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FORMATION OF COMPLEMENTARY AND COOPERATIVE HYDROGEN-BONDING NETWORKS OF SUGAR-BASED BOLAAMPHIPHILES IN WATER

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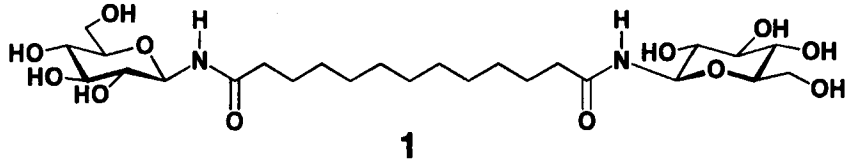
Abstract A 1-D-glucosamide bolaamphiphile with undecamethylene group self-assembled to form a layered structure in water. Complementary and cooperative hydrogen-bonding networks between sugar hydroxyl and amide groups were determined by X-ray crystal analysis.

INTRODUCTION

The hydrogen-bond control is a key methodology to build up stable molecular self-assemblies.[1-3] However, it is difficult to form self-assembling material stabilized by hydrogen bonds in water. We have recently synthesized 1-glucosamide bolaamphiphiles with a D-glucosylamine unit at each end, and have found the stable fiber formation from them.[4] Crystal structure of the bolaamphiphile should give valuable information about hydrogen-bond networks in the fiber. In this study, we have analyzed the crystal structure of 1 and discuss about the layered structure.[5]



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EXPERIMENTAL

The bolaamphiphile 1 crystallized as a thin platelet from boiled water by cooling and evaporation. The crystals were stable up to 222°C. Details of the data collection and structure refinment are given in TABLE I. Hydrogen atoms of the hydroxyl and amides groups were solved by differential-Fourier, and the remaining H atoms were placed at calculated positions.

TABLE I Summary of crystal data for the bolaamphiphile **1**

Crystal data

$C_{25}H_{46}N_2O_{12}$, mol wt 566.30, $P2_1$, $Z = 2$, monoclinic

Cell dimension, $a = 6.220(1)$, $b = 48.25(1)$, $c = 4.922(2)$ Å, $\beta = 105.67(2)°$, $V = 1422.3(6)$ Å^3

Dcalc = 1.32 g cm^{-3}, Dobs = 1.33 g cm^{-3}

Experimental details

Radiation, graphite-monochromated Mo-Kα

No. of reflections measured, 7512

No. of unique reflections, 3308

No. of observed reflections, 2256, $F > 3\sigma(F)$

Range of h, k, l; $-7 \leq h \leq 8$, $-62 \leq k \leq 62$, $-6 \leq l \leq 0$

2θ range, $3 < 2\theta < 55°$

Scan mode, ω scan*

Intensity data were collected by Mac Science MXC18; structure solved by the direct method (*SIR*92 in *CRYSTAN*-GM) and refined by *CRYSTAN*-GM.

Final agreement factors, R-factor = 0.0503, $wR = 0.0782$

* Each peak was observed without overlapping.

RESULTS AND DISCUSSION

The bolaamphiphile **1** forms a layered structure in which the undecamethylene chains are arranged in antiparallel pleated sheet [FIGURE 1(*a*) and (*b*)]. The polar sugar groups are bound together *via* hydrogen bonds, whereas the *n*-alkylene chains form closed packing. The all-*trans* zigzag alkylene chains are parallel [FIGURE 1(*b*) and FIGURE 2(*a*)]. These layered structuers are stabilized by precise intra- and interlayer hydrogen-bonding networks. According to the literature,[6] only eight crystal structures have been reported for cyclic carbohydrate amphiphiles with a single *n*-alkyl chain. There have been no examples of bilayers and no-interdigitizing chains. In this respect, it has been unpredicted that a cyclic sugar-head group allows to form such a stable monolayer structure. Therefore, this is the first example of the monolayered crystal for the carbohydrate amphiphile with a cyclic sugar. There proved to be 24 hydrogen bonds per molecule.

The spanned *n*-alkylene chain in the bolaamphiphile **1** is constrained to be slightly left-handed twisting and bowing with an all-*trans* conformation [FIGURE 2(*a*) and (*b*)]. The twisting and bowing conformation will be caused by the formation of intra- and interlayer hydrogen bonds between sugar hydroxyl and amide groups. The *n*-alkylene chain is flexible compared with the sugar-head group. The distances between the two adjacent *n*-alkylene chains are 4.92 and 6.22 Å. The latter distance is affected by the packing of the pyranose rings that form the hydrogen-bonding networks. The *n*-alkylene chains incline to compensate the void for the closest

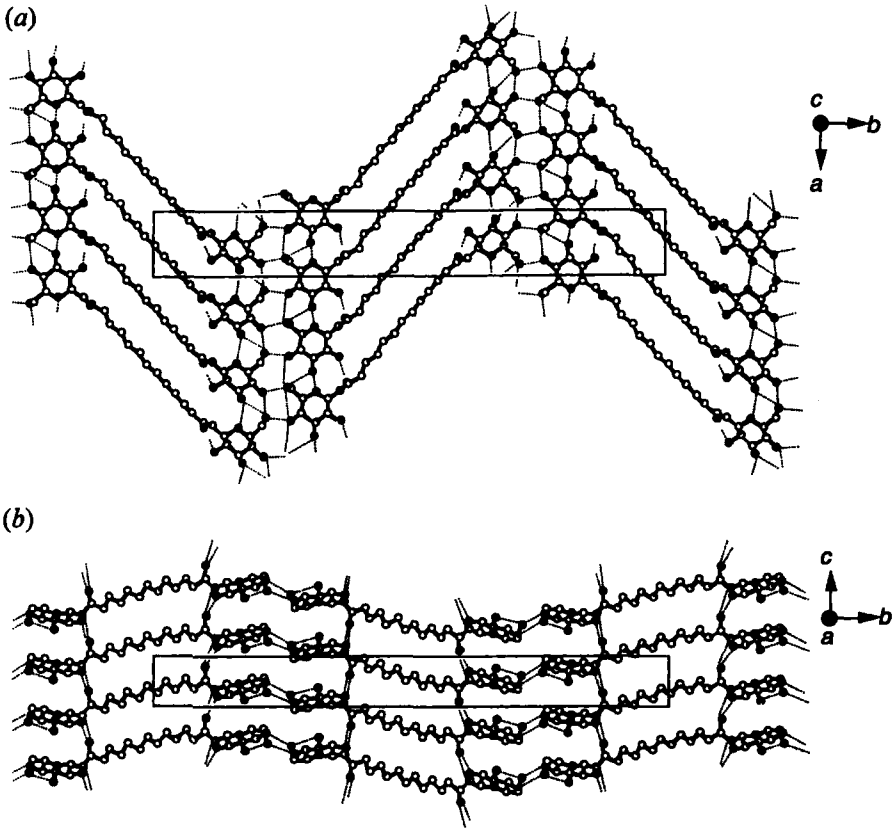

FIGURE 1 Molecular packing of **1**, viewed along (*a*) the *c* axis and (*b*) the *a* axis, representing the intra- and interlayer hydrogen-bonding networks. Hydrogen atoms have been removed for clarity.

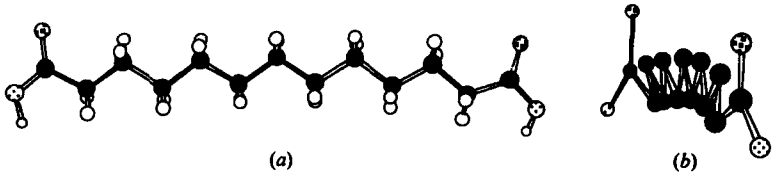

FIGURE 2 The confomation of the undecamethylene chain of **1** in the crystal, viewed along (*a*) the perpendicular axis to zigzag plane of the *n*-alkylene chain, and (*b*) the chain.

packing. The resulting inclination of the *n*-alkylene chain is 48.7° with respect to the *ab* plane normal.

The sugar hydroxyl groups, O(3A)–O(6A) and O(3B)–O(6B), form two-

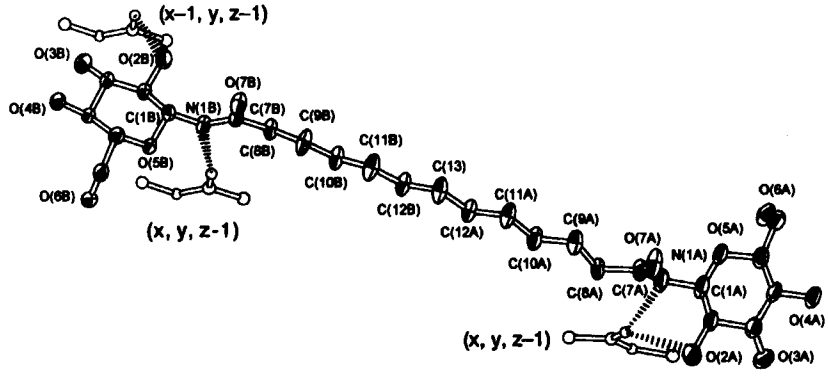

FIGURE 3 Crystal structure of **1** with components of molecules at (x-1, y, z-1) and (x, y, z-1). Thermal ellipsoids are drawn at 50% probability.

dimensional networks of the hydrogen bonds through the *ab* plane [FIGURE 1(*a*)]. On the other hand, the amide groups involving O(2A) and O(2B) form hydrogen bond chains along the *c* axis [FIGURE 1(*b*) and FIGURE 3]. The hydrogen-bond chains of the amide groups are translation motif.[7] It should be noted here that the hydroxyl group O(2A)–H of (x, y, z) bonds to O(7A) of (x, y, z-1) molecule, while the O(2B)–H of (x, y, z) bonds to O(7B) of (x-1, y, z-1) molecule (FIGURE 3). These chains are unsymmetrical for the both parts. The other patterns are similar for both sugar-head groups, except for O(2A) and O(2B). Intralayer "N"-shaped hydrogen bonds are found between the hydroxyl groups and oxygen atoms, O(3)–H···O(5), O(3)–H···O(6) and O(4)–H···O(6). The hydroxyl groups, O(4A)–H···O(6B) and O(4B)–H···O(6A) form interlayer hydrogen bonds. In addition, the hydroxyl groups, ···O(6A)–H···O(4A)–H···O(6B)–H··· O(4B)–H···, form infinite homodromc chains[8] through the *ab* plane.

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