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Non-mesogenic crystal structure of a synthetic 1-D-glucosamide bolaamphiphile

Mitsutoshi Masuda *, Toshimi Shimizu

Department of Organic Materials, National Institute of Materials and Chemical Research, 1-1 Higashi, Tsukuba, Ibaraki 305, Japan

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Abstract

The crystal structure of the synthetic 1-glucosamide bolaamphiphile, *N,N'*-bis(β-D-glucopyranosyl)undecane-1,11-dicarboxamide (**1**) was determined by single-crystal X-ray analysis. The space group is $P2_1$ with cell dimensions: $a = 6.220(1)$, $b = 48.25(1)$, $c = 4.922(2)$ Å, $\beta = 105.67(2)°$, and $Z = 2$. The glucopyranosyl ring is in a $^4C_1$ chair conformation. The bolaamphiphile molecules are arranged in a layered structure with the alkylene chains packed antiparallel in a pleated sheet. The glucosamine moieties are linked by a three-dimensional intermolecular hydrogen-bonding network. The *n*-alkylene chain has an all-*trans* zigzag conformation with a small left-handed twist. © 1997 Elsevier Science Ltd.

Keywords: X-ray; Crystal structure; 1-Glucosamide bolaamphiphile; Layered assembly; Hydrogen-bonding network; All-*trans* zigzag conformation

1. Introduction

The carbohydrate amphiphiles exhibit both thermotropic and lyotropic mesophases, depending on the shape of the molecules [1]. In addition, *N*-alkylaldonamide amphiphiles can form a wide range of well-defined fibrous superstructures [2]. Intermolecular networks of hydrogen bonds play an important role both in the self-assembly of the carbohydrate amphiphiles and in their physical and thermal behavior [1,3–7]. To the best of our knowledge, thirteen X-ray analyses have been reported for the cyclic sugar amphiphiles with single *n*-alkyl chains (carbon number ≥ 5) [1,8–16]. To date, no examples of head-to-head bilayer structures with non-interdigitizing chains have been observed.

Synthetic bolaamphiphiles with a glucopyranose ring at each end form air-stable fibrous assemblies [17]. Cooperative hydrogen-bonding networks in the crystal lattice for the 1-glucosamide bolaamphiphile with *n*-undecamethylene link have been observed [18]. In this paper, we report a head-to-head layered structure of *N,N'*-bis(β-D-glucopyranosyl)undecane-1,11-dicarboxamide containing an all-*trans* hydrocarbon link.

2. Experimental

Synthesis of N,N'-*bis*(β-D-*glucopyranosyl)undecane-1,11-dicarboxamide* (**1**).—The 1-D-glucosamide bolaamphiphile **1** was prepared from the fully acetylated glucosyl bromide via the azide. Commercially available tetra-*O*-acetyl-α-D-glucopyranosyl bromide was treated with NaN_3 to give a crystalline 1-β-azide

* Corresponding author.

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derivative of the tetraacetylated glucose. The ^{1}H NMR spectrum indicated only β-glucose in this azide derivative by the presence of only one doublet (J 8.6 Hz) for the anomeric proton. This compound was hydrogenated in the presence of platinum oxide into a 1-β-amino derivative, which was directly condensed with 1,11-undecane dicarboxylic acid chloride. Purification of the octaacetylated derivatives by silica-gel column chromatography (eluent: 20:1 $CHCl_3$–MeOH) and the succeeding deacetylation gave the crude bolaamphiphile. Purification by silica-gel column chromatography (eluent: 6:4:1 $CHCl_3$–MeOH–H_2O) gave the requisite 1-D-glucosamide bolaamphiphile. The β-anomeric configuration of the product was also confirmed by the anomer proton signal in the ^{1}H NMR spectrum. The purity was confirmed by thin-layer chromatography on silica gel plates (E. Merck Silica Gel F60 254) and MALDI-TOFMS (Shimadzu/Kratos KOMPACT MALDI III) using sinapinic acid as a matrix. *N,N'*-bis(β-D-glucopyranosyl)undecane-1,11-dicarboxamide (**1**): mp 220.4 °C; ^{1}H NMR (270 MHz, D_2O, 50 °C): δ 4.95 (d, J 9.2 Hz, 2 H, H-1), 3.88 (dd, J 12.2 and 2.0 Hz, 2 H, H-6b), 3.72 (dd, J 12.2 and 5.0 Hz, 2 H, H-6a), 3.55 (dd, J 9.2 and 8.9 Hz, 2 H, H-3), 3.51 (m, J 9.3, 5.0, and 2.0 Hz, 2 H, H-5), 3.42 (dd, J 9.3 and 8.9 Hz, 2 H, H-4), 3.39 (dd, J 9.2 and 9.2 Hz, 2 H, H-2), 2.32 (dd, J 7.3 and 7.6 Hz, 4 H, $-CH_2CONH-$), 1.64 (m, 4 H, $-CH_2CH_2CONH-$), 1.29 (m, 14 H, $-CH_2-$). Anal. Calcd for $C_{25}H_{46}N_2O_{12}$ (566.31): C, 52.99; H, 8.18; N, 4.94. Found: C, 53.04; H, 8.20; N, 4.89.

Table 1
Crystal data and summary of experimental details for **1**

Molecular formula	$C_{25}H_{46}N_2O_{12}$
Molecular weight	566.30
Crystal type	Monoclinic
Space group	$P2_1$
Z	2
Lattice constants	
a (Å)	6.220(1)
b (Å)	48.25(1)
c (Å)	4.922(2)
β (°)	105.67(2)
Cell volume (Å^3)	1422.3(6)
Crystal dimensions (mm)	0.80×0.30×0.20
D_{calc} (g·cm^{-3})	1.32
D_{obs} (g·cm^{-3})	1.33
Radiation	Graphite-monochromated Mo-K α
Number of reflections measured	7512
Number of unique reflections	3308
Number of observed reflections	2256 [$F > 3\sigma(F)$]
Index range for data collection	$-7 \le h \le 8$ $-62 \le k \le 62$ $-6 \le l \le 0$
2θ range (°)	$3 \le 2\theta \le 55$
Scan mode	ω-scan
R-factor	0.0504
wR	0.0791

X-ray single-crystal structure analysis.—Crystals of **1** were obtained by slow cooling and evaporation of an aq soln. The data collection was on a Mac Science MXC18 automatic four-circle diffractometer at room temperature. All measurements were carried out by ω-scan method in $3° < 2\theta < 55°$. The unit cell dimensions were determined from 19 strong reflections. The intensities and orientation of the crystal were checked by three non-overlapping standard reflections every 100 reflections. Crystal data and summary of the experimental details are given in Table 1.

The structure was solved by the direct method (SIR92 in CRYSTAN-GM) and refined by CRYSTAN-GM [19,20]. The absolute configuration of the molecule is determined by the known chirality of the D-glucopyranose ring in previous syntheses [21,22]. All the non-hydrogen atoms were refined anisotropically. The hydrogen atoms of hydroxyl and amide groups were located by difference Fourier synthesis, and the remaining hydrogen atoms were placed at calculated positions [d(C–H) = 1.00 Å]. All the located hydrogen atoms were included in the further full-matrix least-square refinement. The atomic coordinates of the non-hydrogen and hydrogen atoms are listed in Table 2.

3. Results and discussion

The crystal of **1** is stable in the atmosphere and transforms directly from crystal to liquid at 220 °C [23]. This is in a striking contrast to the thermotropic liquid crystalline behavior of bolaamphiphilic polyols [3,24].

The molecular structure of **1** is shown in Fig. 1 with atomic numbering. The segments **A** and **B** in **1** show a small conformational difference of less than 10° in torsion angles. The C–C bond lengths of the glucopyranosyl ring are normal, 1.510(7)–1.534(10)

Table 2
Fractional atomic coordinates and equivalent isotropic temperature factor [a,b]

Atom	x/a ($\times 10^{-4}$)	y/b ($\times 10^{-4}$)	z/c ($\times 10^{-4}$)	U_{iso} ($\times 10^{-3}$)
C-1A	14282(9)	6375(1)	4923(13)	48
C-2A	15622(9)	6417(1)	2798(15)	53
C-3A	17289(9)	6652(1)	3850(13)	48
C-4A	16028(8)	6914(1)	4180(14)	47
C-5A	14470(9)	6860(1)	6019(14)	48
C-6A	12945(10)	7101(1)	6120(16)	61
C-7A	12180(10)	5963(1)	5680(14)	53
C-8A	10675(10)	5733(1)	4132(15)	57
C-9A	9265(11)	5589(1)	5785(13)	55
C-10A	7554(11)	5403(2)	3830(13)	57
C-11A	6164(11)	5225(2)	5271(15)	61
C-12A	4389(10)	5063(1)	3114(13)	54
C-13	3004(11)	4866(2)	4378(15)	61
N-1A	12710(9)	6154(1)	3996(14)	54
O-2A	16824(8)	6174(1)	2454(13)	66
O-3A	18576(7)	6704(1)	1888(9)	56
O-4A	17586(7)	7121(1)	5443(12)	62
O-5A	13059(6)	6622(1)	5043(9)	49
O-6A	11609(7)	7173(1)	3370(12)	66
O-7A	12917(9)	5971(1)	8250(10)	72
C-1B	−8880(7)	3418(1)	−890(9)	33
C-2B	−11165(8)	3406(1)	−2967(10)	36
C-3B	−12420(7)	3151(1)	−2343(10)	35
C-4B	−11029(8)	2888(1)	−2259(11)	39
C-5B	−8738(8)	2930(1)	−262(11)	38
C-6B	−7169(8)	2684(1)	−099(13)	46
C-7B	−6516(7)	3817(1)	755(10)	33
C-8B	−5417(9)	4067(1)	−143(11)	42
C-9B	−3324(10)	4159(2)	2076(12)	53
C-10B	−2085(10)	4388(1)	965(12)	50
C-11B	−124(11)	4504(2)	3225(14)	60
C-12B	1158(10)	4725(1)	2089(13)	52
N-1B	−7587(6)	3649(1)	−1338(8)	34
O-2B	−12301(7)	3652(1)	−2666(10)	49
O-3B	−14493(6)	3130 [c]	−4431(9)	49
O-4B	−12181(7)	2671(1)	−1253(12)	60
O-5B	−7673(5)	3169(1)	−1123(7)	35
O-6B	−6833(6)	2619(1)	−2756(10)	57
O-7B	−6465(7)	3774(1)	3245(7)	50
Atom	x/a ($\times 10^{-3}$)	y/b ($\times 10^{-3}$)	z/c ($\times 10^{-3}$)	U_{iso} ($\times 10^{-2}$)
H–N-7A	1227(11)	610(1)	245(15)	4(2)
H–O-2A	1609(17)	605(2)	129(19)	8(3)
H–O-3A	1997(13)	661(2)	253(14)	6(2)
H–O-4A	1722(18)	728(2)	467(22)	10(3)
H–O-6A	−552(16)	268(2)	−381(18)	10(2)
H–N-7B	−732(11)	366(1)	−325(14)	5(2)
H–O-2B	−1334(9)	366(1)	−387(10)	2(1)
H–O-3B	−1568(18)	317(2)	−315(21)	12(3)
H–O-4B	−1189(16)	255(2)	−191(19)	8(3)
H–O-6B	1022(16)	708(2)	356(19)	9(3)

[a] The expression is $U_{iso} = \frac{1}{3}\Sigma\Sigma U_{ij} a_i^* a_j^* \boldsymbol{a}_i \cdot \boldsymbol{a}_j$.
[b] Standard deviations are given in parentheses.
[c] Fixed parameter.

Å, as are the C–OH bond lengths, 1.409(8)–1.433(8) Å.

Two D-glucopyranose rings are in the $^4C_1$ chair conformation as shown in Fig. 1. Selected torsion angles are given in Table 3. The torsion angles within the ring range from 51.7(6) to 65.3(4)° and are similar to those of methyl β-D-glucopyranoside in the crystal lattice (the deviation ≤ 5.5°) [25]. The torsion angles around the *N*-glycosidic linkage (C-7–N-1–C-1–O-5) are −101.0(8) and −107.1(5)° in **A** and **B**, respectively. The corresponding angles are −73.2° (C–O-1–C-1–O-5) and −83.6° (C–N-1–C-1–O-5) for methyl β-D-glucopyranoside [25] and 4-*N*-(β-D-glucopyranosyl)-L-asparagine, respectively [26]. The angles in **1** are close to that of the latter, which also has *N*-glycosidic linkage via the amide group. The puckering parameters (Q) [27] of the two glucopyranose rings (0.587 and 0.596 Å in **A** and **B**, respectively) are similar to the ideal value for β-D-glucopyranose ring with the $^4C_1$ chair conformation (0.598 Å) [28]. However, the θ parameter in **A** (7.1°) deviates more from the ideal value (2.7°) than that in **B** (5.1°). As will be detailed later, the bigger distortion of the ring in **A** should be derived also from the convergent hydrogen-bond formation of the N-1A–H amide and O-2A–H hydroxyl protons to the O-7A carbonyl oxygen.

A schematic illustration of the planes for the sugar, amide, and alkylene chain moieties is given in Fig. 2. The planes through the amide groups (planes D and E) are inclined (13.4 and 16.8°, respectively) to the plane C through eleven carbon atoms of the connecting *n*-alkylene chain. The alkylene chain has an all-*trans* zigzag conformation with a left-handed twist (Fig. 3a). The plane through C-8A, C-9A, and C-10A makes an angle of 30.9° to that through C-8B, C-9B, and C-10B. In addition, the chain is also bowed with a subtending angle of 5.9°, when viewed perpendicular to the plane C (Fig. 3b). On the other hand, both the amide planes D and E are almost parallel (8.5°) to each other.

In Fig. 2, the plane of the amide group (plane D) through N-1A, C-7A, and O-7A forms an angle of 66.1° to the least-square plane F through C-2A, C-3A, C-5A, and O-5A of the glucopyranose ring. The plane of the amide group (plane E) through N-1B, C-7B, and O-7B forms an angle of 72.9° to the least-square plane G of the glucopyranose ring through the C-2B, C-3B, C-5B, and O-5B.

Molecular packing.—Fig. 4a and b show the crys-

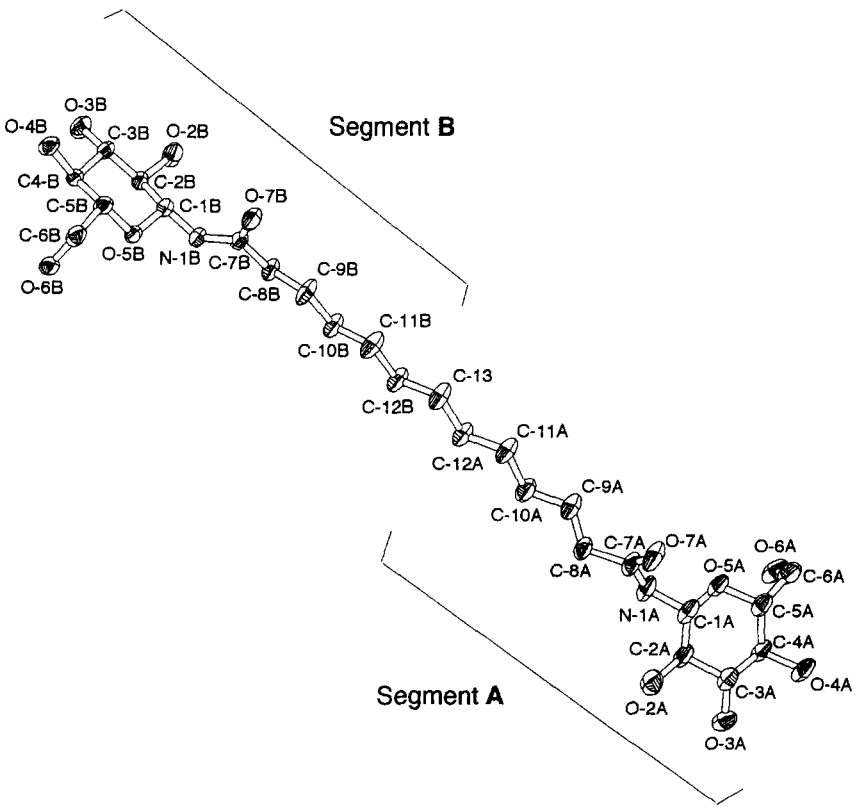

Fig. 1. Molecular structure (ORTEP drawing) and atomic numbering for **1**. Thermal ellipsoids are drawn at 50% probability.

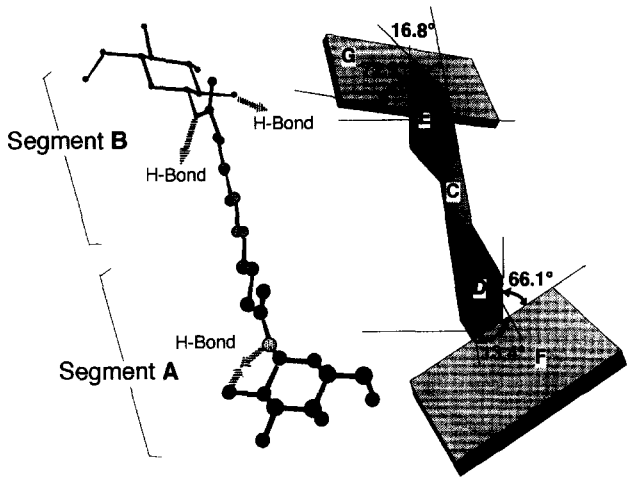

Fig. 2. Schematic illustration of the orientation for five least-square planes C, D, E, F, and G in **1**.

tal packing pattern of **1**. The bolaamphiphile molecules form a head-to-head layered structure in which polar and non-polar regions alternate. The alkylene chains are arranged in an antiparallel pleated sheet. The polar sugar head-groups are hydrogen-bonded, while the *n*-alkylene chains form close hydrocarbon packing with parallel zigzag alkylene chains. The distances between adjacent alkylene chains are 6.22 and 4.92 Å, corresponding to the lengths of the *a*- and *c*-axis in the unit cell, respectively. The 4.9-Å length is typical for the alkylene-chain packing with hydrogen-bonded amide groups [29]. The 6.2-Å distance is the result of the pyranose rings. As a result, the inclination of the alkylene chain is 50° with respect to the normal to the layered plane [9,16]. The packing type categorized by Vand [30] is $T_{\|}$ for **1**. The subcell is outlined in Fig. 4a and b as a distorted triclinic cell with idealized dimension: $a_s = 4.18$, $b_s = 2.53$, $c_s = 4.92$ Å, $\alpha = 90.0$, $\beta = 66.5$, $\gamma = 84.7°$. The volume per CH_2 group is 23.7 Å^3 and similar to that of 1-decyl α-D-glucopyranoside (22.4 Å^3) [12], where the hydrocarbon chains interdigitate to compensate the packing of sugar moieties [9–14]. This crystal structure demonstrates that a stable layered structure containing no hydrocarbon chain disorder is possible with a cyclic head-group.

Hydrogen bonds of the sugar hydroxyl and amide groups.—The intermolecular O–O distances in hy-

Table 3
Selected torsion angles (degrees) in **1** [a]

Torsion angle	Segment **A**	Segment **B**
Sugar		
O-5–C-1–C-2–C-3	62.7(6)	58.9(5)
C-1–C-2–C-3–C-4	−59.0(6)	−53.3(5)
C-2–C-3–C-4–C-5	53.4(6)	52.3(5)
C-3–C-4–C-5–O-5	−51.7(6)	−57.0(5)
C-4–C-5–O-5–C-1	57.5(6)	64.6(4)
C-5–O-5–C-1–C-2	−62.7(6)	−65.3(4)
N-1–C-1–C-2–O-2	−59.7(6)	−59.8(5)
O-3–C-3–C-2–O-2	59.0(6)	65.7(5)
O-4–C-4–C-3–O-3	−65.4(6)	−67.3(5)
O-4–C-4–C-5–C-6	67.7(6)	65.5(6)
O-5–C-5–C-6–O-6	−65.1(6)	−63.2(5)
Amide		
C-1–N-1–C-7–C-8	−173.3(10)	−174.2(6)
C-7–N-1–C-1–O-5	−101.0(8)	−107.1(5)
C-7–N-1–C-1–C-2	141.2(9)	131.7(5)
Alkylene chain		
C-7–C-8–C-9–C-10	169.6(8)	172.6(7)
C-8–C-9–C-10–C-11	174.5(8)	174.1(8)
C-9–C-10–C-11–C-12	175.8(8)	178.0(8)
C-10–C-11–C-12–C-13	176.7(8)	174.4(8)
C-11–C-12–C-13–C-(12) [b]	176.3(8)	174.1(8)
Amide–alkylene chain		
C-9–C-8–C-7–N-1	−155.0(9)	−149.0(7)

[a] Standard deviations are given in parentheses.
[b] The number in parentheses shows the atom number in opposite segment.

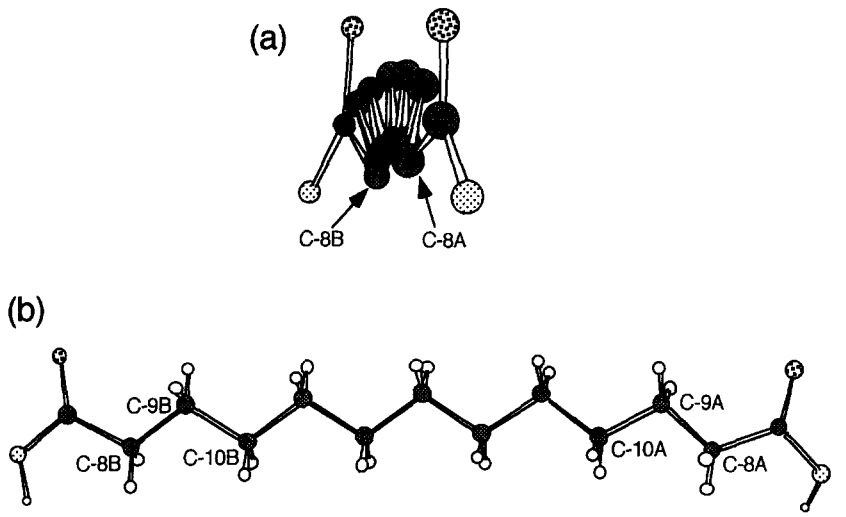

Fig. 3. Conformation of the undecane 1,11-dicarboxamide chain in the crystal lattice of **1** viewed along (a) the zigzag chain axis and (b) the perpendicular axis to the zigzag plane of the *n*-alkylene chain.

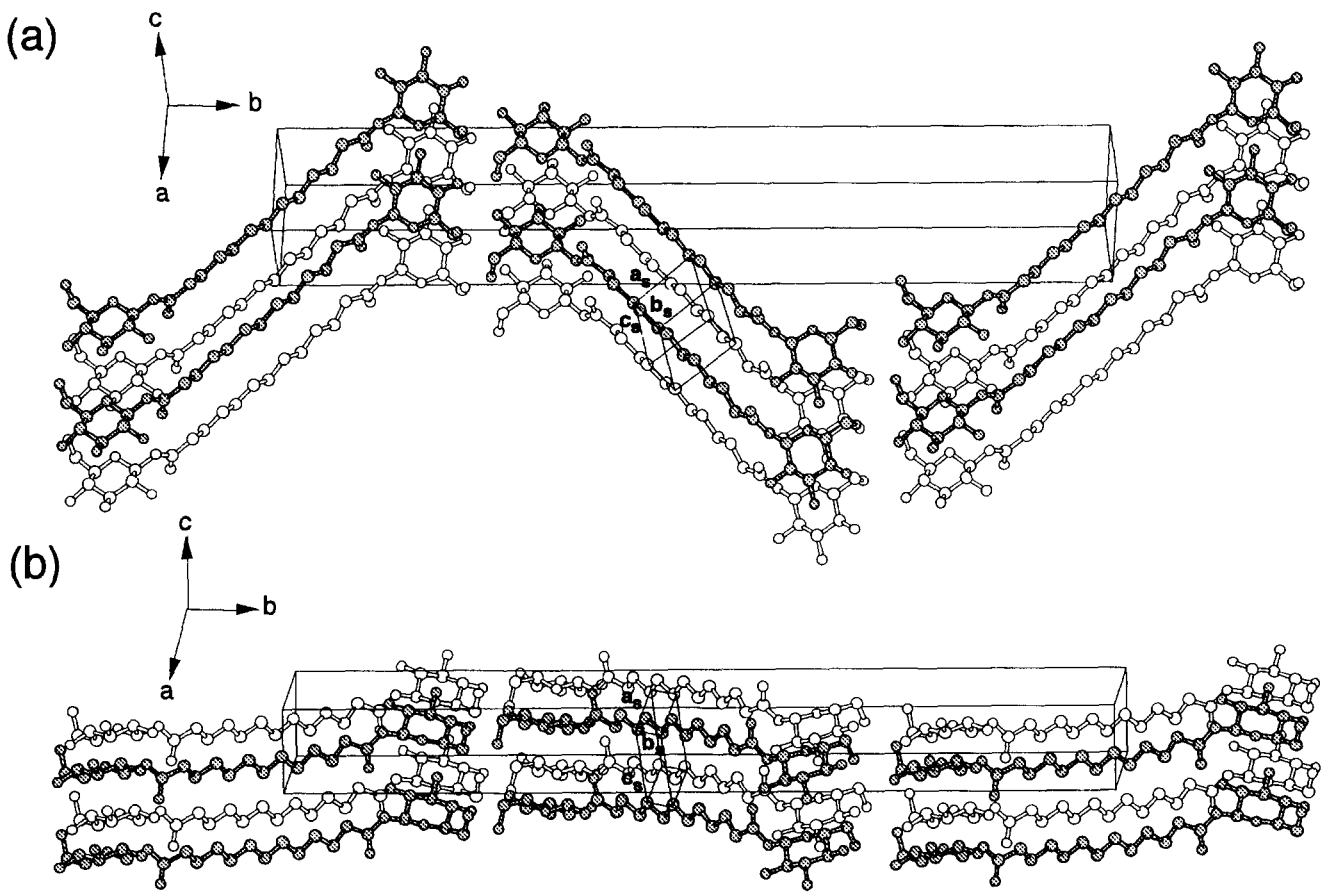

Fig. 4. Molecular packing and sub-cell structure of **1** viewed along (a) the *c*-direction and (b) the *a*-direction. The molecules on this side are shaded, and hydrogen atoms are omitted for clarity.

drogen-bond contacts are listed in Table 4. There exist twenty-four hydrogen bonds per molecule. The hydrogen-bonding network contributes to crystal stability. Two types of hydrogen bonds exist. One set is between the sugar hydroxyl groups except for the O-2A–H and O-2B–H groups, which construct a two-dimensional network in the *ab*-plane (Fig. 4a and Fig. 5a and b). The another is a motif of linear hydrogen bonds involving the amide and hydroxyl (O-2A–H and O-2B–H) groups along the *c*-axis.

Intra- and inter-layer hydrogen bonds are shown in Fig. 5a and b. They are formed between sugars in the equatorial direction of the pyranose rings, roughly in a two-dimensional plane, and are similar in both segments of the molecule, except for O-2A and O-2B. Each hydroxyl group participates in more than two hydrogen bonds as a donor or an acceptor. Especially, O-6A and O-6B participate in three hydrogen bonds. The O-6–H group as donor and the O-3 and O-4 atoms as acceptors form bifurcated three-center hydrogen bonds in both segments [31–33].

Intralayer '*N*'-shaped hydrogen bonds are seen between the hydroxyl groups and the oxygen atoms of adjacent molecules within the layer (O-3–H · · · O-5, O-6–H · · · O-3, and O-6–H · · · O-4). This motif is very similar to that found in the crystal structure of merosingrin [34,35]. Merosingrin is a D-glucopyranose derivative forming a bicyclic compound at the C-1 and C-2 positions. Due to this blocking, the hydroxyl groups at the C-3–C-6 positions only are available for hydrogen bonding. Since the O-2–H groups of **1** are utilized to hydrogen-bond to carbonyl oxygen O-7 of the amide group, the other hydroxyl groups will behave in the same way as merosingrin in hydrogen-bond formation.

Interlayer hydrogen bonds are found between the hydroxyl groups of both segments, O-4A–H · · · O-6B and O-4B–H · · · O-6A. The alternating intra- and inter-layer hydrogen bonds form an infinite chain (· · · O-6A–H · · · O-4A–H · · · O-6B–H · · · O-4B–H · · ·) through the *ab*-plane. This is energetically more favorable than the finite chain [36].

The hydrogen-bond scheme around the amide groups, illustrated in Fig. 6, is arranged in translation motif [29]. It should be noted that the hydroxyl group O-2A–H at (x, y, z) bonds to the carbonyl oxygen O-7A at (x, y, $z-1$), whereas the O-2B–H group at (x, y, z) bonds to O-7B at ($x-1$, y, $z-1$). The FTIR spectrum for the crystal of **1** showed two distinctive amide C=O stretching bands at 1657 and 1642 cm^{-1}. This result suggests a difference in hydrogen-bond stability of the amide groups in **A** and

Table 4
Hydrogen-bond distances (Å) and angles (degrees) [a] with symmetry code [b]

	O–H(i) · · · O	O · · · O (Å)	H · · · O (Å)	O–H · · · O (°)
Glucopyranose ring				
Segment **A**	O-3–H · · · O-5(ii)	2.829(5)	1.98	145
	O-6–H · · · O-3(iii) [c]	2.911(7)	2.14	135
	O-6–H · · · O-4(iii) [c]	2.957 6)	2.13	142
	O-4A–H · · · O-6B(iv) [d]	2.720(8)	1.76	170
Segment **B**	O-3–H · · · O-5(iii)	2.888(5)	1.93	169
	O-6–H · · · O-3(ii) [c]	3.087(5)	2.40	128
	O-6–H · · · O-4(ii) [c]	2.798(6)	2.19	120
	O-4B–H · · · O-6A(v) [d]	2.683(8)	1.74	163
Amide part				
Segment **A**	N-1–H · · · O-7(vi)	2.999(8) [e]	2.08	147 [f]
	O-2–H · · · O-7(vi)	2.905(8)	2.08	141
Segment **B**	N-1–H · · · O-7(vi)	2.994(5) [e]	1.98	167 [f]
	O-2–H · · · O-7(vii)	2.879(6)	1.94	164

[a] The H · · · O distances, and the O–H · · · O and N–H · · · O angles were obtained by normalizing the covalent O–H and N–H distances to the standard value of 0.97 and 1.03 Å, respectively [36].
[b] (i) x, y, z; (ii) $x+1$, y, z; (iii) $x-1$, y, z; (iv) $2-x$, $y+1/2$, $2-z$; (v) $1-x$, $y-1/2$, $2-z$; (vi) x, y, $z-1$; (vii) $x-1$, y, $z-1$.
[c] These are three-center hydrogen bonds.
[d] Interlayer hydrogen bond.
[e] The N-1 · · · O-7 distance.
[f] The N-1–H · · · O-7 angle.

B. The hydrogen bond between the amide groups in **B** will be more stable than that in **A** because the linearity of both N-1–H · · · O-7 and O-2–H · · · O-7 in **B** is higher than that in **A** (Table 4). The linear hydrogen bond is energetically favored over the bent one [32,33]. In addition, the distance of O-7 · · · O-2 in **B** is shorter than that in **A**. Consequently, the bond length of C-7–O-7 in **B** [1.235(5) Å] is longer than that in **A** [1.224(9) Å], and is comparable to that of a double-acceptor type categorized by Taylor [32]. Although the C=O group in **A** is categorized into the double acceptor, the distance corresponds to that of the single acceptor.

In conclusion, the synthetic 1-glucosamide bolaamphiphile **1** can form a hydrogen-bond-stabilized layered structure containing an all-*trans* hydrocarbon link. The three-dimensional network of hydrogen bonds strongly affects the molecular structure and crystal packing. To date, only two X-ray analyses have been reported for β-*N*-glycosylic derivatives [16,26], and several cases for β-glucoside derivatives with long *n*-alkylene chains [1]. To the best of our knowledge, the present results give the first X-ray structure of a bolaamphiphile having a glucopyranose ring at each end [15].

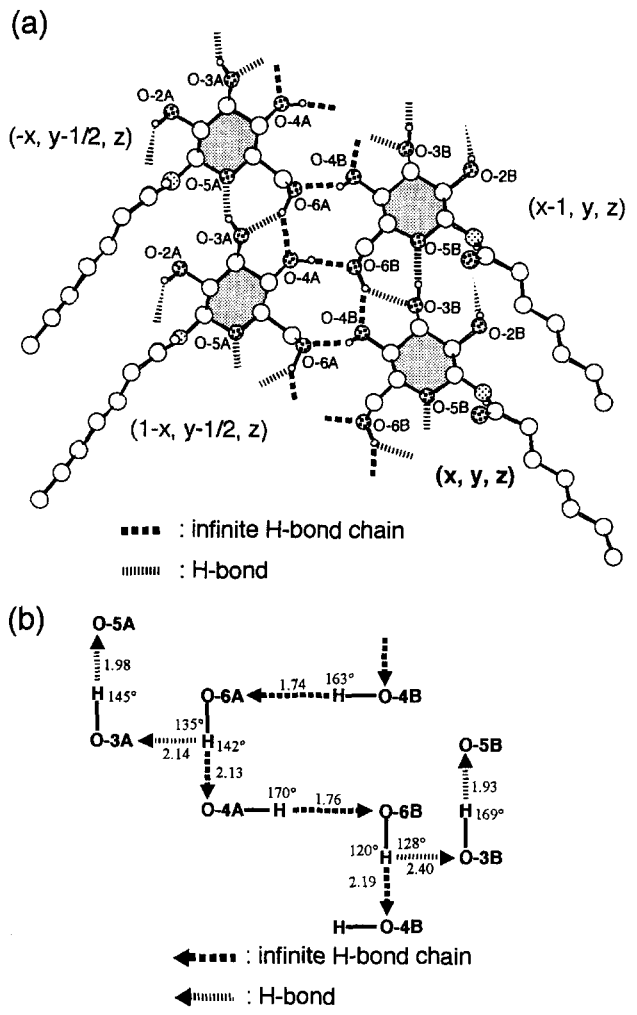

Fig. 5. (a) Two-dimensional network of hydrogen bonds formed between β-D-glucopyranosyl rings of **1** viewed along the *c*-axis. The glucopyranosyl rings are shaded, and the hydrogen atoms of the alkylene chains are omitted for clarity. (b) Schematic representation of hydrogen-bond connectivity. The covalent O–H and N–H bond lengths were normalized to 0.97 and 1.03 Å, respectively [36].

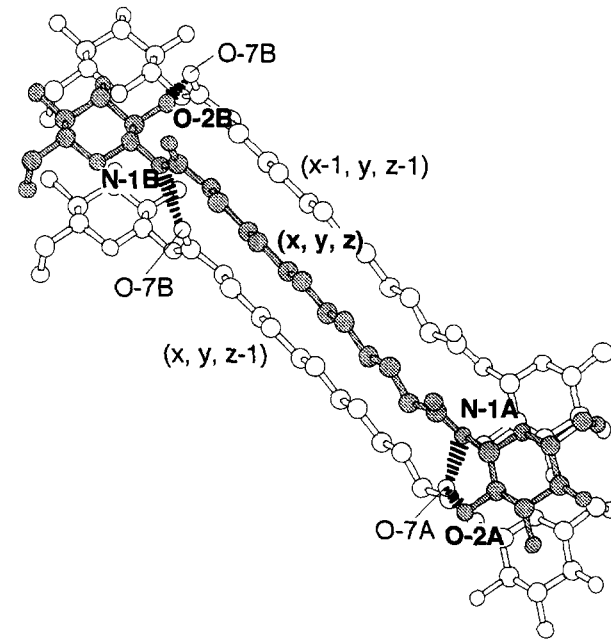

Fig. 6. Hydrogen-bond schemes around the amide groups. The molecule at (*x*, *y*, *z*) is shaded, and the hydrogen atoms are omitted for clarity.

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