the length of a (hypothetical) dimer that is intercalated in the head group region (2×3.6 nm $= 7.2$ nm). Taking into account the tilting of the molecules at the edges of the ribbons which is necessary to obtain efficient space filling (see Figure 4c), the lattice parameter $b = 5.8$ nm most likely corresponds to twice the thickness of the ribbons. Then, the parameter $a = 5.4$ nm should correspond to the lateral distance between the ribbons. Under this assumption in average about five molecules should be arranged side by side across the diameter of each ribbon. Thus, the proposed model seems reasonable, because it is in accordance with the molecular dimensions and explains the experimental findings.

Figure 5a shows another representation of this arrangement: The incompatible hydrophilic and rigid aromatic units separate from each other by forming layers, and every second polar layer is interrupted in regular intervals by columns with an enhanced concentration of lipophilic chains.

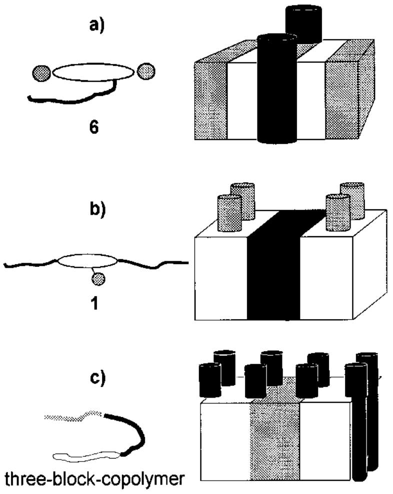

Figure 5. Comparison of the structures of columnar phases of a) **6**, b) **1**, and c) a triblock copolymer. In (a) and (b) gray = hydrophilic groups, white = aromatic cores, black = lipophilic chains; in (c) the different shading distinguishes the incompatible blocks.

This model describes a novel type of thermotropic columnar structure which is in many respects different from those known for disclike molecules or conventional amphiphiles. However, there are remarkable similarities to the model proposed for the columnar mesophase of the lateral amphiphile **1** (Figure 5b). In the rectangular columnar phase of **1** the lipophilic alkyl chains form layers, whereas the lateral hydrophilic groups segregate from the terphenyl rigid cores and form columns between the aromatic regions. Although the self-organization of these two classes of mesogens is unique among low molecular weight materials, there is a close relationship to the supermolecular structures of some linear triblock copolymers. For such compounds microphase separation can lead to formation of columnar structures like that shown in Figure 5c.[1, 9]

This work shows that highly smectogenic bolaamphiphiles with rigid cores can be forced to self-assemble to columnar mesophases if their smectic order is disturbed by large lateral lipophilic substituents. Their phase structure results from the combination of microsegregation and rigidity. It is imaginable that the application of this structural concept to macromolecular systems could lead to new phase structures with useful macroscopic properties.

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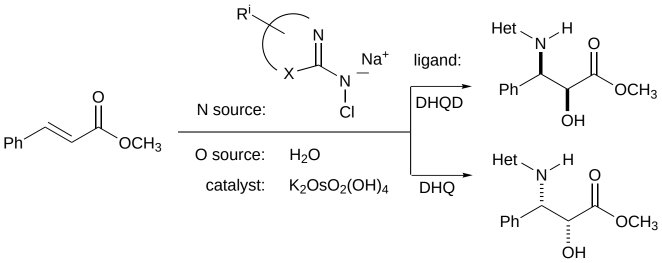
Catalytic Asymmetric Aminohydroxylation with Amino-Substituted Heterocycles as Nitrogen Sources[**]

Lukas J. Goossen, Hong Liu, K. Ruprecht Dress, and K. Barry Sharpless[*]

Dedicated to Professor Theodore Cohen
on the occasion of his 70th birthday

The β-amino alcohol moiety appears in numerous biologically active compounds,[1] and the osmium-catalyzed asymmetric aminohydroxylation (AA) of olefins provides an efficient method for the enantioselective creation of this important functionality.[2] Sulfonamides,[2a, 3] amides,[4] and carbamates[5] have been utilized as nitrogen sources for the AA, and there has been rapid improvement in both scope and selectivity since the initial report.[2a] The *N*-protected amino alcohols obtained were usually converted into free amino alcohols, so that the development of a set of orthogonally cleavable protecting groups had been our major concern.[2–5] Current developments in combinatorial chemistry stimulated us to exploit this reaction for the direct introduction of biomedically relevant heterocyclic substructures to olefins.[6] We now report an enantioselective procedure for the vicinal addition of a hydroxyl group and amino-substituted heterocycles to olefins (Scheme 1).



Scheme 1. Aminohydroxylation with amino-substituted heterocycles. R^i indicates the remaining portion of the heterocycle. Het = heterocycle, DHQ = dihydroquinine, DHQD = dihydroquinidine.

Attempts to extend the scope of the nitrogen sources in the AA to heterocyclic substituted amines had long been frustrated by very poor turnover and side reactions (e.g. ring chlorinations)[7] until Jerina et al. achieved a breakthrough with the use of an adenine derivative as nitrogen source in the aminohydroxylation of a unique olefin.[8] Then, in collabo-

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