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Crystal and molecular structure of *N*-(*n*-octyl)-6-deoxy-D-gluconamide: a novel packing of amphiphilic molecules

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Abstract

N-(*n*-Octyl)-6-deoxy-D-gluconamide crystallizes in the orthorhombic space group $P2_12_12_1$, with $a = 5.4524(5)$, $b = 16.662(3)$, and $c = 36.897(5)$ Å. The structure was determined by X-ray diffraction and refined to $R = 9.2\%$. The asymmetric crystal unit contains two molecules (A,B) with significantly different conformations. In contrast to the crystal structures of the *N*-(*n*-alkyl)-D-gluconamide family, in which the molecules were found arranged in head-to-tail monolayers, molecules A and B form a complex motif with pairwise alternating orientations and interdigitating antiparallel aliphatic chains. The two symmetry independent molecules form considerably different hydrogen bond patterns.

Keywords: Alkyl-gluconamides; Amphiphilic molecules; Aliphatic chain packing; Crystal packing; Hydrogen bonding

1. Introduction

The family of alkylated *N*-(*n*-alkyl)-gluconamides exhibits interesting liquid crystal properties which have been reviewed in [1]. X-ray crystal structures of *N*-(*n*-alkyl)-gluconamides have been determined for various alkyl substituents; in the present context, only those with *n*-aliphatic chain residues are of greater interest, i.e., *n*-heptyl [2],

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n-octyl [3], *n*-decyl [2], and *n*-undecyl [4] derivatives. *N*-(*n*-Alkyl)-gluconamides with alkyl chains longer than eight carbon atoms form monolayers, and those with shorter aliphatic chains tend to form micelles [5]. When crystallized, *N*-(*n*-alkyl)-D-gluconamides always form head-to-tail monolayers with the only variation that the symmetry of this packing is triclinic for alkyl chains with odd numbers of C-atoms and monoclinic (space group $P2_1$) for even numbers [3]. In all crystal structures, the hydrogen bond arrangements exhibit systematic patterns, which include a typical four-membered homodromic cycle of intermolecular hydrogen bonds, O-4-H · · · O-3-H · · · O-5-H · · · O-6-H [1–4,6,7]. The head-to-tail monolayers are not the only packing motif for alkylated saccharides: for other hexose moieties, tail-to-tail bilayers are formed, which are more typical for membrane building molecules, e.g., *N*-(*n*-octyl)-D-gulonamide [8] and *N*-(*n*-octyl)-D-talonamide [9]. In the title compound, the terminal hydroxyl group O-6-H of the saccharide has been removed. This necessarily deletes the homodromic four-membered hydrogen bonded cycle, which involves O-6-H. In consequence, a different molecular packing is formed, which represents a new motif for this type of amphiphilic molecules.

2. Experimental

Preparation of N-(n-*octyl*)-*6-deoxy*-D-*gluconamide.*—(by B.P.):

(1) Catalytic oxidation of 6-deoxy-D-*glucose.*—6-Deoxy-D-glucose (1 g, Sigma) was dissolved in 25 mL aqua dest. (pH 7.1), and 50.5 mg of the catalyst Pd–Bi/C suspended in 25 mL aqua dest. was added (pH 6.82). The solution was held under nitrogen, and oxygen was added at a very slow rate to avoid poisoning of the catalyst. The solution was stirred at 50°C and the gluconic acid formed was neutralized by addition of 1 M NaOH. A constant pH of 9.0 was reached after 6 h (97.7% oxidation). The catalyst was then removed by filtration and the gluconic acid sodium salt was obtained by lyophilisation (1.4 g).

(2) 6-Deoxy-D-*gluconolactone.*—The sodium salt of gluconic acid (1.2 g) was dissolved in 40 mL aqua dest. The free gluconic acid was obtained by stepwise addition of cation exchange resin (BioRad W-X8) in the acidic form. When a pH of 2.6 was reached after 15 min, the ion exchange resin was removed by filtration and the gluconolactone was obtained by lyophilisation (930 mg).

(3) N-(n-*Octyl*)-*6-deoxy*-D-*gluconamide.*—6-Deoxy-D-gluconolactone (930 mg, 5.74 mmol) was dissolved in 20 mL of MeOH. The solution was kept at 75°C, and 1.2 mL octylamine (6.65 mmol) was added. After stirring for 2.5 h at 65°C, the solution was stored in a freeze box for crystallisation. Crystals were removed by filtration and washed with acetone. Yield: 1.2 g (72%).

Growth of crystals.—Single crystals suitable for X-ray diffraction studies were grown by slow evaporation of solutions of *N*-(*n*-octyl)-6-deoxy-D-gluconamide in EtOAc. Crystals usually grow as very thin plates which diffract too weakly for structure determination; only occasionally, more bulky specimen were obtained. For all crystals tested, the Bragg reflections were somewhat diffuse, indicating imperfect crystalline order. However, this is the normal case for membrane building molecules.

Table 1
Crystallographic data for 1 and for comparison for 2 [a] [3]

	1	2
Formula	$C_{14}H_{29}NO_5$	$C_{14}H_{29}NO_6$
M_w	291	307
Crystal system	orthorhombic	monoclinic
Space group	$P2_12_12_1$	$P2_1$
Cell constants		
a (Å)	5.4524(5)	5.2521(1)
b (Å)	16.662(3)	32.426(9)
c (Å)	36.897(5)	4.805(1)
β (°)		94.96(5)
Cell volume (Å^3)	3352.1(8)	815.23
Z	8	2
d_c (g cm^{-3})	1.15	1.25
Number of X-ray data	2227	1393
Observed data	1952 $F_o \geq 3\sigma(F_o)$	1377 $F_o \geq 2(F_o)$
Final R-factor	0.092	0.046

[a] standard errors given in parentheses.

X-ray diffraction experiments.—Although crystals are stable in air, X-ray diffraction experiments were performed on a crystal mounted in a thin-walled glass capillary together with some mother liquor in order to avoid contact with glue. (Crystal dimensions $0.35 \times 0.25 \times 0.10$ mm^3, Enraf-Nonius Turbo-CAD4 diffractometer on a FR571 rotating anode X-ray generator, Ni-filtered CuK_α radiation with $\lambda = 1.542$ Å, data

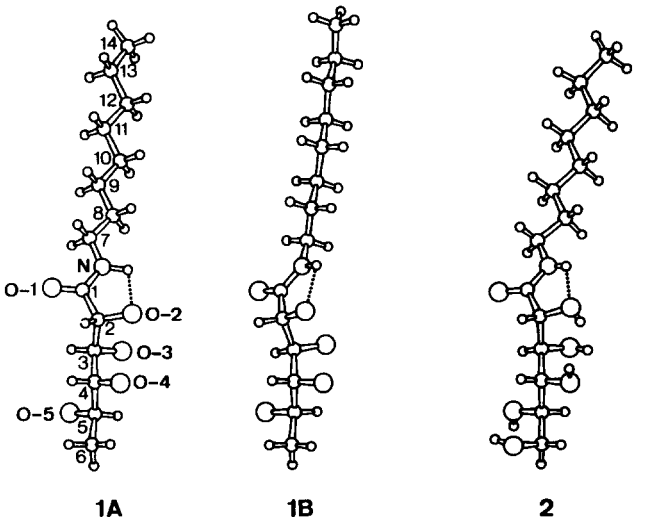

Fig. 1. Molecular structure and atomic labeling for **1A**, **1B**, and **2** [3]. The projection plane is perpendicular to C-3–C-4–C-5. The intramolecular hydrogen bonds are shown; the contacts O-2 · · · O-4 may or may not be associated with intramolecular hydrogen bonds.

collection to a crystallographic resolution of $\lambda/2\sin\theta_{max} = 0.89$ Å, ω-scan mode, empirical absorption correction [10]; crystal data is given in Table 1).

Structure solution and refinement.—The crystal structure was solved with direct methods and refined with standard procedures [11,12] (2 molecules per asymmetric crystal unit). H-atoms bonded to C and N were calculated to ideal positions. Hydroxyl

Table 2
Fractional atomic coordinates and equivalent isotropic displacement parameters U_{eq} in **A** (standard errors given in parentheses)

Atom	x/a	y/b	z/c	U_{eq} (Å^2)
C-6(A)	0.172(3)	0.6665(7)	−0.0889(3)	0.11(1)
C-5(A)	0.323(2)	0.6764(7)	−0.0546(2)	0.08(1)
O-5(A)	0.345(1)	0.7582(3)	−0.0441(2)	0.074(7)
C-4(A)	0.219(2)	0.6260(5)	−0.0239(2)	0.060(9)
O-4(A)	0.207(1)	0.5452(4)	−0.0343(2)	0.085(8)
C-3(A)	0.348(2)	0.6392(6)	0.0120(3)	0.07(1)
O-3(A)	0.612(1)	0.6269(4)	0.0075(2)	0.070(7)
C-2(A)	0.260(2)	0.5819(5)	0.0409(2)	0.062(9)
O-2(A)	0.377(1)	0.5052(3)	0.0378(2)	0.076(7)
C-1(A)	0.295(2)	0.6173(6)	0.0780(3)	0.07(1)
O-1(A)	0.162(2)	0.6733(4)	0.0883(2)	0.083(8)
N-(A)	0.472(2)	0.5886(5)	0.0996(2)	0.074(9)
C-7(A)	0.507(3)	0.6172(7)	0.1351(3)	0.10(1)
C-8(A)	0.723(2)	0.5876(7)	0.1551(3)	0.10(1)
C-9(A)	0.749(3)	0.6173(8)	0.1928(3)	0.11(1)
C-10(A)	0.961(3)	0.5918(9)	0.2146(3)	0.12(2)
C-11(A)	0.961(3)	0.619(1)	0.2534(3)	0.14(2)
C-12(A)	1.180(3)	0.590(1)	0.2757(3)	0.17(2)
C-13(A)	1.180(4)	0.616(1)	0.3155(4)	0.18(2)
C-14(A)	1.386(4)	0.603(2)	0.3384(5)	0.23(2)
C-6(B)	−0.355(2)	0.3854(6)	−0.0912(3)	0.10(1)
C-5(B)	−0.214(2)	0.4091(6)	−0.0568(3)	0.07(1)
O-5(B)	−0.294(1)	0.4922(4)	−0.0487(2)	0.088(8)
C-4(B)	−0.257(2)	0.3578(5)	−0.0254(2)	0.060(9)
O-4(B)	−0.171(1)	0.2773(3)	−0.0351(2)	0.067(7)
C-3(B)	−0.133(2)	0.3865(6)	0.0091(3)	0.07(1)
O-3(B)	0.127(1)	0.3737(4)	0.0065(2)	0.067(7)
C-2(B)	−0.232(2)	0.3542(5)	0.0444(3)	0.07(1)
O-2(B)	−0.201(1)	0.2663(4)	0.0456(2)	0.083(8)
C-1(B)	−0.112(2)	0.3924(6)	0.0750(2)	0.07(1)
O-1(B)	−0.149(2)	0.4671(4)	0.0812(2)	0.087(8)
N-(B)	0.038(2)	0.3504(5)	0.0955(3)	0.10(1)
C-7(B)	0.202(3)	0.3834(8)	0.1223(4)	0.14(2)
C-8(B)	0.224(4)	0.344(1)	0.1550(4)	0.18(2)
C-9(B)	0.398(3)	0.3774(9)	0.1827(3)	0.14(2)
C-10(B)	0.426(4)	0.335(1)	0.2169(5)	0.23(2)
C-11(B)	0.592(4)	0.372(1)	0.2451(4)	0.18(2)
C-12(B)	0.629(5)	0.342(2)	0.2806(5)	0.26(2)
C-13(B)	0.804(4)	0.375(2)	0.3064(5)	0.26(2)
C-14(B)	0.824(5)	0.349(2)	0.3401(5)	0.28(2)

Table 3
Bond distances for molecules **A** and **B** (standard errors given in parentheses)

	A	B
C-6–C-5	1.52(1)	1.54(1)
C-5–O-5	1.42(1)	1.48(1)
C-5–C-4	1.52(1)	1.46(1)
C-4–O-4	1.42(1)	1.47(1)
C-4–C-3	1.52(1)	1.52(1)
C-3–O-3	1.46(1)	1.44(1)
C-3–C-2	1.51(1)	1.51(1)
C-2–O-2	1.43(1)	1.47(1)
C-2–C-1	1.50(1)	1.45(1)
C-1–O-1	1.24(1)	1.28(1)
C-1–N	1.34(1)	1.31(1)
N–C-7	1.41(1)	1.44(2)
C-7–C-8	1.48(2)	1.38(2)
C-8–C-9	1.48(1)	1.50(2)
C-9–C-10	1.47(2)	1.45(2)
C-10–C-11	1.50(2)	1.51(2)
C-11–C-12	1.53(2)	1.41(2)
C-12–C-13	1.53(2)	1.46(2)
C-13–C-14	1.42(3)	1.33(2)

Table 4
Bond angles (°) (standard errors given in parentheses)

	A	B
C-6–C-5–C-4	111.0(8)	115.3(8)
C-5–C-4–C-3	113.3(8)	114.2(8)
O-5–C-5–C-4	111.0(7)	105.1(8)
O-5–C-5–C-6	112.1(9)	109.9(8)
C-4–C-3–C-2	112.1(8)	116.8(8)
O-4–C-4–C-5	110.1(7)	106.9(7)
O-4–C-4–C-3	113.6(7)	110.6(7)
C-3–C-2–C-1	110.8(8)	110.7(8)
O-3–C-3–C-4	109.8(7)	109.7(8)
O-3–C-3–C-2	107.9(8)	111.0(8)
C-2–C-1–N	119.6(9)	119.5(9)
O-2–C-2–C-3	111.3(7)	109.8(7)
O-2–C-2–C-1	111.6(7)	111.1(8)
C-1–N–C-7	122.0(9)	125.2(9)
O-1–C-1–N	120.4(9)	119.6(9)
O-1–C-1–C-2	120.0(9)	120.8(9)
N–C-7–C-8	117.4(9)	118(1)
C-7–C-8–C-9	116(1)	119(1)
C-8–C-9–C-10	119(1)	119(1)
C-9–C-10–C-11	116(1)	118(2)
C-10–C-11–C-12	115(1)	125(2)
C-11–C-12–C-13	115(1)	124(2)
C-12–C-13–C-14	122(1)	123(2)

Table 5
Torsion angles [a] in **1A**, **1B**, and **2** [3]. Torsion angles substantially differing from ±180° are labelled *

Torsion angles (°)	1A	1B	2
C-6–C-5–C-4–C-3	−175.7(8)	175(1)	−179.1(3)
C-5–C-4–C-3–C-2*	−173.8(8)	160(1)	177.4(3)
C-4–C-3–C-2–C-1*	−153.9(8)	175(1)	166.1(3)
C-3–C-2–C-1–N*	−107(1)	−111(1)	−111.7(4)
C-2–C-1–N–C-7	−177(1)	168(1)	177.9(3)
C-1–N–C-7–C-8*	−174(4)	138(1)	−172.8(4)
N–C-7–C-8–C-9	−178(1)	−178(1)	−175.6(4)
C-7–C-8–C-9–C-10	−179(1)	−179(1)	176.8(4)
C-8–C-9–C-10–C-11	−175(1)	−177(2)	178.0(4)
C-9–C-10–C-11–C-12	178(1)	176(2)	177.5(5)
C-10–C-11–C-12–C-13	−180(1)	175(2)	−179.9(4)
C-11–C-12–C-13–C-14	−172(2)	176(2)	178.3(4)

[a] Standard errors given in parentheses.

H-atoms could not be located unambiguously in difference-Fourier maps, and are therefore not included in the structure model. Anisotropic refinement converged with $R = 0.092$, which is in the normal range of related studies.

3. Results

General.—Crystal data of *N*-(*n*-octyl)-6-deoxy-D-gluconamide (**1**) are given in Table 1; for comparision, data published earlier for *N*-(*n*-octyl)-D-gluconamide (**2**) are also shown. Fractional atomic coordinates and equivalent isotropic temperature factors are listed in Table 2. Listings with bond lengths, bond angles and torsion angles are given in Tables 3 to 5. Intra- and inter-molecular contacts suggestive of hydrogen bonds are shown in Table 6.

Molecular conformation.—The conformations of the two symmetry-independent molecules **1A** and **1B** are shown in Figs. 1 and 2 in projections parallel and perpendicular to the carbohydrate backbone; for comparison, the conformation of **2** is also shown. As in all gluconamide structures, the D-glucose moiety and the aliphatic chains adopt the extended all-trans conformation, Table 5.

The characteristic intramolecular hydrogen bond N-H · · · O2, which is observed in all D-gluconamide crystal structures, is also formed in **1A** and **1B**. Based on H-atoms in

Table 6a
N-H · · · O Hydrogen bonds (for normalized H-atom positions)

Contacts	H · · · O (Å)	N · · · O (Å)	Angle (°)	Type
NA-H · · · O2A	2.34	2.72	101	intramolecular
NB-H · · · O2B	2.20	2.66	120	intramolecular
NA-H · · · O1B	2.00	2.97	155	intermolecular

Table 6b
O–O separations (≤ 3.2 Å) suggestive of O–H · · · O hydrogen bonds

Contact	d (Å)	Symmetry
Intra-molecular		
O-2A · · · O-4A	2.89	
O-2B · · · O-4B	2.99	
Inter-molecular		
O-1A · · · O-5A	2.64	$x-0.5, 1.5-y, -z$
O-2A · · · O-1B	3.11	$x+1, y, z$
O-2A · · · O-3B	2.82	x, y, z
O-3A · · · O-5A	2.67	$x+0.5, 1.5-y, -z$
O-3A · · · O-5B	3.10	$x+1, y, z$
O-4A · · · O-5B	2.92	x, y, z
O-4A · · · O-5B	2.91	$x+1, y, z$
O-2B · · · O-4B	3.00	$x+0.5, 0.5-y, -z$
O-2B · · · O-4B	2.69	$x-0.5, 0.5-y, -z$
O-2B · · · O-3B	3.16	$x-0.5, 0.5-y, -z$
O-3B · · · O-4B	2.94	$x+0.5, 0.5-y, -z$

ideal covalent geometries (N–H bond length 1.04 Å [13]), the H · · · O-2 separations are 2.33 and 2.19 Å for molecules **1A** and **1B**, respectively, and the angles at H are 101 and 120°, respectively (Table 6). The intramolecular O-2 · · · O-4 separation is 2.89 Å in **1A** and 2.99 Å in **1B**, which is typical for the all-trans conformation. An intramolecular hydrogen bond between these hydroxyl groups is stereochemically possible, but is observed in only few of the related compounds [in *N*-(*n*-undecyl)-D-gluconamide [4], in 1-deoxy-*N*-methyloctanamido-D-glucitol (MEGA-8) [1], and also in the neutron crystal

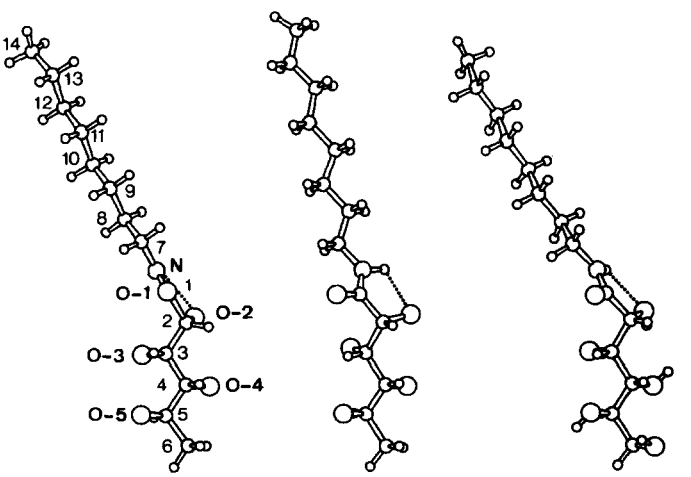

Fig. 2. As Fig. 1, projection plane parallel to C-3–C-4–C-5.

structure of form A of potassium gluconate [14]]. In most of the related compounds, however, *no* intramolecular hydrogen bond O-2 · · · O-4 is formed, despite the short O · · · O separation (as reliably observed by neutron diffraction for *N*-(chloroethyl)-D-gluconamide, O-2 · · · O-4 = 2.97 Å [15]). For **1** it can therefore not be decided from the present data, whether this hydrogen bond is formed or not.

As in **2**, the molecules are bent at the amide link in the form of a 'V'. The geometry of this bending is different for the symmetry-independent molecules **1A** and **1B**. The conformation of **1A** is very similar to that of **2** with all torsion angles comparable exept for C-4–C-3–C-2–C-1, which differs by ~ 12° (compare **1A** and **2** in Figs. 1 and 2). In **1B**, there is a significant distortion in the saccharide moiety, with a pronounced difference for torsion angle C-1–N–C-7–C-8, 138° in **1B**, and −174 and −172° in **1A** and **2**, respectively. This leads to a relatively irregular geometry of the saccharide-alkyl linkage. As a result, the saccharide and alkyl zig-zag chains are almost coplanar in **1B** (angle between the least squares planes of the atoms C-3 to C-6 and C-7 to C-13 = 7°), whereas in **1A** they form a dihedral angle of 103°. The different conformations are presumably adopted to obtain orientations of the alkyl chain suitable for optimal hydrocarbon packing, see below.

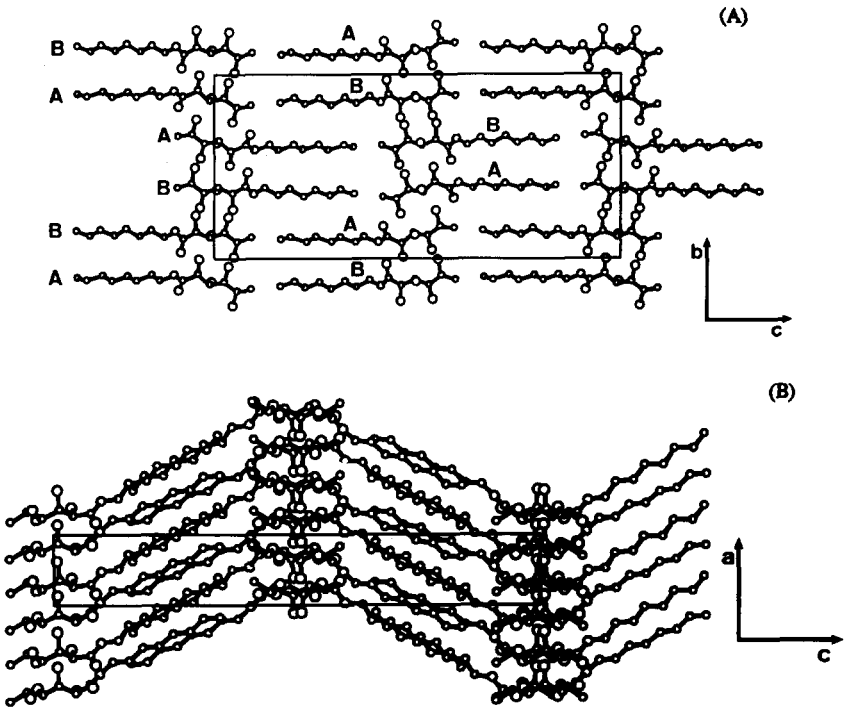

Fig. 3. Crystal packing of *N*-(*n*-octyl)-D-gluconamide: (A) view onto the *b*–*c*-plane, showing the intercalating structure of the carbohydrate moieties and the interdigitating alkyl chains; (B) view onto the *a*–*c*-plane, showing the fishbone pattern.

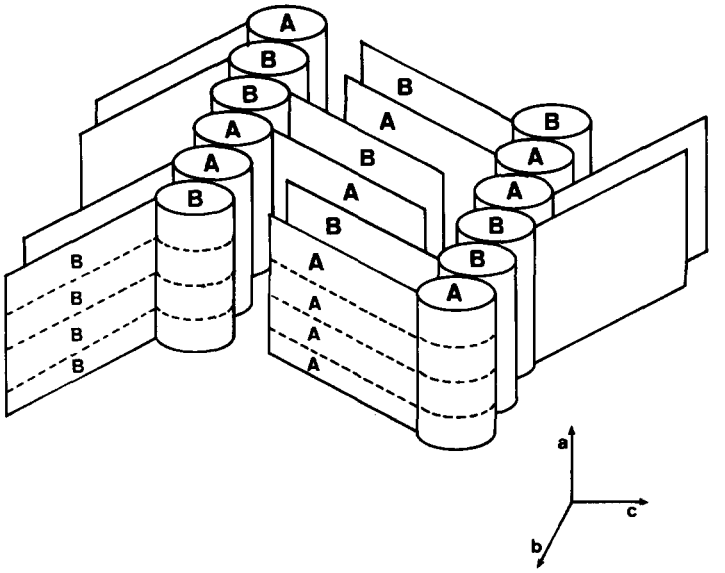

Fig. 4. Schematic picture of the crystal packing. Stacking in the direction of the *a*-axis is drawn as columns; this is a guide to the eye rather than a realistic view. Remarkably, the carbohydrate moieties are arranged in a **AABBAABB** form and the alkyl moieties in a **ABABAB** form.

Crystal packing.—The packing arrangement of **1** is shown in a view down the short *a*-axis in Fig. 3A, down the *b*-axis in Fig. 3B, and in a schematic representation in Fig. 4. In direction of the long *c*-axis, the molecules **A** and **B** are aligned in head-to-tail

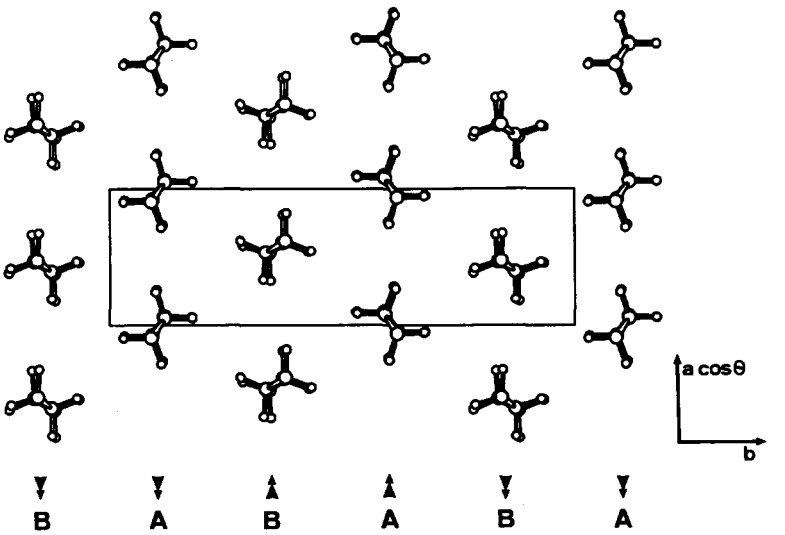

Fig. 5. Aliphatic packing shown in projection along the alkyl chains around $z = 1/4$. Arrows indicate the directionality of the chains: ⇑, C-7 → C-14 running into the projection plane; ⇓, opposite direction. The aliphatic packing is classified as HS1 [17].

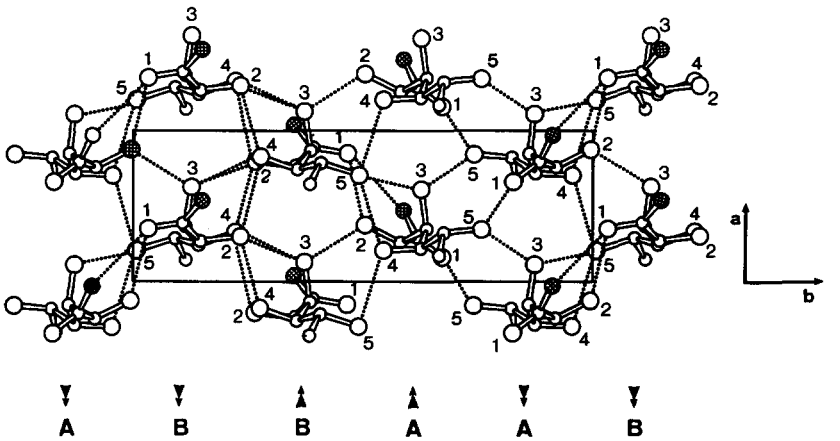

Fig. 6. Intermolecular hydrogen bonding contacts of **1** shown in projection onto the $a-b$-plane. For clarity, only the carbohydrate moiety is drawn: ⇑, the chain C-6 → N is running into the projection plane; ⇓, opposite direction.

fashion **ABAB**. In the b-direction, the packing mode of the carbohydrate moieties is **AABBAABB**, with neighbours **AB** orientated parallel and neighbours **AA** and **BB** orientated antiparallel. This way, carbohydrate moieties form compact layers and the aliphatic chains form interdigitating 'sheets', Fig. 4. A view on the $a-c$-plane (Figs. 3B and 4) shows a fishbone pattern, which is similar to other amphiphilic substances.

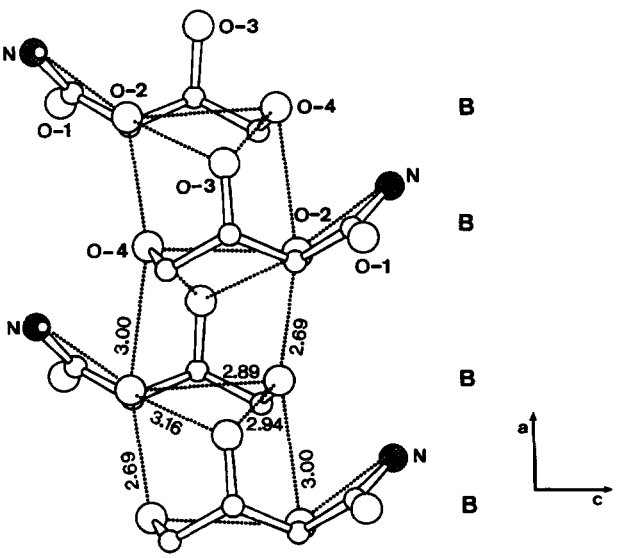

Fig. 7. O · · · O Contacts suggestive of hydrogen bonding between molecules **BB** in projection onto the $a-c$-plane ($y/b = 1/4$). Only relevant atoms are drawn.

Related intercalating packing arrangements with neighbouring antiparallel molecules (↑ ↓ ↑ ↓ ...) were reported for the crystal structures of MEGA-8 [1], and for *N*-gluconamides with isopropyl [16] and cyclohexyl [17] residues, and also for other bilayer forming molecules [18]. Of the particular present packing mode (↑ ↑ ↓ ↓ ↑ ↑), however, no earlier example is known to the authors.

The alkyl chains of **1A** and **1B** are not exactly parallel, but form angles of 29° and 26° with the *b*–*c*-plane (for **1A** and **1B**, respectively). The aliphatic packing is shown in Fig. 5 in a projection along the **1B** chain. Due to the different conformations of the carbohydrate-alkyl linkages, the least squares planes of the alkyl chains of neighbouring parallel molecules **1A** and **1B** are almost perpendicular, 88°, and those of antiparallel molecules **1A** and **1B** are almost parallel. This way a complex, but energetically favorable packing of the alkyl chains is possible, which is classified as orthorhombic 'hybrid substructure' HS1 according to Abrahamson et al. [19] (see also [20]). The dimensions of the aliphatic subcell are $a_s = 4.83$ Å and $b_s = 16.66$ Å, with a cross-sectional area of 20.1 Å^2 per alklyl chain.

The hydrogen bonding network.—As hydroxyl H-atom positions could not be determined, O-H · · · O hydrogen bonds can only be tentatively assigned on the basis of O · · · O contacts, Table 6. The reability of such assignments was recently discussed in detail [21].

The remarkably irregular intermolecular hydrogen bond pattern is shown in a view along the *c*-axis in Fig. 6. Surprisingly, only for molecule **1A**, N-H forms an intermolecular hydrogen bond besides the intramolecular N-H · · · O-2 interaction (intermolecular H · · · O-1B = 2.00 Å, intramolecular H · · · O-2A = 2.34 Å, Table 6), whereas in **1B**, the N-H hydrogen donates only intramolecularly to O-2B. It has been observed earlier in *N*-cyclohexylgluconamide [17], that the gluconamide N-H forms only the heavily bent N-H · · · O-2 interaction, but no intermolecular hydrogen bond.

As there are no direct hydrogen bonds between adjacent molecules in *a*-direction, it is suggestive to describe the hydrogen bonding in terms of network patterns formed within the pairs of layers **AA**, **AB**, and **BB** (compare Fig. 5).

(1) The **AA** *hydrogen bonds.*—Neighboring molecules **AA** are only connected by finite hydrogen bond chains O-3 · · · O-5 · · · O-1, Fig. 6.

(2) The **AB** *hydrogen bonds.*—The hydrogen bonding pattern between molecules **A** and **B** is complex and irregular. Most striking is an infinite chain O-5B · · · O-4A · · · O-5B · · · O-4A running in the direction of the *a*-axis. O-5B forms an additional contact to O-3A, and O-4A an intramolecular contact to O-2A which may or may not represent a hydrogen bond, as was outlined in the section on *Molecular conformation.* Another system of hydrogen bonds is N-A-H · · · O-1BO-2A · · · O-3B, Fig. 6.

(3) The **BB** *hydrogen bonds.*—Unlike **AA** and **AB**, the hydrogen bonds between molecules **BB** form a regular pattern, shown in Fig. 7 in a view on the *a*–*c*-projection plane. Two symmetry related parallel infinite chains O-2 · · · O-4 · · · O-2 · · · O-4 run in the direction of the *a*-axis, and these chains are connected by the intramolecular O-2 · · · O-4 contacts (2.89 Å) to form a ladder-like pattern. This pattern, however, is 'proton-deficient' [22], i.e., the number of O-H hydrogen atoms is not sufficient to satisfy all potential hydrogen bonding contacts simultaneously: the two infinite chains O-2 · · · O-4 · · · O-2 alone would engage all available H-atoms, and no one would be

left for the intramolecular O-2 · · · O-4 contacts. As *intermolecular* O · · · O contacts ≤ 3.0 Å almost certainly are associated with hydogen bonds [21], whereas this is not necessarily true for *intramolecular* contacts, the formation of the two cooperative chains O-2 · · · O-4 · · · O-2 · · · O-4 seems more probable than circular structures with neighbouring unsatisfied short intermolecular O · · · O contacts. In addition, O-2 and O-4 form intermolecular contacts with O-3, which could represent a three center hydrogen bond [22], Fig. 7.

The described patterns are of very unequal strength: the hydrogen bond system between molecules **AA** is relatively weak, whereas the infinite cooperative system **BB** is strong. The irregular pattern **AB** is inbetween these cases. This circumstance certainly is surprising and unfortunately remains unexplained as we were unable to locate H-atom positions.

4. Discussion

It must be expected that the deletion of the O-6 hydroxyl group leads to a different crystal packing mode compared to **2**, because the characteristic homodromic, quadrilateral hydrogen bond pattern (O-3-H · · · O-5-H · · · O-6-H · · · O-4-H · · · O-3) of the *N*-(alkyl)-gluconamide packing can not form. However, the formation of a molecular packing mode which is *that* much different, was not expected.

N-(*n*-Octyl)-D-gluconamides have thermotropic liquid-crystal properties [1,23]. Furthermore, crystal–crystal phase transitions upon heating are observed [4]. Investigations with mannose exhibit different thermal behaviour of the C-6-OH and the C-6-deoxy form, and a comparison of 6-deoxy-L-mannose-*S*,*S*-diacyl-acetal with the stereoisomeric D-mannose form also shows a different thermic behaviour [24]. Deletion of the terminal hydroxyl group of mannose causes absence of a mesophase in a crystal–crystal transition. For **1**, the thermic behaviour in comparison to **2** has not yet been determined.

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