

Liquid Crystalline Bolaamphiphiles with Semiperfluorinated Lateral Chains: Competition between Layerlike and Honeycomb-Like Organization

Xiaohong Cheng,^{†,§} Malay Kumar Das,[‡] Ute Baumeister,[‡] Siegmur Diele,[‡] and Carsten Tschierske^{*,†}

Contribution from the Institute of Organic Chemistry, University Halle, Kurt-Mothes-Str.2, D-06120 Halle, Germany, and Institute of Physical Chemistry, University Halle, Mühlpforte 1, D-06108 Halle, Germany

Received March 29, 2004; E-mail: Tschierske@chemie.uni-halle.de

Abstract: Novel bolaamphiphilic triblockmolecules consisting of a rigid biphenyl unit, with a polar 2,3-dihydroxypropyloxy group and a phenolic OH group at opposite ends, as well as a semiperfluorinated chain in a lateral position have been synthesized via palladium catalyzed cross coupling reactions as the key steps. The thermotropic liquid crystalline behavior of these compounds was investigated by polarized light microscopy, DSC and X-ray scattering, and the influence of the length of the lateral chain on the mesomorphic properties was studied. The compound with the shortest chain as well as the long chain derivatives form lamellar mesophases composed of segregated layers of the bolaamphiphilic moieties and sublayers comprising the fluid lateral chains. The layers within the lamellar phases of the short chain compound adopt a positional correlation, leading to a 2D lattice ($Col_h/p2mm$), whereas the layers of the lamellar phases of the long chain derivatives are noncorrelated (Lam). Compounds with a medium chain length organize into columnar phases, where the nonpolar lateral chains segregate into columns, which are embedded in networks of regular (Col_h) or stretched ($Col_h/c2mm$) hexagonal cylinder shells consisting of the bolaamphiphilic units. In total, an unusual phase sequence was found, where, with respect to the chain length, columnar mesophases occur between two mesophases with layer organization.

Introduction

The design of novel molecules forming new types of liquid crystalline (LC) phases is of contemporary interest for the design of new materials with useful application properties¹ and also for the fundamental understanding of soft-matter self-organization.^{2,3} There are three main routes to tailor the self-organization in LC systems; these are the molecular shape, microsegregation effects, and chirality. In classical LC systems the shape of rigid units plays a dominating role for the organization of the molecules, leading to nematic phases, layer structures (rodlike molecules; smectic phases), and 2D arrangements of columns (disklike molecules; columnar phases).¹ The relatively new concept of bent-core molecules ("banana molecules") has recently lead to a variety of new LC phases characterized by supramolecular chirality and polar order.⁴ Molecular chirality gives rise to helical superstructures which are in competition with the organization provided by the molecular shape.⁵ Segregation is

the fundamental driving force of the self-association of amphiphilic molecules.⁶ Low molecular weight, dendritic or polymeric amphiphiles (e.g. block copolymers), composed of only

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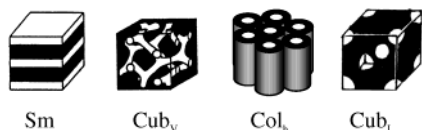


Figure 1. General phase sequence of conventional amphiphiles with respect to the increasing volume fraction of one of the incompatible parts.

two different molecular parts usually change their organization depending on the volume fractions of the two incompatible parts. Thereby, starting from layer structures (smectic phases) for nearly equal volume fractions, the mesophase morphology changes at first to columnar phases and then to mesophases composed of spheroidal aggregates with increasing volume fraction of one of the parts (see Figure 1).^{7–11} Additionally, bicontinuous cubic phases (Cub_v) and perforated layer structures were observed as intermediate phases at the transition from lamellar to columnar organization.^{7,9,10} However, the number of possible structures which can be realized with these binary amphiphiles is limited mainly to these rather simple morphologies.

Mesophase morphologies with higher levels of complexity can be achieved with polyphilic (macro)molecules, combining more than two incompatible units, as successfully demonstrated for ABC-triblock copolymers.^{7,12–15} The combination of am-

phiphilic self-organization with the organizing forces provided by rigid (in most cases rodlike) segments is another route to novel mesophase morphologies. One of the first important steps in this direction was done with polycatenar molecules (rodlike molecules with more than one chain at each terminus), where the parallel organization of extended linear rigid cores is in competition with the space filling of the alkyl chains attached to the ends.¹⁶ Rod-coil molecules¹⁷ and molecules incorporating bulky oligosiloxane¹⁸ or perfluoroalkyl segments^{19–21} also follow this design strategy. Polyphilic molecules, supermolecules, and dendrimers incorporating rodlike segments were found to organize into ABC-triple layer and “onion-like” superstructures.^{18,19,22} In these polyphilic molecules the organizing forces provided by the rigid segments are in line with the

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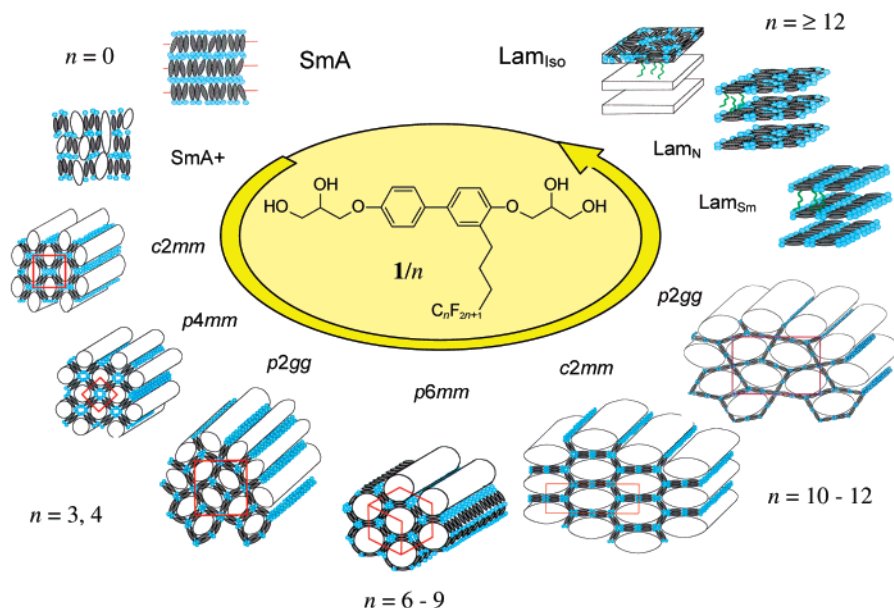


Figure 2. Dependence of the liquid crystalline phases of the bolaamphiphilic tetraols $1/n$ with respect to the length of the lateral semiperfluoroalkyl chains and models for the organization of the molecules $1/n$ into these mesophases (blue = hydrogen bonding networks of the terminal diol groups; white = microsegregated regions of the lateral chains; gray = rigid biphenyl units).^{27b}

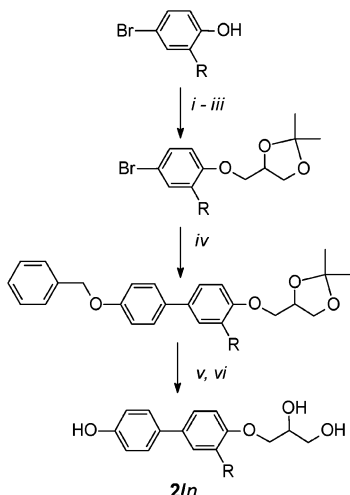
amphiphilic self-organization, enhancing each other. Several attempts have also been made to disturb the self-organization of rodlike segments by lateral substituents²³ or by attaching rigid units laterally to polymer backbones^{24,19n} or to dendritic cores.²⁵ In most cases only a reduction of the molecular order was achieved, i.e., the positional order within smectic phases was lost and these phases were replaced by nematic phases having only orientational long-range order. In few cases, however, smectic phases remain¹⁹ⁿ or columnar phases were found.²⁵ A new hexagonal columnar mesophase (Col_h) was reported for some semirigid main-chain polymers containing long alkyl chains attached laterally to the polymer backbone.²⁶ In this columnar phase the semirigid polymer backbones form cylinder walls, which are filled by the lateral alkyl chains. This might be regarded as a first example, demonstrating that competitive combination of the organization of rigid segments and the organization provided by microsegregation can lead to new mesophase morphologies. A further increase of the mesophase complexity of LC systems can be expected if rigid segments are in competition with a multilevel segregation. An especially wide variety of different complex soft matter superstructures was recently obtained by competitive combination of hydrogen bonding functional groups, calamitic rigid units, and semiper-

fluorinated alkyl chains in the bolaamphiphiles $1/n$.²⁷ Here, the organization of the fluid nonpolar chains is in competition with the organization provided by the rigid biphenyl units and the polar hydrogen bonding networks. As shown in Figure 2, elongation of the lateral chain of compounds $1/n$ gives rise to a transition from a conventional smectic A phase (molecules are aligned, on average, perpendicular to the layer planes, SmA) via a strongly distorted structure (SmA+)^{27a} and a series of columnar phases composed of polygonal cylinders (rhombuses, Col_r/c2mm; squares, Col_{sq}/p4mm; pentagons, Col_p/p2gg; hexagons, Col_h/p6mm; stretched hexagons, c2mm)²⁷ to a novel type of lamellar phases (Lam).²⁸ In the columnar mesophases the fluid nonpolar chains are organized within columns and the bolaamphiphilic units form networks of cylinder shells framing these columns. The space required by the (semiperfluoro)alkyl chains with respect to the length of the bolaamphiphilic moieties determines the shape of the cylinders and gives rise to different types of 2D lattices.^{27,29} If the size of the lateral chains is further extended, then the nonpolar columns fuse together to yield infinite layers. This gives rise to a novel class of lamellar liquid crystalline phases in which the rigid rodlike segments are organized *parallel* to the layer planes (designated as Lam).^{27b,28,30} A stepwise occurrence of orientational and positional order within the polar sublayers is thought to lead to different subtypes

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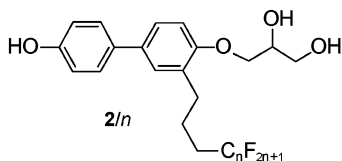
Scheme 1. Synthesis of Compounds $2/n$ ($R = -(CH_2)_3-C_nF_{2n+1}$ with $n = 3, 4, 6, 7, \text{iso-}7, 8, 10, 12$)^a



^a Reagents and conditions: (i) 1. $CH_2=CH-CH_2Br$, K_2CO_3 , CH_3CN , reflux, 2 h; (ii) OsO_4 , *N*-methylmorpholine-*N*-oxide, H_2O , acetone, 25 °C, 2 h; (iii) $Me_2C(OMe)_2$, $Py \cdot TosOH$, CH_2Cl_2 , 25 °C, 24 h; (iv) 4-benzyloxyphenyl boronic acid, $Pd(PPh_3)_4$, $NaHCO_3$, glyme, H_2O , reflux, 6 h; (v) 10% HCl , $EtOH$, 25 °C, 24 h; (vi) H_2 , Pd/C , $EtOAc$, 30 °C, 24 h.

of these lamellar phases. It is a fascinating feature of these materials that a series of 10 distinct new LC phases can be obtained by the minimal structural change provided by the variation of the length of the semiperfluorinated chain.

In this report novel bolaamphiphiles $2/n$ will be described, in which one of the polar 2,3-dihydroxypropyloxy units of $1/n$ is replaced by a single OH group. For these compounds a series of eight different liquid crystalline phases (three lamellar and five columnar) was found with increasing length of the lateral chain. However the structure of three of the columnar phases is different from those observed for compounds $1/n$. An additional unique feature of the series of compounds $2/n$ is that two rectangular columnar mesophases and a hexagonal columnar mesophase appear as intermediate phases between lamellar mesophases of the same type. This is a quite unusual phase sequence, which is quite different from the behavior of conventional amphiphiles, where the columnar phases occur at the transition from lamellar to spheroidal micellar organization (Figure 1).



Results and Discussion

1. Synthesis. Scheme 1 describes the synthesis of compounds $2/n$. The preparation of the 2-substituted 4-bromophenols, used as starting materials, was reported earlier.^{27b} The introduction of the terminal propane-2,3-diol groups was achieved by allylation followed by OsO_4 -catalyzed dihydroxylation.^{31,32} The 1,2-diol groups were protected as cyclic acetals, and then Miyaura–Suzuki couplings³³ were performed with 4-benzyl-

oxybenzene boronic acid, which yielded the biphenyl skeleton. The protecting groups were removed by acidolytic cleavage of the acetonide groups, followed by catalytic hydrogenation of the benzyl groups. All final products were purified by preparative centrifugal thin-layer chromatography with a Chromatotron (Harrison Research) and by repeated crystallization from appropriate solvents and characterized by 1H NMR, ^{13}C NMR, ^{19}F NMR, and elemental analysis. The purity was additionally checked by TLC. Experimental details and analytical data are reported in the Supporting Information.

2. Mesomorphic Properties. 2.1. General Trends. All compounds were investigated by polarized light optical microscopy, differential scanning calorimetry, and X-ray diffraction. The transition temperatures and corresponding enthalpy values are collated in Table 1. With exception of compound $2/3$, all compounds show enantiotropic (thermodynamically stable) liquid crystalline phases, whereas the mesophase of $2/3$ is monotropic (metastable). In comparison with the related tetraols $1/n$,^{27b} the mesophase stability is reduced by 20 °C–50 °C, due to the reduced number of hydrogen bonding sites which reduces the cohesive forces. As was also observed in the series of bolaamphiphilic tetraols $1/n$, the mesophase stability strongly rises with elongation of the lateral chain and the mesophase type is highly dependent upon the length of the semiperfluorinated chain, which is shown graphically in Figure 3. A sequence of eight different liquid crystalline supermolecular organizations was found for this homologous series.

2.2. Lamellar Phases of Compounds $2/7$ – $2/12$. The mesophases of $2/8$ – $2/12$ have already been analyzed in detail in a recent paper.^{28a} Accordingly, upon cooling compounds $2/10$ and $2/12$ from the isotropic liquid state, the optically uniaxial Lam_{Iso} mesophase is formed at first. This mesophase is proposed to be built up by an alternating sequence of layers of the nonpolar lateral chains and layers of the bolaamphiphilic 4'-(2,3-dihydroxypropoxy)biphenyl-4-ol units. Within the layers formed by the bolaamphiphilic moieties, the rodlike biphenyl units are organized without long-range in-plane order (Lam_{Iso} phase). Upon further cooling of compounds $2/10$ and $2/12$ an additional phase transition into an optically biaxial lamellar mesophase takes place. In this lamellar phase the biphenyl units adopt a long-range orientational order within the aromatic sublayers, parallel to the layer planes (Lam_N , see Figure 4c). In the case of compound $2/10$ a third phase transition is observed. It is thought that at the transition into this mesophase (Lam_{Sm}) the biphenyl cores adopt a positional correlation within each layer, whereas between adjacent layers there is only an orientational long-range correlation but no positional correlation. These three phases have nearly identical X-ray diffraction patterns,^{28a} characterized by a sharp spotlike layer reflection on the meridian and associated higher order reflections up to the fourth order as well as a nearly circular diffuse wide angle scattering (similar to the diffraction pattern shown in Figure 6a).^{28a} In the case of compound $2/8$ only one phase, the Lam_{Sm} phase, was detected.

Three different mesophases were found for compound $2/7$. The texture (Figure 5) and X-ray diffraction pattern (Figure 6a) of the high-temperature mesophase are identical to those reported for $2/8$,^{28a} and therefore it is also assigned as Lam_{Sm}

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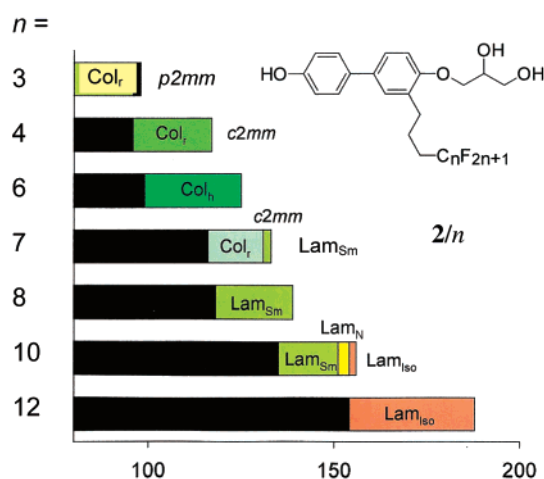
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Table 1. Mesophases, Phase Transition Temperatures, Phase Transition Enthalpies (Lower Lines in Italics), and Other Parameters of the Bolaamphiphiles **2/n**^a

2/n

Comp.	n	Phase Transitions (<i>T</i> / °C)	<i>a</i> /nm	<i>b</i> /nm	<i>d</i> /nm	<i>V</i> _{cell} /nm ³	<i>V</i> _{mol} /nm ³	<i>n</i> _{cell}	<i>n</i> _{cell,calc}	<i>n</i> _{wall}
		<i>ΔH</i> /kJ mol ⁻¹								
2/3	3	Cr 98 (Col _r /p2mm 96) Iso 27.4 5.5	1.57	2.16		1.53	0.517	3.0		
2/4	4	Cr 87 Col _r /c2mm 117 Iso 35.6 7.4	3.13	4.62		6.51	0.554	11.7	12	2.0
2/6	6	Cr 99 Col _h 125 Iso 16.5 5.9	2.90			3.28	0.627	5.2	6	1.7
2/7	7	Cr 116 (Col _r /c2mm 102) Col _r /c2mm 131 Lam _{Sm} 132 Iso 17.5 0.85 6.0 ^b	3.0 ^c 2.96 ^d	8.21 ^c 5.59 ^d		11.1 ^c 7.45 ^d	0.664	16.7 ^c 11.2 ^d	16 ^c 12 ^d	2.1 ^c 1.9 ^d
2/i7	7	Cr <20 Col _r /c2mm 131 Iso 6.4	2.97	5.36	2.8 ^c	7.16	0.664	10.8	12	1.8
2/8	8	Cr 119 Lam _{Sm} 139 Iso 0.9 ^f 6.1			2.96					
2/10	10	Cr 135 Lam _{Sm} 152 Lam _N 153 Lam _{iso} 156 Iso 25.0 1.9 ^b 1.8			3.41					
2/12	12	Cr 154 (Lam _N 142) Lam _{iso} 188 Iso 17.5 0.46 1.8			3.8					

^a The transition temperatures were determined by DSC (first heating scan, 10 K min⁻¹); *a, b* = lattice parameters and *d* = layer distance, derived from the Guinier pattern with exception of the values for **2/3**, which were obtained from the 2D diffraction pattern of an aligned sample; *V*_{cell} = volume of a unit cell with a height of *h* = 0.45 nm;³⁴ *V*_{mol} = crystal volume for a single molecule as calculated using the volume increments reported by Immirzi.³⁵ *n*_{cell} = number of molecules in the unit cell, calculated according to *n*_{cell} = *V*_{cell}/*V*_{mol}; *n*_{cell,calc} = number of molecules arranged in the cross section of the unit cell as theoretically required by the model of the mesophase. This number is calculated from the number of biphenyl units required for the formation of the polygonal frames and the number of columns per unit cell. *n*_{wall} = average thickness of the cylinder walls given by the number of biphenyl units arranged in average side by side in the walls separating two adjacent cylinder cores. Abbreviations: Cr = crystalline solid; Col_r, Col_h, Col₂, Col₃ = rectangular columnar mesophases; the lattice type is given in italics; Col_h = hexagonal columnar phase; Lam_{iso} = lamellar phase with an arrangement of rodlike units without in-plane order; Lam_N = lamellar phase with an arrangement of biphenyl units parallel to the layer planes and with an in-plane orientational order; Lam_{Sm} = lamellar phase for which an arrangement of biphenyl units parallel to the layer planes with an in-plane orientational and positional order, but without positional correlation of adjacent layers, is proposed (see Figure 4d); Iso = isotropic liquid; the perfluorinated segment of compound **2/i7** is branched at the terminal end (*iso*-perfluoroheptyl segment) whereas all other chains are unbranched. ^b Phase transition not resolved. ^c Col_r/c2mm phase. ^d Col_r/c2mm phase. ^e Lam_{Sm} phase. ^f Only partial crystallization was observed.

**Figure 3.** Dependence of the liquid crystalline phases of compounds **2/n** with respect to the length of the semiperfluorinated lateral chain. For clarity, the monotropic low-temperature phases Col_r/c2mm of **2/7** and Lam_N of **2/12** are not shown.

with *d* = 2.8 nm.³⁰ The two low-temperature phases are columnar phases and will be discussed in the following section.

2.3. Centered Rectangular and Hexagonal Columnar Phases of Compounds **2/4–2/7**: Regular and Distorted Hexagonal Cylinders.

The diffraction pattern of **2/7** changes completely at 131 °C (Figure 6b). The new diffraction pattern can be indexed on the basis of a centered rectangular columnar phase (*c2mm*) with the lattice parameters *a* = 2.96 nm and *b* = 5.59 nm. The transition to this *c2mm* phase (designated as Col_{r1}) can also be observed by a change in the birefringence of the optical texture at this temperature (see Figure S1a,b in the Supporting Information). Upon further cooling to 102 °C the texture becomes broken and the birefringence strongly changes again (see Figure S1c,d in the Supporting Information), indicating an additional phase transition. Also the diffraction pattern changes at these transitions (Figure 6c). It can now be explained by the superposition of two differently aligned domains (fiber symmetry of the sample), the normal of the (110) plane of which is tilted by a few degrees (~4°) with respect to the normal of the glass surface. Figure 6d shows the two reciprocal lattices which are in the reflection position. Based on these considerations this pattern can be assigned to a centered rectangular *c2mm* lattice, in which the lattice parameter *a* = 3.0 nm is

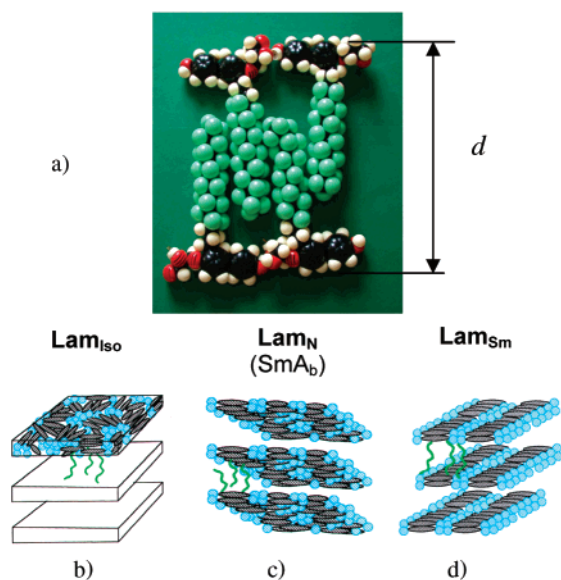


Figure 4. (a) CPK model of four molecules of **2/12** arranged into a smectic layer and (b–d) models of the organization of the molecules in the different lamellar mesophases. On average the aromatic sublayers have a thickness of about twice to three times the width of the aromatic unit; i.e., two to three biphenyl cores are arranged side by side in the cross section of the aromatic sublayers. For clarity only an arrangement of two molecules in the cross section of the layers is shown. The lateral chains of the additional molecules fill the void space within the nonpolar sublayers. Within the nonpolar sublayers the chains are highly disordered; the arrangement in part a shows an idealized intercalated organization of the chains, which represents only one of the numerous possible arrangements in this dynamic equilibrium. Details of the phase assignment of the Lam phases were reported in ref 28a.

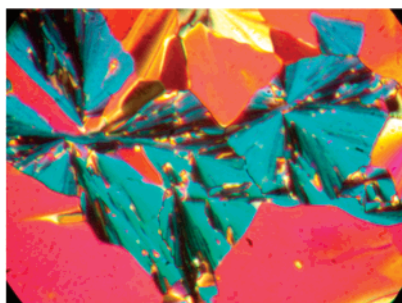


Figure 5. Optical photomicrograph (crossed polarizers, $T = 130\text{ }^{\circ}\text{C}$) of the texture of the Lam_{Sm} phase of compound **2/7**. The textures of the other mesophases are shown in Figure S1 of the Supporting Information.

roughly the same as that in the high-temperature columnar phase ($c2mm$), whereas the parameter b is significantly enlarged (this phase is designated as Col_{I2}). The unusually large lattice parameter $b = 8.21\text{ nm}$ corresponds to five times the molecular length, and this can be explained using a model where the cylinder shells are formed by the organization of eight bolaamphiphilic moieties around the cylinder cores, as shown in Figure 6e. These shells adopt a strongly deformed hexagonal cross sectional shape where two sides are formed by end-to-end dimers as already found for the $c2mm$ phases of tetraols **1/10**–**1/12** (Figure 2).^{27b} The calculated number of molecules per unit cell (n_{cell} , calculated with $h = 0.45\text{ nm}$;³⁴ see Table 1) is about 16.7, which is in good agreement with this model, requiring 16 molecules. Possible structures of the high-temperature columnar phase ($Col_{I1}/c2mm$) will be discussed at the end of this section.

In contrast to the straight chain compound **2/7**, the branched isomeric compound **2/i7** shows only one mesophase. This

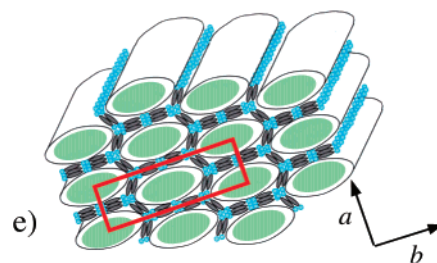
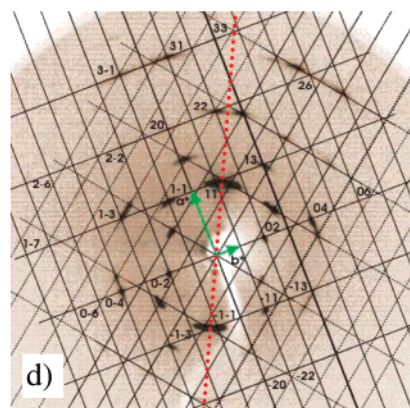
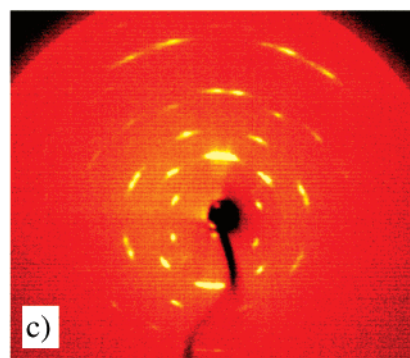
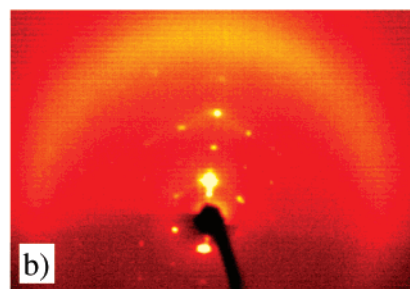
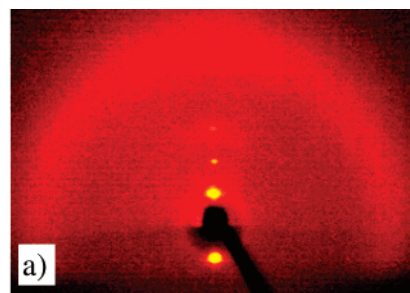


Figure 6. X-ray diffraction pattern of the mesophases of compound **2/7**: (a) Lam_{Sm} phase at $131.5\text{ }^{\circ}\text{C}$; (b) $Col_{I1}/c2mm$ phase at $115\text{ }^{\circ}\text{C}$. (c, d) $Col_{I2}/c2mm$ phase at $93\text{ }^{\circ}\text{C}$ (small angle region); (e) model of the $Col_{I2}/c2mm$ phase showing one of the two alignments parallel to the (110) plane.

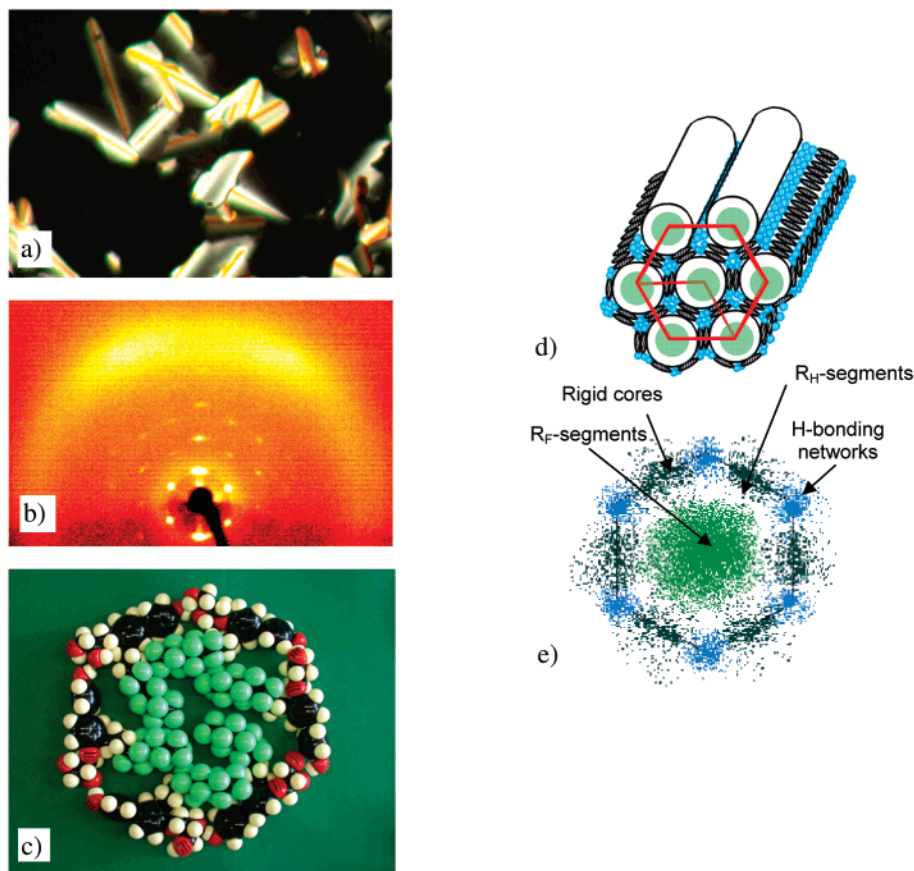


Figure 7. (a) Texture (crossed polarizers) of the Col_h phase of compound **2/6** at 120 °C, dark areas are homeotropically aligned regions; (b) X-ray diffraction pattern of an aligned sample of the Col_h phase at 80 °C; (c) CPK models showing six molecules of **2/6** forming a hexagon; (d) model showing the molecular organization within the mesophase; (e) more realistic picture of the Col_h phase, showing the diffuse character of the microsegregated regions.

compound does not crystallize, even after prolonged storage at room temperature. However, the mesophase stability (i.e., the clearing temperature) is not changed by introduction of the branching. The optical texture as well as the diffraction pattern of **2/7** are very similar to that of the high temperature $c2mm$ phase (Col_{r1}) of the isomeric compound **2/7**. This diffraction pattern can also be indexed on the basis of a $c2mm$ lattice with the lattice parameters $a = 2.97$ nm and $b = 5.36$ nm, which are close to those of the Col_{r1} phase of **2/7**. Miscibility studies additionally confirm that both mesophases belong to the same phase type (no local minimum of the mesophase transition temperature or any phase boundary could be detected in the contact region between both compounds).

The texture of the shorter homologue **2/6** is completely different from those of all other compounds of this series. It is characterized by large homeotropically aligned regions (indicating the optical uniaxiality of this mesophase) containing birefringent filaments as typical for hexagonal columnar phases (see Figure 7a).³⁶ The X-ray diffraction pattern also indicates a hexagonal columnar structure for this mesophase (Figure 7b).

(34) Herein, the value $h = 0.45$ nm was used in all calculations, independent of the actual position of the maximum of the wide angle scattering in the diffraction pattern. The reason is that the bolaamphiphilic units (their average diameter is 0.45 nm) are responsible for the lattice of the cylinder shells, whereas the semiperfluoroalkyl chains (their average diameter is 0.54 nm) fill the channels within this structure as a fluid continuum (the diffuse wide angle reflection forms a closed ring). Hence, only the total volume of these chains is important.

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The lattice parameter was calculated to be $a_{\text{hex}} = 2.90$ nm. It is thought that the structure of this mesophase is essentially the same as that proposed for the Col_h phases of the bolaamphiphilic tetraols **1/n** with a medium chain length ($n = 6–9$; see Figures 2 and 7d).^{27b} In this model the nonpolar lateral chains segregate from the rest of the molecule and form infinite columns which organize into a 2D hexagonal lattice. Around these columns the biphenyl units form cylinder shells with a regular hexagonal cross sectional shape. The terminal diol groups and the phenolic hydroxy groups organize into common hydrogen bonding networks which stabilize this arrangement by providing attractive forces at the ends of the calamitic units. The hexagonal lattice parameter is approximately $3^{1/2}$ times the length of the bolaamphiphilic moiety. This is the same ratio as that found for the Col_h phases of compounds **1/6–1/9**^{27b} and is in accordance with a model in which six bolaamphiphilic cores form hexagonal frames around the nonpolar cylinder cores, as shown in Figure 7c. These hexagonal cylinders organize into a honeycomb-like network (see Figure 7d). It seems that the space required by the lateral chains of this compound perfectly matches the space provided by the arrangement of the bolaamphiphilic segments in these hexagonal frames (Figure 7c).

In Table 1 the values of the number of molecules calculated for the unit cells (n_{cell}) and the number of molecules arranged in the cross section of the cylinder walls (n_{wall}) are collated. The values n_{wall} are between 1.7 and 2.1 for all columnar phases with core–shell structures. Hence, the cylinder walls have a thickness, on average corresponding to approximately two

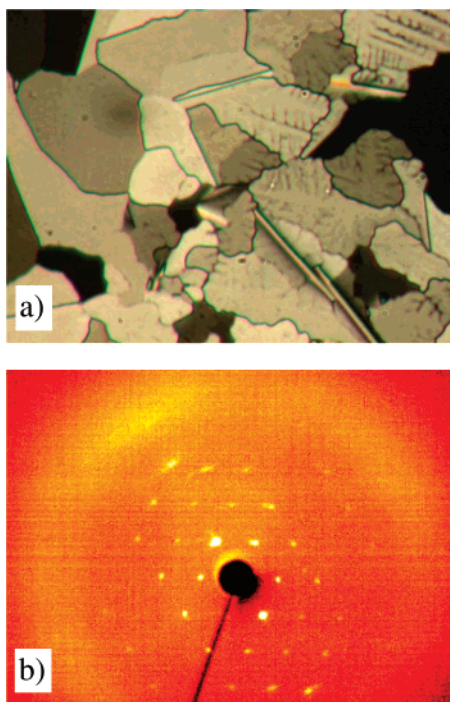


Figure 8. (a) Texture of compound 2/4 (crossed polarizers) at $T = 117$ °C (Iso to $\text{Col}_3/c2mm$ transition, dark areas correspond to residues of the isotropic liquid phase) and (b) X-ray diffraction pattern of an aligned sample of the $\text{Col}_3/c2mm$ phase of compound 2/4 at 109 °C.

parallel arranged biphenyl cores. This average number results from the fact that the mesophases reported herein represent ordered *fluids*, which means that there is a high degree of conformational, rotational, and translational mobility. Hence, there are no well-defined crystal-like structures³⁷ as might be suggested by the shown models. Instead, there are distinct regions with an enhanced concentration of the aromatic cores, regions of the polar hydrogen bonding groups, regions of the aliphatic, and regions of the fluorinated segments, as shown in Figure 7e. Depending upon the degree of incompatibility between the segments, the interfaces between these segregated regions can be quite sharp or more diffuse. Due to this nanoscale disorder, the number of molecules organized in a distinct volume is an average value, and therefore, the number of bolaamphiphilic cores which are organized side-by-side in the cylinder walls (n_{wall} ; see Table 1) is also an *average number*. Depending upon several parameters, this number can be either larger or smaller than a full number. A slight stretching of the cylinders along the c -axis, for example, reduces the average number of bolaamphiphilic cores organized in the cross section of the cylinder walls.^{27b} Compression along the c -axis leads to a larger number (slightly thicker walls), and these additional molecules can provide their lateral chains for improving the space filling within the nonpolar cylinders without changing the overall shape of the cylinder shells.

The texture of compound 2/4 is different again from that found for 2/6. It is characterized by a mosaic-like texture with some spherulitic domains (Figure 8a). The obtained X-ray diffraction pattern, shown in Figure 8b, can be indexed on the basis of a centered rectangular 2D lattice ($c2mm$) with the lattice

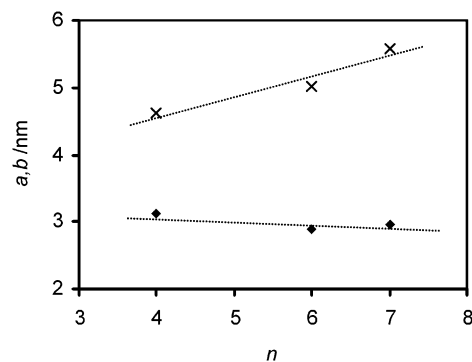


Figure 9. Plot of the lattice parameters a (◆) and b (×) of the $\text{Col}_i/c2mm$ phases of 2/4 (Col_3) and 2/7 (high-temperature phase Col_1) and the corresponding values calculated for the Col_h phase of 2/6 against the length of the lateral chain.

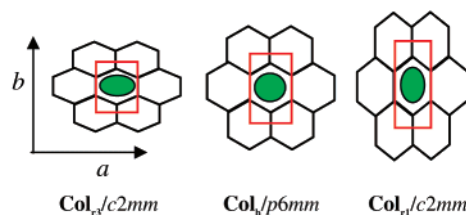


Figure 10. Models showing schematically the deformation of the hexagonal lattice of 2/6 (middle) in the $\text{Col}_3/c2mm$ mesophase of 2/4 and the $\text{Col}_1/c2mm$ phase of 2/7.

parameters $a = 3.13$ nm and $b = 4.62$ nm (designated as Col_3). If these lattice parameters are compared with those of the $c2mm$ lattice of the Col_1 phase (columnar high-temperature phase) of 2/7, then parameter b is reduced whereas a is slightly increased. If the Col_h phase of 2/6 is included in this comparison (formally this Col_h phase can be described as a $c2mm$ lattice in which $a = a_{\text{hex}} = 2.90$ nm and $b = 3^{1/2}a_{\text{hex}} = 5.02$ nm), then there is a continuous change of the parameter b to larger values whereas the parameter a slightly decreases in the sequence 2/4–2/6–2/7 (see Figure 9). This means that the Col_h phase fits quite well into this sequence, and it seems that the centered rectangular columnar mesophases of 2/4 and 2/7 (Col_3 and Col_1 , respectively) result from the deformation of the nondistorted hexagonal lattice of compound 2/6. For the $\text{Col}_1/c2mm$ phase of 2/7, the unit cell is stretched along b , whereas, in the $\text{Col}_3/c2mm$ phase of compound 2/4, it is compressed in this direction (see Figure 10). Accordingly, the $c2mm$ lattices of 2/4 (Col_3) and of the Col_1 phase of 2/7 are thought to result from an organization of six bolaamphiphilic units around cylinder cores with a slightly elliptical shape (the long axis of the ellipsoids is parallel to a for 2/4 and parallel to b for 2/7). Hence the fundamental organization of the molecules in these mesophases is not significantly changed when a comparison to the Col_h phase is made; i.e., in all three phases, six molecules form the hexagonal cylinder shells, which frame the nonpolar columns. The main difference is that in the Col_1 and Col_3 phases the cylinder shells adopt a slightly deformed hexagonal cross sectional shape. This can be achieved by minimal variation of the angles between the cylinder walls and by a slight change of the interdigitation of the hydrogen bonding sites, which modifies the effective length of the bolaamphiphilic units. However, there is no significant change of the number of molecules arranged around the cylinders, which is also indicated by the values n_{cell} (see Table 1). In the Col_h phase it is $n_{\text{cell}} = 5.2$ (only one cylinder

(37) Examples of channel organic coordination solids: (a) Xu, Z.; Lee, S.; Kiang, Y.-H.; Mallik, A. B.; Tsomaia, N.; Mueller, K. T. *Adv. Mater.* **2001**, *13*, 637–641. (b) Moulton, B.; Zaworotko, M. J. *Chem. Rev.* **2001**, *101*, 1629–1658.

per unit cell), and in the Col_{r1} and Col_{r3} phases it is about twice this number ($n_{\text{cell}} = 11.2\text{--}11.7$), because there are two cylinders per unit cell. In this respect these Col_{r1} and Col_{r3} phases are quite distinct from the columnar phases observed in the homologous series of tetraols $1/n$ (Figure 2). In the series of compounds $1/n$, the transition from Col_h to the Col_r phases ($c2mm, p2gg$) arises due to a change of the number of molecules organized around the nonpolar columns, from four (rhombuses) for short homologues via five (pentagons) and six (hexagons) to eight (stretched hexagons) for the higher homologues.^{27b}

Only the low-temperature $c2mm$ mesophase of $2/7$ (Col_{r2}) has a structure which is quite different from the other $c2mm$ phases observed for the triols $2/n$. In this columnar phase, the cylinder shells incorporate eight bolaamphiphilic cores in the cross section and adopt a strongly deformed hexagonal cross sectional shape (two sides of the hexagons are formed by end-to-end pairs) as already found for the $c2mm$ phases of tetraols $1/10\text{--}1/12$ ^{27b} (see Figure 6e). It seems that in the series of triols $2/n$ this type of enlarged cylinders is also possible, but only at reduced temperature.

2.4. Columnar Mesophase of 2/3: A Correlated Layer Structure. The mesophase of $2/3$ is different again from all other compounds. It grows as rectangles (Figure 11a) which coalesce to form a mosaic-like texture. Shearing destroys this texture, and homogeneously aligned strongly birefringent textures were obtained, as it is typical for columnar liquid crystalline phases (Figure 11b). The X-ray diffraction pattern (Figure 11c) of this mesophase is characterized by a sharp reflection on the meridian with the associated higher orders, corresponding to $d = 2.16$ nm. There is an additional reflection on the meridian, corresponding to a periodicity $d_2 = 1.57$ nm, and a weak cross reflection assigned to 11. This diffraction pattern can be assigned to a noncentered rectangular $p2mm$ cell with the lattice parameters $a = 1.57$ nm and $b = 2.16$ nm. These parameters are much smaller than those of all other columnar phases in this homologous series. In the wide angle region of the diffraction pattern, there is a nearly circular diffuse ring, corresponding to a mean distance of $D = 5.1\text{--}5.2$ nm. The overall appearance of the diffraction pattern and the rather small lattice parameters are strongly reminiscent of the diffraction pattern recently found for a correlated layer structure, formed by a tetraol bolaamphiphile of type $1/n$ with a branched lateral chain.³⁸ The value of $a = 1.57$ nm is in good agreement with the molecular length of the bolaamphiphilic rigid core measured between the terminal polar groups ($L = 1.5\text{--}1.7$ nm, depending on the assumed conformation of the 2,3-dihydroxypropyloxy group). The periodicity in the b direction can easily be explained by a layer structure with the layer distance corresponding to $d = 2.16$ nm. As shown in Figure 11d and e, these lattice parameters can be realized by the organization of the molecules $2/3$ in a correlated layer structure, where the aromatic cores lie parallel to the layer planes. The fluid and nearly isotropic distributed semiperfluorinated chains separate the aromatic sublayers. The aromatic sublayers are about three parallel aligned biphenyl units thick, but for clarity only an arrangement of two molecules in the cross section of the layers is shown in Figure 11d. The lateral chain of the third molecule fills the remaining void space within the nonpolar sublayers. The main

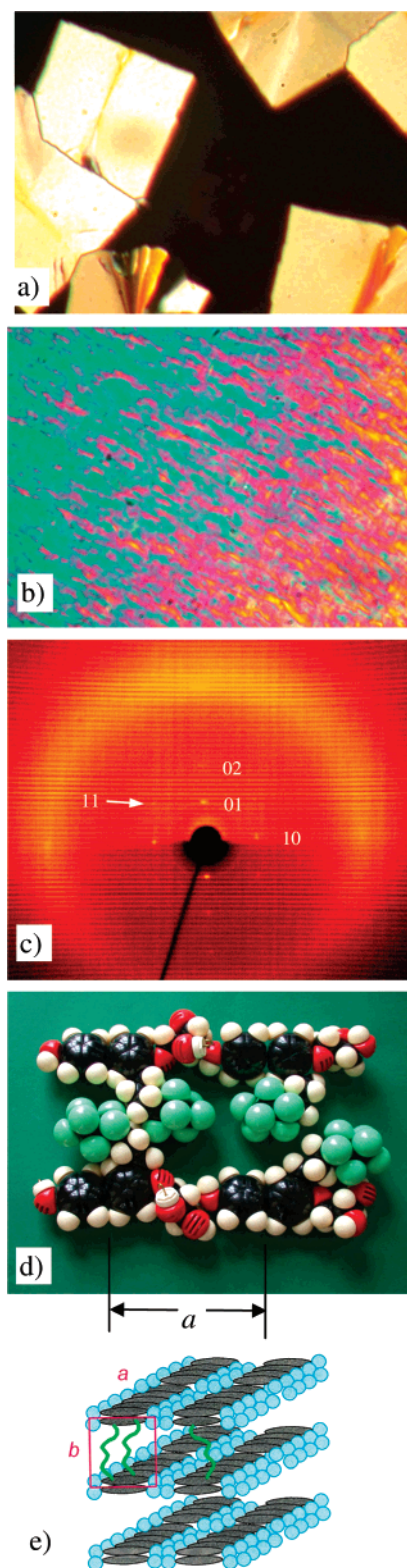


Figure 11. (a) Texture (crossed polarizers) of the Col_r/ $p2mm$ phase of compound $2/3$ at 96 °C as it is growing from the isotropic liquid state, dark areas correspond to residues of the isotropic liquid phase; (b) texture of the Col_r/ $p2mm$ phase of compound $2/3$ at 95 °C after shearing; (c) X-ray diffraction pattern of an aligned sample of the Col_r/ $p2mm$ phase at 92 °C. (d) CPK models showing four molecules of $2/4$ forming a correlated layer structure; for clarity only an arrangement of two molecules in the cross section of the layers is shown, but in reality the aromatic sublayers are about three biphenyl units thick. The lateral chains of the additional molecules fill the void space within the nonpolar sublayers. (e) Model of the molecular organization in the Col_r/ $p2mm$ mesophase.

(38) Prehm, M.; Diele, S.; Das, M. K.; Tschierske, C. *J. Am. Chem. Soc.* **2003**, *125*, 614–615.

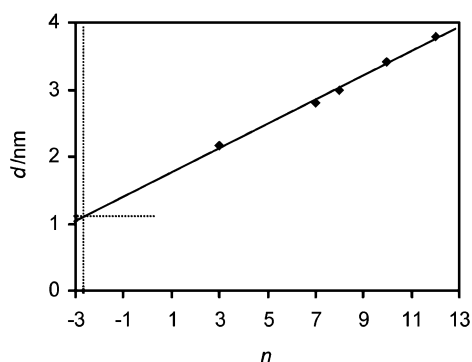


Figure 12. Plot of the d -values (\blacklozenge) of the lamellar mesophases of compounds $2/n$ against the length of the lateral chain. Because of the presence of the $(\text{CH}_2)_3$ spacer unit between aromatic core and R_F chain extrapolation was done to -2.5 .

difference between the lamellar phase of $2/3$ with respect to those of compounds $2/7$ – $2/12$ is that adjacent layers in the mesophase of $2/3$ are positional correlated in an AA fashion, which leads to the noncentered $p2mm$ lattice, whereas there is no such correlation in the Lam phases of compounds $2/7$ – $2/12$. Moreover, if the d -values of the lamellar phases of compounds $2/3$, $2/7$, $2/8$, $2/10$, and $2/12$ are plotted against the chain length, then a linear dependence can be found (see Figure 12). Extrapolation to $n = -2.5$ (this value was chosen because the fluorinated chains are coupled to three CH_2 units and the length of this spacer unit is equivalent to ca. 2.5 CF_2 units) gives a value of ca. 1.1 nm which represents the thickness of the aromatic sublayers. This thickness corresponds to about two to three aromatic cores arranged side-by-side within the cross section of the aromatic sublayers, as typical for all investigated lamellar phases with rigid cores arranged parallel to the layer planes. This linear dependence also confirms that the fundamental phase structures of the lamellar phases of the long chain compounds $2/7$ – $2/12$ and the short chain compound $2/3$ should be principally identical and that the increase of the chain length leads to an expansion of the layer distance. In this organization the area required by one bolaamphiphilic moiety at the polar–nonpolar interface can be calculated from the length ($L = 1.5$ nm) and its average width (0.45 nm) to give a value of 0.68 nm^2 . The cross sectional area of one perfluorinated chain is approximately 0.27–0.35 nm^2 .³⁹ This means that the interfacial area provided by the bolaamphiphilic moieties is nearly equivalent to that required by two intercalated perfluoroalkyl chains and this enables all compounds $2/n$ to adopt a layered organization, although this organization was only found for the short and the long chain compounds.

3. Summary and Conclusions

Eight different liquid crystalline phases were found for the rodlike triol compounds $2/n$ upon elongation of the lateral perfluorinated chain, as shown in Figure 13. In some respects, this phase sequence is related to that observed for the series of the related tetraols $1/n$ (see Figure 2). Namely, a Col_h phase occurs at medium chain lengths, around which other rectangular columnar phases are located. However, there are also striking differences between the two series $1/n$ and $2/n$. First, the shortest

homologue $2/3$ as well as the long chain compounds $2/7$ – $2/12$ adopt layerlike organizations in which the aromatic cores are organized parallel to the layer planes. Second, with the exception of the Col_{12} low-temperature mesophase of $2/7$, in all columnar mesophases with $c2mm$ lattice six molecules are framing the cylinder cores and, hence, these $c2mm$ phases represent slightly distorted Col_h phases.

From the point of view of the chemical structure, the main differences between the series $2/n$ and $1/n$ are the reduced number of hydrogen bonding sites (reduced cohesive forces) and the reduced length of the bolaamphiphilic moiety due to the replacement of one of the 2,3-dihydroxypropoxy groups by a single phenolic OH group. As mentioned above, the area required by the bolaamphiphilic moiety at the aromatic–aliphatic interface is almost twice the cross sectional area of a perfluorinated chain. This means that flat interfaces (layer structures) are, in principle, possible for all compounds $2/n$, irrespectively of the length of the fluorinated chains. Hence, the organization into Lam phases (layer structures with an organization of the rigid cores parallel to the layer planes) is expected to be the fundamental organization within this class of compounds. In fact, however, it is only observed for compounds $2/3$ and $2/7$ – $2/12$. For compound $2/3$ with short lateral chains, there is a strong coupling between adjacent layers which leads to a long-range positional correlation between the layers, giving rise to a noncentered rectangular 2D lattice ($p2mm$). This long-range positional correlation of the layers was not observed for the long chain compounds $2/7$ – $2/12$ (Lam-phases). However, at a certain volume fraction of the lateral chains another organization becomes more favorable. This is a hexagonal columnar mesophase, in which the bolaamphiphilic segments form hexagonal frames around the microsegregated columns of the nonpolar lateral chains. If the space required by the lateral chains of six molecules is exactly the volume provided inside the hexagonal cylinders (formed by six bolaamphiphilic moieties), then the hexagonal columnar phase becomes the preferred type of organization. The stability of this honeycomb-like organization may be due, in large, to an energy gain due to the more favorable hydrogen bonding in the networks connecting three cylinder walls with respect to the hydrogen bonding in the layer structures. The starlike 3-fold connection of the 1,2-diol groups may possibly allow a greater number of geometrically optimal hydrogen bonding to be formed within the hexagonal lattice as compared with a linear connection in the lamellar phases. If the volume available within the cylinders is not equal with the volume provided by six lateral chains, then the organization in hexagonal cylinders becomes less favorable and organization of the molecules into layers was found. At the borderline between these two types of organization, the formation of slightly stretched hexagonal cylinders ($\text{Col}_{13}/c2mm$ phase of compound $2/4$ and $\text{Col}_{11}/c2mm$ phase of $2/7$) seems to be the best compromise. In this way the 3-fold connection of the cylinder walls can be retained, whereas the anisotropic stretching of the hexagons is favorable for a parallel organization of the chains inside the nonpolar columns.

In only one case (low-temperature $\text{Col}_{12}/c2mm$ phase of $2/7$) another mesophase type was found. It is built up of elongated cylinders framed by eight molecules. This mesophase type was also observed for compounds of the series of tetraols $1/n$ ($n = 10$ – 12) at the transition from hexagonal columnar to lamellar

(39) Smart, B. E. In *Organofluorine Chemistry Principles and Commercial Applications*; Banks, R. E., Smart, B. E., Tatlow, J. C., Eds.; Plenum Press: New York, 1994; pp 57–88.

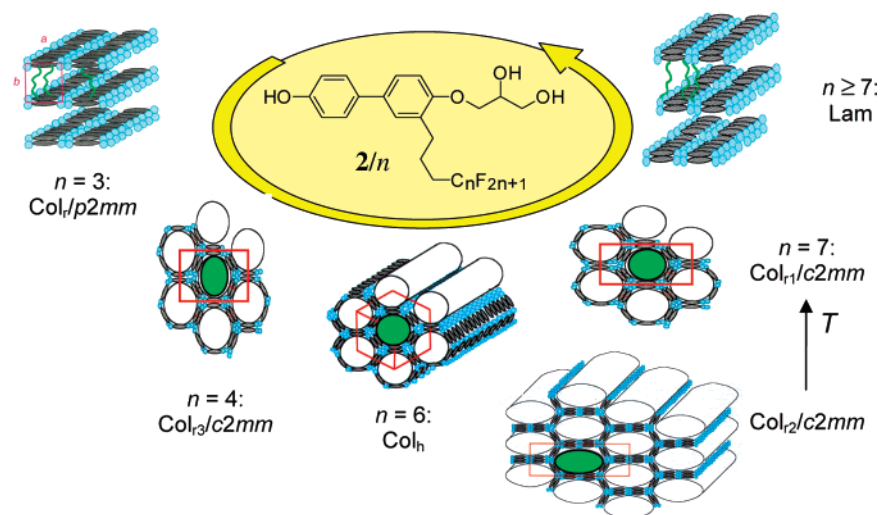


Figure 13. Phase sequence of compounds $2/n$ depending on the chain length (the different types of Lam phases for compounds with $n \geq 7$ are not shown).

organization. However, in the series of the analogous triols $2/n$, it is only a monotropic mesophase occurring below one of the above-mentioned $c2mm$ phases representing slightly distorted hexagonal columnar arrangements. A possible explanation could be that, in order to be stable, these large-cylinder structures require stronger cohesive forces and a higher degree of segregation between aromatic and polar subunits.

In summary, it was shown that columnar liquid crystalline phases with core-shell structures could not only be found as intermediate phases at the transition between two fundamentally different types of lamellar phases, i.e., between smectic (rodlike units are perpendicular to the layer planes) and the just recently discovered laminated phases (rodlike units are parallel to the layer planes), as reported earlier,^{27b} these mesophases can also occur as alternative possibilities to the layerlike organization within laminated mesophases. Here, slight changes of the molecular structure can easily shift this balance between

layerlike and columnar organization. Further investigation of such small structural effects, which have a strong influence upon self-organization of these simple molecules into complex superstructures, will undoubtedly contribute to a better understanding of complex soft matter self-assembly.

Acknowledgment. This work was supported by the Deutsche Forschungsgemeinschaft, the Fonds der Chemischen Industrie and the European Commission (RTN LCDD).

Supporting Information Available: Tables with crystallographic data, figures showing the textures of the mesophases of $2/7$, experimental procedures, and analytical data (NMR, MS, elemental analysis). This material is available free of charge via the Internet at <http://pubs.acs.org>.

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