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A Novel Class of Amphotropic Mesogens Displaying S_A-Polymorphism, Nematic and Lyotropic Columnar Phases

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Two novel amphiphiles without flexible alkyl chains, but instead with extended aromatic units and head groups of different size have been synthesized and investigated by polarized light optical microscopy, differential scanning calorimetry, and X-ray diffraction. They show formation of nematic phases and S_A subtypes as known from polar smectics. On addition of glycerol columnar phases were observed.

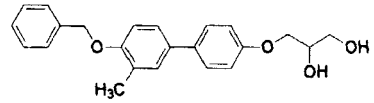
Keywords: calamitic amphiphiles; S_A-polymorphism; lyotropic mesophases; columnar mesophases; amphotropic liquid crystals

INTRODUCTION

Most liquid crystalline phases are formed by molecules which have either an anisometric or an amphiphilic structure. In most of these compounds flexible alkyl chains provide a certain degree of mobility, whereas rigid rod-like, disc-shaped or polar groups are responsible for the order in the mesophases. Mesogens - anisometric as well as amphiphilic - without flexible chains are quite rare. Examples are p-oligophenylenes[1], high molecular weight condensed polyaromatic compounds (carbonaceous materials)[2], some indene derivatives and pseudoazulenes[3], salts of 2-benzyl-3-phenyl-propionic acid[4] and 2-(3-phenyloxyphenyl)propionic acid (fenoprofens)[5], and the class of chromonic liquid crystals[6].

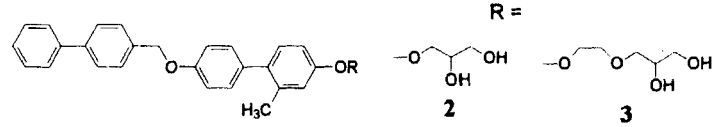
One aim of our work is to study systematically the mesogenic properties of amphiphilic molecules, the flexible alkyl chains of which have completely been replaced by rather rigid, all-aromatic segments. To this purpose we have synthesized a series of novel calamitic mesogens with diol head

groups[7]. 4-(2,3-Dihydroxypropyloxy)-4'-benzyloxybiphenyls with lateral methyl substituents at the biphenyl rigid core, such as **1**, were the first examples of this class of compounds. They showed the same diversity of mesophases as classical amphiphiles forming thermotropic and/or lyotropic smectic A, smectic C, columnar and optical isotropic, probably cubic phases depending on the position of the methyl substituent[7]. In the case of these amphiphiles, the hydrophobic interactions of the alkyl chains are replaced by interactions between aromatic segments and their columnar phases are of the ribbon type.

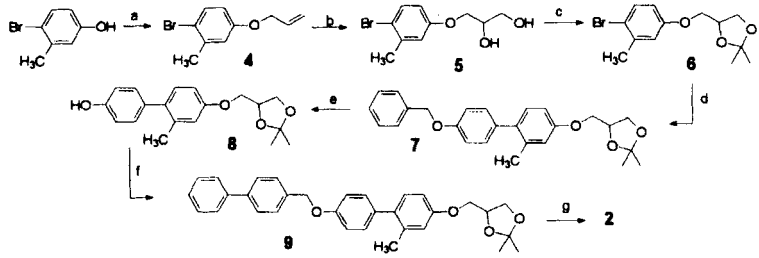


1 cr 128 Col_{ob} 151 is

Here we report on the properties of novel amphiphiles of this type with a more extended aromatic segment. Beside compound **2** with a small and compact 2,3-dihydroxypropyloxy head group also compound **3** with a larger hydrophilic group was synthesized[8].



SYNTHESIS



SCHEME 1 Synthesis of compound **2**; reagents and conditions: a) allyl bromide, K_2CO_3, acetone, reflux, 3 h; b) OsO_4, N-methylmorpholine-N-oxide, acetone, H_2O, 20 °C, 24 h; c) 2,2-dimethoxypropane, pyridinium tosylate, 20 °C, 12 h; d) 4-benzyloxyphenyl boronic acid, $Pd(PPh_3)_4$, $NaHCO_3$, glyme, H_2O, reflux, 6 h; e) H_2, Pd/C, EtOAc, 20 °C; f) 4-phenylbenzyl chloride, K_2CO_3, acetone, reflux, 8 h; g) pyridinium tosylate, H_2O, MeOH, reflux, 3 h.

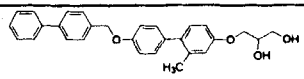
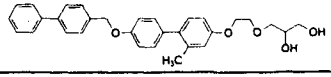
Compound **2** was synthesized according to Scheme 1. WILLIAMSON etherification of 4-bromo-3-methyl phenol with allyl bromide yielded the allyl ether **4**, the double bond of which was dihydroxylated employing VAN RHEENEN's method[9]. After protection of the hydroxy groups, the aryl bromide **6** was coupled with 4-benzyloxyphenyl boronic acid in a SUZUKI reaction[10]. Then the benzyl protecting group was removed by hydrogenolysis, and the phenol thus obtained (**8**) was etherified with commercially available 4-phenylbenzyl chloride. Cleavage of the acetonide protecting group by acidic hydrolysis yielded the desired diol **2**, which was purified by crystallization from n-hexane/ethyl acetate. The synthesis of **3** followed an analogous route, using the tosylate of 2-allyloxyethanol instead of allyl bromide and carrying out the deprotection of the diol group before etherification with 4-phenylbenzyl chloride.

MESOMORPHIC PROPERTIES

Thermotropic properties

The transition temperatures of the compounds **2** and **3** as obtained by polarized light optical microscopy (OM) are summarized in Table 1. On cooling from the isotropic melt, formation of a nematic *schlieren* texture is observed for compound **2**. It converts into a typical S_A fan shaped texture at 168 °C. On further cooling with a rate of ca 5K/min this texture is replaced by a pseudoisotropic one in a distinct transition at 153 °C. On heating with the same rate, separation and coexistence of two immiscible, homeotropically aligned phases can be observed in the temperature range between 153 °C to 156 °C. Above this temperature range only one homogenous phase is observed. These observations are essentially confirmed by DSC investigations (Fig. 1).

TABLE 1 Transition temperatures *T*/°C and corresponding enthalpy values ΔH /kJ mol^{-1} (lower lines in italics) of compounds **2** and **3**.

Comp.		phase transitions
2		cr 148 S_{A2} 153 S_{Ad} 168 N 171 is
		22.6 *4.7* *0.2* *1.5*
3		cr 103 S_A+ 148 is
		22.4 *3.5*

Obviously, compound **2** shows S_A polymorphism. This phenomenon is frequently observed for so called polar smectics[11]. Nevertheless, the behavior of **2** is a surprising result because to our knowledge up to now the

existence of different S_A subtypes within the phase sequence of one compound has never been reported for highly polar amphiphilic molecules, the aggregation of which is based on hydrogen bonding or ionic interactions.

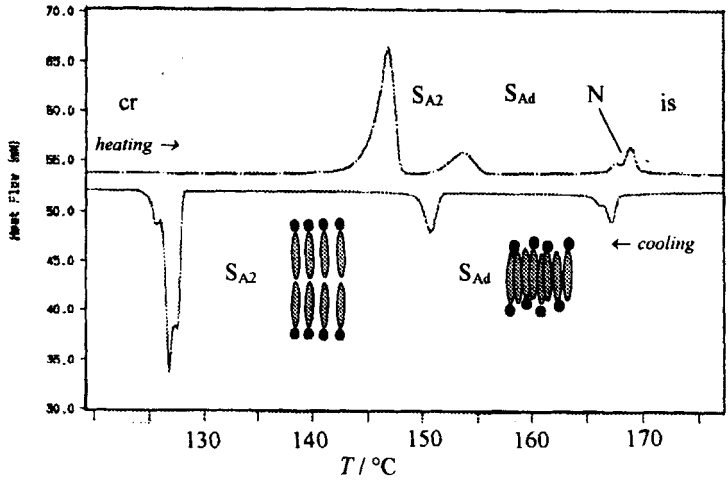


FIGURE 1 DSC plot of compound **2**, heating and cooling rate 5K/min.

The structure of the nematic phase could not be investigated by X-ray diffraction due to the small temperature range of its existence. By cooling down the sample in a magnetic field well oriented domains have been obtained, the patterns of which prove clearly the presence of a smectic A-phase. The *d*-value was found to be 3.2 nm which corresponds to 1.2 molecular lengths. It points to a S_{Ad} structure of the high temperature S_A-phase with a complete overlapping of the aromatic parts. Below 153 °C different patterns have been obtained. In most cases the pattern does not change on cooling until crystallization sets in at 140°C. Sometimes an additional reflection is observed which would provide a *d*-value of 4.8 nm and its intensity changes with temperature. This points to a coexistence of two smectic phases. By chance, repeating measurements gave also a pattern with exclusively a sequence of (00*l*) reflections (l = 1-3) with a period of 4.8 nm (1.8 molecular lengths). This indeed points to the existence of a S_{A2}-phase without or with only slight intercalation, but its appearance depends very sensitively on the boundary conditions (heating or cooling rates, surface interactions). The same feature has been found by microscopic and DSC-studies. It seems that the S_{A2}-phase is the thermodynamically more stable mesophase below 153 °C, however its formation from the S_{Ad}-phase is hindered and strongly depends on the experimental conditions.

Compound **3** does not exhibit a nematic phase and no S_A polymorphism. Although its mesophase displays a typical fan-shaped texture which clearly points to an S_A phase, X-ray studies, however, gave no evidence for a layer structure. Only a diffuse scattering indicating short range order is observed instead of a layer reflection (S_A+). This observation is related to those made with smectic phases of some polyelectrolyte-lipid complexes which were assigned as superundulated layer structures[12].

Mesomorphism in the presence of glycerol

Because of the combination of rigid structure and amphiphilic nature, compounds **2** and **3** fulfill the typical requirements for amphotropic materials[13]. As the high melting points of the compounds do not allow the investigation of water-containing samples, we investigated the influence of glycerol on their aggregation. Glycerol was chosen because of its high boiling point and because it represents the basic unit of the hydrophilic groups of these compounds. Both compounds do not dissolve in excess glycerol, but take up a limited amount of solvent[14]. The results as obtained by OM of the glycerol saturated samples are summarized in Table 2.

TABLE 2 Mesomorphic properties of compounds **2** and **3** in the glycerol saturated state.

Comp.	transition temperatures, *T*/°C
2	cr 118 Col 136 S_{Ad} 193 is
3	cr 85 Col 109 S_A 177 is

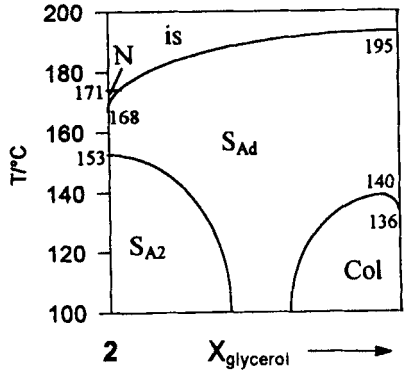


FIGURE 2 Qualitative phase diagram of the system **2**/glycerol as obtained from observation of the contact region.

The qualitative phase diagram in Fig. 2 was constructed by investigation of the contact region between **2** and glycerol. Because these investigations were done in the presence of excess glycerol the amount of glycerol taken up may change as a function of temperature. In the contact region of **2** with glycerol (see Fig. 2) the nematic phase is replaced by the stabilized S_{Ad} phase. The S_{Ad} - S_{A2} transition temperature decreases with increasing solvent content. In a medium concentration range exclusively the S_{Ad} phase is observed. On further increased solvent content an additional mesophase is induced below the S_{Ad}-phase.

In the contact region of **3** with glycerol a continuous stabilization of the smectic phase is observed. No phase boundary was detected in the region of this S_A-phase on increasing solvent concentration. Thus, either the phase type does not change or a continuous transition to another S_A-subtype occurs. However, also in this case an additional mesophase is induced at higher solvent content below the S_A-phase. The lyotropic low temperature phases of **2** and **3** occur from the homeotropically aligned S_A phases with the texture shown in Fig. 3a. On shearing it turns to a nongeometric texture (Fig. 3b). These observations point to columnar phases. From their position in the phase diagram and taking into account the limited solvent uptake, we can assume that the columnar lyomesophases of **2** and **3** should represent ribbon phases (modulated smectic phase) resulting from a breaking up of the smectic layers due to the enlargement of the head group region.

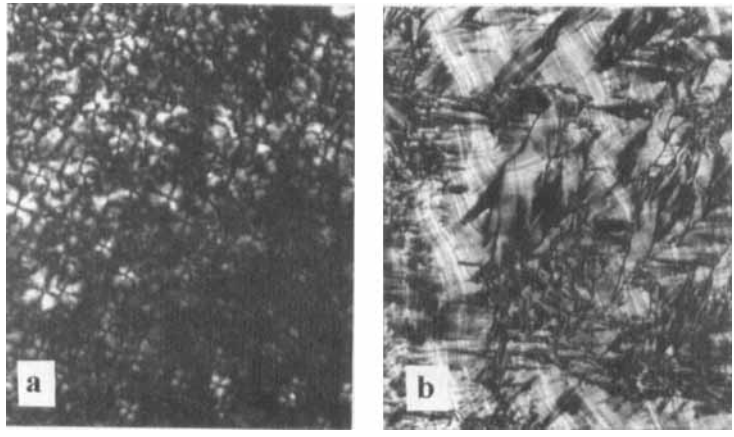


FIGURE 3 Polarized optical photomicrographs of **3** in the glycerol saturated state at 104 °C, a) appearance on cooling from the homeotropically aligned S_A phase, and b) after shearing.

(See Color Plate III at the back of this issue)

These results show once more that rigid amphiphiles without flexible lipophilic chains are able to form a great variety of thermotropic and lyotropic mesophases. Though many questions remain open, their self-organization can be located at the borderline between that of classical amphiphiles, polar smectics and chromonic liquid crystals.

EXPERIMENTAL

4-[2-Methyl-4'-(4-phenylbenzyloxy)biphenyl-4-yloxymethyl]-2,2-dimethyl-1,3-dioxolan 9:
A mixture of 1 g (3.28 mmol) **8**[15], 0.72 g (3.25 mmol) 4-phenylbenzyl chloride (Aldrich) and 6 g (42 mmol) K_2CO_3 in 60 mL acetone was stirred under reflux (monitored by TLC, 5 h). After the reaction was finished, 40 mL water were added, the layers separated and the aqueous phase was extracted three times with 40 mL of $CHCl_3$. The combined extracts were washed with 60 mL portions of 2M Na_2CO_3, water and brine, dried with Na_2SO_4 and the solvent was removed under reduced pressure. The product was purified by crystallization from 50 mL methanol/ethyl acetate (3:2), and 50 mL n-hexane/ethyl acetate (3:2). Yield: 0.56 g (58 %). Transitions/°C: cr 123 (S_A 77 N 96) is. $C_{32}H_{32}O_4$ requires (found): C, 79.97 (79.93); H, 6.71 (6.95 %); ^{1}H-NMR (200 MHz; $CDCl_3$; *J*/Hz): δ = 7.59 - 6.93 (m, 14 H, Ar-H), 6.75 (s, 1 H, Ar-H), 6.74 (m, 1 H, Ar-H), 5.07 (s, 2 H, Ar-CH_2), 4.40 (m, 1 H, sec. CH), 4.11 - 3.80 (m, 4 H, $OCH_2CH(O)CH_2$), 2.18 (s, 1 H, $ArCH_3$), 1.41 (s, 3 H, CH_3), 1.34 (s, 3 H, CH_3).

3-[2-Methyl-4'-(4-phenylbenzyloxy)biphenyl-4-yloxy]propane-1,2-diol 2:
A mixture of 0.5 g (1.04 mmol) of **9**, 0.05 g pyridinium tosylate and 3 mL water in 30 mL methanol was stirred under reflux for 8 h (monitored by TLC). After the reaction had finished, the solvent was removed *in vacuo*. The residue was taken up in 30 mL ethyl acetate and washed with 20 mL portions of sat. aq. $NaHCO_3$, water and brine and dried with Na_2SO_4. The solvent was distilled off and the product was purified by repeated crystallization from 15 mL n-hexane/ethyl acetate (2:1). Yield: 0.09 g (20 %). $C_{29}H_{28}O_4$ requires (found): C, 79.07 (78.69); H, 6.41 (6.46 %); MS, *m/z* (rel. intensity %): 440 (17, M^+), 167 (100); ^{1}H-NMR: (500 MHz; DMSO-D_6; *J*/Hz): δ = 7.68 (m, 4 H, ar. H), 7.56 (d, 2 H, *J* 8.1, H_h, H_i), 7.47 (m, 2 H, Ar-H), 7.37 (m, 1 H, Ar-H), 7.22 (d, 2 H, *J* 8.7, Ar-H), 7.06 (d, 2 H, *J* 8.7, Ar-H), 7.05 (d, 1 H, *J* 8.5, Ar-H), 6.84 (d, 1 H, *J* 2.5, Ar-H), 6.79 (dd, 1 H, *J* 8.5, 2.5, Ar-H), 5.18 (s, 2 H, Ar-CH_2), 4.91 (d, 1 H, *J* 5.2, sec. OH), 4.62 (m, 1 H, prim. OH), 3.98 (m, 1 H, $ArOCH_aH_b$), 3.84 (m, 2 H, $ArOCH_aH_b$), 3.78 (m, 1 H, sec. CH), 3.43 (m, 2 H, CH_2OH), 2.19 (s, 3 H, $ArCH_3$).

6-[2-Methyl-4'-(4-phenylbenzyloxy)biphenyl-4-yloxy]-4-oxahexane-1,2-diol 3
Synthesized as described above from 0.5g (1.57mmol) 6-(4'-hydroxy-2-methylbiphenyl-4-yloxy)-4-oxahexane-1,2-diol[15] and 0.35 g (1.73 mmol) 4-phenylbenzylchloride; Yield: 0.22 g (29 %). $C_{31}H_{32}O_5$ requires (found) C, 76.84 (76.64); H, 6.66 (6.72); ^{1}H-NMR (200 MHz; DMSO-D_6; d, ppm): 7.69 (m, 4 H,

Ar-H), 7.60 - 7.30 (m, 5 H, Ar-H), 7.22 (d, 2 H, J = 8.6 Hz, Ar-H), 7.06 (m, 3 H, Ar-H), 6.85 (s, 1 H, Ar-H), 6.79 (d, 1 H, J = 8.6 Hz, Ar-H), 5.18 (s, 2 H, Ar-CH_2), 4.63 (d, 1 H, J = 5.1 Hz, sec. OH), 4.46 (m, 1 H, prim. OH), 4.08 (m, 2 H, ArOCH_2CH_2O), 3.73 (m, 2 H, ArOCH_2CH_2O), 3.63 - 3.30 (m, $OCH_2CH(OH)CH_2OH$, overlapped by H_2O), 2.17 (s, 3 H, -CH_3). MS m/z (rel. intensity, %): 484 (10, M^+), 167 (100).

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[14] Due to the difficulty to obtain homogeneous samples we were not able to determine the glycerol content. However we have investigated the maximum water uptake of related compounds. These investigations have shown that about 1 mol water is taken up by compounds related to **2** and about 2 mol by compound related to **3**. The amount of glycerol should be in the same order of magnitude. Thus, alternatively one can speak of a guest-host relationship instead of a lyotropic mesomorphism in a traditional sence.
[15] Compounds **4–8** were used as intermediates for the synthesis of other compounds. Experimental details for their synthesis will be published in a forthcoming paper.