New Liquid Crystalline Materials by Combination of Pyramidic and Calamitic Structural Units

Hansjörg Budig,[a] Siegmar Diele,[b] Petra Göring,[b] Reinhard Paschke,[a] Christiane Sauer[b] and Carsten Tschierske*[a]

[a] *Institute of Organic Chemistry, Martin-Luther University Halle, D-06015 Halle/Saale and* [b] *Institute of Physical Chemistry, Martin-Luther University Halle, D-06099 Halle/Saale, Weinbergweg 16, Germany*

Fixing of calamitic rod-like molecules to a cyclotribenzylene unit gives liquid crystalline materials with either columnar or lamellar mesophases.

Thermotropic liquid crystalline phases may be formed by rod-like (calamitic) as well as by disc-shaped molecules. Rod-like molecules give rise to nematic and/or smectic liquid crystalline phases whereas discotic and pyramidic molecules self organize to give discotic nematic phases and/or columnar mesophases.[1–5] Polycatenar and board-like (sanidic) molecules have recently been designed to bridge the gap between these two different types of mesophases.[6,7] The covalent linkage of differently shaped molecules may be an attractive way of creating new supramolecular structures.

In this paper, we describe new compounds consisting of calamitic units covalently linked by spacers of different length with a bowl-shaped cyclotribenzylene central core (2,3,7,8,12,13-hexasubstituted 10,15-dihydro-5*H*-tribenzo[*a,d,g*]cyclononene derivatives). The synthesis of these new compounds was achieved by esterification of cyclotricatechylene or hexakis(11-hydroxyundecyloxy)-10,15-dihydro-5*H*-tribenzo[*a,d,g*]cyclononene with appropriate carboxylic acids incorporating the bicyclohexyl- or 2-phenyl-thiadiazole rigid cores using the carbodiimide method.

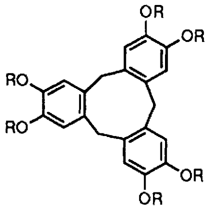
In Table 1 the properties of these compounds are summarized and compared with those of a simple n-alkylderivative, **1**.[3] Comparing **1** and **2** shows that mesophase stability increases if two cyclohexane rings are incorporated in each of the lateral chains. Polarizing microscopy and X-ray investigations have proved that compound **2** without spacer has a broad columnar mesomorphic range. The X-ray pattern of compound **2** exhibits two Bragg reflections in the small angle region. The ratio of their positions is 1.0 : 1.19. This result excludes a smectic layer structure. It supports the existence of a columnar mesophase, which must be different, however, from a hexagonal one. Obviously, the stiffness of the side chains gives rise to the formation of a superdisc[9,10] and, therefore, supports the stacking of the molecules in columns.

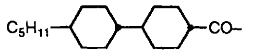
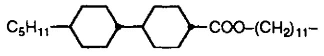
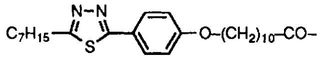
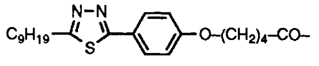
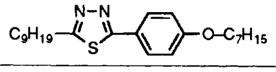
Contrary to this, compound **3** with the cyclotribenzylene unit decoupled from the bicyclohexyl rigid cores by undecamethylene spacers is a crystalline solid without any mesophase. This is also true for the thiadiazole derivative **4**. It seems, that mesomorphic properties are lost, if the rod-like units are decoupled from the central part by a long spacer.

However, compound **5** with medium spacer length forms a liquid crystalline phase. The transition from the isotropic liquid can be seen by the formation of small batonnets that coalesce to a focal conic fan-like texture indicating a smectic A-type mesophase. The X-ray pattern of oriented samples show a crescent-like reflection in the small angle region (and its higher orders) and a diffuse scattering in the wide angle region. The maxima of both scatterings are perpendicular to each other, supposing a S_A-phase. These results indicate, that in these derivatives of cyclotribenzylene a columnar stacking of the molecules is not possible. The competition between the disc-like middle part of the molecule and the calamitic units is increased by the decoupling of both different structural elements. Now the calamitic units may adapt a parallel packing, which leads to the lamellar self organization. Obviously, the cyclotribenzylene moities support this lamellar structure. This conclusion is drawn from the fact that the calamitic compound **6**[8] exhibits a significantly lower mesophase stability than the corresponding cyclotribenzylene derivative **5**.

However, the further lengthening of the spacer (**3** and **4**) yields a loss of the liquid crystalline properties. Obviously, the

Table 1 Phase transition temperatures[a] *T*/°C of the cyclotribenzylene derivatives **1**–**5** and comparison with the calamitic thiadiazole derivative **6**. The values in brackets (lower lines) refer to the enthalpies ΔH [kJ mol^{-1}].



Compound	R	*T*/°C
1	$C_{12}H_{25}$–CO–	c 67 D 139 i[c]
2		c 118 D 355 i (decomp.) (63.8)
3		c 114–115 i
4		c 140–142 i
5		c 144/152 S_A 160 i[d] (43.1) (38.8)
6		c 77 S_C 89 i[e]

[a] Determined by polarizing microscopy using a Mettler FP HT hot stage and control unit in conjunction with a Nikon Optiphot 2 polarizing microscope, abbreviations: c = crystalline, D = discotic mesophase, S_A = smectic A-phase, S_C = smectic C-phase, i = isotropic phase. [b] Correct C, H analyses, and ^{1}H NMR spectra have been recorded for compounds **2**–**5**. [c] See ref. 5. [d] Two different melting points were observed due to different crystalline modifications. [e] See ref. 8.

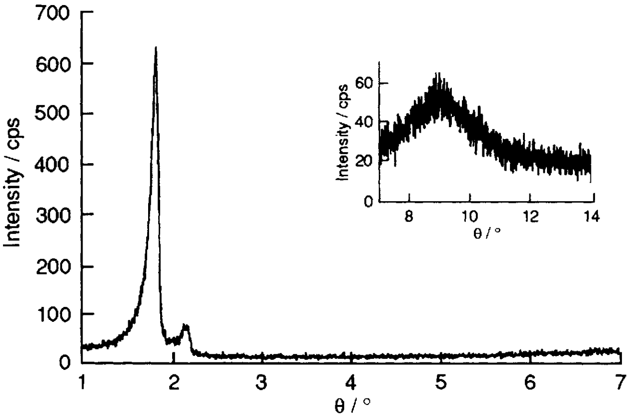


Fig. 1 X-Ray scattering (Guinier-goniometer trace) of compound **2** in the mesophase at 140 °C. The inset displays the scattering at wide angles with a higher resolution.

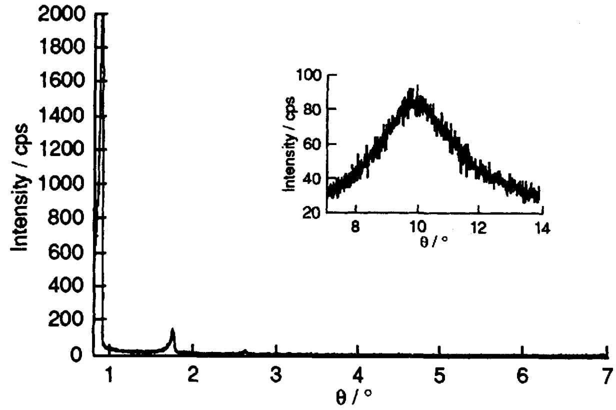


Fig. 2 X-Ray scattering (Guinier-goniometer trace) of compound **5** in the mesophase at 140 °C (supercooled sample). The inset displays the scattering at wide angles with a higher resolution.

long spacer dilutes the system and hinders the formation of mesogenic structures.

The fixing of calamitic rod-like molecules by a cyclotribenzylene unit is a useful approach to new liquid crystalline materials, which—depending on the spacer length—can exhibit either columnar or lamellar mesophases.

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