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First examples of a new class of discogen

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PRELIMINARY COMMUNICATION

First examples of a new class of discogen

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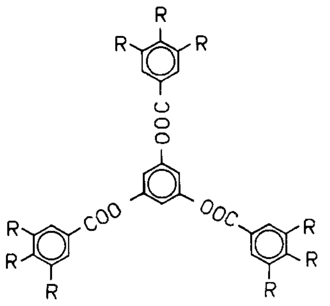
Two examples of a new class of discotic liquid crystals are presented. Their molecular architecture consists of a trisubstituted central core (either a benzene or a cyclohexane ring) and three regional cores, with three decyloxy-chains in the 3,4,5-positions of a particular benzene ring. These regional cores are linked to the central core via ester groups. Polarizing microscopy and calorimetric measurements reveal the existence of monotropic and enantiotropic discotic mesophases respectively. The products exhibit a pronounced hindering of crystallization at room temperature.

Discogens are known to have central cores (aromatics, alicyclics and metal complexes) with four to nine side chains [1]. Several attempts have been made to synthesize discotic liquid-crystalline compounds with only trisubstituted central cores. However, the interpretation of the thermal behaviour of these materials is not clear [2, 3] or an appropriate liquid-crystalline phase does not even exist [1, 4–6]. In this preliminary communication a new principle for the design of discogens together with the thermal and microscopic properties of two representative examples are described.

In general, a central core (aromatic or alicyclic) of the new compounds is substituted in the 1,3,5-positions via ester groups with three regional cores, each of them bearing three alkoxy side chains. A molecular model shows that the resulting nine side chains can be arranged to provide a complete covering of the peripheric area of the molecule (cf. figure 1). The molecular structure can be compared with that of the so-called super discs [1, 7]. However, the three regional cores do not form a space filling ring of rings with only one side chain per outer ring and a total substitution of the central core, as has been described.



1

$R = -O-C_{10}H_{21}$

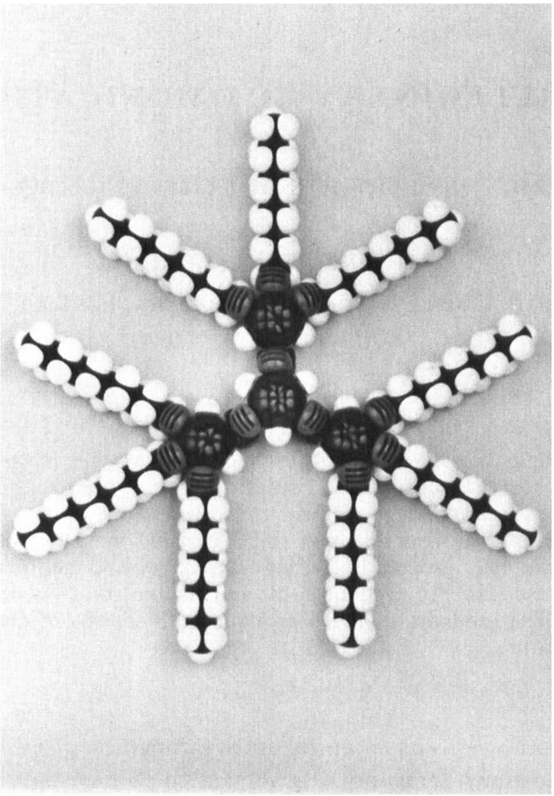


Figure 1. A molecular model for **1**.

With the first compound, 1,3,5-tris(3′,4′,5′-tridecyloxybenzoyloxy)-benzene **1**, calorimetric measurements (Perkin Elmer DSC 7) show during the first heating period three partially resolved peaks at 30·5°C, 38·8°C and 39°C (figure 2, curve (*a*)). On cooling (figure 2, curve (*b*)) a smaller peak appears at 27·3°C. The enthalpy value $\Delta H = 19{\cdot}8\,\mathrm{kJ/mol}$ is similar to that for the hexa-*n*-alkanoates of benzene [8]. The small peak coincides with the appearance of a mosaic texture under the polarizing microscope (Leitz, Laborlux 12-Pol, Mettler hot stage FP 82). A second heating and cooling cycle (figure 2, curves (*c*, *d*)), beginning not later than 4–5 hours after the first measurements, shows only the transitions to the mesophase and isotropic phase at 29·5°C (19·8 kJ/mol) and 27·3°C (19·8 kJ/mol) respectively. This indicates a monotropic mesophase which is metastable for several hours at room temperature. As can be seen under the polarizing microscope, after 4–5 hours the mesophase below 27·3°C or the isotropic melt above 29·5°C begins to crystallize very slowly. No crystallization peak can be detected in the thermogram therefore with a heating rate higher than 0·5°C/min. A third heating curve (cf. figure 3, curve (*a*)) obtained 12 hours after the second measurement then shows the thermogram of the remaining mixture of the meso- and crystalline phases. At 29·4°C the transition of the rest of the mesophase to its isotropic melt occurs, at 36°C a solid/solid transition of a first crystalline phase K_1 to a second modification K_2 appears. The third peak corresponds to the melting temperature $T_{mK_2} = 46{\cdot}8$°C, being the only peak on heating after 22 hours at most.

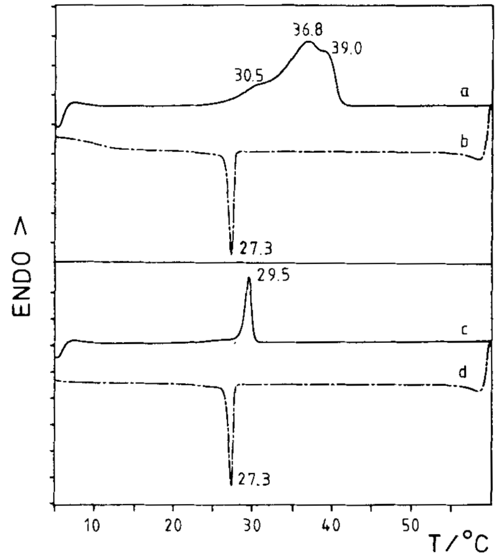


Figure 2. The D.S.C. thermogram of **1**. (*a*, *b*) First heating and cooling; (*c*, *d*) second heating and cooling; cooling and heating rate 5°C/min.

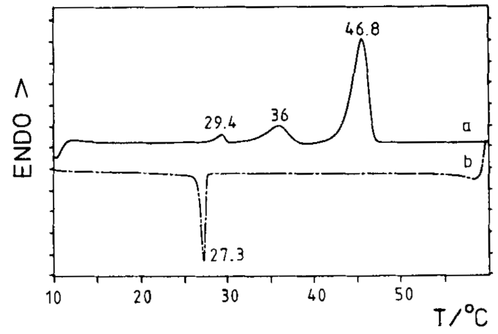
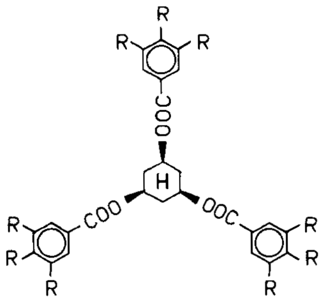


Figure 3. D.S.C. thermogram of **1**. (*a*, *b*) Heating and cooling after 12 hours; cooling and heating rate 5°C/min.

Upon annealing at the clearing point, in addition to a mosaic texture with linear birefringent defects, homeotropic digitated stars can be observed (cf. figure 4(*a*)). Both phenomena are typical for D_{ho} phases [9, 10].



2

R = $-O-C_{10}H_{21}$

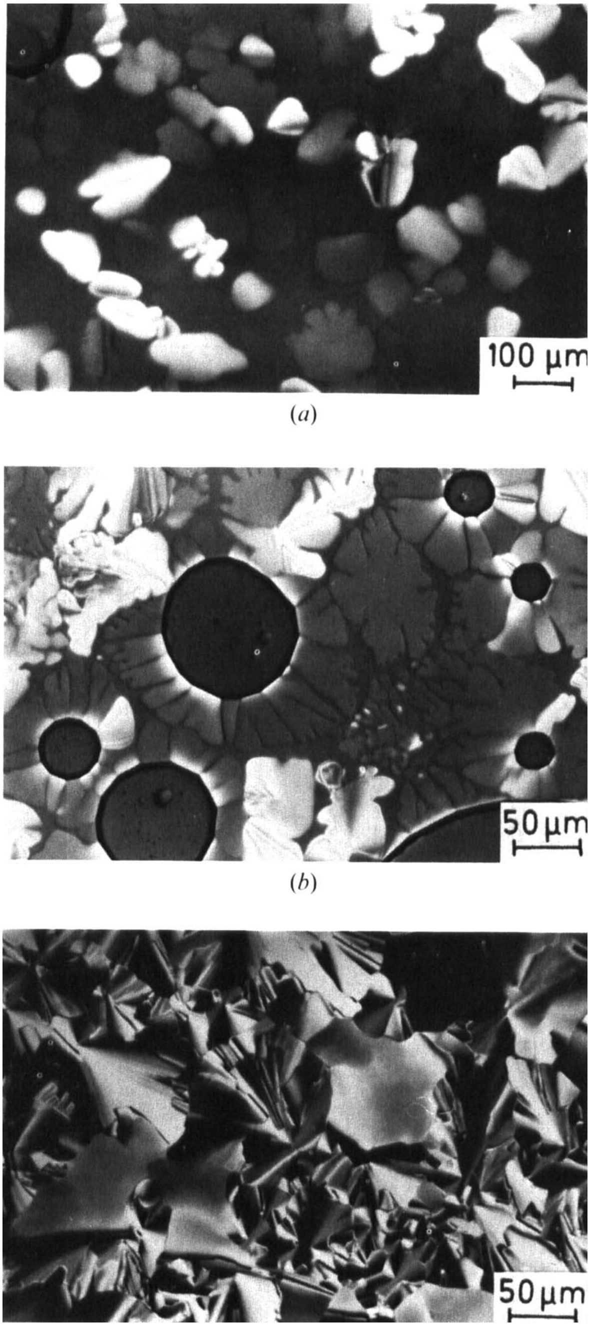


Figure 4. (*a*) Optical texture of **1** after annealing at 29·3°C; between crossed polarizers; (*b*) optical texture of **2** after annealing at 59·3°C; between crossed polarizers; (*c*) optical texture of **2** after annealing at 45°C; between crossed polarizers..

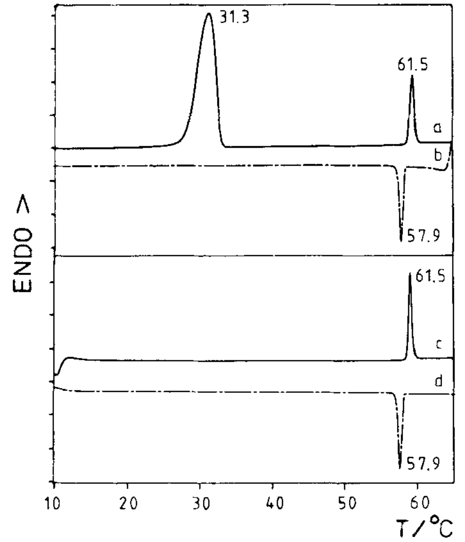


Figure 5. D.S.C. thermogram of **2**. (*a*, *b*) First heating and cooling; (*c*, *d*) second heating and cooling; cooling and heating rate 5°C/min.

The second model compound, cis,cis-1,3,5-tris(3′,4′,5′-tridecyloxybenzoyloxy)-cyclohexane **2**, differs from **1** by changing the central core to the cis-phloroglucitol unit. The calorimetric measurements, confirmed by microscopic observations, yield in the first heating experiment (cf. figure 5, curve (*a*)) the transition scheme

$$\mathrm{K} \xrightarrow[(146{\cdot}5\,\mathrm{kJ\,mol^{-1}})]{31{\cdot}3^{\circ}\mathrm{C}} \mathrm{D} \xrightarrow[(17{\cdot}6\,\mathrm{kJ\,mol^{-1}})]{61{\cdot}5^{\circ}\mathrm{C}} \mathrm{I},$$

where the upper number gives the transition temperature and the lower the enthalpy. On cooling (cf. figure 5, curve (*b*)) only the transition to the mesophase is observed

$$\mathrm{D} \xleftarrow[(16{\cdot}9\,\mathrm{kJ\,mol^{-1}})]{57{\cdot}9^{\circ}\mathrm{C}} \mathrm{I}.$$

Further heating and cooling cycles (cf. figure 5, curves (*c*, *d*)), even after several months, only reveal the transition from the mesophase to the melt and from the melt to the mesophase, respectively. This indicates a metastable existence of the enantiotropic mesophase at room temperature over a long period. Annealing at 59°C, under the polarizing microscope, reveals digitated stars (cf. figure 4(*b*)). Cooling at a rate of 5°C/min results in a texture quite similar to those for the D_{ho} phases of hexa-alkanoylscyllo-inosits [1, 11] (cf. figure 4(*c*)).

Further investigations, including phase diagrams and X-ray measurements, of the two model compounds described here and of other members of the corresponding series of this new class of discogens must be performed. Details of the synthesis and characterization of these materials will be published later.

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