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Smectic, columnar and cubic mesophases in binary systems of hemiphasmidic and calamitic amphiphilic diols

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A first example of an amphiphilic hemiphasmid consisting of a biphenyl rigid core connected to a hydrophilic 5,6-dihydroxy-3-oxahexyloxy group at one end and carrying two lipophilic dodecyloxy chains at the other end has been synthesized by a Pd-catalysed cross coupling reaction. The liquid crystalline properties of this compound have been investigated by polarized light microscopy, by differential scanning calorimetry and by X-ray diffraction. It exhibits a thermotropic hexagonal columnar mesophase which is stabilized on addition of formamide. On addition of ethylene glycol, a bicontinuous cubic mesophase is induced. Furthermore, binary mixtures of this compound with structurally related single chain amphiphiles have been investigated. Besides a smectic A phase, an induced columnar mesophase and a cubic phase were found in these mixtures.

1. Introduction

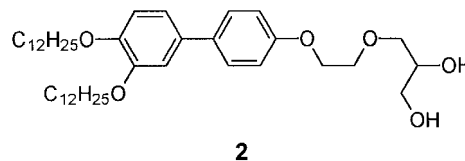
Liquid crystalline phases can be formed by a wide variety of different materials: rod-like and disc-like mesogens, amphiphilic molecules, rigid polymers and block copolymers etc. The combination of the structural units of different classes of mesogenic molecules is a present topic of research. Polycatenar compounds [1], for example, have a structure intermediate between rod-like and disc-like molecules, and the combination of anisometric and amphiphilic molecules can give rise to amphotropic materials [2].

We have recently synthesized amphiphilic biphenyl derivatives such as the compounds **1** (see table 1), which combine a rigid rod-like core with a flexible and lipophilic alkyl chain and a hydrophilic group. Some of these compounds have an unexpected polymorphism. The calamitic compounds **1.11–1.14** ($n = 11–14$), for example, form not only a smectic A phase as expected, but also columnar phases. It has been proposed that the columnar mesophases of these rod-like molecules result from the collapse of the smectic layer structure into ribbons, which are arranged in an oblique 2D-lattice [3, 4]. The short chain homologue **1.8** ($n = 8$) exhibits a

smectic C phase instead of the columnar mesophase and the compound **1.10** ($n = 10$) shows a Col–SmC–SmA trimorphism [4].

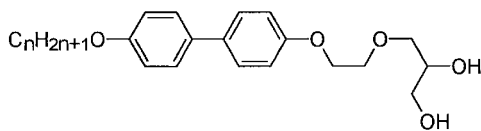
The mesomorphic properties of these amphotropic mesogens were influenced by addition of protic solvents which leads to the stabilization of the SmA phases and to the loss of the columnar and smectic C phases [4].

In this paper we report the synthesis and the thermotropic and lyotropic liquid crystalline behaviour of a double chain compound **2** (see below) incorporating two long alkyl chains instead of only one.



This compound combines typical structural units of three different classes of liquid crystalline compounds: the taper-shaped 3,4-dialkoxyphenyl unit which is often used to obtain columnar mesophases and the calamitic biphenyl unit, which is a typical structural unit of calamitic liquid crystals. Furthermore, due to the hydrophilic diol unit, this molecule is not only anisometric, but also amphiphilic.

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Table 1. Thermotropic phase transition temperatures (°C) of the single chain compounds **1** [4].

Compound	<i>n</i>	Cr	Col _{ob}	SmC	SmA	I
1/8	8	•	146	—	•	153
1/10	10	•	143	•	146	•
1/11	11	•	143	•	147	—
1/14	14	•	139	•	147	—

2. Synthesis

As shown in the scheme, compound **2** was prepared by Suzuki cross coupling [5] of 4-(5,6-dihydroxy-3-oxaheptyloxy)bromobenzene **5** [4] with 3,4-didodecyloxyphenyl boronic acid **4** [6].

3. Thermotropic properties

The compound **2** was first studied by polarized light microscopy. On cooling, a spherulitic texture is formed at 135°C. Crystallization occurs at 81°C, and reheating gives a melting point at 87°C. DSC scans confirmed the microscopic data.

The X-ray diffraction pattern of the mesophase of compound **2** exhibits three sharp reflections in the small angle region and a diffuse scattering in the wide angle

region. The ratio of positions of the reflections is 1:3^{1/2}:2, proving the existence of a hexagonal columnar mesophase with a strongly temperature dependent hexagonal lattice parameter ($a = 5.83$ nm at $T = 100^\circ\text{C}$ and $a = 5.16$ nm at $T = 130^\circ\text{C}$). The length of the molecule in its most extended conformation is $L = 3.2$ nm (CPK-models). This is in agreement with the assumption that the hexagonal columnar phase could consist of extended columnar aggregates built up by hydrogen bonding networks between the polar diol head groups inside the columns, surrounded by the rigid rods and the molten alkyl chains (see figure 6).

According to this model, the stronger cohesive forces are located inside the columns and therefore this phase can be regarded as an inverted phase (Col_{h2}). Assuming a density of $\rho = 1$ g cm⁻³, the number n of molecules arranged in a hypothetical single slice of the columns† with a thickness (h) of 0.45 nm was estimated according to equation (1)

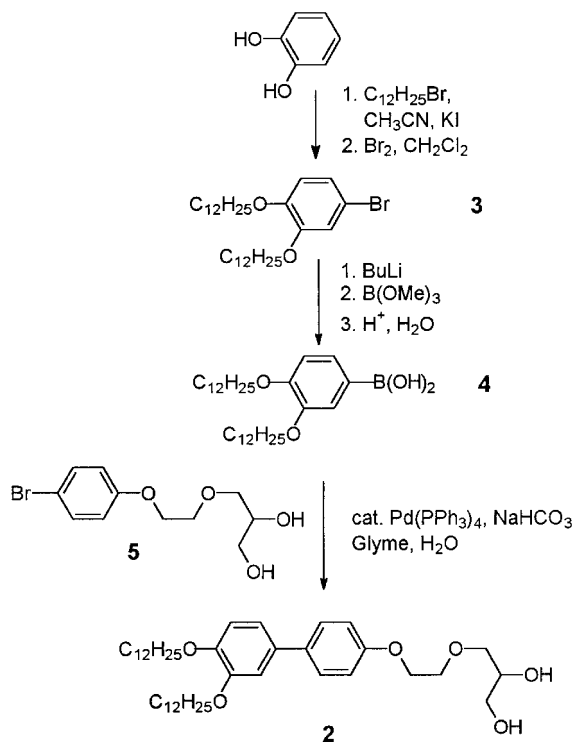
$$n = a^2/2 \cdot 3^{1/2} h N_A/M \rho. \quad (1)$$

Here the parameter a is the hexagonal lattice parameter ($a = 5.83$ nm at $T = 100^\circ\text{C}$), N_A is the Avogadro constant and M is the molecular mass. The estimated value n of about 12 molecules (at $T = 100^\circ\text{C}$) is larger than that found for columnar phases of other wedge shaped amphiphiles [7–10].

4. Lyotropic properties

As in the case of other amphiphilic diols [2, 3, 4, 11, 12] the mesomorphic properties of compound **2** can be

† It should be stressed, that due to the cooperative nature of the hydrogen bonding in polyhydroxy compounds, the individual amphiphiles are randomly distributed along the column axis, in the same way as in hexagonal columnar phases of lyotropic systems. The slices discussed can only give rough information about the number of molecules arranged *on average* side by side. The thickness of the slices was taken to be 0.45 nm, because this value corresponds to the average lateral distance between the centres of alkyl chains usually observed by X-ray scattering from columnar phases.

Scheme. Synthesis of compound **2**.

influenced by the addition of solvents. Protic solvents can interact with the hydrophilic groups and influence the strength of the hydrogen bonding and additionally increase the size of the polar groups. The latter effect can give rise to a change of the interface curvature between the polar and the lipophilic regions. In the case of the single chain compounds **1**, this leads to the disappearance of the columnar phase and to a stabilization of the smectic A phase [4]. However no smectic phase can be detected on addition of protic solvents such as water, ethylene glycol or formamide to compound **2**. For the system **2**/formamide, the clearing temperature of the hexagonal columnar mesophase only continuously rises. The maximum transition temperature of the formamide-saturated sample ($T = 180^\circ\text{C}$) exceeds the clearing temperature of the thermomesophase. No other mesophase is detected at any solvent concentration.

A different behaviour was found for the system **2**/ethylene glycol. Here, the columnar mesophase is only slightly stabilized on addition of ethylene glycol (maximum at $T = 139^\circ\text{C}$). Further increasing the ethylene glycol concentration leads to a decrease in the stability of the columnar mesophase and a highly viscous optically isotropic phase with cornered or angular phase boundaries occurs. From this appearance we can conclude that it is a cubic mesophase. The transition temperatures of the solvent saturated samples of compounds **1.12** and **2** are compared in table 2.

Obviously, ethylene glycol molecules (which may be regarded as building blocks of the polar group of compound **2**) are incorporated into the hydrogen bonding network of these head group units. This increases their cross sectional area and causes the transition from the columnar to the cubic mesophase, which in this case should represent an intermediate phase on the way from the inverted columnar mesophase to a smectic phase. Thus, the phase should be an inverted bicontinuous cubic phase ($\text{Cub}_{\text{V}2}$) with a structure composed of two interwoven networks of cylinders as assumed for bicontinuous

cubic mesophases of other lyotropic systems. The pronounced taper-shaped structure of the double chain compound **2**, in comparison with that of the single chain compounds **1**, however inhibits the formation of smectic layer structures [13].

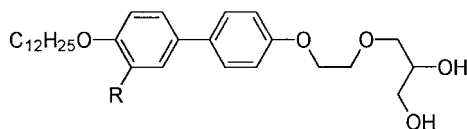
5. Binary mixtures of the double chain amphiphile **2** with single chain diols **1**

Recently we have found that the adjustment of the polar–lipophilic interface curvature in mesophases of polyhydroxy amphiphiles is made possible not only by addition of protic solvents, but also by mixing structurally related polyhydroxy amphiphiles which have different molecular shapes [10, 14]. This method was used for example to distinguish between different types of cubic mesophases [10, 14]. In the following account we apply this method to binary mixtures consisting of the single chain compounds **1** and the double chain compound **2**.

Figure 1 shows the contact region between compound **1.14** with only one tetradecyloxy chain and compound **2** with two dodecyloxy chains at 142°C . As expected, the columnar phases of these two compounds are not completely miscible, because they are of different types (Col_{ob} and Col_{h}). In the contact region the columnar phase of **2** disappears and two new phases occur. The detailed phase diagram of the system **2**/**1.14** is given in figure 2.

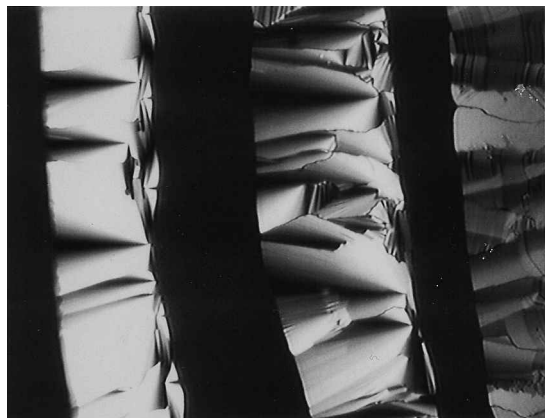
On increasing the concentration of **1.14**, the hexagonal columnar phase of the double chain compound **2** is at first stabilized. At an approximately equimolar ratio of both compounds, the maximum of the clearing temperature ($T = 143^\circ\text{C}$) is reached and afterwards the stability of the columnar phase decreases again. At $x = 0.55$ a SmA phase appears above the columnar phase. At a ratio of approximately 2 mol of **1.14** per mol of **2** the Col_{h} phase disappears and another phase occurs with a spherulitic texture, typical for columnar phases. The X-ray diffraction pattern of this induced phase exhibits a diffuse scattering in the wide angle region. In the small

Table 2. Comparison of the thermotropic and lyotropic phase transition temperatures ($T/^\circ\text{C}$) of the double chain compound **2** and the single chain compound **1.12** [3, 4].



Condition	$R = \text{H}$ (compound 1.12)	$R = \text{C}_{12}\text{H}_{25}\text{O}$ (compound 2)
Pure compound	Cr_1 127 Cr_2 142 Col_{ob} 147 SmA 170 I	Cr_1 83 Cr_2 87 Col_{h} 135 I (21.4) (59.0) (1.4) ^a
Ethylene glycol saturated	Cr 110 SmA 135 I	Cr 86 Col_{h} 129 $\text{Cub}_{\text{V}2}$ 139 I
Formamide saturated	Cr 108 SmA 183 I	Cr 81 Col_{h} 180 I

^a Transition enthalpies ($\Delta H/\text{kJ mol}^{-1}$).



I Col_h SmA Col_x Cub Col_{ob}

Figure 1. Optical photomicrograph of the contact region of compounds **2** and **1.14** at 142°C. From left to right: isotropic liquid of compound **2**, Col_h phase, homeotropically aligned SmA phase, induced columnar phase (Col_x), induced cubic phase (Cub), Col_{ob} phase of compound **1.14**.

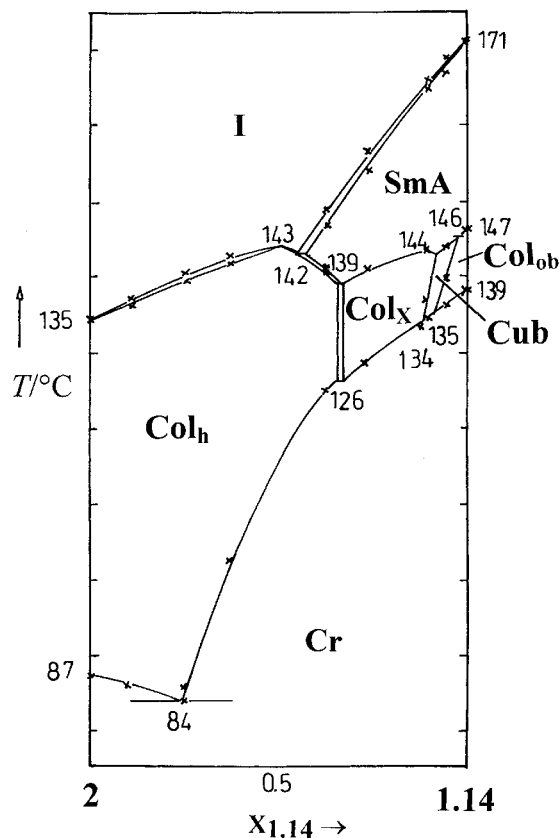


Figure 2. Binary phase diagram of the system **2/1.14**.

angle region, a very strong reflection which corresponds to a d value of 5.35 nm and several additional reflections of very low intensity occur. The reflections detected cannot be indexed on the basis of either a hexagonal or a rectangular lattice. Therefore the phase type cannot be

specified in more detail. This induced columnar phase (Col_x) disappears again on further increasing the concentration of compound **1.14** and is replaced by a small region of an optically isotropic phase. This isotropic mesophase is highly viscous and grows with cornered or angular phase boundaries (see figure 3). As mentioned above, these are typical features of cubic mesophases. The observed reflections (table 3) point to a primitive cubic lattice.

At a ratio of more than 19 mol of **1.14** to one mol of **2** the cubic phase disappears again and only the Col_{ob} phase and the SmA phase of the pure single chain compound **1.14** can be observed. Concerning the concentration range, the cubic phase is observed between two columnar phases. This is remarkable, because in other amphiphilic compounds [7, 10, 14, 15] and in lyotropic systems [13], cubic phases are usually found as intermediates between columnar and lamellar phases or between columnar mesophases and micellar solutions.

The same principal phase diagrams as for the system **2/1.14** were observed for the binary systems of **2** with **1.12** and **1.11**. In the latter of these two cases the cubic phase appears only as a monotropic mesophase, figure 4(b). No cubic mesophase and no induced columnar phase can be observed in mixtures of **2** with **1.10** and **1.8**, figures 4(a) and 5. This indicates that the stabilities of the induced phases decrease with decreasing chain length



Figure 3. Polarized optical microscopic texture observed at the transition from the induced columnar to the cubic phase of the binary mixture of compounds **2** and **1.14** ($x_{1.14} = 0.9$) at 136°C.

Table 3. Observed and calculated X-ray reflections for the induced cubic phase of the binary mixture **2/1.14** ($x_{1.14} = 0.97$).

$\theta_{\text{obs}}/^\circ$	$\theta_{\text{calc}}/^\circ$	hkl
0.81	0.81	111
0.95	0.94	200
1.55	1.56	311
1.65	1.65	222

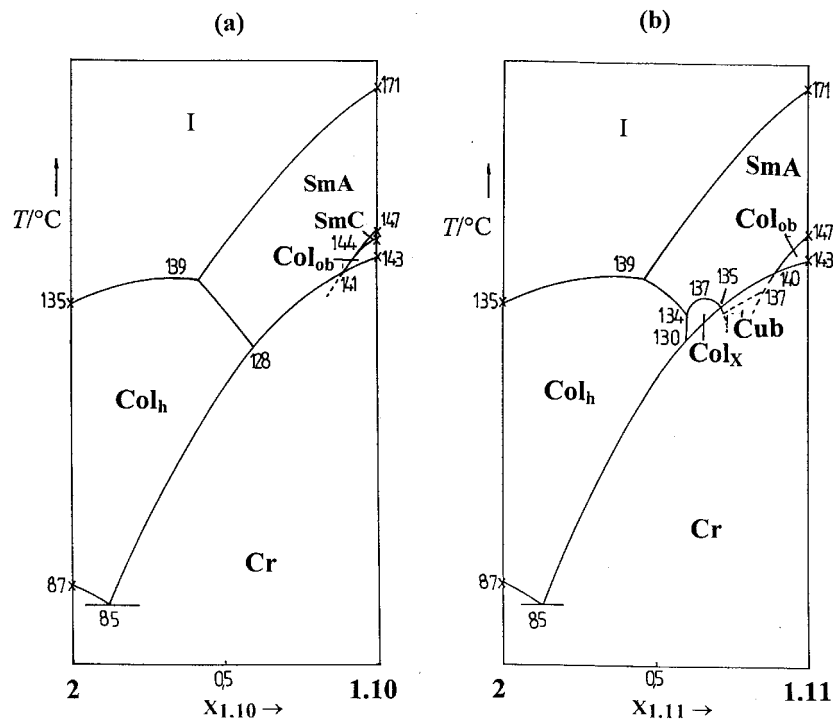


Figure 4. Simplified binary phase diagrams of the systems 2/1.10 (a) and 2/1.11 (b).

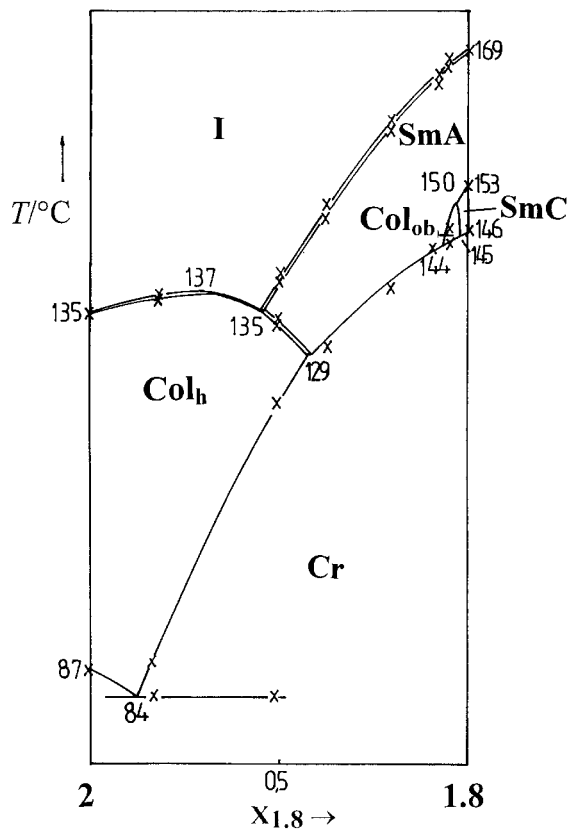


Figure 5. Binary phase diagram of the system 2/1.8.

of the single chain compound in the mixed systems. Another interesting observation was made during investigation of the binary system of 2 with the short chain compound 1.8.

The pure compound 1.8 has a smectic C phase instead of the Col_{ob} phase of the long chain analogues 1.10–1.14 [4]. However, in the mixture with 2 at a concentration of only 0.05 mol of 2 per mol of 1.8, a small region of columnar phase can be induced. The optical texture of this mesophase is the same as that of the Col_{ob} phases of the pure compounds 1.10 and 1.11 [4]. Therefore we assume that this induced columnar phase is of the same type as the Col_{ob} phase found for the pure single chain amphiphiles 1.10–1.14 [4]. This assumption is supported by the fact that in the system 2/1.10, the SmC phase of compound 1.10 is completely replaced by the Col_{ob} phase on increasing the concentration of 2, see figure 4(a). These observations are in accordance with the proposed model for the Col_{ob} phases of the single chain compounds 1.10–1.14 [4]. According to this model, the collapse of the smectic layers with formation of a ribbon phase results from the different space filling of the incompatible microsegregated parts of the molecules and it was assumed that the mean lateral area of the lipophilic regions of the long chain compounds 1.10–1.14 is slightly larger than that of their polar regions, see figure 6. It seems that for the short chain compound 1.8 this difference is not large enough to cause the collapse of the smectic layers into ribbons and consequently only

an SmC phase is found. On addition of **2** however, the mean lateral area of the lipophilic region is increased and this can induce the transition to the Col_{ob} phase.

6. Summary and discussion

In summary, the first example of a taper-shaped double chain amphiphile with an extended calamitic unit has been synthesized. It exhibits a thermotropic hexagonal columnar mesophase. It seems, that the microstructure of this columnar mesophase is largely different from that of the columnar mesophases of the related single chain compounds. Probably, the hexagonal columnar phase of the double chain compound **2** is related to the columnar mesophases of other taper-shaped amphiphiles [7–10, 12, 14], characterized by an average cylindrical diameter of the columns. Due to the elongated rigid biphenyl unit however, the number of molecules arranged in each (hypothetical) slice of these columns is much larger than usual. In contrast, the Col_{ob} phases of the single chain amphiphiles **1** represent typical ribbon phases, which are built up by ribbon-like segments of a collapsed smectic layer structure, see figure 6. This difference of the mesophase structure must be responsible for the different lyotropic phase behaviour of compounds **1** and **2**. The columnar mesophase of compound **2** (Col_h) can be stabilized on addition of protic solvents, whereas the Col_{ob} phases of the single chain analogues are readily destabilized and transformed into a layer structure (SmA phase).

The miscibility experiments have also proven the incompatibility of the two columnar phases. Despite the similarity of the molecular structures and the equal molecular length of the individual amphiphiles (e.g. compounds **2** and **1.12**), no direct transition between their columnar mesophases is possible.

Besides a smectic A phase, an induced columnar phase and a cubic mesophase were found in mixtures of compound **2** at higher concentrations with the related single chain amphiphiles **1**. Regarding the oblique columnar phase of the single chain compounds **1** as a ribbon phase, essentially composed of fragments of layers, and the hexagonal columnar phase of the double chain compound **2** as consisting of cylindrical aggregates, the cubic phase occurs between a layer-like and a cylindrical aggregate morphology. Therefore, it seems likely, that this cubic phase too could have a bicontinuous interwoven network structure.

With respect to the variety of different mesophases found, these amphiphiles and their mixtures behave like the polycatenar [1] and double swallow tailed [16] compounds. We can regard these molecules as a special type of polycatenar compound which can be described as amphiphilic hemiphasmids. Related non-amphiphilic hemiphasmidic compounds incorporating a biphenyl rigid core are non-mesogenic [1]. Obviously a significant mesophase stabilization is provided by the amphiphilic molecular structure, which must be due to at least two effects. First we have the hydrogen bonding networks between the hydrophilic groups which provide temporary cross links and in this way additionally stabilize the mesophases. In this respect the hydrogen bondings act as a kind of dynamic polymer backbone. Remarkably, non-amphiphilic hemiphasmids fixed to a polymer backbone have recently been described [17, 18] Also for these molecules, smectic, columnar and an optically isotropic mesophase [18] have been found. In the case of amphiphilic hemiphasmids a second mesophase stabilizing effect, the strong microsegregation [19] of the polar regions from the lipophilic residues must additionally contribute to their mesophase formation.

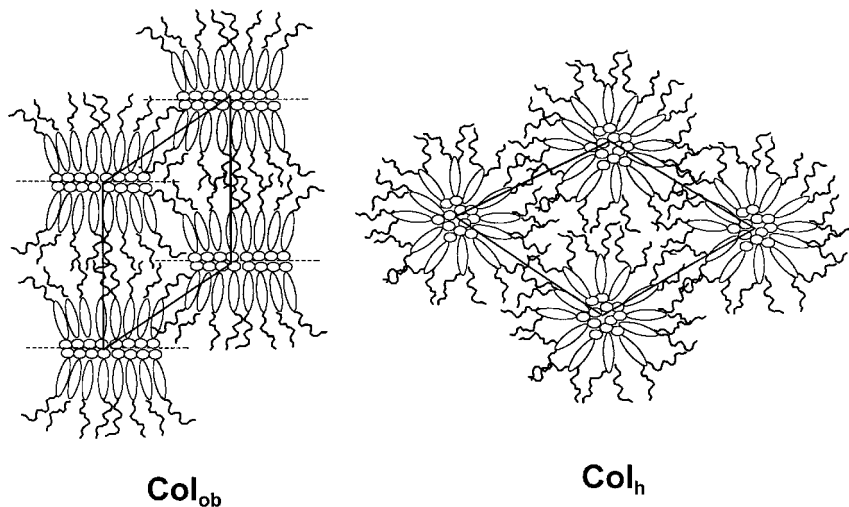


Figure 6. Model of the organization of the single chain molecules **1** in the Col_{ob} phase [4] and of the double chain molecules **2** in the Col_h phase (only the cross sections of the columns are shown).

Thus, compound **2**—which combines structural units of three different classes of mesogenic compounds—maps the borderline between disc-like and rod-shaped, thermotropic and lyotropic, low molecular mass and polymeric mesogenic materials.

7. Experimental

7.1. General considerations

Confirmation of the structures was obtained by ^1H NMR spectroscopy (VARIAN Unity 500, VARIAN Gemini 200 spectrometer), by infrared spectroscopy (SPECORD 71) and by mass spectrometry (AMD 402, 70 eV). The purity was checked by thin layer chromatography (TLC aluminium sheets, silica gel 60 F254 from Merck). Microanalyses were performed using a LECO CHNS-932 elemental analyser.

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). 1,2-Didodecyloxybenzene [20] and 4-bromo-1-(5,6-dihydroxy-3-oxahexyloxy)benzene **5** [4] were obtained as described in the references.

7.2. 3,4-Didodecyloxybromobenzene **3**

1,2-Didodecyloxybenzene (43 mmol, 19.2 g) was dissolved in dry CH_2Cl_2 (200 ml). At 0°C a solution of bromine (43 mmol, 6.9 g) in dry CH_2Cl_2 (100 ml) was added dropwise. The mixture was stirred at this temperature for an additional 4 h and allowed to warm to room temperature. The solution was washed with aqueous NaHCO_3 (3×100 ml), dried with Na_2SO_4 and the solvent evaporated. The residue was crystallized from methanol. Yield 21.3 g, 94%; m.p. $44\text{--}45^\circ\text{C}$. Elemental analysis (%), found (calc. for $\text{C}_{30}\text{H}_{53}\text{O}_2$): C 68.48 (68.55), H 10.09 (10.15). ^1H NMR (CDCl_3 , 200 MHz): $\delta = 6.95$ (1H, d, $J = 2.1$ Hz, Ar-H2), 6.96 (1H, dd, $J = 2.3$ Hz, $J = 9.2$ Hz, Ar-H5), 6.70 (1H, d, $J = 9.2$ Hz, Ar-H4), 3.94 (2H, t, $J = 6.7$ Hz, OCH_2), 3.92 (2H, t, $J = 6.7$ Hz, OCH_2), 1.77 (4H, m, $\text{CH}_2\text{CH}_2\text{O}$), 1.5–1.25 (36H, m, CH_2), 0.86 (6H, t, $J = 6.0$ Hz, CH_3).

7.3. 3,4-Didodecyloxyphenyl boronic acid **4**

A solution of **3** (9.0 g, 17 mmol) in dry THF (150 ml) was cooled with vigorous stirring to -15°C . BuLi (16 ml of a 1.6M solution in hexane, 26.0 mmol) was added dropwise within 2 h keeping the temperature between -15°C and -20°C . The suspension was stirred at -30°C for 1 h and then trimethyl borate (5.4 g, 52.0 mmol) was added using a syringe; the temperature was kept at -35°C during this addition. The reaction mixture was stirred for 2 h at -35°C and then allowed

to warm to room temperature overnight. After addition of 3M hydrochloric acid (30 ml) the mixture was stirred for 1 h at 20°C . The solvent was then evaporated and the residue crystallized from petroleum ether. Yield 90%; m.p. $103\text{--}112^\circ\text{C}$. ^1H NMR (CDCl_3 , 200 MHz): $\delta = 7.79$ (1H, d, $J = 8.0$ Hz, Ar-H), 7.70 (1H, d, $J = 1.4$ Hz, Ar-H2), 6.97 (1H, d, $J = 8.1$ Hz, Ar-H5), 4.11 (2H, t, $J = 6.4$ Hz, CH_2O), 4.01 (2H, t, $J = 6.4$ Hz, CH_2O), 1.75–1.95 (4H, m, $\text{CH}_2\text{CH}_2\text{O}$), 1.1–1.6 (36H, m, CH_2), 0.86 (6H, t, $J = 6.4$ Hz, CH_3).

7.4. 3,4-Didodecyloxy-4'-(5,6-dihydroxy-3-oxahexyloxy)biphenyl **2**

In a two necked flask equipped with reflux condenser and magnetic stirring bar, $\text{Pd}(\text{PPh}_3)_4$ (0.2 g, equivalent to 5 mol %) was added under an argon atmosphere to a mixture consisting of **5** (1.0 g, 3.4 mmol), **4** (1.7 g, 3.5 mmol), glyme (30 ml) and 1M aqueous NaHCO_3 (20 ml). The mixture was stirred at reflux for 5 h. After cooling, the solvent was evaporated and the residue dissolved in hot chloroform (100 ml). The organic phase was separated and petroleum ether added. The precipitate formed was filtered off and the crude product purified by repeated crystallization from petroleum ether/chloroform mixtures. Yield 38%; transitions ($^\circ\text{C}$) Cr_1 81 Cr_2 87 Col_h 135 I. Elemental analysis (%), found (calc. for $\text{C}_{41}\text{H}_{68}\text{O}_6 \cdot 0.5 \text{H}_2\text{O}$): C 72.29 (72.08), H 8.79 (8.71). The water content of the air dried samples was determined by Karl-Fischer titration; water free sample were obtained by heating open samples for one minute at 160°C . ^1H NMR (CDCl_3 , 500 MHz): $\delta = 7.44$ (2H, d, $J = 8.8$ Hz, Ar-H), 7.05 (1H, s, Ar-H), 7.04 (1H, d, $J = 8.0$ Hz, Ar-H), 6.94 (2H, d, $J = 8.8$ Hz), 6.90 (1H, d, $J = 8.0$ Hz, Ar-H), 4.15 (2H, t, $J = 4.6$ Hz, ArOCH_2), 4.03 (4H, t $J = 6.6$ Hz, $\text{ArOCH}_2\text{alkyl}$), 4.00 (4H, t $J = 6.6$ Hz, $\text{ArOCH}_2\text{alkyl}$), 3.88 (3H, m, $\text{ArOCH}_2\text{CH}_2$, CH), 3.74–3.61 (4H, m, $\text{OCH}_2\text{CHOHCH}_2\text{OH}$), 1.81 (4H, m, $\text{CH}_2\text{CH}_2\text{OAr}$), 1.46 (4H, m, $\text{CH}_2\text{CH}_2\text{CH}_2\text{OAr}$), 1.20–1. (32H, m, br, CH_2), 0.87 (6H, t, $J = 7.1$ Hz, CH_3); MS (70 eV): m/z (%) = 656 (100, M^+), 582 (8), 488 (12), 442 (7), 202 (10).

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