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Design of Liquid Crystalline Block Molecules with Nonconventional Mesophase Morphologies: Calamitic Bolaamphiphiles with Lateral Alkyl Chains

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Abstract: Novel bolaamphiphiles, consisting of a biphenyl rigid core, polar 2,3-dihydroxypropoxy groups at each terminal end, and an additional long alkyl chain in a lateral position have been synthesized. The structures of these ternary block molecules were systematically changed by variation of the length and position of the alkyl chain, by introduction of additional spacer units between one of the 2,3-dihydroxypropyl groups and the rigid core, and by replacement of one of the 2,3-dihydroxypropoxy groups by a single hydroxy group. The influence of these structural variations on the liquid crystalline properties of these new materials was investigated by polarized-light microscopy, differential scanning calorimetry, and X-ray diffraction. These investigation have shown that, by elongation of the lateral chain, a transition from a smectic monolayer structure (SmA_1) via a strongly distorted layer structure (SmA^+), a centered rectangular columnar phase (Col_r/*c*2*mm*) and a noncentered rectangular columnar phase (Col_r/*p*2*gg*) to a hexagonal columnar phase (Col_h/*p*6*mm*) takes place. Elongation of the bolaamphiphilic core leads to the loss of the columnar phases, which are replaced by smectic phases, whereas reduction of its length favors the hexagonal columnar phase. This phase sequence is explained as a result of the microsegregation of the lateral alkyl chains from the rigid aromatic cores. The segregated alkyl chains are organized in columns that interrupt the smectic layers. The hydrogen bonding keep the bolaamphiphilic cores fixed end to end, so that they form networks of cylinders around the lipophilic columns. The space required by the alkyl chains with respect to the length of the bolaamphiphilic cores is restricted and largely determines the geometry of the cylinders, which leads to the observed phase sequence. The obtained mesophase morphologies, built up by three distinct sets of subspaces, are related to morphologies of some ternary block copolymers. Furthermore, the investigated compounds represent a novel class of materials, capable of forming supramolecular columnar mesophases.

Introduction

The investigation of the driving forces of molecular self-organization is one of the most exciting and most rapidly growing areas of chemical research. During the past decade the formation of well-defined supramolecular structures based on the microphase separation of incompatible subunits in multiblock copolymers,[1−3] polyelectrolyte−surfactant complexes,[4] and polymer blends[5] has significantly advanced and led to a wide variety of quite exciting morphologies. Such segregation effects are also of great importance for the structure formation in biological systems and for the self-organization of low molecular weight amphiphiles and liquid crystals. In thermotropic liquid crystals, for example, the segregation of flexible chains from rigid anisometric (calamitic or disklike) units is a main driving force for the formation of positional ordered (smectic, columnar, cubic) liquid crystalline phases.[6] Therefore, conventional liquid crystalline materials are designed in such a way that the effects of microsegregation, the preorganization of the molecular subunits, and the parallel alignment of rigid anisometric units contribute cooperatively to their self-organization, enhancing each other. For example, calamitic rigid units and flexible alkyl

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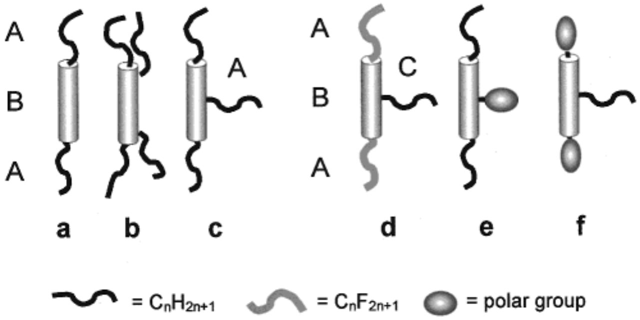

Figure 1. Schematic presentation of the molecular structures of mesophase forming binary (a−c) and ternary block molecules (d−e) comprising a calamitic middle block: (a) conventional calamitic mesogen; (b) polycatenar mesogen; (c) calamitic mesogen with lateral alkyl chain; (d) calamitic mesogen with semifluorinated side chains and lateral alkyl chain; (e) facial amphiphile; (f) bolaamphiphile with lateral alkyl chain.

chains are usually combined in such a manner that the two incompatible molecular parts are located in well-defined separate molecular regions and they are connected in a strictly linear way (see Figure 1, **a**).[7] This designing principle leads to the formation of predominately layer structures (smectic phases) consisting of segregated sublayers of the parallel aligned rigid cores and sublayers of conformational disordered alkyl chains.[8] If, however, additional alkyl chains are grafted in lateral positions at the rigid core, the layer arrangement is strongly disturbed.[9] This is not only due to the steric effect which disfavors the alignment of the calamitic cores but also to the incompatibility of the lateral alkyl chains with the aromatic cores and especially to their complete compatibility with the terminal alkyl chains. Thereby, the influence of lateral chains strongly depends on their position with respect to the terminal chains. If they are located at the terminal ends, adjacent to the terminal chains (polycatenar mesogens **b**), they enlarge the volume fraction of the flexible chains, which can give rise to a curvature of the aromatic−aliphatic interface, leading to columnar and cubic mesophases.[10,11] In contrast, the connection of aliphatic chains to other lateral positions, more close to the center of the calamitic cores (**c**), leads to the complete loss of positional order; i.e., smectic phases are replaced by nematic phases, accompanied by a drastic decrease of the mesophase stability.[9] If however, the lateral groups are incompatible with the terminal chains, the layer structures can remain. For example, calamitic mesogens, carrying two semifluorinated terminal chains and very bulky aliphatic lateral groups form stable smectic phases (**d**).[12] Even a mesophase stabilizing effect can be achieved, if the lateral groups provide additional cohesive intermolecular forces. This was recently shown for calamitic mesogens with two terminal alkyl chains and a lateral aromatic electron-acceptor group[9b] as well as for molecules with a polar lateral group, capable of hydrogen bonding, such as the 1,2-diol group (facial amphiphiles **e**).[13] The size of the polar lateral group of the facial amphiphiles was further increased by introduction of oligooxyethylene chains, which led to the induction of different types of rectangular columnar mesophases (Col_r).[14] The formation of these columnar phases was explained as the result of the inset of an additional segregation process occurring between the rigid aromatic cores and the polar lateral groups, whereby the lateral groups become organized in separate cylinders, which interrupt the smectic layers in regular intervals.[14]

Herein we report novel ternary block molecules of type **f** (see Figure 1), in which the positions of the polar diol groups and the alkyl chains were exchanged with respect to the facial amphiphiles **e**.[15] In such bolaamphiphiles,[16] the strongest attractive forces (H-bonding) are positioned at both terminal ends of the rigid calamitic cores. This, and the strong segregation of the polar 1,2-diol groups from the biphenyl cores into separate sublayers, lead to a dramatic stabilization of smectic phases.[17−19] Hence, the parent compound of this series without a lateral substituent (compound **1/0**; see Figure 2) forms an extremely stable smectic A phase with monolayer structure (SmA_1).[20] Therefore, such molecules can provide the unique possibility to change the mesophase structure from a layer structure to more complex ones by introduction of long lateral alkyl chains. Because the lateral alkyl chains represent a third incompatible unit, incompatible with both, the polar terminal diol groups[21] and the rigid biphenyl units,[6] these molecules represent ternary block molecules.[22] Furthermore, in such molecules, microsegregation and rigidity are combined in such a way that they compete with each other. This means that segregation of the

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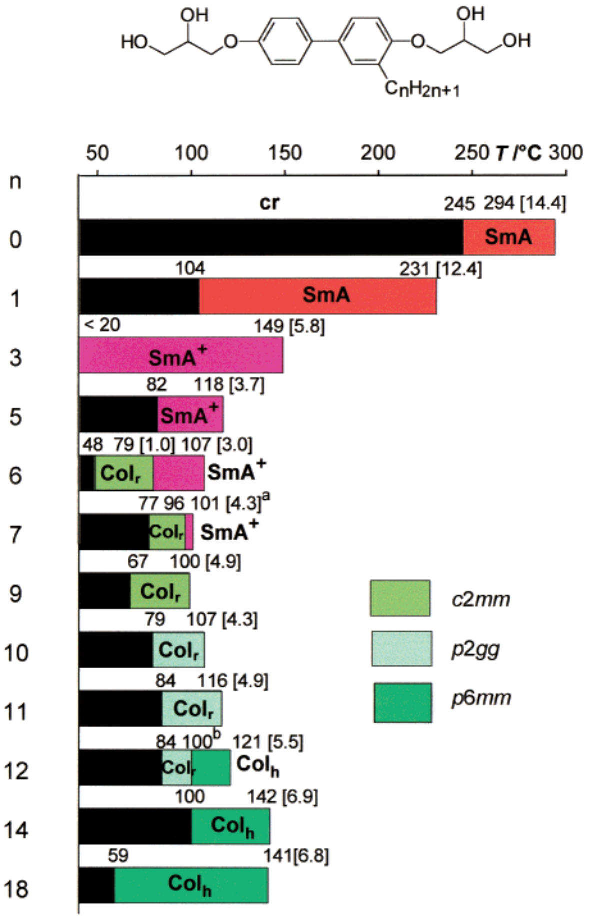
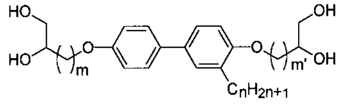
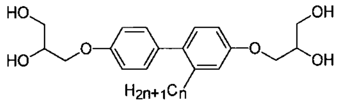


Figure 2. Mesophases, phase transition temperatures (T/°C), and phase transition enthalpies (ΔH/kJ mol^{-1}, values in brackets) of the bolaamphiphiles **1/n**. Abbreviations: cr (black columns), crystalline solid state; SmA, smectic A-phase; SmA$^+$, disordered SmA phase (see text); Col$_r$, rectangular columnar mesophase; Col$_h$, hexagonal columnar mesophase. (a) Enthalpy value refers to the transition Col$_r$-SmA$^+$-is. (b) No transition enthalpy was found for this transition by DSC.

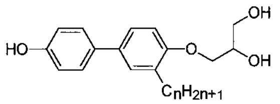
lipophilic chains would disturb the parallel alignment of the rigid cores and vice versa. We hoped that this competitive combination of microsegregation and rigidity may open new possibilities for the design of new and unusual supramolecular arrangements.



m' = 1: **m/n**
m = 1: **m'/n**



1/n'



P/n

For this purpose, we have synthesized the bolaamphiphilic biphenyl derivatives **m/n** in which the length of the lateral alkyl chain (n) and the length of the spacer unit between one of the diol groups and the biphenyl core (m) were systematically changed. Additionally, the triols **P/n** and some selected compounds, in which the position of the alkyl chains (compounds **1/n′**) or the position of the spacer unit were shifted (compounds **m′/n**), have been synthesized. The influence of these structural variations on the liquid crystalline properties of these new materials was investigated by polarized-light optical microscopy, differential scanning calorimetry, and X-ray diffraction.

Results and Discussion

1. Synthesis. The bolaamphiphiles **1/4**−**1/18** were prepared as shown in Scheme 1,[25] using Kumada[29] and Suzuki[30] coupling reactions as key steps. [4-(2,2-Dimethyl-1,3-dioxolan-4-yl-methyl)benzene]boronic acid (**I**) was the key intermediate for the synthesis of these compounds. The preparation of this new boronic acid required some special reaction conditions. So, the halogen metal exchange reaction of the aryl bromide **VII/0**[31] with n-butyllithium had to be carried out at −100 °C followed by quenching with trimethyl borate at −90 °C in order to minimize side reactions due to metalation in a position ortho to the acetonide unit. The acid-sensitive acetonide group additionally required a special workup procedure using a phosphate buffer adjusted to pH 4.5−5 at 0 °C. The coupling reactions of this boronic acid with the appropriate aryl bromides **VII/n** were carried out using standard conditions with Pd[PPh$_3$]$_4$, in aqueous glyme and NaHCO$_3$ as base.[30] Only in the case of **1/18** were these conditions not successful, due to the poor solubility of the highly lipophilic aryl bromide **VII/18**. In this case, the system 2-(di-*tert*-butylphosphino)biphenyl, Pd(OAc)$_2$, KF in THF was applied.[32] In the final step, the acetonide groups of the obtained biphenyl derivatives **VIII/n** were cleaved (pyridinium tosylate/MeOH for $n < 18$, for $n = 18$: HCl in EtOH) and the bolaamphiphiles **1/n** were purified by repeated crystallization.

The isomeric 2-substituted tetraol **1/11′** was prepared in an analogous way, starting with 3-chloroanisole. The schemes describing the synthesis of all other compounds, the detailed experimental procedures, and the analytical data are collected in the Supporting Information.

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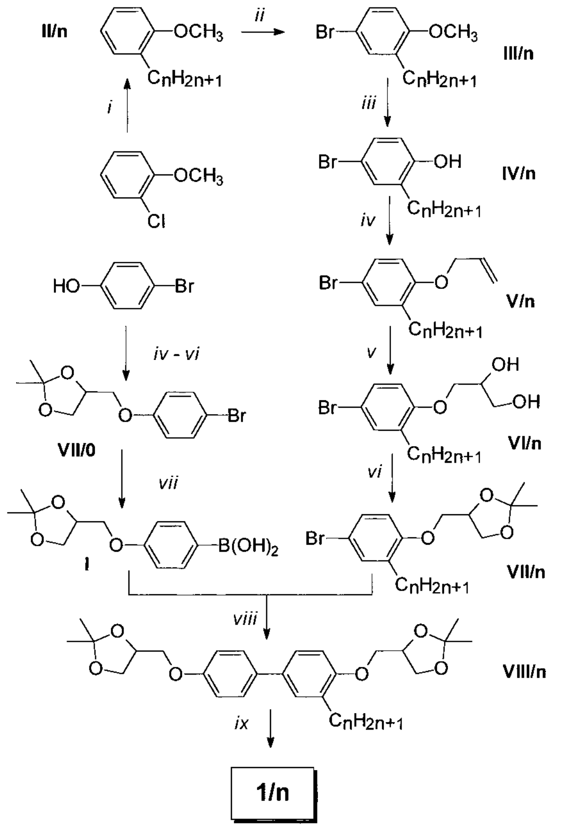
Scheme 1. Synthesis of the Bolaamphiphiles **1**/**n**[a]



[a] Reagents and conditions: (i) (1) $C_nH_{2n+1}MgBr$, Ni(dppp)Cl_2, Et_2O, reflux; (2) H_2O, HCl.[29] (ii) NBS, CH_3CN, 20 °C.[23] (iii) BBr_3, CH_2Cl_2, 20 °C.[24] (iv) $BrCH_2CH{=}CH_2$, K_2CO_3, CH_3CN, reflux.[27] (v) NMMNO, catalytic OsO_4, acetone, 20 °C.[26] (vi) $Me_2C(OMe)_2$, catalytic Py TosOH, 20 °C.[28] (vii) (1) BuLi, −100 °C; (2) $B(OMe)_3$, −90 °C; (3) H_2O, phosphate buffer pH 4−5. (viii) Pd$[PPh_3]_4$, $NaHCO_3$, H_2O, glyme, reflux[30] or catalytic Pd$(OAc)_2$, catalytic 2-(di-*tert*-butylphosphinyl)-biphenyl, KF, THF, 20 °C.[32] (ix) H_2O, MeOH, Py TosOH or EtOH, aqueous HCl.

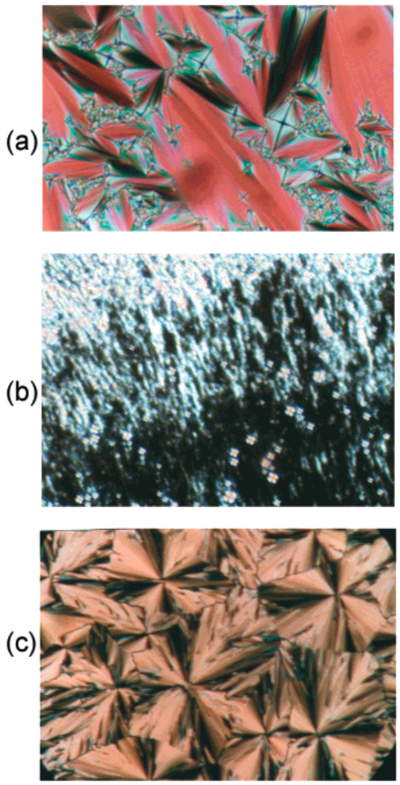


Figure 3. Optical photomicrographs (crossed polarizers) of the mesophases of **3/9**: (a) fan texture of the SmA$^+$ phase at 90 °C; (b) oily streaks texture of the SmA$^+$ phase after shearing at 90 °C; (c) Col$_r$ phase at 70 °C.

2. Influence of the Length of the Lateral Chain on the Mesophase Morphology. All synthesized compounds, even **1/18** with the extremely long lateral chain, show thermotropic liquid crystalline phases, whereby the mesophase type dramatically depends on the molecular structure. In Figure 2, the influence of the length of the lateral chain on the liquid crystalline properties of the bolaamphiphilic tetraols **1/n** is shown. As expected, the introduction of the lateral methyl group at position 3 of the biphenyl core of **1/0**[20] causes a drastic decrease of the melting and clearing temperature. By elongation of the lateral substituent to a length of $n = 9$ the liquid crystalline phases are further destabilized. Also, the transition enthalpies of the transition from the mesophases to the isotropic liquid state strongly decrease by elongation of the lateral chain from 14.4 (**1/0**) to 3.0 kJ mol^{-1} (**1/6**); afterward, the transition temperatures and the enthalpy values slightly rise again.

Smectic Phases. Smectic A-phases, characterized by their typical fan-shaped textures were observed for **1/0**−**1/7**. They easily align homeotropically, appearing completely black between crossed polarizers. Additionally, oily streaks and small orthogonal extinction crosses can be observed, which confirm this phase assignment (see, for example, Figure 3a,b). X-ray diffraction of the SmA phase of **1/1** provided a diffuse scattering in the wide-angle region, corresponding to the mean distance between disordered aromatic cores and a sharp reflection in the small-angle region. A layer thickness of $d = 1.8$ nm, corresponding to 0.83 molecular lengths ($L = 2.1$) at 90 °C was measured. This indicates a smectic monolayer structure (SmA$_1$) as typical for bolaamphiphilic molecules. The intensity of the layer reflection decreases on elongation of the lateral chain (**1/3** > **1/5**) and, remarkably, beside the sharp layer reflection, a diffuse scattering is found in the small-angle region. For **1/6,** only the diffuse scattering in the small-angle region remains (beside the diffuse scattering in the wide angle region). The diffuse scattering, however, indicates the loss of a layer periodicity and characterizes the nematic state, although the mesophase was clearly classified as a SmA phase by the textures. This contradiction has also been reported for some polyelectrolyte−lipid complexes and has been explained by a superundulated layer structure.[33] In the case under consideration, the increasing size of the lateral alkyl chains could lead to the distortion of the layers and to the formation of locally disordered inhomogenities, which could represent distinct regions with locally enhanced concentration of the lipophilic chain. Aligned samples cannot be obtained by applying a magnetic field. This is also a hint on the highly disordered character of this mesophase. Only in one exceptional case (**1/3**), it was possible to get a fairly well aligned sample by surface alignment on a glass substrate. Preliminary investigations of this sample suggest that the diffuse scattering occurs perpendicular to the layer reflection. This points to an electron density modulation perpendicular to the layers, which is in line with the proposed inset of the segregation of the lipophilic alkyl chains from the rigid aromatic cores. However, further detailed investigations are necessary to obtain a more detailed picture of the structure of this unusual mesophase. [34]

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(34) This problem will be treated in a separate paper in more detail.

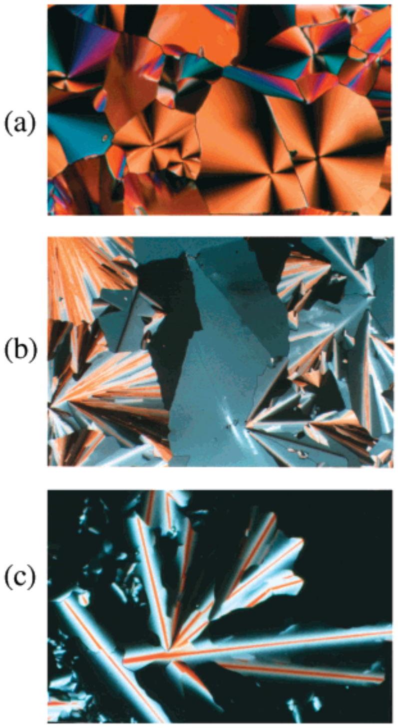

Figure 4. Optical photomicrographs (crossed polarizers) of (a) the $\mathrm{Col_r}$ phase (*c*2*mm*) of **2/9** at 70 °C, (b) the $\mathrm{Col_r}$ phase (*p*2*gg*) of **1/11** at 110 °C, and (c) the hexagonal columnar phase of **1/14** at 130 °C.

Columnar Phases. For **1/6** and **1/7**, an additional phase transition can be observed within the liquid crystalline state at 79 and 96 °C, respectively. This phase transition is accompanied by significant changes of the texture. In regions with a fan texture, the fans get broken and in the homeotropically aligned regions the occurrence of a strongly birefringent texture can be observed (see, for example, Figure 3c). For the higher homologues, the smectic phases get completely lost ($n \geq 9$). Instead, textures as typical for columnar phases occur on cooling from the isotropic liquid state. In dependence on the chain length three different types of textures can be found. Spherulitic and mosaic-like textures are typical for **1/9** (similar to Figure 4a). The textures of the mesophases of **1/10** and **1/11** have a distinct appearance, characterized by mosaic-like regions and regions with broken spherulites (Figure 4b). Compounds **1/12**, **1/14**, and **1/18** have large pseudoisotropic areas, occasionally interrupted by lancetlike birefringent regions, as shown in Figure 4c. The pseudoisotropic areas indicate the optically uniaxiality of this mesophase, and the textures are very similar to those observed for hexagonal columnar phases of disklike molecules. For **1/14** and **1/18**, this texture remains on cooling, until crystallization sets in. However, **1/12** slightly changes its texture on cooling. At ~100 °C, the homeotropically aligned regions become slightly birefringent, which points to an additional phase transition.

So, it seems that in dependence on the length of the lateral chains there are at least three different types of columnar mesophases. To determine their structure, the mesophases were investigated by X-ray diffraction with the Guinier film method (Huber), and additionally, well-aligned monodomains were investigated by means of a two-dimensional detector (HI-STAR, Siemens). Depending on the chain length, three completely different types of columnar phases were found.

(a) Centered Rectangular Columnar Phases of Compounds 1/6−1/9 and 3/9. The Guinier pattern of the low-temperature mesophases of **1/6** and **1/7** as well as the mesophase of **1/9** shows a diffuse wide-angle scattering which excludes crystalline phases or highly ordered smectic phases. In the low-angle regions few (two or three) nonequidistant reflexes were found (see Table 1 in the Supporting Information). However, it was not possible to get aligned samples with one of these compounds. Only in the case of **3/9**, which differs from **1/9** by the slightly longer spacer between one of the diol groups and the biphenyl core, was it possible to get fairly well aligned samples. The diffraction pattern of the low-temperature mesophase of **3/9** (see Figure 5a) can be indexed on the basis of a centered rectangular 2D lattice (space group *c*2*mm*) with the lattice parameter $a = 3.58$ and $b = 3.74$ nm. The length of this molecule in its most stretched conformation between the ends of the headgroups amounts to 2.4 nm. Thus, both lattice parameters are in between the molecular length and twice it. As the relative positions of these reflections in the columnar phases of **1/6−1/9** are almost identical to those in the diffraction pattern of the columnar phase of **3/9**, we have indexed their diffraction pattern in the same way, which means on the basis of a two-dimensional *c*2*mm* lattice. The obtained lattice parameters are in good agreement with the molecular dimensions (see Table 1). Only the ratio between the parameters *a* and *b* is different for the different compounds.

To deduce a suitable model for these columnar phases, the number of molecules located in the unit cell with a height of 0.45 nm (corresponding to the average distance between the molecules as indicated by the position of the diffuse wide-angle scattering) have been calculated by two different methods (see Table 1), [35] yielding values of about eight molecules. Figure 5b

Table 1. Compound Parameters[a]

compd	L/nm	phase type	a/nm	b/nm	$V_{\mathrm{cell}}/\mathrm{nm}^3$	$V_{\mathrm{mol}}/\mathrm{nm}^3$	M/g mol^{-1}	n_1	n_2	n_{av}
1/6	2.1	$\mathrm{Col_r}$, *c*2*mm*	3.43	3.22	4.97	0.479	419	10.4	7.1	8.8
1/9	2.1	$\mathrm{Col_r}$, *c*2*mm*	3.21	3.43	4.95	0.553	461	8.9	6.5	7.7
1/10	2.1	$\mathrm{Col_r}$, *p*2*gg*	5.5	6.2	15.35	0.578	475	26.5	19.5	23.0
1/11	2.1	$\mathrm{Col_r}$, *p*2*gg*	5.4	5.8	14.09	0.603	489	23.4	17.3	20.4
1/11′	2.1	$\mathrm{Col_r}$, *p*2*gg*	5.38	5.38	13.02	0.603	489	21.6	16.1	18.9
1/12	2.1	$\mathrm{Col_r}$, *p*2*gg*	5.33	6.17	14.80	0.628	503	23.6	17.7	20.7
1/12	2.1	$\mathrm{Col_h}$	3.36		4.40	0.628	503	7.0	5.3	6.2
1/14	2.1	$\mathrm{Col_h}$	3.59		5.02	0.677	531	7.4	5.7	6.6
1/18	2.1	$\mathrm{Col_h}$	3.66		5.22	0.777	587	6.7	5.4	6.1
3/9	2.4	$\mathrm{Col_r}$,,*c*2*mm*	3.58	3.74	6.03	0.603	489	10.0	7.4	8.7
4′/9	2.5	$\mathrm{Col_r}$, *c*2*mm*	3.82	3.65	6.27	0.628	503	10.0	7.5	8.7
P/11	1.7	$\mathrm{Col_h}$	2.94		3.37	0.513	415	6.6	4.9	5.8

[a] Molecular lengths (L, distances between the head groups in the most extended conformation, CPK models), phase types, lattice parameters (a, b), calculated volumes of the unit cells, assuming a height of 0.45 nm (V_{cell}), molecular volumes (V_{mol}), calculated using volume increments,[35] molecular masses (M), and number of molecules in each 0.45-nm-thick section of the unit cells (n_1 was calculated from the molar volume; n_2 was calculated according to the formula $n_2 = V_{\mathrm{cell}}(N_A/M)\rho$, assuming a density ρ of 1 g cm^{-3}, where N_A is the Avogadro constant; n_{av} is the average value of n_1 and n_2) of the columnar mesophases of the investigated bolaamphiphiles.

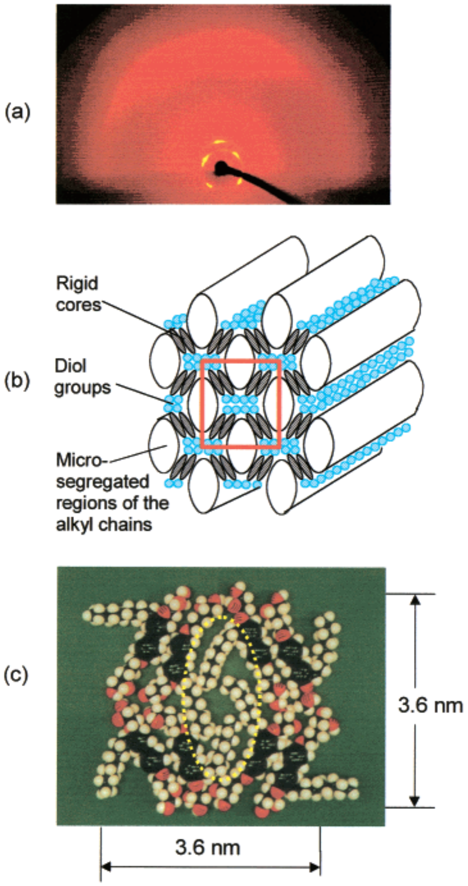

Figure 5. (a) X-ray diffraction pattern of an aligned sample of the columnar phase of **3/9** at 62 °C; (b) arrangement suggested for the molecules **3/9** in the rectangular columnar phase with the two-dimensional space group *c*2*mm*; (c) CPK models showing an arrangement of eight molecules **3/9** arranged in such a manner that the alkyl chains form a separate region surrounded by the bolaamphiphilic cores.

shows a possible arrangement of the molecules **3/9** in the columnar mesophase. Accordingly, the fluid alkyl chains are segregated in infinite columns. These columns interrupt the smectic layers in regular intervals with formation of ribbonlike segments. The biphenyl cores are held together via hydrogen bonding at both of their terminal ends and form cylinders around the lipophilic columns. Thereby, each column is enclosed by four bolaamphiphilic cores. So, on average, two biphenyl cores are arranged side by side within each of the cylinder walls separating the columns. The H-bonding networks at the ends of the biphenyl units are organized in separate ribbons where about eight diol groups are arranged on average in their cross section. The dimensions of this arrangement (∼3.6 nm × 3.6 nm according to CPK models; see Figure 5c) are in good agreement with the experimentally determined lattice parameter for **3/9**. Related models can be constructed for **1/6**−**1/9**. It seems that this special organization allows an efficient space filling for molecules with a medium length of the lateral chain (n = 6−9). However, there is an upper limit of the space available within these cylinders, enclosed between the four bolaamphiphilic cores. If the lateral chains are further elongated, the supramolecular organization is expected to change.

(b) Noncentered Rectangular Columnar Phases of Compounds 1/10−1/12. Indeed, the diffraction patterns of **1/10** and **1/11** and of the low-temperature phase of **1/12** are quite different from those of the mesophases of **1/6**−**1/9** and **3/9**, but similar to one another. Aligned samples were obtained for the mesophase of **1/11**[15] (Figure 6a,b). The outer diffuse scattering forms a closed ring, indicating a strong deviation of the molecular long axis from a preferred direction. In the small-angle regions a lot of spotlike reflections can be found, which can be indexed on the basis of a noncentered rectangular 2D lattice of the two-dimensional space group *p*2*gg* (the X-ray data are collected in Table 2 of the Supporting Information). Remarkably, the lattice parameters (a = 5.5 nm and b = 6.2 nm) are much larger than those of the Col$_r$ phases of **1/6**−**1/9** and **3/9** and also significantly larger than twice the molecular length (L = 2.1 nm).

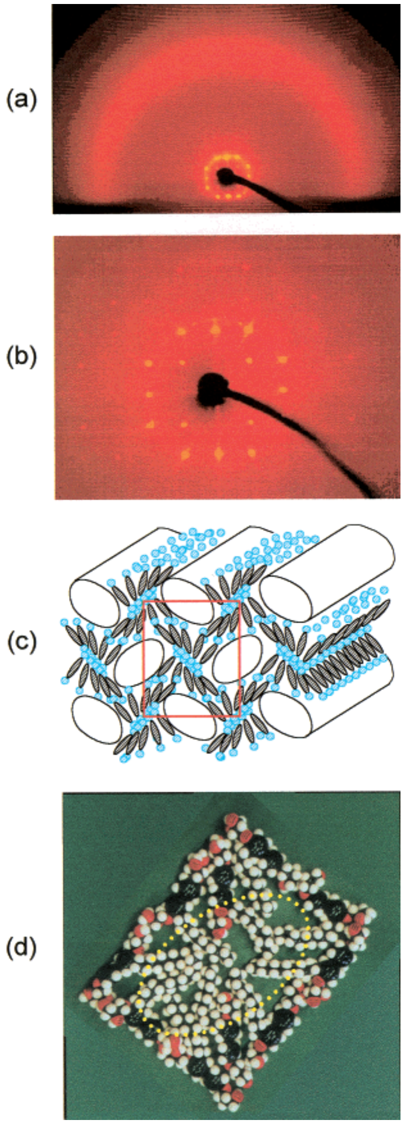

Figure 6. (a) X-ray diffraction pattern of aligned samples of the columnar mesophases of **1/11** at 113 °C; (b) model of a possible arrangement of the molecules **1/11** in the rectangular columnar phase with the two-dimensional space group *p*2*gg*; (c) CPK models showing an arrangement of 10 molecules of **1/11,** organized in such a manner that their bolaamphiphilic cores enclose the microsegregated regions of the alkyl chains.

In the columnar phase of **1/11**, ∼20 molecules are arranged on average side by side in the cross section of each unit cell (see Table 1). Taking into account the special symmetry requirements of the *p*2*gg* space group, the herringbone arrangement shown in Figure 6c,d is in good agreement with the experimentally determined lattice parameter. In this model, the molecules are organized in bilayer ribbons with ∼10 molecules

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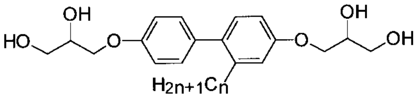
(35) Immrizi, A.; Perini, B. *Acta Crystallogr. Sect. A* **1977**, *33*, 216.

Table 2. Transition Temperatures (T/°C) and Corresponding Enthalpy Values (ΔH/kJ mol^{-1})^a of Compounds **1/1′** and **1/11′**



compd	n	phase transitions
1/1′	1	cr 97 SmA 164 is [16.4] [5.4]
1/11′	11	cr$_1$ 64 cr$_2$ 78 (Col$_r$ 76) is [16.3] [12.1] [3.8]

^{a} Values in brackets.

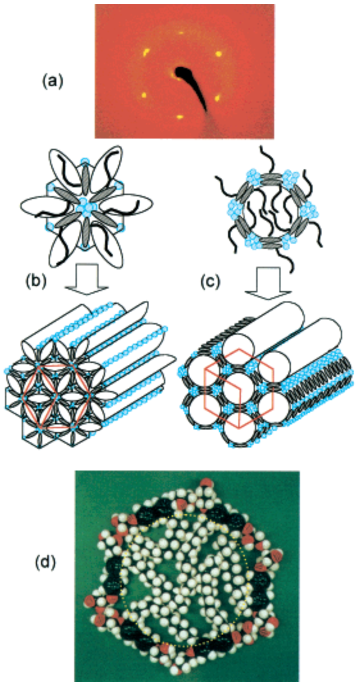
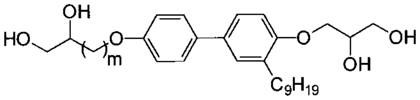


Figure 7. (a) X-ray diffraction pattern of an aligned sample of the hexagonal columnar phase of **1/14** at 135 °C; (b) starlike arrangement of the molecules in a Col$_h$ phase; (c) arrangement of cylinders; (d) CPK models showing six molecules of **1/14** arranged in such a manner that the bolaamphiphilic cores enclose the microsegregated regions of the alkyl chains.

in the cross section, i.e. ~5 molecules are arranged in their lateral diameter. In this way, the lipophilic regions are significantly enlarged and simultaneously the diameter of the cylinders containing the hydrogen-bonding networks can remain rather large. Compound **1/12** shows this type of columnar arrangement only in the low-temperature mesophase. At higher temperatures, a different columnar phase was found. Also, on further elongation of the lateral chain, the mesophase type changes again.

(c) Hexagonal Columnar Phases of Compounds 1/12−1/18. The high-temperature mesophase of **1/12** and the mesophases of **1/14** and **1/18** show the typical diffraction pattern of hexagonal columnar phases (see Figure 7a; the X-ray data are collected in Table 3 of the Supporting Information), which is in accordance with the phase assignment made by polarizing microscopy. The hexagonal lattice parameter amount a_{hex} = 3.36−3.66 nm for **1/12**−**1/18** (L = 2.1 nm) and slightly increase with elongation of the chains (see Table 1). In all Col$_h$ phases, about six molecules are arranged in average in the cross section of each cylinder (see Table 1). It is also remarkable that the lateral chains of the molecules **1/n** forming the Col$_h$ phases (n = 12−18) have twice the length of those forming the Col$_r$ phases with *c*2*mm* lattice (n = 6−9).

Table 3. Transition Temperatures (T/°C) and Corresponding Enthalpy Values (ΔH/kJ mol^{-1})^a of Compounds **m/9**



compd	m	phase transitions
9/9	9	cr 83 SmA$^+$ 96 is [27.1] [7.6]
6/9	6	cr 80 SmA$^+$ 84 is [23.6] [4.1]
4/9	4	cr 79 (SmA$^+$ 72) is [26.1] [2.3]
3/9	3	cr 79 (Col$_r$ 74) SmA$^+$ 92 is [20.7] [1.8] [3.1]
2/9	2	cr 66 Col$_r$ 78 is [14.9] [3.8]
1/9	1	cr 67 Col$_r$ 98 is [11.6] [4.9]

Two different arrangements of these molecules in the Col$_h$ phases are conceivable. (i) They can be arranged radially as schematically shown in Figure 7b. Here, in contrast to the rectangular columnar phases with *c*2*mm* lattice, only two, instead of four alkyl chains are located side by side in the cross section of the elliptical lipophilic cylinders. Because the chain length of these compounds is doubled in comparison to the molecules forming the *c*2*mm* lattice, the cross-sectional area of the lipophilic cylinders should be approximately the same in both phases. However, in the Col$_h$ phase, the cylinder walls have a thickness of only one aromatic core. (ii) The other possibility is shown in Figure 7c: The bolaamphiphilic cores form hexagonal cylinders around the circular lipophilic columns of the alkyl chains. Such an arrangement of six molecules of **1/14**, forming a hexagon around the segregated lipophilic chains, is displayed in Figure 7d, which shows that a quite good space filling within the cylinders is indeed possible. The cylinder model allows the segregation of the lipophilic chains into regions with a significantly larger and more circular cross-sectional area, so that their interfaces to the aromatic regions are reduced. Additionally, in this model, each of the columns of the hydrogen-bonding networks has six diol groups in the cross section. In the radial model (Figure 7b), only half of the number of diol groups are arranged in polar columns with this diameter, whereas the other polar cylinders are smaller. As the cooperative effect of hydrogen bonding between alcoholic OH groups leads to a preference of large aggregates,[36] the cylinder model seems more favorable.[37] However, on the basis of our present experimental results, we are not able to certainly exclude one of the two possible arrangements.

3. Influence of the Position of the Lateral Chain. The influence of the position of the lateral chain on the mesomorphic properties was investigated with **1/1′** and **1/11′** (see Table 2). In both cases, the mesophase stability of the 2-substituted

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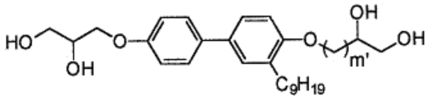
(36) (a) Frank, H. S.; Wen, W.-Y. *Discuss. Faraday Soc.* **1957**, *24*, 133. (b) Bellamy, L. J.; Pace, R. L. *Spectrochim. Acta* **1966**, 525. (c) Kleeberg, H. In *Intermolecular Forces, An Introduction to Modern Methods and Results*; Huyskens, P. L., Luck, W. A. P., Zeegers, T., Eds.; Springer: Berlin, 1991; p 251.

(37) Additionally, if the molecules under discussion are regarded as amphiphiles with an especially large headgroup (both diol groups and the biphenyl core are assumed to form the headgroup region), it can be expected that the alkyl chains are organized inside the cylinders formed by the polar groups as shown in model 7c. This organization is related to normal-type columnar mesophases of lyotropic[44] and thermotropic systems: (a) Borisch, K.; Tschierske, C.; Göring, P.; Diele, S. *Chem. Commun.* **1998**, 2711. (b) Fischer, S.; Fischer, H.; Diele, S.; Pelzl, G.; Jankowski, K.; Schmidt, R. R.; Vill, V. *Liq. Cryst.* **1994**, *17*, 885. (c) Borisch, K.; Tschierske, C.; Göring, P.; Diele, S. *Langmuir* **2000**, *16*, 6701.

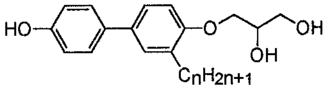
Table 4. Transition Temperatures (T/°C) and Corresponding Enthalpy Values (ΔH/kJ mol^{-1})[a] of Compounds **m′/9**



compd	m'	phase transitions
9′/9	9	cr 120 (SmA$^{(+)}$ 76) is
6′/9	6	cr 84 (SmA$^{(+)}$ 74) is [30.3] [1.0]
4′/9	4	cr 70 (Col$_r$ 61) is [25.9] [2.2]
1/9	1	cr 67 Col$_r$ 100 is [11.6] [4.9]

[a] Values in brackets.

Table 5. Transition Temperatures (T/°C) and Corresponding Enthalpy Values (ΔH/kJ mol^{-1})[a] of Compounds **P/n**



compd	n	phase transitions
P/0	0	cr 239 SmA 260 is [50.1][b] [2.6]
P/1	1	cr 155 SmA 172 is [29.6] [11.3]
P/3	3	cr 107 (SmA$^{(+)}$ 75) is [27.9] [2.7]
P/9	9	cr 126 (Col$_h$ 85) is [48.0]
P/11	11	cr 109 (Col$_h$ 102) is [42.3] [7.5]

[a] Values in brackets. [b] Sum of the transitions between different crystalline modifications: cr$_1$ 99 cr$_2$ 200 cr$_3$ 218 cr$_4$ 239.

molecules **1/1′** and **1/11′** is significantly reduced in comparison to the related 3-substituted **1/1** and **1/11** (see Figure 2). This is in accordance with results obtained with other amphiphilic[31] and non-amphiphilic liquid crystals[38] and could be due to changes of the conformation of the biphenyl unit (dihedral angle between the planes of the adjacent benzene rings) and to a stronger disturbance of the parallel alignment of the rigid cores by substituents in a central position. However, the mesophase type remains unchanged; i.e., both methyl-substituted compounds exhibit SmA phases, and even more interestingly, the columnar phase of the undecyl-substituted molecule **1/11′** has the same *p*2*gg* lattice ($a = b = 5.38$ nm,[39] the X-ray data are collected in Table 2 of the Supporting Information) as that of the isomeric **1/11** (see Figure 6c). This indicates that the position of the lateral chain has obviously no influence on the mesophase type. This behavior is completely different from that observed with polycatenar compounds for which a shifting of one alkyl chain from a peripheral to a central position at the rigid core leads to the loss of columnar and cubic mesophases and leads to nematic phases without positional long-range order.[9b,10]

4. **Influence of the Length of the Bolaamphiphilic Core. (a) Spacer Length.** The influence of the length of the spacer unit, connecting the rigid core with one of the diol headgroups, was investigated with the bolaamphiphiles **m/9** bearing a nonyl chain in position 3 at the biphenyl unit (Table 3). Centered rectangular columnar mesophases (*c*2*mm* lattice) with well-developed spherulitic textures were observed for **1/9**, **2/9** (Figure 4a), and **3/9** (Figure 3c) with rather short spacer units. In the case of **3/9** an additional SmA$^+$ phase was found above the columnar phase, and **4/9**, **6/9**, and **9/9** with longer spacers have exclusively SmA$^+$ phases (Table 3). For the SmA$^+$ phase of **3/9**, only a diffuse scattering in the small-angle region can be observed beside the diffuse wide-angle scattering, as typical for the distorted SmA$^+$ phase of **1/6**. However, in the diffraction pattern of the SmA$^+$ phase of **9/9**, a sharp reflection can be observed ($d = 2.5$ nm, $L = 3.2$) beside the diffuse small-angle scattering of low intensity. Hence, increasing the length of the aliphatic spacer reduces the disturbance of the layer arrangement. In the series of compounds **4′/9**, **6′/9**, and **9′/9**, which have the spacer at the other end, neighboring the lateral alkyl chain, the same phase sequence can be observed (see Table 4). The main difference is that **4′/9** has a columnar phase whereas the isomeric **4/9** is smectic. This shows that in the **m′/9** series the formation of columnar phases is slightly more facilitated than in the **m/9** series. However, in both series, the columnar phases are replaced by SmA$^{(+)}$ phases[40] on elongation of the spacer units; i.e., the effect of elongation of the bolaamphiphilic backbone is reverse to the effect of elongation of the lateral alkyl chain.

(b) Size of the Polar Groups. Quite surprisingly, even the phenols **P/n**, in which one of the 2,3-dihydroxypropoxy groups is replaced by a phenolic OH group, show liquid crystalline properties (see Table 5). Due to the lower hydrogen-bonding density, the stability of their mesophases is reduced in comparison to the related tetraols **1/n**. Again, the length of the lateral chain determines the mesophase type. Hexagonal columnar phases can be observed for the homologues **P/9** and **P/11** with long lateral chains, and the stability of this mesophase rises with elongation of the chains. The comparison with the tetraols **1/9** and **1/11** indicates that reduction of the length of the bolaamphiphilic core by replacement of one of the 2,3-dihydroxypropoxy groups by a single OH group leads to a transition from rectangular columnar phases (*c*2*mm* and *p*2*gg*, respectively) to hexagonal columnar arrangements. This shows that reduction of the length of the bolaamphilic central unit has the same effect as elongation of the lateral chains. This observation is in line with our models of the mesophase structures. Because less space is available within the cylinders built up by the significantly shorter cores of **P/9** and **P/11** ($L = 1.7$ nm), the length of the alkyl chains required to fill this space is reduced. Indeed, the hexagonal lattice parameter of **P11** amounts to $a_{\mathrm{hex}} = 2.94$ nm, which is significantly smaller than that of the columnar phases of the tetraol **1/12**.

Summary and Conclusions

The investigations have shown that attachment of a lateral alkyl chain to a bolaamphiphilic rigid core and its successive elongation leads to a transition from a smectic monolayer structure (SmA$_1$) via strongly distorted layer structures (SmA$^+$) to a variety of quite interesting new columnar phases. There are at least three different columnar phases that differ in the symmetry and in the values of their lattice parameter, so that on elongation of the lateral chain, the phase sequence SmA$_1$ − SmA$^+$ − Col$_r$(*c*2*mm*) − Col$_r$(*p*2*gg*) − Col$_h$(*p*6*mm*) can be observed (Figure 8).

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(38) (a) Gray, G. W.; Hird, M.; Toyne, K. J. *Mol. Cryst. Liq. Cryst.* **1991**, *195*, 221. (b) Hird, M.; Toyne, K. J.; Hindmarrsh, P.; Jones, J. C.; Minter, V. *Mol. Cryst. Liq. Cryst.* **1995**, *260*, 227. (c) Andersch, J.; Tschierske, C.; Diele, S.; Lose, D. *J. Mater. Chem.* **1996**, *6*, 1297.

(39) Because the texture of **1/11′** is identical with that of **1/11** and because of the fact that no homeotropically aligned regions can be obtained, it can be assumed that this mesophase is optical biaxial. Therefore, this mesophase cannot be a tetragonal phase, though the lattice parameters *a* and *b* are identical.

(40) Due to rapid crystallization of **6′/9** and **9′/9**, the confirmation of the smectic phase type (SmA$_1$ vs SmA$^+$) by X-ray scattering was not possible with these molecules.

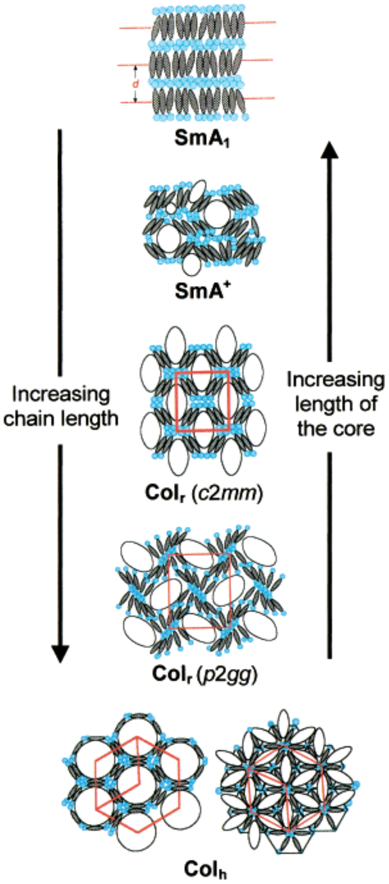

Figure 8. Change of the mesophase morphology of the bolaamphiphilic molecules in dependence of the length of the lateral chains with respect to the length of the rigid bolaamphiphilic core.

This phase sequence should be the result of the segregation of the three incompatible building blocks, the attractive forces provided by hydrogen bonding and the rigid rodlike shape of the biphenyl cores. The well-defined layer structure of the parent bolaamphiphile **1/0**, built up by biphenyl cores on the one side and hydrogen-bonding networks on the other side, is disturbed by the lateral alkyl substituents. It leads to the distorted layer structures of the SmA^+ phases, first. On further elongation of the lateral chains, the tendency of segregation between the aromatic cores and chains increases and leads to columns of microsegregated regions, arranged in a two-dimensional lattice. Simultaneously, the layers of the biphenyl units and the hydrogen-bonding networks are interrupted in regular intervals, leading to ribbons of biphenyl cores and ribbons of hydrogen-bonding networks arranged in a regular way. The attractive hydrogen-bonding networks at both molecular ends of the rigid bolaamphiphilic cores fix the molecules side by side. In this way, the bolaamphiphilic cores form networks of cylinders, filled with the fluid alkyl chains. So, the alkyl chains are enclosed in constrained environments. Therefore, the space required by the lipophilic chains with respect to the length of the bolaamphiphilic cores determines the mesophase type. The transition from the *c*2*mm* lattice ($n = 6-9$) to the *p*6*mm* lattice ($n = 12-18$) can take place either by enhancement of the number of lipophilic columns (accompanied by the reduction of the number of calamitic cores in the cross section of the aromatic ribbons; see model 7b) or by an increase in the size of the lipophilic regions, which requires that the number of calamitic cores surrounding the lipophilic columns is enhanced to six, on average (see model 7c). Obviously, for the organization of the compounds with an intermediate chain length ($n = 10-12$), the herringbone-like organization within the *p*2*gg* lattice represents the best compromise between the *c*2*mm* and the *p*6*mm* lattice. Hence, the phase sequence on increasing the length of the lateral chains can be explained by rather simple geometric considerations.

This explanation also allows us to understand the effect of the spacer units in **m/9** and **m′/9**. As elongation of the spacers increases the length of the bolaamphiphilic core, the space available for the accommodation of the lateral alkyl chains is enlarged. Furthermore, the aliphatic spacers are compatible with the lateral chains. In this way, the segregation tendency of the lateral chains is reduced. As a consequence, the columnar phases get lost and they are replaced by $SmA^{(+)}$ phases. On the other hand, the reduction of the size of the bolaamphiphilic core by replacement of one of the 2,3-dihydroxypropoxy groups by an OH group (**P/9** and **P/11**) leads to the change of the mesophase type in the other direction; i.e., Col_r phases are replaced by Col_h phases.

The fact that the mesophase type does not change by variation of the position of the lateral chain (**1/11** vs **1/11′**) is very important. It confirms that, although in compounds **1/n** the lateral substituents are positioned adjacent to one of the terminal groups as in polycatenar mesogens, their organization should be quite distinct from them. The main difference is the incompatibility of the lateral alkyl chains with the terminal diol groups[21] which requires their segregation into different subspaces.

It should also be pointed out that the hydrogen-bonding networks between the hydroxy groups are highly dynamic,[36,41] allowing a high degree of fluidity in these systems. Also the alignment of the biphenyl cores is by far not so perfect as suggested by the shown models. The high degree of local disorder is also confirmed by the diffuse scattering in the wide-angle region of all diffraction pattern. Because of this dynamic character, slight variations of the volume fraction of the lipophilic chains can be compensated by changes of the dimensions of the cylinders, before at a certain critical volume fraction the mesophase type suddenly changes.

The proposed morphologies of the columnar mesophases are quite different from those of all other liquid crystalline systems. In the columnar phases of disklike molecules[42] and polycatenar compounds[10] as well as in the thermotropic[43] and lyotropic columnar mesophases[44] of conventional amphiphilic molecules, the columns are surrounded by a *continuum*, in most cases consisting of fluid alkyl chains (or formed by solvent molecules as in the case of normal lyotropic systems). In the new phases reported herein, space is subdivided into three distinct sets of subspaces: columns of hydrogen-bonding networks, ribbons of aromatic cores, and cylinders filled with the alkyl chains. This is due to the fact that these molecules are built up by three instead of only two chemically incompatible building blocks and due to their nonlinear combination, which enhance the complexity of the self-organized systems. Interestingly, similar

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morphologies have very recently been reported for flexible ternary block copolymers, namely, ABC heteroarm star terpolymers.[3b] In these polymer systems, beside lamellar morphologies, tetragonal[45] and hexagonal morphologies, built up by three sets of distinct cylinders, also have been found in dependence on the volume fraction of the three incompatible blocks.[3b,46] The main difference of the mesophases of the low molecular mass block molecules reported herein is that their organized structures have a significantly smaller length scale (∼2−5 nm; nanophase separation[47]) than those of the polymer systems (∼100 nm; microphase separation[1]). Additionally, they have a lower viscosity and can respond much faster to external stimuli, which is favorable for potential applications. As another difference, in low molecular weight systems, the unfavorable contribution of the entropy of mixing requires a larger incompatibility of the segments to obtain segregation. Herein, we have successfully shown that the competitive combination of polar/apolar microsegregation and rigid/flexible incompatibility can overcome this problem. It turned out to be an appropriate designing principle for low molecular weight molecules, which are able to self-assemble to well-organized states of soft matter with complex morphologies. Furthermore, the investigated compounds represent a novel class of materials, capable of forming supramolecular columnar mesophases[48] and providing an interesting new pathway for the transition from a layerlike to a columnar organization of soft matter.[49] By further variation of the molecular structure, many other new and exciting mesophase morphologies should be detected in the future. These investigations are presently on the way.

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Supporting Information Available: Schemes describing the synthesis of **P/n**, **m/n**, and **m′/n**, the experimental procedures, and analytical data of all compounds and tables with X-ray data of **1/6**, **1/9**, **3/9**, **4′/9**, **1/11**, **1/11′**, **1/12**, **1/14**, **1/18**, and **P/11**. This material is available free of charge via the Internet at http://pubs.acs.org.

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(45) The formation of a tetragonal 2D lattice instead of a rectangular one should be due to the flexibility of the copolymer.

(46) Moreover, a Col$_h$ phase, with a structure related to the organization suggested in Figure 7c has recently been reported for a LC-main-chain polymer, built up by linear chains of rodlike rigid cores comprising long lateral alkyl chains. The segregation of the lateral alkyl chains from the polymer backbones is the driving force for this organization. However, in contrast to our systems, where the aromatic cores are arranged perpendicular to the column long axes, in the Col$_h$ phase of this polymer system, the rigid polymer backbones are arranged parallel to the column long axes: Watanabe, J.; Sekine, N.; Nematsu, T.; Sone, M.; Kricheldorf, H. R. *Macromolecules* **1996**, *29*, 4816.

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