Hydrogen-Bond-Assisted Layered Assembly and Hydrocarbon-Chain Kink Defect of a Synthetic 1-Galactosamide Bolaamphiphile

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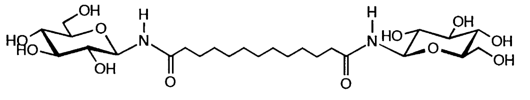
A hydrogen-bond-assisted layered assembly of the synthetic 1-galactosamide bolaamphiphile, *N,N'*-bis(β-D-galactopyranosyl)decane-1,10-dicarboxamide has been characterized by single crystal analysis. The molecular structure includes a "kink" conformation of the connecting decamethylene chain based on a *gauche-trans-gauche'* sequence.

The crystal structures of alkylated cyclic sugars hitherto determined have head-to-head bilayers with interdigitizing alkyl chains although the number of reports is few.[1] To date, there have been no examples of non-interdigitizing chains.[2] In this respect, it has been unpredicted that bolaamphiphiles with a cyclic sugar-head group at each end allow to form a stable monolayer structures. We have recently demonstrated the formation of fibrous supramolecular assemblies from a glucose-based bolaamphiphile **1** with single *n*-alkylene chain[3] and the hydrogen-bonded networks in the crystal lattice.[4] In the present study, we have synthesized a 1-galactosamide derivative **2**.[5] The molecular self-assembly of **2** in the crystal lattice was characterized and compared with that of **1** by single crystal analyses. In particular, it can be expected that the stereochemistry of the terminal aldopyranose and the chain length of the connecting links affect the hydrogen-bonded networks and conformational order in the hydrocarbon chains, respectively.[6] To the best of our knowledge, the only other X-ray structure reported with sugar-based bolaamphiphiles is that of open-chain gluconamide-based bolaamphiphile **3**.[7]



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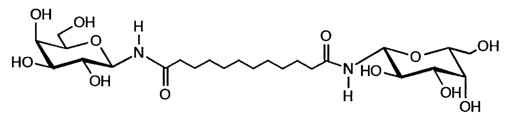

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The novel bolaamphiphile **2** has a D-galactosylamine ring at each end, which connects to 1,10-decane dicarboxylic acid via β-N-glycosidic bond. It proved to be less soluble in water (≈ 1.4% w/v, at 33 °C) than the 1-glucosamide derivative **1** (≈11% w/v, at 30 °C). Self-assembling properties are similar between the glucose- and the galactose-based bolaamphiphiles. The former with even-numbered alkylene carbons gave fibrous assemblies in water,[3] whereas the compound **2** a needle crystal. A successfully obtained single crystal of **2** from a saturated aqueous solution was subjected to X-ray measurement.[8]

The molecular structure of **2** is shown in Figure 1. The connecting long alkylene chain includes a *gauche-trans-gauche'*

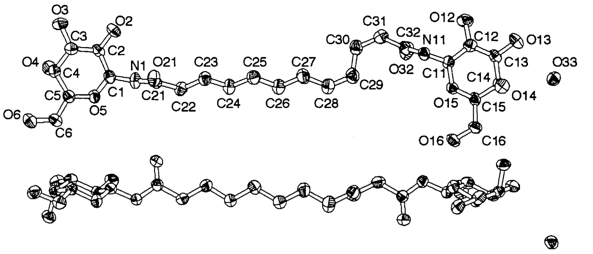

Figure. 1 The molecular structure (ORTEP drawing) and the atomic numbering for **2**. Thermal ellipsoids are drawn at 50% probability.

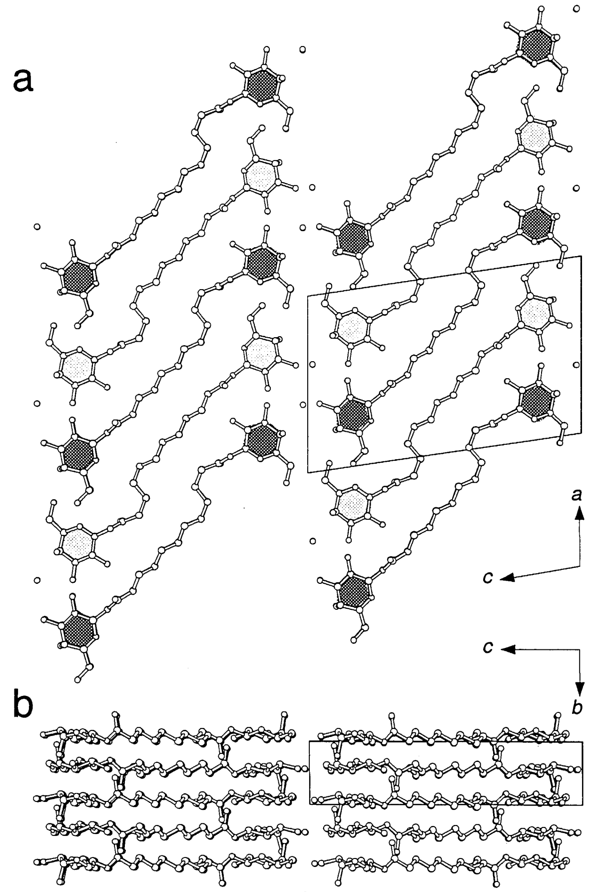

Figure. 2 The crystal structure of **2** projected on the *ac* plane (a) and projected on the *bc* plane (b). Sugar rings are drawn shaded for clarity.

sequence, together with almost extended *trans* conformation through the carbon atoms C22—C28. Both the torsion angles C27–C28–C29–C30 and C29–C30–C31–C32 are synclinal (-67° and 65°, respectively). As a result, the connecting bridge takes a "kink" conformation.[9] This conformational defect presents a striking contrast to an all-*trans* zigzag conformation of the alkylene bridge observed in **1**.[4] However, such a situation affects no remarkable influence on both the orientation of the amide groups and the conformation of the galactose ring. The two amide groups retain an antiparallel orientation (the dihedral angle O21–C21–C32–O32, -178.6°). On the other hand, a slight deviation (15.2°) from the anti-orientation is reported with the two amide groups of **3**.[7] The axial hydroxyl groups at the C4 and C14 positions are almost parallel to the carbonyl groups C32=O32 (the dihedral angle O21–C21–C32–O32, 12.2°) and C21=O21 (the dihedral angle O32–C32–C4–O4, -13.9°), respectively.

Figure 2 shows crystal packing structures projected on the *ac* plane (a) and projected on the *bc* plane (b). The molecules are packed in a layered assembly, with the plane of the pyranose ring almost parallel to the layer plane. The alkylene chain C22—C28 have an inclination of 48° with respect to the normal to the layer plane. This inclination angle is good agreement with that of **1** in a layered structure (49°).[4] The intermolecular void created by the "kink" conformation are filled with the primary alcohol groups of the pyranose rings. Thus, the "kink" conformation of the hydrophobic moieties forms a close packing of the molecules. The present bolaamphiphiles do not arrange in a pleated sheet like **1**, but pack in parallel with each other all over the layers. The layers are stacked in staggered fashion, *i.e.* the next inverse sheet is shifted by about half the thickness of the two neighboring molecules in the *b*-direction.

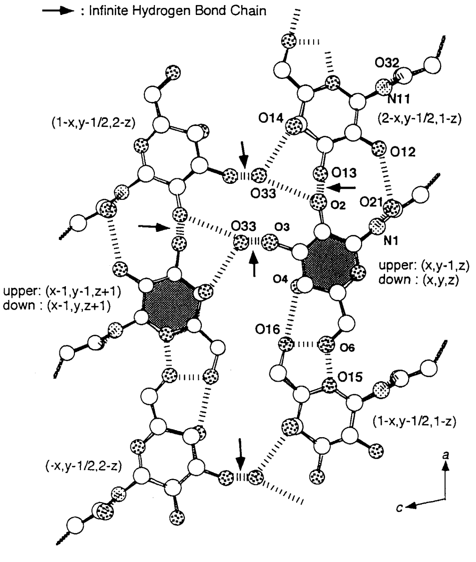

Figure. 3 The hydrogen bonding networks formed between the sugar-head and the amide groups of **2**, projected on the *ac* plane. Sugar rings are drawn shaded for clarity.

Interlayer and intralayer hydrogen-bonded networks effectively stabilize the layered structure (Figure 3). Especially, the hydrogen bonds involving the hydroxyl group at the C4 and C14 axial positions increase the sugar-sugar interaction along the *b*-axis. The intermolecular hydrogen bonds form infinite zigzag chains, O2···O13 within the layers and O3···O33(water) in the hydrophilic region between the sugar rings of the adjacent layers. Furthermore, finite hydrogen bonds are observed for O2···O33(water)···O14 between a water molecule and sugar rings and for O15···O6···O16···O4 between the adjacent molecules within the layer. In this way, the sugar-head groups of **2** form three-dimensional hydrogen-bonded networks, whereas that of **1** two-dimensional ones. In addition, we found two types of hydrogen bonding motifs around the amide groups, which are similar to that of **1**. Both the hydroxyl group at the C12 position of (2-x,y-1/2,1-z) and one amino group N1–H of (x,y-1,z) hydrogen-bond to the carbonyl oxygen O21 of (x,y,z) cooperatively. The another motif is formed between the carbonyl oxygen O32 of (2-x,y-3/2,1-z) and the amide proton N11–H of (2-x,y-1/2,1-z).

References and Notes

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5 The compound **2** gave satisfactory spectra and C,H, and N analytical data.

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8 Crystal data for **2**: $C_{24}H_{44}O_{12}N_2{\cdot}H_2O$: monoclinic, $P2_1$; a = 13.624(2), b = 4.832(3), c = 21.178(3) Å, β = 98.57(1)°, V = 1378.8(8) $Å^3$, Z = 2, Dc = 1.485 gcm^{-3}, T = 296 K. A Rigaku AFC7R diffractometer was used to collect 2341 data points of which 1775 data with $[F > 3\sigma(F)]$ were used in the solution and refinement. X-ray data were corrected for absorption $[\lambda(\text{Cu-K}\alpha)=1.54178$ Å]. All measurements were performed using the ω–2θ scan method in $6 < 2\theta < 120°$. The structure was solved by direct methods (*SHELXS86*) and expanded using Fourier techniques (*DIRDIF94*). The non-hydrogen atoms were refined anisotropically. The amide N1–H hydrogen atom and the hydroxyl hydrogen atoms of O2–H, O3–H, O6–H, O12–H, and O13–H, were located on a differential Fourier map. Other hydrogen atoms were placed at calculated positions. Structure refined to R_F = 0.065 and R_{WF} = 0.064; GOF = 3.13, highest final difference peak, 0.07 $eÅ^{-3}$.

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