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Molecular structures and hydrogen-bond networks in crystals of synthetic 1-D-galactosamide bolaamphiphiles

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Abstract

The crystal structures of synthetic 1-galactosamide bolaamphiphiles, *N*,*N*′-bis(β-D-galactopyranosyl)decane-1,10-dicarboxamide (**1**) and *N*,*N*′-bis(β-D-galactopyranosyl)dodecane-1,12-dicarboxamide (**2**), were determined by single-crystal X-ray analysis. The space groups are $P2_1$, $Z = 2$ with cell dimensions: $a = 13.624(2)$, $b = 4.832(3)$, $c = 21.178(3)$ Å, $\beta = 98.57(1)°$ for **1**; $a = 13.521(2)$, $b = 4.838(1)$, $c = 23.706(2)$ Å, $\beta = 104.945(10)°$ for **2**. The galactopyranosyl rings of **1** and **2** are in a $^4C_1$ chair conformation. The bolaamphiphile molecules are arranged in a layered structure for **1** and **2**, with the alkylene chains packed parallel all over the layers. The hydroxyl groups of the galactopyranosyl rings in **1** and **2** form identical three-dimensional hydrogen-bond networks. The connecting decamethylene spacer of **1** has a kink conformation, while the dodecamethylene chain of **2** an all-trans zigzag conformation. © 2000 Elsevier Science Ltd. All rights reserved.

Keywords: X-ray; Crystal structure; 1-Galactosamide bolaamphiphile; Layered assembly; Hydrogen-bond network; Kink conformation; All-trans zigzag conformation

1. Introduction

Bola-amphiphilic lipids (bolaamphiphiles), which are known as cell-membrane components of *archaebacteria* [1,2], form highly stable monolayer membranes. Many studies have dealt with self-assembling morphologies of diverse bolaamphiphiles [3–5]. In particular, the bolaamphiphiles can form non-spherical molecular assemblies, such as nanoscale fibers [6,7], microtubules [8–11] and helical ribbons [12,13], with solid surfaces through intermolecular interactions between two hydrophilic headgroups [14]. The morphology of the ribbons made from 1-glucosamide bolaamphiphiles strongly depends on the length and even–odd carbon number of the oligomethylene spacer. Stereochemistry of the sugar headgroups was also expected to affect the morphology. We have previously reported the crystal structure of a 1-galactosamide bolaamphiphile **1** [15] in comparison with that of the 1-glucosamide bolaamphiphile **3** [16]. Herein we describe the detailed crystal structures of homologous 1-galacotosamide bolaamphiphiles **1** and **2** with *n*-deca- and *n*-dodecamethylene spacers, respectively. The hydrogen-bond scheme between the galactosamide moieties and the spacer-length effect on the *n*-alkylene chain conformations are discussed.

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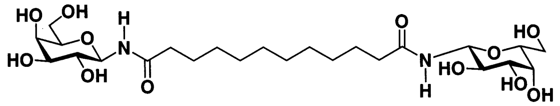

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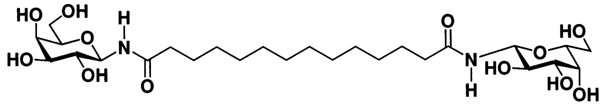

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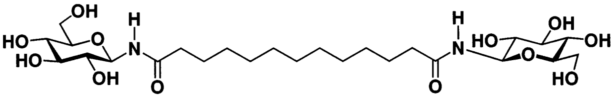

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2. Experimental

Syntheses of both *N*,*N*′-bis(β-D-galactopyranosyl)decane-1,10-dicarboxamide (**1**) and *N*,*N*′-bis(β-D-galactopyranosyl)dodecane-1,12-dicarboxamide (**2**) were reported elsewhere [17].

Table 1
Crystal data and summary of experimental details for **1** and **2**

	1	**2**
Molecular formula	$C_{24}H_{44}N_2O_{12}\cdot H_2O$	$C_{26}H_{48}N_2O_{12}\cdot H_2O$
Molecular weight	570.63	592.68
Crystal type	monoclinic	monoclinic
Space group	$P2_1$	$P2_1$
Z	2	2
Lattice constant		
a (Å)	13.624(2)	13.521(2)
b (Å)	4.832(3)	4.838(1)
c (Å)	21.178(3)	23.706(2)
β (°)	98.57(1)	104.945(10)
Cell volume (Å^3)	1378.8(8)	1498.1(5)
Crystal dimensions (mm)	$0.080\times0.05\times0.20$	$0.09\times0.01\times1.10$
D_{calcd} (g cm^{-3})	1.37	1.31
Radiation	Cu K$_\alpha$	Cu K$_\alpha$
Number of reflections measured	2448	2664
Number of unique reflections	2338	2544
Number of reflections used in refinement	1792 [$F>2.9\sigma(F)$]	2118 [$F>3\sigma(F)$]
Index range for data collection	$0\leq h\leq 9$	$0\leq h\leq 9$
	$0\leq k\leq 5$	$0\leq k\leq 5$
	$-23\leq l\leq 23$	$-26\leq l\leq 25$
2θ Range (°)	$6\leq 2\theta\leq 120$	$6\leq 2\theta\leq 120$
Scan mode	$\omega/2\theta$ scan	$\omega/2\theta$ scan
R factor	0.058	0.037
wR	0.062	0.039

Single-crystal X-ray structural analysis.— Crystals of **1** and **2** were obtained by slow cooling and evaporation of aqueous solutions. Compound **2** only gave thin, brittle needle crystals. The crystals analyzed were 0.1 mm bigger than the collimator size used since it was too difficult to cut them. These experimental conditions had no serious influence on the data collection. The data collection was carried out on a Rigaku AFC-7R automatic four-circle diffractometer at 302 K. All measurements were carried out by $\omega/2\theta$-scan method in $6°\leq 2\theta\leq 120°$. The unit cell dimensions were determined from 24 and 25 strong reflections for **1** and **2**, respectively. The intensities and orientations of both crystals were checked by three non-overlapping standard reflections every 150 reflections. Crystal data and summary of the experimental details are given in Table 1.

The structures were solved by the direct method (SIR92 [18] and MULTAN88 [19] for **1** and **2**, respectively) and expanded using Fourier techniques (DIRDIF94) [20]. The absolute configurations of the molecules were determined by the known chirality of the D-galactopyranose ring in previous syntheses [21,22]. All of 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 hydrogen atoms located were included in the further full-matrix least-squares refinement. All the hydrogen atoms of the amide and the hydroxyl groups of H–N-1A, H–N-1B, H–O-4A, H–O-6A, H–O-2B, and H–O-6B in **1**, and all of these in **2** were located on differential Fourier maps. The atomic coordinates of the non-hydrogen and hydrogen atoms are listed in Table 2.

3. Results and discussion

The molecular structures and packing of **1** and **2** are shown in Figs. 1 and 2, respectively. The molecular conformations and packing of **1** and **2** are similar, except for the alkylene

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

Molecule	Atom	*x*/*a*	*y*/*b*	*z*/*c*	$B_{\mathrm{eq}}/B_{\mathrm{iso}}$ (Å^2)
1	C-1A	1.6611(4)	0.304(4)	0.2222(3)	3.2(1)
	C-2A	1.6085(4)	0.383(3)	0.1557(3)	3.0(1)
	C-3A	1.6661(4)	0.256(3)	0.1071(3)	3.2(1)
	C-4A	1.7735(5)	0.344(4)	0.1187(3)	3.1(1)
	C-5A	1.8174(4)	0.284(4)	0.1881(3)	3.1(1)
	C-6A	1.9211(4)	0.396(4)	0.2084(3)	3.8(2)
	C-7A	1.5668(5)	0.252(4)	0.3105(3)	3.3(1)
	C-8A	1.5285(5)	0.390(4)	0.3656(3)	3.4(1)
	C-9A	1.4402(5)	0.255(4)	0.3874(3)	3.7(2)
	C-10A	1.4081(5)	0.402(4)	0.4439(3)	3.7(2)
	C-11A	1.3198(5)	0.270(4)	0.4683(3)	3.9(2)
	C-12A	1.2922(5)	0.411(4)	0.5278(3)	3.9(2)
	N-1A	1.6117(4)	0.414(3)	0.2726(3)	3.5(1)
	O-2A	1.5082(3)	0.284(4)	0.1461(2)	3.54(10)
	O-3A	1.6176(3)	0.320(4)	0.0431(2)	3.8(1)
	O-4A	1.7778(3)	0.633(4)	0.1028(2)	3.8(1)
	O-5A	1.7586(3)	0.412(4)	0.2313(2)	3.4(1)
	O-6A	1.9839(3)	0.289(4)	0.1661(2)	4.3(1)
	O-7A	1.5601(4)	−0.002(4)	0.3017(2)	4.3(1)
	C-1B	0.8117(4)	0.320(4)	0.7728(3)	3.1(1)
	C-2B	0.7075(5)	0.235(3)	0.7808(3)	3.3(1)
	C-3B	0.6820(4)	0.353(3)	0.8424(3)	3.0(1)
	C-4B	0.7581(5)	0.267(4)	0.8992(3)	3.1(1)
	C-5B	0.8604(4)	0.346(4)	0.8854(3)	3.2(1)
	C-6B	0.9438(5)	0.265(4)	0.9368(3)	3.9(2)
	C-7B	0.8731(5)	0.387(4)	0.6727(3)	3.4(1)
	C-8B	0.8951(5)	0.256(4)	0.6118(3)	3.9(2)
	C-9B	0.9866(5)	0.376(4)	0.5886(3)	4.0(2)
	C-10B	1.0813(5)	0.313(4)	0.6326(3)	4.5(2)
	C-11B	1.1746(5)	0.426(4)	0.6102(3)	4.8(2)
	C-12B	1.1998(5)	0.293(4)	0.5499(3)	4.4(2)
	N-1B	0.8441(4)	0.219(4)	0.7162(3)	3.3(1)
	O-2B	0.6458(4)	0.347(4)	0.7265(2)	5.5(1)
	O-3B	0.5825(3)	0.273(4)	0.8510(2)	3.8(1)
	O-4B	0.7555(3)	−0.030(4)	0.9090(2)	3.7(1)
	O-5B	0.8799(3)	0.219(4)	0.8268(2)	3.15(9)
	O-6B	1.0385(4)	0.353(4)	0.9231(3)	4.1(1)
	O-7B	0.8772(4)	0.642(4)	0.6800(2)	4.6(1)
	O-w	1.3896(3)	0.326(4)	0.0169(2)	3.9(1)
	H–N–1A	1.635(8)	0.61(3)	0.285(5)	13.6(4)
	H–O–4A	1.848(7)	0.71(3)	0.094(4)	10.3(5)
	H–O–6A	2.040(6)	0.42(2)	0.168(4)	7.7(6)
	H–N–1B	0.813(6)	0.03(2)	0.702(4)	8.3(6)
	H–O–2B	0.580(6)	0.31(3)	0.736(4)	10.2(5)
	H–O–6B	1.030(8)	0.44(2)	0.905(5)	6.3(4)
2	C-1C	0.2981(3)	0.386(1)	0.7957(2)	2.44(7)
	C-2C	0.3634(3)	0.4654(10)	0.8554(2)	2.25(7)
	C-3C	0.3158(3)	0.3390(10)	0.9015(2)	2.33(7)
	C-4C	0.2061(3)	0.432(1)	0.8919(2)	2.31(6)
	C-5C	0.1481(3)	0.373(1)	0.8290(2)	2.35(7)
	C-6C	0.0412(3)	0.492(1)	0.8114(2)	3.12(9)
	C-7C	0.3689(3)	0.321(1)	0.7120(2)	2.78(8)
	C-8C	0.3955(3)	0.462(1)	0.6610(2)	2.95(9)
	C-9C	0.4911(3)	0.339(1)	0.6474(2)	3.42(10)
	C-10C	0.5183(3)	0.481(1)	0.5962(2)	3.31(9)
	C-11C	0.6132(3)	0.352(1)	0.5831(2)	3.50(10)

Table 2 (*Continued*)

Molecule	Atom	x/a	y/b	z/c	B_{eq}/B_{iso} (Å^2)
	C-12C	0.6420(3)	0.482(1)	0.5311(2)	3.36(9)
	C-13C	0.7378(3)	0.355(1)	0.5195(2)	3.63(10)
	N-1C	0.3364(3)	0.4903(9)	0.7486(1)	2.67(8)
	O-2C	0.4647(2)	0.3596(8)	0.8639(1)	3.10(6)
	O-3C	0.3769(2)	0.4084(8)	0.9583(1)	3.04(6)
	O-4C	0.2060(2)	0.7181(8)	0.9061(1)	3.13(6)
	O-5C	0.1980(2)	0.4959(8)	0.7882(1)	2.75(6)
	O-6C	−0.0142(2)	0.3830(9)	0.8500(1)	3.61(7)
	O-7C	0.3756(3)	0.0722(8)	0.7199(1)	4.23(7)
	C-1D	1.2276(3)	0.412(1)	0.2068(2)	2.27(7)
	C-1D	1.3320(3)	0.316(1)	0.2018(2)	2.61(7)
	C-3D	1.3477(3)	0.4382(10)	0.1451(2)	2.39(7)
	C-4D	1.2625(3)	0.352(1)	0.0928(2)	2.41(7)
	C-5D	1.1611(3)	0.440(1)	0.1043(2)	2.38(7)
	C-6D	1.0683(3)	0.359(1)	0.0567(2)	3.03(8)
	C-7D	1.1680(3)	0.4873(10)	0.2933(2)	2.38(7)
	C-8D	1.1328(3)	0.356(1)	0.3426(2)	3.19(9)
	C-9D	1.0302(3)	0.467(1)	0.3468(2)	3.9(1)
	C-10D	0.9949(3)	0.344(1)	0.3974(2)	4.1(1)
	C-11D	0.8949(3)	0.467(1)	0.4038(2)	4.3(1)
	C-12D	0.8647(3)	0.349(1)	0.4571(2)	4.0(1)
	C-13D	0.7673(3)	0.476(1)	0.4669(2)	3.8(1)
	N-1D	1.2006(3)	0.3125(8)	0.2579(1)	2.45(7)
	O-2D	1.4032(2)	0.421(1)	0.2509(1)	4.73(8)
	O-3D	1.4448(2)	0.3516(8)	0.1380(1)	3.11(6)
	O-4D	1.2613(2)	0.0619(8)	0.0841(1)	3.13(6)
	O-5D	1.1509(2)	0.3125(7)	0.1574(1)	2.30(5)
	O-6D	0.9750(2)	0.4465(9)	0.0689(1)	3.37(7)
	O-7D	1.1666(2)	0.7379(8)	0.2872(1)	3.61(7)
	O-w	0.6086(2)	0.4184(9)	0.9850(1)	3.26(7)
	H–N–1C	0.341(3)	0.66(1)	0.744(2)	2.9(8)
	H–O–2C	0.501(3)	0.50(1)	0.862(2)	4.8(7)
	H–O–3C	0.385(3)	0.25(1)	0.974(2)	3.6(8)
	H–O–4C	0.158(3)	0.76(1)	0.909(2)	4.2(7)
	H–O–6C	−0.066(4)	0.49(1)	0.848(2)	6.5(7)
	H–N–1D	1.197(3)	0.12(1)	0.264(2)	3.1(8)
	H–O–2D	1.456(3)	0.47(1)	0.248(2)	3.7(8)
	H–O–3D	1.483(3)	0.49(1)	0.140(2)	3.6(8)
	H–O–4D	1.288(3)	0.03(1)	0.068(2)	3.7(7)
	H–O–6D	0.986(3)	0.60(1)	0.092(2)	5.3(7)
	H–O–wa	0.556(3)	0.41(1)	0.970(2)	5.3(7)
	H–O–wb	0.633(3)	0.29(1)	1.007(2)	3.3(8)

[a] The expression is $B_{eq} = 4/3\Sigma U_{ij} B_{ij} \mathbf{a}_i \mathbf{a}_j$.

[b] Standard deviations are given in parentheses.

chain conformations. The C–C bond lengths are normal, 1.50(1)–1.53(1) and 1.507(6)–1.536(6) Å for **1** and **2**, respectively, as are the C–OH, 1.414(9)–1.45(1) and 1.402(6)–1.442(5) Å for **1** and **2**, respectively.

All D-galactopyranose rings proved to be in a $^4C_1$ chair conformation. The puckering parameters (Q) [23] of all the rings are similar in both sides of the molecules, and close to the ideal value of β-D-galactopyranose ring with a $^4C_1$ chair conformation (Table 3) [24]. However, the θ parameters of the rings in segments A and C (C-1–C-5, and O-5) show bigger distortion from an ideal value (3.7°) than those in segments B and D. The parameter ϕ does not have important meaning since the θ

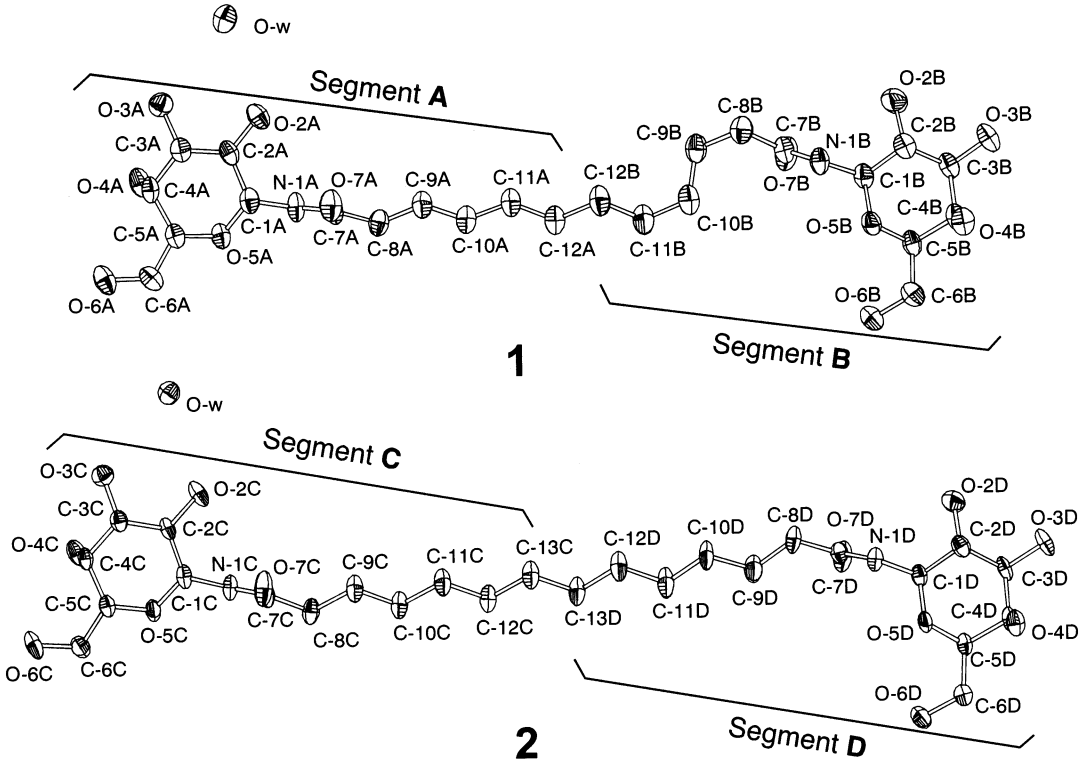

Fig. 1. Molecular structures (ORTEP drawing) and atomic numbering for **1** and **2**. Thermal ellipsoids are drawn at 50% probability.

values are very close to zero [24]. The torsion angles within the four rings in **1** and **2** range from 52.4 to 66.2°, and are similar to those of methyl β-D-galactopyranoside **4** in the crystal lattice (deviation ≤ 6.2°) [25]. On the other hand, the angles of O-5–C-5–C-6–O-6 in segments A and C are different from those in segments B and D and that in methyl β-D-galactopyranoside (63.9°), as shown in Table 4.

The connecting *n*-alkylene spacer of **1** includes a gauche–trans–gauche′ sequence, together with almost extended trans conformation through the carbon atoms C-7A–C-12A and C-10A–C-12B. Both the torsion angles C-12B–C-11B–C-10B–C-9B and C-10B–C-9B–C-8B–C-7B are synclinal (− 67 and 65°, respectively). Consequently, the *n*-alkylene chain takes a kink conformation. This conformational defect presents a striking contrast to the all-trans zigzag conformation of the alkylene spacers observed both in **2** and **3** [15]. The conformational defects, such as gauche or kink, in the crystalline state of amphiphiles are often observed in the chain next to the hydrogen-bonded headgroup [26–28]. The headgroups act as a semirigid framework, and therefore introduce constraints to the system. A reason for the kink defect in **1** stems from the impossibility of interdigitation of the *n*-alkylene chains within the monolayered structure. In contrast, the single-head single-chain glycoside lipids can allow the chain to interdigitate [29–31]. The limiting molecular area of the galactosamide ring is larger than that of the *n*-alkylene chain. Consequently, dominant packing of hydrogen-bonded galactosamide moieties significantly affects the flexible chain conformation and eventually induces an inclination or a kink conformation of the alkylene spacers in the crystal. High thermal parameters around C-10B–C-12B and C-8D–C-11D in **1** and **2**, respectively, suggest that the atoms close to the amide links have a tendency to deviate from the extended conformation.

However, this situation has no remarkable influence on either the orientation of amide groups or the conformations of the galactopyranosyl rings. The two amide groups at both sides of the molecules retain an antiparallel orientation; that is, the two amide planes of the both sides form an angle of 10.7° in **1**, and that of 4.17° in **2**. On the other hand, a slight

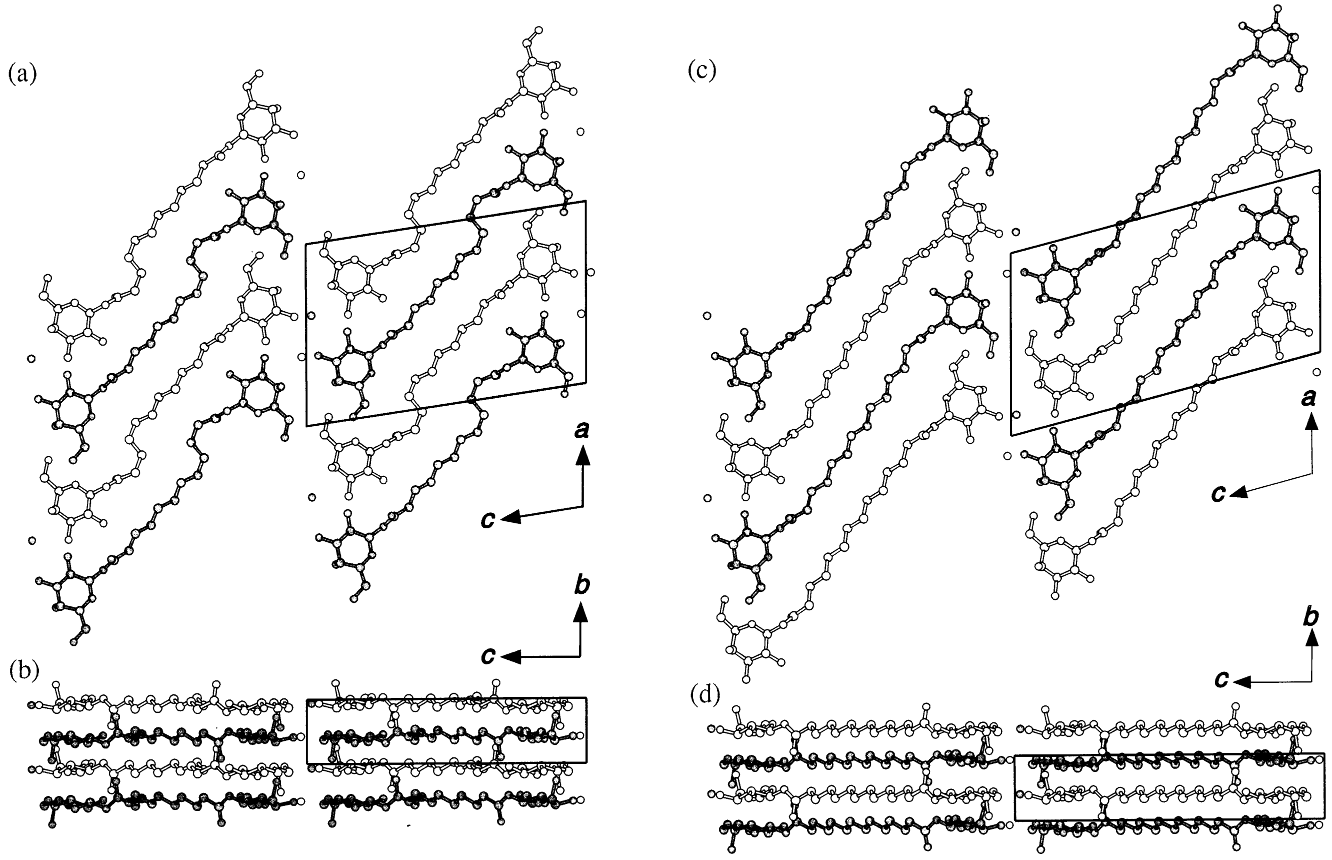

Fig. 2. Molecular packing of **1** and **2**, viewed along (a), (c) the *b* axis, and (b), (d) the *a* axis, respectively. Hydrogen atoms were omitted for clarity.

deviation (15.2°) from the anti-orientation has been reported with the two amide groups of a gluconamide-based bolaamphiphile [27]. The least-squares planes of the pyranose rings of **1** and **2** are almost parallel to each other (2.9 and 2.4°, respectively). This finding is quite different from unparallel orientation (59°) of the pyranose rings for **3**. Both subtending angles of the extended alkylene chains for **1** and **2** are smaller than that of **3** (Table 5).

Molecular packing.—Fig. 2 shows molecular packing of head-to-head layered assemblies viewed along the *a* and *b* axes. The bolaamphiphiles **1** and **2** are stacked in brick motif; i.e., the next inverse sheet is shifted by half the thickness of the two neighboring molecules in the *b* direction. Both alkylene chains C-8A–C-10B and C-8C–C-8D have similar inclinations with respect to the layer plane normal as observed in **3** (Table 4). However, the observed kink conformation of **1** induces the reduction in the inclination angle compared with the all-trans conformation of **2**. The present bolaamphiphiles **1** and **2** are not arranged in a pleated sheet like **3**, but are packed in parallel with each other all over the layers. No difference in the lengths of the *a* and *b* axes between **1** and **2** suggests almost identical coordinates of the galactopyranosyl rings.

Adjacent alkyl chains of **2** are arranged in an $O_{\perp}$-type packing. The idealized dimensions

Table 3
Puckering parameters for the bolaamphiphiles **1** and **2** in crystal

Molecule		Q	θ (°)	ϕ (°)
1	Segment A	0.591	5.11	50.47
	Segment B	0.593	3.65	16.49
2	Segment C	0.591	4.88	62.04
	Segment D	0.615	2.93	27.09
4 [a]		0.586	3.7	21.5

[a] Ideal β-galactopyranose [24].

Table 4
Selected torsion angles (°) in **1** and **2** [a]

Torsion angle	**1**		**2**	
Segment	**A**	**B**	**C**	**D**
Sugar				
O-5–C-1–C-2–C-3	60.8(7)	58.8(7)	61.5(5)	60.3(5)
C-1–C-2–C-3–C-4	−55.3(8)	−55.3(8)	−56.6(5)	−57.2(5)
C-2–C-3–C-4–C-5	52.6(9)	53.8(8)	52.8(5)	56.1(5)
C-3–C-4–C-5–O-5	−53.9(8)	−57.2(8)	−54.6(5)	−58.1(5)
C-4–C-5–O-5–C-1	61.8(9)	63.8(9)	61.3(5)	64.9(5)
C-5–O-5–C-1–C-2	−65.3(8)	−63.7(7)	−64.5(5)	−66.2(5)
N-1–C-1–C-2–O-2	−59.0(9)	−60.2(9)	−60.1(5)	−61.2(5)
O-3–C-3–C-2–O-2	57.6(6)	64.3(9)	59.3(5)	64.9(5)
O-4–C-4–C-3–O-3	−54.1(6)	−58.3(8)	−52.4(5)	58.1(5)
O-4–C-4–C-5–C-6	−52.6(9)	−57.9(8)	−51.7(5)	−56.9(5)
O-5–C-5–C-6–O-6	−177.6(7)	−59.5(10)	−179.4(4)	−59.2(5)
Amide				
C-1–N-1–C-7–C-8	−173.0(6)	−173.5(6)	−173.4(4)	−174.7(4)
C-7–N-1–C-1–O-5	−126.4(7)	−117.3(7)	−123.6(4)	−110.5(4)
C-7–N-1–C-1–C-2	112.9(8)	121.3(8)	115.7(5)	129.0(4)
Alkylene chain				
C-7–C-8–C-9–C-10	178.8(7)	66.3(9)	−180.0(4)	178.2(4)
C-8–C-9–C-10–C-11	−179.3(7)	179.2(7)	−179.5(4)	176.6(5)
C-9–C-10–C-11–C-12	176.4(7)	−67(1)	178.5(4)	177.0(5)
C-10–C-11–C-12–C-13	176.3(7)	178.8(7)	179.0(4)	177.4(5)
C-11–C-12–C-13–C-(12) [b]	178.0(7) [c]		178.8(4)	179.3(5)
C-12–C-13–(C-13–C-12) [b]			178.7(5)	
Amide-alkylene chain				
C-9–C-8–C-7–N-1	151.4(7)	−138.9(7)	−140.(4)	−131.5(5)

[a] Standard deviations are given in parentheses.

[b] The number in parentheses shows the atom number in opposite segment.

[c] The dihedral angle of C-11A–C-12A–C-12B–C-12B.

Table 5
Structural parameters of the alkylene chains for the bolaamphiphiles in crystal

Molecule	Alkylene chain length	Inclination angle (°)	Average volume per CH_2 group (Å^3)	Twisting angle (°) [a]	Subtending angle (°) [b]
1	10	48 [c]	20.9	8.3	1.4
2	12	55	22.4 [d]	7.8	3.0
3 [16]	11	49	23.8	30.9	5.9

[a] Calculated from the dihedral angle between the two planes defined by C-8A–C-10A and C-10B–C-12B for **1**, and C-8C–C-10C and C-8D–C-10D for **2**.

[b] The chains are bowed with these subtending angles.

[c] Calculated from all-trans part of the alkylene chain.

[d] Calculated from subcell lattices.

of the subcell are: $a_s = 4.84$, $b_s = 7.32$, $c_s = 2.53$ Å. The volume per CH_2 group ($V_{\mathbf{2}\ CH_2} = 22.4$ Å^3) of **2** is similar to that of **3**. However, we were unable to estimate the subcell dimensions of **1** from the crystal structure.

The average volume of the CH_2 groups for **1** ($V_{\mathbf{1}\ CH_2,\ average} = 20.9$ Å^3) was calculated as follows:

$$V_{\mathbf{1}\ CH_2,\ average} = (V_{\mathbf{1}\ cell} - V_{\mathbf{1}\ sugar})/(CH_2 \text{ number in cell of } \mathbf{1})$$

where the $V_{1\,\text{cell}}$ and $V_{1\,\text{sugar}}$ are unit cell volume and the sugar volume, respectively, in the cell of **1**. The $V_{1\,\text{sugar}}$ is expected to be similar to that for **2** ($V_{2\,\text{sugar}} = 960.5$ Å^3) since the packing and hydrogen-bond scheme of galacotosamide between **1** and **2** are identical. The $V_{2\,\text{sugar}}$ was calculated from unit cell volume ($V_{2\,\text{cell}}$) and average volume of the CH$_2$ groups ($V_{2\,\text{CH}_2}$) for **1** as follows:

$$V_{1\,\text{sugar}} \approx V_{2\,\text{sugar}} = V_{2\,\text{cell}} - V_{2\,\text{CH}_2} \times (\text{CH}_2\ \text{number in cell of}\ \mathbf{2})$$

As a result, the packing density of the CH$_2$ group for the gauche-including conformation in **1** is larger than that of the all-trans conformations in **2** and **3** [16].

The intermolecular void around C-6A–O-5A–C-1A–N-1A–C-7A in **1** created by packing of sugar and alkylene chain is filled with the kink conformation. As a result, the minimum distance of intermolecular atomic contact for O-5A···C-10B (3.85 Å) in **1** is shorter than that for O-5C···C-9D (4.29 Å) in **2**.

Hydrogen bonds of the sugar hydroxyl and amide groups.—The three-dimensional hydrogen-bond networks in both crystals of **1** and **2** are based on an identical scheme (Fig. 3). The intra- and interlayer networks effectively stabilize the layered structure. However, the scheme is totally different from the two-dimensional scheme of the 1-glucosamide bolaamphiphile **3** [16]. Irrespective of the conformational difference in the *n*-alkylene spacer, the galactosamide moieties in **1** and **2** form the same hydrogen-bond scheme at both sides of the molecules. X-ray analysis of **2** gave whole hydrogen atoms of the sugar hydroxyl and amide groups, whereas only six hydrogen atoms of the amide and hydroxyl group were resolved for **1** (Table 6 and Fig. 3). Both crystals include one water molecule per bolaamphiphile.

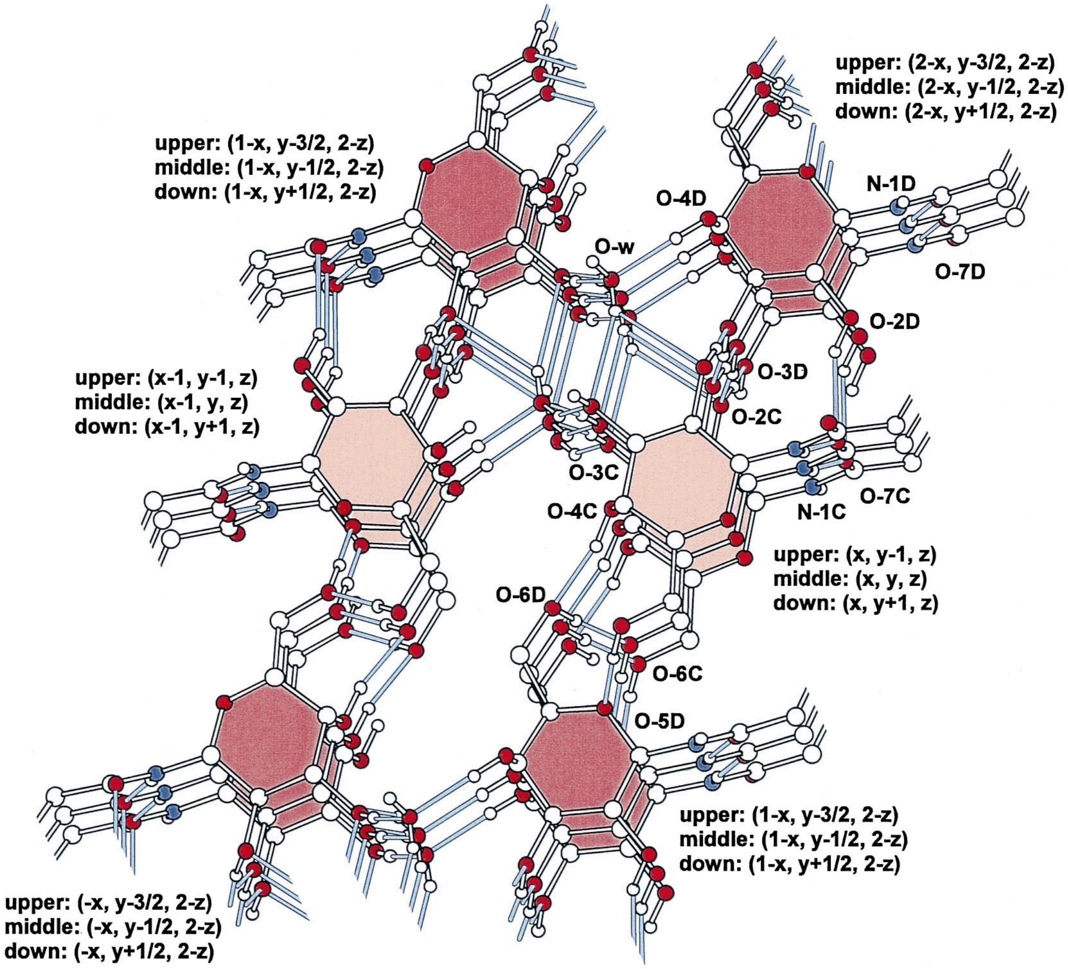

Fig. 3. Three-dimensional hydrogen-bond networks formed between β-D-galactosamide rings of **2**, viewed along the *b* direction.

Table 6
Hydrogen-bond distances (Å) and angles (°) [a] of **1** and **2** with symmetry code [b]

D–H(i)···A	D···A (Å)		H···A (Å)		D–H···A (°)	
	1	**2** [e]	**1**	**2** [e]	**1**	**2** [e]
Galactopyranose ring						
O-w–Ha···O-2(i) [c]	2.960(7)	3.034(5)		2.38		125
O-w–Ha···O-3(i) [c]	3.071(7)	3.028(5)		2.12		158
O-w–Hb···O-3(ii) [d]	2.768(8)	2.792(5)		1.90		151
O-3A–H···O-w(ii) [d]	2.700(8)	2.708(5)		1.74		174
O-4B–H···O-w(iii)	2.780(7)	2.778(4)		1.83		166
O-2A–H···O-3B(iv)	2.673(7)	2.680(5)		1.73		167
O-3B–H···O-2A(iv)	2.782(6)	2.749(6)	1.84	1.80	164	163
O-4A–H···O-6B(v)	2.849(7)	2.877(4)	1.88	1.92	171	167
O-6B–H···O-6A(v)	2.815(8)	2.812(5)	1.85	1.85	175	171
O-6A–H···O-5B(vi)	2.770(7)	2.753(4)	1.82	1.80	168	165
Amide part						
N-1B–H···O-7B(viii)	2.945(9)	2.928(5)	2.12	1.92	135	164
N-1A–H···O-7A(vii)	2.991(9)	2.973(6)	2.10	1.97	143	163
O-2B–H···O-7B(iv)	2.871(7)	2.976(5)	2.14	2.11	130	148

[a] The H···A distances and D–H···A angles were obtained by normalizing the covalent O–H and N–H distance to the standard values of 0.97 and 1.03 Å, respectively [32].

[b] (i) x, y, z; (ii) $1-x, y-3/2, 2-z$; (iii) $2-x, y-3/2, 2-z$; (iv) $2-x, y-1/2, 1-z$; (v) $1-x, y-1/2, 1-z$; (vi) $1-x, y-3/2, 1-z$; (vii) $x, y+1, z$; (viii) $x, y+1, z$.

[c] These are three-center hydrogen bonds.

[d] Interlayer hydrogen bond.

[e] Segment symbols A and D for **1** correspond to C and D, respectively, for **2**.

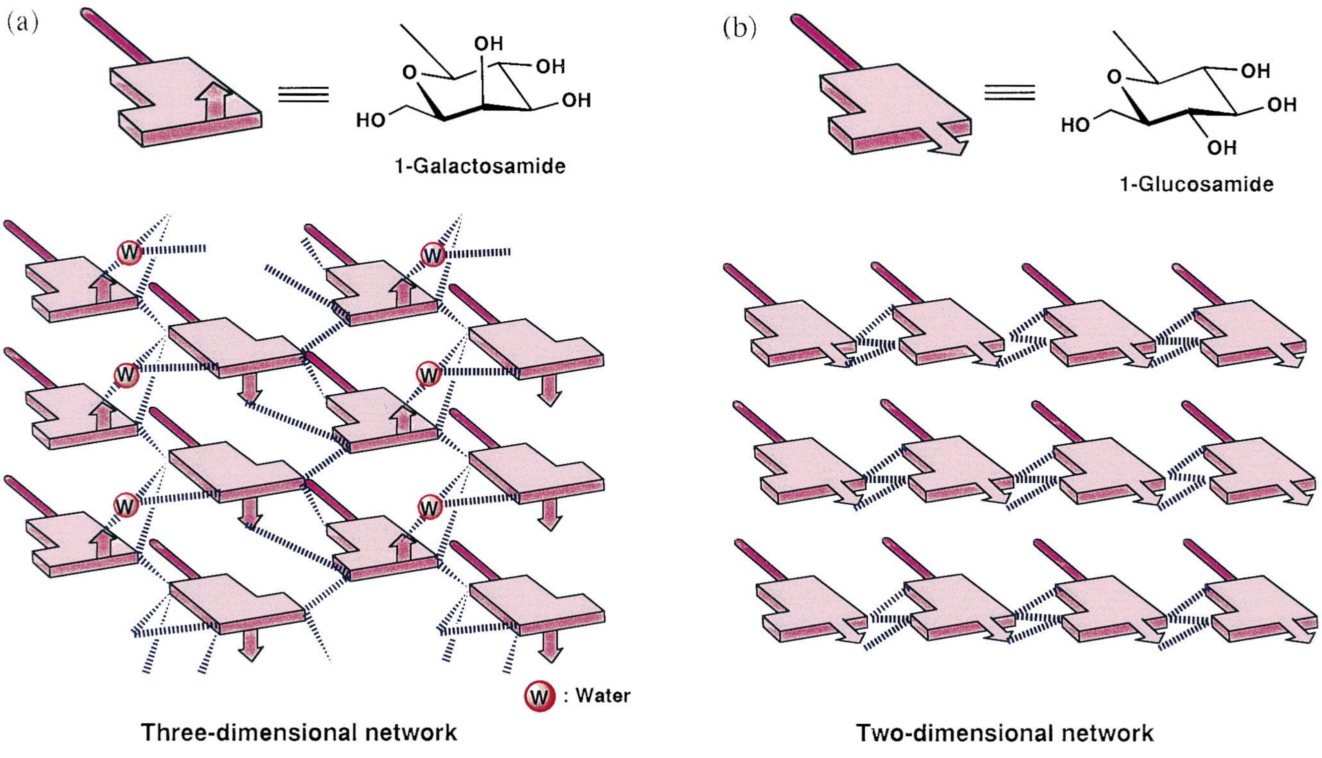

Fig. 4. Schematic illustration of the intralayer hydrogen-bond networks of the aldopyranosyl moieties in (a) 1-galactosamide and (b) 1-glucosamide bolaamphiphiles.

The hydrogen bonds involving the O-4C–H and O-4D–H hydroxyl groups increase the interaction between the sugars along the *b* axis. The axial hydroxyl group of segment C forms a finite hydrogen-bond network as O-4C–H···O-6D–H···O-6C–H···O-5C, while that of segment D forms O-4D–H···O-w. The hydrogen bonds form infinite zigzag chains, O-2C–H···O-3D and O-3C–H···O-2D within the layer, and O-3C–H···O-w and O-w–Hb···O-3C between the layers. As a result, O-w and O-3C form ladder-shaped infinite hydrogen-bond chains along with the *b* axis, as shown in Fig. 3. These infinite hydrogen bonds are energetically more favorable than the finite chain [32]. Fig. 4 represents a schematic illustration of the hydrogen-bond networks for **1** and **2**. The sugar headgroups of **1** and **2** form three-dimensional hydrogen-bond networks. In contrast, the headgroups of **3** provide an example of two-dimensional ones (Fig. 4). Three-center hydrogen-bond configuration [32] has been found for the O-w–Ha group (donor), and the O-2C and O-3C atoms (acceptors), as observed in **3**. The hydrogen-bonded crystal water functions as a glue between the layers.

In addition, we found two types of hydrogen-bond schemes around the amide groups. One found in segments B and D is a single acceptor type. The other found in segments A and C is a double acceptor type [33], as observed in **3**. The hydroxyl group at the C-2D position of $(2-x,\ y-3/2,\ 2-z)$ and the adjacent amide proton N-1C–H of $(x,\ y-1,\ z)$ hydrogen-bond to the carbonyl oxygen O7-C of $(x,\ y,\ z)$, while the amide proton N-1D–H of $(x,\ y+1,\ z)$ to O-7D $(x,\ y,\ z)$ with translation motif. We have found in total 26 hydrogen bonds in **2**, which is similar to 24 hydrogen bonds in **3**.

4. Supplementary material

Full crystallographic details have been deposited with the Cambridge Crystallographic Data Centre. These data may be obtained, on request, from The Director, CCDC, 12 Union Road, Cambridge CB2 1EZ, UK (Tel.: +44-1223-336408; fax: +44-1223-336033; e-mail: deposit@ccdc.cam.ac.uk or www: http://www.ccdc.cam.ac.uk).

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