Liquid Crystals
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713926090

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Online publication date: 06 August 2010

To cite this Article Borisch, Konstanze , Diele, Siegmar , Goring, Petra , Muller, Henning and Tschierske, Carsten(1997) 'Amphiphilic N-benzoyl-1-amino-1-deoxy-D-glucitol derivatives forming thermotropic lamellar, columnar and different types of cubic mesophases', Liquid Crystals, 22: 4, 427 — 443
To link to this Article: DOI: 10.1080/026782997209144
URL: http://dx.doi.org/10.1080/026782997209144

LIQUID CRYSTALS, 1997, VOL. 22, NO. 4, 427–443

Amphiphilic *N*-benzoyl-1-amino-1-deoxy-D-glucitol derivatives forming thermotropic lamellar, columnar and different types of cubic mesophases

by KONSTANZE BORISCH†, SIEGMAR DIELE‡, PETRA GORING‡, HENNING MÜLLER† and CARSTEN TSCHIERSKE†*

†Martin-Luther-Universität Halle, Institut für Organische Chemie, Kurt-Mothes-Str. 2, D-06120 Halle, Germany

‡Martin-Luther-Universität Halle, Institut für Physikalische Chemie, Mühlpforte 1, D-06108 Halle, Germany

(*Received 12 August 1996; in final form 31 October 1996; accepted 28 November 1996*)

Novel amphiphilic glucamine derivatives have been synthesized. These are *N*-benzoyl-1-deoxy-1-methylamino- D-glucitols and *N*-benzoyl-1-amino-1-deoxy-D-glucitols carrying one, two or three aliphatic chains ($C_nH_{2n+1}O$– with $n=3$, 6 and 12) grafted to the benzamido group. The thermotropic mesophases of these compounds were studied by thermal polarizing optical microscopy and differential scanning calorimetry, and some also by X-ray scattering. Depending on the number and the length of the alkyl chains lamellar, bicontinuous cubic, hexagonal columnar or inverted micellar cubic mesophases were detected by analogy with lyotropic systems. In the contact region between lamellar phases of the single chain amphiphiles and micellar cubic phases of the mesomorphic triple chain compounds, hexagonal columnar phases can be induced. A hexagonal columnar phase was also induced in the contact region between a bicontinuous and a micellar cubic mesophase. The lyotropic liquid crystalline behaviour of the dodecyloxy substituted *N*-benzoyl-1-deoxy-1-methylamino-D-glucitols was investigated by the solvent penetration method using ethylene glycol as protic solvent. On increasing the solvent content, the double chain compound forms a cubic and a lamellar mesophase and the triple chain compound forms a hexagonal columnar lyomesophase. The dodecyloxy substituted compounds were also investigated with respect to their behaviour as thin films at the air–water interface using a Langmuir film-balance. Different types of π/A-isotherms were observed whereby the molecular areas at collapse were determined either by the size of the carbohydrate head group (single chain compounds) or by the number of alkyl chains (double and triple chain compound).

1. Introduction

The observation of a double melting of certain long chain alkylglucopyranosides by E. Fischer [1] was the first indication of thermotropic liquid crystalline properties in amphiphilic carbohydrates. Presently extensive research in this area is carried out in many laboratories and several different classes of amphiphilic carbohydrates have been prepared and investigated [2, 3]. It was realized that the formation of large dynamic intermolecular hydrogen bonding networks involving the hydroxyl groups of the carbohydrate head groups, as well as the segregation of the hydrophilic and the hydrophobic parts of the individual molecules into different regions, are the driving forces for their self organization. Therefore, the type of mesophase formed strongly depends on the number of alkyl chains attached to the carbohydrate moiety. Single chain carbohydrates usually form only lamellar (smectic) mesophases[a] with a double-layer arrangement of the individual molecules, whereas those with two alkyl chains often organize into cylindrical aggregates which form columnar mesophases (H_{II}) [3, 5]. More recently however, some carbohydrates [5] and other polyhydroxy amphiphiles [6, 7] exhibiting optically isotropic cubic thermotropic mesophases have been reported (figure 1). The reasons for their appearance and the structures of these cubic mesophases are however not yet clear.

Unlike thermotropic cubic phases, the appearance of lyotropic cubic phases in surfactant–solvent systems is often observed and well understood. According to a

*Author for correspondence.

[a] Cubic phases were observed for single chain carbohydrates with a disaccharide head group or with a 1,3-bis (β-D-glucosyloxy)propyl head group [4].

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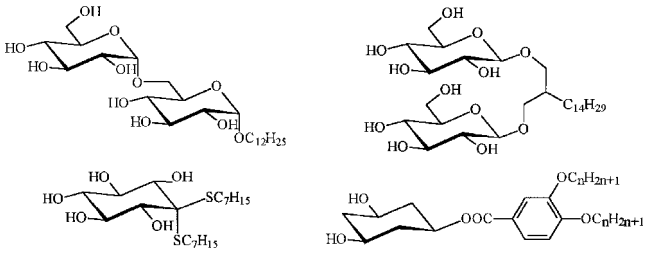


Figure 1. Amphiphilic carbohydrate derivatives and polyhydroxyamphiphiles forming cubic thermo-mesophases.

simple packing model of Israelachvili [8], the kinds of mesophases observed in these lyotropic systems mainly depend on the ratio of the surface area of the hydrated head group at the micellar interface to the size of the lipophilic parts. Depending on this ratio, spherical, cylindrical or double layer micelles can be predicted, which at lower solvent concentration can organize into different lyotropic mesophases. As evident from the theoretical phase diagram (figure 2), not only lamellar and columnar arrangements are possible, but also cubic phases can be found [9–11].

Two principally different structural types of cubic phases exist dependent on the solvent concentration [12]. Bicontinuous cubic phases (V-phases) which can be described as interwoven, but unconnected networks of branched columns, occur as intermediate phases between the lamellar phase and the columnar phases. The discontinuous cubic phases (I-phases) are located between the hexagonal columnar phases and the micellar solutions and consist of densely packed closed micelles. The question arose as to whether the same phase sequences can be observed in the case of the thermotropic phases of amphiphilic carbohydrates as a function of the number and size of the alkyl chains.

Accordingly, our aim was to design amphiphilic molecules having a thermotropic cubic phase consisting of inverted closed micelles (I_{II}-phase). In order to achieve this, the hydrophobic region of the carbohydrate amphiphiles has to be enlarged. Three types of triple-chain carbohydrates have already been reported (figure 3) [13–15]. However, they exhibit either columnar phases [13, 15] or do not display any thermotropic behaviour [14]. In two of the reported compounds the alkyl chains were fixed to some of the hydroxyl groups of the carbohydrate moiety. Thus, by increasing the number of chains the number of hydroxyl groups is simultaneously reduced, and the attractive interactions *via* hydrogen bonding are decreased.

Here we describe novel amphiphilic 1-amino-1-deoxy-D-glucitol- and 1-deoxy-1-methylamino-D-glucitol derivatives[b], in which one, two and even three alkyl chains are fixed *via* an aromatic linking unit[c] to a carbohydrate

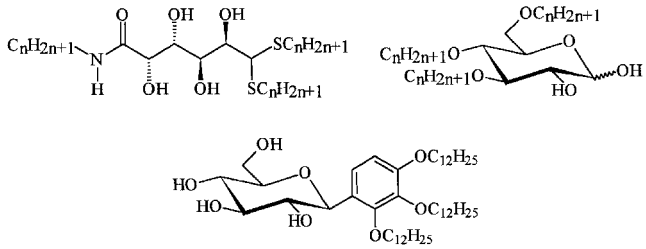


Figure 3. General formulae of the triple chain carbohydrates reported in the literature.

[b] Thermotropic [16] and lyotropic [17] properties of single chain *N*-alkanoyl-1-deoxy-1-methylamino-D-glucitol derivatives have been reported. More recently the amphotropic behaviour of double chain *N*-acyl-*N*-alkyl-1-amino- D-glucitols has been described [18].

[c] After submission of this manuscript a first triple chain *C*-glycoside bearing three alkyl chains grafted on an aromatic core was reported. However, it exhibits a columnar thermomesophase. This is probably due to the rather large cyclic carbohydrate head group [15].

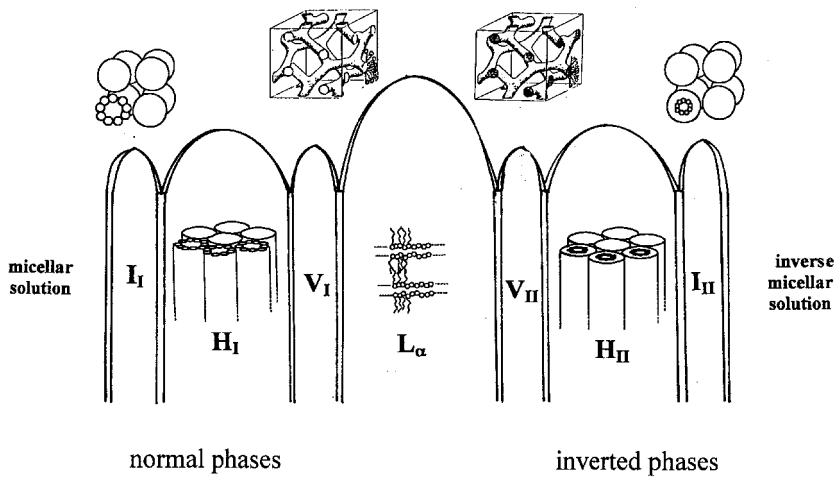
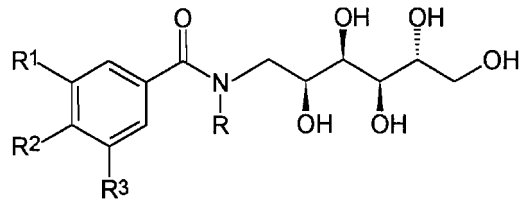


Figure 2. Schematic representation of the major lyotropic liquid crystalline phase types occurring as a function of the water content; abbreviations: L_α = lamellar α-phase, V = bicontinuous cubic mesophase (the structure of the *Ia*3*d*-type is displayed), H = hexagonal columnar phase, I = discontinuous (micellar) cubic phase (a primitive cubic lattice is displayed); subscripts: I = normal phases, II = inverted phases.

moiety. Thus, the number of hydroxyl groups is kept constant by increasing the number of chains.

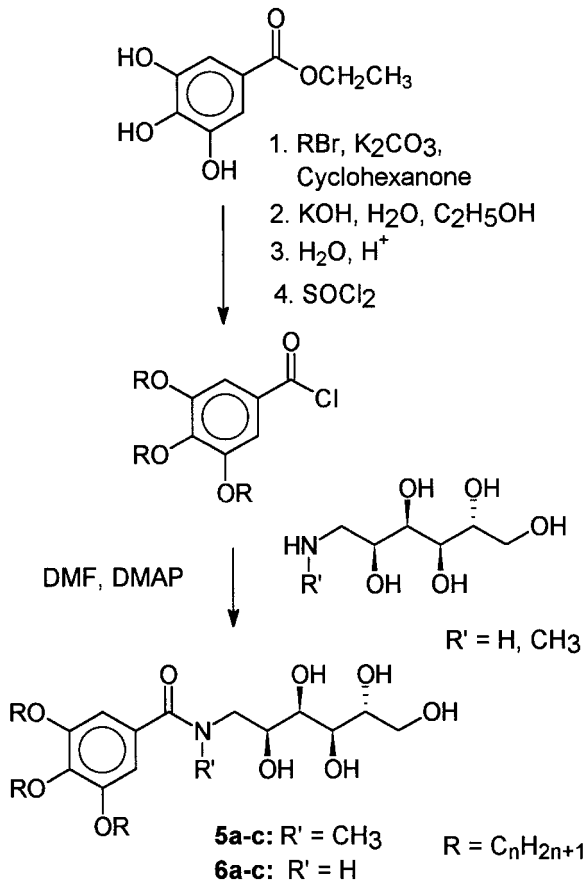


	R = CH_3	R = H
R^1, R^3 = H; R^2 = OC_nH_{2n+1}	**1**	**2**
R^3 = H; R^1, R^2 = OC_nH_{2n+1}	**3**	**4**
R^1, R^2, R^3 = OC_nH_{2n+1}	**5**	**6**

2. Results and discussion

2.1. *Synthesis*

The synthesis of the 3,4,5-trialkoxybenzamides **5** and **6** is displayed in the scheme. In an analogous manner, the other *N*-benzoyl-1-deoxy-1-methylamino-D-glucitols **1** and **3**, as well as the *N*-benzoyl-1-amino-1-deoxy-D-glucitols **2** and **4**, were obtained by aminolysis of the appropriately substituted benzoyl chlorides with a ten fold excess of *N*-methylglucamine or glucamine, respectively. The glucitols obtained were purified by repeated crystallization.



Scheme Synthesis of the *N*-(3,4,5-trialkoxybenzoyl)-1-deoxy-1-methylamino-D-glucitols **5a–c** and the *N*-(3,4,5-trialkoxybenzoyl)-1-amino-1-deoxy-D-glucitols **6a–c**.

2.2. *Thermotropic properties of the pure compounds*

The liquid crystalline properties of the synthesized compounds were investigated by thermal optical polarizing microscopy and by differential scanning calorimetry. The mesophases of the 1-deoxy-1-methylamino-D-glucitol derivatives were additionally studied by means of X-ray scattering. The thermotropic transition temperatures of the glucamides and *N*-methylglucamides are listed in tables 1, 2 and 4[d].

If the transition temperatures of the glucamides **2**, **4** and **6** are compared with those of the corresponding *N*-methylglucamides **1**, **3** and **5**, the latter always display lower clearing temperatures and decreased melting temperatures. This is probably due to the reduction of the possible hydrogen bonding sites and the increase in the lateral steric repulsive effects caused by the *N*-methyl substituent. In the following sections, the mesomorphic properties of the single chain, the double chain and the triple chain compounds will be discussed in more detail.

2.2.1. *Single chain compounds*

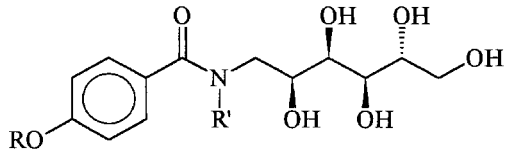
The single chain compounds **1** and **2** (table 1) exhibit mesophases with focal-conic fan textures. They can be homeotropically aligned giving pseudo-isotropic regions separated by oily streaks. Both textures are consistent with a lamellar α-phase (L_α).

The X-ray studies of compound **1a** and **1b** confirmed these results. The patterns exhibit a strong reflection in the small angle region and a diffuse scattering in the wide angle region, indicating a layer structure without order in the layers. In the case of compound **1a**, the second order of the layer reflection was observed. The intensity (I_{002}) compared with that of the first order reflection (I_{001}) was $I_{002}/I_{001} \sim 10^{-2}$. The layer spacings are temperature dependent and larger than the length of the molecule:

1a: $L = 2{\cdot}45$ nm; $d(T = 95°C) = 3{\cdot}27$ nm;
$d(T = 105°C) = 3{\cdot}19$ nm;
1b: $L = 3{\cdot}1$ nm $d(T = 105°C) = 4{\cdot}0$ nm;
$d(T = 170°C) = 3{\cdot}5$ nm.

[d] There are some deviations from the values reported in the preliminary communication [19] which are due to two factors. First, the melting points depend on the thermal history of the samples, because different crystalline modifications can be obtained. In this paper the temperatures of the highest observed melting transitions are given. Second, in the temperature range of the clearing temperatures, thermal decomposition sets in. Improved values have been obtained using higher heating rates.

Table 1. Thermotropic transition temperatures (°C) and transition enthalpies (lower lines, kJ mol^{-1}) of *N*-(4-alkoxybenzoyl)-1-deoxy-1-methylamino-D-glucitols **1a**, **b** and *N*-(4-alkoxybenzoyl)-1-amino-1-deoxy-D-glucitols **2a**, **b**. Cr=crystalline solid, is=isotropic liquid; for an explanation of the other abbreviations, see figure 2.



Compound	*R*	*R'*	Phase transition/°C Transition enthalpies/kJ mol^{-1}
1a	C_6H_{13}	CH_3	Cr 120 (L_α 119) is 35·7
1b	$C_{12}H_{25}$	CH_3	Cr 112 L_α 186 is (dec.) 26·2 2·0
2a	C_6H_{13}	H	Cr 197 (L_α 193) is 77·8
2b	$C_{12}H_{25}$	H	Cr 182 L_α 250 is (dec.) 59·6 1·2

Therefore a bilayer structure with interdigitation of either the alkyl chains or the carbohydrate moieties must be assumed. Because it is not possible to derive a structural model on the basis of the Fourier transform of one or two reflections we have calculated the structure factor, F^2 (001), for different packing models of compound **1b**, first with an interdigitation of the chains and secondly with an overlapping of glucamide units[e]. In the first case, the ratios F^2 (002)/F^2 (001) have always been found to be between 1 and 10^{-1} which contradicts the experimental results. In the second case the best fit between experimental and calculated values was obtained ($I_{002}/I_{001} \sim 10^{-2}$) if about 40% of the alkyl chains exist as *gauche*-conformers. This is reasonable since the overlapping glucamide parts generate free volume in the region of the alkyl chains, which is compensated by highly disordered chains. Additional support for the model with overlapping glucamide units is given by the X-ray studies of the double chain compound **3a** (see next section) which yields the same layer spacing ($d=3{\cdot}19$ nm at $T=120$°C) as for compound **1a**. Here, the existence of two chains rules out *a priori* the assumption of a model with interdigitated chains.

2.2.2. *Double chain compounds*

Three different mesophases were observed for the double chain compounds **3** and **4** (table 2).

Compounds **3b** and **4b**, with long dodecyloxy chains, display a spherulitic texture which is typical for a hexagonal columnar mesophase (identical with the texture of compound **6b**, which is displayed in figure 6).

The X-ray diffraction pattern of the mesophase of compound **3b** exhibits three sharp reflections in the small angle region and a diffuse scattering appears in the wide angle region. The ratio of reflection positions is $1:3^{\frac{1}{2}}:2$ proving the existence of a hexagonal columnar mesophase with a strongly temperature dependent hexagonal lattice parameter ($a=5{\cdot}31$ nm at $T=65$°C and $a=4{\cdot}44$ nm at $T=185$°C). This hexagonal columnar phase should consist of extended columnar aggregates associated by hydrogen bonding networks between the glucamide head groups surrounded by the molten alkyl chains. Assuming a density of $\rho=1$ g cm^{-3}, the number *n* of molecules arranged side by side in a single slice of the columns[f] with a thickness *h* of 0·45 nm was estimated according to equation (1)

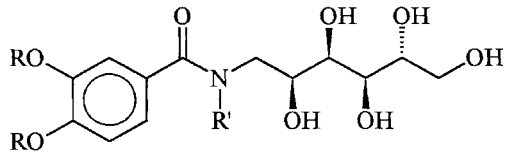
$$n=\frac{a^2}{2}3^{\frac{1}{2}}h\frac{N_A}{M}\rho \qquad (1)$$

where *a* is the hexagonal lattice parameter ($a=4{\cdot}88$ nm at $T=120$°C), N_A the Avogadro constant and *M* the

[e] An overlapping of only the pentahydroxyhexyl part of the 1-deoxy-1-methylamino-D-glucitol units was assumed. The *N*-methylamido group should be excluded from the intercalation for steric reasons.

[f] It should be stressed that due to the cooperative nature of the hydrogen bonding in polyhydroxy compounds, no small disc-shaped aggregates are formed, which then assemble into columns. Instead, 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 information about the number of molecules arranged *on average* side by side. The thickness of the slices was defined to be 0·45 nm. This is a reasonable value corresponding to the average lateral distance between the centres of alkyl chains usually observed by X-ray scattering for columnar phases.

Table 2. Thermotropic transition temperatures (°C) and transition enthalpies (lower lines, kJ mol^{-1}) of *N*-(3,4-dialkoxybenzoyl)-1-deoxy-1-methylamino-D-glucitols **3a**, **b** and *N*-(3,4-dialkoxybenzoyl)-1-amino-1-deoxy-D-glucitols **4a**, **b**. Abbreviations: see figure 2 and table 1.



Compound	*R*	*R'*	Phase transition/°C Transition enthalpies/kJ mol^{-1}
3a	C_6H_{13}	CH_3	Cr 93 L_α 130 is 29·5 0·7
3b	$C_{12}H_{25}$	CH_3	Cr 54 H_{II} 194 is (dec.) 22·5 0·9
4a	C_6H_{13}	H	Cr 172 V_{II} 185 is 73·5 0·7
4b	$C_{12}H_{25}$	H	Cr 162 H_{II} 254 is (dec.) 91·2 0·9

molecular mass. The estimated value $n=8$ (at $T=120$°C) corresponds with the packing coefficient $P=0{\cdot}62$ using the increment method $P=V_{mol}/V_{cell}$ according to Kitaigorodski [20]. The number of molecules arranged in one slice of constant thickness is larger than found for other wedge shaped polyhydroxy amphiphiles [21–24]. It remains open whether the diameter of the cylindrical columns is enlarged (uniform interface curvature) or the columns are deformed to give non-circular cylinders (ribbons). On account of the fact that the degree of deformation and the orientation of deformation change along the axis of the aggregates and with time, or that they are arranged randomly oriented in the hexagonal lattice, the cross sections of these aggregates are circular on average, giving rise to the typical scattering pattern of hexagonal columnar phases [25].

The *N*-methyl-3,4-dihexyloxybenzamide **3a** (which has significantly shorter alkyl chains) forms a mesophase with an optical texture typical for L_α-phases (focal-conic fan texture which can be homeotropically aligned to give large pseudo-isotropic areas and oily streaks). The layer spacing $d=3{\cdot}19$ nm at 120°C corresponds to the ratio $d/L=1{\cdot}3$ and therefore an interdigitated bilayer structure is assumed. Because two aliphatic chains are grafted to the carbohydrate moiety, an interdigitation of the alkyl chains can be ruled out and a layered mesophase with deeply interdigitated glucamide units is likely.

No birefringence between crossed polarizers could be observed for the 3,4-dihexyloxybenzamide **4a** without the *N*-methyl group. Calorimetric measurements indicate, besides the melting point, an additional phase transition at 185°C (figure 4) which is accompanied by a sudden significant decrease in viscosity, strongly suggesting the existence of a cubic mesophase. The X-ray diffraction pattern of this cubic phase (figure 5) can be explained by a body centred cubic lattice of space group *Ia*3*d* ($a_{cub}=8{\cdot}31$ nm at 175°C).

Consideration of the influence of the chain length on the mesophase type reveals that increase of the chain lengths of the double chain glucamide **4a** gives rise to a columnar phase (compound **4b**). On the other hand, the corresponding *N*-methylglucamide **3a** with hexyloxy chains has a lamellar phase (table 2). Therefore we assume that the cubic phase of **4a** is a bicontinuous cubic phase (V_{II}-phase) appearing as an intermediate phase between the lamellar and columnar structures. These cubic phases can be described as interwoven networks of branched cylinders or ribbons.

2.2.3. *Triple chain compounds*

The *n*-propyl derivatives **5a** and **6a** are not liquid crystalline. Two different mesophases were found for the other triple chain carbohydrates (table 4). The compounds with hexyloxy chains (compounds **5b** and **6b**) form hexagonal columnar mesophases (figure 6). The lattice parameter of compound **5b** is significantly less temperature dependent than that of the double chain compound **3b**; $a=3{\cdot}49$ nm at $T=100$°C and $a=3{\cdot}54$ nm at $T=130$°C. The same estimation as described above leads to a number *n* of molecules per slice of 5. This value is also obtained using the assumed density $\rho=1\,g\,cm^{-3}$ and corresponds to those values found in columnar phases of other polyhydroxy compounds. Obviously, the three hexyloxy chains can effectively surround the polar regions of the hydrogen bonded networks. Therefore, the packing cannot be further improved by enlarging the alkyl chains. Consequently no columnar mesophases were detected for the long

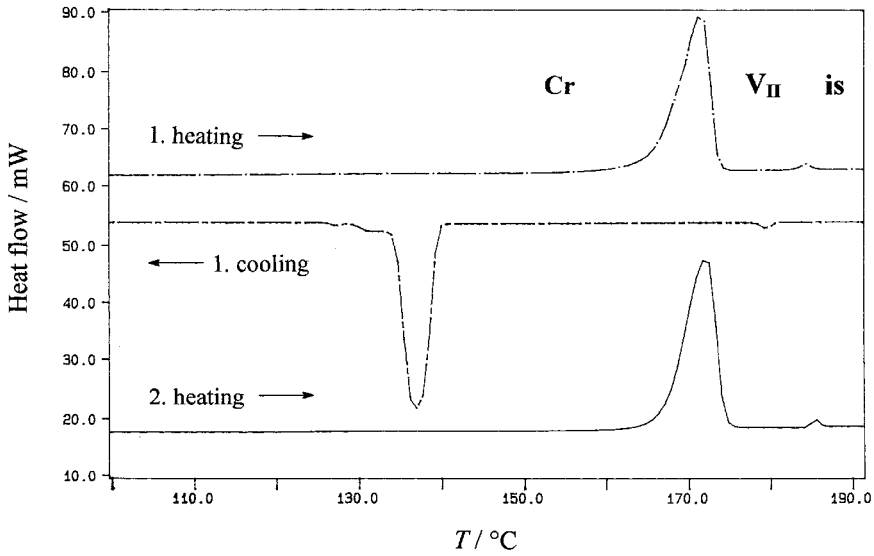


Figure 4. DSC heating and cooling traces of compound **4a** ($10\,K\,min^{-1}$).

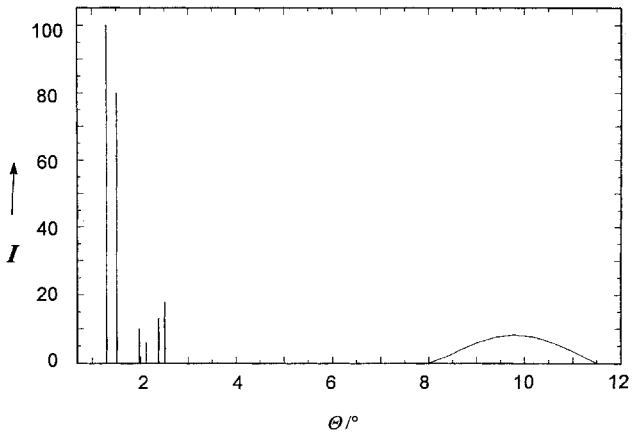


Figure 5. Schematic presentation of the X-ray pattern of the cubic mesophase of compound **4a** at 175°C.

Table 3. Structural parameter of the V_{II}-phase of **4a**.

θ_{obs}	θ_{calc}	*h k l*
1·30	—	2 1 1
1·51	1·50	2 2 0
1·98	1·97	3 2 1
2·11	2·12	4 0 0
2·38	2·38	4 2 0
2·50	2·49	3 3 2

chain 3,4,5-tridodecyloxybenzamides **5c** and **6c**. These compounds display highly viscous and optically isotropic mesophases between their melting points and the transitions to the isotropic liquid.

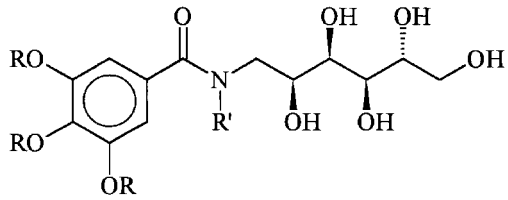
The optically isotropic mesophase of compound **5c** was investigated by X-ray scattering. The pattern displays several reflections in the small angle region (figure 7), which can be indexed on the basis of a primitive cubic cell with a lattice parameter of 8·55 nm at 90°C. The space group can be either *Pm*3*n* or *P*43*n* (table 5).

The different mesophases found for the glucamides dependent on the length and the number of chains grafted to the aromatic unit, and also the formation of cubic mesophases for the tris(dodecyloxy)benzamides, can be explained using the well known packing considerations for lyotropic systems [8–12]. Considering the chemical structures of all the compounds investigated, the glucamide moieties act as the hydrophilic head groups, whereas the alkyl chains correspond to the hydrophobic parts of the molecules. As expected, layer structures were found if both parts occupy approximately the same volumes, as for example in the case of the single chain glucamides **1** and **2** and the double chain glucamides with short chains (compound **3a**). Increasing the length or the number of alkyl chains gives rise to an increased volume of the hydrophobic region. Since the hydrophilic groups remain constant, a curvature of the interface between the two amphipatic (hydrophilic and hydrophobic) regions is obtained. By analogy with lyotropic systems, a mesophase consisting of columnar aggregates results for compounds **3b**, and **4b** with two dodecyloxy chains and for the compounds **5b** and **6b** with three hexyloxy chains.

Further enlarging the chains of the 3,4,5-trialkoxybenzamides increases the interfacial curvature and so—again as for lyotropic systems—could give rise to the formation of closed inverse micelles. We therefore assume that the cubic phases of the triple chain compounds **5c** and **6c** are inverse discontinuous cubic mesophases (I_{II}-phases).

Taking into account the lattice parameter ($a = 8{\cdot}55$ nm at 90°C), it can be calculated that about 430 molecules

Table 4. Thermotropic transition temperatures (°C) and transition enthalpies (lower lines, kJ mol^{-1}) of *N*-(3,4,5-trialkoxybenzoyl)-1-deoxy-1-methylamino-D-glucitols **5a**–**c** and *N*-(3,4,5-trialkoxybenzoyl)-1-amino-1-deoxy-D-glucitols **6a**–**c**. Abbreviations: see figure 2 and table 1.



Compound	*R*	*R'*	Phase transition/°C Transition enthalpies/kJ mol^{-1}
5a	C_3H_7	CH_3	Cr 127 is 49·5
5b	C_6H_{13}	CH_3	Cr 94 H_{II} 145 is 40·2 1·3
5c	$C_{12}H_{25}$	CH_3	Cr 75 I_{II} 185 is (dec.) 112·3 1·1
6a	C_3H_7	H	Cr 180 is 67·2
6b	C_6H_{13}	H	Cr 105 H_{II} 199 is (dec.) 61·0 1·3
6c	$C_{12}H_{25}$	H	Cr 94 I_{II} 227 is (dec.) 59·0 1·2

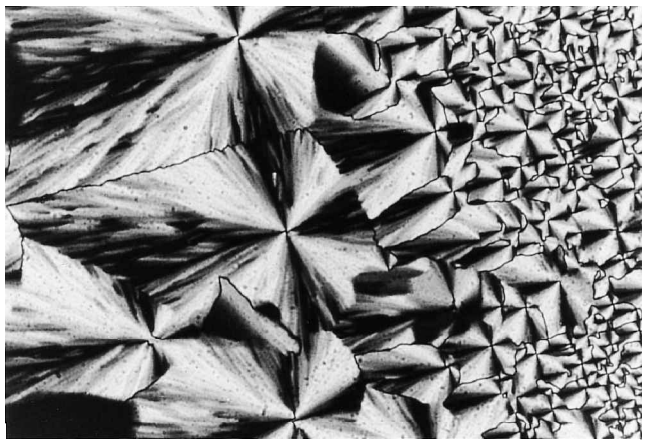


Figure 6. Optical photomicrograph (crossed polarizers) of the H_{II}-phase of compound **6b** at 170°C.

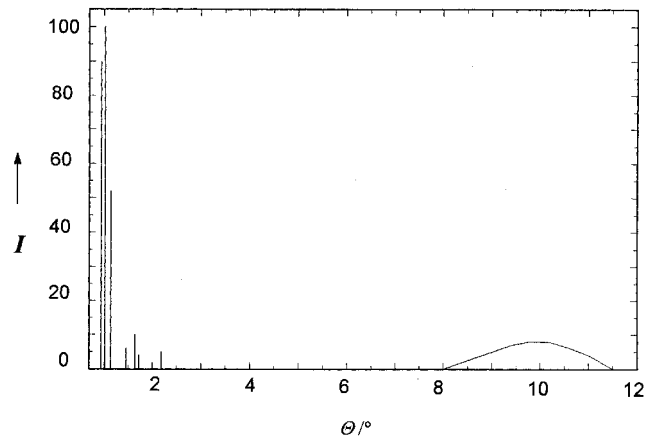


Figure 7. Schematic presentation of the X-ray pattern of the cubic mesophase of compound **5c** at 90°C.

should be arranged in each unit cell of the cubic mesophase of compound **5c**. If one assumes the existence of spherical micelles, their diameter (8·55 nm) would be significantly larger than twice the length of a single molecule in its most extended conformation ($L = 3{\cdot}1$ nm). Therefore we assume that the cubic lattice is built up by prolate-like micelles (short rods). Fontell *et al.* [26] suggested a structure for lyotropic cubic phases located between the micellar solution and the normal hexagonal phase. They proposed that these cubic phases have the same structure as solid γ-O_2 and β-F_2 at 50 K and N_2 at room temperature and 49 kbar. In this structure the

Table 5. Structural parameter of the I_{II}-phase of **5c**.

θ_{obs}	θ_{calc}	*h k l*
0·94	—	1 1 1
1·02	1·03	2 0 0
1·14	1·15	2 1 0
1·46	1·46	2 2 0
1·64	1·63	3 1 0
1·72	1·71	3 1 1
2·19	2·19	3 3 0

cubic unit cell is built up from eight rod-shaped aggregates with an axial ratio around two (prolate micelles). One of these rod-shaped micelles is placed in each corner of the unit cell, one in the centre, and two at each surface of the cell. We propose that the thermotropic cubic phases of **5c** and **6c** also have that structure, with the difference that they are built up by inverted micelles. Under this assumption the micelles must consist of *c.* 54 molecules, which seems reasonable.

In order to confirm the suggested inverted micellar structures of the cubic mesophases of the triple chain compounds **5c** and **6c**, binary mixtures of these compounds with each other, with other glucamides and with protic solvents were investigated.

2.3. *Induced thermotropic mesophase in mixtures*

As shown by Marques *et al.* [27] the curvature of the mixed micelles of ternary mixtures consisting of two different surfactants and water depends on the mixing ratio. Therefore it has been reported recently that the liquid crystalline phase behaviour in ternary lyotropic systems can be continuously varied by mixing two differently structured surfactants [28]. The question arose whether it is also possible to influence the interfacial curvature of the thermotropic mesophases of the amphiphilic carbohydrate derivatives under investigation by mixing differently structured glucamides having different mesophases.

2.3.1. *Single chain plus triple chain compounds*

In the contact region between the cubic phases of the triple chain compounds **5c** and **6c** and the smectic phases of the compounds **1**, **2** and **3a**, optically anisotropic bands with spherulitic textures develop (e.g. figure 8).

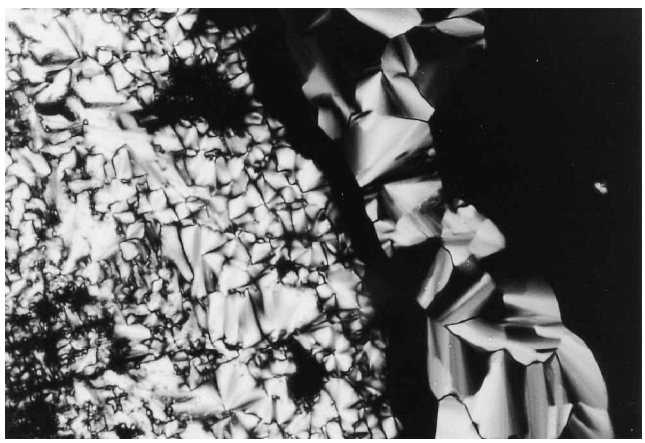


Figure 8. Optical photomicrograph (crossed polarizers) of the H_{II}-phase developing in the contact region between the optically isotropic micellar cubic I_{II}-phase of compound **5c** (right-hand side) and the lamellar α-phase of compound **1b** (left-hand side) at 152°C.

The textures of the induced mesophases are the same for all mixtures and their maximum isotropization temperatures are summarized in table 6. From the observed texture we decided on columnar mesophases.

To confirm this assumption, more detailed investigations of the binary system **1b/5c** have been carried out. A phase diagram was constructed by investigation of defined mixtures (figure 9). On increasing the content of the triple chain compound **5c** in the lamellar phase of the single chain carbohydrate **1b**, the clearing temperature decreases. In a broad concentration region from 30–70 per cent of **5c**, a novel mesophase with a spherulitic texture develops. The optical texture of this mesophase corresponds to that observed for the hexagonal columnar phases of some double chain and triple chain compounds (e.g. **3b** and **6b**). The maximum stability of this induced phase is found at an equimolar ratio **1b/5c**.

In the region between the lamellar and the columnar phases, the appearance of a bicontinuous cubic phase (V_{II}-phase) is to be expected. Careful inspection of the contact region and investigation of binary mixtures in this concentration range however gave no indication of a cubic phase. The whole isotropic region which occurs in the contact region between the hexagonal phase and the lamellar phase (figure 8) is of low viscosity.

The hexagonal columnar structure of the induced mesophase was confirmed by X-ray scattering as indicated above. The equivalence of the hexagonal structure of the pure double chain compound **3b** and the induced

Table 6. Phase types and maximum clearing temperatures (°C) of the mesophases induced in binary mixtures of compounds I and II, which have structurally different mesophases, as determined by the penetration technique. Abbreviations: see figure 2 and table 1.

Compounds I (phase $T_{cl,max}$/°C)	Compounds II (phase $T_{cl,max}$/°C)	Induced phase, $T_{cl,max}$/°C
5c (I_{II} 185)	**1a** (L_α 119)	H_{II} 162
	1b (L_α 186)	H_{II} 171
	2a (L_α 193)	H_{II} 190
	2b (L_α 250)	H_{II} 203
	3a (L_α 130)	H_{II} 154
	4a (V_{II} 185)	H_{II} 189
6c (I_{II} 227)	**1a** (L_α 119)	H_{II} 191
	1b (L_α 186)	H_{II} 205
	2a (L_α 193)	H_{II} 213
	2b (L_α 250)	H_{II} 233
	3a (L_α 130)	H_{II} 182
	4a (V_{II} 185)	H_{II} 210
4a (V_{II} 185)	**1a** (L_α 119)	—
	1b (L_α 186)	—
	2a (L_α 193)	—
	2b (L_α 250)	—
	3a (L_α 130)	—

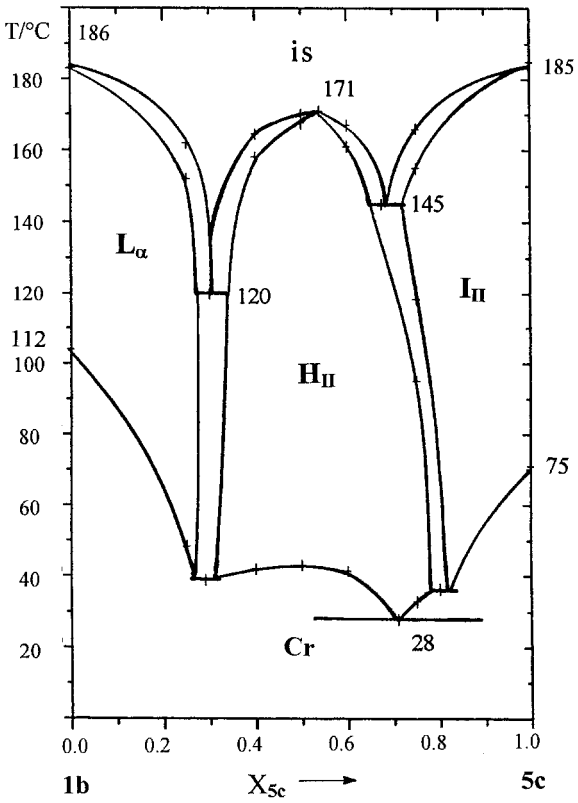


Figure 9. Binary phase diagram of the system **1b/5c**.

phase has been additionally demonstrated by the equality of their lattice parameters, as well as by their temperature dependence as given in figure 10. This means that in the contact region, the smectic layer is curved to such an extent that a columnar phase can appear. Because only the interfacial curvature of closed micelles needs to be large enough to induce columns, it is most likely that the cubic phase of the triple chain amphiphile **5c** is a discontinuous I-phase. Since the hydrophobic units are significantly larger than the hydrophilic units, the columnar and the cubic phases are both of the inverse type (H_{II} and I_{II}, respectively).

2.3.2. *Bicontinuous cubic phase plus micellar cubic phase*

It was mentioned earlier that the double chain compound **4a** with two hexyloxy chains displays a cubic mesophase different from the cubic phases of the triple chain amphiphiles **5c** and **6c**. We assumed that the cubic phase of **4a** could be a bicontinuous cubic phase consisting of interwoven networks of branched columnar aggregates or ribbons (V_{II}-phase). If this is true, then—by analogy with the phase sequence in lyotropic systems (see figure 2)—a columnar phase should develop in the contact zone between the bicontinuous cubic phase and the discontinuous (micellar) phase of **5c**. Indeed, a broad region of a hexagonal columnar phase is induced between these two compounds (figure 11). The binary

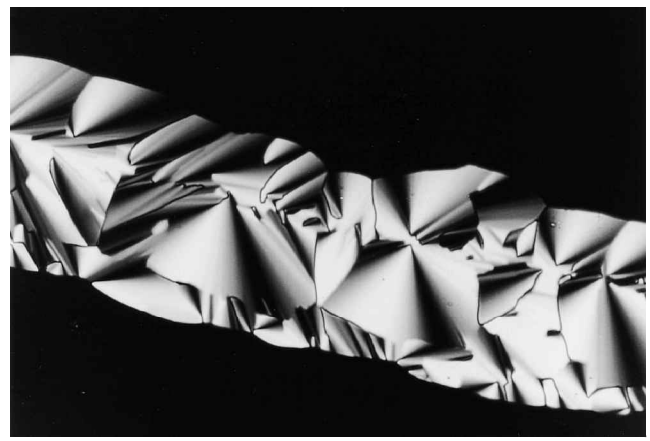


Figure 11. Optical photomicrograph (crossed polarizers) of the H_{II}-phase occurring in the contact region between the I_{II}-phase of compound **5c** (upper part) and the V_{II}-phase of compound **4a** (lower part) at 181°C.

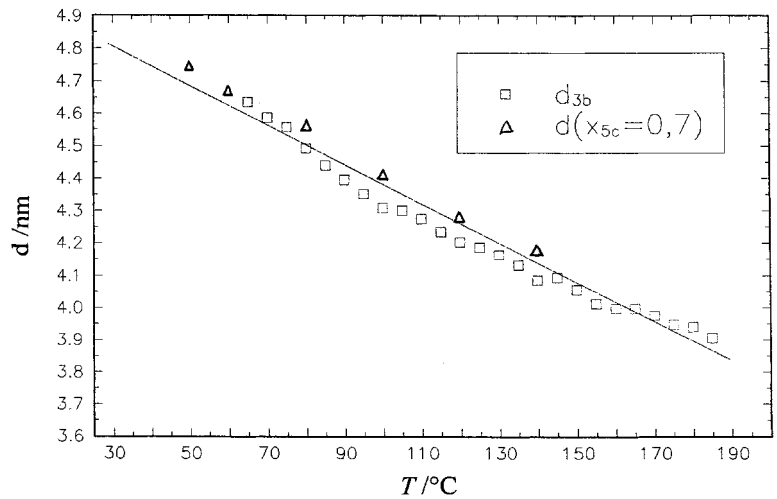


Figure 10. Temperature dependence of the hexagonal lattice parameter *d* of the double chain compound **3b** (□) and of a mixture ($X_{5c}=0{\cdot}7$) of the compounds **1b** and **5c** (△).

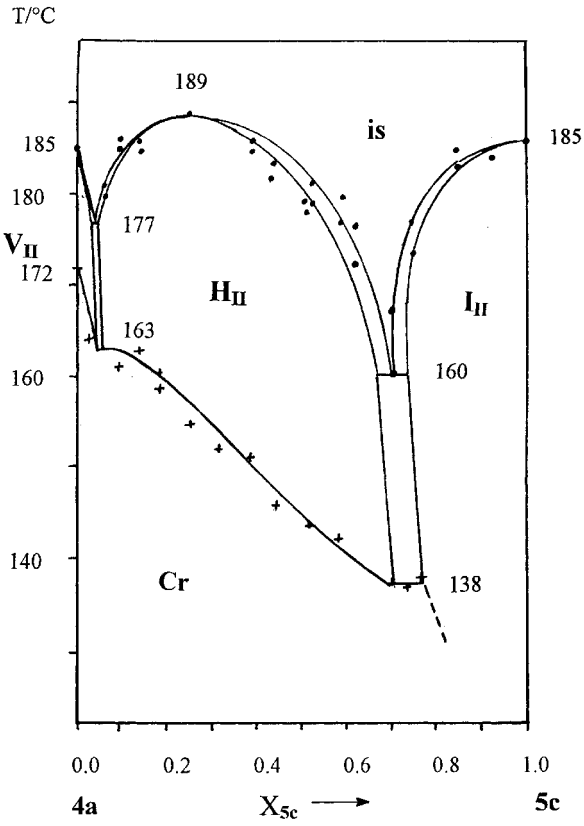


Figure 12. Binary phase diagram of the system **4a/5c**.

phase diagram of the system **4a/5c** is shown in figure 12. The columnar phase occurs in a very wide concentration range between $X_{5c}=0{\cdot}05$ and $X_{5c}=0{\cdot}7$ which means that contamination of the cubic phase of **4a** with only five molecules **5c** per 100 molecules **4a** gives rise to a columnar structure.

The hexagonal columnar structure was again confirmed by X-ray investigation of an equimolar mixture. The maximum clearing temperature of the induced columnar phase was slightly above the clearing temperatures of the mesophases of the single components. To the best of our knowledge, this is the first time that a thermotropic columnar mesophase has been induced simply by mixing two structurally different cubic phases.

No columnar phase can be observed in the contact region between the cubic phase of the double chain compound **4a** and the lamellar phases of **3a** or **1b**. This observation is also in accordance with an inverted bicontinuous structure of the cubic phase of **4a**.

2.4. *Lyotropic properties*

In order to get more information about the structures of the cubic phases of the triple chain compounds, we have additionally studied the behaviour of the dodecyloxy substituted glucamides and *N*-methylglucamides in the presence of ethylene glycol as protic solvent[g] [29]. The transition temperatures of the ethylene glycol saturated samples, as well as the maximum transition temperatures of the induced phases in the contact regions, were determined by polarizing optical microscopy (table 7).

Table 7. Phase transition temperatures (°C) of the ethylene glycol saturated samples of compounds **1b**, **3b**, **4b**, **5c** and **6c** and the maximum transition temperatures of the lyomesophases T_{max} as determined from contact preparations. Abbreviations: see figure 2 and table 1.

Compound	Phase transition of the ethylene glycol saturated samples/°C	T_{max}/°C
1b	Cr 141 is	—
3b	Cr 50 L_α 136 is	V_{II}–L_α: 134; L_α–is: 152
4b	Cr 134 L_α 149 is	V_{II}–is: 171; L_α–is: 184
5c	Cr 56 H_{II} 128 is	H_{II}–is: 146
6c	Cr 72 H_{II} 142 is	H_{II}–is: 181

No mesophase was induced by addition of ethylene glycol to the single chain compound **1b**. With increasing solvent concentration, the clearing temperature of the lamellar phase decreases.

In the contact region between the columnar phases of the double chain compounds **3b** and **4b** and ethylene glycol, cubic and lamellar α-phases were found. The photomicrograph of the contact region of compound **3b**/ethylene glycol at 140°C is shown in figure 13. The simplified principal phase diagram of this binary system is displayed in figure 14. A broad region of a lamellar phase is induced in the ethylene glycol rich region. Up to 134°C, a (bicontinuous) cubic phase occurs as the intermediate phase between the hexagonal columnar phase and the lamellar phase. At elevated temperatures however, a direct transition from the columnar to the lamellar phase occurs on increasing the solvent concentration. The cubic phase was identified by the occurrence of a highly viscous and optically isotropic band with stepped phase boundaries (observed between 70° crossed polarizers). Furthermore the transition to the cubic phase can be slightly supercooled (2–3 K).

The same behaviour was observed for the binary system **4b**/ethylene glycol (figure 15). However, in this case, independent of the temperature, no direct transition from the columnar to the lamellar phase was found on

[g] Due to experimental difficulties, only preliminary investigations have been carried out. Because the transition temperatures of all compounds are significantly above 100°C, we used ethylene glycol instead of water for these investigations. Not all compounds could be investigated, because most of the short chain derivatives are highly soluble in this solvent. Therefore we have restricted our investigations to the dodecyloxy substituted derivatives **1b**, **3b**, **4b**, **5c** and **6c**.

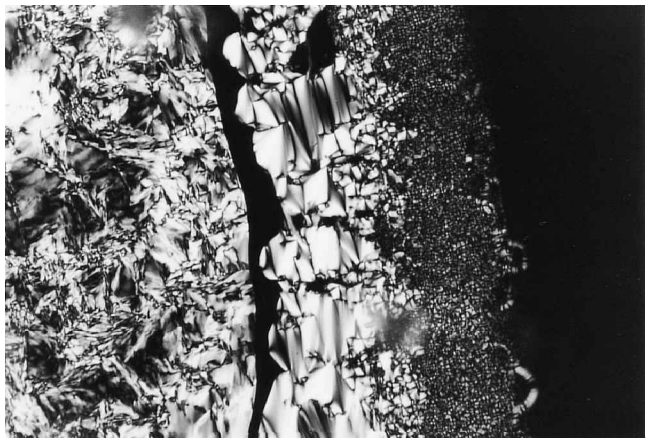


Figure 13. Optical photomicrograph (crossed polarizers) of the contact region between the H_{II}-phase of compound **3b** (left-hand side) and ethylene glycol (right-hand side) at 140°C.

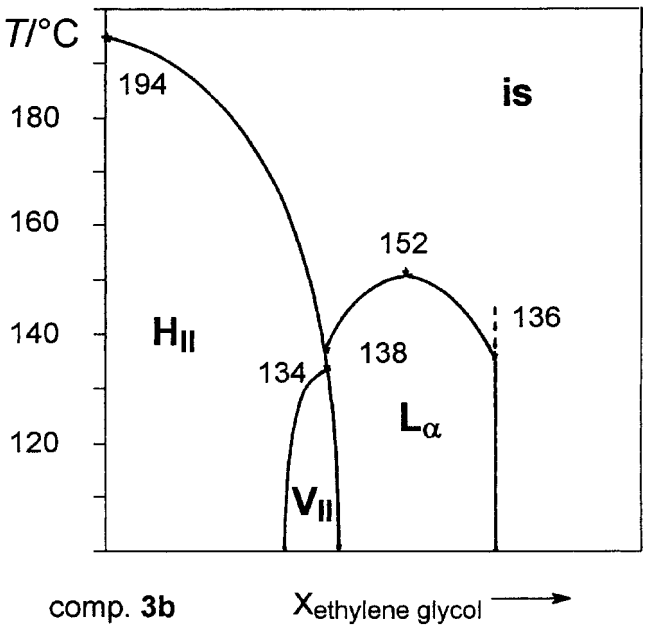


Figure 14. Simplified principal phase diagram of the binary system **3b**/ethylene glycol as obtained from solvent penetration experiments.

changing the solvent concentration. The cubic phase always occurs between the H_{II}-phase and the L_α-phase up to 171°C and then directly turns into an isotropic liquid (rounded phase boundaries).

In the contact region between the cubic phases of the triple chain compounds **5c** and **6c** and ethylene glycol only a hexagonal columnar phase develops (see figure 16).

We explain the observed lyotropic phase behaviour in the following way. The polar ethylene glycol molecules are incorporated into the hydrogen bonding networks

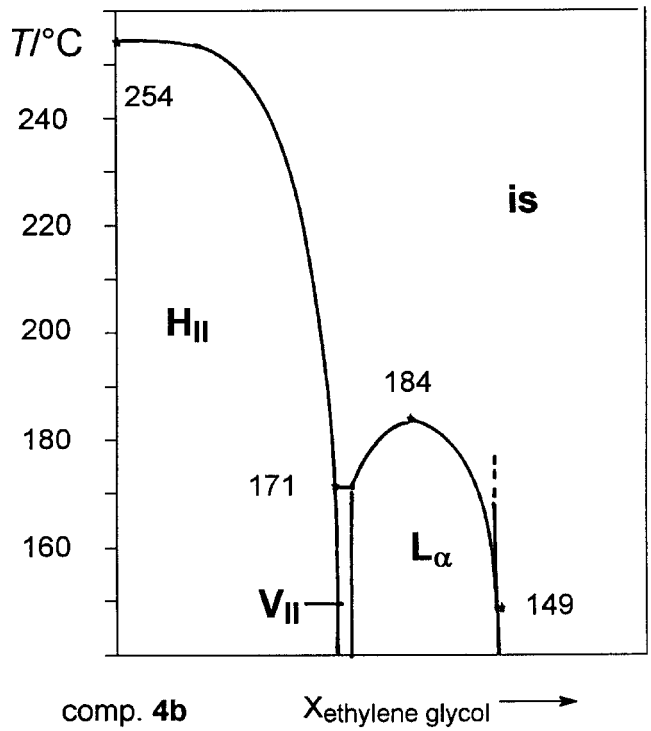


Figure 15. Simplified principal phase diagram of the binary system **4b**/ethylene glycol as obtained from solvent penetration experiments.

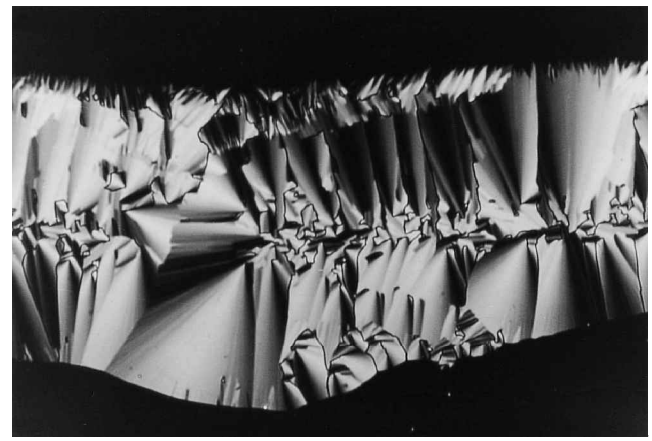


Figure 16. Optical photomicrograph (crossed polarizers) of the H_{II}-phase which appears in the contact region between the I_{II}-phase of compound **5c** (upper part) and ethylene glycol (lower part) at 140°C.

of the hydroxyl groups, therefore the size of the hydrophilic head groups increases and accordingly the curvature of the (inverse) aggregates is diminished. This gives rise to a transition from the curved hexagonal columnar phase *via* a bicontinuous cubic phase (V_{II}) to the non-curved lamellar-α mesophase (compounds **3b** and **4b**) and from the strongly curved closed inverted micelles in the discontinuous cubic I_{II}-phases of the compounds **5c**

and **6c** to the less curved cylindrical aggregates of the hexagonal columnar phase. This gives additional hints about the inverted micellar type of the cubic mesophases of the triple chain carbohydrates **5c** and **6c**.

2.5. *Monolayer behaviour*

The relative sizes of the hydrophilic and the hydrophobic parts of these new carbohydrate amphiphiles should not only influence their aggregation behaviour as bulk materials, but should also influence their self organization at interfaces. We investigated the monolayer behaviour of the insoluble long chain *N*-methylglucamides as thin films at the air water interface by means of a Langmuir film-balance [30].

Figure 17 compares the π/A-isotherms obtained for the single chain, the double chain and the triple chain *N*-methylglucamides **1b**, **3b** and **5c** which all have the same chain length (C_{12}).

These compounds form stable monomolecular films at the air water interface. The number of alkyl groups has a remarkable influence on the shape of the isotherms. The single chain compound **1b** forms a highly compressible condensed film. Collapse takes place at 43 mN m^{-1} and an area of 34 Å^2/molecule. The area at the collapse is significantly larger than expected for a dense packing of the hydrophobic 4-alkoxyphenyl groups (18–22 Å^2/molecule). We assume that the densely packed (hydrated) hydrophilic carbohydrate moieties determine the molecular area at the collapse point. The liquid-like type of isotherm may result from the dehydration of the carbohydrate moieties and conformational changes during compression.

The double chain compound **3b** also forms a condensed film, but it is much less compressible than that

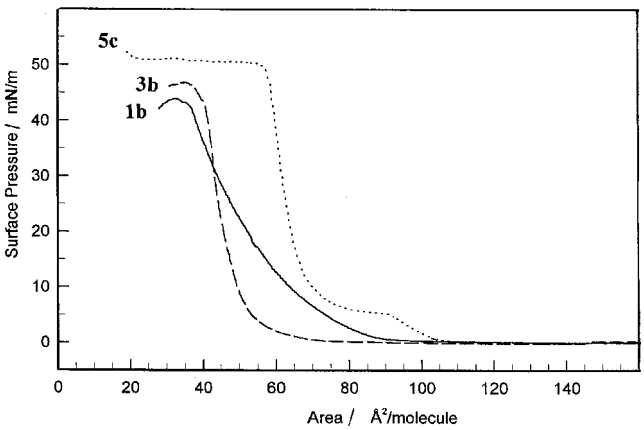


Figure 17. Pressure–area isotherms (T=20°C) of *N*-(4-dodecyloxybenzoyl)-1-deoxy-1-methylamino-D-glucitol **1b**, *N*-(3,4-didodecyloxybenzoyl)-1-deoxy-1-methylamino-D-glucitol **3b** and *N*-(3,4,5-tridodecyloxybenzoyl)-1-deoxy-1-methylamino-D-glucitol **5c**.

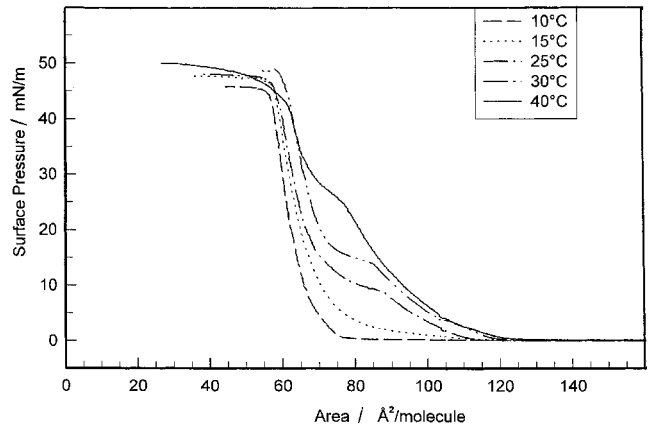


Figure 18. Temperature dependence of the pressure–area isotherms of *N*-(3,4,5-tridodecyloxybenzoyl)-1-deoxy-1-methylamino- D-glucitol **5c**.

of the single chain compound **1b**. The collapse takes place at 47 mN m^{-1} and an area of 36 Å^2/molecule. This area corresponds to a dense packing of the alkyl chains (2×18 Å^2/molecule). Interestingly the area at the collapse is nearly the same for the single chain amphiphile and the double chain compound. This means that the diameter of the hydrated head group and that of two aliphatic chains are nearly identical.

The triple chain compound **5c** forms a condensed film with the same slope as the double chain compound **3b**. The collapse appears at an area of 59 Å^2/molecule, which is consistent with a dense packing of three aliphatic chains. Additionally to the condensed film, a liquid expanded film appears at lower film pressures. The transition from the liquid expanded to the condensed film is first order and displays the usual temperature dependence (figure 18).

The different monolayer properties of the amphiphiles can be correlated with their lyotropic mesophase behaviour. Though the solvents are different, the results of the monolayer investigations on water are consistent with the conclusions drawn from the lyomesophases in ethylene glycol. The diameter of the hydrated *N*-methylglucamide group seems to be larger than the diameter of a single alkyl chain. A balanced ratio is found for the double chain amphiphiles. Accordingly the lyomesophases of the double chain glucamides are lamellar layer structures. The pressure–area isotherms of the triple chain *N*-methylglucamide **5c** is determined only by the diameter of the alkyl chains. This means that the diameter of the hydrophobic part is larger than that one of the hydrated head group, which is consistent with the observed inverted hexagonal columnar lyomesophase.

3. Experimental

3.1. *Techniques*

Transition temperatures were measured using a Mettler FP 82 HT hot stage and control unit in conjunc-

tion with a Nikon Optiphot 2 polarizing microscope and values confirmed using differential scanning calorimetry (Perkin-Elmer DSC-7, heating and cooling rate: 10 K min^{-1}). Reversibility studies using DSC showed that the compounds tend to decompose slowly at their clearing temperatures (glucamides above 180°C, *N*-methylglucamides above 130°C).

X-ray diffraction patterns were obtained using a Guinier diffractometer (Huber) operating with a Cu($K\alpha_1$) beam. Mesophase induction and lyotropic properties were investigated by the penetration technique and by studies of binary mixtures.

The maximum temperatures of the lyomesophases were determined on samples made by carefully grinding the compounds with an excess of ethylene glycol. These mixtures were investigated by calorimetry and by optical polarizing microscopy.

Pressure–area isotherms were recorded using an R & K film balance equipped with a teflon-coated Langmuir trough and a continuous Wilhelmy type measuring system. The temperature of the experimental system was 20°C. The substances were dissolved in chloroform; typically the concentrations were between 1 and 2 mmol dm^{-3}. The measurements were started 10 min after spreading. Water used for measuring the surface properties was of Millipore quality.

3.2. *Materials*

Ethyl 4-hydroxybenzoate, ethyl 3,4-dihydroxybenzoate (Aldrich), ethyl 3,4,5-trihydroxybenzoate (Fluka), 1-amino-1-deoxy-D-glucitol (Aldrich), 1-deoxy-1-methylamino-D-glucitol (Aldrich), 1-bromopropane, 1-bromohexane, and 1-bromododecane (Merck) were used as obtained. Ethylene glycol used for the determination of the lyotropic properties was distilled and stored over molecular sieves (3 Å).

The substituted carboxylic acids were obtained by etherification of the ethyl hydroxybenzoates with the bromoalkanes and potassium carbonate in cyclohexanone [31] followed by saponification. The resulting alkoxybenzoic acids were purified by repeated crystallization. Confirmation of the structures of the products was obtained by ^{1}H and ^{13}C NMR spectroscopy (Varian Gemini 200 and Varian Unity 500) and mass spectrometry (Intectra GmbH, AMD 402, electron impact, 70 eV).

Microanalyses were performed using a CHNF-932 (LECO Co.) elemental analyzer. Owing to the hygroscopic properties of some compounds, moisture was absorbed during sample preparation and therefore no correct combustion analyses were obtained for these compounds. In these cases the water content was determined by Karl-Fischer titration [32] and the amount of absorbed water was taken into account for the calculation of the required values. The purity of all compounds was checked by thin layer chromatography (Merck, silica gel 60 F 254). Measurements of optical rotation were carried out with a Perkin Elmer Polarimeter 341.

3.3. *General procedure for the synthesis of N-benzoyl-1-deoxy-1-methylamino-*D*-glucitols and N-benzoyl-1-amino-1-deoxy-*D*-glucitols* (**1**–**6**)

The substituted benzoic acid (3 mmol) and thionyl chloride (10 ml) were heated under reflux for 3 h. The excess of thionyl chloride was distilled off and the residue was dissolved in 15 ml of dry methylene chloride. 1-Deoxy-1-methylamino-D-glucitol (30 mmol) or 1-amino-1-deoxy-D-glucitol (30 mmol) was dissolved in 30 ml of dry dimethylformamide under inert conditions, and DMAP (10 mg) was added. The solution of the benzoyl chloride in methylene chloride was added drop by drop at 80°C. The resulting solution was heated at this temperature for 3 h and kept for an additional 24 h at room temperature. The solvent was then evaporated and the residue washed twice with water.

3.4. *N-(4-hexyloxybenzoyl)-1-deoxy-1-methylamino-*D*-glucitol* (**1a**)

This was synthesized from 4-hexyloxybenzoic acid (0·67 g) and 1-deoxy-1-methylamino-D-glucitol (5·85 g) and crystallized twice from acetone. Yield: 26 per cent; transition temperatures (°C): Cr 120 (L_α 119) is (isotropic); $[\alpha]_D^{25} = -1{\cdot}2$ ($c = 1$, methanol); TLC: $R_f = 0{\cdot}30$ (eluent chloroform–ethanol, 10:3); (Found: C 59·48, H 8·35, N 3·69. $C_{20}H_{33}O_7N$. 0·3 H_2O requires C 59·33, H 8·36, N 3·46 per cent); δ_H (500 MHz; DMSO-d_6; 25°C) 0·87 (t, 3H, CH_3), 1·29 (m, 4H, CH_2), 1·45 (m, 2H, CH_2), 1·73 (m, 4H, CH_2), 2·96 (s, 3H, N–CH_3), 3·28–3·66 (m, 8H, CH–OH, CH_2–OH, CH_2–N, OH), 3·97 (t, 2H, OCH_2), 4·25 (br, 2H, OH), 4·44 (br, 2H, OH), 4·82 (d, 1H, OH), 6·91 (d, 2H, H–ar), 7·37 (d, 2H, H–ar).

3.5. *N-(4-dodecyloxybenzoyl)-1-deoxy-1-methylamino-*D*-glucitol* (**1b**)

This compound was synthesized from 4-dodecyloxybenzoic (0·92 g) and 1-deoxy-1-methylamino-D-glucitol (5·85 g) and was crystallized twice from methanol. Yield: 40 per cent; transition temperatures (°C): Cr 112 L_α 186 is (dec.); $[\alpha]_D^{25} = -1{\cdot}9$ ($c = 0{\cdot}8$, methanol); TLC: $R_f = 0{\cdot}27$ (eluent chloroform–ethanol, 10:3); (Found: C 64·28, H 9·58, N 2·80. $C_{26}H_{45}O_7N$ requires C 64·57, H 9·38, N 2·90 per cent); δ_H (200 MHz; DMSO-d_6; 25°C) 0·83 (t, 3H, CH_3), 1·25 (br, 18H, CH_2), 1·69 (br, 2H, CH_2), 2·97 (s, 3H, N–CH_3), 3·30–3·85 (m, 8H, CH–OH, CH_2–OH, CH_2–N, OH), 3·96 (t, 2H, OCH_2), 4·28 (br, 2H, OH), 4·42 (br, 2H, OH), 4·87 (d, 1H, OH), 6·9 (d, 2H, H–ar), 7·36 (d, 2H, H–ar).

3.6. *N-(4-hexyloxybenzoyl)-1-amino-1-deoxy-*D-*glucitol* (**2a**)

This was synthesized from 4-hexyloxybenzoic acid (0·67 g) and 1-amino-1-deoxy-D-glucitol (5·43 g) and was crystallized twice from methanol–chloroform (1:1). Yield: 76 per cent; transition temperatures (°C): Cr 197 (L_α 193) is; TLC: R_f=0·18 (eluent chloroform–ethanol, 10:3); (Found: C 59·50, H 8·18, N 3·48. $C_{19}H_{31}O_7N$ requires C 59·05, H 8·35, N 3·62 per cent); δ_H (500 MHz; DMSO-d_6; 25°C) 0·86 (t, 3H, CH_3), 1·32 (m, 6H, CH_2), 1·70 (br, 2H, CH_2), 3·21–3·75 (m, 8H, CH–OH, CH_2–OH, CH_2–N, OH), 4·0 (t, 2H, O–CH_2), 4·30 (br, 2H, OH), 4·4 (br, 2H, OH), 4·44 (br, 1H, OH), 6·98 (d, 2H, H–ar), 7·78 (d, 2H, H–ar), 8·16 (t, 1H, NH).

3.7. *N-(4-dodecyloxybenzoyl)-1-amino-1-deoxy-*D-*glucitol* (**2b**)

This compound was synthesized from 4-dodecyloxybenzoic acid (0·92 g) and 1-amino-1-deoxy-D-glucitol (5·43 g) and was crystallized twice from methanol–chloroform (1:1). Yield: 79 per cent; transition temperatures (°C): Cr 182 L_α 250 is (dec.); TLC: R_f=0·17 (eluent chloroform–ethanol, 10:3); (Found: C 61·31, H 9·09, N 3·04. $C_{25}H_{43}O_7N$. H_2O requires C 61·58, H 9·3, N 2·87 per cent); δ_H (200 MHz; DMSO-d_6; 25°C) 0·85 (t, 3H, CH_3), 1·25 (m, 18H, CH_2), 1·70 (m, 2H, CH_2), 3·23–3·74 (m, 8H, CH–OH, CH_2–OH, CH_2–N, OH), 4·0 (t, 2H, OCH_2), 4·32 (br, 2H, OH), 4·42 (br, 2H, OH), 4·88 (d, 1H, OH), 6·95 (d, 2H, H–ar), 7·8 (d, 2H, H–ar), 8·21 (t, 1H, NH).

3.8. *N-(3,4-dihexyloxybenzoyl)-1-deoxy-1-methylamino-*D-*glucitol* (**3a**)

This was synthesized from 3,4-dihexyloxybenzoic acid (0·97 g) and 1-deoxy-1-methylamino-D-glucitol (5·85 g) and was crystallized twice from methanol. Yield: 23 per cent; transition temperatures (°C): Cr 93 L_α 130 is (dec.); $[\alpha]_D^{28}$ = +2·7 (c=1, methanol); TLC: R_f=0·43 (eluent chloroform–ethanol, 10:3); (Found: C 62·49, H 9·08, N 2·51. $C_{26}H_{45}O_8N$ requires C 62·50, H 9·08, N 2·80 per cent; δ_H (500 MHz; DMSO-d_6; 25°C) 0·86 (t, 6H, CH_3), 1·30 (m, 4H, CH_2), 1·45 (m, 4H, CH_2), 1·68 (m, 12H, CH_2), 2·96 (s, 3H, N–CH_3), 3·26–3·56 (m, 8H, CH–OH, CH_2–OH, CH_2–N, OH), 3·89–3·97 (m, 4H, OCH_2), 4·25 (br, 2H, OH), 4·44 (br, 2H, OH), 4·84 (d, 1H, OH), 6·93 (br, 3H, H–ar). EI-Ms m/z (per cent): 499 (2·1) [M^+], 322 (3·6), 305 (100), 221 (25), 137 (21·4).

3.9. *N-(3,4-didodecyloxybenzoyl)-1-deoxy-1-methylamino-*D-*glucitol* (**3b**)

This was synthesized from 3,4-didodecyloxybenzoic acid (1·47 g) and 1-deoxy-1-methylamino-D-glucitol (5·85 g) and was crystallized twice from methanol. Yield: 60 per cent; transition temperatures (°C): Cr 61 H_{II} 194 is (dec.); $[\alpha]_D^{35}$ = +4·8 (c=1, chloroform); TLC: R_f=0·40 (eluent chloroform–ethanol, 10:3); (Found: C 68·08, H 10·31, N 2·00. $C_{38}H_{69}O_8N$ requires C 68·33, H 10·41, N 2·10 per cent); δ_H (500 MHz; DMSO-d_6; 25°C) 0·83 (t, 6H, CH_3), 1·12 (m, 32H, CH_2), 1·23 (m, 4H, CH_2), 1·67 (m, 4H, CH_2), 2·95 (s, 3H, N–CH_3), 3·32–3·55 (m, 8H, CH–OH, CH_2–OH, CH_2–N, OH), 3·94 (br, 4H, OCH_2), 4·32 (br, 2H, OH), 4·44 (br, 2H, OH), 4·92 (br, 1H, OH), 6·93 (br, 1H, H–ar), 7·09 (br, 2H, H–ar).

3.10. *N-(3,4-dihexyloxybenzoyl)-1-amino-1-deoxy-*D-*glucitol* (**4a**)

This compound was synthesized from 3,4-dihexyloxybenzoic acid (0·97 g) and 1-amino-1-deoxy-D-glucitol (5·43 g) and was crystallized twice from methanol. Yield: 54 per cent; transition temperatures (°C): Cr 172 V_{II} 185 is; $[\alpha]_D^{28}$ = +8·7 (c=0·8, chloroform); TLC: R_f=0·19 (eluent chloroform–ethanol, 10:3); (Found: C 61·62, H 8·80, N 2·89. $C_{25}H_{43}O_8N$ requires C 61·83, H 8·92, N 2·88 per cent); δ_H (500 MHz; DMSO-d_6; 25°C) 0·86 (t, 6H, CH_3), 1·29 (m, 8H, CH_2), 1·43 (m, 4H, CH_2), 1·70 (m, 4H, CH_2), 3·23–3·77 (m, 8H, CH–OH, CH_2–OH, CH_2–N, OH), 3·94 (q, 4H, OCH_2), 4·27 (t, 2H, OH), 4·42 (dd, 2H, OH), 4·85 (d, 1H, OH), 6·98 (d, 1H, H–ar), 7·43 (dd, 2H, H–ar), 8·2 (t, 1H, NH). EI-Ms m/z (per cent): 485 (14·3) [M^+], 335 (14·3), 305 (100), 221 (36·4), 137 (25·7).

3.11. *N-(3,4-didodecyloxybenzoyl)-1-amino-1-deoxy-*D-*glucitol* (**4b**)

This was synthesized from 3,4-didodecyloxybenzoic acid (1·47 g) and 1-amino-1-deoxy-D-glucitol (5·43 g) and was crystallized twice from methanol. Yield: 48 per cent; transition temperatures (°C): Cr 162 H_{II} 254 is (dec.); $[\alpha]_D^{25}$ = +7·1 (c=0·9, chloroform); TLC: R_f=0·30 (eluent chloroform–ethanol, 10:3); $C_{37}H_{67}O_8N$: calc. 653·4867, found 653·4886 (MS); δ_H (500 MHz; DMSO-d_6; 25°C) 0·83 (t, 6H, CH_3), 1·23 (br, 32H, CH_2), 1·41 (br, 4H, CH_2), 1·65 (m, 4H, CH_2), 3·29–3·74 (m, 8H, CH–OH, CH_2–OH, CH_2–N, OH), 3·98 (m, 4H, OCH_2), 4·24 (t, 2H, OH), 4·42 (dd, 2H, OH), 4·80 (d, 1H, OH), 6·95 (d, 1H, H–ar), 7·34 (br, 2H, H–ar), 8·15 (t, 1H, NH); EI-Ms m/z (per cent): 653 (4·7) [M^+], 617 (3·1), 574 (6·4), 473 (100), 154 (25), 137 (24·7).

3.12. *N-(3,4,5-tripropyloxybenzoyl)-1-deoxy-1-methylamino-*D-*glucitol* (**5a**)

This was synthesized from 3,4,5-tripropyloxybenzoic acid (0·89 g) and 1-deoxy-1-methylamino-D-glucitol (5·85 g), and was crystallized twice from hexane. Yield: 40 per cent; m.p.: 127°C; $[\alpha]_D^{30}$ = −3·9 (c=1, methanol); TLC: R_f=0·44 (eluent chloroform–ethanol, 10:3); $C_{23}H_{39}O_9N$: calc. 473·2625, found 473·2656 (MS); δ_H (200 MHz; DMSO-d_6; 25°C) 0·97 (t, 9H, CH_3), 1·57–1·76

(m, 6H, CH_2), 2·94 (s, 3H, N–CH_3), 3·45–3·54 (m, 8H, CH–OH, CH_2–OH, CH_2–N, OH), 3·81–3·93 (m, 6H, CH_2O), 4·28 (br, 2H, OH), 4·5 (br, 2H, OH), 4·95 (br, 1H, OH), 6·74 (br, 2H, H–ar); EI-MS *m/z* (per cent): 473 (7·5) [M^+], 279 (100), 237 (37·3), 195 (7·8), 153 (13·3).

3.13. *N-(3,4,5-trihexyloxybenzoyl)-1-deoxy-1-methylamino-*D*-glucitol* (**5b**)

Synthesized from 3,4,5-trihexyloxybenzoic acid (1·3 g) and 1-deoxy-1-methylamino-D-glucitol (5·85 g), it was crystallized twice from methanol. Yield: 26 per cent; transition temperatures (°C): Cr 94 H_{II} 145 is (dec.); $[\alpha]_D^{30} = -7{\cdot}0$ ($c = 1$, methanol); TLC: $R_f = 0{\cdot}42$ (eluent chloroform–ethanol, 10:3); (Found: C 63·94, H 9·41, N 2·27. $C_{32}H_{57}O_9N$ requires C 64·08, H 9·58, N 2·34 per cent); δ_H (500 MHz; DMSO-d_6; 25°C) 0·88 (t, 9H, CH_3), 1·30 (m, 12H, CH_2), 1·41 (t, 6H, CH_2), 1·58–1·70 (m, 6H, CH_2), 2·95 (s, 3H, N–CH_3), 3·42–3·64 (m, 8H, CH–OH, CH_2–OH, CH_2–N, OH), 3·85 (t, 2H, CH_2O), 3·92 (t, 4H, CH_2O), 4·26 (t, 2H, OH), 4·42 (br, 2H, OH), 4·87 (br, 1H, OH), 6·65 (br, 2H, H–ar); δ_C (200 MHz; $CDCl_3$; 25°C) 173·39 (CO), 153·07, 139·63, 129·93, 105·80 (C–ar), 73·44, 72·28, 71·80, 70·18 (CH–OH), 64·05 (CH_2–OH), 39·52 (N–CH_3), 69·31, 69·24, 31·53, 30·22, 25·72, 22·56 (CH_2), 13·97 (CH_3); EI-Ms *m/z* (per cent): 599 (10·7) [M^+], 405 (100), 321 (35·7), 254 (7·1), 153 (12·1).

3.14. *N-(3,4,5-tridodecyloxybenzoyl)-1-deoxy-1-methylamino-*D*-glucitol* (**5c**)

Synthesized from 3,4,5-tridodecyloxybenzoic acid (2·0 g) and 1-deoxy-1-methylamino-D-glucitol (5·85 g), it was crystallized twice from methanol. Yield: 64 per cent; transition temperatures (°C): Cr 75 I_{II} 185 is (dec.); $[\alpha]_D^{30} = +6{\cdot}4$ ($c = 1$, chloroform); TLC: $R_f = 0{\cdot}57$ (eluent chloroform–ethanol 10:3); (Found: C 70·44, H 11·58, N 1·62. $C_{50}H_{93}O_9N$ requires C 70·46, H 11·00, N 1·64 per cent); δ_H (500 MHz; DMSO-d_6; 25°C) 0·84 (t, 9H, CH_3), 1·25 (m, 48H, CH_2), 1·45 (m, 6H, CH_2), 1·60–1·75 (m, 6H, CH_2), 2·94 (s, 1H, N–CH_3), 3·27–3·55 (m, 8H, CH–OH, CH_2–OH, CH_2–N, OH), 3·85 (t, 2H, CH_2O), 3·94 (m, 4H, CH_2O), 4·26 (t, 2H, OH), 4·42 (br, 2H, OH), 4·88 (br, 1H, OH), 6·65 (br, 2H, H–ar); EI-Ms *m/z* (per cent): 851 (6·7) [M^+], 674 (100), 657 (93·3), 506 (66·7), 489 (36·7), 338 (20), 3·3 (55), 71 (23·3), 57 (46·7).

3.15. *N-(3,4,5-tripropyloxybenzoyl)-1-amino-1-deoxy-*D*-glucitol* (**6a**)

Synthesized from 3,4,5-tripropyloxybenzoic acid (0·89 g) and 1-amino-1-deoxy-D-glucitol (5·43 g), it was crystallized twice from methanol. Yield: 47 per cent; m.p.: 180°C; $[\alpha]_D^{30} = -1{\cdot}1$ ($c = 1$, methanol); TLC: $R_f = 0{\cdot}25$ (eluent chloroform–ethanol 10:3); (Found: C 57·37, H 8·24, N 3·01. $C_{22}H_{37}O_9N$ requires C 57·50, H 8·12, N 3·05 per cent); δ_H (500 MHz; DMSO-d_6; 25°C) 0·98 (t, 9H, CH_3), 1·62 (m, 4H, CH_2) 1·74 (m, 2H, CH_2), 3·22–3·41 (m, 8H, CH–OH, CH_2–OH, CH_2–N, OH), 3·86 (t, 2H, OCH_2), 3·95 (t, 4H, CH_2O), 4·28 (t, 2H, OH), 4·4 (dd, 4H, OH), 4·8 (d, 1H, OH), 7·14 (s, 2H, H–ar), 8·27 (t, 1H, NH); EI-Ms *m/z* (per cent): 459 (23·4) [M^+], 279 (100), 237 (44·3), 195 (10), 153 (13·6).

3.16. *N-(3,4,5-trihexyloxybenzoyl)-1-amino-1-deoxy-*D*-glucitol* (**6b**)

Synthesized from 3,4,5-trihexyloxybenzoic acid (1·3 g) and 1-amino-1-deoxy-D-glucitol (5·43 g), it was crystallized twice from acetone. Yield: 65 per cent; transition temperatures (°C): Cr 105 H_{II} 199 is (dec.); $[\alpha]_D^{30} = -4{\cdot}2$ ($c = 1$, methanol); TLC: $R_f = 0{\cdot}40$ (eluent chloroform–ethanol 10:3); $C_{31}H_{55}O_9N$: calc. 585·3877, found 585·3845 (MS). δ_H (500 MHz; DMSO-d_6; 25°C) 0·86 (t, 9H, CH_3), 1·30 (m, 12H, CH_2O), 1·42 (m, 6H, CH_2), 1·62–1·70 (m, 6H, CH_2), 3·22–3·58 (m, 8H, CH–OH, CH_2–OH, CH_2–N, OH), 3·84 (t, 2H, CH_2O), 3·95 (t, 4H, CH_2O), 4·29 (br, 2H, OH), 4·42 (br, 2H, OH), 4·82 (br, 1H, OH), 7·14 (s, 2H, H–ar, 8·29 (t, 1H, NH); EI-Ms *m/z* (per cent): 585 (22·6) [M^+], 405 (100), 321 (90·5), 237 (26·8), 169 (26·6), 153 (26·5).

3.17. *N-(3,4,5-tridodecyloxybenzoyl)-1-amino-1-deoxy-*D*-glucitol* (**6c**)

Synthesized from 3,4,5-tridodecyloxybenzoic acid (2·0 g) and 1-amino-1-deoxy-D-glucitol (5·43 g), it was crystallized twice from methanol. Yield: 36 per cent; transition temperatures (°C): Cr 94 I_{II} 227 is (dec.); $[\alpha]_D^{25} = -0{\cdot}9$ ($c = 0{\cdot}9$, chloroform); TLC: $R_f = 0{\cdot}38$ (eluent chloroform–ethanol 10:3); (Found: C 69·49, H 10·82, N 1·61. $C_{49}H_{91}O_9N$. 0·5 H_2O requires C 69·46, H 10·94, N 1·65 per cent); δ_H (200 MHz; DMSO-d_6; 25°) 0·82 (t, 9H, CH_3), 1·13–1·70 (m, 60H, CH_2), 3·28–3·63 (m, 8H, CH–OH, CH_2–OH, CH_2–N, OH), 3·85 (t, 2H, CH_2O), 3·97 (t, 4H, CH_2O), 4·28 (t, 2H, OH), 4·4 (br, 2H, OH), 4·83 (d, 1H, OH), 7·13 (s, 1H, H–ar), 8·29 (t, 1H, NH); EI-Ms *m/z* (per cent): 837 (33·9) [M^+], 674 (100), 657 (55·9), 506 (62·7), 489 (39), 338 (16·9), 170 (71·2), 71 (49·2), 57 (62·7).

4. Summary and conclusions

Novel liquid crystalline carbohydrates have been synthesized. Dependent on the number and the length of the alkyl chains, they can form lamellar, inverted bicontinuous cubic, inverted hexagonal columnar and inverted micellar cubic mesophases. Thus, the thermotropic mesomorphism of these amphiphilic carbohydrate derivatives is dependent on the number and length of the lipophilic chains and is comparable with the well known dependence of the lyotropic mesomorphism of detergent solutions on concentration.

To the best of our knowledge, the triple chain benzamides **5c** and **6c** represent the first amphiphilic carbohydrate derivatives which have thermotropic cubic mesophases consisting of inverse micelles (I_{II}-phase) [33]. This is especially remarkable, since the trialkoxybenzoyl group has been widely used as a taper-shaped structural unit in other amphiphiles. However most of the compounds reported display only columnar mesophases [23, 24, 34, 35].

Also the 3,4-dihexyloxybenzamide **4a** (table 2) has a cubic phase. This compound, with only two short chains, should not be able to form inverted micelles and therefore the cubic phase of this compound should differ from those of the triple chain compounds **5c** and **6c**, not only with respect to the different cubic lattices (**4a**: body centred, **5c**: primitive), but also in the shape of the aggregates forming the cubic arrangement. We assume that the cubic phase of the double chain amphiphile **4a** is a bicontinuous cubic phase (V_{II}-phase) appearing as an intermediate phase between lamellar and columnar structures. Thus it should be an interwoven network of branched cylinders or ribbons. The inverted cubic phase of the triple chain compound **5c** should consist of prolate-like micelles.

Furthermore it was possible to induce thermotropic columnar mesophases in the contact region between amphiphilic carbohydrates which form different mesophases. Hexagonal columnar mesophases were observed between lamellar phases and micellar cubic phases and also between structurally different types of cubic phases (V_{II}- and I_{II}-phases). This mesophase induction may be used as a tool for the structure determination of cubic phases of other amphiphilic compounds. This can be achieved simply by mixing the unknown cubic phases with a reference compound of known structure and observing the mesophases developing in the contact region. Careful interpretation of the results can give first hints about the structure of the unknown cubic phase[h].

This work was supported by the Deutsche Forschungsgemeinschaft and the Fonds der Chemischen Industrie.

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[h] The results can give only hints as to the phase structure and should be confirmed by additional methods. It should always be kept in mind that specific intermolecular interactions can give rise to undesired effects. Therefore, the chemical structures of the reference compound and the compounds investigated should be as similar as possible to exclude misleading interpretations.

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