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The scope and limitations of liquid-crystalline behaviour in monosaccharide amphiphiles Comparison of the thermal behaviour of several homologous series of D-glucose derived compounds with an amino-linked alkyl chain

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The scope and limitations of liquid-crystalline behaviour in monosaccharide amphiphiles

Comparison of the thermal behaviour of several homologous series of D-glucose derived compounds with an amino-linked alkyl chain

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A short review of the scope and limitations of liquid-crystalline behaviour in carbohydrate derivatives is presented. In order to investigate the influence of structure variations on the thermal behaviour of monosaccharide amphiphiles, six homologous series of D-glucose and 2-deoxy-D-glucose derivatives with an amino-linked *n*-alkyl chain were prepared. The observed thermal behaviour could be readily explained with the aid of a refinement of the qualitative model that was presented earlier [1]. All compounds were found to be mesogenic, and the observed mesophase was smectic A_d (i.e. a partially overlapping bilayer structure) in all cases.

1. Introduction

Interest in the physical properties of amphiphilic compounds derived from mono (and oligo) saccharides is increasing steadily. Many different compounds can be synthesized in excellent yields via short reaction sequences. Small structural changes that may lead to large differences in properties are, therefore, easily implemented. Research thus far has been focused chiefly on biological activity [2–5] and surfactant properties [6–10]. More than a dozen compounds are now commercially available for the solubilization and reconstitution of membrane proteins. Larger scale use of these materials as non-ionic surfactants in biodegradable detergents as well as for the purpose of enhanced oil recovery probably will be only a matter of time.

Another interesting feature of these compounds is their potential for liquid-crystalline behaviour. First reported by Fischer and Helferich [11] in 1911 and characterized by Noller and Rockwell [12] in 1938, this phenomenon was totally neglected until the early 1980s, when Jeffrey [13–18] repeatedly brought the matter to the attention of the scientific community. Based on very few data he predicted carbohydrate amphiphiles to be a vast source of new liquid-crystalline materials. Very recent work by a number of research groups has unequivocally established the validity of Jeffrey's predictions. The general types of compounds that may display liquid-crystalline behaviour have been shown to range from the so-called bolaamphiphiles [19] (two

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cyclic [20] or acyclic [21] monosaccharide moieties linked by one or two alkyl chains) to fully acylated hexose [22] and inositol [23–25] derivatives. In between these extremes, compounds have been reported with

a monosaccharide moiety with one alkyl or acyl chain (C- [26–28], O- [29–34], N- [35–38], or S- [39, 40] linked) usually, but not necessarily [32], at the anomeric position; there is one report of an ω-hydroxy function on the alkyl group [21];

a monosaccharide [1, 41–44] or inositol [44] moiety with two alkyl chains.

The alkyl chain may be branched [25, 40]; deoxy- [1, 43] and anhydrosugars [26, 45, 46] may be employed. In addition to the compounds that are now known to display liquid-crystalline behaviour, probably thousands of compounds have been reported in the literature which are carbohydrate mesogens but have not been recognized as such, particularly for those cases where so-called softening points or double melting points have been observed.

Although from this we might conclude that nearly any combination of (a) carbohydrate moiety(ies) and (one) alkyl chain(s) will lead to mesogenic compounds, this is definitely not the case. The influences of small structural changes on the occurrence, the temperature range and the type of mesophase were found to be huge [1, 25, 38, 47]. The aim of our research is to find a model which will explain the observed behaviour and that may be used to predict the behaviour of new compounds [1]. We report here on the synthesis and behavioural characteristics of several homologous series of D-glucose and 2-deoxy-D-glucose derived amphiphiles with an amino-linked alkyl chain and compare them with the *n*-alkyl D-gluconamides [36] and the 1-(*n*-alkanoylmethyl)amino-1-deoxy-D-glucitols [38].

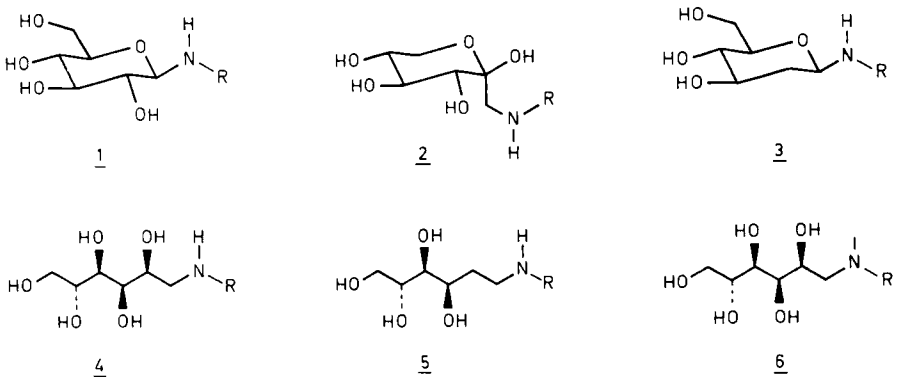
2. Results and discussion

2.1. *Synthesis*

Six homologous series of compounds (*n*-heptyl through *n*-hexadecyl) were prepared. The *n*-alkyl 1-amino-β-D-glucopyranosides (**1**) [48] were prepared by stirring D-glucose and the appropriate *n*-alkylamine in absolute ethanol. The 1-(*n*-alkylamino)-1-deoxy-β-D-fructopyranosides (**2**) were obtained by an Amadori rearrangement [49] of **1**. First the oxalic acid salts of **2** were formed upon refluxing **1** and a slight excess of oxalic acid in dioxane/methanol. Treatment with 1N sodium hydroxide gave free **2**. The *n*-alkyl 1-amino-2-deoxy-β-D-glucopyranosides (**3**) were formed by reaction of 2-deoxy-D-glucose and *n*-alkylamine in absolute ethanol. The 1-(*n*-alkylamino)-1-deoxy-D-glucitols (**4**) may be synthesized directly by reductive amination of D-glucose [50] or by sodium cyanoborohydride reduction [51] of **1**. The products **4** were isolated as HCl salts and were treated with a slight excess of 5N potassium hydroxide to give free **4**. Similarly, sodium cyanoborohydride reduction of **3** leads to the 1-(*n*-alkylamino)-1,2-dideoxy-D-glucitols (**5**). The 1-(*n*-alkylmethylamino)-1-deoxy-D-glucitols (**6**) were obtained by prolonged refluxing of 1-deoxy-1-(methylamino)-D-glucitol with the appropriate *n*-alkyl bromide in ethanol in the presence of larger than two equivalents of potassium carbonate [52].

2.2. *The mesophase*

So far only two types of mesophases have been observed for carbohydrate mesogens. Derivatives with one alkyl chain may form smectic A_d (S_{A_d}) mesophases, i.e. they form bimolecular layers with partially overlapping sugar moieties in the core



(*a*) R = *n*-heptyl, (*b*) R = *n*-octyl, (*c*) R = *n*-nonyl, (*d*) R = *n*-decyl, (*e*) R = *n*-undecyl, (*f*) R = *n*-dodecyl, (*g*) R = *n*-tridecyl, (*h*) R = *n*-tetradecyl, (*i*) R = *n*-pentadecyl, (*k*) R = *n*-hexadecyl.

Scheme I.

of the layers [53] and the alkyl chains pointing outwards. These S_{A_d} phases were found to be identical to the lyotropic lamellar mesophase [54, 55]. Derivatives with two or more alkyl chains may form disk-like mesophases; several types of ordering of these disks have been reported [56].

The initial characterization of the mesophases was carried out by textural observations with the polarizing microscope [57, 58]. Definite clues as to the nature of a mesophase were obtained from X-ray experiments [59] and by miscibility studies with compounds, the mesophases of which have already been determined [60]. Compounds **1–6** are no exception, they all form a S_{A_d} mesophase. Characteristics textures of this mesophase are batonnets which coalesce to a focal-conic fan-like texture with pseudo-isotropic areas, and also oily streaks (illustrated in figures 1 and 2). Powder X-ray measurements (Guinier–Simon camera) of several samples were kindly performed by Mr. F. van der Horst of the Department of Solid State Physics (University of Groningen). In all cases a layer spacing was found that corresponds to $l < d < 2l$, where l is the molecular length of the fully extended molecule and d is the calculated layer thickness.

2.3. *Thermal behaviour*

In the crystalline state most carbohydrate mesogens are packed in a similar fashion [13, 15, 61–65]: a bilayer structure with the carbohydrate moieties placed head-to-head, held together by extensive hydrogen-bonded networks, and the fully interdigitized, extended alkyl chains pointing away (at an angle) and held together by weak van der Waals interactions. In some cases [33, 66–69] head-to-tail packing in monolayers is observed. No general explanation for this anomalous behaviour has been proposed, but for the *N*-alkyl D-aldonamides it is probably due to the dominant hydrogen bond forming amide functionalities. The tendency to form a layered crystal lattice is a prerequisite for the formation of smectic mesophases [70]. Fairly strong, lateral cohesive forces (stacking forces), e.g. (induced) dipole interactions, between molecules are an additional requirement [70].

Jeffrey [17] explained the thermal behaviour of carbohydrate mesogens by assuming a two-stage melting process. The alkyl chains melt first with the carbohydrate part of the crystal lattice remaining largely intact, thus forming the core of the mesophase

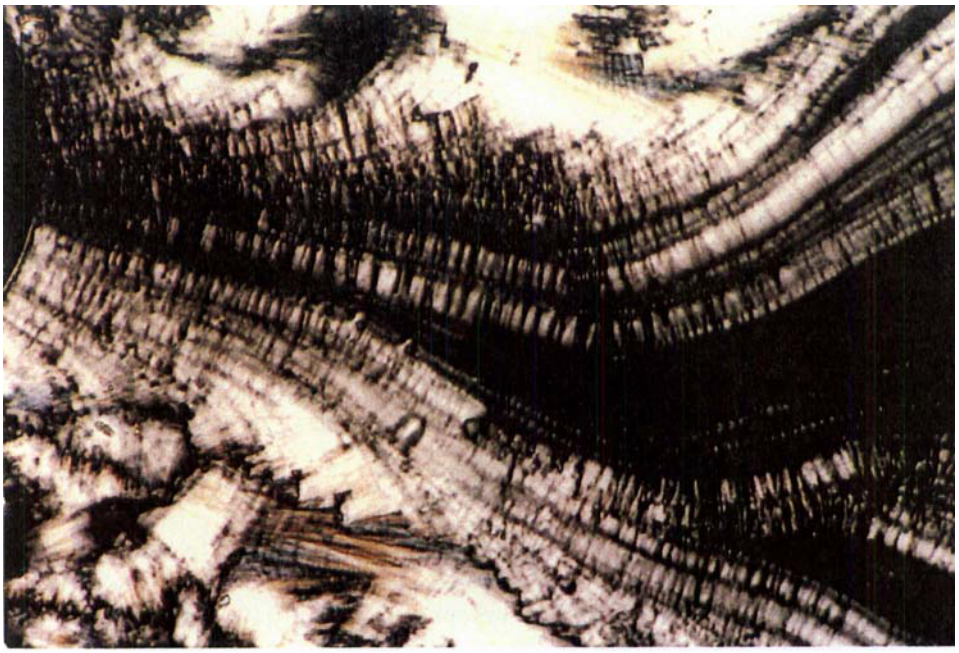


Figure 1. The oily streak texture of 1-deoxy-1-(*n*-tetradecylmethylamino)-D-glucitol (**6h**).

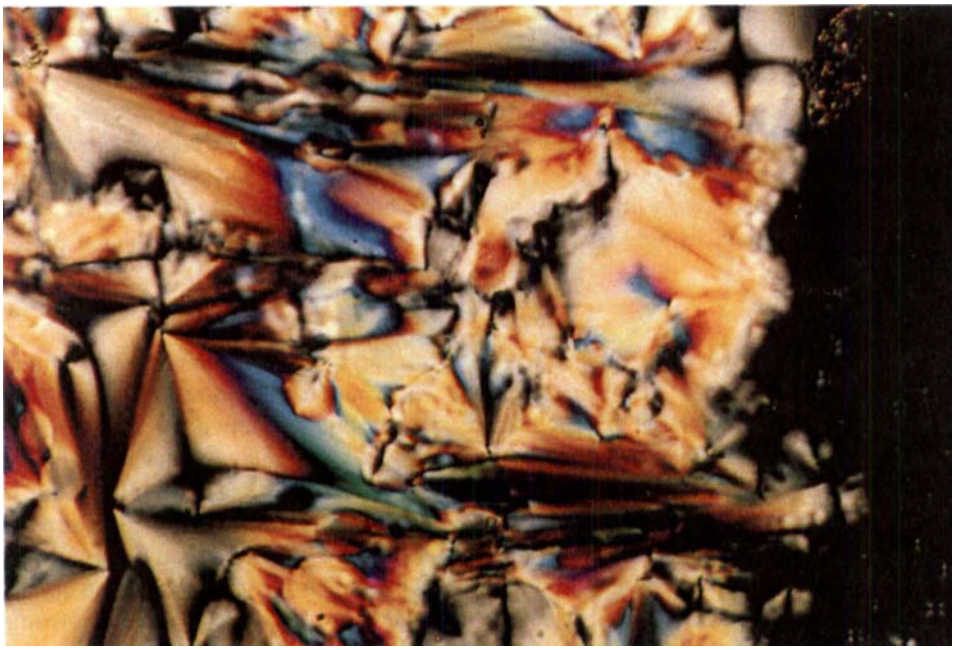


Figure 2. The focal conic fan-like texture of 1-deoxy-1-(*n*-tridecylamino)-D-glucitol (**4g**).

layers. At the clearing point the hydrogen-bonded networks break down and an isotropic liquid is formed. However, our studies of ten homologous series of aldose dialkyl dithioacetals [1] have revealed that this model fails to explain both the behavioural pattern within a homologous series and the observed similarities and differences between compounds that only differ in the configuration of the carbohydrate moiety.

The observed behaviour is better explained when we assume that the melting point is determined by the strength of the hydrogen-bonded network. At the melting point the three-dimensional crystal lattice is broken down completely and new hydrogen-bonded aggregates are formed (compare with, for example, the 4-alkoxybenzoic acids [71] and the 2-(4′-alkyl-cyclohexyl)-1,3-propanediols [72]) which form layers or columns in a manner very similar to other mesogenic amphiphiles [73]. At the clearing point the stacking forces can no longer hold together the two dimensional ordering and an isotropic liquid is formed. The aggregates are not necessarily broken down at this point. In this model compounds **1**–**6** form bimolecular aggregates (dimers). Powder X-ray data [20] indicate that there is only partial overlap of the carbohydrate moieties of the molecules. This means that some of the hydroxyl groups are not involved in dimer formation and we propose that these provide (by dynamic hydrogen-bonding between dimers) the lateral cohesive forces which stabilize the mesophase layers. This suggestion is supported by the fact that the mesogenic properties of carbohydrate amphiphiles are lost completely when they are mixed with non-carbohydrate mesogens [53]. This qualitative model suggests that the melting and clearing points are more or less independent entities, meaning that small structural variations may have different or even opposing influences on the two transition temperatures.

Compounds **1** and **2** do form a mesophase upon melting (~ 100°C) but, as decomposition also starts immediately upon melting, quantitative investigations are not possible. The decomposition of **1** is a complicated process (cf. the Maillard reaction [74]) which probably involves the hydroxyl group at C-2. Indeed the 2-deoxy compounds **3** are much more stable and can be subjected to several heating and cooling cycles without significant decomposition. All compounds **3** are monotropic, i.e. as a result of significant supercooling of the isotropic liquid, formation of a metastable mesophase is observed prior to recrystallization. The enthalpies of the mesophase–isotropic transitions were too small to be detected by differential scanning calorimetry. Transition temperature data were obtained with a hot stage mounted on a polarizing microscope. These data and the DSC data for the melting points are given in table 1. Figure 3 shows a plot of the transition temperature for compounds **3** as a function of the alkyl chain length. For these the clearing points during heating and cooling show considerable differences (5–7°C). We have never observed this phenomenon in carbohydrate mesogens before, and can offer no explanation at this time. Compounds **3** have melting points which are in the same range as those of **1** and **2** (disregarding the pronounced odd–even effect) implying that the hydroxyl group at C-2 is not involved in the hydrogen-bonded network in the crystal. Qualitative rapid heating and cooling runs of the long chain **1** and **2** indicate clearing points of approximately 125°C. The clearing points of compounds **3** are ~ 40–45°C lower. The hydroxyl group at C-2 thus plays an important role in the stabilization of the mesophase.

The transition temperature data for **4**–**6** are listed in tables 2–4. Compounds **4** exhibit by far the largest mesophase ranges of all the compounds investigated here. Compound **4a** is monotropic but **4b–j** are enantiotropic. The clearing points rise rapidly with increasing alkyl chain lengths, to reach a maximum for the *n*-dodecyl

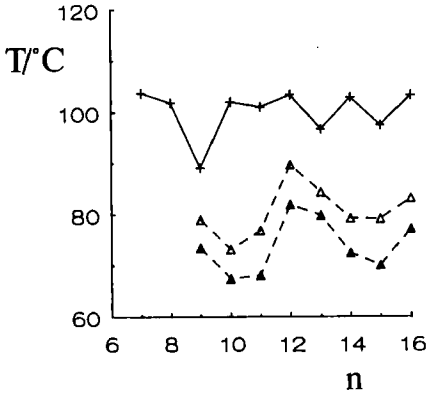


Figure 3. The transition temperatures for **3a–j** plotted as a function of the alkyl chain length, *n*; +, melting point; △, clearing point (up); ▲, clearing point (down).

derivative **4f**. The slightly lower clearing points for even longer alkyl chains are attributed to a tendency to coil [75], thus decreasing the mesophase stability. This behaviour is typical for most homologous series of carbohydrate mesogens reported so far. Compounds **5** have significantly lower transition temperatures; the melting points are lowered by ~25–30°C, the clearing points by ~45–55°C. This behaviour suggests that for the open-chain compounds the hydroxyl group at C-2 takes part in the hydrogen-bonded network of the crystal lattice and also, even more strongly, has a role in the stabilization of the mesophase structure. Compounds **6** have a methyl group on the nitrogen instead of a hydrogen atom, which dramatically lowers both the melting (~40°C) and the clearing points (60–80°C). The lowering of the melting points is caused by removing a possible participant in the hydrogen-bonded network and/or by the more difficult packing of the molecules due to the introduction of a disturbance of the rod-like shape. The latter is probably the most significant factor for the destabilization of the mesophases of **6** compared to **4**. This phenomenon has been described earlier for compounds with discotic [76] and

Table 1. The transition temperatures and enthalpies for a homologous series of *n*-alkyl 1-amino-2-deoxy-β-D-glucopyranosides (**3a–j**)

Compound	M.p.†/°C	ΔH/kJ mol^{-1}†	C.p.‡§/°C	ΔH/kJ mol^{-1}
3a	102·1–105·3	43·8	–	–
3b	100·1–103·5	49·8	–	–
3c	86·9–91·2	37·2	79·0 (73·5)	–
3d	101·2–102·8	62·8	73·2 (67·4)	–
3e	99·8–102·2	27·2‖	76·9 (68·1)	–
3f	102·6–104·8	70·3	89·7 (81·9)	–
3g	95·1–98·4	55·8	84·3 (79·8)	–
3h	102·0–103·8¶	78·6	79·3 (72·5)	–
3i	97·2–99·2¶	64·7	79·2 (70·1)	–
3j	102·7–103·8¶	55·5	83·2 (77·2)	–

†Measured at 5 K min^{-1} with a Perkin–Elmer DSC 7.
‡Measured at 5 K min^{-1} with a Mettler FP92 hot stage.
§Values in parentheses observed on cooling.
‖Melting point preceded by several crystal-to-crystal transitions.
¶Compounds melt through a transient liquid crystal phase.

Table 2. The transition temperatures† and enthalpies† for a homologous series of 1-(*n*-alkylamino)-1-deoxy-D-glucitols (**4a–j**)

Compound	M.p.‡/°C	ΔH/kJ mol^{-1}	C.p.‖/°C	ΔH/kJ mol^{-1}
4a	125·5–128·1	58·6	– (113·8)	1·0
4b	120·5–122·9	61·6	142·5 (141·9)	1·4
4c	124·3–127·0	70·2	154·6 (149·9)	1·7
4d	123·2–125·1	63·4	165·6 (164·8)	1·8
4e	123·1–126·0	73·9	167·9 (164·2)	1·6
4f	122·5–124·0	63·8	173·6 (172·3)	1·5
4g	125·5–127·5	73·4	173·0 (172·0)	1·3
4h	123·8–125·0	70·4	173·4 (172·1)	1·2
4i	126·5–128·1	83·4	172·8 (172·3)	1·0
4j	124·8–126·6	63·1	170·9 (171·4)	0·4

†Measured at 5 Kmin^{-1} with a Perkin–Elmer DSC 7.
‡For each compound at least one crystal-to-crystal transition was observed prior to melting.
§Solidification of all compounds upon cooling takes place via several crystal-to-crystal transitions.
‖Values in parentheses obtained on cooling.

Table 3. The transition temperatures† and enthalpies† for a homologous series of 1-(*n*-alkylamino)-1,2-dideoxy-D-glucitols (**5a–j**)

Compound	M.p./°C	ΔH/kJ mol^{-1}	C.p.‡/°C	ΔH/kJ mol^{-1}
5a	105·5–106·9	46·7	– –	–
5b	98·2–101·6	40·2	– (97·8)	1·1
5c	97·0–98·9	40·8	– (105·9)§	–‖
5d	104·5–107·7	51·7	114·2 (112·9)	0·4
5e	102·1–106·6	55·5	119·0 (118·8)	1·3
5f	105·4–108·1	53·6	123·4 (123·6)	1·2
5g	106·1–108·0	–¶	127·8 (128·9)	1·0
5h	107·8–110·9	–¶	124·2 (125·1)	0·9
5i	109·7–111·3	–¶	128·7 (129·1)	0·8
5j	107·0–108·2	–¶	122·3 (122·6)	0·7

† Measured at 5 Kmin^{-1} with a Perkin–Elmer DSC 7.
‡ Values in parentheses obtained upon cooling.
§ Measured with a Mettler FP 82 hot stage.
‖ No peak visible in DSC.
¶ Due to exothermal crystal-to-crystal transition, no reliable value was determinable.

cholesteric [77] mesophases. The differences in thermal behaviour are illustrated in figures 4–6.

Compounds **4** can also be compared with the *n*-alkyl-D-gluconamides (**7**) [36, 37] and compounds **6** with the 1-(*n*-alkanoylmethylamino)-1-deoxy-D-glucitols (**8**) [38]. Compounds **7** form monolayers in the crystal as a result of the very strong hydrogen-bond forming amide functionality and favourable packing conditions [67, 69]. Significantly higher melting points are observed for **7**, the clearing points are also somewhat higher, again indicating the stabilizing effect on the mesophase of a functionality capable of hydrogen-bonding which is not involved in dimer formation. Compounds **6** and **8** have similar melting points. The clearing points of **8** are 20–30°C higher than those of **6**, but still much lower than for **4**, indicating that the carbonyl function (a hydrogen-bond acceptor) does have a stabilizing effect on the

Table 4. The transition temperatures† and enthalpies† for a homologous series of 1-(*n*-alkylmethylamino)-1-deoxy-D-glucitols (**6a–j**)

Compound	M.p./°C	ΔH/kJ mol^{-1}	C.p.‡/°C	ΔH/kJ mol^{-1}
6a	76·1–78·9	34·5	– (62·8)	0·8
6b	80·1–83·2	51·7	– (71·3)	1·0
6c	79·9–83·0	41·9	85·7 (85·9)	1·1
6d	79·9–83·8	39·8	95·2 (94·1)	1·0
6e	84·2–87·1	50·5	93·9 (94·8)	1·0
6f	85·8–88·6	50·2	100·2 (100·7)	0·9
6g	88·2–91·6	49·8	102·6 (100·6)	0·8
6h	88·0–92·0	58·1	105·9 (106·3)	0·8
6i	91·6–94·4	63·8	100·9 (100·7)	0·7
6j	90·9–94·3	51·5		

†Measured at 5 K min^{-1} with a Perkin–Elmer DSC 7.
‡Values in parentheses obtained upon cooling.

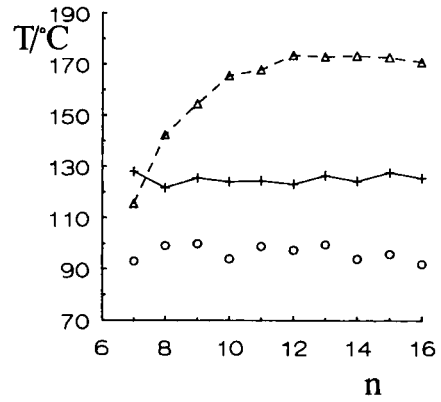


Figure 4. The transition temperatures, for **4a–j** plotted as a function of the alkyl chain length, *n*; +, melting point; △, clearing point; ○, freezing point; ○, freezing point.

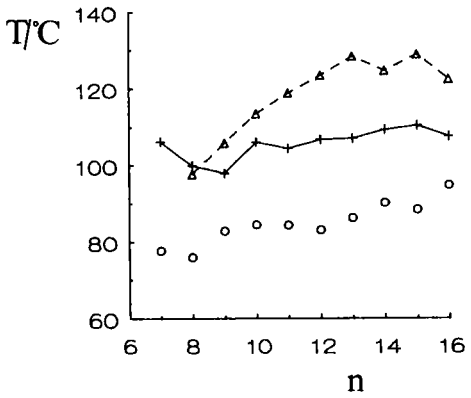


Figure 5. The transition temperatures for **5a–j** plotted as a function of the alkyl chain length, *n*; +, melting point; △, clearing point; ○, freezing point.

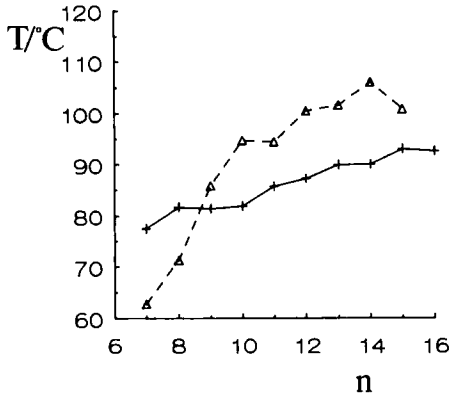
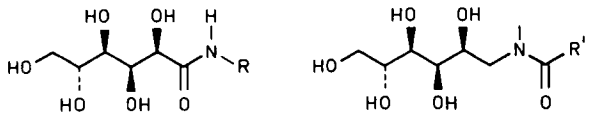


Figure 6. The transition temperatures for **6a–j** plotted as a function of the alkyl chain length, *n*; +, melting point; △, clearing point.



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Scheme II.

Table 5. Comparison of the transition temperatures for the *n*-dodecyl derivatives of acyclic compounds **5–8** with those of 1-(*n*-dodecylamino)-1-deoxy-D-glucitol

Compound **4f**	m.p. 123°C	c.p. 173°C
	δ m.p./°C	δ c.p./°C
Compound **5f**	−18	−50
Compound **6f**	−36	−73
Compound **7f**	+32	+16
Compound **8f**	−29	−48

mesophase by itself, although it is much smaller than the effect of an -OH or -NH functionality.

The data for compounds **4–8** are summarized in table 5 for the *n*-dodec(ano)yl derivatives **4f–8f**. These clearly demonstrate that small structural changes may lead to large differences in thermal behaviour that are well explained by our qualitative model. The magnitudes of the influences of a structural change are not the same for the melting and clearing points, but so far the influences have always been in the same direction. Further investigations are needed to find out whether the latter phenomenon is accidental or structural.

3. Experimental

All reagents and solvents were purchased from one of the large chemical suppliers and used without purification. Satisfactory elemental analyses of several, arbitrarily chosen, compounds were obtained from the microanalytical division of the Department

of Chemistry, University of Groningen, The Netherlands. NMR spectra were recorded on a Varian VXR 300. Thermomicroscopy was performed with the Mettler FP 800 system, the hot stage was mounted on a Nikon microscope. Quantitative thermal analyses were performed in a Perkin Elmer Delta Series DSC 7. DSC peak shapes indicated that all investigated compounds were more than 99·5 per cent pure.

*n-Alkyl 1-amino-β-*D*-glucopyranosides* (**1a–j**) [48]. A mixture of 3·6 g (0·02 mol) D-glucose (anhydrous) and 0·02 mol of the appropriate *n*-alkylamine in 40 ml of absolute EtOH was stirred at ambient temperature for 24 hours. The mixture was then heated at 50°C until it started to turn yellow (signifying the onset of decomposition) Rapid heating to reflux dissolved nearly all of the remaining solids. Solid residue was separated by decantation, crude **1** crystallizes from the solution in ~90 per cent yield upon cooling. In order to obtain optimum yields of **1a** and **1b** the warm solutions must be saturated with diethyl ether. Crude **1** usually contained traces of unreacted D-glucose which may be removed by recrystallization (MeOH/acetone for **1a–e**, MeOH for **1f–j**). The white crystalline compounds decompose slowly (the rate depends upon the purity and alkyl chain length), eventually leading to a dark brown tar-like substance.

*n-Alkyl 1-amino-1-deoxy-β-*D*-fructopyranosides* (**2a–j**) [49]. A mixture of 0·01 mol **1** and 1 g (0·011 mol) oxalic acid in 100 ml of dry 1,4-dioxane and 30 ml MeOH was refluxed for 10–15 min. Any remaining solids were removed by decantation. Crystalline **2**.HO_2CCO_2H containing 10–25 per cent of dioxane precipitated from the solution upon cooling to room temperature. Pure **2a–e** were obtained in ~80 per cent yield by carefully titrating a suspension/solution of **2**.HO_2CCO_2H in methanol with 1N NaOH in MeOH, followed by removal of the sodium oxalate by filtration over Cellite (P4 glass filter), evaporation of the solvent and recrystallization from acetone or methanol/diethyl ether. Pure **2f–j** were obtained in > 95 per cent yield by dropwise addition of aqueous NaOH to a stirred suspension of **2**.HO_2CCO_2H in H_2O until the pH remains constant at ~7·5. The precipitate was filtered off, washed with cold water, dried and recrystallized from MeOH. The stability of the compounds is similar to that of the corresponding **1**.

*n-Alkyl 1-amino-2-deoxy-*D*-glucopyranosides* (**3a–j**). A mixture of 2·46 g (0·015 mol) 2-deoxy-D-glucose and 0·015 mol of the appropriate *n*-alkylamine in 40 ml of EtOH was stirred for 24 hours at room temperature. For **3a–e** the resulting clear solution was saturated with diethyl ether and cooled to 5°C to give yellowish crystals in ~90 per cent yield. Compounds **3f–j** were heated to dissolve all of the remaining solids and subsequently cooled to 5°C to precipitate the products (yields > 90 per cent).

NMR data (CD_3OD) for *n*-octyl 1-amino-2-deoxy-β-D-glucopyranoside (**3b**): ^1H: δ 0·94 (*t*, 3 H, H–8′, 8′, 8′), 1·35 (*m*, 10 H, H–3′, 3′/7′ (7′), 1·51 (*m*, 2 H, H–2′, 2′), 2·12 (*ddd*, 1 H, H–3), 2·63 (*m*, 1 H, H–2a), 2·95 (*m*, 1 H, H–2b), 3·22 (*dd*, 1 H, H–4), 3·60 (*m*, 1 H, H–5), 3·73 (*dd*, 1 H, H–6a), 3·88 (*dd*, 1 H, H–6b), 4·14 (*dd*, 1 H, $J_{1,2a}$, $J_{1,2b}$, 1·8, 10·6 Hz), 4·70 (*s*, ±3 H, OH's); ^{13}C: δ 14·4 (C–8′), 23·5 (C–7′), 28·3, 30·2, 30·5, 31·0, 32·9 (C–2′/C–6′), 40·6 (C–2), 46·4 (C–1′), 63·1 (C–6), 73·3 (2×), 78·8 (C–3/C–5), 87·4 (C–1). Integration of H–1 indicates the presence of 10–15 per cent of the α anomer in methanol solution.

*1-(n-Alkylamino)-1-deoxy-*D*-glucitols* (**4a–j**) [51]. Nitrogen was bubbled through a solution/suspension of 2 g of **1** in 40 ml of MeOH. After a few minutes 500 mg (0·008 mol) $NaCNBH_3$ and 540 mg (0·009 mol) glacial acetic acid were added and the mixture was stirred under N_2 at room temperature for 5–7 hours. The solution was then carefully acidified to pH of 2 with concentrated HCl (THIS IS HAZARDOUS

BECAUSE HYDROGEN CYANIDE IS EVOLVED!!). After leaving the resulting suspension overnight, MeOH was removed *in vacuo*, 30 ml of H_2O were added and 5N KOH solution was added until the pH remains constant at 8–9. The precipitate was filtered with suction, washed with ice-cold H_2O and dried in the air. Recrystallization from ethanol led to analytically pure **4** in ~90–95 per cent yields.

NMR data (CD_3OD) for 1-deoxy-1-(*n*-octylamino)-1-deoxy-D-glucitol (**4b**): ^1H: δ 0·94 (*t*, 3 H, H-8′, 8′, 8′), 1·36 (*bs*, 10 H, H-3′, 3′/H-7′, 7′), 1·56 (*m*, 2 H, H-2′, 2′), 2·64 (*m*, 2 H, H-1′, 1′), 2·78 (*m*, 2 H, H-1, 1), 3·63–3·96 (several *m*, 6 H, H-2/H-6, 6), 4·70 (*s*, ± 5 H, OH's); ^{13}C: δ 14·3 (C-8′), 23·6 (C-7′), 28·4, 30·3, 30·6 (2 ×), 32·9 (C-2′/C-6′), 50·7 (C-1′), 52·5 (C-1), 65·0 (C-6), 72·8 (3 ×), 73·1 (C-2/C-5).

*1-(n-Alkylamino)-1,2-dideoxy-*D*-glucitols* (**5a–j**). These compounds were prepared from compounds **3** using exactly the same procedure as described for compounds **4a–j**. Yields were approximately 90 per cent.

NMR data (CD_3OD) for 1-(*n*-heptylamino)-1,2-dideoxy-D-glucitol (**5a**): ^1H: δ 0·95 (*t*, 3 H, H-7′, 7′, 7′), 1·37 (*m*, 8 H, H-3′, 3′/H-7′, 7′), 1·54 (*m*, 2 H, H-2′, 2′), 1·77 (*m*, 1 H, H-2a), 1·85 (*m*, 1 H, H-2b), 2·66 (*dt*, 2 H, H-1, 1), 2·83 (*m*, 2 H, H-1′, 1′), 3·38 (*dd*, 1 H, H-3), 3·61–3·75 (several *m*, 2 H, H-4, H-6a), 3·83 (*dd*, 1 H, H-6b), 3·98 (*ddd*, 1 H, H-5); ^{13}C: δ 14·4 (C-7′), 23·7 (C-6′), 28·3, 30·2, 30·3, 32·9 (C-2′/C-5′), 33·8 (C-2), 47·6 (C-1′), 50·5 (C-1), 65·1 (C-6), 70·5, 73·1, 74·7 (C-3/C-5).

*1-(n-Alkylmethylamino)-1-deoxy-*D*-glucitols* (**6a–j**) [52]. A mixture of 1·95 g (0·01 mol) 1-(methylamino)-1-deoxy-D-glucitol, 0·01 mol of the appropriate *n*-alkylbromide and 5·6 g (0·04 mol) K_2CO_3 was refluxed in 40 ml EtOH until the alkylbromide could no longer be detected by TLC (Al_2O_3, $MeCl_2$: MeOH = 9 : 1, detection by iodine vapour), usually 3–4 days. The hot suspension was filtered and compounds **6** crystallized from the resulting clear solution upon cooling. Recrystallization from ethanol yielded analytically pure product in 60–65 per cent yield.

NMR data (CD_3OD) for 1-deoxy-1-(methyloctylamino)-D-glucitol (**6b**): ^1H: δ 0·93 (*t*, 3 H, H-8′, 8′, 8′), 1·34 (*bs*, 10 H, H-3′, 3′/7′, 7′), 1·53 (*m*, 2 H, H-2′, 2′), 2·33 (*s*, 3 H, N-CH_3), 2·48 (*m*, 2 H, H-1′, 1′), 2·58 (*d*, 2 H, H-1, 1), 3·65–3·91 (several *m*, 6 H, H-2/6, 6), 4·69 (*s*, ± 4 H, *OH*'s); ^{13}C, δ 14·4 (C-8′), 23·5 (C-7′), 27·7, 28·4, 30·2, 30·4 (C-3′/6′), 32·8 (C-2′), 43·0 (C-1′), 59·5 (N-*C*H_3), 61·4 (C-1), 64·7 (C-6), 71·5 (C-2), 72·8, 72·8, 73·4 (C-3, 4, 5).

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