Molecular design of amphitropic liquid crystalline carbohydrates–amphiphilic *N*-methyl-glucamides exhibiting lamellar, columnar or cubic mesophases

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Amphiphilic 1-deoxy-1-(*N*-methylbenzamido)-D-glucitols display smectic, hexagonal columnar or discontinuous cubic thermotropic liquid crystalline phases depending on the number of alkyl chains attached to the benzamido group.

The observation of a double melting of certain long-chain alkylglucopyranosides by Fischer and Helferich[1] was the first indication for the exhibition of thermotropic liquid crystalline properties by amphiphilic carbohydrates. Presently, extensive research is carried out in many laboratories, and many different classes of amphiphilic carbohydrates have been prepared and investigated.[2] It was realized that the formation of large dynamic intermolecular hydrogen-bonding networks between the hydroxy groups of the carbohydrate head groups as well as the segregation of the hydrophilic and the hydrophobic parts of the individual molecules are the driving forces for their self organization. The kind of formed mesophase depends strongly on the balance between the hydrophobic chains and the hydrophilic head groups. Therefore the number of alkyl chains attached to the carbohydrate moiety determines the structure of the mesophase: single-chain carbohydrates usually form lamellar (smectic) thermotropic mesophases and those with two alkyl chains often organize to cylindrical aggregates which arrange into columnar mesophases.[3] Less attention has been drawn to three-chain carbohydrates. They exhibit either columnar phases[4] or do not display any thermotropic behaviour.[5]

We have synthesized 1-deoxy-1-(*N*-methyl-benzamido)-D-glucitols **1–3** in which one, two or three alkyl chains are fixed *via* an aromatic linking unit to the carbohydrate moiety (Fig. 1).†‡ In this way the number of hydroxy groups present is not influenced by increasing the number of chains.

These compounds were investigated by optical microscopy, calorimetry and X-ray diffraction. On cooling compound **1** from the isotropic melt at 183 °C the formation of a fan texture with homeotropic regions was observed between crossed polarizers. This indicates a smectic A-type mesophase, which was confirmed by X-ray diffraction.

The two-chain compound **2** displays a special kind of fan texture which is often observed for hexagonal columnar phases. The X-ray diffraction pattern exhibits three sharp reflections in the low-angle region. The ratio of their positions is $1 : \sqrt{3} : 2$, proving the existence of a hexagonal columnar mesophase, with a hexagonal lattice parameter of 48.5 Å.

Contrary to these two compounds, no birefringence was found on cooling the three-chain compound **3** until crystallization occurs at 62 °C. However at 174 °C a significant increase of the viscosity was observed. Calorimetric measurements indicate the presence of a phase transition at this temperature, which is a strong hint towards the existence of a cubic mesophase.

The X-ray diffraction pattern exhibits a strong reflection in the low-angle region together with three reflections of very weak intensity. The reflections obtained result from a cubic structure with a lattice parameter of 85.5 Å. This lattice parameter exceeds considerably the length of the molecule, as found in other cases. Cubic phases are often observed in lyotropic systems in defined temperature and concentration ranges.[6] In these lyotropic liquid crystalline systems two different structures of cubic phases are known. The first consists of two networks of cylinders interwoven but not connected with each other, which appears as an intermediate phase between lamellar and hexagonal phases. The other type consists of cubic arrangements of globular aggregates (discontinuous/micellar phase). These two types of cubic phases could also be

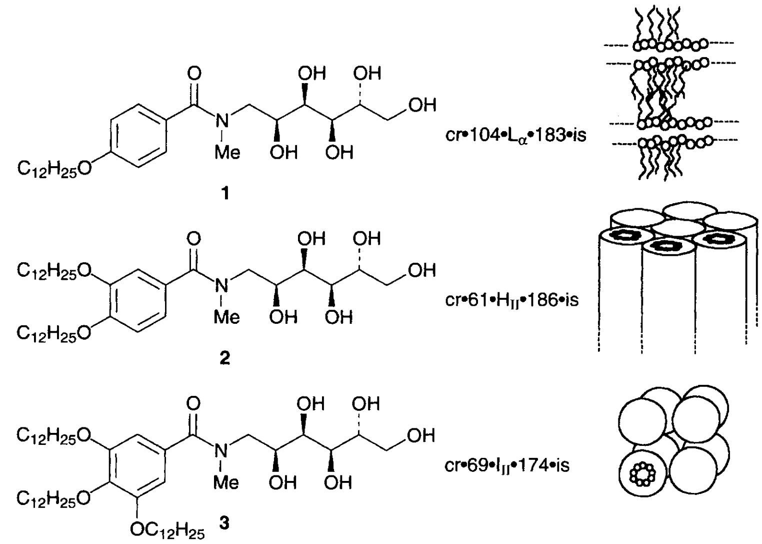

Fig. 1 Structures and transition temperatures (°C) of compounds **1–3** as determined by polarizing microscopy; cr = crystalline solid, L_α = lamellar α-phase, H_{II} = inverted hexagonal columnar phase, I_{II} = inverted micellar cubic phase, is = isotropic liquid

considered for the thermotropic cubic phase of the amphiphilic carbohydrate **3**. However a distinction between them is not possible on the basis of our X-ray experiments. Nevertheless, some arguments point to a cubic arrangement of inverted micelles (discontinuous I_{II}-phase) as shown in Fig. 1.

First we can consider the observed change of the mesophase type by increasing the chain number. Considering the chemical structure of compounds **1–3**, the glucamide moieties act as the hydrophilic head groups whereas the alkyl chains correspond to the hydrophobic part of the molecules. If both parts occupy approximately the same volumes as for example in the case of the single-chain glucamide **1**, a smectic layer structure is found. Increasing the number of alkyl chains gives rise to a curvature of the interface between the two antipathic regions. Thus the columnar mesophase consisting of cylindrical aggregates results for compound **2**. Introduction of a third alkyl chain in compound **3** should further increase the interface curvature and therefore can give rise to the formation of inverse globular aggregates (I_{II}-phase).

The second argument concerns the change of the mesophase by addition of ethylene glycol: using the penetration method the appearance of a hexagonal columnar phase was found in the contact zone of the three-chain compound **3** with ethylene glycol [Fig. 2(*a*)]. Here the relative size of the hydrophilic head group is increased by solvation and the curvature of the spherical aggregates is diminished and this gives rise to the transition from spherical to less curved cylindrical aggregates.

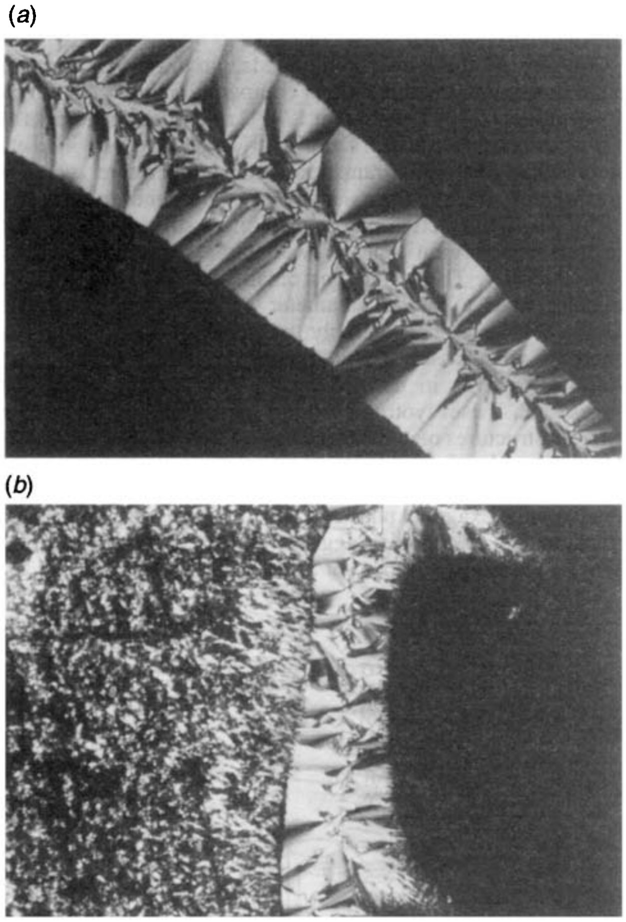

Fig. 2 Optical photomicrographs (crossed polarizers) of the H_{II}-phases which appear (*a*) in the contact region between compound **3** (lower part, optical isotropic I_{II}-phase) and ethylene glycol (upper part, isotropic liquid) at 100 °C and (*b*) in the contact region between compound **3** (right-hand side, optical isotropic I_{II}-phase) and compound **1** (left-hand side, lamellar α-phase) at 115 °C

Finally, we have found by mixing the three-chain compound **3** with the single-chain compound **1** that the hexagonal phase, which is intermediate between the smectic and cubic phases, is induced [Fig. 2(*b*)].

All these observations are in accord with the proposed inverse micellar structure of the cubic mesophase of the *N*-methylglucamide **3**.

Thermotropic cubic phases are rare and there are only a few reports on other carbohydrate derivatives which display thermotropic cubic mesophases.[§] However it seems that compound **3** is the first example which displays a thermotropic cubic mesophase consisting of inverse micelles.

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Footnotes

[†] The thermotropic[7] and the lyotropic[8] phase behaviour of simple *n*-alkanoates of *N*-methylamino-1-deoxy-D-glucitol has been reported by Pfannemüller and coworkers.

[‡] Compounds **1–3** were synthesized by treatment of the corresponding benzoyl chlorides with an excess of *N*-methylglucamine in dry DMF. Expected C, H analyses and ^1H NMR spectra were obtained *e.g.* for **3**: ^1H NMR (200 MHz, $CDCl_3$, 25 °C, $SiMe_4$) δ 0.88 (t, 9 H, CH_3), 1.14–1.66 (m, 60 H, CH_2), 2.78 (br, 1 H, OH), 3.06 (s, 3 H, NCH_3), 3.32 (br, 1 H, OH) 3.5–3.9 (m, 9 H, C*H*OH, C*H*$_2$OH, CH_2N, OH), 3.93 (t, 6 H, CH_2O), 4.08 (br, 1 H, OH), 4.83 (br, 1 H, OH), 6.59 (s, 2 H, aromatic H).

[§] Single-chain carbohydrates with large head groups have been described to exhibit a bicontinuous cubic phase.[9] Also some inosose-*S,S*-diacetals display a cubic mesophase below a hexagonal columnar phase. Because their stability increases with decreasing chain length also in this case a bicontinuous type phase behaviour must be assumed.[10] Additionally, some double-chain diols[11] display cubic phases whereas in the series of related three-chain diols[12] only the hexagonal columnar phase was observed. Therefore these cubic phases should be of the bicontinuous type, too.

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