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Formation of Columnar and Cubic Mesophases by Calamitic Molecules: Novel Amphotropic Biphenyl Derivatives

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Novel amphiphilic 4,4′-disubstituted biphenyl derivatives incorporating a hydrophilic 5,6-dihydroxy-3-oxahexyloxy group and a lipophilic chain have been synthesized by Pd-catalyzed cross-coupling reactions of phenyl boronic acids with 4-(5,6-dihydroxy-3-oxahexyloxy)bromobenzenes. The thermotropic and lyotropic mesomorphic behavior of these compounds were investigated by polarizing microscopy, by differential scanning calorimetry, and by means of X-ray diffraction. Thereby the influence of the length of the alkyl chain, the type of connecting unit between alkyl-chain and the rigid core (O vs CH_2), and the influence of lateral substituents and of the molecular chirality on the mesomorphic properties were investigated. All compounds have smectic A-phases as the high-temperature mesophases. Additionally, columnar phases were found for the long chain 4′-alkoxy-4-(5,6-dihydroxy-3-oxahexyloxy)biphenyls **2c**−**f** without lateral substituent and for the 4-(5,6-dihydroxy-3-oxahexyloxy)-4′-dodecyloxy-3′-methylbiphenyl **10**. All other laterally substituted biphenyl derivatives **9** and **11**−**15** and the 4′-alkyl substituted compound **8** display only smectic phases. The influence of protic solvents (formamide and ethylene glycol) on the liquid crystalline properties was studied. The columnar mesophases and S_C-phases are destabilized by addition of protic solvents whereas the S_A-phases are stabilized. Furthermore, binary mixtures of the amphiphilic biphenyl derivatives with each other have been investigated. Complete miscibility was found for the S_A-phases and the columnar phases of the compounds **2c**−**f**. However the columnar phases of the nonsubstituted compounds **2c**−**f** and the 3′-methyl substituted derivative **10** do not have an uninterrupted miscibility. Cubic phases (*Pn*3*m* or *Pn*3) and additional columnar phases were induced in the contact regions. Thus, the same diversity of different kinds of mesophases as in lyotropic systems and in the thermotropic phase sequence of polycatenar compounds is found. It is proposed that the cubic and columnar mesophases of these rodlike molecules result from the collapse of the smectic layer structures into ribbons.

Introduction

The liquid crystalline state which combines order and mobility on a molecular level is of great interest for material science as well as for life science. It can be found in different classes of compounds such as anisometric (rod-shaped or disklike) molecules, amphiphilic molecules and in block copolymers, in pure materials (thermotropic phases), and in mixed systems with appropriate solvents (lyotropic phases). The mobility is caused by the thermal motion of the molecules whereas the order is provided by a combination of molecular anisometry, attractive forces and micro segregation. The combination of micro segregation[1] and molecular anisometry could lead to interesting new materials with unusual properties. Thus, rod−coil molecules[2] and rod−coil block copolymers[3] have been synthesized. Furthermore, in low molecular weight molecules rodlike and disklike rigid units have been combined with perfluorinated segments,[4] oligosiloxane units,[5] and with hydrophilic groups.[6] In a project aimed at the synthesis of novel amphotropic liquid crystals we have combined rigid biphenyl and *p*-terphenyl rods with flexible and lipophilic alkyl chains and with flexible, but polar oligooxyethylene chains terminated with hydroxy groups.[7,8] The hydroxy groups provide attractive intermolecular interactions[9] which enhance the segregation tendency of the polyether chains. These molecules can be regarded as low molecular weight block molecules composed of three distinct units incompatible with each other (polyphilic molecules).[4f] Columnar mesophases have for example been found for 4,4″-dialkoxyterphenylderivatives with laterally attached polyether chains.[7,8b] The fixation of a polyether chain in a terminal position at a rigid core[8,10] however can lead to a pronounced layer like organization.[8a]

More recently we have synthesized the amphiphilic biphenyl derivatives **1**−**4** carrying an alkyl chain at one end and a polyether chains at the other terminus.[8] Those compounds, incorporating an 1,2-diol group and additionally at least one oxyethylene unit (comp. **2e-4**) display two mesophases (see Figure 1). In the cases of compounds **3** and **4** with long polyether chains an S_A/S_C-dimorphism was observed.[8] In contrast to **3** and **4** the low-temperature phase of compound **2e** displays an optical texture which is not typical for an S_C-phase.

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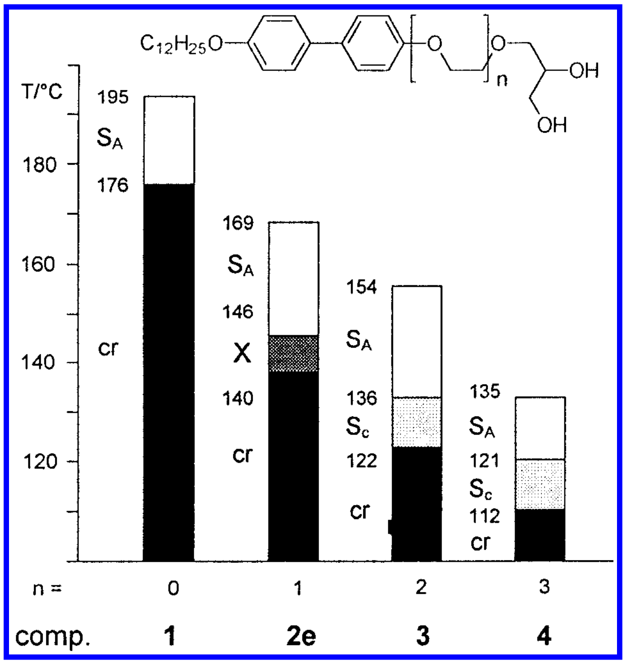
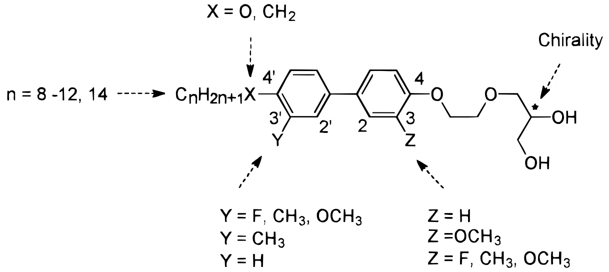


Figure 1. Comparison of the phase transition temperatures of the 4-dodecyloxybiphenyl derivatives **1**, **2e**, **3**, and **4** with different hydrophilic groups (values taken from ref. 8).

Furthermore, the X-ray pattern of a nonoriented sample in the unknown mesophase is characterized by several sharp reflections in the small angle region. In the wide angle region a diffuse scattering suggests the liquid like behavior concerning the lateral molecular distances. Therefore this unknown phase could not be a smectic low-temperature phase. Because the positions of the reflections in the small angle region exclude a hexagonal columnar arrangement, it was assumed, that this phase can be a rectangular or an oblique columnar phase.[8]

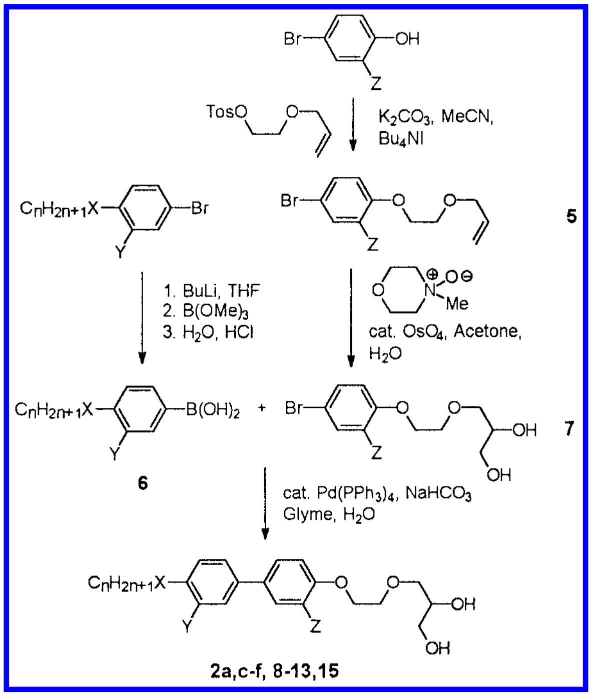
To clarify the reason for the unusual phase behavior of this compound, novel amphiphilic biphenyl derivatives were synthesized and the influence of various structural variations on their mesomorphic behavior was investigated. Thereby the length of the alkyl chain, the type of connecting unit between alkyl-chain and rigid core (O vs CH_2), the influence of lateral substituents in two different positions, and the influence of optical activity on the thermotropic and lyotropic mesomorphic behavior, as well as binary mixtures of these compounds, were investigated.



2. Synthesis

The desired compounds were prepared by Suzuki cross-coupling[11] of the 4-(5,6-dihydroxy-3-oxahexyloxy)bromobenzenes **7** with appropriate phenyl boronic acids **6** (see Scheme 1). The racemic 4-(5,6-dihydroxy-3-oxahexyloxy)bromobenzenes **7** were obtained by OsO_4-catalzed dihydroxylation[12] of the corresponding allyl ethers **5**. Compound **2b** was synthesized using another approach which will be reported in a separate paper, 1-(5,6-dihydroxy-3-oxahexyloxy)-4-iodo-2-methylbenzene (**7c**) was used for the synthesis of compound **14**. The optically active diol *(S)*-**7a** was obtained by enantioselective Sharpless dihydroxylation[13] using β-AD-Mix in 64% enantiomeric excess (determined by ^1H and ^{19}F NMR analysis of the diastereomeric Mosher's ester[14]). The final products were purified by chromatography, followed by recrystallization from petroleum ether/ethyl acetate/chloroform mixtures.

SCHEME 1: Synthesis of the Compounds 2a, 2c−f, 8−13, and 15.



3. Results

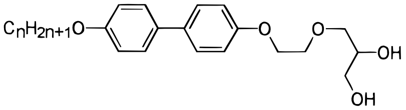
3.1. Thermotropic Properties of the Pure Compounds. *Influence of the Length of the Terminal Alkoxy Chain.* The thermotropic phase transition temperatures of the alkoxy substituted compounds **2** in dependence on the length of the alkoxy chains are given in Table 1. All investigated compounds **2** exhibit an enantiotropic polymorphism with a smectic A-phase as high-temperature mesophase.

Compounds **2a**-**2c** which have the shortest alkyl chains display a smectic C-phase below the S_A-phase. By cooling the S_C-phase of **2c** an additional phase transition to another mesophase can be found; the typical S_C-schlieren texture passes over in a fanlike texture, which is known for columnar mesophases (Figure 2a). The same texture is found on cooling the homeotropically aligned S_A-phase of **2d**, but no additional S_C-phase appears. The optical textures observed for the low-temperature mesophases of the other homologues **2e** and **f** (Figure 2b) differ from those of **2c** and **d**.

The DSC heating traces of the compounds **2** are shown in Figure 3. It can be seen, that all compounds have at least two different crystalline phases cr_1 and cr_2 beside the liquid crystalline phases. Remarkably the transition from the mesomorphic state to cr_2 cannot be supercooled as obvious from the heating and cooling scan of compound **2e** shown in Figure 4.

To obtain information about the structure of the mesophases X-ray measurements were done. In the S_A-phase of all homologue the diffraction pattern exhibit the characteristic feature of smectic phases without order in the layers. The layer reflection and its second order and a diffuse halo at about 10°

TABLE 1: Phase Transition Temperatures (°C) and Associated Enthalpy Values (kJ/mol, Lower Lines in Brackets) of the Pure 4-Alkoxy-4′-(5,6-dihydroxy-3-oxapentyl)biphenyles 2a−f and Clearing Temperatures of the S_A-Phases of the Solvent Saturated Samples



compd	n	cr_1	cr_2	Col	S_C	S_A-is	T_{cl} ethylene glycol saturated	T_{cl} formamide saturated
2a	8	115/121[a]	146		153	169	125	152
		(8.0/4.3)	(18.1)		(0.7)	(12.7)		
2b	9	118	146		150	171	128	161
		(14.3)	(19.5)		(0.7)	(12.3)		
2c	10	120	143	146	147	171	130	173
		(14.9)	(19.4)		(0.9)[b]	(11.9)		
2d	11	128	143	147		171	132	178
		(23.3)	(17.8)	(0.9)		(11.8)		
2e[c]	12	127	142	147		170	135	183
		(19.7)	(17.6)	(0.9)		(10.8)		
(S)-**2e**	12	128	143	149		171	134	184
		(20.1)	(17.9)	(1.0)		(10.4)		
2f	14	130	139	147		171	146	189
		(23.6)	(17.7)	(0.7)		(8.7)		

[a] Different crystalline modifications. [b] Not resolved. [c] Values obtained from a new sample. They slightly differ (1−2 K) from the values given in ref 8.

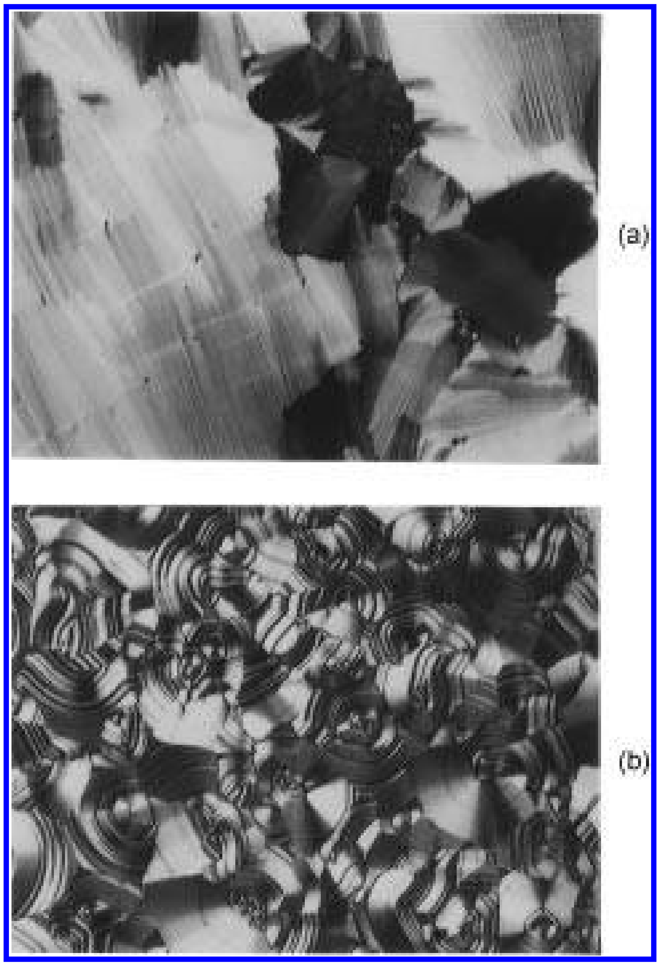


Figure 2. Optical photomicrographs (crossed polarizers) of the textures of the thermotropic columnar phase of compound **2c** at (a) 145 °C and **2f** at (b) 145 °C.

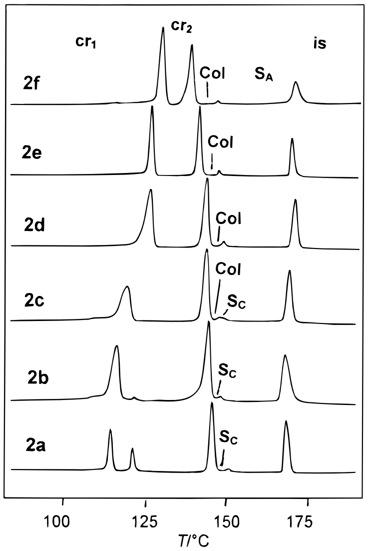


Figure 3. DSC-heating curves (10 K min^{-1}) of the compounds **2**.

appear. The observed smectic layer thickness is significantly larger than the length of the molecules ($d/L \approx 1.7$) proving the existence of bimolecular smectic layers. In Figure 5, the d-values for the S_A-phases are plotted as a function of the number n of carbon atoms in the alkyl chains. The layer spacing is nearly a linear function of n, but the increase of the d-value with n is essential smaller than expected for a bilayer structure (0.11 nm/CH_2-group instead of 0.25 nm/CH_2-group). It supposes that the alkyl chains are strongly disordered or interdigitated.

Upon cooling, the S_A-phase of **2c**−**f** into the unknown phase the reflections of the S_A-phase are maintained, but additional sharp scatterings of very low intensity at small angles appear, which, however, could not be indexed assuming a hexagonal or rectangular cell. Therefore a two-dimensional oblique lattice is assumed. The evaluation of the pattern with this assumption leads to a good agreement of the observed and calculated reflections and is given in Table 2 for compound **2f**. The lattice parameters of the columnar mesophase of this compound amount $a = 6.23$ nm; $b = 5.68$ nm; $\gamma = 71.5°$. Here the b-parameter corresponds approximately to the maximal layer thickness of the S_A-phase ($d = 5.8$ nm).

Comparing the pattern of the homologues **2c**−**f** in the columnar phase, it is obvious that the number of the detected reflections in the small angle region depends on the length of

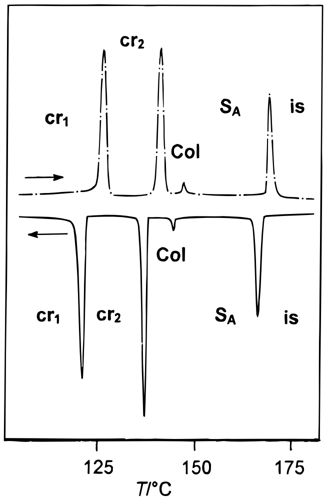


Figure 4. DSC heating and cooling trace (10 K min^{-1}) of compound **2e**.

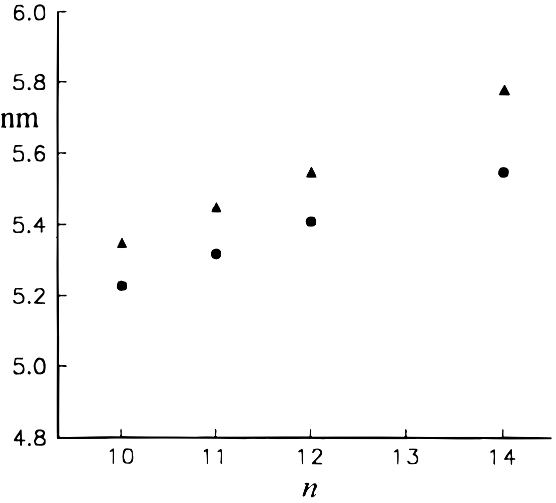


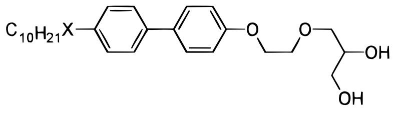
Figure 5. Layer spacing (*d*) of the S_A-phases of compounds **2c**−**f** as a function of the number of carbon atoms in the alkyl chains as obtained on cooling after the transition from the isotropic liquid (●) and before the phase transition (▲).

TABLE 2: Observed Reflections in the Columnar Phase of Compound 2f

θ_{exp}(deg)	θ_{cal}(deg)	*hk*
0.746		10
0.818		01
0.916		11
1.455	1.457	21; $\bar{2}\bar{1}$
1.502	1.492	20; $\bar{2}0$
1.575	1.569	12; $\bar{1}\bar{2}$

the alkyl chains. Whereas in the diffraction pattern of compound **2f** six sharp scatterings were found, the pattern of **2c** exhibits only two reflections preventing a doubtless evaluation. It can be assumed that all phases are of the same type, because the ratio of the observed reflections relative to the first one is the same. Miscibility studies of these compounds with each other also confirm this assumption (see below).

Alkyl Derivative **8**. An exclusively smectic polymorphism is found for the undecyl derivative **8**, which has the same chain length as the decyloxy compound **2c.** On cooling the S_A-phase, an S_C-phase and a smectic low-temperature phase can be observed. The textures of the S_A- and S_C-phase correspond to the known fan shape respectively broken fan shape textures. The low-temperature phase is characterized by a paramorphotic fan shape texture, which is known for ordered tilted smectic phases. In agreement with the observed texture, the X-ray pattern of this low-temperature phase shows only one outer sharp scattering beside the inner layer reflections (up to the sixth order) pointing to a smectic F or smectic I phase. A definite distinguish between S_F and S_I can be given only on the basis of oriented samples which have not been obtained.



2c: X = O : cr 143 Col 146 S_C 147 S_A 171

8: X = CH_2: cr 108 $S_{I/F}$ 119 S_C 120 S_A 165

Molecular Chirality. The transition temperatures and the textures of the mesophases of the racemic compound **2e** and its enantiomerically enriched sample *(S)*-**2e** are nearly identical (Table 1). It seems that, in this class of compounds, there is no significant influence of molecular chirality on the mesomorphic properties. Therefore no further investigations have been carried out.

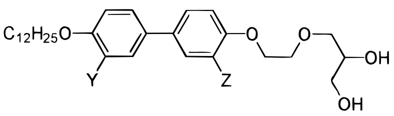
Lateral Substituents. Lateral substituents (F, CH_3, and OCH_3) were placed either in ortho-position to the polar headgroup (3-substituted derivatives **13**−**15**) or in ortho-position to the terminal alkyl chain (3′-substituted compounds **9**−**11**). Compound **12** contains two lateral substituents. All compounds with a lateral group neighboring the polar group have only S_A-phases. Exclusively S_A-phases were also found if polar groups (F or MeO) are placed close to the alkyl chain.

A broad region of a columnar phase is observed for the 3′-methyl substituted compound **10** between 80 and 102 °C. However, the texture of this mesophase (Figure 6) differs significantly from those of the columnar phases of the compounds **2c**−**f**. Likewise the X-ray pattern shows differences from those of the columnar phases of compounds **2c**−**f**. Again, several sharp reflections were detected in the small angle region (Figure 7), but the ratio of the Bragg angles of the reflections is different. In the wide angle region an amorphous scattering at about 10° was found. Also miscibility investigations point to another type of columnar phase (see below). Further X-ray studies at oriented samples are under way, to elucidate the structure.

3.2. Lyotropic Properties in the Presence of Protic Solvents. Because the compounds under consideration represent amphiphilic molecules, we have studied their behavior in the presence of protic solvents. Since the transition temperatures of the pure compounds exceed 100 °C, we did not use water, but other protic solvents with elevated boiling points were used for these investigations. Ethylene glycol and formamide were chosen. The transition temperatures of the solvent saturated samples of the compounds **2** and **9**−**15** are included in Tables 1 and 3. Generally the solvent saturated samples display decreased melting temperatures of the crystalline phases and the smectic A-phase is the only mesophase observed. The influence of these two solvents on the clearing temperatures is different. With exception of the short chain derivatives **2a** and **b**, the S_A-phases are stabilized on addition of formamide, whereas on addition of ethylene glycol the clearing temperatures of all compounds are depressed.

To get a deeper insight in the influence of protic solvents on the mesomorphic properties the lyotropic phase behavior of compound **2c** was investigated in more detail. The binary phase diagram of **2c** with formamide constructed from DSC- heating and -cooling scans is displayed in Figure 8. The interpretation

TABLE 3: Phase Transition Temperatures (°C) and Associated Enthalpy Values (kJ/mol, Lower Lines in Brackets) of the Pure Laterally Substituted 4-Alkoxy-4′-(5,6-dihydroxy-3-oxapentyl)biphenyles 9-15 and Clearing Temperatures of the S_A-Phases of the Solvent Saturated Samples



compd	*Y*	*Z*	cr	Col	S_A-is	T_{cl} ethylene glycol saturated	T_{cl} formamide saturated
9	F	H	98 (41.6)		155 (5.1)	124	163
10	CH_3	H	80 (41.4)	102 (0.1)	141 (2.4)	133	181
11	CH_3O	H	78 (42.0)		131 (4.3)	104	152
12	CH_3	CH_3O	59/75/92[a] (2.1/4.1/41.3)		109 (1.8)	99	159
13	H	F	117 (44.7)		137 (5.5)	120	169
14	H	CH_3	108 (24.5)		139 (7.9)	125	159
15	H	CH_3O	69/85[a] (17.7/22.4)		130 (5.2)	97	145

[a] Different crystalline modifications.

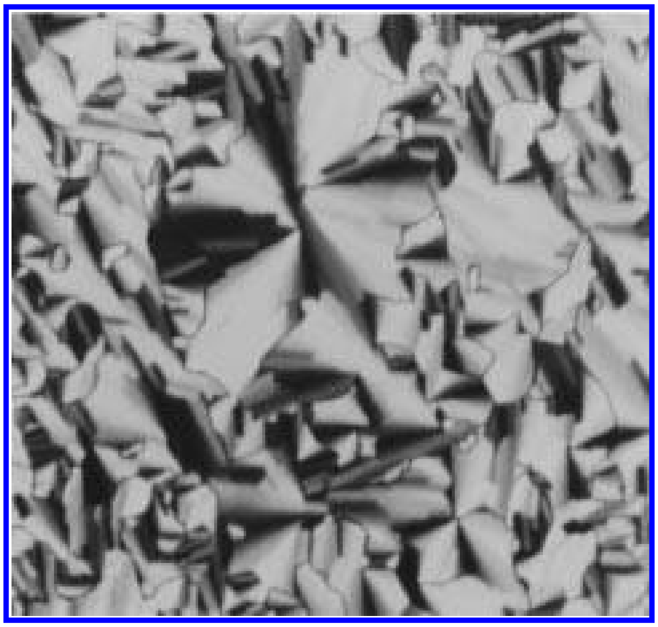


Figure 6. Optical micrograph (crossed polarizers) of the texture of the thermotropic columnar phase at 100 °C as obtained by cooling the homeotropically aligned S_A-phase of compound **10**.

of the DSC-curves is based on microscopic observations. At first considering the S_A-is-transition, a slight increase of the clearing temperature is observed on increasing the formamide content of the sample. A maximum ($T = 185$ °C) is reached at a molar ratio of approximately 6 mol formamide/mol diol **2c**. On further addition of formamide, the clearing temperature slightly decreases again. The solvent-saturated sample has a clearing temperature of 173 °C. In contrast to the smectic A-phase, the S_C-phase and the columnar mesophase are strongly destabilized and disappear at further increased solvent content. The S_C-phase can be observed up to a solvent content of ca. 3.6 mol formamide/mol **2c**, whereas the columnar phase already disappears at a ratio as small as 0.25 mol formamide per mol diol **2c**.

Similar behavior was found for the long chain derivatives **2d**−**f**. As a representative example, the simplified principal phase diagram of the system **2f**/formamide, obtained from solvent penetration experiments (contact preparations), is given in Figure 9. Here, the columnar phase is destabilized and a smectic C-phase is induced at a certain formamide concentration.

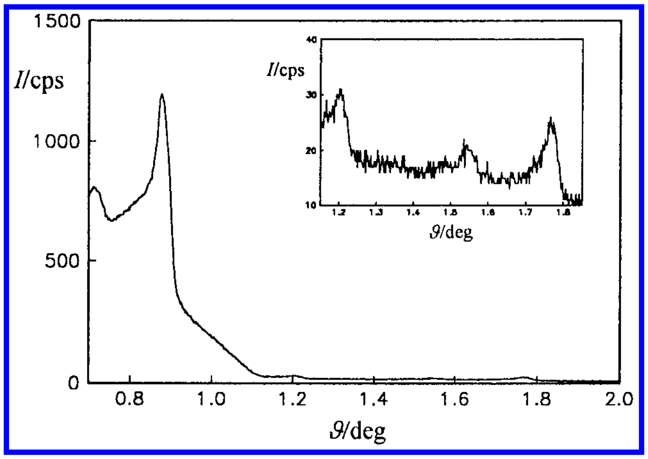


Figure 7. Small angle part of the X-ray diffraction pattern of the columnar phase of compound **10**.

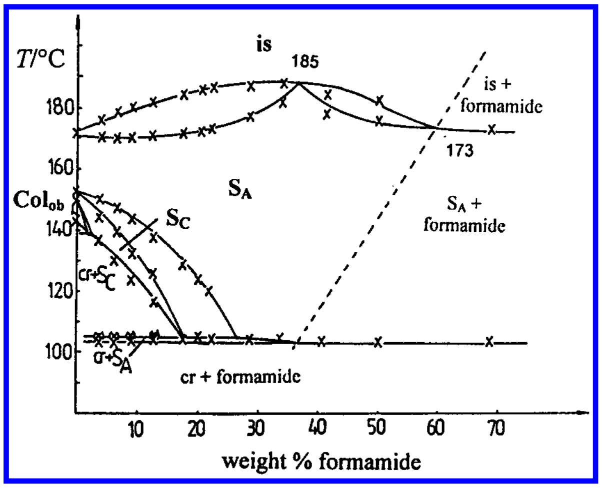


Figure 8. Phase diagram of the system **2c**/formamide.[8b]

Also, the columnar mesophase of the methyl substituted compound **10** is destabilized in favor of the S_A-phase on addition

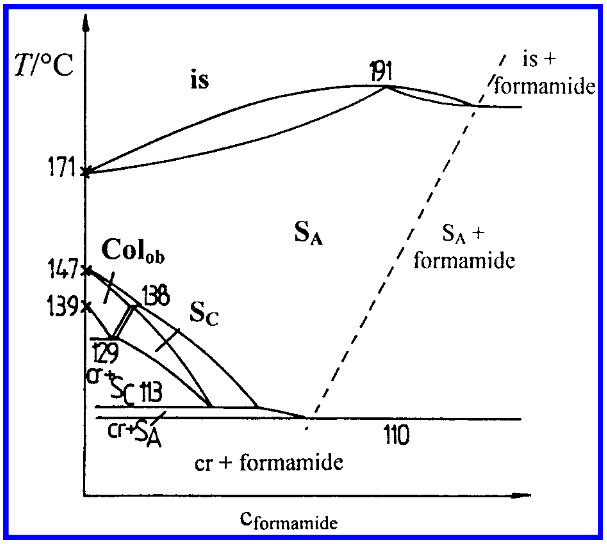


Figure 9. Simplified phase diagram of the system **2f**/formamide.

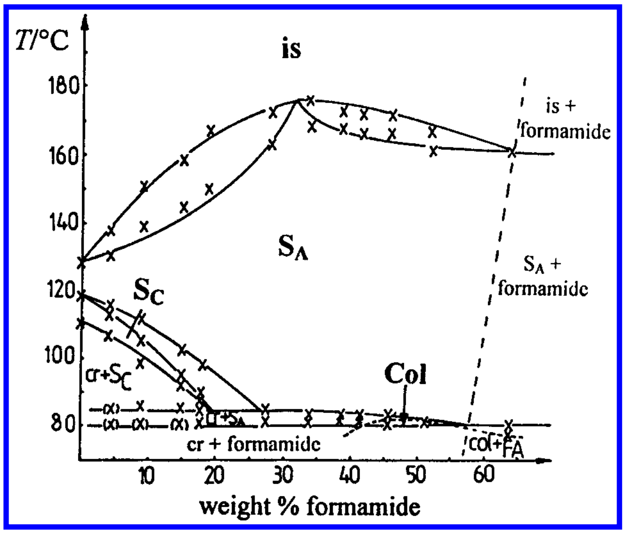


Figure 10. Phase diagram of the system **4**/formamide.

of protic solvents. However, contrary to the derivatives **2**, no smectic C-phase can be detected at any solvent concentration.

The influence of the size of the hydrophilic group on the lyotropic phase behavior is obvious from the comparison of the phase diagrams of the mono(oxyethylene) derivative **2c** with formamide (Figure 8) and the phase diagram of the tris(oxyethylene) derivative **4** with formamide (Figure 10). In both cases, the S_A-phase is stabilized at first and then destabilized, and the S_C-phases are strongly destabilized and disappear with increasing formamide content. It is, however, remarkable that a new monotropic mesophase can be induced in the formamide rich region of the phase diagram of the tris(oxyethylene)-derivative **4** (Figure 10). This induced mesophase is characterized by a typical spherulitic texture (see Figure 11) which is often observed for columnar mesophases. Because of the fact that this mesophase occurs at a large excess of formamide (8−22 mol formamide/mol of **4**) and taking in account the rather large size of the hydrophilic group of compound **4**, we assume that this phase can be a hexagonal columnar phase (direct phase H_I) consisting of cylindrical micelles as often observed in lyotropic systems or a ribbon phase as recently proposed for thermomesophases of rod−coil molecules with extended oligo(oxyethylene) chains.[2] Because of the metastable character this mesophase could not be proved using X-ray method.

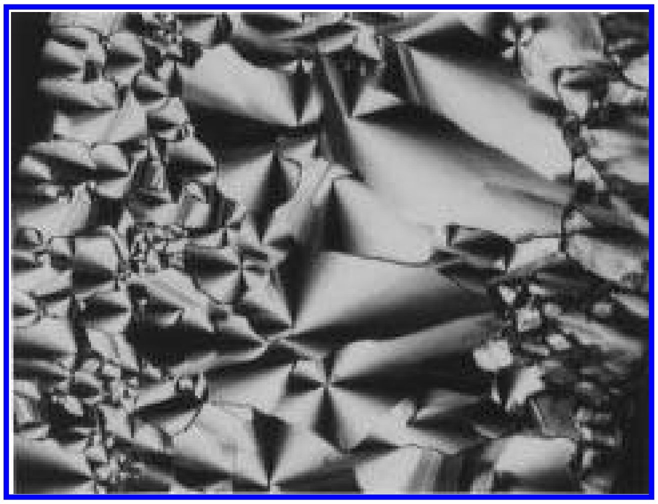


Figure 11. Optical micrograph (crossed polarizers) of the induced lyotropic columnar phase of compound **4** with formamide ($T = 83$ °C, 45 wt % formamide).

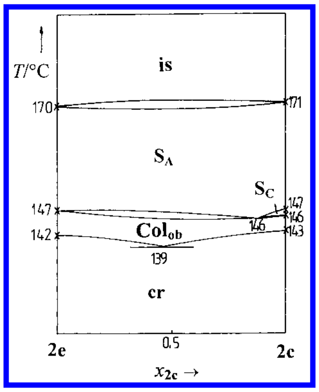


Figure 12. Phase diagram of the binary system **2e**/**2c**.

3.3. Binary Mixtures of Different Biphenyl Derivatives.

Recently we have found, that the adjustment of the polar-lipophilic interface curvature in thermotropic mesophases of polyhydroxy amphiphiles is possible by mixing structurally related polyhydroxy amphiphiles which have a different molecular shape.[15] This method was for example used to distinguish between different types of cubic mesophases.[15] In the following we want to apply this method to get additional information about the structure of the columnar mesophases of compounds **2** and **10**.

At first, binary mixtures of the compounds **2c**−**f** differing only in the alkyl chain length have been investigated. The simplified binary phase diagram (obtained from contact preparations) for the system **2c**/**2e** is given in Figure 12. Complete miscibility between the smectic A-phases and the columnar phases of the two components was found. Neither a phase boundary in the columnar phase range nor a minimum in the Col−S_A-transition curve could be detected. In the contact region, the optical textures of the columnar phases gradually change. This can also be observed for the other binary systems and confirms that all the columnar phases in this class of compounds have an identical structure, despite of the fact that they display different textures.

In a second step we investigated binary mixtures of the compounds **1, 2e,** and **3** with each other. These compounds have identical alkyl chain length and differ only in the number of oxyethylene units between diol unit and rigid core, (i.e., in the size of the hydrophilic group). Though the S_A-phases of the compounds **2e** and **3** are completely miscible, a sharp phase boundary with an extended two phase region separates the smectic C-phase of **3** from the columnar phase of **2e** (Figure

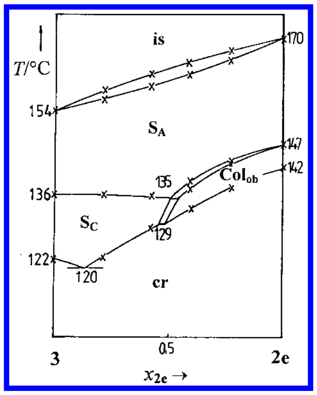


Figure 13. Binary phase diagram of the system **3**/**2e**.

13). This means that the columnar phase gets lost on increasing the average size of the hydrophilic groups in the mixed system. Much more important is the fact that, in the contact region of the diol **1** without polyether chain and the S_C-phase of the diethylene glycol derivative **3**, the typical texture of the columnar mesophase of compound **2e** is observed in the temperature range between 124 and 131 °C. No columnar phase can be detected for the pure compound **3** down to 122 °C. Probably some of the compound **1** dissolves in the S_C-phase of **3** and induces the columnar mesophase. This means that the columnar phase appears if the average size of the hydrophilic groups is decreased. It is also possible that, in the contact region, the melting point of **1** is depressed and therefore a hidden monotropic columnar phase can be observed. Unfortunately, the S_A-phase of the pure compound **1** crystallizes at 176 °C and cannot be supercooled at all. Therefore we can only speculate on the existence of a monotropic Col_{ob} phase of this compound. Nevertheless, this observation indicates that the Col_{ob}-phase can only be found for biphenyl derivatives with a relatively small polar group.

The columnar phases of the compounds **2c**−**f** are depressed and replaced by the S_A-phase upon addition of the biphenyl derivatives **13**−**15** with polar or nonpolar lateral substituents next to the hydrophilic group and also upon addition of the compounds **9** and **11** that have polar substituents in neighborhood to the alkyl chain.

The binary phase diagrams of the methyl substituted compound **10** with the 4′-alkoxybiphenylderivatives **2** are much more complicated. The detailed phase diagram of the system **2e**/**10** is given in Figure 14. Again, complete miscibility is found between the smectic A-phases of both compounds. However, the columnar phases of these two compounds do not have an uninterrupted miscibility. This confirms the assumption that the two columnar phases could be of a different type. In the contact region two induced phases occur. Upon increasing the ratio **2e**/**10**, the columnar phase of the methyl-substituted compound **10** is at first stabilized, but in the middle concentration range (x_{2e} = 0.4−0.7), another phase occurs. This phase appears optically isotropic. It grows with cornered phase boundaries, and it is significantly more viscous than the neighboring columnar mesophases. These are typical features of cubic phases. More detailed inspection between crossed polarizers reveals the presence of a very dim mosaic like texture consisting of homogeneous areas, some of them appearing not completely dark. Such a pattern has been observed for other thermotropic cubic phases[16] and probably could be caused by the polycrystalline nature of the samples. This optically isotropic mesophase was investigated by X-ray diffraction by the Guinier film method. In the small angle region seven sharp reflections appear, which could be indexed on the basis of a cubic lattice (Table 4). According to the observed systematic extinctions, the space groups *Pn*3*m* and *Pn*3 are compatible with the experimental results. The obtained lattice constant a = 9.22 nm is much larger than twice the estimated molecular length (2L ~ 6.4 nm from CPK-models).

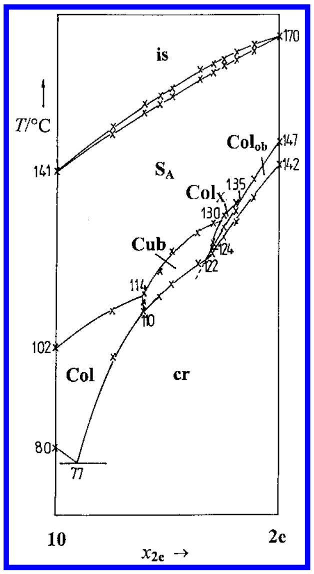


Figure 14. Binary phase diagram of the system **10**/**2e**.

Figure 15. Texture (crossed polarizers) of the columnar phase (Col_X) appearing in the binary system**10/2e** at x_{2e} = 0.75 and T = 130 °C.

TABLE 4: Observed Reflections of the Binary Mixture x_{2e} = 0.46, x_{10} = 0.54 in the Cubic Phase

Θ_{exp}(deg)	Θ_{cal}(deg)	*hkl*
0.83		111
0.97	0.96	200
1.16	1.17	211
1.36	1.35	220
1.58	1.59	311
1.65	1.66	222
1.79	1.79	321

At a molar fraction of x_{2e} ~ 0.75, another columnar phase (Col_X) is induced in a very small region between the cubic and Col_{ob} phases. This induced phase has a spherulitic texture (Figure 15). The small existence range prevents a further characterization by X-ray studies.

The principal phase diagrams (obtained from contact preparations) of the binary systems of the methyl-substituted compound **10** with other homologues **2** are displayed in Figures 16a−c. Interestingly, increasing the chain length of the compounds **2**

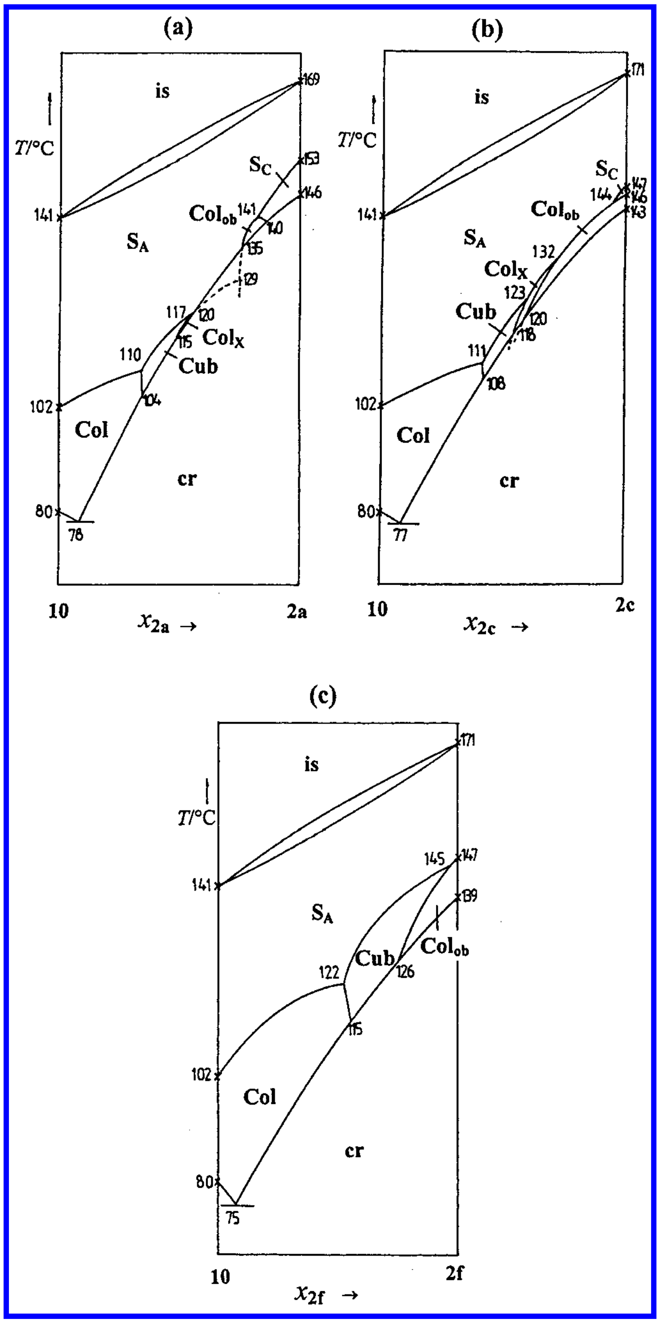


Figure 16. Simplified binary phase diagrams of the systems (a) **10**/**2a**, (b) **10**/**2c**, and (c) **10**/**2f**.

leads to increased stability of the induced columnar (**2a**, 129 °C; **2c**, 132 °C; **2e**, 135 °C) and the induced cubic phases (**2a**, 117 °C; **2c**, 123 °C; **2e**, 130 °C; **2f**, 145 °C). In the binary system **10/2f**, however, no induced columnar phase is observed. It seems that the cubic phase is more strongly stabilized and therefore completely replaces the columnar phase (Col$_X$) in this binary system.

On mixing the short chain compounds **2a** and **2c** with **10** their S$_C$-phases disappear (Figures 16a and b). The S$_C$-phase of compound **2a** is replaced by a second induced mesophase which occurs beside the Col$_X$-phase (see Figure 16a). The optical texture of this induced columnar phase corresponds to that one of the Col$_{ob}$ mesophase of the pure compounds **2c** and **d** (Figure 2a). Therefore, we assume that this induced phase could correspond to the columnar mesophases (Col$_{ob}$) of the pure compounds **2**.

4. Discussion

In summary we have found that single chain amphiphiles incorporating biphenyl rigid rods (compounds **2c**–**f** and **10**) can form columnar phases despite of the fact that they are neither disklike nor tapered shaped and the parallel arrangement of the individual molecules should favor smectic layer structures. The preliminary X-ray studies performed at nonoriented samples point to a two-dimensional oblique structure of these columnar phases.

From the different textures, from X-ray results, and from miscibility studies we conclude that the Col$_{ob}$ phases of the compounds **2c**–**f** differ significantly from that one of the 3′-methyl-substituted compound **10**.

In the columnar phases of the compounds **2c**–**f** the *d*-value of the smectic phase above the columnar phase corresponds to one of the lattice parameter of the columnar phase. Therefore, we assume that these columnar mesophases may result from the collapse of the smectic layer structure into ribbons. Such ribbon structures[17,18] have already been described for thermotropic phases of soaps.[19] They are also under discussion in relation to mesophases of polycatenar[20b] and double-swallow-tailed[21] compounds, mesogens with fluorinated terminal chains,[22] and facial calamitic amphiphiles.[24] Ribbon phases can also appear as intermediate phases between single-layer and double-layered smectic phases of polar calamitic 4-nitrobenzoates and 4-cyanobenzoates[23] and in mixtures consisting of amphiphilic and bolaamphiphilic mesogens.[24] In most cases the collapse of layers results from a frustration caused by the different space filling of incompatible parts of the individual molecules (e. g., headgroup lattice and alkyl chains in the case of alkali metal carboxylates, rigid cores, and alkyl chains in the case of polycatenar and swallow-tailed compounds).

In the compounds **1**–**15** the hydrophilic groups strongly interact via large dynamic hydrogen bonding networks and give rise to stable bilayer structures. These bilayer structures are further reinforced by the rigid biphenyl cores, which prefer a parallel arrangement within the smectic layers.[10,25] The polar and the rigid parts can segregate from the flexible lipophilic alkyl chains into different regions. At elevated temperatures, the space filling of these regions seems to be nearly equivalent, and therefore, an S$_A$ bilayer structure is observed. It is well-known that the molecular motion and bond reorientation processes are temperature dependent. The decrease of the temperature can differently influence the hydrogen bonding networks, the arrangement of the biphenyl units, and the conformation of the alkyl chains. This could give rise to a different cross section of the polar and the lipophilic regions in dependence on the temperature. It was observed that the columnar phase is only found for the derivatives with long lipophilic chains and that it is lost by increasing the size of the hydrophilic groups either by elongation of the oxyethylene chains or by hydration with protic solvents. Therefore, it seems likely that in the columnar mesophase the cross section of the polar regions is smaller than that of the lipophilic regions.[26] The columnar phase occurs on cooling the S$_A$-phase. This would mean that the average cross section of the hydrophilic groups decreases to a greater degree upon cooling than that of the lipophilic alkyl chains. This fact can be explained, if one assumes a reorganization of the hydrogen bonding network at the transition from the smectic to the columnar phase, which allows a more efficient packing in the polar region. The resulting different space filling within the segregated regions gives rise to a frustration within the layers which causes their collapse with formation of ribbons arranged in a oblique lattice.

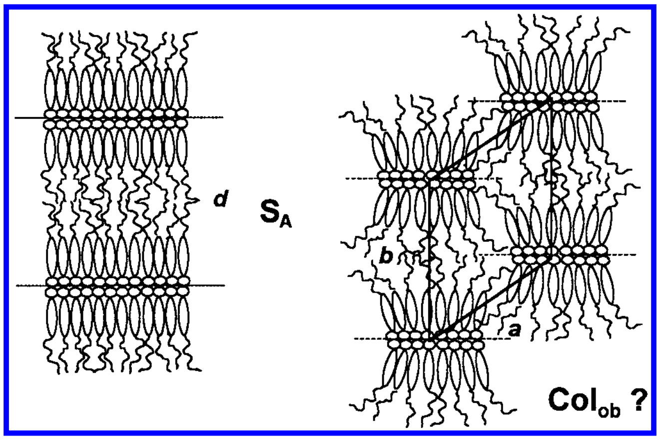


Figure 17. Schematic representation of a possible arrangement of the molecules in the Col_{ob}-phases of the compounds **2**.

Because of the fact that one of the lattice parameter of the Col_{ob}-phase agrees well with the layer thickness of the neighboring S_A-phase, it seems likely that the molecules have a nontilted arrangement. However, in the case of the appearance of a smectic C-phase above the columnar phase of compound **2c** and on addition of protic solvents to the compounds **2d−f,** a tilted arrangement of the molecules cannot be totally excluded at present.

With only one exception, all laterally substituted compounds exclusively display the smectic A-phase. It supposes that the additional lateral steric effect connected with a decrease of the core−core interactions and an increase of the cross section in this molecular moiety prevents the formation of the ribbons. The only one exception from this is found in the 3′-methyl-substituted compound **10**. From investigation of the columnar phase of compound **10** and from miscibility studies with compounds **2**, we found that the columnar phase of **10** significantly differs from the columnar phases of the compounds **2c−f**.

In mixed systems consisting of the 3′-methyl-substituted compound **10** and the compounds **2** without lateral substituents, the smectic C-phases of compounds **2a−c** are replaced by the Col_{ob}-phase. Probably the methyl-substituted compound **10** increases the average cross section of the lipophilic chain region which causes the transition from a S_C-phase to the Col_{ob}-phase.

Most remarkable is the fact that in all cases a cubic phase is induced in these mixed systems. The cubic phase in the system **2e/10** can have either a *Pn*3*m* or a *Pn*3 space group. The position of this cubic phase between two columnar mesophases (regarding the concentration) is quite unusual. However, with respect to the temperature regime (see Figure 14), the cubic phase occurs on cooling a smectic A-phase before the transition to a columnar phase or crystallization. Cubic phases can often be observed as intermediate phases between smectic and columnar mesophases.[27,28] In most cases *Ia*3*d* and *Im*3*m* cubic lattices have been found. Cubic phases with a *Pn*3*m* lattice[29] have, for example, been detected in some lyotropic systems as intermediate phases between the smectic and the inverted columnar mesophase.[27,30] It was proposed that these cubic phases consist of two interwoven tetrahedral networks containing the polar regions arranged in a double diamond lattice as shown in Figure 18, separated by the F-minimal surface.

In the mixed systems **2/10**, the cubic phase occurs neighboring a smectic A-phase and close to a columnar mesophase composed of ribbons. A cubic phase composed of ribbons was recently proposed for an *Im*3 cubic phase of a ternary lyotropic system between a lamellar and a rectangular columnar mesophase.[31]

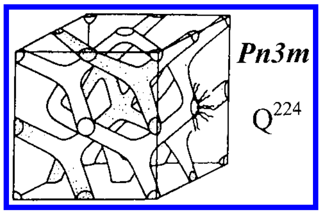


Figure 18. Model proposed for cubic mesophases of inverted lyotropic systems with a *Pn*3*m* lattice.[27]

From the discussion given for this ternary lyotropic system, it can be assumed that the cubic phase occurring in the mixed system **2/10e** could also be built up by interwoven networks of ribbons.

With respect to the mesophases observed (smectic, columnar, and cubic), the same diversity of different kinds of mesophases, as in the lyotropic and thermotropic phase sequence of amphiphilic molecules and block copolymers and as in the thermotropic phase sequence of polycatenar compounds, is found. The proposed model of the arrangement of the individual molecules in the mesophases is similar to that of polycatenar compounds.[20] The main difference is that not the individual molecules but extended hydrogen bonded bilayer-aggregates form the ribbons and that only one terminal chain is attached to each rigid core. In this respect, the compounds **2** and **10** are related to the rodlike hydrogen-bonded dimers of 3′-substituted 4′-alkoxybiphenylcarboxylic acids[28,32] and to the ion pair complexes formed by silver(I) complexes of 4-alkoxystilbazoles, associated to alkylsulfonate anions,[33] which both show cubic mesophases.

To clarify the complex phase behavior of this type of compounds, further synthetic activities, and detailed investigations are in progress.

5. Experimental Section

5.1. General Considerations. Confirmation of the structures of intermediates and products was obtained by ^{1}H spectroscopy (VARIAN Unity 500, VARIAN Gemini 200 spectrometer), by infrared spectroscopy (SPECORD 71), and by mass spectrometry (Intectra GmbH, AMD 402, electron impact, 70 eV). The purity of all compounds was checked by thin-layer chromatography (TLC aluminum sheets, silica gel 60 F254 from Merck). Microanalyses were performed using an LECO CHNS-932 elemental analyzer.

Transition temperatures were measured using a Mettler FP 82 HT hot stage and control unit in conjunction with a Nikon Optiphot-2 polarizing microscope and were confirmed using differential scanning calorimetry (Perkin-Elmer DSC-7). X-ray studies were performed by means of a Guinier-goniometer (Fa. HUBER). 4-Bromo-2-fluorophenol (Aldrich), 4-bromo-2-methoxyphenol (Lancaster), 4-iodo-2-methylphenol (Aldrich), β-AD-mix (Aldrich), osmium tetroxide (Berlin Chemie), and *N*-methyl morpholine-N-oxide solution (Aldrich) were used as obtained. 2-Allyloxyethanol,[34] 4-undecyloxy bromobenzene,[35] 1-toluylsulfonyloxy-2-oxa-5-hexene,[36] 4-alkoxy bromobenzenes,[37,38] 4-octyloxyphenylboronic acid (**6a**),[39] 4-decyloxyphenylboronic acid (**6b**),[40] and compound **2b**[41] were obtained according to the procedures described in the corresponding references.

5.2. Etherification of Phenols: General Procedure. The appropriate substituted phenol (58 mmol) was dissolved in 200 mL dry acetonitrile. K_2CO_3 (24 g, 175 mmol), the appropriate 1-bromoalkane (60 mmol), and Bu_4NI (100 mg) were added and the mixture was stirred at 100 °C for 4−8 h. Afterward the solvent was removed in vacuo and the residue was dissolved in water (100 mL) and ether (150 mL). The organic layer was separated and the aqueous solution was extracted twice with ether (50 mL). The combined solutions were washed with water (100 mL) and with brine (50 mL). After drying (Na_2SO_4), the solvent was removed. The products were purified either by column chromatography or by repeated crystallization from ethanol.

4-Bromo-1-tetradecyloxybenzene. Yield 81%; mp 40 °C; ^{1}H NMR ($CDCl_3$, 500 MHz) $\delta = 7.36$ (2H, d, *J* = 8.2, Ar−H), 6.95 (2H, d, *J* = 8.2, Ar−H), 3.99 (2H, t, *J* = 6.8 Hz, CH_2O), 1.75 (2H, m, CH_2CH_2O), 1.51−1.25 (22H, m, CH_2), and 0.88 (3H, t, *J* = 6.5 Hz, CH_3).

4-Bromo-1-dodecyloxy-3-fluorobenzene. Yield 78%, oily liquid; ^{1}H NMR ($CDCl_3$, 500 MHz) $\delta = 7.2$ (1H, d, *J* = 10.7 Hz, Ar−H), 7.14 (1H, d, *J* = 6.5 Hz, Ar−H), 6.8 (1H, t, Ar−H), 3.97 (2H, t, *J* = 6.6 Hz, $ArOCH_2$), 1.78 (2H, m, $ArOCH_2CH_2$), 1.26 (18 H, m, CH_2), 0.87 (3H, t, *J* = 6.9 Hz, CH_3).

4-Dodecyloxy-1-iodo-3-methylbenzene. Yield 85%, oily liquid; ^{1}H NMR ($CDCl_3$, 200 MHz) $\delta = 7.39$ (2H, d, Ar−H), 6.54 (1H, d, *J* = 9.2 Hz, Ar−H), 3.89 (2H, t, *J* = 6.3 Hz, $ArOCH_2$), 2.15 (3H, s, Ar−CH_3), 1.76 (2H, m, $ArOCH_2CH_2$), 1.25 (18H, m, CH_2), 0.87 (3H, t, *J* = 6.7 Hz, CH_3).

4-Bromo-1-dodecyloxy-3-methoxybenzene. Yield 98%; mp 39 °C; ^{1}H NMR ($CDCl_3$, 200 MHz) $\delta = 6.96$ (2H, m, Ar−H), 6.71 (1H, d, *J* = 8.2 Hz, Ar−H), 3.95 (2H, t, *J* = 6.8 Hz, $ArOCH_2$), 3.82 (3H, s, $ArOCH_3$), 1.78 (2H, m, $ArOCH_2CH_2$), 1.24 (18H, m, CH_2), 0.86 (3H, t, *J* = 6.8 Hz, CH_3).

5.3. Phenylboronic Acids (6). A solution of the appropriate bromobenzene derivative (25 mmol) in dry THF (150 mL) was cooled with violent stirring to −78 °C. BuLi (16 mL of a 1.6 M solution in hexane, 26.0 mmol) was added dropwise within 2 h while the temperature was kept below −60 °C. The suspension was stirred at −70 °C for 3 h and then trimethylborate (5.4 g, 52.0 mmol) was added via a syringe. The temperature was kept below −60 °C during the addition. The reaction mixture was stirred for 2 h at −70 °C and then allowed to warm to room temperature. After addition of 3 M hydrochloric acid (30 mL), the mixture was stirred for additional 1 h at 20 °C. Afterward the solvent was evaporated and the residue was extracted with ethyl acetate (2 × 100 mL). The combined organic phases were washed with water (100 mL) and brine (50 mL) and were dried with Na_2SO_4. After the evaporation of the solvent, the residue was recrystallized from petroleum ether. Some of the boronic acids were obtained as mixtures containing oligomeric boronic acids. These mixtures can be used for the cross-coupling reaction without further purification.

4-Undecyloxyphenylboronic Acid (6c). Yield 75%; mp 80−81 °C; ^{1}H NMR ($CDCl_3$, 200 MHz) $\delta = 8.13$ (2H, d, *J* = 8.6 Hz, Ar−H), 6.98 (2H, d, *J* = 8.6 Hz, Ar−H), 4.02 (2H, d, *J* = 6.7 Hz, CH_2O), 1.81 (2H, m, CH_2CH_2O), 1.2−1.5 (16H, m, CH_2), 0.87 (3H, t, *J* = 6.6 Hz, CH_3).

4-Dodecyloxyphenylboronic Acid (6d). Yield 69%; mp 60−68 °C;^{1}H NMR ($CDCl_3$, 200 MHz) $\delta = 8.16$ (2H, d, *J* = 8.6 Hz, Ar−H), 6.99 (2H, d, *J* = 8.6 Hz, Ar−H), 4.03 (2H, t, *J* = 6.6 Hz, CH_2O), 1.82 (2H, m, CH_2CH_2O), 1.2−1.5 (18H, m, CH_2), 0.89 (3H, t, *J* = 6.4 Hz, CH_3).

4-Tetradecyloxyphenylboronic Acid (6e). Yield 66%; mp 67 °C; ^{1}H NMR ($CDCl_3$, 200 MHz) $\delta = 8.13$ (2H, d, *J* = 8.6 Hz, Ar−H), 6.99 (2H, d, *J* = 8.6 Hz, Ar−H), 4.04 (2H, t, *J* = 6.6 Hz, CH_2O), 1.82 (2H, m, CH_2CH_2O), 1.2−1.6 (22H, m, CH_2), 0.86 (3H, t, *J* = 6.4 Hz, CH_3).

4-Undecylphenylboronic Acid (6f). Yield 66%; mp 50 °C; ^{1}H NMR ($CDCl_3$, 200 MHz) $\delta = 8.14$ (2H, d, *J* = 8.6 Hz, Ar−H), 7.49 (2H, d, *J* = 8.6 Hz, Ar−H), 2.69 (2H, t, *J* = 6.6 Hz, CH_2−Ar), 1.65 (2H, m, CH_2CH_2−Ar), 1.2−1.3 (16H, m, CH_2), 0.88 (3H, t, *J* = 6.4 Hz, CH_3).

4-Dodecyloxy-3-fluorphenylboronic Acid (6 g). Yield 59%; ^{1}H NMR ($CDCl_3$, 200 MHz) $\delta = 7.91$ (1H, d, *J* = 8.6 Hz, Ar−H), 7.86 (1H, d, *J* = 11.5 Hz, Ar−H), 7.05 (1H, dd, *J* = 8.0 Hz, *J* = 8.0 Hz, Ar−H), 4.11 (2H, t, *J* = 6.5 Hz, CH_2O), 1.87 (2H, m, CH_2CH_2O), 1.2−1.6 (18H, m, CH_2), 0.88 (3H, t, *J* = 6.7 Hz, CH_3); ^{19}F NMR ($CDCl_3$, 188 MHz) $\delta = -137.46$ (dd, *J* = 11.5 Hz, *J* = 8.0 Hz, Ar−F).

4-Dodecyloxy-3-methylphenylboronic Acid (6h). Yield 83%; ^{1}H NMR ($CDCl_3$, 200 MHz) $\delta = 8.03$ (1H, d, *J* = 8.2 Hz, Ar−H), 7.96 (1H, s, Ar−H), 6.90 (1H, d, *J* = 8.2 Hz, Ar−H), 4.03 (2H, t, *J* = 6.4 Hz, CH_2O), 2.30 (3H, s, CH_3O), 1.83 (2H, m, CH_2CH_2O), 1.2−1.9 (18H, m, CH_2), 0.87 (3H, t, *J* = 6.3 Hz, CH_3).

4-Dodecyloxy-3-methoxyphenylboronic Acid (6i). Yield 52%; mp 118−120 °C; ^{1}H NMR ($CDCl_3$, 200 MHz) $\delta = 7.84$ (1H, dd, *J* = 1.4 Hz, *J* = 8.0 Hz, Ar−H), 7.70 (1H, d, *J* = 1.2 Hz, Ar−H), 7.01 (1H, d, *J* = 8.0 Hz, Ar−H), 4.11 (2H, t, *J* = 6.8 Hz, CH_2O), 4.00 (3H, s, CH_3O), 1.5−2.0 (20H, m, CH_2), 0.86 (3H, t, *J* = 6.3 Hz, CH_3).

5.4. 4-Halo-1-(5,6-dihydroxy-3-oxahexyloxy)benzene Derivatives (7a−d). The appropriate substituted 4-halophenol (13 mmol) was dissolved in dry acetonitrile (50 mL). K_2CO_3 (4.6 g, 33 mmol), 1-toluylsulfonyloxy-2-oxa-5-hexene (3.4 g, 13 mmol), and Bu_4NI (10 mg) were added, and the mixture was stirred at 100 °C for 4−8 h. Afterward, the solvent was removed in vacuo, and the residue was dissolved in water (50 mL) and ether (100 mL). The organic layer was separated, washed with water (50 mL), and with brine (50 mL). After drying (Na_2SO_4), the solvent was removed. The products were purified by column chromatography (chloroform/methanol 10:1). The solvent was evaporated and the oily residues were used without further purification for the dihydroxylation. For this purpose, the 4-halo-1-(3-oxa-5-hexenyloxy)benzene derivative obtained (5.0 mmol) was dissolved in acetone (90 mL). To this solution *N*-methylmorpholine-*N*-oxide (7.0 mmol, 10.7 mL of an 60% solution in water) and osmium tetroxide solution (1 mL of 0.01 M% solution in *tert*-butyl alcohol) were added. The resulting mixture was stirred for 100 h at room temperature. After this time, starting materials could no longer be detected and the mixture was worked up as follows: sodium bisulfite (saturated solution, 30 mL) was added and the resulting slurry was vigorously stirred for 1 h at room temperature. Afterward the solids were filtered off through a pad of Celite. The Celite was washed with acetone (100 mL), and the solution was evaporated. The residue was dissolved in warm ethyl acetate (200 mL) and the solution was washed with water (100 mL) and brine (25 mL) and was finally dried over Na_2SO_4. After evaporation of the solvent, the residue was purified by column chromatography with chloroform /methanol mixtures. The solvent was evaporated, and the highly viscous oily residues were used as obtained.

4-Bromo-1-(5,6-dihydroxy-3-oxahexyloxy)benzene (7a). Yield 63%; mp 30 °C; elemental analysis (%), found (calcd for $C_{11}H_{15}BrO_4$) C 45.06 (45.38), H 5.34 (5.19); ^{1}H NMR ($CDCl_3$, 200 MHz) $\delta = 7.35$ (2H, d, *J* = 9 Hz, Ar−H), 6.77 (2H, d, *J* = 9.0 Hz, Ar−H), 4.07 (2H, t, *J* = 4.6 Hz, $ArOCH_2CH_2O$), 3.9−3.5 (7H, m, $ArOCH_2CH_2O$, $OCH_2CHOHCH_2OH$).

4-Bromo-1-(5,6-dihydroxy-3-oxahexyloxy)-2-fluorobenzene (7b). Yield 28%; ^{1}H NMR ($CDCl_3$, 500 MHz) $\delta = 7.15$ (1H, dd, *J* = 2.4 Hz, *J* = 10.7 Hz, Ar−H), 7.10 (1H, d, *J* = 8.8 Hz, Ar−H), 6.79 (1H, dd, *J* = 8.8 *J* = 8.8 Hz, Ar−H), 4.07 (2H, t, *J* = 4.5 Hz, $ArOCH_2CH_2O$), 3.9−3.3 (9H, m, ArOCH$_2$C*H*$_2$O, OC*H*$_2$C*H*OHC*H*$_2$OH, OH); ^{19}F NMR (CDCl$_3$, 188 MHz) $\delta = -132.27$ (Ar−F, dd, $J = 8.8$ Hz, $J = 10.7$ Hz).

1-(5,6-Dihydroxy-3-oxahexyloxy)-4-iodo-2-methylbenzene (7c). Yield 38%; ^{1}H NMR (CDCl$_3$, 200 MHz) $\delta = 7.3-7.5$ (2H, m, Ar−H), 6.52 (1H, d, $J = 9.1$ Hz, Ar−H), 4.03 (2H, t, $J = 11.6$ Hz, ArOC*H*$_2$CH$_2$O), 3.9−3.4 (7H, m, ArOCH$_2$C*H*$_2$O,OC*H*$_2$C*H*OHC*H*$_2$OH), 2.92 (2H, s, broad, OH), 2.14 (3H, s, CH$_3$).

4-Bromo-1-(5,6-dihydroxy-3-oxahexyloxy)-2-methoxybenzene (7d). <sen>Yield 38%; ^{1}H NMR (CDCl$_3$, 500 MHz) $\delta = 6.9-7.0$ (2H, m, Ar−H), 6.72 (1H, d, $J = 4.3$ Hz, Ar−H), 4.09 (2H, t, $J = 4.6$ Hz, ArOC*H*$_2$CH$_2$O), 3.42 (s, 3H, OCH$_3$), 3.5−3.9 (7H, m, ArOCH$_2$C*H*$_2$O,OC*H*$_2$C*H*OHC*H*$_2$OH).

***(S)*-4-Bromo-1-(5,6-dihydroxy-3-oxahexyloxy)benzene [*(S)*-7a].** β-AD-Mix (10 g) was dissolved in H$_2$O/*tert*-butanol (1:1, 80 mL). The solution was cooled to 0 °C. At this temperature, 4-bromo-1-(3-oxa-5-hexenyloxy)benzene (1.5 g, 6.0 mmol) was added. The resulting mixture was stirred for 24 h at 0−1 °C. After this time, starting materials could no longer be detected and the mixture was worked up as described for the racemic **7a**. The ^{1}H NMR-spectrum corresponds to that one of the racemic compound. The enantiomeric purity was determined by Mosher's method: ee = 64%.

5.5. Pd^0-Catalyzed Cross Coupling of Aryl Bromides with Phenyl Boronic Acids: General Procedure. In a two-necked flask equipped with a reflux condenser and a magnetic stirring bar, Pd(PPh$_3$)$_4$ (0.2 g, 5 mol %) was added under an argon atmosphere to a mixture consisting of the halobenzene derivative (3.4 mmol), the boronic acid (3.5 mmol), glyme (30 mL), and 1 M NaHCO$_3$ solution (20 mL). The mixture was stirred at reflux temperature for 5 h. After cooling, the solvent was evaporated and the residue was dissolved in hot chloroform (100 mL). The organic phase was separated, and petroleum ether was added. The precipitate formed was sucked off, and the crude product obtained was purified by repeated crystallization from petroleum ether/ethyl acetate/chloroform mixtures.

4-(5,6-Dihydroxy-3-oxahexyloxy)-4′-octyloxybiphenyl (2a). Synthesized from **6a** and **7a**. Yield 39%; transitions (°C) cr$_1$ 115, cr$_2$ 121, cr$_3$ 146, S$_C$ 153, S$_A$ 169 is; elemental analysis (%), found (calcd for C$_{25}$H$_{36}$O$_5$) C 72.29 (72.08), H 8.79 (8.71); ^{1}H NMR (CDCl$_3$, 500 MHz) $\delta = 7.43$ (4H, m, Ar−H), 6.93 (4H, m, Ar−H), 4.15 (2H, t, $J = 4.6$ Hz, ArOC*H*$_2$CH$_2$O), 3.97 (2H, t, $J = 6.6$ Hz, ArOCH$_2$), 3.92−3.84 (3H, m, ArOCH$_2$C*H*$_2$O, CH), 3.74−3.61 (4H, m, OC*H*$_2$CHOHC*H*$_2$OH), 1.78 (2H, m, C*H*$_2$CH$_2$OAr), 1.45 (2H, m, C*H*$_2$CH$_2$CH$_2$OAr), 1.4−1.2 (10H, m, CH$_2$), 0.87 (3H, t, $J = 7.1$ Hz, CH$_3$).

4-(5,6-Dihydroxy-3-oxahexyloxy)-4′-nonyloxybiphenyl (2b). Transitions (°C) cr$_1$ 118, cr$_2$ 146, S$_C$ 150, S$_A$ 171 is; elemental analysis (%), found (calcd for C$_{26}$H$_{38}$O$_5$) C 72.28 (72.53), H 8.94 (8.89); ^{1}H NMR (DMSO-D6, 200 MHz) $\delta = 7.50$ (4H, m, Ar−H) 6.97 (4H, m, Ar−H), 4.63 (1H, d, $J = 5.1$ Hz, sec OH), 4.47 (1H, t, $J = 5.7$, prim OH), 4.10 (2H, t, $J = 4.7$, ArOC*H*$_2$CH$_2$O), 3.97 (2H, t, $J = 6.3$ Hz, ArOCH$_2$), 3.74 (2H, t, $J = 4.7$, ArOCH$_2$C*H*$_2$), 3.6−3.3 (5H, m, OC*H*$_2$C*H*OHC*H*$_2$-OH), 1.69 (2H, m, ArOCH$_2$C*H*$_2$), 1.26 (12H, m, CH$_2$), 0.85 (3H, t, $J = 6.3$, CH$_3$); MS (70 eV) *m/z* (%) = 430 (71, M$^+$), 312 (12), 186 (100).

4′-Decyloxy-4-(5,6-dihydroxy-3-oxahexyloxy)biphenyl (2c). Synthesized from **6b** and **7a**. Yield 16%; transitions (°C) cr$_1$ 120, cr$_2$ 143, Col$_{ob}$ 146, S$_C$ 147, S$_A$ 171; elemental analysis (%), found (calcd for C$_{27}$H$_{40}$O$_5$) C 72.03 (72.94), H 8.90 (9.07); ^{1}H NMR (CDCl$_3$, 500 MHz) $\delta = 7.43$ (4H, m, Ar−H), 6.93 (4H, m, Ar−H), 4.15 (2H, t, $J = 4.6$ Hz, ArOC*H*$_2$CH$_2$O), 3.97 (2H, t, $J = 6.6$ Hz, CH$_2$OAr), 3.93−3.83 (3H, m, ArOCH$_2$C*H*$_2$O, CH), 3.74−3.61 (4H, m, OC*H*$_2$CHOHC*H*$_2$OH), 2.67 (1H, s, broad, OH, 2.07 (1H, s, broad, OH), 1.78 (2H, m, C*H*$_2$CH$_2$-OAr), 1.45 (2H, m, C*H*$_2$CH$_2$CH$_2$OAr), 1.4−1.2 (12H, m, CH$_2$), 0.87 (3H, t, $J = 7.1$ Hz, CH$_3$); MS (70 eV) *m/z* (%) = 444 (100, M$^+$), 186 (33).

4-(5,6-Dihydroxy-3-oxahexyloxy)-4′-undecyloxybiphenyl (2d). Synthesized from **6c** and **7a**. Yield 51%; transitions (°C) cr$_1$ 128, cr$_2$ 143, Col$_{ob}$ 147, S$_A$ 171; elemental analysis (%), found (calcd for C$_{28}$H$_{42}$O$_5$) C 73.34 (73.33), H 9.26 (9.23); ^{1}H NMR (CDCl$_3$, 200 MHz) $\delta = 7.47$ (4H, m, Ar−H), 6.97 (4H, m, Ar−H), 4.17 (2H, t, $J = 4.9$ Hz, ArOC*H*$_2$CH$_2$O), 3.99 (2H, t, $J = 6.4$ Hz, CH$_2$OAr), 3.9−3.7 (3H, m, ArOCH$_2$C*H*$_2$O, CH), 3.8−3.6 (4H, m, OC*H*$_2$CHOH−C*H*$_2$OH), 2.70, (1H, d, $J = 5.0$ Hz, CHO*H*), 2.12 (1H, dd, $J = 6.6$ Hz, $J = 6.6$ Hz, CH$_2$O$_H$) 1.79 (2H, m, C*H*$_2$CH$_2$OAr), 1.6−1.2 (16H, m, CH$_2$), 0.89 (3H, t, $J = 6.7$ Hz, CH$_3$); MS (70 eV) *m/z* (%) = 458 (100, M$^+$), 186 (54).

***(S)*-4-(5,6-Dihydroxy-3-oxahexyloxy)-4′-dodecyloxybiphenyl [*(S)*-2e].** Synthesized from **6d** and *(S)*-**7a**. Yield 48%; transitions (°C) cr$_1$ 128, cr$_2$ 143, Col$_{ob}$ 149, S$_A$ 171 is; elemental analysis (%), found (calcd for C$_{29}$H$_{44}$O$_5$) C 73.63 (73.69); H 9.31(9.38); $[\alpha]_D = 6.8°$ (25 °C, $c = 0.001$ g/mL in CHCl$_3$); ee = 64%; ^{1}H NMR (CDCl$_3$, 200 MHz) $\delta = 7.44$ (4H, m, Ar−H), 6.93 (4H, m, Ar−H), 4.15 (2H, t, $J = 4.9$ Hz, ArOC*H*$_2$-CH$_2$O), 3.97 (2H, t, $J = 6.5$ Hz, ArOCH$_2$), 3.9−3.8 (3H, m, ArOCH$_2$C*H*$_2$O, CH), 3.7−3.55 (4H, m, OC*H*$_2$CHOHC*H*$_2$OH), 1.78 (2H, m, C*H*$_2$CH$_2$OAr), 1.6−1.2 (18H, m, CH$_2$), 0.86 (3H, t, $J = 6.5$ Hz, CH$_3$) MS (70 eV) *m/z* (%) = 471 (100, M$^+$), 353 (12), 303 (12), 185 (80).

4-(5,6-Dihydroxy-3-oxahexyloxy)-4′-tetradecyloxybiphenyl (2f). Synthesized from **6e** and **7a**. Yield 47%; transitions (°C) cr$_1$ 130, cr$_2$ 139, Col$_{ob}$ 147, S$_A$ 171; elemental analysis (%), found (calcd for C$_{31}$H$_{48}$O$_5$) C 73.17(73.73), H 9.23(9.66); ^{1}H NMR (CDCl$_3$, 500 MHz) $\delta = 7.44$ (4H, m, Ar−H), 6.93 (4H, m, Ar−H), 4.15 (2H, t, $J = 4.6$ Hz, ArOC*H*$_2$-CH$_2$O), 3.97 (2H, t, $J = 6.6$ Hz, ArOCH$_2$), 3.92−3.83 (3H, m, ArOCH$_2$C*H*$_2$O, CH), 3.74−3.61 (4H, m, OC*H*$_2$CHOHC*H*$_2$OH), 1.78 (2H, m, C*H*$_2$CH$_2$OAr), 1.45 (2H, m, C*H*$_2$CH$_2$CH$_2$OAr), 1.4−1.2 (20H, m, CH$_2$), 0.87 (3H, t, $J = 7.1$ Hz, CH$_3$); MS (70 eV) *m/z* (%) = 499 (100, M$^+$), 465 (10), 185 (57).

4-(5,6-Dihydroxy-3-oxahexyloxy)-4′-undecylbiphenyl (8). Synthesized from **6f** and **7a**. Yield 44%; transitions (°C) cr$_1$ 75, cr$_2$ 100, cr$_3$ 108, S$_{I/F}$ 119, S$_C$ 120, S$_A$ 165 is; elemental analysis (%), found (calcd for C$_{28}$H$_{42}$O$_4$) C 76.31(75.98), H, 9.69(9.56); ^{1}H NMR (CDCl$_3$, 500 MHz) $\delta = 7.48$ (2H, d, $J = 8.8$ Hz, Ar−H), 7.43 (2H, d, $J = 8.3$ Hz, Ar−H), 7.20 (2H, d, $J = 8.3$ Hz, Ar−H), 6.95 (2H, d, $J = 9.0$ Hz, Ar−H), 4.17 (2H, t, $J = 4.6$ Hz, ArOC*H*$_2$CH$_2$O), 3.92−3.84 (3H, m, ArOCH$_2$, CH), 3.74−3.61 (6H, m, ArOCH$_2$C*H*$_2$O, OC*H*$_2$-CHOHC*H*$_2$OH), 2.61 (2H,t, $J = 7.8$ Hz, ArCH$_2$), 1.61 (2H, m, ArCH$_2$C*H*$_2$), 1.4−1.2 (16H, m, CH$_2$), 0.87 (3H, t, $J = 6.8$ Hz, CH$_3$); MS (70 eV) *m/z* (%) = 442 (100, M$^+$), 324 (45), 301 (10), 183 (74).

4-(5,6-Dihydroxy-3-oxahexyloxy)-4′-dodecyloxy-3′-fluorbiphenyl (9). Synthesized from 4-dodecyloxy-3-fluorphenyl boronic acid **6g** and **7a**. Yield 36%; transitions (°C) cr 98, S$_A$ 155 is; elemental analysis (%), found (calcd for C$_{29}$H$_{43}$FO$_5$) C, 70.67(70.99); H, 8.77(8.83); ^{1}H NMR (CDCl$_3$, 200 MHz) $\delta = 7.43$ (3H, m, Ar−H), 6.97 (4H, m, Ar−H), 4.15 (2H, t, $J = 4.5$ Hz, ArOC*H*$_2$CH$_2$O), 4.04 (2H, t, $J = 6.6$ Hz, ArOCH$_2$), 3.95−3.85 (3H, m, ArOCH$_2$C*H*$_2$O, CH), 3.78−3.6 (4H, m, OC*H*$_2$-CHOHC*H*$_2$OH), 1.85 (2H, m, C*H*$_2$CH$_2$OAr), 1.5−1.2 (18H, m, CH$_2$), 0.86 (3H, t, $J = 6.8$ Hz, CH$_3$); ^{19}F NMR (CDCl$_3$, 188

MHz) $\delta = -135.93$ (t, Ar−F); MS (70 eV) *m*/*z* (%) = 490 (100, M^+), 322 (36), 204 (96).

4-(5,6-Dihydroxy-3-oxahexyloxy)-4′-dodecyloxy-3′-methylbiphenyl (10). Synthesized from 4-dodecyloxy-3-methylphenyl boronic acid **6h** and **7a**. Yield 39%; transitions (°C) cr 80, Col$_r$ 102, S$_A$ 141 is; elemental analysis (%), found (calcd for $C_{30}H_{46}O_5$) C, 73.76(74.04); H, 9.51(9.53); ^{1}H NMR ($CDCl_3$, 500 MHz) $\delta = 7.45$ (2H, d, $J = 8.8$ Hz, Ar−H), 7.29 (2H, m, Ar−H), 6.94 (2H, d, $J = 8.8$ Hz, Ar−H), 6.83 (1H, d, $J = 8.1$ Hz, Ar−H), 4.15 (2H, t, $J = 4.6$ Hz, $\mathrm{ArOC}\mathit{H}_2\mathrm{CH_2O}$), 3.97 (2H, t, $J = 6.6$ Hz, $\mathrm{CH_2OAr}$), 3.92−3.83 (3H, m, $\mathrm{ArOCH_2C}\mathit{H}_2\mathrm{O}$, CH), 3.75−3.61 (4H, m, $\mathrm{OC}\mathit{H}_2\mathrm{CHOHC}\mathit{H}_2\mathrm{OH}$), 2.25 (3H, s, $\mathrm{CH_3}$−Ar), 1.79 (2H, m, $\mathrm{C}\mathit{H}_2\mathrm{CH_2OAr}$), 1.46 (2H, m, $\mathrm{C}\mathit{H}_2\mathrm{CH_2CH_2OAr}$), 1.4−1.2 (16H, m, $\mathrm{CH_2}$), 0.86 (3H, t, $J = 7.1$ Hz, $\mathrm{CH_3}$); MS (70 eV): *m*/*z* (%) = 486 (100, M^+), 452 (9), 412 (6), 318 (14, $M^+-C_{12}H_{25}$), 200 (52).

4-(5,6-Dihydroxy-3-oxahexyloxy)-4′-dodecyloxy-3′-methoxybiphenyl (11). Synthesized from 4-dodecyloxy-3-methoxyphenyl boronic acid **6i** and **7a**. Yield 51%; transitions (°C) cr 78, S$_A$ 131 is; elemental analysis (%), found (calcd for $C_{30}H_{46}O_6$) C, 71.40(71.68); H, 9.22(9.22); ^{1}H NMR ($CDCl_3$, 500 MHz) $\delta = 7.45$ (2H, d, $J = 8.8$ Hz, Ar−H), 7.04 (2H, m, Ar−H), 6.9−7.0 (3H, m, Ar−H), 4.15 (2H, t, $J = 4.6$ Hz, $\mathrm{ArOC}\mathit{H}_2\mathrm{CH_2O}$), 4.02 (2H, t, $J = 6.8$ Hz, $\mathrm{CH_2OAr}$), 3.92−3.83 (6H, m, $\mathrm{ArOCH_2C}\mathit{H}_2\mathrm{O}$, CH, $\mathrm{CH_3OAr}$), 3.74−3.61 (4H, m, $\mathrm{OC}\mathit{H}_2\mathrm{CHOHC}\mathit{H}_2\mathrm{OH}$), 1.84 (2H, m, $\mathrm{C}\mathit{H}_2\mathrm{CH_2OAr}$), 1.45 (2H, m, $\mathrm{C}\mathit{H}_2\mathrm{CH_2CH_2OAr}$), 1.4−1.2 (16H, m, $\mathrm{CH_2}$), 0.87 (3H, t, $J = 7.1$ Hz, $\mathrm{CH_3}$); MS (70 eV) *m*/*z* (%) = 502 (100, M^+), 334 (35, $M^+-C_{12}H_{25}$), 216 (38).

4-(5,6-Dihydroxy-3-oxahexyloxy)-4′-dodecyloxy-3-methoxy-3′-methylbiphenyl (12). Synthesized from 4-dodecyloxy-3-methylphenylboronic acid **6h** and **7d**. Yield 71%; transitions (°C) cr$_1$ 59; cr$_2$ 75; cr$_3$ 92; S$_A$ 109 is; elemental analysis (%), found (calcd for $C_{31}H_{48}O_6$) C, 70.03(72.06); H, 9.33(9.36); ^{1}H NMR ($CDCl_3$, 500 MHz) $\delta = 7.29$ (2H, m, Ar−H), 7.04 (2H, m, Ar−H), 6.92 (1H, d, $J = 8.8$ Hz, Ar−H), 6.83 (1H, d, $J = 8.8$ Hz, Ar−H), 4.19 (2H, t, $J = 4.6$ Hz, $\mathrm{ArOC}\mathit{H}_2\mathrm{CH_2O}$), 3.97 (2H, t, $J = 6.3$ Hz, $\mathrm{CH_2OAr}$), 3.94−3.86 (6H, m, $\mathrm{ArOCH_2C}\mathit{H}_2\mathrm{O}$, CH, $\mathrm{OCH_3}$), 3.72−3.61 (4H, m, $\mathrm{OC}\mathit{H}_2\mathrm{CHOHC}\mathit{H}_2\mathrm{OH}$), 2.26 (3H, s, $\mathrm{CH_3}$−Ar), 1.80 (2H, m, $\mathrm{C}\mathit{H}_2\mathrm{CH_2OAr}$), 1.47 (2H, m, $\mathrm{C}\mathit{H}_2\mathrm{CH_2CH_2OAr}$), 1.4−1.2 (16H, m, $\mathrm{CH_2}$), 0.87 (3H, t, $J = 7.1$ Hz, $\mathrm{CH_3}$); MS (70 eV) *m*/*z* (%) = 516 (100, M^+), 398 (18), 230 (38).

4-(5,6-Dihydroxy-3-oxahexyloxy)-4′-dodecyloxy-3-fluorbiphenyl (13). Synthesized from **6d** and **7b**. Yield 23%; transitions (°C) cr 117, S$_A$ 137; elemental analysis (%), found (calcd for $C_{29}H_{43}FO_5$) C, 71.07(70.99); H, 9.06(8.83); ^{1}H NMR ($CDCl_3$, 500 MHz) $\delta = 7.42$ (2H, d, $J = 8.8$ Hz, Ar−H), 7.27−7.20 (2H, m, Ar−H), 7.00 (1H, t, $J = 8.6$ Hz, Ar−H), 6.93 (2H, d, $J = 8.8$ Hz, Ar−H), 4.21 (2H, t, $J = 4.6$ Hz, $\mathrm{ArOC}\mathit{H}_2\mathrm{CH_2O}$), 3.97 (2H, t, $J = 6.6$ Hz, $\mathrm{CH_2OAr}$), 3.92−3.85 (3H, m, $\mathrm{ArOCH_2C}\mathit{H}_2\mathrm{O}$,CH), 3.74−3.62 (4H, m, $\mathrm{OC}\mathit{H}_2\mathrm{CHOHC}\mathit{H}_2\mathrm{OH}$), 1.78 (2H, m, $\mathrm{C}\mathit{H}_2\mathrm{CH_2OAr}$), 1.45 (2H, m, $\mathrm{C}\mathit{H}_2\mathrm{CH_2CH_2OAr}$), 1.4−1.2 (16H, m, $\mathrm{CH_2}$), 0.87 (3H, t,$J = 7.1$ Hz, $\mathrm{CH_3}$); ^{19}F NMR ($CDCl_3$, 188 MHz) $\delta = -135.32$ (t, $J = 8.8$ Hz, Ar−F); MS (70 eV) *m*/*z* (%) = 490 (98, M^+), 372 (28), 204 (100, HO−PhF−PhOH).

4-(5,6-Dihydroxy-3-oxahexyloxy)-4′-dodecyloxy-3-methylbiphenyl (14). Synthesized from **6d** and **7c.** Yield 61%; transitions (°C) cr 108, S$_A$ 139; elemental analysis (%), found (calcd for $C_{30}H_{46}O_5$) C, 73.54(74.03); H, 9.36(9.53); ^{1}H NMR ($CDCl_3$, 500 MHz) $\delta = 7.42$ (2H, d, $J = 8.8$ Hz, Ar−H), 7.30 (2H, m, Ar−H), 6.91 (2H, d, $J = 8.6$ Hz, Ar−H), 6.84 (1H, d, $J = 8.3$ Hz, Ar−H), 4.15 (2H, t, $J = 4.6$ Hz, $\mathrm{ArOC}\mathit{H}_2\mathrm{CH_2O}$), 3.97 (2H, t, $J = 6.6$ Hz, $\mathrm{CH_2OAr}$), 3.93−3.85 (3H, m, $\mathrm{ArOCH_2C}\mathit{H}_2\mathrm{O}$, CH), 3.74−3.62 (4H, m, $\mathrm{OC}\mathit{H}_2\mathrm{CHOHC}\mathit{H}_2\mathrm{OH}$), 2.27 (3H, s, $\mathrm{CH_3}$−Ar), 1.78 (2H, m, $\mathrm{C}\mathit{H}_2\mathrm{CH_2OAr}$), 1.45 (2H, m, $\mathrm{C}\mathit{H}_2\mathrm{CH_2CH_2OAr}$), 1.4−1.1 (16H, m, $\mathrm{CH_2}$), 0.86 (3H, t, $J = 7.1$ Hz, $\mathrm{CH_3}$); MS (70 eV) *m*/*z* (%) = 486 (100, M^+), 368 (11), 200 (45).

4-(5,6-Dihydroxy-3-oxahexyloxy)-4′-dodecyloxy-3-methoxybiphenyl (15). Synthesized from **6d** and **7d**. Yield 49%; transitions (°C): cr$_1$ 69, cr$_2$ 85, S$_A$ 130; elemental analysis (%), found (calcd for $C_{30}H_{46}O_6$) C, 70.49(71.68); H, 8.94(9.22); ^{1}H NMR ($CDCl_3$, 500 MHz) $\delta = 7.43$ (2H, d, $J = 8.8$ Hz, Ar−H), 7.04 (2H, m, Ar−H), 6.92 (3H, m, Ar−H), 4.19 (2H, t, $J = 4.9$ Hz, $\mathrm{ArOC}\mathit{H}_2\mathrm{CH_2O}$), 3.97 (2H, t, $J = 6.6$ Hz, $\mathrm{CH_2OAr}$), 3.92−3.87 (m, 6H, $\mathrm{ArOCH_2C}\mathit{H}_2\mathrm{O}$, CH, $\mathrm{OCH_3}$), 3.72−3.61 (4H, m, $\mathrm{OC}\mathit{H}_2\mathrm{CHOHC}\mathit{H}_2\mathrm{OH}$), 1.78 (2H, m, $\mathrm{C}\mathit{H}_2\mathrm{CH_2OAr}$), 1.45 (2H, m, $\mathrm{C}\mathit{H}_2\mathrm{CH_2CH_2OAr}$), 1.4−1.2 (16H, m, $\mathrm{CH_2}$), 0.87 (3H, t, $J = 7.1$ Hz, $\mathrm{CH_3}$); MS (70 eV): *m*/*z* (%) = 502 (100, M^+), 468 (8, $M^+-CH_2{=}COHCH_2OH$), 428 (10), 384 (33), 216 (52, HO−PhOMe−Ph−OH).

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References and Notes

(1) (a) Percec, V.; Heck, J.; Johansson, G.; Tomazos, D.; Kawasumi, M.; Ungar, G. *J. Macromol. Sci., Pure Appl. Chem.* **1994**, *A31*, 1031. (b) Stebani, U.; Lattermann, G. *Macromol. Rep.* **1995**, *A32* (Suppl. 3) 385. (c) Pegenau, A.; Göring, P.; Tschierske, C. *J. Chem. Soc, Chem. Commun.* **1996**, 2563. (d) Cameron, J. H.; Facher, A.; Lattermann, G.; Diele, S. *Adv. Mater.* **1997**, *9*, 398.

(2) (a) Lee, M.; Oh, N.-K.; Zin, W. C. *J. Chem. Soc., Chem. Commun.* **1996**, 1787. (b) Lee, M.; Oh, N.-K.; Lee, H.-K.; Zin, W.-C. *Macromolecules* **1996**, *29*, 5567.

(3) Chen, J. T.; Thomas, E. L.; Ober C. K.; Hwang, S. S. *Macromolecules* **1995**, *28*, 1688.

(4) (a) Doi, T.; Sakurai, Y.; Tamatani, A.; Takenaka, S.; Kusabashi, S.; Nishihata Y.; Terauchi, H. *J. Mater. Chem.* **1991**, *1*, 169. (b) Nguyen, H. T.; Sigaud, G.; Achard, M. F.; Hardouin, F.; Twieg R. J.; Betterton, K. *Liq. Cryst.* **1991**, *10*, 389. (c) Pelzl, G.; Diele, S.; Lose, D.; Ostrovski B. I.; Weissflog; W. *Cryst. Res. Technol.* **1997**, *32*, 99. (d) Pensec, S.; Tournilhac, F.-G.; Bassoul, P. *J. Phys. II Fr.* **1996**, *6***,** 1597. (e) Dahn, U.; Erdelen C.; Ringsdorf, H.; Festag, R.; Wendorff, J. H.; Heiney, P. A.; Maliszewskyj, N. C. *Liq. Cryst.* **1995**, *19*, 759. (f) Tournilhac, F.; Bosio, L.; Nicoud J.-F.; Simon, J. *J. Chem. Phys. Lett.* **1988**, *145*, 452. (g) Pensec, S.; Tournilhac, F.-G.; Bassoul, P.; Durliat, C. *J. Phys. Chem. B* **1998**, *102*, 52. (h) Percec, V.; Johansson, G.; Ungar G.; Zhou, J. *J. Am. Chem. Soc.* **1996**, *118*, 9855.

(5) Kuschel, F.; Mädicke, A.; Diele, S.; Utschick, H.; Hisgen B.; Ringsdorf, H. *Polym. Bull.* **1990**, *23***,** 373 and references therein.

(6) Tschierske, C. *Prog. Polym. Sci.* **1996**, *21*, 775.

(7) Hildebrandt, F.; Schröter, J. A.; Tschierske, C.; Festag, R.; Wittenberg, M.; Wendorff, J. H. *Adv. Mater.* **1997**, *9*, 564.

(8) (a) Neumann, B.; Sauer, C.; Diele, S.; Tschierske, C. *J. Mater. Chem.* **1996,** *6*, 1087. (b) Tschierske, C.; Schröter, J. A.; Lindner, N.; Sauer, C.; Diele, S.; Festag, R.; Wittenberg, M.; Wendorff, J.-H. *SPIE* 1998, **3319**, 8.

(9) (a) Lawrence, A. S. C. *Mol. Cryst. Liq. Cryst.* **1969**, *7*, 1. (b) Diele, S.; Vorbrodt H.-M.; Zaschke, H. *Mol. Cryst. Liq. Cryst. Lett.* **1984**, *102*, 181. (c) Tschierske, C.; Brezesinski, G.; Kuschel F.; Zaschke, H. *Mol. Cryst. Liq. Cryst. Lett.* **1989**, *6*, 139. (d) van Doren, H. A.; van der Geest, R.; Kellog R. M.; Wynberg, H. *Recl. Trav. Chim. Pays-Bas* **1990**, *109*, 197. (e) Lattermann, G.; Staufer, G. *Liq. Cryst.* **1989**, *4*, 347. (f) Lattermann, G.; Staufer G.; Brezesinski, G. *Liq. Cryst.* **1991**, *10*, 169. (g) Praefcke, K.; Marquardt, P.; Kohne, B.; Stephan, W. *J. Carbohydr. Chem.* **1991**, *10*, 539. (h) Eckert, A.; Kohne, B.; Praefcke, K. *Z. Naturforsch.* **1988**, *43b*, 878. (i) Praefcke, K.; Kohne, B.; Eckert, A.; Hempel, J. *Z. Naturforsch.* **1990**, *45b*, 1084.

(10) (a) Lühmann, B.; Finkelmann, H. *Colloid Polym. Sci.* **1986**, *264*, 189. (b) Lühmann, B.; Finkelmann, H. *Colloid Poymer Sci.* **1987**, *265*, 506. (c) Schafheutle, M. A.; Finkelmann, H. *Liq. Cryst.* **1988**, *3*, 1369.

(11) (a) Miyaura, N.; Suzuki, A. *Chem. Rev.* **1995**, *95*, 2457. (b) Miyaura, N.; Yanagi, T.; Suzuki, A. *Synth. Commun.* **1981**, *11*, 513. (c) Hird, M.; Gray, G. W.; Toyne, K. J. *Mol. Cryst. Liq. Cryst.* **1991**, *206*, 187.

(12) van Rheenen, V.; Kelly R. C.; Cha, D. F. *Tetrahedron Lett.* **1976**, 1973.

(13) Kolb, H. C.; VanNieuwenhze M. S.; Sharpless, K. B. *Chem. Rev*. **1994**, *94*, 2483.

(14) Dale, J. A.: Mosher, H. S. *J. Am. Chem. Soc*. **1973**, *95*, 512.

(15) (a) Borisch, K.; Diele, S.; Göring, P.; Tschierske, C. *J. Chem. Soc., Chem. Commun.,* **1996**, 237. (b) Borisch, K.; Diele, S.; Göring, P.; Müller H.; Tschierske, C. *Liq. Cryst*. **1997**, *22*, 427. (c) Borisch, K.; Diele, S.; Göring, P.; Kresse H.; Tschierske, C. *Angew. Chem*. **1997**, *109*, 2188. *Angew. Chem., Int. Ed. Engl*. **1997**, *36***,** 2087. (d) Borisch, K.; Diele, S.; Göring, P.; Kresse H.; Tschierske, C. *J. Mater. Chem*. **1998**, 8, 529.

(16) Demus, D.; Kunicke, G.; Neelsen, J.; Sackmann, H. *Z. Naturforsch*. **1968**, *23a*, 84.

(17) Hagslätt, H.; Söderman O.; Jönsson; B. *Liq. Cryst*. **1994**, *17*, 157.

(18) Charvolin, J. *J. Chim. Phys*. **1983**, *80*, 15.

(19) (a) Skoulios A.; Luzzati, V. *Acta Crystallogr*. **1961**, *14*, 278. (b) Gallot, B.; Skoulios, A. *Acta Crystallogr*. **1962**, ***15***, 11.

(20) (a) Malthete, J.; Nguyen, H. T.; Destrade, C. *Liq. Cryst*. **1993**, *13*, 171. (b) Nguyen, H. T.; Destrade C.; Malthete, J. *Adv. Mater*. **1997**, *9*, 375.

(21) Weissflog, W.; Wiegeleben, A.; Diele, S.; Demus, D. *Liq. Cryst*. **1984**, *19*, 983.

(22) (a) Nguyen, H. T.; Sigaud, G.; Achard, M. F.; Hardouin, F. *Liq. Cryst.* **1991**, *103*, 89. (b) Lobko, T. A.; Ostrovskii, B. I. *Mol. Mater*. **1992**, *1*, 99. (c) Lobko, T. A.; Ostrovskii, B. I.; Pavluchenko, A. I.; Sulianov, S. N. *Liq. Cryst*. **1993**, *15*, 361.

(23) Hardouin, F.; Levelut, A. M.; Achard M. F.; Sigaud, G. *J. Chim. Phys*. **1983**, *80*, 53.

(24) Sauer, C.; Diele, S.; Tschierske, C. *Liq. Cryst*. **1997**, *6*, 911.

(25) (a) Tschierske, C.; Lunow, A.; Joachimi, D.; Hentrich, F.; Girdziunaite, D.; Zaschke, H.; Mädicke, A.; Brezesinski G.; Kuschel, F. *Liq. Cryst*. **1991**, *9*, 821. (b) Pietschmann, N.; Lunow, A.; Brezesinski, G.; Tschierske, C.; Kuschel F.; Zaschke, H. *Colloid Polym. Sci*. **1991**, *269*, 636. (c) Hentrich, F.; Tschierske, C.; Diele S.; Sauer, C. *J. Mater. Chem*. **1994**, *4*, 1547.

(26) In this respect the columnar phases can be regarded as inverted phases.

(27) Seddon, J. M.; Templer, R. H. *Handbook of Biological Physics*, Lipowsky, R., Sackmann, E., Eds.; Elsevier Science B. V.: New York, **1995**; Vol 1, p 97−160.

(28) Levelut, A. M.; Clerc, M. *Liq. Cryst*. **1998**, *24*, 105 and references therein.

(29) Thermotropic cubic-phases with a *Pn3* or *Pn3m* space group have been discussed for dibenzoylhydrazines. Demus, D.; Gloza, A.; Hartung, H.; Hauser, A.; Raphtel I.; Wiegeleben, A. *Kristallogr. Tech*. **1981**, *16*, 1445.

(30) Longley, W.; McIntosh, T. J. *Nature* **1983**, *303*, 612.

(31) Hendrikx, Y.; Pansu, B. *J. Phys II Fr*. **1996**, *6*, 33.

(32) (a) Gray, G. W.; Jones B.; Marson, F. *J. Chem. Soc*. **1957**, 393. (b) Diele, S.; Brand P.; Sackmann, H. *Mol. Cryst. Liq. Cryst*. **1972**, *17*, 163. (c) Etherington, G.; Langley, A. J.; Leadbetter, A. J.; Wang, X. J. *Liq. Cryst*. **1988**, *3*, 155.

(33) Bruce, D. W.; Donnio, B.; Hudson, S. A.; Levelut, A.-M.; Megtert, S.; Petermann, D.; Veber, M. *J. Phys. II Fr*. **1995**, *5*, 289.

(34) Hurd C. D.; Pollack, M. A. *J. Am. Chem. Soc*. **1938**, *60*, 1908.

(35) Brown, J. H.; Marvel, C. S. *J. Am. Chem. Soc*. **1937**, *59*, 1176.

(36) Molander, G. A.; Harring, L. S. *J. Org. Chem*. **1990**, *55*, 6171.

(37) Ohta, K.; Takagi, A.; Muroki, H.; Yamamoto, I.; Matsuzaki, K. *Mol. Cryst. Liq. Cryst*. **1987**, *147*, 15.

(38) Gray, G. W.; Hird, M.; Lacey, D.; Toyne, K. J. *J. Chem. Soc., Perkin Trans. 2* **1989**, 2041.

(39) Gray, G. W.; Hird, M.; Toyne, K. J. *Mol. Cryst. Liq. Cryst*. **1991**, 195, 221.

(40) Andersch, J.; Tschierske, C.; Diele, S.; Lose, D. *J. Mater. Chem*. **1996**, *6*, 1297.

(41) Manuscript in preparation.