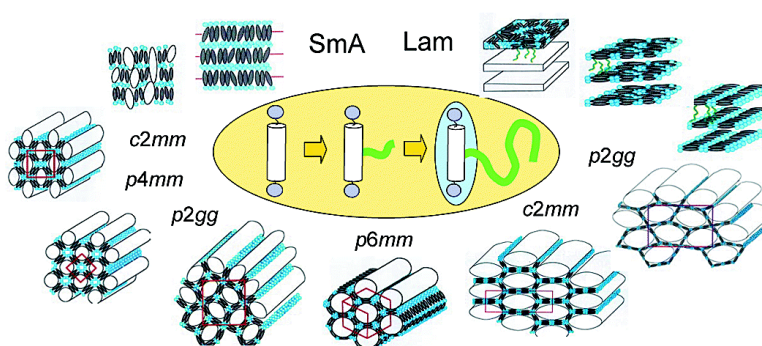


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J. Am. Chem. Soc., **2003**, 125 (36), 10977-10996 • DOI: 10.1021/ja036213g • Publication Date (Web): 14 August 2003

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Calamitic Bolaamphiphiles with (Semi)Perfluorinated Lateral Chains: Polyphilic Block Molecules with New Liquid Crystalline Phase Structures

Xiaohong Cheng,[†] Marko Prehm,[†] Malay Kumar Das,[‡] Jens Kain,[‡] Ute Baumeister,[‡] Siegmund Diele,[‡] Dag Leine,[‡] Alfred Blume,[‡] and Carsten Tschierske^{*†}

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

Received May 19, 2003; E-mail: Tschierske@chemie.uni-halle.de

Abstract: Novel bolaamphiphiles consisting of a rigid biphenyl unit, two terminal polar 1,2-diol units and laterally attached (semi)perfluorinated chains have been synthesized via palladium-catalyzed cross coupling reactions as the key step. The thermotropic liquid crystalline behavior of these compounds was investigated by polarized light optical microscopy, DSC, and X-ray scattering, and the influences of the length, number, structure, and position of the lateral chain on the mesomorphic properties were studied. A wide variety of unique liquid crystalline phases were found upon elongation of the lateral semiperfluorinated chains. For short- and medium-chain length a series of columnar phases were observed, and upon further elongation of the lateral chain a series of novel mesophases with layer structures were found. In the columnar phases, the nonpolar lateral chains segregate into columns, which are embedded in honeycomb-like networks of cylinders consisting of the biphenyl units. Strings of hydrogen-bonding networks of the diol groups provide cohesive forces, which maintain the overall structure. Changing the length of the lateral chains influences the diameter of the columns and thus determines the number of biphenyl units which are required to surround these columns. The number of these units [four (*c2mm*, *p4mm*), five (*p2gg*), six (*p6mm*), eight (*c2mm*) or 10 (*p2gg*)] defines the shape of the cylinders as well as the lattice type of the columnar phase. It is proposed that the columnar phases with a *p2gg* lattice result from the regular organization of pairs of cylinders which have a pentagonal cross sectional shape. In the mesophases with layer structure the aromatic rodlike cores are arranged parallel to the layer planes, and the onset of orientational and positional ordering of the biphenyl segments leads to a sequence of subtypes for these lamellar phases (Lam_{1so} – Lam_N – Lam_X).

Introduction

In the past 20–30 years liquid crystalline materials have received significant attention. The combination of order and mobility in these systems leads to novel functional materials which have had a great impact on recent development of mobile information technologies.¹ Although more than 100 000 liquid crystalline compounds have been synthesized thus far, their basic structures are quite similar. They represent either anisometric molecules with a specific rodlike or disklike shape, or amphiphilic molecules, as well as oligomers, polymers, and dendrimers derived from these fundamental structures.² There are two main driving forces for self-organization in such systems: (i) segregation of incompatible molecular parts into separate subspaces,³ accompanied by aggregation of compatible

or complimentary units, and (ii) minimization of the free volume, which in the case of rigid molecules or supermolecular aggregates with a rodlike or disklike shape leads to a parallel alignment of these anisometric units.² The self-organized structures of such conventional LC materials are quite simple: flexible binary amphiphiles give rise to a sequence of lamellar, bicontinuous cubic, columnar, and spheroidal cubic mesophases with respect to the volume fraction of the incompatible parts (e.g., surfactant solvent systems,⁴ thermotropic mesophases of amphiphiles,⁵ flexible block copolymers,⁶ and low-molecular mass block molecules⁷). These mesophases are characterized

[†] Institute of Organic Chemistry.

[‡] Institute of Physical Chemistry.

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by positional order in one, two, or three dimensions. Rodlike and disklike molecules on the other hand align parallel and give rise to orientational order, which leads to the formation of nematic phases (orientational ordering only), and smectic or columnar LC phases if there is additional positional order.^{2,8} New and more complex mesophase morphologies can arise if these driving forces are combined in a competitive way, or if there are other forces which compete with these fundamental organizations. Chirality, for example, favors a helical organization of molecules, which is in competition with a layered organization, leading to quite complex superstructures (TGB phases, blue phases, and other complex 3D ordered structures).⁹ In bent-core mesogens, as another example, a polar order results from the directed organization of the molecules in layers, which is in competition with a layerlike organization, leading to frustrated phase structures and supramolecular chirality.¹⁰

From the field of multiblock copolymers, it is known that increasing the number of incompatible units fixed to one another is an alternative way to amazingly complex morphologies.^{11,12} However, this concept is less explored in low-molecular mass LC materials. There are some reports about rodlike,^{13,14} taper-shaped, and dendritic polyphilic molecules,^{15,16} where different incompatible units were connected in a linear fashion. However, this molecular topology inherently favors the organization provided by the molecular shape, leading predominantly to the formation of triple-layer structures for calamitic molecules and formation of onion-like columns or spheroids for taper-shaped molecules. Another approach aims at the *competitive* combination of the organization provided by rigid segments with a polyphilic molecular structure.^{3a,b,17–20}

Rigid bolaamphiphiles with flexible lateral alkyl chains $1/n^{21}$ represent one class of compounds in which this approach was very successfully used to obtain novel liquid crystalline phases

with complex morphologies. These compounds can be regarded as block molecules consisting of three incompatible units: a rigid rodlike aromatic unit, two hydrophilic terminal groups, and a lipophilic lateral alkyl chain. All three structural units are incompatible with respect to one another, and therefore, they are forced to organize within different subspaces. Furthermore, a strong competition arises between the parallel alignment of the rodlike biphenyl units and the steric interaction caused by the lateral alkyl chains. The space requirement of the lateral

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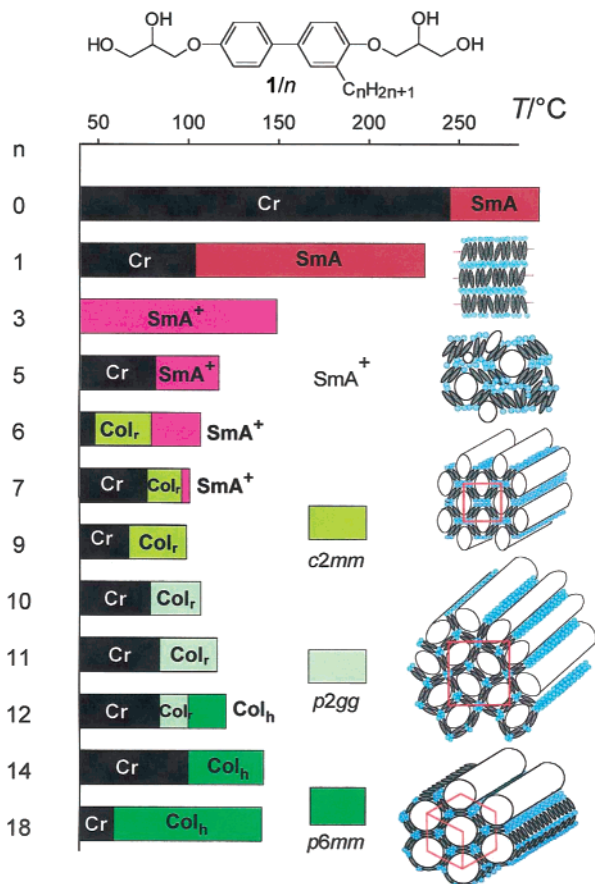


Figure 1. Dependence of the liquid crystalline phases of compounds **1/n** with respect to the length of the lateral alkyl chains and models for the organization of the molecules **1/n** in their mesophases.^{21b} Cr = crystal, SmA = smectic A phase (liquid crystalline phase with layer structure, without long-range positional order in the layers and with an arrangement of the biphenyl units parallel to the layer normal), SmA⁺ = disordered mesophase (typical SmA texture, but a diffuse reflection is found adjacent or instead of the sharp layer reflection in the small-angle region of the X-ray diffraction pattern),^{21b} Col_r = centered (*c2mm*) or noncentered (*p2gg*) rectangular columnar phases;²⁶ Col_h = hexagonal columnar phase (*p6mm*).²⁷ Models: blue = hydrogen-bonding networks of the terminal diol groups; white = microsegregated regions of the lateral alkyl chains; gray = rigid biphenyl units.

chains disturbs the original layer structure.²² However, the cooperative and dynamic networks of intermolecular hydrogen bonding²³ between the diol groups provide sufficient cohesive energy to inhibit a complete collapse of the molecular order and support the segregation of the incompatible parts,²⁴ leading to a series of novel mesophases. As shown in Figure 1,

elongation of the lateral chain of the compounds **1/n** gives rise to a transition from a smectic monolayer structure ($n = 0, 1$: SmA₁) via a mesophase with a strongly distorted structure ($n = 3-7$: SmA⁺), a centered rectangular columnar phase ($n = 6-9$: Col_r/*c2mm*), and a noncentered rectangular columnar phase ($n = 10-12$: Col_r/*p2gg*) to a hexagonal columnar phase ($n \geq 12$: Col_h/*p6mm*).^{21b} This phase sequence results from the microsegregation of the lateral alkyl chains from the rigid aromatic units which occurs above a certain minimum length for these chains (≥ 3). The segregated alkyl chains organize into distinct regions. For short-chain compounds (**1/3**, **1/5**) and for medium-chain compounds at higher temperatures (**1/6**, **1/7**), there is no long-range correlation between these lipophilic regions. This leads to a special type of mesophase which is characterized by a typical SmA-like optical texture and by an X-ray diffraction pattern in which a diffuse scattering in the small-angle region appears adjacent to or instead of the sharp layer reflection (SmA⁺).^{21b} Longer chains organize in infinite columns which adopt a positional long-range order in two dimensions, leading to columnar phases. In these mesophases the bolaamphiphilic units form networks of cylinder shells around the lipophilic columns (see Figure 1).²⁵ The terminal diol groups are organized into hydrogen-bonding networks which stabilize this arrangement by providing attractive forces at the ends of the calamitic units. The space required by the alkyl chains with respect to the length of the bolaamphiphilic units determines the number of biphenyl units which have to be organized in the shells around the lipophilic cylinder cores. This influences the geometry of the cylinders and gives rise to the above-mentioned sequence of two-dimensional (2D) lattices.^{21b}

To further extend this designing principle, we have synthesized rigid bolaamphiphiles with perfluorinated (compounds **4/n**) and semiperfluorinated lateral chains (compounds **2/n**, **3/n**, **5/n-7/n**, see Scheme 1). There are several distinct effects of (semi)-perfluorinated chains which can influence the self-organization of such molecules.^{7b,14,16,19,28,29} First, the perfluorinated segments are incompatible with hydrogenated molecular parts and also with polar segments. This fluorophobic effect usually increases segregation and stabilizes the mesophases. Second, perfluorinated chains have a significantly larger volume than alkyl chains. Finally, such chains have preferred conformations (helical) which are different from those adopted by alkyl chains (all-trans).³⁰ For these reasons, it was hoped that the introduction of perfluorinated segments would lead to further novel mesophases being observed. The structure of all compounds is based on the bolaamphiphilic^{31,32} 4,4'-bis(2,3-dihydroxypropoxy)-biphenyl unit.³³ Systematically changing the length, the degree

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(25) To avoid confusion the term (*cylinder*) *shell* is used for the shell of bolaamphiphilic units arranged around a lipophilic column [(*cylinder*) *core*]. In the resulting 2D lattice shells of adjacent cylinders form the (*cylinder*) *walls*, i.e. these cylinder walls separate the cylinder cores.

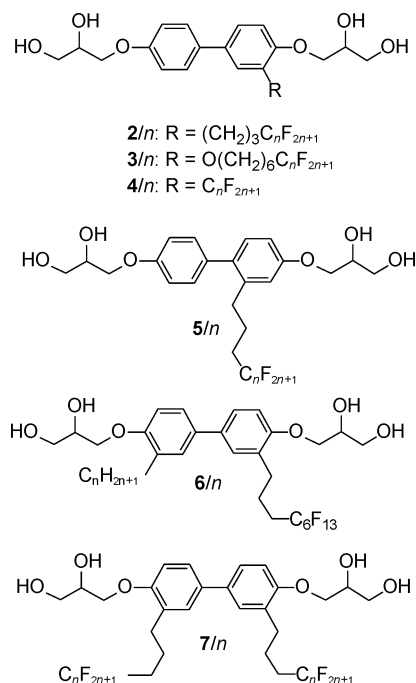
(26) The model of the *p2gg* phase has been revised (see section 2.2) and is different from the earlier proposed structures.²¹

(27) In ref 21b two different models were discussed for the Col_h phases of compounds **1/12-1/18**, but on the basis of the new model for the *p2gg* phases and the other results reported herein the alternative star-like model can be excluded.

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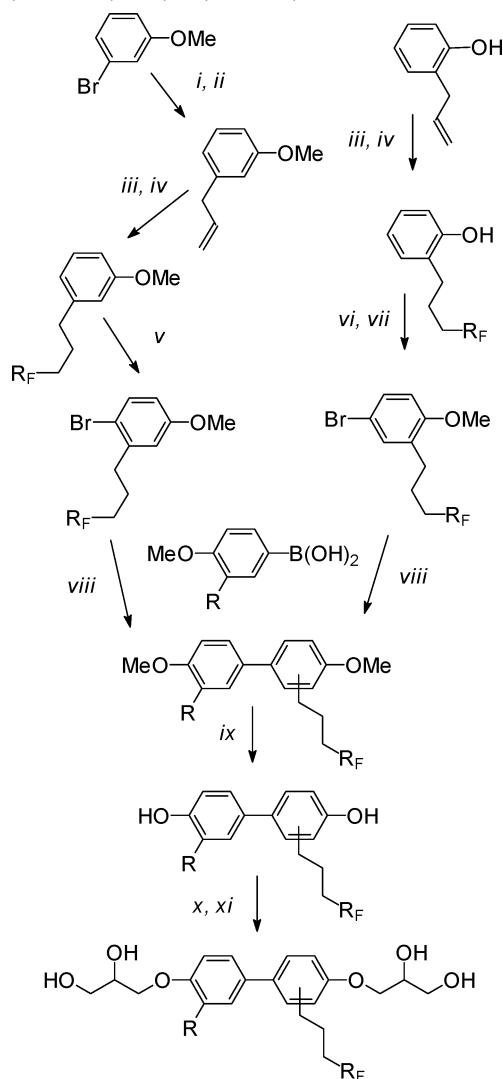
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Scheme 1. Structural Formulas of the Molecules under Investigation

of fluorination (compounds $2/n$ – $4/n$), and the position (compounds $5/n$) of the lateral chain gives rise to a series of different liquid crystalline phases with unique structures.

Results and Discussion

1. Synthesis. Scheme 2 describes the synthesis of most of the compounds. Compounds $2/n$, $5/n$, $6/n$, and $7/n$ containing perfluorinated lateral chains attached via a propylene spacer were synthesized by the Pd^0 -catalyzed addition of 1-iodoperfluoroalkanes^{16a,34} to 2-allylphenol or 3-allylanisole, followed by para-selective bromination using $\text{HBr}/\text{AcOH}/\text{DMSO}$ ³⁵ (phenols) or $\text{NBS}/\text{CH}_3\text{CN}$ ³⁶ (anisoles). Then a Suzuki-coupling³⁷ with appropriate benzene boronic acids gave the biphenyl cores, and finally the introduction of the terminal propane-2,3-diol groups led to the desired compounds.^{38,39} The first step in the synthesis of compounds $4/n$ with perfluorinated chains directly attached to the aromatic core was a coupling reaction between 2-iodoanisole and 1-iodoperfluoroalkanes in the presence of reactive Cu -powder.⁴⁰ This was followed by bromination with NBS in trifluoroacetic acid⁴¹ and continued according to Scheme

Scheme 2. Synthesis of Compounds $2/n$, $5/n$ ($R = \text{H}$), $6/n$ ($R = \text{C}_n\text{H}_{2n+1}$) and $7/n$ ($R = (\text{CH}_2)_3\text{C}_n\text{F}_{2n+1}$)^a

^a Reagents and conditions: *i*) Mg , Et_2O , reflux; *ii*) 1. $\text{CH}_2=\text{CHCH}_2\text{Br}$, Et_2O , 0°C , 2. HCl , H_2O , 0°C ; *iii*) $\text{Pd}(\text{PPh}_3)_4$, R_FI , 25°C , 36 h; *iv*) 1. LiAlH_4 , Et_2O , reflux, 2 h, 2. H_2O , H_2SO_4 , 0°C ; *v*) NBS , CH_3CN , 25°C , 24 h; *vi*) DMSO , HBr/AcOH , 5°C ; *vii*) CH_3I , K_2CO_3 , CH_3CN , reflux, 2 h; *viii*) $\text{Pd}(\text{PPh}_3)_4$, NaHCO_3 , glyme, H_2O , reflux, 6 h; *ix*) BBr_3 , CH_2Cl_2 ; *x*) $\text{CH}_2=\text{CH}-\text{CH}_2\text{Br}$, K_2CO_3 , CH_3CN , reflux, 6 h; *xi*) OsO_4 , *N*-methylmorpholine-*N*-oxide, H_2O , acetone, 25°C 2 h.

2. To further elongate the lateral chain, compounds $3/n$, in which the perfluorinated segments are attached via a hexamethyleneoxy spacer, were synthesized by etherification of bis-4,4'-(2,2-dimethyl-1,3-dioxolan-4-ylmethoxy)-3-biphenylol⁴² with appropriate 1H,1H,2H,2H,3H,3H,4H,4H,5H,5H,6H,6H-perfluoroalkylhalides.⁴² All final products were purified by preparative centrifugal thin-layer chromatography with a Chromatotron (Harrison Research) and, if possible, by repeated crystallization from appropriate solvents and characterized by ^1H , ^{13}C , and ^{19}F NMR and elemental analysis. The purity was additionally checked by TLC. Experimental details and analytical data are reported in the Supporting Information.

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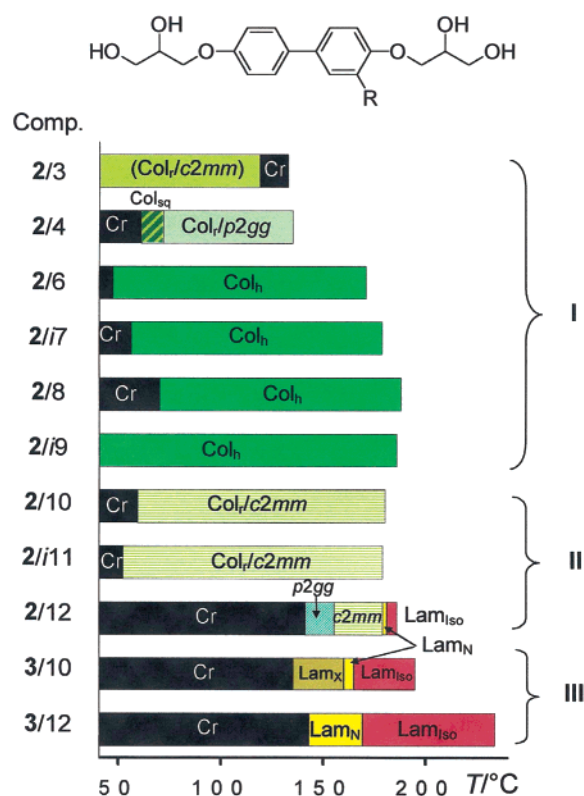


Figure 2. Dependence of the liquid crystalline phases of compounds **2/n** and **3/n** with respect to the length of the semiperfluorinated lateral chain (**2/n**: R = (CH₂)₃C_nF_{2n+1}; **3/n**: R = O(CH₂)₆C_nF_{2n+1}).

2. Mesomorphic Properties

2.1. General Trends. The obtained compounds were investigated by polarized light optical microscopy, differential scanning calorimetry, and X-ray diffraction. The transition temperatures and corresponding enthalpy values for all compounds are collated in Tables 1–3. All materials with one (semi)perfluorinated lateral chain show thermotropic liquid crystalline phases. The mesophase stability and the mesophase type are strongly dependent upon the length of the semiperfluorinated chain. However, the type of attachment of the perfluorinated chains to the aromatic units (direct connection in compounds **4/n** or via spacer units in all other compounds) and the position of the chains (position 2 in compounds **5/n** or position 3 in all other compounds) are less important. Figure 2 graphically shows the dependence of the phase transitions on the chain length for the 3-substituted compounds **2/n** and **3/n**. Three distinct groups of compounds can be distinguished with regard to the phase behavior. Compounds **2/3**–**2/9** (group I) have either rectangular or hexagonal columnar mesophases, similar to those found for the alkyl-substituted compounds **1/n**. Compounds **2/10**–**2/12** with a medium length of the semiperfluorinated chain (group II) have mesophases with unusually large lattice parameters, and two additional lamellar mesophases (Lam) were found for compound **2/12**. Compounds **3/10** and **3/12** (group III) which have the longest chains show exclusively lamellar phases.

2.2. Influence of the Length of the Semiperfluorinated Chain on the Mesophase Morphology: Columnar Mesophases of Group I Compounds. In this section the mesomorphic properties of compounds **2/3**–**2/9** will be discussed. A

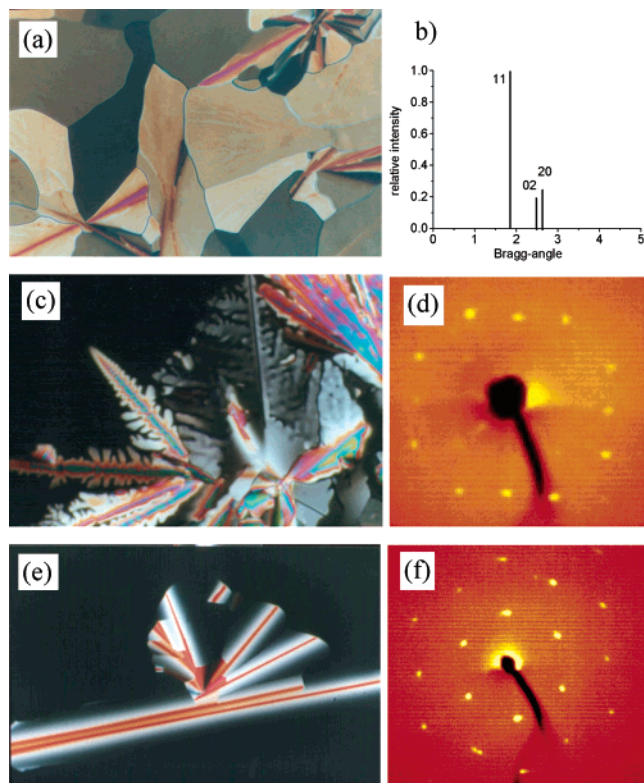
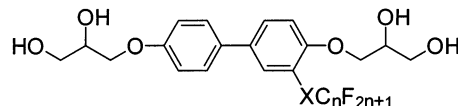


Figure 3. Optical photomicrographs (left, crossed polarizers) and X-ray diffraction pattern (right) of the columnar mesophases of group I compounds: (a, b) Col_r phase (c2mm) of **2/3** at 115 °C; (c) Col_r phase (p2gg) of **2/4** growing into the isotropic liquid at 135 °C (black areas are residual regions of the isotropic liquid); (d) Col_r phase (p2gg) of **2/4** at 127 °C; (e) Col_h phase of **2/7** at 170 °C (here, the black areas are homeotropic domains in which the columns are perfectly aligned perpendicular to the glass substrates); (f) Col_h phase of **2/7** at 175 °C.

comparison with the corresponding hydrocarbon analogues **1/n** (see Figure 1) with the same number of C-atoms in the lateral chain shows that most fluorinated compounds **2/n** have reduced melting points, but all have significantly enhanced mesophase stabilities. This gives rise to significantly enlarged mesophase regions for all fluorinated compounds with the exception of compound **2/3**, which exhibits only monotropic (metastable) behavior. It is also interesting to note that branching of the terminal chains (compound **2/7** and **2/9**) appears to have no significant influence upon the mesophase behavior. Compounds **2/7**, **2/6**, and **2/8** all exhibit the same mesophase type (Col_h), and the clearing temperature of **2/7** lies between those of compounds **2/6** and **2/8** which contain unbranched chains.

Compounds of group I exhibit four different types of columnar mesophases. Typical textures and small-angle X-ray diffraction pattern of the three main phase types are shown in Figure 3. Diffuse scattering in the wide-angle region of all X-ray diffraction patterns confirm the liquid crystalline nature of these mesophases. Mosaic-like textures and spherulitic textures were detected for compound **2/3** (Figure 3a). The powder-like X-ray diffraction pattern of this mesophase (Figure 3b) is characterized by three non-equidistant sharp reflections in the small-angle region, which were indexed on the basis of a centered rectangular 2D lattice. In accordance with results obtained during previous investigations of bolaamphiphiles with lateral alkyl chains^{21b} the c2mm 2D space group has been assumed. The lattice parameters were then calculated to be $a = 3.3$ nm and $b = 3.4$ nm. These lattice parameters are between the single

Table 1. Mesophases, Phase Transition Temperatures, Phase Transition Enthalpies (lower lines in italics), and Other Parameters of the Bolaamphiphiles $2/n-4/n^a$


Comp	X	n	Phase Transitions ($T / ^\circ\text{C}$)	a/nm	b/nm	d/nm	$V_{\text{cell}}/\text{nm}^3$	$V_{\text{mol}}/\text{nm}^3$	n_{cell}	$n_{\text{cell,calc}}$	n_{wall}	f_R
			$\Delta H/\text{kJ mol}^{-1}$									
2/3	(CH ₂) ₃	3	Cr ₁ 104 Cr ₂ 133 ^b (Col _r /c2mm 119) Iso <i>15.2 6.2 6.5</i>	3.3	3.4		5.05	0.603	8.4	8	2.1	0.33
2/4	(CH ₂) ₃	4	Cr 61 Col _{sq} 67 Col _r /p2gg 135 Iso <i>11.2 -^d 5.3</i>	5.4 ^e	5.9 ^e		14.34 ^e	0.640	22.4 ^e	20 ^e	2.2 ^e	0.36
2/6	(CH ₂) ₃	6	Cr 47 Col _h 171 Iso <i>12.4 8.5</i>	3.47			4.69	0.713	6.6	6	2.2	0.43
2/i7	(CH ₂) ₃	7	Cr 56 Col _h 179 Iso <i>9.8 9.7</i>	3.5			4.77	0.749	6.4	6	2.1	0.46
2/8	(CH ₂) ₃	8	Cr 70 ^b Col _h 188 Iso <i>5.3 9.3</i>	3.47			4.69	0.786	6.0	6	2.0	0.48
2/i9	(CH ₂) ₃	9	Cr <20 Col _h 186 Iso <i>8.2</i>	3.45			4.64	0.823	5.6	6	1.9	0.51
2/10	(CH ₂) ₃	10	Cr 59 Col _r /c2mm 180 Iso <i>13.8 8.0</i>	3.7	9.6		15.98	0.859	18.6	16	2.3	0.53
2/i11	(CH ₂) ₃	11	Cr 52 Col _r /c2mm 179 Iso <i>10.8 7.6</i>	3.7	9.7		16.15	0.896	18.0	16	2.3	0.55
2/12	(CH ₂) ₃	12	Cr 141 Col _r /p2gg 155 Col _r /c2mm 180 Lam _N 181 Lam _{iso} 185 Iso <i>25.5 1.3 2.7^e 1.1</i>	4.0 ^f	9.7 ^f		17.46 ^f	0.933	18.7 ^f	16 ^f	2.3 ^f	0.56
							39.85 ^e	0.933	42.7 ^e	40 ^e	2.1 ^e	0.56
3/10	O(CH ₂) ₆	10	Cr 135 ^h Lam _X 166 Lam _N 167 Lam _{iso} 195 Iso <i>67.8 2.6^l 1.1</i>				3.94					0.57
3/12	O(CH ₂) ₆	12	Cr 143 ^k (Lam _X 141) Lam _N 169 Lam _{iso} 235 Iso <i>69.5 1.0 1.9 1.8</i>			4.5						0.59
4/4	-	4	Cr 113 (SmA 81) Iso <i>19.1 1.7</i>									0.28
4/8	-	8	Cr 97 M1 134 Col _h 158 Iso <i>17.8 -^d 5.8</i>	3.41 ^l			4.53 ^l	0.712	6.4 ^l	6	2.1 ^l	0.43

^a The transition temperatures were determined by DSC (first heating scan, 10 K min⁻¹); a, b, d = lattice parameters, V_{cell} = volume of a unit cell with a height of $h = 0.45$ nm;⁴³ V_{mol} = volume for a single molecule as calculated using the crystal volume increments reported by Immirzi;⁴⁴ n_{cell} = number of molecules in a unit cell, calculated according to $n = V_{\text{cell}}/V_{\text{mol}}$; $n_{\text{cell,calc}}$ = number of molecules arranged in the cross section of a 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 polygon and the number of columns per unit cell; n_{wall} = average thickness of the cylinder walls given by the average number of biphenyl units arranged side by side in the walls separating two adjacent cylinder cores;²⁵ f_R = volume fraction of the lateral chains; abbreviations: Lam_{iso} = lamellar phase with an arrangement of rodlike units parallel to the layer planes and without additional order; Lam_N = lamellar phase with an arrangement of biphenyl units parallel to the layer planes and with an in-plane orientational order; Lam_X = lamellar phase for which an arrangement of biphenyl units parallel to the layer planes with an in-plane orientational and possibly also an positional order is proposed (see Figure 15); Col_{sq} = square columnar mesophase; Col_r = rectangular columnar phases, the lattice type is additionally given; M1 = mesophase with unknown structure; Iso = isotropic liquid; the perfluorinated segments of compounds 2/i7, 2/i9 and 2/i11 are branched at their terminal ends (*iso*-perfluoroalkyl segments) whereas all other chains are linear. ^b This phase transition was only observed in the first heating scan. ^c Values for the Col_r/p2gg phase. ^d This phase transition was only observed by X-ray diffraction. ^e The phase transitions Col_r/c2mm-Lam_N-Lam_{iso} are not resolved. ^f Values for the Col_r/c2mm phase. ^g Value for the Lam_{iso} phase. ^h On cooling additional transitions to crystalline mesophases can be observed at 101 °C and 77 °C. ⁱ The phase transitions Lam_X-Lam_N-Lam_{iso} are not resolved. ^k On cooling, an additional transition to a crystalline mesophases can be observed at 122 °C. ^l Value for the Col_h phase.

molecular length ($L = 2.1$ nm)⁴⁵ and twice that length. The number of molecules located within a hypothetical unit cell with

a height of 0.45 nm⁴³ has been calculated according to the equation $n = V_{\text{cell}}/V_{\text{mol}}$, yielding a value of approximately eight

(43) 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 only fill the channels within this structure. Because the cross section of the perfluorinated segments is larger than the rest of the molecules, there is a drift of the maximum of the diffuse scattering in the X-ray diffraction pattern to larger D -values with increasing degree of fluorination. However, this shift is due to a change of a molecular parameter rather than due to a change of the structure. Because the diameter of the fluorinated segments is larger than that of the nonfluorinated bolaamphiphilic moieties, which form the cylinder walls, there is a mixing of the chains of adjacent (hypothetical) unit cells along the cylinder, i.e. the perfluorinated chains in one unit cell also contribute to the space filling in the adjacent unit cell. This is in line with the models of the mesophases (see Figures 4f, 6c, and 10b), where some vacant space is available for parts of the chains from the neighboring cells.

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 (45) The molecular lengths are calculated as the distance between the ends of the terminal propane-2,3-diol units and have a value between 1.7 and 2.1 nm, depending on the conformation assumed for the propane-2,3-diol units. The molecular length of 2.1 nm is found in all cylinder structures of compounds 1/n, 2/n, and 5/n. It seems that the organization into cylinders leads to a maximum stretching of the bolaamphiphilic cores due to the confined geometry in which the flexible chains are enclosed. To get minimal interfaces the cross section of the cylinders should be as large as possible, which leads to a stretching of the cylinder walls. In contrast, a value of only 1.7 nm was found for a correlated layer structure.⁶¹ Within layer structures, expansion of the lipophilic regions is easily achieved by changing the thickness of the nonpolar sublayers, so that the conformation of the hydrogen bonding is more independent from the organization of the nonpolar chains. Here the molecules organize in such a way that a maximum number of hydrogen-bonding sites are utilized most efficiently. This is obviously achieved if the propane-2,3-diol groups adopt a compact conformation with strong interdigitation.

molecules per unit cell (see Table 1). A cylinder model, in which approximately four molecules are arranged in the cross-section of each cylinder and two cylinders are arranged in the unit cell, provides the most accurate fit to these data. This organization of cylinders with an elliptical cross-sectional area in a $c2mm$ lattice is similar to the model proposed for the $Col_r/c2mm$ phases of 1/6–1/9 shown in Figure 1.

The high-temperature mesophase of 2/4 shows a quite different optical texture. Upon cooling from the isotropic, a fern-like texture is observed (see Figure 3c) which coalesces to form mosaic-like and spherulitic regions. To determine the structure of this and other mesophases X-ray scattering investigations were performed on aligned samples. The alignment was achieved by slow cooling (0.01 K min^{-1}) of a droplet of the sample (diameter ca. 1–1.5 mm) on a glass plate. Surface interactions at the sample-glass interface or at the sample-air interface cause a special alignment of the cylinders within the columnar phases: their long axes are packed in planes parallel to the surfaces of the sample. Within these planes, the cylinder axes are orientationally disordered around the layer normal with a more or less equal distribution of domains with different orientations. The incident X-ray beam (wavelength of the Cu $K\alpha$ line, 0.154 nm) is applied parallel to the substrate glass plate, and the scattering beam intensity was recorded in transmission using a 2D detector (HI-Star, Siemens). The X-ray diffraction pattern of an aligned sample of compound 2/4 at 127°C clearly excludes a centered cell due to the appearance of the 21 and 12 reflections (see Figure 3d). These reflections can be explained if a $p2gg$ 2D noncentered rectangular lattice is assumed. The lattice parameters were then calculated to be $a = 5.4 \text{ nm}$ and $b = 5.9 \text{ nm}$. These values are more than twice the molecular length ($L = 2.1 \text{ nm}$), and approximately 22 molecules are arranged in the cross section of the unit cell.⁴³

The model shown in Figure 4a was first proposed for the $p2gg$ lattice of compounds 1/10–1/12.²¹ Generally, a $p2gg$ lattice requires a herringbone-like arrangement within the lattice, which was realized in the model in Figure 4a by including two elliptical cylinders per unit cell, separated by bilayer-like aggregates of the bolaamphiphilic units.²¹ However, such a model does not fit with the cylinder-shell models of the other columnar mesophases discussed in this article. Alternatively, the formation of a $p2gg$ lattice is also possible by the regular organization of four cylinders per unit cell. This is achieved if the large cylinders shown in Figure 4a are divided into pairs of cylinders at the same geometrical positions. Such a model with four cylinders per unit cell can easily explain the large lattice parameter found.

The $p2gg$ lattice is located between the $Col_r/c2mm$ phase and the Col_h ($p6mm$) phase. The $c2mm$ lattice is formed by the arrangement of four molecules around a cylinder, whereas the $p6mm$ lattice has six molecules arranged around each cylinder. Therefore, it can be assumed that in the $p2gg$ lattice each cylinder is surrounded by the bolaamphiphilic units of either five or six molecules. If a six-molecule arrangement for the $p2gg$ lattice is assumed, then the cylinder shell must adopt an elongated quadrilateral shape. This shape is formed by the organization of an end-to-end dimer on two sides and a single molecule on the others, as shown in Figure 4b. However, a much simpler lattice, such as the $c2mm$ lattice or an alternative $p2gg$ lattice (however, this two-cylinder-lattice should not be confused

with the previously discussed lattice shown in Figure 4a), composed of only two cylinders per unit cell is more likely. These small lattices, shown in Figure 4c, are more likely as they only contain one type of hydrogen-bonding network (three-wall connections), whereas the $p2gg$ lattice described in Figure 4b contains three distinct types of hydrogen-bonding networks, i.e. two-, three-, and four-wall connections.

A similar $p2gg$ lattice containing four cylinders arranged in pairs is possible when five biphenyl units form the cylinder shell. These biphenyl units would form a pentagonal shape around the cylinder cores as shown in Figure 4, d–f. When a pentagonal cross-sectional shape is adopted, the formation of pairs of cylinders is the only possible structure by which a regular 2D organization of this type of column can be realized, i.e. smaller lattices are not possible. Furthermore, in this structure only two types of hydrogen bonding are combined, three-wall connections (as found in the $p6mm$ lattice of the higher homologues) and four-wall connections (as found in the $c2mm$ lattice of the shorter homologue). In this respect a $p2gg$ lattice formed by the organization of pentagons is intermediate between the $c2mm$ and the $p6mm$ lattice. As shown in Figure 4f, the model consisting of slightly distorted pentagonal cylinders is in very good agreement with measured lattice parameters.⁴⁵ This model also predicts the large value of the number of molecules contained within the unit cell ($n_{\text{cell}} = 22$). Assuming that the wall thickness in the network structure is approximately twice the width of the biphenyl units, a theoretical value $n_{\text{cell,calc}} = 20$ can be calculated (five molecules in each cylinder shell and four cylinders forming the unit cell) which is very close to the experimental value n_{cell} . Therefore, it is suggested, that the $p2gg$ lattices of compounds 1/10–1/12 and compound 2/4 are organized in this type of arrangement. Moreover, it is proposed that in this class of compounds the $p2gg$ lattice containing four cylinders in each unit cell is an indication of a regular 2D organization of pairs of cylinders with *pentagonal cross-sectional shape*.^{46,47} In these $p2gg$ mesophases, the specific pentagonal shape is provided by the self-organization of the rigid biphenyl cores, and it is not averaged out by rotation around the long axis of the cylinders, because this rotation is inhibited by the segregation of the intermolecular hydrogen-bonding networks of the terminal diol groups from the rigid aromatic cores. This segregation fixes the positions of the biphenyl cores (and H-bonding networks) within the cylinder walls.

On further cooling, an additional phase transition was observed in the X-ray diffraction pattern of compound 2/4 at approximately 67°C . At this temperature the spotlike reflections in the small-angle region are replaced by a single sharp ring at $\theta = 2.09^\circ$, corresponding to $d = 2.14 \text{ nm}$ (the diffuse wide-angle scattering remains). It is interesting to note that this reflection shows clear maxima positioned at the equator and at the meridian. A possible explanation for this observation (square columnar phase Col_{sq}) will be given in section 2.4.

Mesophase textures of compounds 2/6–2/i9 are identical and can be optically characterized by the observation of large

(46) In the $p2gg$ phase of the hydrocarbon compounds 1/10–1/12 a number of 19–23 molecules per unit cell was calculated,²¹ which is also in perfect agreement with the pentagonal cylinder model.

(47) This model corresponds to an elemental tiling of 2D space with the topological class $[3^2 \cdot 4 \cdot 3 \cdot]$, for details see: (a) Grünbaum, B.; Shepard, G. C. *Tillings and Patterns*; W. H. Freeman: New York, 1986. (b) Simon, J.; Bassoul, P. *Design of Molecular Materials: Supramolecular Engineering*; John Wiley: Chichester, 2000.

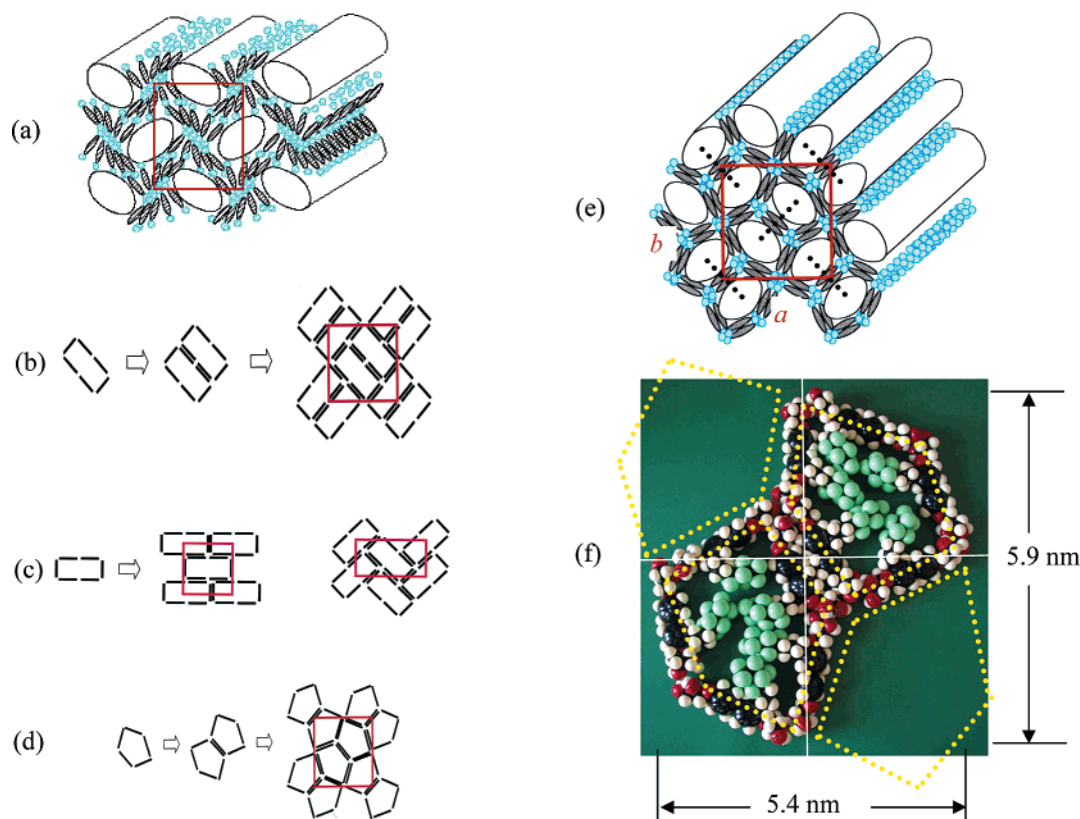


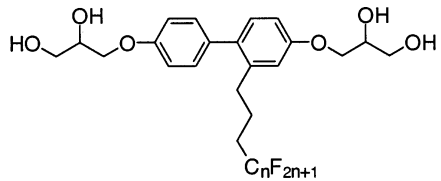
Figure 4. Models for the molecular arrangement of $1/10$ – $1/12$ and $2/4$ in rectangular columnar mesophases. (a) Model with only two elliptical columns per unit cell as initially proposed for the $p2gg$ phases of compounds $1/10$ – $1/12$;²¹ (b) $p2gg$ lattice containing four columns per unit cell as formed by the organization of pairs of cylinders with a quadrilateral cross-sectional shape (only the biphenyl units are shown); (c) other 2D lattices of columnar phases arising from the regular organization of cylinders with a quadrilateral cross-sectional shape (additional oblique lattices are possible); (d) $p2gg$ lattice containing four columns per unit cell as formed by the organization of pairs of cylinders with a pentagonal cross-sectional shape; (e) revised molecular model for the arrangement of $1/10$ – $1/12$ and $2/4$ in the $Col_r/p2gg$ phases; the dotted lines indicate the pairs of columns; (f) CPK models showing 10 molecules of $2/4$ forming a pair of pentagons (central pair of the model shown in d and e).

homeotropic aligned regions containing birefringent filaments, typical for hexagonal columnar phases (see Figure 3e). X-ray diffraction also proof a hexagonal columnar structure for these mesophases and the diffraction pattern of compound $2/i7$ is shown in Figure 3f as an example. The lattice parameters are calculated to be between $a_{\text{hex}} = 3.45$ nm and $a_{\text{hex}} = 3.50$ nm for all investigated Col_h -phases. In all cases approximately six molecules are arranged (on average) in the cross section of each cylinder (see Tables 1 and 2). In this mesophase six biphenyl units form the cylinder shells around the nonpolar cores as shown in Figure 1 (for the Col_h phases of compounds $1/12$ – $1/18$).²⁷

Therefore, with respect to the changes in chain length, the phase sequence $Col_r/c2mm$, $Col_r/p2gg$, $Col_h/p6mm$ was found, which is the same as that found for the alkyl-substituted compounds $1/n$.^{21b} Also similar molecular arrangements for the mesophases of the fluorinated group I compounds $2/3$ – $2/i9$ and the hydrocarbon compounds $1/n$ can be proposed. These mesophases represent cylinder structures in which the semiperfluorinated lateral chains form infinite columns around which the rigid bolaamphiphilic units form a shell. These bolaamphiphilic units are connected end-to-end and side-by-side by elongated hydrogen-bonding networks between the diol groups, and these are arranged parallel to the nonpolar columns. The relative volume required by the semifluorinated chains with respect to the length of the rigid segments determines the number

of biphenyl units organized in the shells around the cylinder cores, and this number increases from four in the $Col_r/c2mm$ and $Col_{sq}/p4mm$ phases (see section 2.4) via five in the $Col_r/p2gg$ phases to six in the $Col_h/p6mm$ phases. Hence, the number of biphenyl units arranged around the nonpolar cylinder cores is well defined, and this leads to distinct polygonal shapes of the cylinder shells. These shapes must enable a regular and uniform packing in 2D space as well as a segregation of the biphenyl units from the diol groups, which allows interconnection of the biphenyl units to occur exclusively at their H-bonding sites (commensurate packing).

Although the phase sequence observed is the same as that found for the hydrocarbon analogues $1/n$, the overall chain length necessary to achieve these columnar phases is significantly reduced. The Col_h phase, for example, occurs for the fluorinated compound $2/6$ (with a total of nine C-atoms in the lateral chain), whereas the same phase is not observed in the $1/n$ series until the lateral hydrocarbon chain contains at least 12 CH_2 groups (compound $1/12$). This observation can be explained due to the much larger volume occupied by semifluorinated chains when compared to that of the corresponding alkyl chains. Indeed, the volume fraction of the lateral chains (f_R , see Table 1), required for the formation of the different types of columnar phases is identical for the bolaamphiphiles with fluorinated and nonfluorinated lateral chains: $Col_r/c2mm$:

Table 2. Mesophases, Phase Transition Temperatures, Phase Transition Enthalpies (lower lines in italics) and Other Parameters of the Bolaamphiphiles **5/n**^a


comp.	<i>n</i>	<i>T</i> /°C	ΔH /kJ mol ⁻¹	<i>a</i> /nm	$V_{\text{cell}}/\text{nm}^3$	$V_{\text{mol}}/\text{nm}^3$	n_{cell}	$n_{\text{cell,calc}}$	n_{wall}	f_R	
5/4	4	Cr ₁ 107	Cr ₂ 121	2.14	2.06	0.640	3.2	4	1.6	0.36	
		<i>(Col_{sq}/p4mm 102) Iso</i>									
		<i>15.5</i>	<i>14.0</i>								
5/6	6	Cr < 20	Col _h 134	3.48	4.72	0.713	6.6	6	2.2	0.43	
5/8	8	<i>6.0</i>		3.47	4.69	0.786	6.0	6	2.0	0.48	
		Cr < 20 Col _h 161 Iso									
		<i>6.1</i>									
5/10	10	Cr 80	M2 114	3.47 ^b	4.69 ^b	0.859	5.5 ^b	6	1.8 ^b	0.53	
		Col _h 147	Iso								
		<i>11.6</i>	<i>1.6</i>	<i>2.0</i>							

^a Abbreviations: Col_{sq} = columnar mesophase with square lattice; M2 = unknown mesophase. ^b Refers to the Col_h phase.

$f_R = 0.28$ – 0.36 ; Col_r/p2gg: $f_R = 0.36$ – 0.43 ; Col_h/p6mm: $f_R = 0.43$ – 0.53 .

The organization into hexagonal columnar phases can be found over the broadest range of volume fraction of the lateral chains, which indicates that it is especially favorable. Furthermore, it is remarkable that the diameter of the columns of the Col_h phases does not change upon elongation of the lateral chain from compound **2/6** to compound **2/i9**. This shows that the diameter of the columns is wholly defined by the length of the bolaamphiphilic units forming the cylinder shells. Therefore, it can be deduced that the additional space required by the larger chains is provided by the stretching of the cylinders along the cylinder long axis, leading to a reduction in the average number of molecules per cylinder segment with $h = 0.45 \text{ nm}^{43}$ from $n_{\text{cell}} = 6.6$ (compound **2/6**) to $n_{\text{cell}} = 5.6$ (compound **2/i9**) for the series **2/n** (and from $n_{\text{cell}} = 6.6$ to $n_{\text{cell}} = 5.5$ for compounds **5/n**, see Table 2, section 2.4). This stretching of the cylinders is accompanied by a slight reduction in the thickness of the cylinder walls. This means, that the number of biphenyl units located side by side within the walls separating the columns (n_{wall} , see Table 1) can vary to optimize the overall space filling within the nonpolar regions of the cylinders. In most cases, an average of two biphenyl units are arranged side by side. For the Col_h phases the value is between 2.2 and 1.8, but in some cases this value can be as low as 1.6 (Col_{sq} phase of compound **4/4**, see section 2.4, Table 2) or as high as 2.3 (*c2mm* mesophases of the group II compounds, see section 2.5). It is also important to note here, that all these structures are highly dynamic and the positions of the molecules within the columns are not fixed. This means that there is no formation of disklike entities or any long-range correlation of the positions of the biphenyl units along the cylinder shells, i.e. there is no perfect order as the models shown might suggest. Therefore, the number of biphenyl units arranged side by side in the cross section of the cylinder walls is an average value and noninteger numbers are allowed.

Before discussing compounds **2/n** and **3/n** with longer chains (group II and III) a discussion of the connection of the

semifluorinated chains with the rigid biphenyl units (compounds **4/n**) and position of the lateral chain (compounds **5/n**) will be made.

2.3. Compounds with Directly Attached Perfluorinated Chains. Two compounds **4/4** and **4/8** have been synthesized, in which the perfluorinated chain is directly attached to the biphenyl units (see Table 1). Compound **4/4**, which has the shortest chain of all synthesized molecules shows a fanlike texture, typical for SmA phases. This is the only bolaamphiphilic compound, reported herein, which shows a smectic A phase where the biphenyl units are thought to be arranged in average perpendicular to the layer plane,⁴⁸ but this phase is only monotropic, so further investigations were not possible.

Compound **4/8** shows a Col_h phase and an additional low-temperature phase (M1), which was not investigated in detail. This material shows an unusually low-melting transition for compounds which contain a perfluorinated alkyl chain attached directly to the mesogenic core. When the transition temperatures and mesophase type for compound **4/8** (C₈-chain) is compared with compounds of the **2/n** series it was found to fit between **2/4** (C₇-chain, Col_r/p2gg) and **2/6** (C₉-chain, Col_h). This means that the volume fraction of the lateral chain with respect to the length of the bolaamphiphilic unit is the dominating factor which determines the mesophase structure. There is no significant influence of the type of connection between the fluorinated segment and the biphenyl unit on mesophase type and mesophase stability.

2.4. Influence of the Position of the Lateral Chain: A Square Columnar Phase. For bolaamphiphiles with lateral alkyl chains, it was found that the position of substitution at the biphenyl unit only has an influence upon the mesophase stability, and not the mesophase type.^{21b} To check if this also applies for the perfluorinated compounds a series of compounds **5/4**, **5/6**, **5/8**, and **5/10** have been synthesized, in which the semiperfluorinated chain is attached at the 2-position on the aromatic core. Compounds **5/6** and **5/8** which are related to the isomeric compounds **2/6** and **2/8** show Col_h phases; however,

(48) Also a SmA+ structure^{21b} could be possible for this mesophase.

these materials have significantly reduced clearing temperatures (see Table 2). This reduction in clearing temperature was also observed in other amphiphilic⁴⁹ and non-amphiphilic liquid crystals⁵⁰ when the lateral chain is moved to a more central position. Two possible explanations for this phenomenon have been proposed: (i) that changing the position of the lateral substitution would cause a change of the conformation of the biphenyl unit, i.e. a change in the dihedral angle between the planes of the adjacent benzene rings and (ii) that a change of substitution would disturb the parallel alignment of the rigid units.

However, compound **5/4** is different from **5/6** and **5/8**. This compound shows a texture (Figure 5a) which is quite different from that of the isomeric compound **2/4**. The mesophase is optically uniaxial, and the texture is similar to those found for the hexagonal columnar phases in series **2/n** and **4/n**. However, the 2D X-ray diffraction pattern of an aligned sample (Figure 5b) indicates a liquid crystalline phase with a square lattice ($p4mm$), which is in full accordance with the optical uniaxiality of this mesophase.⁵¹ The lattice parameter can be calculated to $a_{sq} = 2.14$ nm, which is close to the molecular length in a stretched conformation ($L = 2.1$ nm).⁴⁵ The model shown in Figure 5c is in good agreement with the experimentally determined lattice parameter. Accordingly, the arrangement of the molecules in this mesophase is similar to those found in the centered rectangular columnar $c2mm$ phase of compound **2/3**. In both mesophases four bolaamphiphilic units form the cylinder shells around the nonpolar columns of the semifluorinated chains. The main difference is that the columns in the Col_{sq} phase have a circular to square-like⁵² instead of an elliptical cross-sectional shape. This enhances the symmetry and gives rise to the change in lattice type. Hence, the Col_{sq} -phase of **5/4** can be regarded as an intermediate stage in the transition from the $c2mm$ lattice to the $p2gg$ lattice. In this square-columnar phase the space between the four bolaamphiphilic units is filled to the maximum possible extent, and therefore the columns adopt a square cross section. However, it was found that in this mesophase approximately 3.2 molecules are contained within the unit cell. It is thought that this unusually low number of molecules contained within the unit cell arises due to an overcrowding of the interior of the columns in this square phase. This leads to an expansion of the columns along their long axes (as discussed in section 2.2. for the Col_h phases), and therefore a reduction in the number of molecules organized in the cross section of the cylinder walls is found. The same results were obtained from the CPK model shown in Figure 5d. The length of each side of this square is ca. 2.3 nm, which means that the

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(50) (a) Gray, G. W.; Hird, M.; Toyne, K. J. *Mol. Cryst. Liq. Cryst.* **1991**, *195*, 221–237. (b) Hird, M.; Toyne, K. J.; Hindmarsh, P.; Jones, J. C.; Minter, V. *Mol. Cryst. Liq. Cryst.* **1995**, *260*, 227–240. (c) Andersch, J.; Tschierske, C.; Diele, S.; Lose, D. *J. Mater. Chem.* **1996**, *6*, 1297–1307. (51) Earlier reports about Col_{sq} phases: (a) Ohta, K.; Watanabe, T.; Hasebe, H.; Morizumi, Y.; Fujimoto, T.; Lelievre, D.; Simon, J. *Mol. Cryst. Liq. Cryst.* **1991**, *196*, 13–26. (b) Praefcke, K.; Marquardt, P.; Kohne, B.; Stephan, W. *Mol. Cryst. Liq. Cryst.* **1991**, *203*, 149–158. (c) Komatsu, T.; Ohta, K.; Watanabe, T.; Ikemoto, H.; Fujimoto, T.; Yamamoto, I. *J. Mater. Chem.* **1994**, *4*, 537–540. (d) Hatusaka, K.; Ohta, K.; Yamamoto, I.; Shirai, H. *J. Mater. Chem.* **2000**, *11*, 423–433.

(52) In Figure 5c, the cross-sectional shape of the cylinder cores is represented by a circle; however, the shape of the cylinder shells is a square. Therefore, the cylinder cores must, in actual fact, have a cross-sectional shape which is between a circle (minimized interfacial areas) and a square (maximal space filling), i.e. it should be a "square with rounded corners". Related arguments also concern the models of all other columnar phases discussed herein.

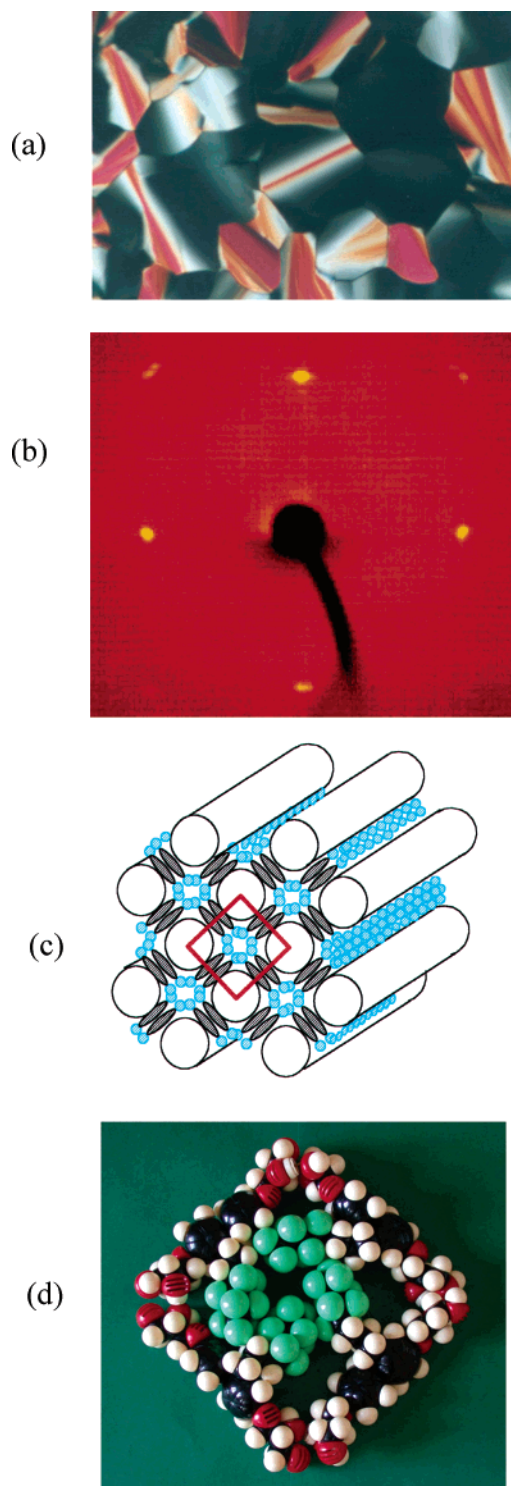


Figure 5. (a) Texture (crossed polarizers) of the Col_{sq} phase of compound **5/4** at 95 °C; (b) X-ray diffraction pattern of an aligned sample of the Col_{sq} phase at 99 °C (small-angle region); (c) model of the organization of the molecules in the Col_{sq} phase (two biphenyl units are shown in each cylinder wall; however, in reality this number is only about 1.6). (d) CPK models showing four molecules of **5/4** forming a square.

lattice parameter of 2.14 nm can only be realized if the effective thickness of the cylinder walls is less than the usually observed value of two molecules.

A Col_{sq} phase could also be one possible explanation for the low-temperature phase observed in the isomeric compound **2/4**. Although no well-aligned samples have been obtained for this

mesophase, the observation of a sharp ring in the small-angle region could result from the 10 and 01 reflections of a Col_{sq} phase (multidomain sample). Assuming such an indexing would lead to $a = 2.14$ nm, which exactly corresponds to the lattice parameter found for the Col_{sq} phase of **5/4**. This means that changing the position of the $(\text{CH}_2)_3\text{C}_4\text{F}_9$ chain has a stabilizing effect upon the $\text{Col}_{\text{sq}}/p4mm$ phase with respect to the $\text{Col}_l/p2gg$ phase. This would seem to suggest that a chain in the 2-position requires less space than that in the 3-position and hence enables a slightly more efficient packing. Probably, the more pronounced T-like shape of **5/4** is also favorable for the organization in a square lattice.

A similar influence of the position of the chain on the mesophase type is evident if the isomeric compounds **2/10** and **5/10** are compared. Compound **5/10** exhibits a broad region of a Col_h phase, whereas the isomeric compound **2/10** exhibits a mesophase with a novel $c2mm$ lattice (see section 2.5). However, at low temperature a mesophase with unknown structure (M2) was found for **5/10**, which could possibly be related to the mesophase type found for **2/10**.

2.5. Mesophases of Group II Compounds: Columnar Phases with Large Lattice Parameters. Compounds **2/10**, **2/i11**, and **2/12** show two new columnar phases. The texture of the mesophase of **2/10** (Figure 6a) is different from any other known liquid crystalline phase. In the X-ray pattern only reflections with $h + k = 2n$ have been observed in the small-angle region (Figure 6b). These reflections can be assigned to a centered rectangular lattice ($c2mm$) with the lattice parameters $a = 3.7$ nm and $b = 9.6$ nm. An additional weak reflection on the meridian corresponding to a periodicity $d = 3.4$ nm could be explained by a contribution of a differently aligned monodomain. The lattice parameter b in this $c2mm$ phase is much larger than that found for the $c2mm$ phase of compound **2/3**. One possible explanation for the organization of molecules within this columnar mesophase is shown in Figure 6, c and d. In this model the bolaamphiphilic units again form shells around the cylinder cores of microsegregated semiperfluorinated chains. In this phase the shells contain eight bolaamphiphilic units in the cross section instead of six as found for the Col_h phases. As regular octagons cannot efficiently pack into a 2D lattice, the shell adopts a deformed hexagonal shape. Within these hexagons two opposite sides are stretched, i.e. two sides of these hexagons are formed by an end-to-end dimer. This causes a reduction of the symmetry, leading to a change of the lattice type from $p6mm$ to $c2mm$. Within this $c2mm$ lattice the lattice parameter a has the same order of magnitude as a_{hex} for the Col_h phases of compounds **2/n**, (about $3^{1/2} L$), whereas the parameter b is significantly enlarged and has a value equivalent to 4–5 times the molecular length. This can be seen in Figure 6c, and these lattice parameters predicted are in excellent agreement with the experimental data.

The optical texture of compound **2/i11** (see Figure 7a, b) is quite different from **2/10**. However, both diffraction patterns can be indexed on the basis of a centered rectangular $c2mm$ lattice, and the lattice parameters obtained for these two compounds are almost identical. Therefore, the model for the organization of the molecules in this mesophase is similar to that shown in Figure 6c.⁵³ The apparent differences in the diffraction patterns are thought to arise due to differing alignments within the rotationally disordered sample. In com-

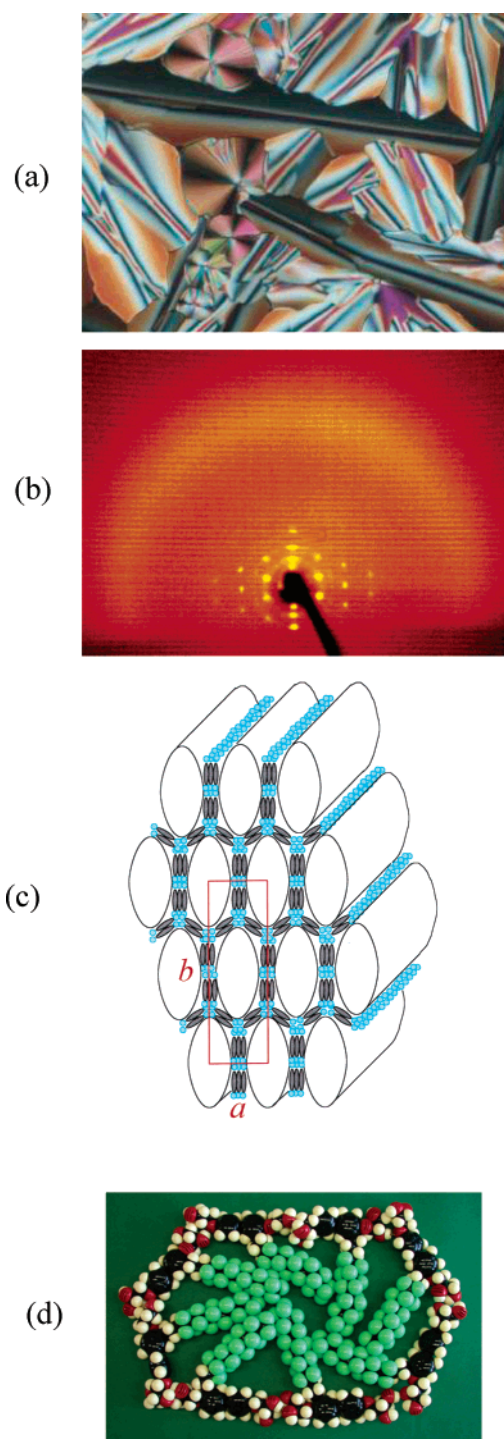


Figure 6. (a) Texture of the mesophase of compound **2/10** as obtained on cooling from the isotropic liquid at $T = 170$ °C; (b) X-ray diffraction pattern of an aligned sample of **2/10** at 150 °C; (c) molecular arrangement within the rectangular columnar mesophase Col_l with a $c2mm$ 2D space group; (d) CPK model of eight molecules **2/10** arranged so that the semiperfluorinated chains form a central region around which eight bolaamphiphilic units are arranged.

ound **2/i11** the crystallographic (110) plane of the lattice is parallel to the surfaces; thus, the sample is rotationally disordered about the normal to this plane. Figure 7c shows two

(53) In contact preparations of compounds **2/10** and **2/i11** a continuous change of the isotropization temperature was found without any minimum. This may be another indication that both materials show a mesophase structure of the same type. Also in the contact region between **2/i7** (Col_h) and **3/12** (Lam) only one single new columnar mesophase is induced, as expected.

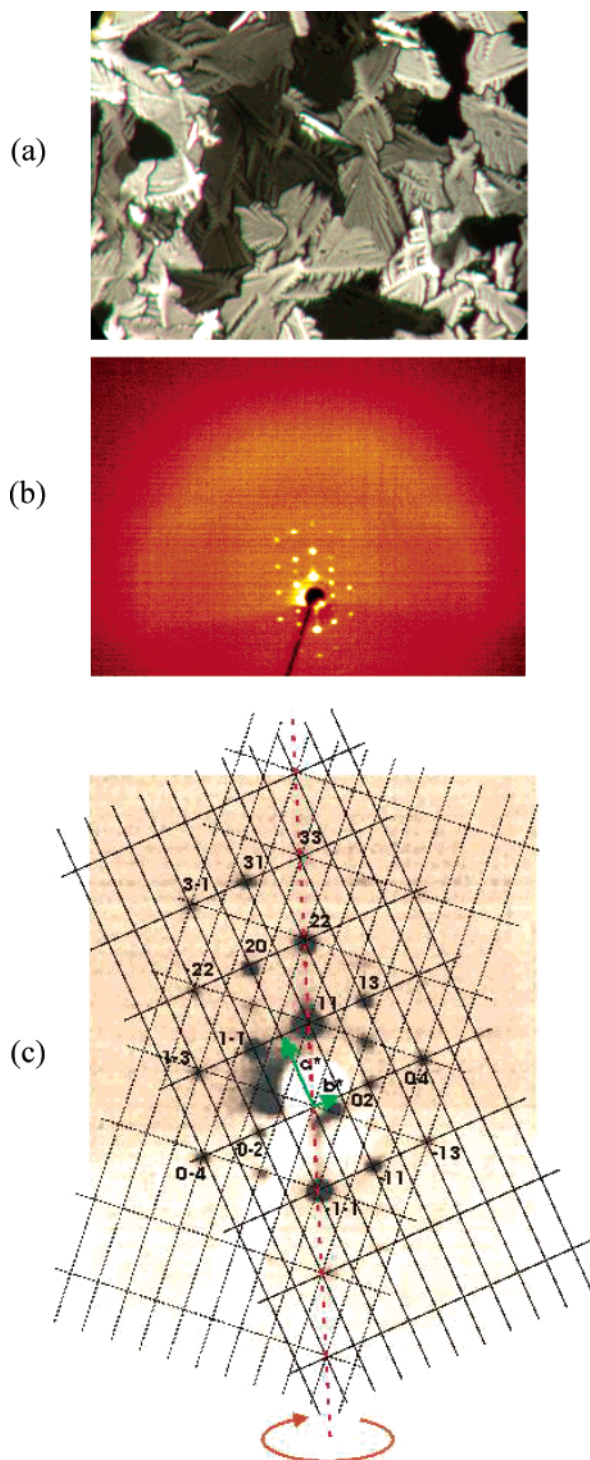


Figure 7. (a) Texture of the mesophase of compounds **2/i11** as obtained on cooling from the isotropic liquid at 178 °C; (b) X-ray diffraction pattern of an aligned sample of **2/i11** at 177 °C; (c) the same pattern showing the two orientations of the 2D reciprocal lattice.

orientations of the reciprocal lattice that give rise to the diffraction pattern. The different reflection intensities observed for both orientations may be due to a “nonperfect” disorder in the sense that a nonequally distributed orientation of the cylinder axes exists around the normal of the (110) plane. In the sample of **2/10** the (010) plane is parallel to the surface, and the rotation axis is perpendicular to this plane. Since this axis lies within one mirror plane of the lattice, the reflections of both orientations

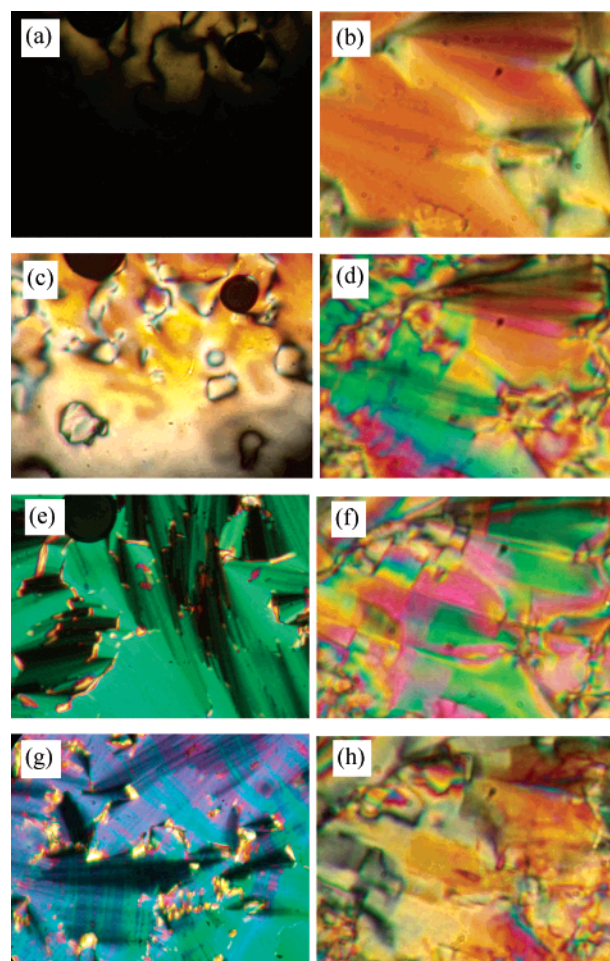


Figure 8. Optical textures (crossed polarizers) of compound **2/12** as observed on cooling a homeotropically aligned sample (layers are parallel to the surfaces of the glass substrates, left) and a sample showing a fan-shaped texture (layers are perpendicular to the glass substrates, right): (a) Lam_{iso} phase at 181.5 °C (in the upper part the schlieren texture of the Lam_{N} phase develops); (b) Lam_{iso} phase at 183 °C; (c, d) Lam_{N} phase at 181 °C; (e, f) $\text{Col}_r/c2mm$ phase at 160 °C; (g) transition from the $\text{Col}_r/c2mm$ phase (lower right corner) to the $\text{Col}_r/p2gg$ phase (upper left corner) at 155 °C; (h) $\text{Col}_r/p2gg$ phase at 145 °C.

fall together. This different sample alignment could also be a possible explanation for the different optical textures observed between crossed polarizers.

Compound **2/12** shows four different mesophases (see Figures 8 and 9). The two high-temperature mesophases are lamellar phases (Lam_{iso} and Lam_{N} phases) which are described in the next section. Figure 8 shows changes in the textures of these lamellar mesophases upon cooling (between crossed polarizers), and the corresponding X-ray diffraction patterns of aligned samples are shown in Figure 9.

The mesophase which is observed below the lamellar phases appears to have a 2D lattice. The diffraction pattern of this mesophase (Figure 9b) can also be assigned to a $c2mm$ lattice, where the lattice parameters are $a = 9.7$ nm, $b = 4.0$ nm. The value of b is slightly larger than that observed for the $c2mm$ phase of **2/i11** ($b = 3.7$ nm). At first glance the diffraction pattern looks quite distinct from those obtained for the $c2mm$ lattices of **2/10** and **2/i11**. This is due to the almost perfect cylindrical averaging in the sample, which is again aligned parallel to the (110) plane of the lattice as in the case of **2/i11**.

A complete change of the diffraction pattern (see Figure 9c)

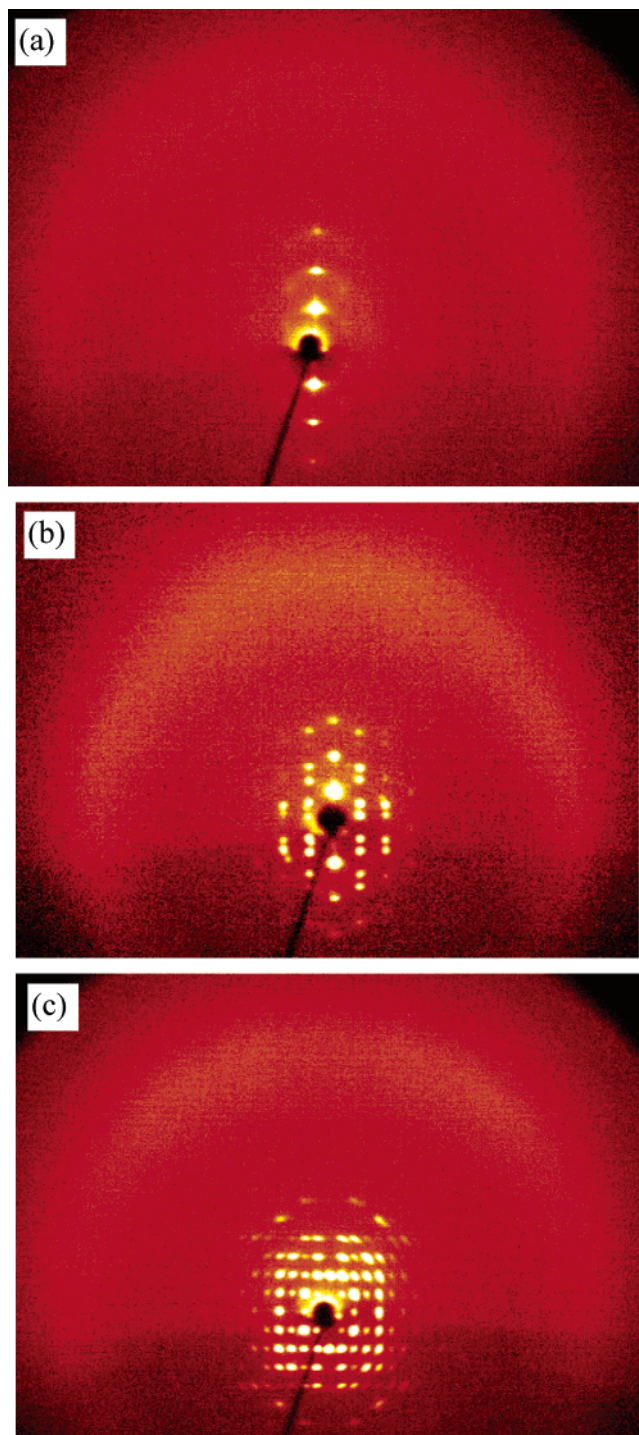


Figure 9. X-ray diffraction pattern of an aligned sample of **2/12** (a) $\text{Lam}_{1\text{so}}$ phase at 184 °C; (b) $\text{Col}_h/c2mm$ phase at 167 °C and (c) $\text{Col}_h/p2gg$ phase at 151 °C.

and of the texture (see Figure 8, g and h) was observed on further cooling at 155 °C. The diffuse outer scattering remains, but more than 100 sharp spots appear in the small-angle region of the diffraction pattern. These reflections can be assigned to a noncentered rectangular lattice with the space group $p2gg$ and lattice parameters $a = 11.5$ nm and $b = 7.7$ nm. These lattice parameters are much larger than those found for all other mesophases of compounds $1/n-5/n$. Such large lattice parameters would suggest that this $p2gg$ lattice results from the organization of four columns in the unit cell, as proposed in

section 2.2 for the $p2gg$ phase of $2/4$. When a comparison of the area of the high-temperature $c2mm$ lattice ($S = 38.8$ nm², two columns per cell) and the lower-temperature $p2gg$ lattice ($S = 88.8$ nm², four columns per cell) of $2/12$ is made, it is apparent that the area of this $p2gg$ lattice is more than twice the area of the $c2mm$ lattice. This is thought to arise due to an increase in the number of molecules within the cross section of each column. Calculations based on these areas give a value of 9.3 molecules per column in the $p2gg$ phase. If it is additionally assumed that a more efficient packing of molecules occurs at lower temperature, then it is reasonable to assume that this number is in fact 10 molecules per column. As each unit cell contains four columns, then a number of $n_{\text{cell,calc}} = 40$ molecules is expected to be located in each unit cell with a height of $h = 0.45$ nm. A value of $n_{\text{cell}} = 42.7$ was calculated from the experimental data, and this is in good agreement with the ideal value proposed. As suggested in section 2.2 the occurrence of a $p2gg$ lattice in this class of compounds is a strong indication for a columnar mesophase formed by the organization of cylinders with a pentagonal cross-sectional shape. Furthermore, a pentagon can be easily built up by a number of 10 molecules if each side of the pentagon is formed by two molecules. Therefore, the most probable arrangement for this $p2gg$ lattice is a regular and commensurate packing of four cylinders, each cylinder having a pentagonal cross-sectional shape made up of 10 molecules in the cross section in which each side of the pentagon is formed by end-to-end dimers as shown in Figure 10a. Figure 10b shows the CPK model of 10 molecules of $2/12$ arranged in a pentagon, and the lattice parameters measured for the model are in good agreement with the experimental values obtained. The formation of such an unusual structure is thought to arise due to an increase in the stiffness of the perfluorinated chains upon reducing the temperature.

These results show that further elongation of the lateral chains leads to a further expansion of the cylinders which gives rise to a transition from the Col_h phases to new columnar phases with a cylinder-shell morphology and very large unit cell parameters. In these mesophases at least two sides of the cylinder shells are elongated, and these sides are formed by two end-to-end connected bolaamphiphilic units. These columnar phases are thought to represent intermediary phases at the transition from hexagonal cylinder structures to a novel type of lamellar organization, and these lamellar phases will be discussed in the next section.

2.6. Lamellar Mesophases of Group III Compounds. As mentioned in the previous section compound **2/12** forms not only two distinct columnar mesophases, but also two lamellar high-temperature mesophases. Much broader regions of these lamellar mesophases were found for compounds **3/10**⁵⁴ and **3/12** which have longer lateral chains. In this section attention will be focused on the lamellar phases of these two compounds. Both compounds contain three different mesophases with layered structure.

The DSC heating and cooling scans of **3/12** are shown in Figure 11, and the textures of the different mesophases are collated in Figure 12. Upon cooling the first mesophase behaves like a conventional SmA phase. This is characterized by a typical fanlike texture (Figure 12b) which can be easily aligned

(54) Preliminary communication: Prehm, M.; Cheng, X. H.; Diele, S.; Das, M. K.; Tschierske, C. *J. Am. Chem. Soc.* **2002**, *124*, 12072–12073.

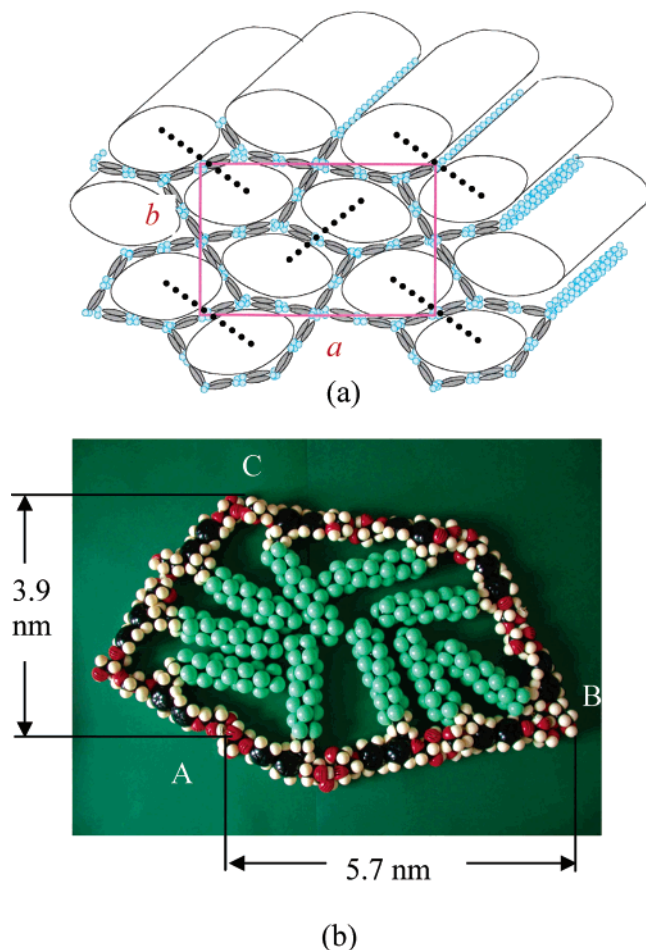


Figure 10. (a) Possible molecular arrangement of the molecules in the rectangular columnar mesophase Col_r of compound **2/12** with a $p2gg$ 2D space group, the dotted lines indicate pairs of columns; (b) CPK models showing an arrangement of 10 molecules **2/12** in a pentagon, in which each side is formed by end-to-end connected dimers (the upper right cylinder within the frame of the $p2gg$ lattice in (a) is shown, the hydrogen-bonding site A is located in the center of the unit cell, the distances A–B and A–C correspond to $0.5a$ and $0.5b$, respectively).

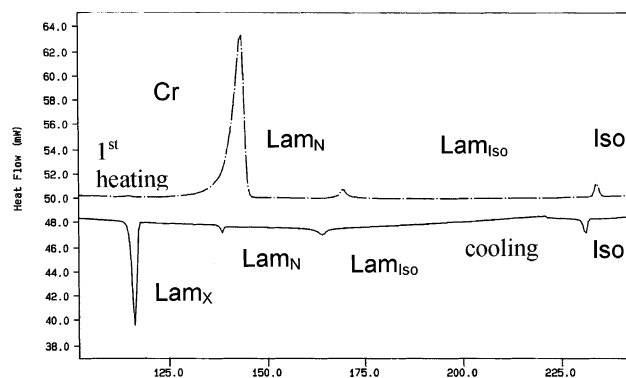


Figure 11. DSC heating and cooling scans of compound **3/12** (10 K min^{-1}).

homeotropically (in this alignment the layers are parallel to the glass surfaces of the measuring cell) and which appears almost completely black between crossed polarizers, but contains some oily streaks and some other defects due to a nonperfect alignment when viewed through crossed polarizers (Figure 12a). Upon further cooling of this homeotropically aligned sample a fluid schlieren texture appears (Figure 12c), indicating the transition to a fluid, optically biaxial mesophase. A characteristic

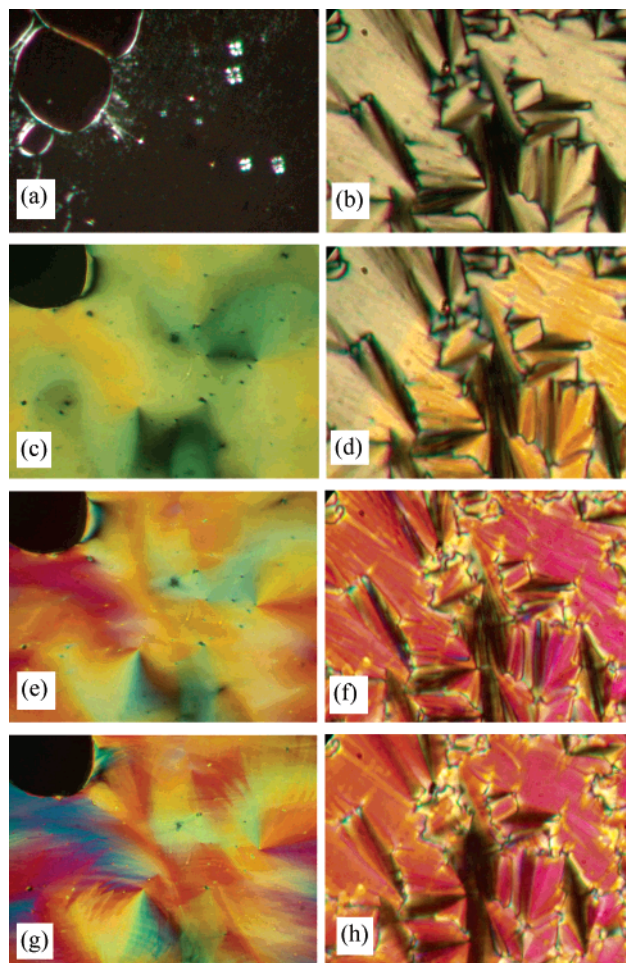


Figure 12. Optical textures (crossed polarizers) of compound **3/12** observed on cooling a homeotropically aligned sample (left) and a sample with fan-shaped texture (right): (a, b) Lam_{Iso} phase at $180\text{ }^\circ\text{C}$; (c) Lam_N phase at $168\text{ }^\circ\text{C}$; (d) Lam_{Iso} – Lam_N transition at $169\text{ }^\circ\text{C}$; (e, f) Lam_N phase at $163\text{ }^\circ\text{C}$; (g, h) Lam_X phase at $139\text{ }^\circ\text{C}$.

feature of this schlieren textures is the absence of any four-brush-disclinations. This excludes a SmC -like organization in which the molecules are tilted with respect to the layer planes, as often found below the SmA phases in conventional LC materials. Upon cooling, in the regions with a fan-shaped texture a strong change in the birefringence can be observed at the phase transition; however, the fans themselves are unaffected (see Figure 12, d and f). These textural features are typical for transitions from uniaxial SmA phases to biaxial SmA_b phases^{55,56} in which the layer structure remains unchanged; however, there is a change of the ordering within the layers.

Upon transition to the third mesophase the fan texture remains unaffected (see Figure 12h), whereas in the schlieren texture a distinct featherlike pattern appears, as well as an increase in birefringence (Figure 12g). There is also an associated increase in the viscosity of the sample at the transition to this low-temperature mesophase.

However, the X-ray diffraction patterns of all three phases are almost identical, and are characterized by a diffuse scattering

- (55) Brand, H. R.; Cladis, P. E.; Pleiner, H. *Macromolecules* **1992**, *25*, 7223–7226.
 (56) (a) Pratibha, R.; Madhusudana, N. V.; Sadashiva, B. K. *Science* **2000**, *288*, 2184–2187. (b) Hegmann, T.; Kain, J.; Pelzl, G.; Diele, S.; Tschierske, C. *Angew. Chem., Int. Ed.* **2001**, *40*, 887–890. (c) Sadashiva, B. K.; Reddy, A.; Pratibha, R.; Madhusudana, N. V. *Chem. Commun.* **2001**, 2140–2141.

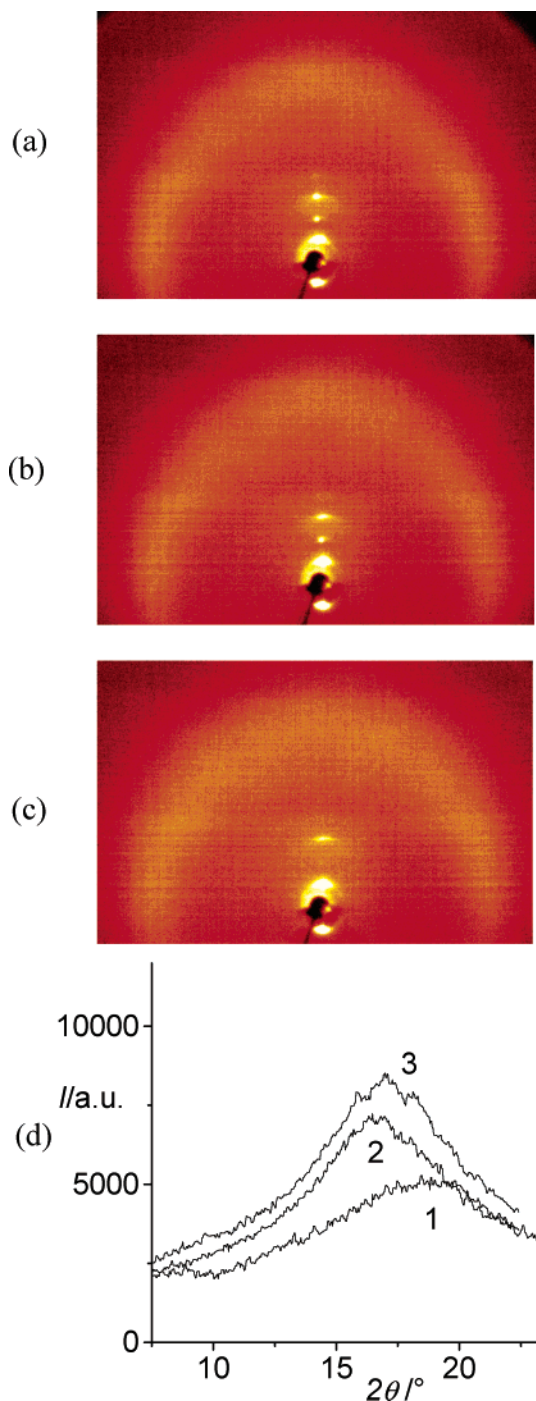


Figure 13. X-ray diffraction pattern of an aligned sample of compound 3/10 (a) at 147 °C (Lam_X), (b) at 167 °C (Lam_X), (c) at 185 °C (Lam_{Iso}), and (d) scans of the pattern obtained at 185 °C along the meridian (1) and along the equator (2, 3).

in the wide-angle region, and in the small-angle region by several sharp equidistant reflections on the meridian, indicating the presence of well-defined fluid layer structures. The X-ray diffraction patterns for the mesophases of 3/10 are shown in Figure 13. The layer thickness is 3.94 nm for 3/10 and strongly increases by elongation of the lateral chain (3/12: $d = 4.5$ nm).⁵⁷

(57) This strong increase of d with the chain length is unexpectedly large compared to observations made with smectic phases of conventional LC materials. A detailed discussion of this effect is however difficult, because not only the degree of intercalation of the chains, but also the thickness of the aromatic sublayers can change, depending on the chain length, and both have a strong influence upon the layer distances.

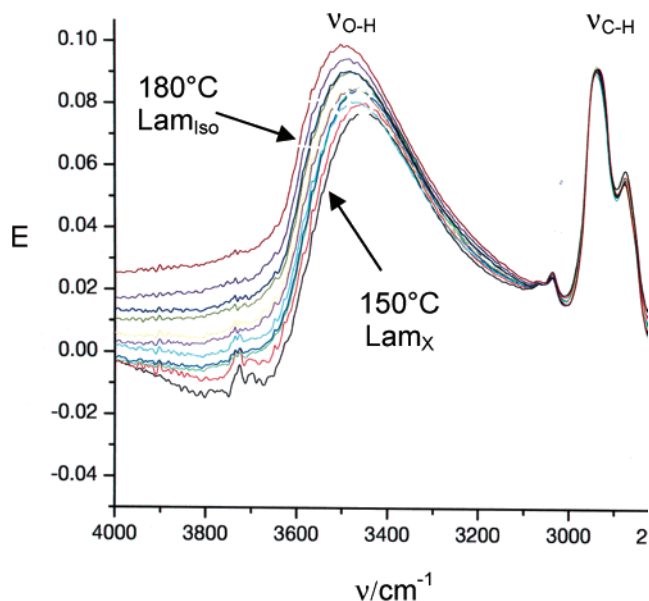


Figure 14. Temperature dependence of the ν_{O-H} stretching frequency in the IR spectra of compound 3/10 in the region measured between 150 and 180 °C at 3 K intervals.

However, the layer thickness does not change at the transitions between the different phases. Only the number of higher-order reflections increases with decreasing temperature. Another important feature of the X-ray diffraction pattern of aligned samples is the diffuse wide-angle scattering which forms a noncircular ring with maxima corresponding to $D = 0.53$ nm at the equator and to $D = 0.48$ nm at the meridian. The maximum at the equator is thought to be due to the perfluorinated chains, whereas the maxima at the meridian result from the rest of the molecule. Therefore, it is assumed that the perfluorinated chains are aligned in average parallel to the meridian (layer normal), whereas the aromatic parts are aligned perpendicular to it.

Compound 3/10 was investigated by IR spectroscopy between 150 and 180 °C to include all three mesophases. This investigation focused on the O–H stretching frequency region of the IR spectra; however, no significant changes in the spectra were observed (see Figure 14). The OH stretching region for all phases was characteristic of extended intermolecular hydrogen-bonding networks^{23,58} and would seem to indicate that structural changes are due to the reorganization of the biphenyl units rather than to significant changes in the hydrogen-bonding networks. This is supported by the observation of low enthalpies (Figure 11) at the transitions between the different lamellar phases and into the isotropic liquid.

The optical observations in conjugation with the X-ray patterns give rise to the proposed molecular arrangements, shown in Figure 15, a–d. The layer structure arises due to segregation of the nonpolar lateral chains from the bolaamphiphilic units (biphenyl units and terminal diol groups) into distinct sublayers, however, unlike conventional smectic phases, the calamitic biphenyl units are organized *parallel to the layer planes*. The aromatic layers are separated by the nonpolar layers of the lateral chains. These chains are strongly disordered

(58) Siegel, G. G.; Huyskens, P. L. In *Intermolecular Forces, An Introduction to Modern Methods and Results*; Huyskens, P. L., Luck, W. A. P., Zeegers, T., Eds.; Springer: Berlin, 1999; pp 387–395.

(liquidlike) but with a certain preferred direction of the fluorinated segments perpendicular to the layer planes (the maximum of the diffuse scattering at the equator is very close to the value for the mean distance between perfluorinated chains corresponding to $D = 0.54$ nm). The experimentally determined layer distance requires that the chains are intercalated and that the thickness of the aromatic sublayers should correspond to, on average, approximately 3 times the width of the biphenyl unit. The diffraction pattern and the layer distances do not change at the phase transitions, and therefore, the biphenyl units remain parallel to the layer planes in all three lamellar phases. It is suggested that the symbol Lam should be used for each of these special types of lamellar mesophases, to distinguish them from the conventional smectic phases of rodlike mesogens and the smectic phases of the bolaamphiphiles $1/0-1/9$, and $4/4$, in which the rodlike cores are aligned perpendicular to the layer planes (SmA) or tilted (SmC). As indicated by the IR investigations, the phase transitions seems to be accompanied by a change of the shape and distribution of the hydrogen-bonding networks rather than by a change in the size of the networks as all phases have quite large dynamic hydrogen-bonding networks. In the isotropic liquid phase these networks are thought to be randomly distributed in space, whereas in the Lam phases they are concentrated within the sublayers of the bolaamphiphilic moieties. Hence, there are clusters of molecules in all mesophases.

Three subtypes of Lam phases were observed, which show different optical properties as a function of temperature. The high-temperature phase is optically uniaxial as observed for SmA and lyotropic L_α phases, and upon cooling a transition to an optically biaxial Lam phase is observed. These two mesophases and the transition between them will be discussed first. There are two different organizations which could explain the uniaxiality of the high-temperature phase. One possible structure for the uniaxial phase is a lamellar organization in which there is no other ordering within the plane.⁵⁹ The bolaamphiphilic moieties are organized in clusters which are irregularly distributed within the layers, as shown in Figure 15b. Because there is an isotropic distribution of the calamitic units within the layer planes this phase is assigned as Lam_{Iso} ($D_{\infty h}$ symmetry). At the transition to the optically biaxial mesophase below the Lam_{Iso} phase, the biphenyl units adopt a long-range orientational ordering within the aromatic sublayers, and the individual layers become orientationally correlated to one another. Therefore, biaxiality is observed throughout the bulk (see Figure 15c). This phase can be regarded as a lamellar phase built up of quasi-2D layers with nematic-like ordering within the plane, separated by layers of the fluid lateral chains, and therefore this mesophase is designated *laminated nematic* (Lam_N) and exhibits a D_{2h} symmetry. Another model for the optically uniaxial phase is also possible, in which a nematic order within the aromatic sublayers is already present, but in which an orientational correlation between adjacent layers does not exist (noncorrelated Lam_N phase). This arrangement would also be optically uniaxial, and the transition to the optical biaxial mesophase in this case would arise due to the onset of the orientational correlation between the layers, which may be caused by a reduction in the conformational (internal) mobility of the molecules at reduced

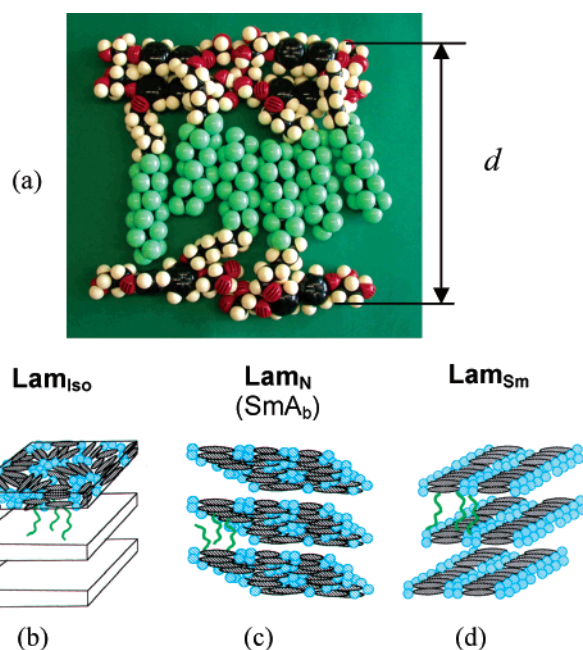


Figure 15. (a) CPK model of six molecules of 3/10 arranged into layers. On average the aromatic sublayers have a thickness 3 times the width of the aromatic unit. The marked d -spacing corresponds to the experimentally determined value. (b–d) Models of the organization of the molecules in the different lamellar mesophases. The rigid bolaamphiphilic units (gray) are arranged parallel to the layer planes, and the space between the layers is filled by the fluid lateral semiperfluoroalkyl chains. The Lam_{Sm} structure shown in (d) represents a possible structure of the Lam_X low-temperature phase of compounds 3/ n .

temperature. This would lead to a preferred direction within the fluorinated sublayers, and as a consequence correlation between the layers would arise. However, there is no direct experimental evidence for either of these two possibilities, but replacement of the biphenyl unit by an elongated p -terphenyl unit⁶⁰ leads to a complete loss of the optically uniaxial phase and a strong stabilization of the biaxial mesophase, which is predicted by using the Lam_{Iso} model of the uniaxial mesophase. Therefore, it seems likely that the optically uniaxial high-temperature phase is a Lam_{Iso} phase and that the formation of a long-range orientational order within the individual layers is coupled with the formation of long-range orientational correlation between adjacent layers.

The structure of the low-temperature mesophases Lam_X for compounds 3/10 and 3/12 is even more difficult to understand and still remains somewhat unclear. A crystallization in one of the sublayers can be excluded due to the presence of diffuse scattering in the wide-angle region of the X-ray diffraction pattern. If an analogy is drawn with the phase sequence Iso–N–Sm, seen for calamitic molecules upon decreasing temperature, it can be assumed that the same sequence occurs in the 2D sublayers of the bolaamphiphilic units. Hence, it is thought that in the low-temperature phase an additional periodicity occurs parallel to the aromatic sublayers arising from the organization of the hydrogen-bonding networks into stripes. These stripes are separated by ribbons of biphenyl units organized in a parallel fashion. Such a phase should exhibit a reflection at the equator of the diffraction pattern; however, this has not been observed. A possible explanation for the absence of this reflection may be that the number of scattering units

(59) A related mesophase was reported for anthracene derivatives: Norvez, S.; Tournilhac, F. G.; Bassoul, P.; Hersonn, P. *Chem Mater* **2001**, *13*, 2552–2561.

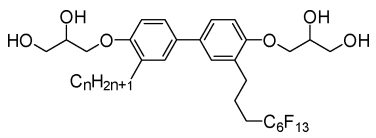
(60) Cheng, X. H.; Tschierske, C. Unpublished results.

contributing to the overall scattering volume is small and that the electron density modulation parallel to the layer planes is much lower than perpendicular to the layers. Both effects would cause this reflection to have very low intensity. There are two possible organizations of layers with such an additional in-plane periodicity; the layers could be either correlated or noncorrelated, positionally. A correlated layer structure was recently reported for a molecule, related to **3/n** but with a branched semiperfluorinated lateral chain, and as expected, a 2D lattice as typical for a columnar phase ($Col_r/p2mm$) was indicated by several reflections out of the meridian of the diffraction pattern.⁶¹ This shows that such a 2D lattice should be detectable by X-ray diffraction. Therefore, the other possible structure, i.e. a mesophase without positional correlation between adjacent layers (but with orientational correlation), designated herein as Lam_{Sm} (see Figure 15d), seems more likely for this mesophase.⁶² Theoretically, a streaky vertical reflection should be observed on the equator of the diffraction pattern of such a mesophase, but according to the arguments given above such a reflection might not be detected due to its low intensity. Therefore, it is proposed that a Lam_{Sm} structure is the most likely possibility for the Lam_X phase, but further investigations are necessary to completely understand this special type of mesophase.⁶³

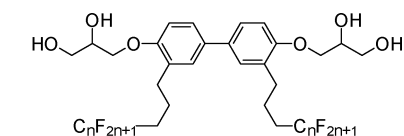
Apart from a temperature dependence, the chain length (i.e. the space required by the lateral chains) also has a significant influence on the subtype of Lam phases observed. The broadest regions of the Lam_{Iso} and Lam_N phases were found for **3/12**, whereas a stabilization in the Lam_X phase was observed on reducing the chain length. This leads to a rather small region of the Lam_N phase for compound **3/10**.⁵⁴ It seems that the space required by the lateral chains in the nonpolar sublayers also has an influence upon the organization of the rigid calamitic units within the aromatic sublayers. It is thought that upon increasing the chain length there is not only an increase of the layer distance d but also an expansion of the area required by the chains within the layer planes. This leads to an increased separation of the rigid units, which disfavors the occurrence of orientational and positional in-plane ordering. For this reason compound **2/12**, which has a shorter chain than compounds **3/n**, has only very short Lam_{Iso} - and Lam_N -phase regions. However, this compound does not exhibit a Lam_X phase, but instead, different columnar mesophases; this has already been discussed in section 2.5.

2.7. Compounds with Two Lateral Chains. Three different types of bolaamphiphiles with two lateral chains have also been synthesized. Compounds **6/n** (see Table 3) have a semiperfluorinated chain and an alkyl chain, whereas compounds **7/n** have two semiperfluorinated chains. Compound **6/1** is similar to **2/6**, but has an additional methyl group attached to the aromatic core. As with compound **2/6** it forms a hexagonal columnar phase, but the mesophase stability is significantly reduced. All bolaamphiphiles with two long lateral chains rapidly crystallize at high temperatures without the observation of any liquid

Table 3. Transition Temperatures ($T/^\circ\text{C}$) of the Bolaamphiphiles **6/n**

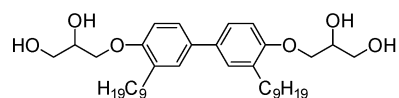


cmpd	n	$T/^\circ\text{C}$
6/1	1	Cr 97 Col _h 134 Iso
6/6	6	Cr 137 Iso
6/12	12	Cr 134 Iso



7/6: $n = 6$ mp.: 147 °C

7/i7: $n = 7$ mp.: 143 °C



1/9,9: mp.: 123 °C

crystalline phase. This shows that enlargement of the nonpolar regions is not possible by attaching two lateral chains to a biphenyl unit.

3. Summary and Conclusions

In this investigation novel complex mesophase morphologies were obtained by careful molecular design. This was achieved by attaching a nonpolar chain laterally to a rigid rodlike bolaamphiphilic core. Rodlike bolaamphiphiles are known to form extremely stable smectic monolayer phases due to the parallel organization of the rodlike moieties, the segregation of the polar terminal groups from the aromatic units, and the cohesive forces provided by the hydrogen-bonding networks between terminal diol groups.^{32d,e,33} Introduction and successive enlargement of lateral alkyl-, semiperfluoroalkyl-, or perfluoroalkyl chains disturb the parallel organization of the biphenyl cores within these layer structures. However, the cohesive forces (H-bonding) inhibit the complete collapse of positional ordering to yield nematic or isotropic liquid phases as usually observed.²² Instead, a variety of new columnar phases with core-shell morphologies and novel types of smectic phases, in which rodlike aromatic units are organized parallel to the layer planes (Lam), were observed. As shown in Figure 16, all the columnar phases occur as intermediary phases at the transition between conventional SmA phases and the novel laminated phases (Lam).

As shown in Table 4, there is a remarkably strong correlation between the mesophase type and the volume fraction of the lateral chain. The elongation of the lateral chain causes distinctive changes in the molecular shape, amphiphilic pattern, and segregation regime. Molecules with very long chains (group III) organize in Lam phases and behave similarly to single-headed amphiphiles. In these molecules the whole bolaamphiphilic unit (the biphenyl unit together with the two polar groups) can be regarded as polar "headgroup". In the meso-

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

(62) A related phase, designated as sliding columnar phase was recently proposed as a possibility of the organization of DNA strands in LC phases of DNA–lipid complexes: Lubensky, T. C.; O'Hern, C. S. In *Slow Dynamics in Complex Systems*; Tokuyama, M., Oppenheim, I., Eds.; The American Institute of Physics: Woodbury, NY, 1999; pp 105–116.

(63) A related phase sequence was also found for bolaamphiphilic triols: Cheng, X. H.; Das, M. K.; Diele, S.; Tschierske, C. *Angew. Chem., Int. Ed.* **2002**, *41*, 4031–4035.

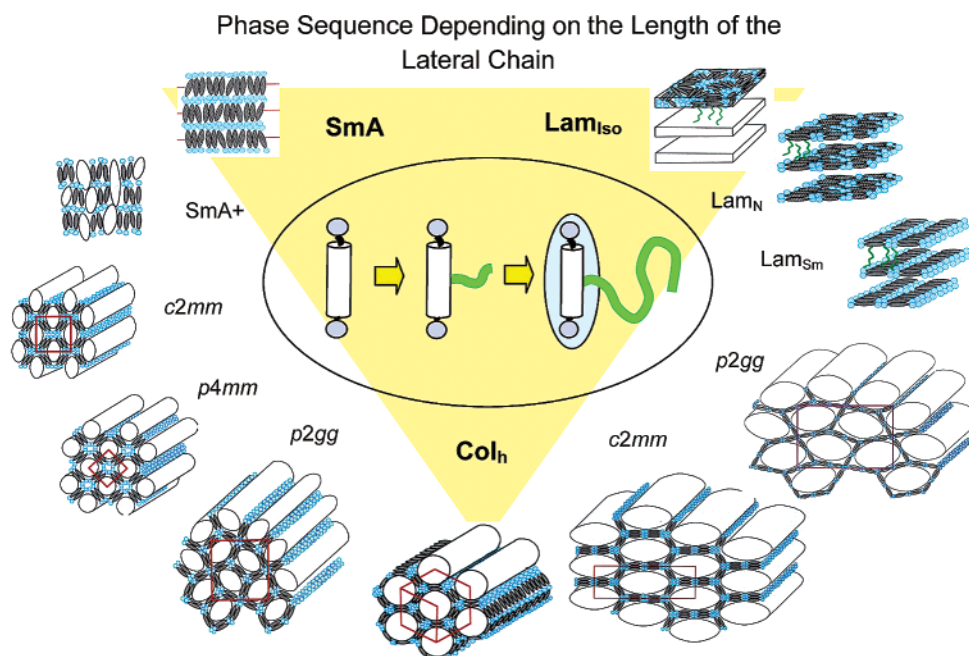


Figure 16. Liquid crystalline phases formed by the rigid bolaamphiphiles with respect to the size of the nonpolar lateral chain.

Table 4. Correlation between Volume Fraction of the Nonpolar Lateral Chain (f_R) and Observed Mesophase Type for the Bolaamphiphiles $1/n-5/n$

Mesophase	Shape of the cylinder shell	Number of molecules forming the cylinder shell	Cylinders per unit cell	f_R
SmA, SmA+				≤ 0.28
Col _h /c2mm		4	2	0.28 - 0.36
Col _{sq} /p4mm		4	1	≈ 0.36
Col _h /p2gg		5	4	0.36 - 0.43
Col _h /p6mm		6	1	0.43 - 0.53
Col _h /c2mm		8	2	0.53 - 0.56
Col _h /p2gg		10	4	
Lam _{iso} , Lam _N , Lam _X				≥ 0.56

phases of these materials an equivalent space filling of the polar units and the intercalated nonpolar chains allows these molecules to adopt an organization in layer structures. At enhanced

temperature the rodlike polar groups are rotationally disordered, i.e. their specific shape is not recognized (Lam_{iso}), but by reducing the temperature, the rigid rodlike structure of these

“headgroups” becomes important, and this leads to a stepwise onset of orientational (Lam_N) and possibly also positional order within these sublayers.

Compounds with intermediate chain lengths form numerous different columnar phases that arise from a mismatch of the space required by the nonpolar chains (R_H , R_F) and the polar molecular parts (see Table 4). The fluid nonpolar parts are organized in the interior of the columns, whereas the rigid bolaamphiphilic units form shells around these columns. In this respect these phases can be regarded as type I (normal type) columnar phases,⁶⁴ as for example often found in lyotropic systems.⁴ However, in contrast to conventional amphiphiles, the “headgroups” have a distinct rigid and bolaamphiphilic substructure, which is recognized during self-organization in columns. The segregation of the biphenyl units from the attached diol groups, as well as the rigid rodlike shape of the polar group only allows organization into certain distinct 2D structures. Furthermore, within the cylinder shells, only commensurate structures are possible, which means, that the cylinder shells must contain a well-defined number (4, 5, 6, 8, or 10) of the bolaamphiphilic units organized around the nonpolar cylinder cores. The resulting columns must be able to arrange in 2D space regularly, and within the resulting 2D lattice the interconnection between the cylinder walls occurs exclusively at the H-bonding sites. Two of these columnar mesophases are especially remarkable; these are the $p2gg$ lattices (compounds **2/4** and **2/12**), in which the columns adopt a pentagonal cross-sectional shape, and the $c2mm$ lattice of compounds **2/10–2/12**, in which eight molecules are organized into a deformed hexagon. These unusual mesophases have never been observed for any other liquid crystalline system. It is also remarkable that in this class of compounds no cubic or any other 3D-ordered mesophase has been detected at the transition between columnar and lamellar organization, as is typical for most other LC systems. In these systems it appears that there is a direct transition from cylinders to layers. Cylinders with eight molecules in the cross section seem to represent the largest of the stable cylinder structures; however, under special conditions (e.g. at reduced temperature) a larger cylinder can also be observed (e.g., the $p2gg$ phase of **2/12**).

Another interesting feature to note about these systems is that the rigid units are located at the interfaces between the individual columns (i.e., at the Wigner–Seitz lattice), whereas the fluid chains are located at the interior of the resulting networks of cylinders.⁶⁵ In columnar LC phases formed by conventional disklike LC molecules the Wigner–Seitz lattice is located within the fluid continuum between the columns, and the rigid parts are located in the centers. In this respect the mesophases reported here are the reverse of the mesophases of polycatenar mesogens (rodlike molecules with multiple or branched terminal chains)⁶⁶

and rod–coil molecules,⁶⁷ where ribbonlike aggregates of calamitic units form the interiors of the columns which are surrounded by the fluid continuum of the attached alkyl chains.

The columnar phases reported herein represent channel structures, built up by the bolaamphiphilic units and filled with the semiperfluorinated chains. Channel structures have also been reported for crystal structures of shape-persistent organic macrocycles,^{68–71} the solid-state structures of some H-bonding organic molecules⁷² and coordination polymers.^{73,74} Mesoporous channel structures were also obtained by surfactant based sol–gel synthesis.⁷⁵ However, in contrast to these solid-state structures, the mesophases reported here represent *fluid, self-organized systems* (ordered fluids) as indicated by the rheologic properties (fluidity) and the X-ray diffraction patterns (diffuse wide-angle scattering).⁷⁶ This means that there is a high mobility in these systems, provided by rapid molecular motions and rotations of the whole molecules, as well as conformational mobility. Therefore, the interfaces between the segregated regions are diffuse. This means that the different regions shown in the models represent regions with an enhanced concentration of one of the incompatible components with respect to that of the other. Hence, these structures are highly ordered on a macroscopic scale but are rather disordered on a microscopic scale.

To the best of our knowledge, there are only two other LC systems with morphologies related to those reported herein. These are semirigid LC-main-chain polymers containing long lateral alkyl chains. Some of these polymers form columnar mesophases (Col_h) with special cylinder morphologies, where the semirigid polymer backbones form the cylinder walls, filled by the lateral alkyl chains.⁷⁷ Other polymers of this type form smectic mesophases, where the semirigid polymer backbones are segregated and organized parallel to the layer planes as in the Lam phases.^{78–80} Another class of mesophases is formed by the organization of rigid aromatic molecules with peripheral

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(65) A liquid crystalline macrocycle, which represents a disklike molecule built up by a rigid frame and an interior of fluid alkyl chains, was recently reported, but only a nematic phase is formed by this compound: Höger, S.; Enkelmann, V.; Bonrad, K.; Tschierske, C. *Angew. Chem., Int. Ed.* **2000**, *39*, 2267–2270.

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(74) (a) Zaworotko, M. J. *Chem. Commun.* **2001**, 1–9. (b) Abourahma, H.; Moulton, B.; Kravtsov, V.; Zaworotko, M. J. *J. Am. Chem. Soc.* **2002**, *124*, 9990–9991.

(75) (a) Attard, G. S.; Glyde, J. C.; Göltner, C. G. *Nature* **1995**, *378*, 366–368. (b) Raimondi, M. E.; Seddon, J. M. *Liq. Cryst.* **1999**, *26*, 305–339. (c) Huo, Q.; Margolese, D. I.; Stucky, G. D. *Chem. Mater.* **1996**, *8*, 1147–1160.

(76) Columnar phases formed by taper-shaped or dendritic LC molecules with polyether chains or crown ether units at the apex can also be regarded as channel structures incorporating three distinct subspaces (central polar core, aromatic inner shell, and aliphatic or perfluoroalkyl outer shell). However, with these compounds segregation leads to onion-like structures. In such structures the rotation of the tapered segments around the column long axis is not restricted, and therefore Col_h phases were observed.^{15c,16b}

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polar groups (some dyes and drugs) in water.⁸¹ In these chromonic lyomesophases, the space required by the water molecules coordinated around these rigid cores (instead of the nonpolar chains in compounds $1/n-5/n$) determines the mesophase type. Hollow-pipe structures (related to the columnar phases of groups I and II materials) and optically biaxial brickwork-layer structures (related to the Lam phases of group III materials) have been proposed for the organization of such molecules.⁸¹ However, in these LC materials only two distinct sets of subspaces exist, whereas most of the mesophases reported herein have three distinct sets of subspaces, i.e. columns of the lateral chains, ribbons of the aromatic units, and strings of H-bonding networks. In this respect these morphologies are unique in LC systems but are related to those observed in some ABC triblock copolymers.^{11,12}

This report shows that it is possible to design complex mesophase morphologies, related to those of multiblock copolymers also with low-molecular mass LC materials. A major challenge in such low-molecular weight systems is to overcome

the unfavorable effect of the entropy of mixing, and this can be achieved if the individual blocks have a high degree of incompatibility with respect to one another. The competitive combination of cohesive hydrogen-bonding, the fluorophobic effect, and the rigid-flexible incompatibility have turned out to be a successful approach in this direction. Remarkably, the wide variety of different phases was obtained using one, single, basic molecular structure, where the only structural change involved the elongation of the laterally attached chain. This shows that careful design of quite simple block molecules by tiny changes of the molecular structure can lead to unexpectedly complex superstructures.

Acknowledgment. This work was supported by the Deutsche Forschungsgemeinschaft, the Fonds der Chemischen Industrie and the European Commission (RTN LCDD); we are grateful to Dr. A. G. Cook for a critical review of the manuscript.

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

JA036213G

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