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Tailoring thermotropic cubic mesophases: amphiphilic polyhydroxy derivatives†

Konstanze Borisch,[a] Siegmar Diele,[b] Petra Göring,[b] Horst Kresse[b] and Carsten Tschierske*[a]

[a]*Institut für Organische Chemie, Martin-Luther-Universität Halle-Wittenberg, Kurt-Mothes Str. 2, D-06120 Halle, Germany*

[b]*Institut für Physikalische Chemie, Martin-Luther-Universität Halle-Wittenberg, Mühlpforte 1, D-06108 Halle, Germany*

Novel amphiphilic polyhydroxy compounds [*N*-(3,4-dialkoxybenzoyl)-1-amino-1-deoxy-D-glucitols (glucamides), *N*-(3,4-dialkoxybenzoyl)-1-deoxy-1-methylamino-D-glucitols, *N*-(3,4,5-trialkoxybenzoyl)-1-deoxy-1-methylamino-D-glucitols (*N*-methylgucamides), 1-benzoylaminopropane-2,3-diols, 2-benzoylaminopropane-1,3-diols, 2-(3,4,5-tridodecyloxybenzoylamino)-2-(hydroxymethyl)propane-1,3-diol and (3,4,5-tridodecyloxybenzoyl)bis(2,3-dihydroxypropyl)amine] have been synthesized. Their thermotropic liquid crystalline phases were investigated by means of polarizing microscopy, differential scanning calorimetry and X-ray diffraction. Depending on the chain length, and the size of the hydrophilic polyhydroxy units, different mesophases have been found: smectic A phases (S_A), inverted bicontinuous cubic phases (Cub_{V2}, *Ia*3*d*), hexagonal columnar phases (Col_{H2}) and micellar cubic mesophases (Cub_{I2}, *Pn*3*m* or *P*43*n*). In strong analogy to lyotropic systems, the type of thermotropic mesophase depends on the ratio between the volume of the lipophilic moiety and the surface area of the hydrophilic moiety at the hydrophilic–lipophilic interface. The crossing from zero interface curvature (S_A phase) to the finite negative curvature of the inverted cylindrical aggregates of the columnar mesophase takes place *via* bicontinuous cubic mesophases. The cylindrical aggregates of the columnar mesophase are stable over a rather broad range of variation of the structural parameter. At a certain degree of the size of the lipophilic moiety in respect to the surface area of the hydrophilic group, however, the transition from the hexagonal columnar to a micellar cubic mesophase takes place. On the basis of proton conductivity measurements and from packing considerations we propose that this cubic lattice is built up by eight closed micelles per unit cell which have a rod-like shape and represent small segments of extended columns. Therefrom we can propose a model for the transformations between these different thermotropic mesophases.

Cubic mesophases represent ordered supermolecular arrangements which are optically isotropic. They are common in surfactant–solvent and lipid–solvent systems[1] and have attracted considerable interest due to their application in the pharmaceutical industry, their potential use in drug release systems and as templates for the preparation of mesoporous silicates and also because of their biological significance.[2] Well-defined cubic structures can also be found in amphiphilic block copolymers[3] and polyelectrolytes.[4]

As shown in Fig. 1 several different cubic phases can be observed in lyotropic systems when the concentration of the surfactant is changed. They can either occur as intermediate phases between lamellar and hexagonal columnar phases (bicontinuous cubic phases, V-phases), or between the hexagonal columnar phases and the micellar solutions (discontinuous cubic phases, I-phases).[5,6] The first type can be regarded as interwoven networks of branched columns, the second one has a different microstructure. It is assumed to consist of a cubic arrangement of closed spherical or nonspherical micelles. The value of the interface curvature between hydrophilic regions and lipophilic regions was recognized as the key factor determining the morphology of the polymolecular aggregates forming the mesophase (layers, columns, closed micelles),[7] whereas the sign of the interface curvature distinguishes between normal (type 1, the interface curvature is directed away from the regions with stronger cohesive interactions) and inverted phase types (type 2, the interface curvature is directed toward the regions with stronger cohesive forces). From a crystallographic point of view one can distinguish between different cubic lattices: primitive (*Pn*3*m*/Q^{224}, *Pm*3*n*/Q^{223}), body centred (*Ia*3*d*/Q^{230}, *Im*3*m*/Q^{229}) and face centred (*Fm*3*m*/Q^{225}, *Fd*3*m*/Q^{227}). The different types of cubic lattices found up to now in the different regions of the lyotropic phase sequence are collected in the principal phase diagram given in Fig. 1.[1,8–10] It has to be mentioned that additional intermediate mesophases (ribbon-phases, rhombohedral, tetragonal and ortorhombic phases[11,12] and isotropic hexagonal phases[13]) can be found between the lamellar phase and the normal and inverted columnar phases.

In contrast to lyotropic cubic systems relatively few thermotropic compounds with cubic phases are known. They have been found for nitro- and cyano-substituted biphenyl carboxylic acids,[14,15] dibenzoylhydrazides,[16] strontium soaps,[17] polycatenar compounds,[18–21] discotic molecules,[22,23] silver complexes,[24,25] a spherical compound,[26] a few calamitic compounds[27,28] and polypeptides.[29] In most cases, bicontinuous structures with a body centred lattice (*Ia*3*d*, *Im*3*m*) have been found for these cubic phases.[18,15] More recently different types of thermotropic cubic phases have been observed for amphiphilic oligoethylene imines,[30] diols[31,32] and carbohydrate derivatives.[33–36] In the case of double chain carbohydrates body centred cubic phases (*Ia*3*d*) were usually found whereas cubic phases with primitive cubic lattices (*Pm*3*n* or *P*43*n*) have only recently been detected for the thermotropic phases of some triple chain amphiphilic carbohydrates[36] and diol compounds[32] and also for some dendrimers.[37] From packing considerations it was concluded that the cubic phases of these compounds should represent inverted micellar cubic mesophases.

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* E-mail: coqfx@mlucom.urz.uni-halle.de

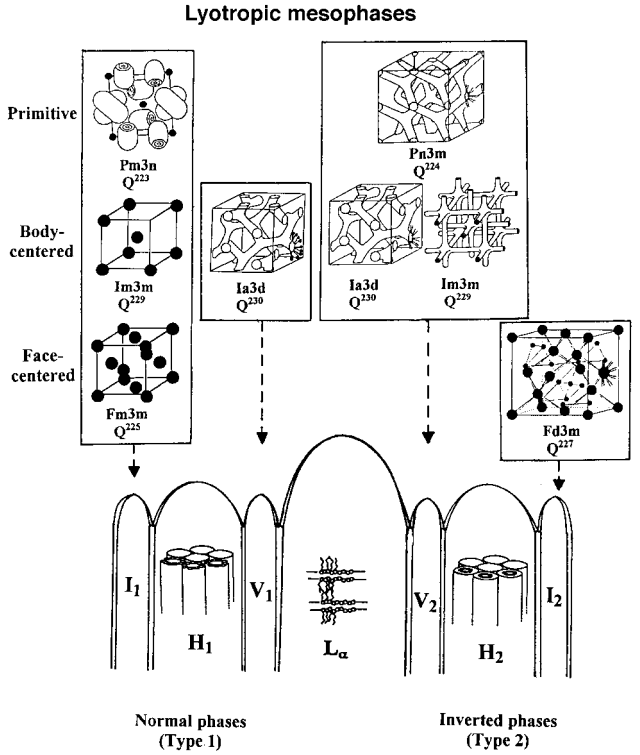
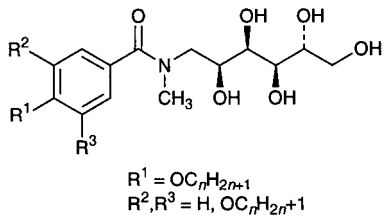


Fig. 1 Schematic representation of the major lyotropic liquid crystalline phase types occurring in detergen–solvent and lipid–solvent systems depending on the solvent concentration (refs. 1,8); abbreviations: L_α = lamellar α-phase, V = bicontinuous cubic mesophase, H = hexagonal columnar phase, I = discontinuous (micellar) cubic phase; subscripts: 1 = normal phase (type 1, the interface curvature is directed away from the regions with stronger cohesive interactions), 2 = inverted phases (type 2, the interface curvature is directed toward the regions with stronger cohesive forces). The positions of the known types of lyotropic cubic phases in the ideal phase diagram are shown together with their space-groups and space-group numbers. Curiously, some inverse systems exhibit phase sequences which are not in accord with this figure. It is unknown why in some systems the sequences H_2–V_2 or V_2–L_α occur on increasing the surfactant concentration (ref. 1). The 'rod-like' versions of the bicontinuous cubic phases are shown. They can also be regarded as bilayers draped on the underlying minimal surfaces (refs. 1,41). Additional to the shown cubic phases a chiral cubic phase with the space group $P4_332$ (Q^{212}) was found in a ternary lipid–protein–water system (ref. 9). Recently, a novel variant of the cubic phases with the space group *Im*3 has been found in a ternary lyotropic system between a rectangular and a lamellar phase (ref. 10).



It seems that the mesophases of the pure carbohydrate- and polyhydroxy-amphiphiles represent thermotropic analogues of the different lyotropic mesophases occurring in detergent–solvent systems. In order to confirm this analogy, we have initiated a systematic study of the influence of slight variations of the lipophilic and the polar regions of amphiphilic polyhydroxy compounds on the appearance of the different types of thermotropic cubic mesophases.‡ For this purpose we have synthesized novel double chain and triple chain glucamides, *N*-methylglucamides, 2,3-dihydroxypropylamides and some related acylated amino alcohols with different numbers of alkyl chains and hydroxy groups.[39,40] The results of the investigation of these compounds are summarized in this report.

Results and Discussion

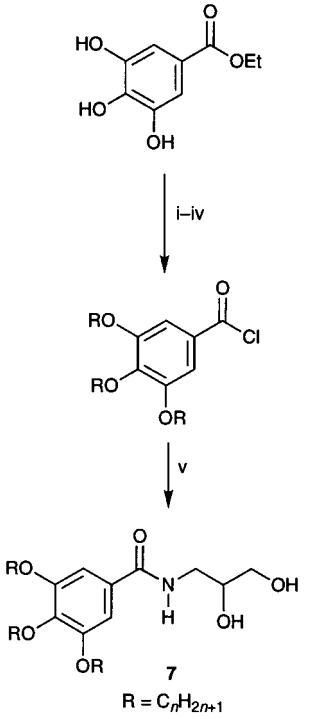
Syntheses

The homologous *N*-benzoyl-1-amino-1-deoxy-D-glucitol derivatives **1**, *N*-benzoyl-1-deoxy-1-methylamino-D-glucitols **2** and **3** were synthesized according to the procedure given for the hexyl and dodecyl derivatives.[36] The other materials were synthesized by aminolysis of substituted benzoyl chlorides with an excess of 1-aminopropane-2,3-diol (compounds **5–7**) (Scheme 1), 2-aminopropane-1,3-diol (compounds **8** and **9**) and 2-amino-2-(hydroxymethyl)propane-1,3-diol (compound **10**) respectively. The tetraol **11** was obtained by aminolysis of 3,4,5-tridodecyloxybenzoyl chloride with diallylamine, followed by OsO_4-catalyzed dihydroxylation of the olefinic double bonds. The final compounds were purified by column chromatography and repeated crystallization. Details are given in the Experimental part.

Amphiphilic carbohydrate derivatives

Optically isotropic mesophases of double chain carbohydrates—bicontinuous cubic phases. At first we investigated the homologues series of the double chain glucamides **1** and the analogous *N*-methylglucamides **2** (Tables 1 and 2). In both series of compounds optically isotropic mesophases were found for one or two compounds with a medium chain length.

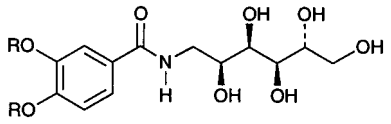
In the case of the glucamides **1** the pentyloxy derivative **1/5** and the hexyloxy derivative **1/6** have optically isotropic mesophases. The isotropic mesophase of **1/6** has recently been investigated and it was found that this phase is a cubic mesophase with a body centred lattice (*Ia3d*; a_{cub} = 8.31 nm at 175 °C).[36] The lower homologues (compounds **1/4** and **1/5**) display smectic A phases (beside an isotropic mesophase in the case of **1/5**) and the higher homologue **1/7** with two



Scheme 1 *Reagents and condition*: i, RBr, K_2CO_3, cyclohexanone; ii, KOH, H_2O, EtOH; iii, H_2O, H^+; iv, $SOCl_2$; v, DMF, DMAP, 2,3-dihydroxypropylamine

‡ In a related study the influence of the alkyl chain size on the lyotropic mesophase structure of 1-alkanoyl-1-deoxy-1-methylamino-D-glucitols has been investigated (ref. 38).

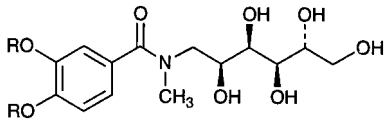
Table 1 Transition temperatures and associated enthalpy values (lower lines; in italics) of the *N*-(3,4-dialkoxybenzoyl)-1-amino-1-deoxy-D-glucitols **1**[a]



compound	R	T/°C ΔH/kJ mol^{-1}
1/4	C_4H_9	K 174 (S_A 156) Iso *66.3* *0.7*
1/5	C_5H_{11}	K 172 (M 162 S_A 168) Iso *68.7* *0.5*
1/6[b,c]	C_6H_{13}	K 172 Cub_{V2} 185 (Col_{H2} 185) Iso *73.5* *0.7*
1/7	C_7H_{15}	K 169 Col_{H2} 203 Iso *72.9* *1.1*
1/9	C_9H_{19}	K 166 Col_{H2} 239 Iso *94.8* *2.6*
1/12[b]	$C_{12}H_{25}$	K 162 Col_{H2} 254 Iso *91.2* *0.9*

[a]Abbreviations: K = crystalline solid, S_A = smectic A phase, Col_{H2} = inverted hexagonal columnar mesophase, Cub_{V2} = inverted bicontinuous cubic mesophase, M = optically isotropic (probably cubic) mesophase of unknown structure, Iso = isotropic liquid; values in parentheses refer to metastable (monotropic) mesophases. In the compound numbering **X/Y**, **X** represents the compound type, and **Y** the length of the alkyl chain. [b]Ref. 36. [c]The texture of a columnar mesophase is only detected on cooling (see text).

Table 2 Transition temperatures, associated enthalpy values (lower lines) and lattice parameter of the smectic phase (d_{lam}) and of the hexagonal columnar mesophases (a_{hex}) at the measurement temperatures (lower lines in brackets) of the *N*-(3,4-dialkoxybenzoyl)-1-deoxy-1-methylamino-D-glucitols **2**[a]



compound	R	T/°C ΔH/kJ mol^{-1}	d_{lam}/nm (T/°C)	a_{hex}/nm (T/°C)
2/6[b]	C_6H_{13}	K 93 S_A 130 Iso 29.5 0.7	3.19 (120)	—
2/7[c]	C_7H_{15}	K 96 M 118 (S_A 118) Iso *27.5* *0.4*	—	—
2/8	C_8H_{17}	K 87 Col_{H2} 155 Iso *18.5* *0.1*	—	4.27 (80)
2/9	C_9H_{19}	K 68 Col_{H2} 174 Iso *18.0* *0.2*	—	4.46 (80)
2/12[b]	$C_{12}H_{25}$	K 54 Col_{H2} 194 Iso *22.5* *0.9*	—	4.88 (120)
2/16	$C_{16}H_{33}$	K 82 Col_{H2} 194 Iso *45.7* *1.2*	—	—

[a]Abbreviations as in Table 1. [b]Ref. 36. [c]The fan-like texture of a S_A phase is only detected on cooling (see text). The value of the transitions to the isotropic liquid was found by microscopic investigations. In the DSC heating cycle an endotherm was detected at 125 °C.

heptyloxy chains has a hexagonal columnar mesophase. Thus, with respect to the chain length, the cubic phase occurs as an intermediate phase between the S_A phase and the inverted hexagonal columnar phase. In analogy to lyotropic systems it can therefore be concluded that this cubic phase should be an inverted bicontinuous cubic phase (V_2-phase). It should consist of two interwoven yet non-connected networks of cylinders containing the hydrogen bonding networks of the carbohydrate

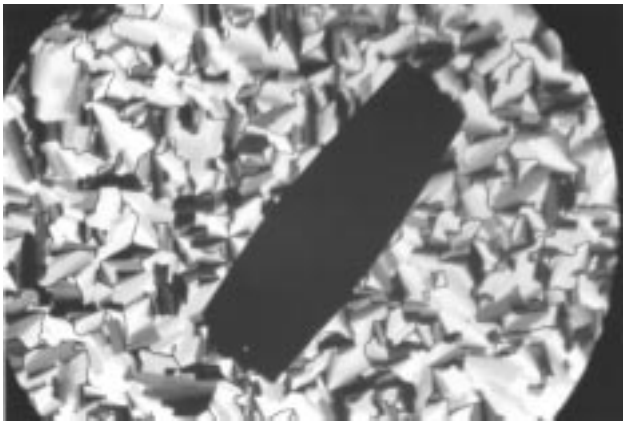


Fig. 2 Optical photomicrograph (crossed polarizers) of the isotropic mesophase of compound **1/6** growing from the hexagonal columnar mesophase at 184 °C

head groups. They are connected three-by-three and separated by a gyroid minimal surface[41] within the lipophilic continuum of the alkyl chains (see Fig. 1).

More detailed investigation of the cubic to liquid phase transition has been done. On heating, a direct transition from the cubic phase to the liquid state occurs at 185 °C. On fast cooling from the liquid however, a spherulitic texture occurs at the same temperature. This texture is typical for hexagonal columnar phases and is identical with the optical texture of the hexagonal columnar mesophases of the glucamides **1/7–1/12**. Immediately after this phase transition took place the cubic phase appear as highly viscous isotropic domains with cornered boundaries (see Fig. 2). These domains grow rapidly and coalesce to a homogeneous area. On re-heating a direct transition from the highly viscous cubic phase to the fluid liquid was found at 185 °C. The spherulitic texture cannot be found on very slow cooling (<2 K min^{-1}). Obviously the formation of the cubic phase can be supercooled and therefore a columnar phase is observed first as a metastable (monotropic) phase. Interestingly the clearing temperature of the columnar mesophase and the transition temperature of the cubic phase to the liquid state seem to be identical ($\Delta T < 1$ K).

The lower homologue **1/5** displays an enantiotropic smectic A phase which turns into an isotropic mesophase on cooling below 162 °C. This phase transition can also be supercooled (down to 158 °C); however this S_A phase is a thermodynamically stable (enantiotropic) phase in the temperature range between 162 and 168 °C. Remarkably, the appearance of the isotropic domains is different from that of the Cub_{V2} phase of compound **1/6**. They appear as circular domains (the same texture as shown in Fig. 3). Due to rapid crystallization of this compound no X-ray investigation of its isotropic mesophase can be carried out to confirm a cubic structure.

No transition to an optically isotropic mesophase was found on cooling the S_A phase of the dibutoxy derivative **1/4** down to 146 °C. At this temperature rapid crystallization sets in.

Also the *N*-methylglucamide **2/7** has an optically isotropic mesophase. This mesophase again occurs intermediate between a smectic A phase (compound **2/6**) and a hexagonal columnar phase (compound **2/8**). Comparing the homologous series of the glucamides **1** with the *N*-methylglucamides **2** indicates that in the series of the *N*-methylglucamides **2** the isotropic mesophase occurs at a longer chain length. Therefore, one can conclude that the *N*-methylglucamide group is slightly larger than the glucamide group. However, it has to be considered that the transition temperatures of the glucamides are significantly higher than those of the corresponding *N*-methylglucamides (due to the additional hydrogen bonding of the N—H group) and therefore their alkyl chains have an increased

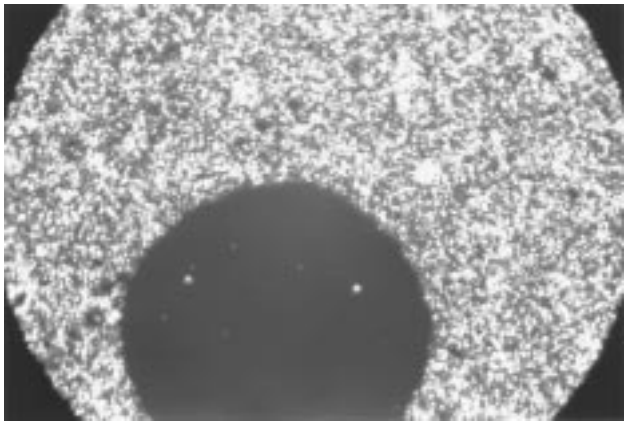


Fig. 3 Optical photomicrograph (crossed polarizers) of the optically isotropic mesophase of compound **2/7** growing from the S_A phase at 90 °C

mobility which gives rise to a larger effective volume of their lipophilic region.

Also for the *N*-methylglucamide **2/7** a direct transition from the isotropic mesophase to the liquid state can only be found in the heating cycles. On cooling from the liquid state a fan-like texture with homeotropic regions and oily streaks can be observed and not a spherulitic texture as found in the case of the glucamide **1/6**. These textural features are typical for a smectic A phase. Immediately after the appearance of the S_A phase small circular and optically isotropic domains occur (see Fig. 3), which rapidly grow and coalesce with formation of a uniform optically isotropic area. The viscosity of these circular domains is significantly larger than that of the surrounding S_A phase. Thus, it can easily be distinguished from the homeotropically aligned regions of the S_A phase. On re-heating only a direct transition to the fluid isotropic phase was found at 118 °C and no S_A phase occurs. Obviously, the formation of the isotropic mesophase is again kinetically hindered. This kinetic effect points to a three dimensional structure of this mesophase.

This and the high viscosity of the isotropic mesophase represent typical features of cubic mesophases.

The inverted bicontinuous structure of the isotropic mesophase of compound **1/6** can be confirmed by miscibility experiments. The binary phase diagram of the system **2/7**–**3/12** is shown in Fig. 4.

Because the structural parameter continuously changes in the contact region between these two compounds, the meso-

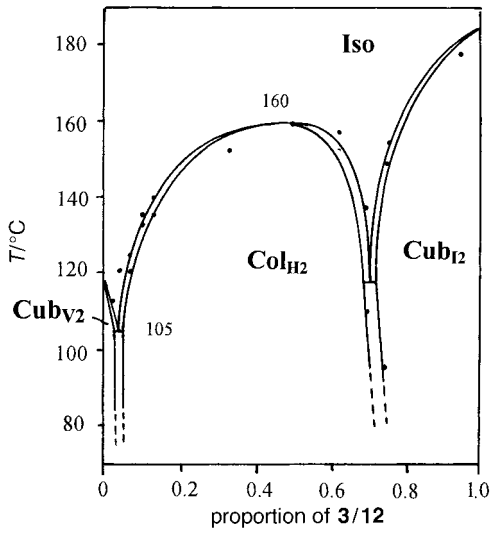


Fig. 4 Binary phase diagram of the system **2/7**–**3/12**

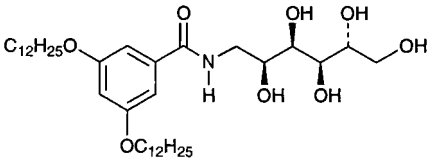
phase type also changes. In analogy to lyotropic systems (Fig. 1), an inverted hexagonal columnar phase (Col_{H2}) can be found between the isotropic mesophase of compound **2/7** and the inverted micellar cubic phase (Cub_{I2}) of compound **3/12**. Thus, the same type of binary phase diagram as for compound **1/6** (forming a Cub_{V2} phase) with **3/12** was found.[36] Therefore, we conclude that this isotropic mesophase should represent an inverted bicontinuous network structure (Cub_{V2}). However, due to the low number and intensity of scatterings in the SAXRS we were not yet able to determine the type of cubic lattice.

Micellar cubic mesophases of triple chain carbohydrate amphiphiles. Now let us turn to triple chain compounds, which have an increased size of the lipophilic moiety and should form strongly curved aggregates. The phase transition temperatures of the triple chain *N*-methylglucamides **3** are summarized in Table 3.

In contrast to the analogous double chain compounds **2**, in this homologous series the compounds with a short and medium chain length (**3/6** and **3/8**) have a hexagonal columnar mesophase and an optically isotropic mesophase occurs on elongation of the alkyl chains, *i.e.* on increasing the interface curvature between polar and lipophilic regions. Therefore it can be concluded that this phase represents a cubic phase consisting of a cubic arrangement of closed inverted micelles.

The nonyloxy derivative **3/9** and the decyloxy derivative **3/10** display a columnar–cubic dimorphism. In contrast to the double chain carbohydrates, the triple chain glucamides have the cubic phases as high temperature mesophases above the hexagonal columnar phase. The X-ray pattern of these cubic phases can be indexed on the basis of primitive cubic lattices (*e.g.* $a_{cub} = 7.93$ nm at 121 °C for compound **3/9**). The space group can be either *Pm*3*n* or *P*43*n*. Interestingly, the cubic lattice parameter amounts to approximately twice the hexagonal lattice parameter of the hexagonal columnar phase below (*e.g.* $a_{hex} = 4.08$ nm at 90 °C for **3/9**). The same relationship between the hexagonal and cubic lattice parameter is found for other triple chain amphiphiles and will be discussed below.

***N*-(3,5-Didodecyloxybenzoyl)-1-amino-1-deoxy-D-glucitol 4/12.** The 3,5-disubstituted glucamide **4/12** shows exclusively a hexagonal columnar mesophase.

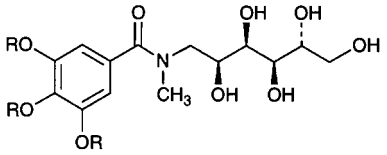


K_1 45 K_2 87 Col_{H2} 175 Iso
6.5 *40.4* *0.5*

If one compares this compound with the related 3,4-disubstituted double chain compound **1/12** and the triple chain carbohydrates **3/12**, a significantly lower mesophase stability is found for **4/12**. The absence of a cubic mesophase leads to the assumption that this 3,5-disubstitution pattern gives rise to behaviour more similar to the 3,4-disubstituted compound than to the triple chain compound **3/12.**

The columnar mesophases of the double and triple chain glucamides. The hexagonal columnar phases of the amphiphilic polyhydroxy compounds consist of extended aggregates of hydrogen bonding networks surrounded by the molten alkyl chains. Comparison of the hexagonal lattice parameter of the double chain compound **2/8** ($a_{hex} = 4.27$ nm at $T = 80$ °C) and the triple chain compound **3/8** ($a_{hex} = 3.83$ nm at $T = 80$ °C) which have both the same chain length and the same molecular

Table 3 Transition temperatures, associated enthalpy values (lower lines) and lattice parameter of the hexagonal columnar mesophases (a_{hex}) and the cubic mesophases (a_{cub}) at the measurement temperatures (lower lines in brackets) of the *N*-(3,4,5-trialkoxybenzoyl)-1-deoxyl-1-methylamino-D-glucitols **3**[a]



compound	R	T/°C ΔH/kJ mol^{-1}	a_{hex}/nm (T/°C)	a_{cub}/nm (T/°C)
3/6[b]	C_6H_{13}	K 94 Col_{H2} 145 Iso *40.2* *1.3*	3.49 (100)	—
3/8	C_8H_{17}	K 75 Col_{H2} 147 Iso *48.8* *0.7*	3.83 (80)	—
3/9	C_9H_{19}	K 50 Col_{H2} 102 Cub_{I2} 143 Iso *62.1* *1.1* *0.8*	4.08 (52)	7.93 (121)
3/10	$C_{10}H_{21}$	K 59 Col_{H2} 89[c] Cub_{I2} 158 Iso *55.2* *0.3* *0.6*	—	—
3/12[b]	$C_{12}H_{25}$	K 75 Cub_{I2} 185 Iso *112.3* *1.2*	—	8.55 (90)

[a]Abbreviations: Cub_{I2} = inverted micellar cubic mesophase, other abbreviations as in Table 1. [b]Ref. 36. [c]This phase transition refers to the heating cycle. On cooling the cubic–columnar transition occurs is at 56 °C.

length (L = 2.55 nm as estimated from CPK models) indicates that the (average) diameter of the columns of the double chain compound is significantly larger then the diameter of the columns of the triple chain compound. Further examples are collected in Table 4. 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 with a thickness (h) of 0.45 nm was estimated according to eq. (1).

$$n = (a^2/2)\sqrt{3}h(N_A/M)\rho \quad (1)$$

The parameter a is the hexagonal lattice parameter, N_A the Avogadro constant and M the molecular mass. The estimated values of n amount to about 5 for the triple chain compounds **3/6–3/8**. This value corresponds to those values found in columnar phases of other tapered polyhydroxy compounds.[42–45]

Obviously, the three alkoxy chains can effectively surround the polar regions of the hydrogen bonding networks and a nearly circular shape of the columns can be assumed.

In contrast, in the columnar mesophases of all investigated double chain compounds (**1/8–1/12**) a much larger number, about eight molecules per slice, was observed. This number is larger than found for other wedge shaped polyhydroxy amphiphiles. Probably the columns of these double chain compounds are non-circular (see Fig. 5). Taking into account the fact that the orientation of the deformations can change along the axis of the columns and/or that they are arranged randomly oriented in the hexagonal lattice, the cross sections of these aggregates should be circular on average, giving rise to the typical scattering pattern of hexagonal columnar phases.[46]

Table 4 Comparison of the hexagonal lattice parameter (a_{hex}), the molecular length (L) (as determined from CPK models assuming an all *trans*-conformation of the chains) and the number of molecules (n) arranged in each slice of the columnar mesophases (with a high of 0.45 nm) of the double chain and triple chain amphiphiles with the same length of the alkyl chains

		triple chain amphiphile			double chain amphiphile		
R	L/nm	Comp.	a_{hex}/nm (T/°C)	n	Comp.	a_{hex}/nm (T/°C)	n
$C_8H_{17}O$	2.55	**3/8**	3.83 (80)	5.0	**2/8**	4.27 (80)	7.7
$C_9H_{19}O$	2.7	**3/9**	4.08 (52)	5.4	**2/9**	4.46 (80)	8.0
$C_6H_{13}O$	1.9	**7/6**	3.13 (75)	4.7	**6/6**	3.48 (84)	7.2

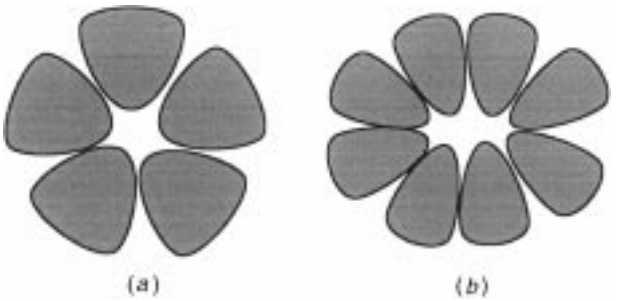


Fig. 5 Cross section of the columnar mesophases of (*a*) the triple chain amphiphiles and (*b*) the double chaing amphiphiles

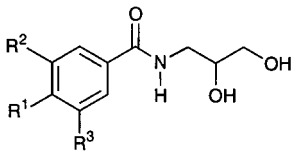
Amphiphilic diols, triols and tetraols

Single chain, double chain and triple chain 1-benzamidopropane-2,3-diol derivatives. In a next step we decided to investigate the influence of the structure of the hydrophilic parts of the amphiphilic molecules on their mesophase behaviour. At first we synthesized and investigated single chain, double chain and triple chain 1-benzamidopropane-2,3-diol derivatives (compounds **5–7** in Table 5). These compounds are structurally related to the glucamides **1–3**, but they have only two instead of five hydroxy groups. In this way the number of attractive hydrogen bonds is decreased and consequently the phase transition temperatures are shifted to lower values.

As in the case of related D-glucamides,[35] three different types of mesophases were found for the 1-benzamidopropane-2,3-diol derivatives depending on the number of alkyl chains. Compound **5/12** with only one dodecyloxy chain forms a smectic A phase, a hexagonal columnar phase (Col_{H2}) is found for the double chain compound **6/12** and a cubic phase was detected for compound **7/12** with three dodecyloxy chains (Table 5).

The inverted micellar structure of the cubic phase of compound **7/12** was at first proven by means of miscibility experiments. The optical microscopic picture of the contact region between the smectic phase of **5/12** and the cubic phase

Table 5 Transition temperatures, associated enthalpy values (lower lines) and lattice parameter of the smectic phase (d), of the hexagonal columnar mesophases (a_{hex}) and the cubic mesophases (a_{cub}) at the measurement temperatures (lower lines in brackets) of the 1-benzoylaminopropane-2,3-diols **5–7**[a]



compound	R^1	R^2	R^3	T/°C ΔH/kJ mol^{-1}	d/nm (T/°C)	a_{hex}/nm (T/°C)	a_{cub}/nm (T/°C)
5/12	$OC_{12}H_{25}$	H	H	K_1 80 K_2 89 S_A 132 Iso *11.6 36.6 0.8*	4.03 (85)	—	—
6/6	OC_6H_{13}	OC_6H_{13}	H	K 79 Col_{H2} 87 Iso *22.0 0.3*	—	3.48 (84)	—
6/12	$OC_{12}H_{25}$	$OC_{12}H_{25}$	H	K 98 Col_{H2} 148 Iso *60.4 1.4*	—	4.2 (105)	—
7/6	OC_6H_{13}	OC_6H_{13}	OC_6H_{13}	K 49 Col_{H2} 91 Iso *23.6 1.4*	—	3.13 (75)	—
7/7	OC_7H_{15}	OC_7H_{15}	OC_7H_{15}	K 46 Col_{H2} 92 Iso *25.7 1.5*	—	3.16 (45)	—
7/8	OC_8H_{17}	OC_8H_{17}	OC_8H_{17}	K 59 Col_{H2} 74[b] Cub_{I2} 85[c] Iso *38.6 0.6 0.4*	—	3.33 (50)	6.89 (75)
7/9	OC_9H_{19}	OC_9H_{19}	OC_9H_{19}	K 49 Cub_{I2} 104[d] Iso *24.4 0.3*	—	—	7.06 (65)
7/12	$OC_{12}H_{25}$	$OC_{12}H_{25}$	$OC_{12}H_{25}$	K_1 45 K_2 69 Cub_{I2} 126 Iso *36.0 11.5 0.7*	—	—	7.94 (45)

[a]Abbreviations as in Tables 1–3. [b]This phase transition refers to the cooling cycle. On heating the columnar–cubic phase transition is observed at 79 °C due to the 'overheating' of this phase transition. [c]On cooling the cubic phase appears at 77 °C. [d]This value was found by microscopic investigations. In the DSC–heating cycle an endotherm was detected at 107 °C.

of compound **7/12** between crossed polarizers is shown in Fig. 6. In the contact region between the cubic phase of the triple chain diol **7/12** and the smectic phase of the single chain diol **5/12** a hexagonal columnar phase is induced (large spherulites in the centre of Fig. 6). The detailed phase diagram of the system **5/12–7/12**, obtained by investigation of binary mixtures, is shown in Fig. 7.

The induction of a columnar mesophase in the contact region of these two compounds is an important piece of evidence for the proposed inverse micellar structure of the cubic mesophase of the triple chain diol **7/12**. The X-ray diffraction pattern of this cubic phase can be indexed on the basis of a primitive cubic lattice (*Pm*3*n* or *P*43*n*) with a lattice parameter $a_{cub} = 7.45$ nm at $T = 90$ °C.

The dependence of the mesophase type on the chain length (see Table 5) was investigated for the triple chain diols **7**. The

Fig. 6 Optical photomicrograph (crossed polarizers) of the Col_{H2} phase developing in the contact region between the micellar cubic Cub_{I2} phase of compound **7/12** (optical isotropic region at the right-hand side) and the S_A phase of compound **5/12** (left-hand side) at 95 °C

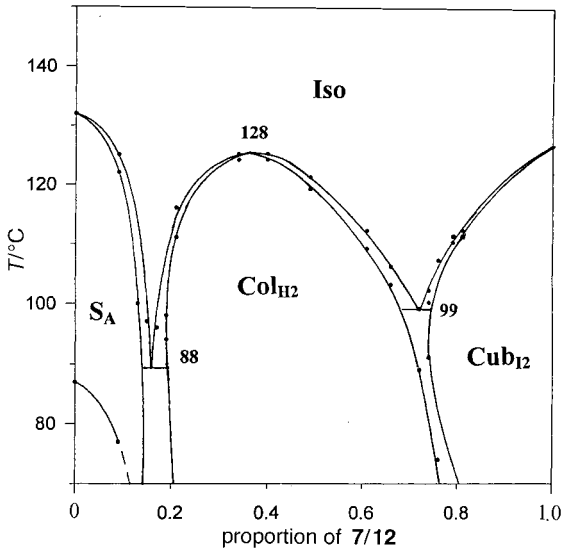


Fig. 7 Binary phase diagram of the system **5/12–7/12**

short chain diols **7/6** and **7/7** have columnar mesophases; a columnar/cubic dimorphism was found for the octyloxy derivative **7/8**. Fig. 8 shows the transition from the hexagonal columnar phase to the cubic mesophase as it can be seen on heating compound **7/8** between crossed polarizers.

The higher homologues **7/9** and **7/12** have exclusively cubic mesophases. The cubic phases of **7/8** and **7/12** have the same kind of primitive cubic lattice (*Pm*3*n* or *P*43*n*). As an example the diffraction pattern of the cubic phase of compound **7/12** is shown in Fig. 9.

The DSC heating and cooling traces of compound **7/8** are shown in Fig. 10. It indicates that the crystalline state can be strongly supercooled. Even after prolonged storage only partial crystallization takes place. Therefore any heating cycle after

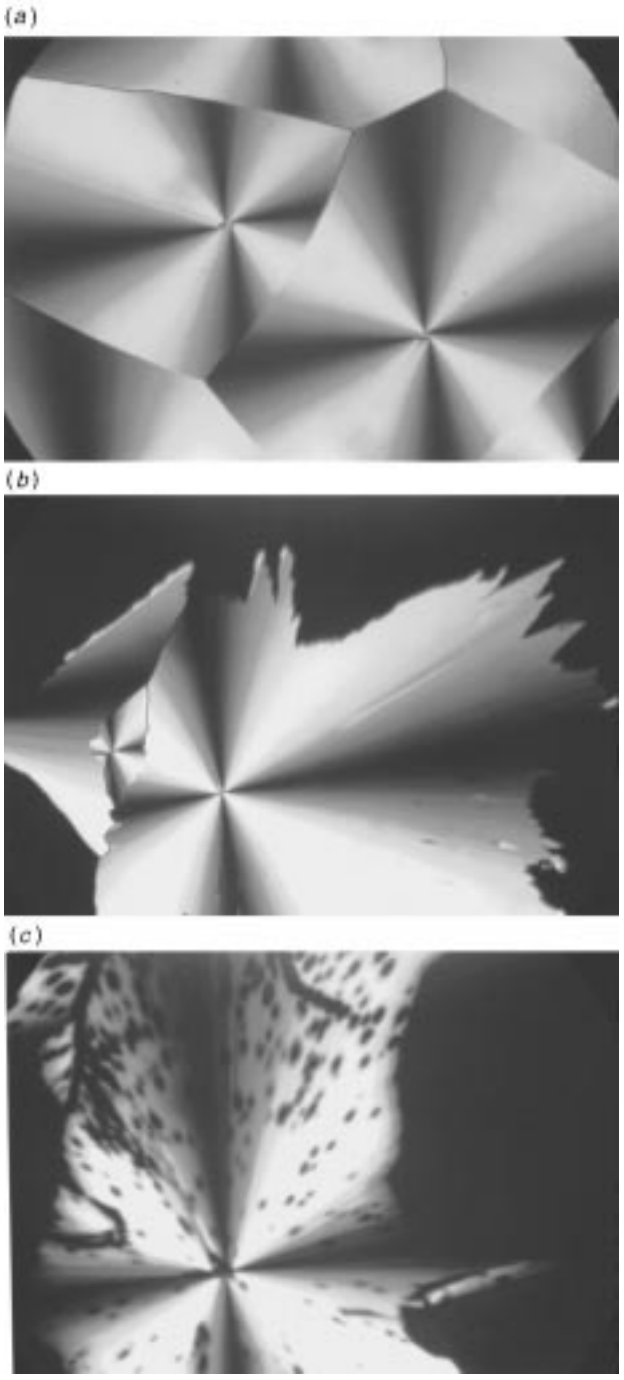


Fig. 8 Optical photomicrographs (crossed polarizers) of the Cub_{I2} phase developing on heating the Col_{H2} phase of compound **7/8**. (*a*) Col_{H2} phase at 74 °C; Cub_{I2} phase (black regions) growing into the Col_{H2} phase at (*b*) 78 and (*c*) 79 °C (the reduced sharpness of this picture is due to the rapid growing of the cubic domains during the time of exposition).

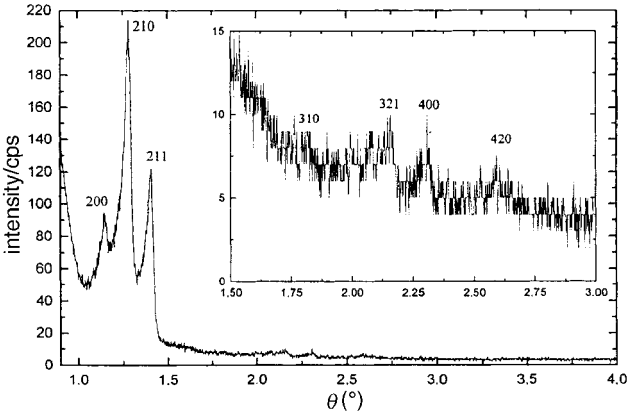


Fig. 9 X-Ray pattern of the micellar cubic mesophase of compound **7/12** at 70 °C

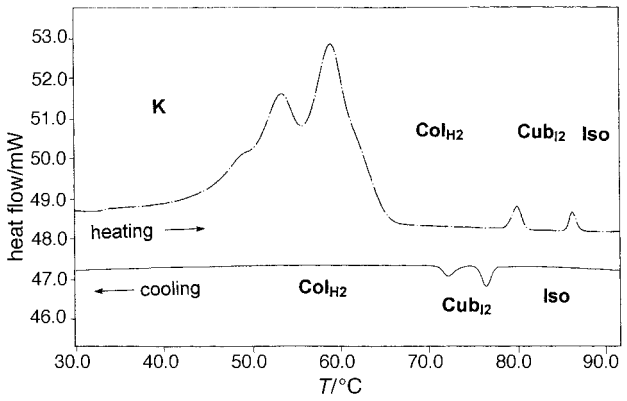


Fig. 10 DSC heating and cooling trace of **7/8** (10 K min^{-1})

the first one gives significantly lower melting enthalpies and sometimes also different melting temperatures. All melting temperatures and enthalpies given in Tables 1–3, 4, 6 and 8 refer to the first heating cycles.

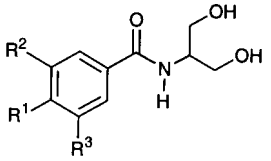
Due to the three dimensional structure of the cubic phases the formation of these isotropic phases can be kinetically hindered. On cooling, the transition from the liquid to the cubic phase is often supercooled and on heating the transition from the columnar to the cubic phase can be overheated. Therefore different values can result for the heating and cooling cycles depending on the heating–cooling rates (see for example Fig. 10). If the cubic phase represents the high temperature mesophase, only on cooling does the transition from the three-dimensional structure (cubic phase) to the columnar mesophase occur without supercooling effects. Therefore, the values for this transition were taken from the cooling cycles. All other reported values correspond to the heating cycles.

There is another interesting point concerning the transition from the optically isotropic mesophases to the fluid liquid state. This transition can be detected microscopically by the sudden increase of the fluidity. In many cases however (*e.g.* compound **7/9**) the corresponding endotherm in the DSC heating curve is detected at higher temperatures then observed by microscopy. The reason for this behaviour is not clear. However, related phenomena were reported for several other compounds with transitions from three-dimensional ordered mesophases to isotropic liquids[47] (cubic phases of long chain nitro-biphenyl carboxylic acids, TGB-phases and blue phases of chiral liquid crystals).

Comparing the homologous series of the triple diols **7** with that of the corresponding triple chain *N*-methylglucamides **3** reveals that the same phase sequence is found in both series of compounds; however the transition from the columnar to the cubic phase occurs in the series of compounds **7** which already have a chain length of eight instead of nine or ten carbon atoms. This means, that the effective size of the 1-amidopropane-2,3-diol unit at the hydrophilic–lipophilic interface should be slightly smaller than that of the 1-methyl-amidoglucitol group. This is also evident from the comparison of the double chain compounds **2/6** and **6/6**. The *N*-methylglucamide **2/6** is a smectic liquid crystal whereas the diol **6/6** forms a columnar mesophase.

2-Benzamidopropane-1,3-diols. In the next step, two selected examples of 2-benzamidopropane-1,3-diols (compounds **8/6** and **9/12**, Table 6) have been synthesized. These compounds

Table 6 Transition temperatures and associated enthalpy values (lower lines) of the 2-benzoylaminopropane-1,3-diol **8/6** and **9/12**[a]



compound	R^1	R^2	R^3	T/°C ΔH/kJ mol^{-1}
8/6	OC_6H_{13}	OC_6H_{13}	H	K_1 64 K_2 108 [Cub_{V2} 50 (Col_{H2} 50)] Iso *4.5* *31.6*
9/12	$OC_{12}H_{25}$	$OC_{12}H_{25}$	$OC_{12}H_{25}$	K 67 (Col_{H2} 62[b]) Cub_{I2} 104[c] Iso *39.3* *2.1* *0.4*

[a]Abbreviations as in Tables 1–3. [b]This phase transition refers to the cooling cycle. On heating the columnar–cubic phase transition is observed at 72 °C due to the 'overheating' of this phase transition. [c]Found by microscopic investigations. In DSC heating cycles the phase transition occurs at 108 °C.

differ from the 1-benzamidopropane-2,3-diols **6/6** and **7/12** only in the position of their hydroxy groups to each other.

Interestingly, the triple chain 1,3-diol **9/12** displays a columnar/cubic dimorphism, whereas the corresponding 1,2-diol **7/12** with the same number and length of the chains forms a micellar cubic phase exclusively. This means that the 1,3-diol unit represents a significantly larger hydrophilic group than the corresponding 1,2-diol unit. This is in accordance with the different molecular areas found in the densely packed monomolecular layers of 1,2-diols (0.21 nm^2 per molecule)[48] and 1,3-diols (0.24 nm^2 per molecule)[49] at the air–water interface. The double chain compound **8/6** has only monotropic liquid crystalline properties. On rapid cooling from the isotropic melt, at first the typical texture of a hexagonal columnar phase appears, which at 50 °C immediately turns into an isotropic phase. On heating, a direct transition into the isotropic liquid takes place and no columnar phase can be detected. This behaviour is analogous to that found for the double chain glucamide **1/6** and therefore it is very likely that the optically isotropic mesophase of this compound represents a bicontinuous cubic phase (Cub_{V2} phase). Due to the monotropic character and the rapid crystallization, no X-ray investigations were possible to confirm the proposed cubic structure of this phase.

Because the lipophilic residues of the double chain 1,3-diol **8/6** and the related 1,2-diol **6/6** are identical, the occurrence of a bicontinuous cubic phase instead of a columnar phase again can be explained by the larger size of the 1,3-diol unit of **8/6** in comparison to the 1,2-diol unit of compound **6/6**.

Investigation of the micellar cubic phases of the triple chain amphiphiles. In order to prove the inverted micellar structure of the cubic phases of the triple chain amphiphiles, proton conductivity investigations have been carried out. If the cubic phases under discussion are built up by closed inverted micelles, then the hydrogen bonding networks between the head-groups should be located inside the micelles and therefore they should be isolated from each other by the lipophilic regions of the alkyl chains. In a bicontinuous cubic phase and in the columnar phase however, the hydrogen bonding network should be extended over large distances. Since these hydrogen bonding networks can act as proton conductors, the conductivity of non-oriented samples is expected to decrease at the transition from the hexagonal columnar to the inverted micellar cubic mesophase. Those compounds with a columnar/cubic dimorphism are therefore especially useful for these investigations.

Indeed, a strong decrease of the specific conductivity is found in all cases investigated at the transition from the hexagonal columnar phase to the cubic phase. The dependence of the specific conductivity κ on the inverse temperature $1/T$ for compounds **7/8** and **9/12** is shown in Fig. 11. This experimental finding strongly supports the inverted micellar structure of the cubic phases of the triple chain amphiphiles under investigation.

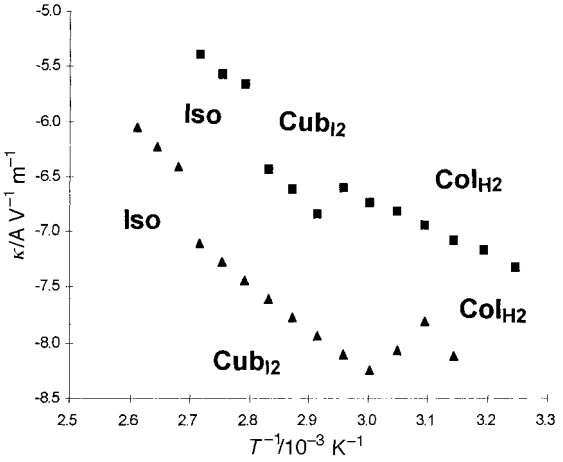


Fig. 11 Plot of the specific conductivity κ of (■) **7/8** and (▲) **9/12** *versus* the reciprocal absolute temperature $1/T$

The next question concerns the shape of these closed micelles. Spherical, oblate and prolate shapes are under discussion for micellar cubic phases of lyotropic systems. If one assumes the existence of spherical micelles, than one micelle is located in each corner of a simple cubic unit cells (see Fig. 12). Therefore, the diameter of these micelles should be equal to the cubic lattice parameter. In this case the diameter of the micelles would be significantly larger than twice the length of the single molecules (see Table 7). This contradiction between molecular size and cell dimensions is often observed in cubic phases. Therefore, Fontell *et al.*[50] suggested an alternative structure for lyotropic micellar cubic phases located between the micellar solution and the normal hexagonal phase (Cub_{I1}) of lyotropic systems. They proposed that the cubic unit cell is built up by eight short rod-like aggregates with an axial ratio of less than 2 : 1. 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. The micelles centred at the corners and in the centre should be statistically disordered or freely rotating, whereas those at the surfaces are only rotationally disordered.[50]

We propose that the thermotropic cubic phases of the triple chain compounds **3/9, 3/10, 3/12** and **7/8–7/12** have the same structure. However, they are built up by *inverted* micelles and appear in the *absence of any solvent*. Thus, the cubic lattice should be built up by non-spherical micelles (short rods), each consisting of approximately 40–50 individual molecules. In order to organize these molecules in each of these closed

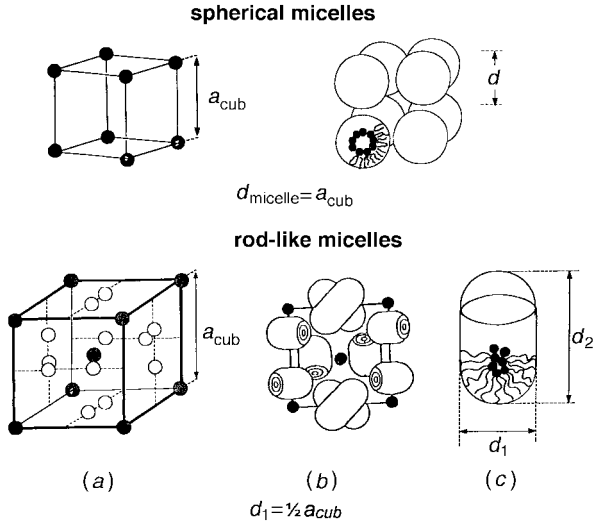


Fig. 12 Two possible models of the structure of the thermotropic inverted micellar cubic mesophases Cub_{I2} of the compounds under discussion. The model based on rod-like closed micelles refers to a proposal by Fontell *et al*. for normal micellar cubic phases in lyotropic systems (ref. 50). (*a*) Arrangement of the micelles in the primitive cubic lattice. The rod-like micelles are indicated a circles, the statistically disordered micelles at the corners and in the centre are indicated by black dots. (*b*) View upon a face of the cubic lattice. (*c*) Schematic presentation of a rod-like micelle.

Table 7 Comparison of the lattice parameter of the micellar cubic mesophases (a_{cub}) and of the hexagonal columnar mesophases (a_{hex}) of the compounds **3/9**, **7/8**, **9/12** and **10/12**, which have a Cub_{I2}/Col_{H2} dimorphism[a]

compound	a_{cub}/nm (T/°C)	L/nm	n_{cell}	d_1/nm	n_{mic}	a_{hex}/nm (T/°C)
3/9	7.93 (121)	2.7	414	40	52	4.08 (52)
7/8	6.89 (75)	2.2	340	3.4	42	3.33 (50)
10/12	7.99 (67)	2.6	395	4.0	49	4.05 (40)

[a]Abbreviations: L = molecular length according to CPK models (extended all *trans*-conformation of the alkyl chains), n_{cell} = number of molecules in each unit cell of the cubic lattice (calculated using the equation $n = V_{cell}(N_A/M)\rho$ and assuming a density of $\rho = 1$ g cm^{-3}); n_{mic} = number of molecules in each rod-like micelle of the cubic mesophase.

cylindrical micelles they should have an axial ratio d_2/d_1 in the order of about 1.5 : 1.[51]

The proposed model (Fig. 12) requires that two micelles are arranged side by side at each cell surface of the cubic lattice. Therefore the short diameter of these rods (d_1) should amount to not more than one half of the cubic lattice parameter a_{cub}. Indeed in all investigated compounds with a Col_{H2}/Cub_{I2} dimorphism the hexagonal lattice parameter of the columnar phases amounts to approximately half the lattice parameter of the cubic mesophase (see Table 7). Thus, in all these cases the short diameter (d_1) of the rod-like micelles in the cubic mesophase is nearly identical to the diameter of the columns in the hexagonal columnar mesophase below. Therefrom we can conclude that these short rod-like micelles should result from the collapse of the extended columns of the Col_{H2} phase into small segments. Probably the arrangement of eight rod-like micelles in each unit cell of such a cubic lattice represents an energetic minimum which could be stabilized, for example by quadrupole interactions.[50] If spherically micelles were to form, their packing coefficient in a simple cubic lattice would amount to only 0.52. Therefore it can be expected that spherical micelles should preferably arrange in a body centred (0.68) or in a face centred lattice (0.74) which allow more efficient packing. Such arrangements have indeed been found in lyotropic systems for some micellar cubic phases of the type 1;[8] however they have never been observed for an inverted system (see Fig. 1). Interestingly, *Pm*3*n* lattices have also been found for thermotropic cubic phases of cone-shaped dendrimers.[37] Here eight nearly spherical (spherical and tetrahedral distorted) micelles were found in the cubic lattice. Because these compounds differ in chemical structure, they could not be compared directly with the compounds described herein.

Triple chain benzamides with other hydrophilic groups. The influence of the hydrophilic group on the mesomorphic properties is obvious from the comparison of the tridodecyloxy benzamides **3/12, 7/12, 9/12, 10/12** and **11/12** given in Table 8. All compounds have the same hydrophobic residue and differ only in the number of hydroxy groups and their position with respect to each other.

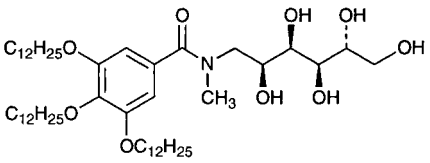
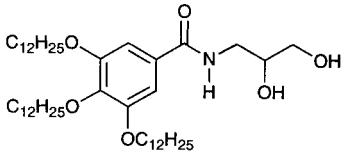
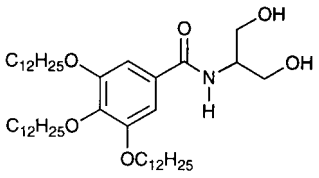
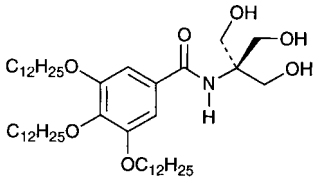
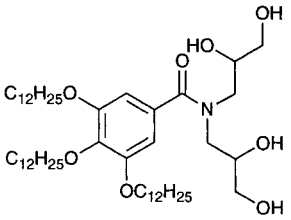
It clearly shows that increasing the number of hydroxy groups destabilizes the inverted micellar cubic mesophase in favour of the hexagonal columnar phase. Hence, the tetraol **11/12** displays exclusively a columnar phase in contrast to the triol **10/12** and the diols **7/12** and **9/12**.

The important influence of the position of the hydroxy groups has already been discussed for the diols **7/12** and **9/12**. Comparing the *N*-methylglucamide **3/12** with the tetraol **11/12** reveals that, despite the fact that the number of hydroxy groups of **3/12** is larger, it has a micellar cubic mesophase whereas the tetrahydroxy compound **11/12** is only columnar. In the case of **11/12** the connecting position is between the four hydroxy groups. Here, all hydroxy groups are positioned close to the hydrophilic–lipophilic interface giving rise to a large area of the hydrophilic group at the interface. In the open chain carbohydrate derivative **3/12** however, the lipophilic residue is attached to a terminal position of the polar group. In this case, not all hydroxy groups are located directly at this interface and therefore the hydrophilic group appears to be smaller. This clearly shows that not only the number of hydroxy groups but also their position in respect to the lipophilic–hydrophilic interface is an important factor governing the hydrophilic–lipophilic interface curvature and thus the type of mesophase. Therefore, the area at the polar–apolar interface which is occupied by the *N*-methylglucamide group is even nearly comparable with that of the 1-amidopropane-2,3-diol group in compound **6/12**. The small diameter of the *N*-methylglucamido head group may be a result of the hindered rotation about the —CH(OH)—CH(OH)— bonds which is much more difficult than that of alkyl or oxyethylene groups, due to the larger steric interactions of OH compared to H.

Conclusions

In summary we have investigated the influence of structural variations of amphiphilic benzamides on their thermotropic phase behaviour. Lamellar (S_A), columnar (Col_{H2}) and two types of cubic mesophases (Cub_{V2} and Cub_{I2}) have been detected. The same diversity of different microstructures as known for lyotropic lipid–water systems,[1] for polycatenar thermotropic compounds[18] and for polyelectrolytes[4] can be found in the thermotropic phase sequence of these amphiphilic polyhydroxy derivatives. In strong analogy to lyotropic systems the type of thermotropic mesophase depends on the surface area of the hydrophilic parts of these molecules at the hydrophilic–lipophilic interface and the size of the lipophilic groups, which determine the mean interface curvature. The cylindrical aggregates of the columnar mesophase are stable over a rather broad range of variation of the structural parameter. The average diameter of the columns of the double chain compounds is significantly larger than that of the corresponding triple chain compounds. This could be due to a non-circular

Table 8 Comparison of the thermotropic phase transition temperatures of the 3,4,5-tridodecyloxybenzamides **3/12**, **7/12**, **9/12**, **10/12** and **11/12** with different hydrophilic groups[a] and enthalpy values of the phase transitions of compounds **10/12** and **11/12** (lower lines)

		T/°C ΔH/kJ mol^{-1}					
compound	structure	K		Col_{H2}		Cub_{12}	Iso
3/12[b]		●	75	—	—	● 185	●
7/12		●	45/69	—	—	● 127	●
9/12		●	67	●	(62)	● 104[c]	●
10/12		●	63[d] *65.3*	●	64 *1.3*	● 87[e] *1.0*	●
11/12		●	40 *67.8*	●	142 *1.6*	— —	●

[a]Abbreviations: see Table 1. [b]Ref. 36. [c]Obtained by microscopic investigations. In the DSC heating cycles the phase transition occurs at 108 °C. [d]Only partial crystallization was found. [e]Obtained by microscopic investigations, in the DSC heating cycle the phase transition was found at 93 °C.

cross section of the cylinders formed by the double chain compounds. On introduction of the third chain, an efficient packing in circular columns becomes possible. At a certain degree of the interface curvature however, the transition from the hexagonal columnar to a micellar cubic mesophase takes place. This can be found for compounds consisting of three long aliphatic chains and a polar group with a small area at the polar–non-polar interface. On the basis of proton conductivity measurements and from packing considerations we propose that this cubic lattice is built up by eight closed micelles which have a rod-like shape and represent small segments of the extended columns of a columnar mesophase.

The transition from the cylinders of the columnar phase to the non-curved lamellar phase occurs *via* bicontinuous cubic mesophases (Cub_{V2}).

Therefrom we can propose a model for the transition between the different mesophases. If one starts with the inverted columnar mesophase of the triple chain compounds, the decrease in the number of alkyl chains gives rise to a noncircular cross section of the columns. Probably there is a strong undulation within the columns of the double chain compounds which increases with decreasing chain length. These columns can fuse with formation of an interwoven network structure ordered in a three-dimensional cubic lattice. On further decreasing the chain length, the interface curvature becomes zero by turning into a smectic layer structure.

On increasing the alkyl chain length of appropriate triple chain compounds, density fluctuations could occur in the polar regions of the columns leading to a disruption of the hydrogen bonding networks within the columns with formation of short rod-like micelles. Probably the arrangement of eight such rod-like micelles in a primitive cubic lattice represents an energetic minimum which allows an efficient packing of the molecules. The analogy of these thermotropic mesophases with the inverted phases of lyotropic systems is obvious. The hydrogen bonding networks correspond to the aqueous regions in

detergent–water systems. It can therefore be assumed that all other phases which are known from lyotropic systems[1,8,10] can also be observed in the thermotropic phase sequence of appropriately designed polyhydroxy amphiphiles. Furthermore the mesomorphic organization of these compounds can be largely influenced by addition of protic solvents.[36] Because these protic solvents are incorporated into the head group region, significant changes of the mesophase types occur. Thus the molecules reported represent typical examples of amphotropic compounds,[52] which bridge the gap between the thermotropic liquid crystalline phases of rod-like, polycatenar and disc-like molecules on the one hand and the lyotropic mesophases of detergent–water mixtures on the other.

Experimental section

Techniques

Transition temperatures (given in °C throughout) were measured using a Mettler FP 82 HT hot stage and control unit in conjunction with a Nikon Optiphot 2 polarizing microscope and these were confirmed using differential scanning calorimetry (Perkin-Elmer DSC-7, heating and cooling rate: 10 K min^{-1}). The accuracy of the transition temperatures is about ± 0.5 K. All phase transitions, except those of cubic and crystalline phases, were completely reversible. If not otherwise stated the transition enthalpies of enantiotropic phases were obtained from the first heating scan, those of monotropic phases from the second heating scan. The accuracy of the enthalpy values is about ± 0.2 kJ mol^{-1}.

X-Ray diffraction patterns were obtained on a Guinier diffractometer (Huber) operating with a Cu-Kα_1 beam. The refraction patterns were recorded with a film camera.

Phase diagrams were established by the penetration experiments and by investigation of binary mixtures. These mixtures were investigated by optical polarizing microscopy between crossed polarizers.

Measurements of the conductivity (AC, $f = 1$ kHz) were carried out on cooling the samples from the isotropic melt in a microcapacitor ($A = 2$ cm^2, $d = 0.02$ cm) without orientation.

Materials

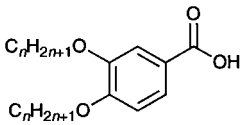
Ethyl 4-hydroxybenzoate, ethyl 3,4-dihydroxybenzoate (Aldrich), ethyl 3,4,5-trihydroxybenzoate (Fluka), 1-aminoethanol (Merck), 1-aminopropane-2,3-diol (Merck), 2-aminopropane-1,3-diol (Aldrich), 2-amino-2-hydroxymethylpropane-1,3-diol (Serva), 1-deoxy-1-methylamino-D-gluctitol (Aldrich), diallylamine (Aldrich) and the 1-bromoalkanes (Merck) were used as obtained.

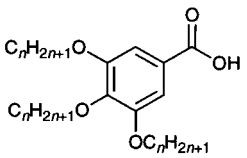
The substituted carboxylic acids were obtained by etherification of ethyl 3,4-dihydroxybenzoate or ethyl 3,4,5-trihydroxybenzoate with alkyl bromides and potassium carbonate in cyclohexanone,[53] followed by saponification. The resulting alkoxybenzoic acids were purified by repeated crystallization from methanol. The melting temperatures of the benzoic acids, together with the reported values from the literature are collected in Table 9.

Confirmation of the structures of the products was obtained by ^1H and ^{13}C NMR spectroscopy (Varian Gemini 200, Varian Unity 400 and Varian Unity 500) and mass spectrometry (Intectra GmbH, AMD 402, electron impact, 70 eV). *J* Values are given in Hz throughout.

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 correct combustion analyses were not obtained for some compounds. In these cases the water content was determined by Karl–Fischer titration[54] and the amount of absorbed water was taken into account. The purity of all compounds was checked by thin layer chromatography (Merck, silica gel 60 F 254). Measurements of the optical rotation were carried out with a Perkin-Elmer Polarimeter 341.

Table 9 Melting temperatures of the 3,4-dialkoxybenzoic acids and the 3,4,5-trialkoxybenzoic acids and reference values from the literature





	mp/°C			mp/°C		
n	found	reported	ref.	found	reported	ref.
4	146					
5	142					
6	130	128	19*d*	39		
7	129	127	19*d*	41	40–41	55
8	123	125	19*d*	53		
9	124	124	19*d*	46		
10	127	123	19*d*	51		
12	120	121	19*d*	56	58	56

Synthesis of the benzamides 1–10

The appropriately substituted benzoic acid (1.5 mmol) and thionyl chloride (10 ml) were refluxed for 3 h. The excess thionyl chloride was distilled off and the residue was dissolved in dry methylene chloride (15 ml). The amino alcohol (15 mmol) was dissolved in dry dimethylformamide (30 ml) under inert conditions and DMAP (10 mg) was added. To this solution the benzoyl chloride dissolved in methylene chloride was added with stirring at 80 °C. The resulting mixture was heated at this temperature for 4 h and was stirred for additional 24 h at room temp. Afterwards the solvent was evaporated *in vacuo* and the residue was purified by crystallization or by column chromatography.

***N*-(3,4-Dibutoxybenzoyl)-1-amino-1-deoxy-D-glucitol 1/4.** Synthesized from 3,4-dibutyloxybenzoic acid (0.4 g, 1.5 mmol) and 1-amino-1-deoxy-D-glucitol (2.7 g, 15 mmol). The residue was crystallized from methanol; Yield: 0.37 g (57%), K 174 (S_A 156) Iso (found: C, 58.78; H, 7.91; N, 3.39. $C_{21}H_{35}O_8N$ requires: C, 58.73; H, 8.21; N, 3.26%); $[\alpha]_D^{20}$ 3.3 (*c* 0.3, chloroform); δ_H (200 MHz; [$^2H_6$]DMSO; 27 °C) 0.96 (6H, t, J 6, CH_3), 1.44–1.49 (4H, m, CH_2), 1.69–1.76 (4H, m, CH_2), 3.40–3.78 (8H, m, C*H*OH, CH_2OH, CH_2N), 4.05 (4H, t, *J* 4, OCH_2), 4.32 (2H, t, *J* 4, OH), 4.44 (2H, m, OH), 4.87 (1H, d, *J* 5, OH), 7.0 (1H, d, *J* 7, H-ar), 7.44 (2H, t, *J* 2, H-ar), 8.2 (1H, br, NH); δ_C (100 MHz; [$^2H_6$]DMSO; 27 °C) 166 (CO), 151, 148, 127, 121, 113 (C-ar), 72, 69, 68, 63 (CH_2OH, CHOH), 68 (CH_2), 43 (CH_2N), 31, 18 (CH_2), 14 (CH_3); *m*/*z* 429 (M^+ 5%).

***N*-(3,4-Dipentyloxybenzoyl)-1-amino-1-deoxy-D-glucitol 1/5.** Synthesized from 3,4-dipentyloxybenzoic acid (0.4 g, 1.5 mmol) and 1-amino-1-deoxy-D-glucitol (2.7 g, 15 mmol). The residue was crystallized from methanol; Yield: 0.34 g (50%), K 172 (M 162 S_A 168) Iso (found: C, 60.11; H, 8.49; N, 3.02. $C_{23}H_{39}O_8N$ requires: C, 60.36; H, 8.60; N, 3.06%); $[\alpha]_D^{30}$ 13.5 ($c = 0.2$, chloroform); δ_H (200 MHz; [$^2H_6$]DMSO; 27 °C) 0.88 (6H, t, *J* 6, CH_3), 1.32–1.48 (8H, m, CH_2), 1.64–1.74 (4H, m, CH_2), 3.41–3.78 (8H, m, C*H*OH, CH_2OH, CH_2N), 3.97 (4H, t, *J* 4, OCH_2), 4.30 (2H, t, *J* 4, OH), 4.44 (2H, dd, *J* 5, OH), 4.84 (1H, d, *J* 5, OH), 7.0 (1H, d, *J* 4, H-ar), 7.44 (2H, t, *J* 2, H-ar), 8.2 (1H, t, *J* 5, NH); δ_C (100 MHz; [$^2H_6$]DMSO; 27 °C) 168 (CO), 153, 149, 128, 122, 114 (C-ar), 73, 71, 70, 65 (CH_2OH, CHOH), 68 (CH_2), 41 (CH_2N), 30, 29, 23 (CH_2), 15 (CH_3); *m*/*z* 458 (M^{+1} 100%).

***N*-(3,4-Diheptyloxybenzoyl)-1-amino-1-deoxy-D-glucitol 1/7.** Synthesized from 3,4-diheptyloxybenzoic acid (0.5 g, 1.5 mmol) and 1-amino-1-deoxy-D-glucitol (2.7 g, 15 mmol). Crystallized twice from methanol; Yield: 0.40 g (52%), K 169 Col_{H2} 203 Iso; (found: C, 62.82; H, 8.94; N, 2.58. $C_{27}H_{47}O_8N$ requires: C, 63.12; H, 9.23; N, 2.73%); $[\alpha]_D^{20}$ 40 (*c* 0.3, chloroform); δ_H (500 MHz; [$^2H_6$]DMSO; 30 °C) 0.85 (6H, t, *J* 6, CH_3), 1.26–1.45 (16H, m, CH_2), 1.68–1.71 (4H, m, CH_2), 3.35–3.76 (8H, m, C*H*OH, C*H*$_2$OH, C*H*$_2$N), 3.97 (4H, q, *J* 5, OCH_2), 4.33 (2H, t, *J* 6, OH), 4.42 (1H, d, *J* 5, OH), 4.46 (1H, d, *J* 5, OH), 4.87 (1H, d, *J* 5, OH), 6.96 (1H, d, *J* 4, H-ar), 7.42 (2H, t, *J* 2, H-ar), 8.2 (1H, t, *J* 6, NH); δ_C (126 MHz; [$^2H_6$]DMSO; 30 °C) 166 (CO), 151, 148, 126, 120, 112 (C-ar), 72, 69, 68, 63 (CH_2OH, CHOH), 68 (CH_2), 31, 29, 28, 25, 22 (CH_2), 14 (CH_3); *m*/*z* 513 (M^+ 9.3%).

***N*-(3,4-Dinonyloxybenzoyl)-1-amino-1-deoxy-D-glucitol 1/9.** Synthesized from 3,4-dinonyloxybenzoic acid (0.6 g, 1.5 mmol) and 1-amino-1-deoxy-D-glucitol (2.7 g, 15 mmol). The residue was crystallized twice from chloroform–methanol, 10 : 1; Yield: 0.37 g (43%), K 166 Col_{H2} 239 Iso (found: C, 65.10; H, 9.72; N, 2.31. $C_{31}H_{55}O_8N$ requires: C, 65.35; H, 9.73; N, 2.46%); $[\alpha]_D^{20}$ 8.9 (*c* 0.8, chloroform); δ_H (500 MHz; [$^2H_6$] DMSO; 30 °C) 0.85 (6H, t, *J* 7, CH_3), 1.25–1.42 (24H, m, CH_2), 1.68–1.70 (4H, m, CH_2), 3.36–3.75 (8H, m, C*H*OH, C*H*$_2$OH, C*H*$_2$N), 3.98 (4H, q, *J* 6, OCH_2), 4.25 (2H, t, *J* 6, OH), 4.36 (1H, d, *J* 5, OH), 4.39 (1H, d, *J* 5, OH), 4.79 (1H, d, *J* 4, OH), 6.95 (1H, d, *J* 9, H-ar), 7.42 (2H, br, H-ar), 8.16 (1H, s, NH); δ_C (126 MHz; [$^2H_6$]DMSO; 30 °C) 166 (CO), 151, 148, 127, 120, 113 (C-ar), 72, 71, 70, 69, 68, 63 (CH_2OH, CHOH), 68 (CH_2), 29, 25, 22 (CH_2), 14 (CH_3); *m*/*z* 569 (M^+ 10%).

***N*-(3,4-Diheptyloxybenzoyl)-1-deoxy-1-methylamino-D-glucitol 2/7.** Synthesized from 3,4-diheptyloxybenzoic acid (0.5 g, 1.5 mmol) and 1-deoxy-1-methylamino-D-glucitol (2.9 g, 15 mmol). Purified by column chromatography (eluent chloroform–ethanol, 10 : 3) and crystallization from methanol; Yield: 0.21 g (27%), K 96 M 118 (S_A 118) Iso (found: C, 62.62; H, 9.34; N, 2.47. $C_{28}H_{49}O_8N$ requires: C, 62.89; H, 9.58; N, 2.72%); $[\alpha]_D^{20}$ −3.0 (*c* 1, methanol); δ_H (500 MHz; [$^2H_6$]DMSO; 30 °C) 0.86 (6H, t, *J* 6, CH_3), 1.26–1.39 (16H, m, CH_2), 1.65–1.72 (4H, m, CH_2), 2.95 (3H, s, NCH_3), 3.30–3.56 (8H, m, C*H*OH, C*H*$_2$OH, C*H*$_2$N), 3.92–3.97 (4H, m, OCH_2), 4.27–4.44 (4H, br, OH), 4.86 (1H, br, OH), 6.94 (3H, br, H-ar); δ_C (126 MHz; [$^2H_6$]DMSO; 30 °C) 170 (CO), 149, 148, 129, 120, 112 (C-ar), 72, 68, 63 (CH_2OH, CHOH), 68 (CH_2), 31 (NCH_3), 29, 28, 25, 22 (CH_2), 14 (CH_3); *m*/*z* 527 (M^+ 1.8%).

***N*-(3,4-Dioctyloxybenzoyl)-1-deoxy-1-methylamino-D-glucitol 2/8.** Synthesized from 3,4-dioctyloxybenzoic acid (0.6 g, 1.5 mmol) and 1-deoxy-1-methylamino-D-glucitol (2.9 g, 15 mmol). Purified by column chromatography (eluent chloroform–ethanol, 10 : 3) and crystallized from methanol; Yield: 0.28 g (34%), K 87 Col_{H2} 155 Iso (found: C, 63.69; H, 9.62; N, 2.32. $C_{30}H_{53}O_8N\cdot 0.5H_2O$ requires: C, 63.98; H, 9.66; N, 2.49%); $[\alpha]_D^{20}$ −5.9 (*c* 1, methanol); δ_H (500 MHz; [$^2H_6$]DMSO; 30 °C) 0.85 (6H, t, *J* 6, CH_3), 1.25–1.43 (20H, m, CH_2), 1.67–1.72 (4H, m, CH_2), 2.95 (3H, s, NCH_3), 3.30–3.55 (8H, m, C*H*OH, C*H*$_2$OH, C*H*$_2$N), 3.92–3.97 (4H, m, OCH_2), 4.27–4.45 (4H, br, OH), 4.87 (1H, br, OH), 6.95 (3H, br, H-ar); δ_C (126 MHz; [$^2H_6$]DMSO; 30 °C) 170 (CO), 149, 148, 129, 120, 113 (C-ar), 71, 68, 63 (CH_2OH, CHOH), 68 (CH_2), 31 (NCH_3), 29, 26, 22 (CH_2), 14 (CH_3); *m*/*z* 555 (M^+ 2.1%).

***N*-(3,4-Dinonyloxybenzoyl)-1-deoxy-1-methylamino-D-glucitol 2/9.** Synthesized from 3,4-dinonyloxybenzoic acid (0.6 g, 1.5 mmol) and 1-deoxy-1-methylamino-D-glucitol (2.9 g, 15 mmol). Purified by columnn chromatography (eluent chloroform–ethanol, 10 : 3) and crystallized twice from methanol; Yield: 0.25 g (29%), K 68 Col_{H2} 174 Iso (found: C, 64.53; H, 9.72; N, 2.17. $C_{32}H_{57}O_8N\cdot 0.5H_2O$ requires: C, 64.83; H, 9.86; N, 2.36%); $[\alpha]_D^{20}$ −5.8 (*c* 1, methanol); δ_H (500 MHz; [$^2H_6$]DMSO; 30 °C) 0.85 (6H, t, *J* 7, CH_3), 1.25–1.43 (24H, m, CH_2), 1.65–1.72 (4H, m, CH_2), 2.95 (3H, s, NCH_3), 3.32–3.56 (8H, m, C*H*OH, C*H*$_2$OH, C*H*$_2$N), 3.92–3.97 (4H, m, OCH_2), 4.27–4.44 (4H, br, OH), 4.87 (1H, br, OH), 6.95 (3H, br, H-ar); δ_C (126 MHz; [$^2H_6$]DMSO; 30 °C) 171 (CO), 149, 148, 129, 120, 113 (C-ar), 71, 70, 68, 63 (CH_2OH, CHOH), 68 (CH_2), 31 (NCH_3), 29, 25, 22 (CH_2), 14 (CH_3); *m*/*z* 583 (M^+ 3.6%).

***N*-(3,4-Dihexadecyloxybenzoyl)-1-deoxy-1-methylamino-D-glucitol 2/16.** Synthesized from 3,4-dihexadecyloxybenzoic acid (0.9 g, 1.5 mmol) and 1-deoxy-1-methylamino-D-glucitol (2.9 g, 15 mmol). The residue was crystallized twice from methanol; Yield: 0.60 g (51%), K 82 Col_{H2} 194 Iso (found: C, 68.42; H, 10.90; N, 1,79. $C_{46}H_{85}O_8N\cdot 1.5H_2O$ requires: C, 68.45; H, 10.99; N, 1.74%); $[\alpha]_D^{30}$ 2.1 (*c* 0.6, chloroform); δ_H (400 MHz; [$^2H_6$]DMSO; 40 °C) 0.84 (6H, t, *J* 6, CH_3), 1.22–1.42 (52H, m, CH_2), 1.67–1.70 (4H, m, CH_2), 2.95 (3H, s, NCH_3), 3.39–3.55 (8H, m, C*H*OH, C*H*$_2$OH, C*H*$_2$N), 3.92–3.97 (4H, m, OCH_2), 4.24–4.41 (4H, br, OH), 4.82 (1H, d, *J* 5, OH), 6.94 (3H, br, H-ar); δ_C (126 MHz; [$^2H_6$]DMSO; 40 °C) 171 (CO), 149, 148, 129, 120, 113 (C-ar), 72, 71, 70, 68, 63 (CH_2OH, CHOH), 31 (NCH_3), 29, 25, 22, 21 (CH_2), 14 (CH_3); *m*/*z* 779 (M^+ 0.6%).

***N*-(3,4,5-Trioctyloxybenzoyl)-1-deoxy-1-methylamino-D-glucitol 3/8.** Synthesized from 3,4,5-trioctyloxybenzoic acid (0.8 g, 1.5 mmol) and 1-deoxy-1-methylamino-D-glucitol (2.9 g, 15 mmol). Purified by column chromatography (eluent chloroform–ethanol, 10 : 3); Yield: 0.26 g (25%), K 75 Col_{H2} 147 Iso (found: C, 66.04; H, 10.11; N, 1.94. $C_{38}H_{69}O_9N\cdot 0.3H_2O$ requires: C, 66.21; H, 10.18; N, 2.03%); $[\alpha]_D^{20}$ −0.5 (*c* 1, methanol); δ_H (500 MHz; [$^2H_6$]DMSO; 30 °C) 0.86 (9H, t, *J* 6, CH_3), 1.25–1.42 (30H, m, CH_2), 1.62–1.70 (6H, m, CH_2), 2.94 (3H, s, NCH_3), 3.30–3.48 (8H, m, C*H*OH, C*H*$_2$OH, C*H*$_2$N), 3.86 (2H, t, *J* 6, OCH_2), 3.92 (4H, t, *J* 6, OCH_2), 4.28–4.45 (4H, br, OH), 4.88 (1H, br, OH), 6.62 (2H, br, H-ar); δ_C (50 MHz; [$^2H_6$]DMSO; 27 °C) 166 (CO), 152, 138, 132, 119 (C-ar), 72, 71, 68, 63 (CH_2OH, CHOH), 68 (CH_2), 51 (CH_2N), 31 (NCH_3), 30, 29, 26, 22 (CH_2), 14 (CH_3); *m*/*z* 683 (M^+ 15%).

***N*-(3,4,5-Trinonyloxybenzoyl)-1-deoxy-1-methylamino-D-glucitol 3/9.** Synthesized from 3,4,5-trinonyloxybenzoic acid (0.8 g, 1.5 mmol) and 1-deoxy-1-methylamino-D-glucitol (2.9 g, 15 mmol). Purified by column chromatography (eluent chloroform–methanol, 10 : 1); Yield: 0.16 g (15%), K 50 Col_{H2} 102 Cub_{I2} 143 Iso (found: C, 68.13; H, 10.67; N, 2.06. $C_{41}H_{75}O_9N$ requires: C, 67.83; H, 10.41; N, 1.93%); $[\alpha]_D^{20}$ −6.1 (*c* 1, methanol); δ_H (200 MHz; [$^2H_6$]DMSO; 27 °C) 0.87 (9H, t, *J* 6, CH_3), 1.28–1.71 (42H, m, CH_2), 2.96 (3H, s, NCH_3), 3.49–3.52 (8H, m, C*H*OH, C*H*$_2$OH, C*H*$_2$N), 3.87–3.98 (6H, m, OCH_2), 4.25–4.55 (4H, br, OH), 4.80–5.05 (1H, br, OH), 6.60–6.80 (2H, br, H-ar); δ_C (100 MHz, [$^2H_6$]DMSO, 27 °C) 166 (CO), 152, 138, 132, 103 (C-ar), 72, 71, 68, 63 (CH_2OH, CHOH), 31 (N-CH_3), 30, 29, 28, 25, 22 (CH_2), 14 (CH_3); *m*/*z* 725 (M^+ 28.6%).

***N*-(3,4,5-Tridecyloxybenzoyl)-1-deoxy-1-methylamino-D-glucitol 3/10.** Synthesized from 3,4,5-tridecyloxybenzoic acid (0.9 g, 1.5 mmol) and 1-deoxy-1-methylamino-D-glucitol (2.9 g, 15 mmol). The residue was purified by chromatography (eluent chloroform–methanol, 10 : 1) and crystallized twice from acetone; Yield: 0.19 g (15%), K 59 Col_{H2} 89 Cub_{I2} 158 Iso (found: C, 68.60; H, 10.54; N, 1.89. $C_{44}H_{81}O_9N$ requires: C, 68.80; H, 10.63; N, 1.82%); $[\alpha]_D^{30}$ −5.6 (*c* 1, methanol); δ_H (200 MHz;

[$^2H_6$]DMSO; 27 °C) 0.87 (9H, t, *J* 6, CH_3), 1.27–1.72 (48H, m, CH_2), 2.96 (3H, s, NCH_3), 3.44–3.52 (8H, br, C*H*OH, CH_2OH, CH_2N), 3.84–3.98 (6H, m, OCH_2), 4.31–4.51 (4H, br, OH), 4.85–5.05 (1H, br, OH), 6.60–6.76 (2H, br, H-ar); δ_C (100 MHz, [$^2H_6$]DMSO, 27 °C) 165 (CO), 152, 138, 132, 104 (C-ar), 72, 71, 68, 63 (CH_2OH, CHOH), 31 (N-CH_3), 30, 29, 25, 22 (CH_2), 14 (CH_3); *m*/*z* 767 (M^+ 11.4%).

***N*-(3,5-Didodecyloxybenzoyl)-1-amino-1-deoxy-D-glucitol 4/12.** Synthesized from 3,5-didodecyloxybenzoic acid (0.7 g, 1.5 mmol) and 1-amino-1-deoxy-D-glucitol (2.7 g, 15 mmol). Crystallized twice from methanol; Yield: 0.10 g (10%), K_1 45 K_2 87 Col_{H2} 175 Iso (found: C, 67.44; H, 10.59; N, 2.0. $C_{37}H_{67}O_8N\cdot 0.2H_2O$ requires: C, 67.59; H, 10.33; N, 2.13%); $[\alpha]_D^{20}$ 2.3 (*c* 1, methanol); δ_H (500 MHz; [$^2H_6$]DMSO; 30 °C) 0.84 (6H, t, *J* 6, CH_3), 1.23–1.39 (36H, m, CH_2), 1.65–1.69 (4H, m, CH_2), 3.35–3.74 (8H, m, C*H*OH, CH_2OH, CH_2N), 3.95 (4H, t, *J* 6, OCH_2), 4.32 (2H, t, *J* 4, OH), 4.41 (1H, d, *J* 5, OH), 4.46 (1H, d, *J* 5, OH), 4.85 (1H, d, *J* 5, OH), 6.56 (1H, s, H-ar), 6.96 (2H, s, H-ar), 8.28 (1H, t, *J* 5, NH); δ_C (50 MHz; [$^2H_6$]DMSO; 27 °C) 166 (CO), 159, 136, 106, 104 (C-ar), 72, 71, 69, 68, 63 (CH_2OH, CHOH), 68 (CH_2), 31, 29, 25, 22 (CH_2), 14 (CH_3); *m*/*z* 653 (M^+ 5.0%).

1-(4-Dodecyloxybenzoylamino)propane-2,3-diol 5/12. Synthesized from 4-dodecyloxybenzoic acid (0.5 g, 1.5 mmol) and 1-aminopropane-2,3-diol (1.4 g, 15 mmol). The residue was purified twice by column chromatography (eluent: chloroform–ethanol 10 : 3; chloroform–methanol 10 : 1). Yield: 0.38 g (33%); K_1 80 K_2 89 S_A 132 Iso (found C, 69.74; H, 9.85; N, 3.70. $C_{22}H_{37}O_4N$ requires: C, 69.62; H, 9.83; N, 3.69%); δ_H (200 MHz, $CDCl_3$; 27 °C) 0.85 (3H, t, *J* 6, CH_3), 1.2–1.5 (18H, m, CH_2), 2.2–2.4 (2H, m, CH_2), 3.1–3.2 (2H, m, OH), 3.6 (5H, m, CH_2NH, C*H*OH, CH_2OH), 3.95 (2H, t, *J* 6,OCH_2), 6.55 (1H, t, *J* 3, NH), 6.9 (2H, d, *J* 2, H-ar), 7.7 (2H, d, *J* 2, H-ar); δ_C (126 MHz; [$^2H_6$]DMSO; 30 °C) 166 (CO), 161, 129, 126, 114 (C-ar), 71 (CHOH), 67 (OCH_2), 64 (CH_2OH), 43 (CH_2NH), 31, 29, 28, 25, 22 (CH_2), 14 (CH_3).

1-(3,4-Dihexyloxybenzoylamino)propane-2,3-diol 6/6. Synthesized from 3,4-dihexyloxybenzoic acid (0.5 g, 1.5 mmol) and 1-aminopropane-2,3-diol (1.4 g, 15 mmol). The residue was purified twice by column chromatography (eluent: chloroform–ethanol, 10 : 3; chloroform–methanol, 10 : 1) and crystallized twice from methanol. Yield: 0.22 g (24%); K 79 Col_{H2} 87 Iso (found C, 65.76; H, 9.40; N, 3.20. $C_{22}H_{37}O_5N\cdot 2H_2O$ requires: C, 65.28; H, 9.24; N, 3.47%); δ_H (200 MHz, [$^2H_6$] DMSO; 20 °C) 0.9 (6H, t, *J* 6, CH_3), 1.25–1.5 (12H, m, CH_2), 1.65–1.75 (4H, m, CH_2), 3.5 (5H, m, CH_2NH, C*H*OH, CH_2OH, 5H), 3.9 (4H, t, *J* 3, OCH_2), 4.6 (1H, t, OH), 4.8 (1H, d, *J* 5, OH), 6.9 (1H, d, *J* 9, H-ar), 7.45 (2H, d, *J* 3, H-ar), 8.3 (1H, br, NH); δ_C (100 MHz; [$^2H_6$]DMSO; 27 °C) 166 (CO), 151, 148, 127, 121, 113, 112 (C-ar), 71 (CHOH), 69, 68 (OCH_2), 63 (CH_2OH), 43 (CH_2NH), 31, 29, 25, 22 (CH_2), 14 (CH_3); *m*/*z* 395 (M^+ 23.5%).

1-(3,4-Didodecyloxybenzoylamino)propane-2,3-diol 6/12. Synthesized from 3,4-didodecyloxybenzoic acid (0.7 g, 1.5 mmol) and 1-aminopropane-2,3-diol (1.4 g, 15 mmol). Purified by column chromatography (eluent: chloroform–methanol, 10 : 1) and crystallized four times from methanol. Yield: 0.44 g (52%); K 98 Col_{H2} 148 Iso (found: C, 72.22; H, 10.97; N, 2.47. $C_{34}H_{61}O_5N$ requires: C, 72.42; H, 10.90; N, 2.48%); δ_H (200 MHz, [$^2H_6$]DMSO; 27 °C) 0.9 (6H, t, *J* 6, CH_3) 1.2–1.5 (36 H, m, CH_2), 1.6–1.8 (4H, m, CH_2), 3.5–3.7 (5H, m, CH_2NH, C*H*OH, CH_2OH), 4.0 (4H, t, *J* 6, OCH_2), 4.6 (1H, t, *J* 5, OH), 4.8 (1H, d, *J* 5, OH), 7.0 (1H, d, *J* 9, H-ar), 7.5 (2H, br, H-ar), 8.3 (1H, br, NH); δ_C (50 MHz; [$^2H_6$]DMSO; 25 °C) 166 (CO), 151, 148, 127, 121, 113, 112 (C-ar), 71 (CHOH), 69, 68 (OCH_2), 64 (CH_2OH), 43 (CH_2NH), 31, 29, 25, 22 (CH_2), 14 (CH_3); *m*/*z* 563 (M^+ 78.3%).

1-(3,4,5-Trihexyloxybenzoylamino)propane-2,3-diol 7/6. Synthesized from 3,4,5-trihexyloxybenzoic acid (0.6 g, 1.5 mmol) and 1-aminopropane-2,3-diol (1.4 g, 15 mmol). Purified by column chromatography (eluent: chloroform–ethanol 10 : 3) followed by preparative thin layer chromatography (Chromatotron, eluent: chloroform). Yield: 0.19 g (26%); K 49 Col_{H2} 91 Iso (found: C, 67.50; H, 9.69; N, 2.78. $C_{28}H_{49}O_6N$ requires: C, 67.85; H, 9.96; N, 2.83%); δ_H (500 MHz, [$^2H_6$]DMSO; 30 °C) 0.88 (9H, t, *J* 4, CH_3), 1.2–1.45 (18H, m, CH_2), 1.6–1.75 (6H, m, CH_2), 3.3–3.4 (5H, m, CH_2NH, C*H*OH, CH_2OH), 3.85 (2H, t, *J* 6, OCH_2), 4.0 (4H, t, *J* 6, OCH_2), 4.53 (1H, t, *J* 6, OH), 4.75 (1H, d, *J* 5, OH), 7.15 (2H, s, H-ar), 8.3 (1H, t, *J* 6, NH); δ_C (126 MHz; [$^2H_6$]DMSO; 30 °C) 166 (CO), 152, 140, 129, 106 (C-ar), 72 (CHOH), 70, 68 (OCH_2), 64 (CH_2OH), 43 (CH_2NH), 31, 30, 29, 25, 22 (CH_2), 14 (CH_3); *m*/*z* 495 (M^+ 7.4%).

1-(3,4,5-Triheptyloxybenzoylamino)propane-2,3-diol 7/7. Synthesized from 3,4,5-triheptyloxybenzoic acid (0.7 g, 1.5 mmol) and 1-aminopropane-2,3-diol (1.4 g, 15 mmol). Purified by column chromatography (eluent: chloroform–ethanol 10 : 3) and by preparative thin layer chromatography (Chromatotron, eluent: chloroform). Yield: 0.22 g (27%); K 46 Col_{H2} 92 Iso (found: C, 68.97; H, 10.44; N, 2.57. $C_{31}H_{55}O_6N$ requires: C, 69.22; H, 10.31; N, 2.61%); δ_H (500 MHz, [$^2H_6$]DMSOt; 30 °C) 0.86 (9H, t, *J* 5, CH_3), 1.2–1.45 (24H, m, CH_2), 1.6–1.75 (6H, m, CH_2), 3.1–3.3, 3.5–3.7 (5H, m, CH_2NH, C*H*OH, CH_2OH), 3.87 (2H, t, *J* 6, OCH_2), 3.98 (4H, t, *J* 6, OCH_2), 4.52 (1H, t, *J* 6, OH), 4.75 (1H, d, *J* 5, OH), 7.1 (1H, s, H-ar), 8.3 (1H, t, *J* 6, NH); δ_C (126 MHz; [$^2H_6$]DMSO; 30 °C) 166 (CO), 152, 140, 129, 106 (C-ar), 72 (CHOH), 70, 68 (OCH_2), 64 (CH_2OH), 43 (CH_2NH), 31, 30, 29, 28, 25, 22 (CH_2), 14 (CH_3); *m*/*z* 537 (M^+ 81.4%).

1-(3,4,5-Trioctyloxybenzoylamino)propane-2,3-diol 7/8. Synthesized from 3,4,5-trioctyloxybenzoic acid (0.8 g, 1.5 mmol) and 1-aminopropane-2,3-diol (1.4 g, 15 mmol). Purified twice by column chromatography (eluent: chloroform–ethanol, 10 : 3; chloroform–methanol, 10 : 1). Yield: 0.41g (47%); K 59 Col_{H2} 74 Cub_{I2} 85 Iso (found: C, 70.26; H, 10.75; N, 2.30. $C_{34}H_{61}O_6N$ requires: C, 70.41; H, 10.61; N, 2.42%); δ_H (500 MHz, [$^2H_6$]DMSO; 30 °C) 0.85 (9H, t, *J* 6, CH_3), 1.2–1.35 (24H, m, CH_2), 1.4–1.48 (6H, m, CH_2), 1.6–1.65 (2H, m, CH_2), 1.7–1.75 (4H, m, CH_2), 3.1–3.2, 3.3–3.4, 3.5–3.7 (m, 5H, CH_2NH, C*H*OH, CH_2OH), 4.50 (1H, t, *J* 6, OH), 4.75 (1H, d, *J* 5, OH), 7.25 (1H, s, H-ar), 8.3 (1H, t, *J* 6, NH); δ_C (126 MHz; [$^2H_6$]DMSO; 30 °C) 166 (CO),152, 140, 129, 106 (C-ar), 72 (CHOH), 70, 68 (OCH_2), 64 (CH_2OH), 43 (CH_2NH), 31, 31, 30, 29, 25, 22 (CH_2), 14 (CH_3); *m*/*z* 579 (M^+ 100).

1-(3,4,5-Trinonyloxybenzoylamino)propane-2,3-diol 7/9. Synthesized from 3,4,5-trinonyloxybenzoic acid (0.8 g, 1.5 mmol) and 1-aminopropane-2,3-diol (1.4 g, 15 mmol). Crystallized three times from methanol. Yield: 0.33 g (35%); K 49 Cub_{I2} 104 Iso (found: C, 70.76; H, 10.61; N, 2.19. $C_{37}H_{67}O_6N\cdot 0.2\ H_2O$ requires: C, 71.04; H, 10.86; N, 2.24%); δ_H (500 MHz, [$^2H_6$]DMSO; 30 °C) 0.84 (9H, t, *J* 7, CH_3), 1.2–1.35 (30H, m, CH_2), 1.4–1.48 (6H, m, CH_2), 1.58–1.66 (2H, m, CH_2), 1.68–1.74 (4H, m, CH_2), 3.12–3.2, 3.3–3.4, 3.58–3.64 (5H, m, CH_2NH, C*H*OH, CH_2OH), 3.87 (2H, t, *J* 6, OCH_2), 3.95 (4H, t, *J* 6, OCH_2), 4.5 (1H, t, *J* 6, OH), 4.75 (1H, d, *J* 5, OH), 7.15 (2H, s, H-ar), 8.3 (1H, t, *J* 6, NH); δ_C (126 MHz; [$^2H_6$]DMSO; 30 °C) 168 (CO), 152, 140, 129, 106 (C-ar), 72 (CHOH), 71, 69 (OCH_2), 64 (CH_2OH), 43 (CH_2NH), 31, 30, 29.0, 26, 22 (CH_2), 14 (CH_3); *m*/*z* 621 (M^+ 100%).

1-(3,4,5-Tridodecyloxybenzoylamino)propane-2,3-diol 7/12. Synthesized from 3,4,5-tridodecyloxybenzoic acid (1.0 g, 1.5 mmol) and 1-aminopropane-2,3-diol (1.4 g, 15 mmol). Purified by chromatography (eluent: chloroform–ethanol, 10:3) and crystallized twice from methanol. Yield: 0.82 g (73%); K_1 45 K_2 69 Cub_{I2} 126 Iso (found: C, 73.98; H, 11.67; N, 1.87. $C_{46}H_{85}O_6N$ requires: C, 73.85; H, 11.45; N, 1.87%); δ_H (500 MHz, [$^2H_6$]DMSO; 40 °C) 0.84 (9H, t, *J* 6, CH_3), 1.2–1.8 (CH_2, m, 60H), 3.35–3.65 (5H, m, C*H*$_2$NH, C*H*OH, C*H*$_2$OH), 3.8–4.0 (6H, br, OCH_2), 4.45 (1H, t, *J* 6, OH), 4.68 (1H, d, *J* 4, OH), 7.18 (2H, s, H-ar), 8.24 (1H, br, NH); δ_C (126 MHz; [$^2H_6$]DMSO; 40 °C) 166 (CO), 152, 140, 135, 129, 106 (C-ar), 72 (CH-OH), 70, 68 (OCH_2), 64 (CH_2OH), 43 (CH_2NH), 31, 30, 29, 25, 22 (CH_2), 14 (CH_3); *m*/*z* 747 (M^+ 100%).

2-(3,4-Dihexyloxybenzoylamino)propane-1,3-diol 8/8. Synthesized from 3,4-dihexyloxybenzoic acid (0.5 g, 1.5 mmol) and 2-aminopropane-1,3-diol (1.4 g, 15 mmol). Purified by column chromatography (eluent: chloroform–ethanol 10:3) and by preparative thin layer chromatography (Chromatotron, eluent: chloroform). Yield: 0.35 g (59%); K_1 64 K_2 108 (Cub_{V2} 50) Iso (found: C, 66.48; H, 9.37; N, 3.37. $C_{22}H_{37}O_5N$ requires: C, 66.79; H, 9.43; N, 3.54%); δ_H (500 MHz, [$^2H_6$]DMSO; 25 °C) 0.87 (6H, t, *J* 6, CH_3), 1.2–1.35 (8H, m, CH_2), 1.4–1.5 (4H, m, CH_2), 1.65–1.75 (4H, m, CH_2), 3.5 (5H, t, *J* 6, C*H*NH, C*H*$_2$OH), 3.9–4.05 (4H, m, OCH_2), 4.6 (2H, t, *J* 5, OH), 6.98 (1H, d, *J* 8, H-ar), 7.45 (2H, m, H-ar), 7.74 (1H, d, *J* 3, NH); δ_C (50 MHz; [$^2H_6$]DMSO; 27 °C) 163 (CO), 151, 148, 127, 121, 103, 102 (C-ar), 69 (OCH_2), 61 (CH_2OH), 54 (CHNH), 31, 29, 25, 22 (CH_2), 13 (CH_3); *m*/*z* 395 (M^+ 20.7%).

2-(3,4,5-Tridodecyloxybenzoylamino)propane-1,3-diol 9/12. Synthesized from 3,4,5-tridodecyloxybenzoic acid (1.0 g, 1.5 mmol) and 2-aminopropane-1,3-diol (1.4 g, 15 mmol). Crystallized twice from methanol. Yield: 0.65 g, (58%); K 67 (Col_{H2} 62) Cub_{I2} 104 Iso (found: C, 73.82; H, 11.64; N, 1.78. $C_{46}H_{85}O_6N$ requires: C, 73.83; H, 11.46; N, 1.87%); δ_H (200 MHz, [$^2H_6$]DMSO; 27 °C) 0.95 (9H, t, *J* 6, CH_3), 1.2–1.8 (60H, m, CH_2), 3.5 (5H, t, *J* 6, C*H*$_2$NH, C*H*$_2$OH), 3.95 (6H, m, OCH_2), 4.6 (2H, t, *J* 5, OH), 7.2 (1H, s, H-ar), 7.85 (1H, br, NH); δ_C (126 MHz; [$^2H_6$]DMSO; 40 °C) 165 (CO), 152, 140, 129, 106 (C-ar), 72 (OCH_2), 68 (CH_2OH), 54 (CHNH), 31, 30, 29, 26, 25, 22 (CH_2), 14 (CH_3); *m*/*z* 747 (M^+ 100%).

2-(3,4,5-Tridodecyloxybenzoylamino)-2-(hydroxymethyl)propane-1,3-diol 10/12. Synthesized from 3,4,5-tridodecyloxybenzoic acid (1.0 g, 1.5 mmol) and 2-amino-2-(2-hydroxymethyl)propane-1,3-diol (1.8 g, 15 mmol). Purified by column chromatography (eluent: chloroform–ethanol, 10:3) and crystallized twice from methanol. Yield: 0.29 g, (25%); K 63 Col_{H2} 64 Cub_{I2} 87 Iso (found: C, 71.25; H, 10.98; N, 1.68. $C_{47}H_{87}O_7N\cdot 0.6H_2O$ requires C, 71.55; H, 11.27; N, 1.78%); δ_H (500 MHz, [$^2H_6$]DMSO; 40 °C) 0.84 (9H, t, *J* 7, CH_3), 1.2–1.45 (54H, m, CH_2), 1.6 (2H, m, CH2), 1.8 (4H, m, CH_2), 3.65 (6H, d, *J* 6, $C(CH_2)_3$, 3.9 (2H, t, *J* 6, OCH_2), 4.0 (4H, *J* 6, OCH_2), 4.7 (3H, t, *J* 6, OH), 7.05 (2H, s, H-ar), 7.15 (1H, s, NH); δ_C (125 MHz; [$^2H_6$]DMSO; 40 °C) 167 (CO), 152, 140, 130, 106 (C-ar), 72 (OCH_2), 68 (CH_2OH), 62 ($C(CH_3)_3$), 31, 29, 26, 22 (CH_2), 13 (CH_3); *m*/*z* 777 (M^+ 17.9%).

Synthesis of *N,N*-bis(3,4-dihydroxypropyl)-3,4,5-tridodecyloxybenzamide 11/12

The 3,4,5-tridodecyloxybenzoic acid (1.0 g, 1.5 mmol) and thionyl chloride (10 ml) were refluxed for 3 h. The excess thionyl chloride was distilled off and the residue was dissolved in dry methylene chloride (15 ml). Diallylamine (1.5 g, 15 mmol) and DMAP (10 mg) were added. The resulting mixture was heated for 4 h at 80 °C and was stirred for an additional 24 h at room temp. Afterwards the solvent was evaporated *in vacuo* and the residue was purified by column chromatography (eluent chloroform–methanol, 10:1) to give *N*,*N*-diallyl-3,4,5-tridodecyloxybenzamide. Yield: 0.86 g (76%); mp 32 °C. *N*,*N*-Diallyl-3,4,5-tridodecyloxybenzamide (0.75 g, 1 mmol) and *N*-methylmorpholine *N*-oxide (0.23 g of a 60% solution in water, 2 mmol) were dissolved in acetone (20 ml). OsO_4 (5 ml of a 0.01 M solution in *tert*-butyl alcohol) was added and the mixture was stirred at room temp. for 24 h. Afterwards Na_2SO_3 (5 ml of a saturated solution) was added and the resulting slurry was stirred for 2 h at 25 °C. The mixture was filtered over a silica bed. The residue was washed twice with acetone (50 ml). The organic solutions were combined and the solvent was evaporated. The residue was dissolved in diethyl ether, washed with water (25 ml), 5% H_2SO_4 (25 ml), saturated $NaHCO_3$ solution (25 ml) and brine (25 ml). The organic layer was dried with Na_2SO_4 and the solvent was distilled off. The residue was crystallized twice from methanol. Yield: 0.31 g (38%); K 40 Col_{H2} 142 Iso (found: C, 71.12; H, 10.85; N, 1.68. $C_{26}H_{57}O_9N$ requires: C, 71.42; H, 11.15; N, 1.70%); δ_H (200 MHz, [$^2H_6$]DMSO; 40 °C) 0.84 (9H, *J* 6, CH_3), 1.24–1.69 (60H, m, CH_2), 2.47–2.51 (10H, m, N(C*H*$_2$C*H*OHC*H*$_2$OH)$_2$), 3.85–3.95 (6H, m, OCH_2), 4.46 (2H, br, OH),4.88 (2H, br, OH), 6.69 (2H, s, H-ar); δ_C (50 MHz; [$^2H_6$]DMSO; 40 °C) 171 (CO), 152, 132, 106 (C-ar), 69, 68, 51 [N($CH_2CHOHCH_2OH)_2$], 72, 41, 39, 38, 31, 30, 29, 26, 21 (CH_2), 14 (CH_3); *m*/*z* 821 (M^+ 16%).

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References

1 J. M. Seddon and R. H. Templer, in *Handbook of Biological Physics*, vol. 1, ed. R. Lipowsky and E. Sackmann, Elsevier, Amsterdam, 1995.
2 G. Lindblom and L. Rilfors, *Biochim. Biophys. Acta*, 1989, **988**, 221.
3 (*a*) A. E. Skoulios, in *Developments in Block Copolymers*, vol. 1, ed. I. Goodman, Applied Science Publishers, London, 1982, p. 81; (*b*) A. E. Skoulios, in *Advances in Liquid Crystals*, vol. 1 ed. G. H. Brown, Academic Press, New York, 1975, p. 169.
4 M. Antonietti and C. Göltner, *Angew. Chem.*, 1997, **109**, 944.
5 (*a*) V. Luzzati and A. P Spengt, *Nature (London), 1967,* **215**, 701; (*b*) J. M. Seddon and R. H. Templer, *Phil. Trans. R. Soc. Lond.*, 1993, **A344**, 377.
6 G. J. T. Tiddy, *Phys. Rep.*, 1980, **57**, 1.
7 J. N. Israelachvili, D. J. Mitchell and B. W. Ninham, *J. Chem. Soc., Faraday Trans. 2*, 1976, **72**, 1525.
8 A. Gulik, H. Delacroix, G. Kirschner and V. Luzzati, *J. Phys. II Fr.*, 1995, **5**, 445.
9 P. Mariani, V. Luzzati and H. Delacroix, *J. Mol. Biol.*, 1988, 165.
10 Y. Hendrikx and B. Pansu, *J. Phys. II Fr.*, 1996, **6**, 33.
11 V. Luzzati, in *Biological Membranes*, Vol. 1, ed. D. Chapman, Academic Press, London 1968, pp. 71–123
12 P. Kekicheff and B. Cabane, *J. Phys.*, 1987, **48**, 1571.
13 M. Clerc, *J. Phys. II Fr.*, 1996, **6**, 961.
14 (*a*) G. W. Gray, B. Jones and F. Marson, *J. Chem. Soc.*, 1957, 393; (*b*) D. Demus, G. Kunicke, J. Neelsen and H. Sackmann, *Z. Naturforsch., Teil A*, 1968, **23**, 84; (*c*) S. Diele, P. Brandt and H. Sackmann, *Mol. Cryst. Liq. Cryst.*, 1992, **17**, 163; (*d*) S. Kutsumizu, M. Yamada and S. Yano, *Liq. Cryst.*, 1994, **16**, 1109.
15 (*a*) G. Etherington, A. J. Leadbetter, X. J. Wang, G. W. Gray and T. Tajbakhsh, *Liq. Cryst.*, 1986, **1**, 209; (*b*) S. Yano, Y. Mori and S. Kutsumizu, *Liq. Cryst.*, 1991, **9**, 907.
16 (*a*) H. Schubert, J. Hausschild, D. Demus and S. Hoffmann, *Z. Chem.*, 1978, **18**, 256; (*b*) D. Demus, A. Gloza, H. Hartung, I. Rapthel and A. Wiegeleben, *Cryst. Res. Technol.*, 1981, **16**, 1445.
17 P. A. Spengt and A. E. Skoulios, *Acta Crystallogr.*, 1966, **21**, 892.
18 H.-T. Nguyen, C. Destrade and J. Malthete, *Adv. Mater.*, 1997, **9**, 375.
19 (*a*) Y. Fang, A. M. Levelut and C. Destrade, *Liq. Cryst.*, 1990, **7**, 265; (*b*) A. M. Levelut and Y. Fang, *Colloq. Phys.*, 1990, **C7**, 299; (*c*) J. Malthete, H. T. Nguyen and C. Destrade, *Liq. Cryst.*, 1993, **13**, 171; (*d*) H. T. Nguyen, C. Destrade and J. Malthete, *Liq. Cryst.*,

1990, **8**, 797; (*e*) C. Destrade, H. T. Nguyen, C. Alstermark, G. Lindsten, M. Nilsson and B. Otterholm, *Mol. Cryst. Liq. Cryst*., 1990, **180B**, 265.
20 H. T. Nguyen, G. Sigaud, M. F. Achard, F. Hardouin, R. J. Twieg and K. Betterton, *Liq. Cryst*., 1991, **10**, 389.
21 W. Weissflog, G. Pelzl, I. Letko and S. Diele, *Mol. Cryst. Liq. Cryst*., 1995, **260**, 157.
22 J. Billard, H. Zimmermann, R. Poupko and Z. Luz, *J. Phys. Fr*., 1989, **50**, 539.
23 B. Kohne, K. Praefcke and J. Billard, *Z. Naturforsch., Teil B*, 1986, **41**, 1036.
24 (*a*) D. W. Bruce, D. A. Dunmur, S. A. Hudson, E. Lalinde, P. M. Maitlis, M. P. McDonald, R. Orr, P. Styring, A. S. Cherodian, R. M. Richardson, J. L. Feijoo and G. Ungar, *Mol. Cryst. Liq. Cryst*., 1991, **206**, 79; (*b*) D. W. Bruce, S. C. Davis, D. A. Dunmur, S. A. Hudson, P. M. Maitlis and P. Styring, *Mol. Cryst. Liq. Cryst*., 1992, **215**, 1; (*c*) D. W. Bruce and S. A. Hudson, *J. Mater Chem*., 1994, **4**, 479; (*d*) D. W. Bruce, B. Donnino, D. Guillon, B. Heinrich and M. Ibn-Elhaj, *Liq. Cryst*., 1995, **19**, 537; (*e*) D. W. Bruce, B. Donnino, S. A. Hudson, A. M. Levelut, S. Megtert, D. Petermann and M. Veber, *J. Phys. II (Fr.)*, 1995, **5**, 289.
25 M. J. Baena, P. Espinet, M. C. Lequerica and A. M. Levelut, *J. Am Chem. Soc*., 1992, **114**, 4182.
26 C. Soulie, P. Bassoul and J. Simon, *J. Chem. Soc., Chem. Commun*., 1993, 114.
27 V. Vill, F. Bachmann, J. Thiem, I. F. Pelyvas and P. Pudlo, *Mol. Cryst. Liq. Cryst*., 1992, **213**, 57.
28 S. Yano, Y. Moriand and S. Kutsumizu, *Liq. Cryst*., 1991, **9**, 907.
29 A. Douy and B. Gallot, *Makromol. Chem*., 1986, **187**, 465.
30 (*a*) U. Stebani, G. Lattermann, M. Wittenberg, R. Festag and J. H. Wendorff, *Adv. Mater*., 1994, **6**, 572; (*b*) U. Stebani, G. Lattermann, R. Festag, M. Wittenberg and J. H. Wendorff, *J. Mater. Chem*., 1995, **5**, 2247.
31 (*a*) G. Lattermann and G. Staufer, *Mol. Cryst. Liq. Cryst*., 1990, **191**, 199; (*b*) G. Staufer, M. Schellhorn and G. Lattermann, *Liq. Cryst*., 1995, **18**, 519; (*c*) M. Schellhorn and G. Lattermann, *Liq. Cryst*., 1994, **17**, 529; (*d*) M. Schellhorn and G. Lattermann, *Macromol. Chem. Phys*., 1995, **196**, 211.
32 K. Borisch, S. Diele, P. Göring, H. Kresse and C. Tschierske, *Angew. Chem*., 1996, **109**, 2188, *Angew. Chem., Int. Ed. Engl*., 1996, **36**, 2087.
33 K. Praefcke, B. Kohne, A. Eckert and J. Hempel, *Z. Naturforsch., Teil B*, 1990, **45**, 1084.
34 S. Fischer, H. Fischer, S. Diele, G. Pelzl, K. Jankowski, R. R. Schmidt and V. Vill, *Liq. Cryst*., 1994, **17**, 855.
35 K. Borisch, S. Diele, P. Göring and C. Tschierske, *Chem. Commun*., 1996, 237.
36 K. Borisch, S. Diele, P. Göring and C. Tschierske, *Liq. Cryst*., 1997, **22**, 427.
37 V. S. K. Balagurusamy, G. Ungar, V. Percec and G. Johansson, *J. Am. Chem. Soc*., 1997, **119**, 1539.
38 C. Hall, G. J. T. Tiddy and B. Pfannemüller, *Liq. Cryst*., 1991, **9**, 527.
39 Thermotropic properties of single chain *N*-alkanoyl-1-deoxy-1-methylamino-D-glucitols have been reported: J. W. Goodby, M. A. Marcus, E. Chin, P. L. Finn and B. Pfannemüller, *Liq. Cryst*., 1988, **3**, 1569. More recently the amphotropic behaviour of double chain *N*-acyl-*N*-alkyl-1-amino-D-glucitols has been described: H. van Doren and K. R. Terpstra, *J. Mater. Chem*., 1995, **5**, 2153. Smectic and columnar liquid crystalline salts of glucamine derivatives have been obtained on addition of carboxylic acids: V. Vill, H. Kelkenberg and J. Thiem, *Liq. Cryst*., 1992, **11**, 459.
40 Columnar mesophases were found for simple benzamides: U. Beginn and G. Lattermann, *Mol. Cryst. Liq. Cryst*., 1994, **241**, 215; and for *N*-(3,4-didecyloxybenzoyl)-2-aminoethanol: U. Stebani and G. Lattermann, *Macromol. Rep*., 1995, **A32** (Suppl. 3), 385.
41 S. Anderson, S. T. Hyde, K. Larsson and S. Lidin, *Chem. Rev*., 1988, **88**, 221.
42 K. Praefcke, A.-M. Levelut, B. Kohne and A. Eckert, *Liq. Cryst*, 1989, **6**, 267.
43 K. Praefcke, P. Marquardt, B. Kohne, W. Stephan, A.-M. Levelut and E. Wachtel, *Mol. Cryst. Liq. Cryst*., 1991, **203**, 149.
44 V. Percec, J. Heck, D. Tomazos, F. Falkenberg, H. Blackwell and G. J. Ungar, *J. Chem. Soc., Perkin Trans 1*, 1993, 2799.
45 (*a*) G. Lattermann and G. Staufer, *Liq. Cryst*., 1989, **4**, 347; (*b*) M. Ebert, R. Kleppinger, M. Soliman, M. Wolf, J. H. Wendorff, G. Lattermann and G. Staufer, *Liq. Cryst*., 1990, **7**, 553.
46 H. Hagslätt, O. Söderman and B. Jönsson, *Liq. Cryst*., 1994, **17**, 157.
47 J. W. Goodby, D. A. Dunmur and P. J. Collings, *Liq. Cryst*., 1995, **5**, 703 and references cited.
48 D. Joachimi, A. Öhlmann, W. Rettig and C. Tschierske, *J. Chem. Soc. Perkin Trans 2*, 1994, 2011.
49 W. Rettig, G. Brezesinski, A. Mädicke, C. Tschierske, H. Zaschke and F. Kuschel, *Mol. Cryst. Liq. Cryst*., 1990, **193**, 115.
50 (*a*) K. Fontell, K. K. Fox and E. Hansson, *Mol. Cryst. Liq. Cryst. Lett*., 1985, **1**, 9; (*b*) K. Fontell, *Colloid Polym. Sci*., 1990, **268**, 264.
51 A values of 1.35 : 1 was obtained by fluorescence quenching experiments of normal cubic mesophases of lyotropic systems: L. B.-A. Johansson and O. Söderman, *J. Phys. Chem*., 1987, **91**, 5275; a value of 1.5 : 1 was found by the same method in poly(oxyethylene) surfactant water systems: B. Medhage, M. Almgren and L. Alsins, *J. Phys. Chem*., 1993, **97**, 7753.
52 C. Tschierske, *Prog. Polym. Sci*., 1996, **21**, 775 and references cited.
53 (*a*) L. Claisen and O. Eisleb, *Ann. Chem*., 1913, **401**, 29; (*b*) D. Coates and G. W. Gray, *J. Chem. Soc., Perkin Trans 2*, 1976, 863.
54 R. Dunkel, M. Hahn, K. Borisch, B. Neumann, H.-H. Rüttinger and C. Tschierske, *Liq. Cryst*., in the press.
55 V. Percec, D. Tomazos, J. Heck, H. Blackwell and G. Ungar, *J. Chem. Soc., Perkin Trans 2*, 1994, 31.
56 H. Meier, E. Praß, G. Zerban and F. Kosteyn, *Z. Naturforsch., Teil B*, 1998, **43**, 889.

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