Carbohydrate Research, 242 (1993) 11–20
Elsevier Science Publishers B.V., Amsterdam

Molecular and crystal structure of the bola-amphiphile *N*-[8-(D-gluconamido)octyl]-D-gluconamide

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(Received December 28th, 1990; accepted in final form August 25th, 1992)

ABSTRACT

The crystal structure of the title compound [**5**; space group $P2_1$; $a = 8.375(5)$, $b = 51.52(2)$, $c = 5.647(3)$ Å; $\beta = 89.64(4)°$] was determined by X-ray diffraction methods and refined to $R = 0.107$. There are two molecules in the asymmetric unit, which adopt nearly identical conformations. Each molecule has two parts that differ only in the torsion angle N–C-7–C-8–C-9, which can be synclinal (−64°) or *anti* (168°). The molecules are arranged in sheets and the packing is stabilised by strong intra- and inter-molecular hydrogen bonds, some of which form a homodromic arrangement.

INTRODUCTION

The study of biological membranes is assisted by a comparison of their properties with those of synthetic membranes constructed from amphiphiles, including monosaccharides linked by an amide group to an alkyl chain[1]. Under certain conditions, *N*-alkyl-D-gluconamides and their enantiomers form helices with opposite screws. The formation of helical fibers is limited to chiral amphiphiles (chiral bilayer effect)[2].

The crystal structures of four *N*-alkyl-D-gluconamides have been elucidated, namely, *N*-heptyl (**1**), *N*-octyl (**2**), *N*-decyl[3,4] (**3**), and *N*-undecyl[5] (**4**), and the molecules are all arranged in an enantiomerpolar[6] head-to-tail fashion.

We have prepared bola-amphiphiles[7] with alkyl chains and two terminal D-gluconamide groups and the corresponding *meso* compounds with one D- and one L-gluconamide group, of which *N*-[8-(D-gluconamido)octyl]-D-gluconamide (**5**) was crystallised for an X-ray study in order to elucidate the packing features of the D-gluconamide moiety. In contrast to the related *N*-alkyl-D-gluconamides, no

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phase transition was detected by differential thermal analysis for **5** until the melting point was reached at 202°C.

EXPERIMENTAL

N-[8-(D-Gluconamido)octyl]-D-gluconamide (**5**), *N-[8-(L-gluconamido)octyl]-D-gluconamide* (**6**), *and N-[8-(amino-octyl]-D-gluconamide* (**7**).—A solution of D-glucono-1,5-lactone (1.96 g, 11 mmol) in Me_2SO (10 mL) was added to a solution of 1,8-diamino-octane (2.9 g, 20 mmol) in MeOH (80 mL) boiling under reflux. The first 5 mL was added dropwise and the remainder in one portion after 1 h. Boiling under reflux was continued for 10 min, the solution was cooled to room temperature, and the precipitate was collected and washed with MeOH and ether. Recrystallisation from MeOH gave **5** (750 mg, ~ 60%); mp 202°C. *Anal.* Calcd. for **5** $C_{20}H_{40}N_2O_{12}$ (500.55): C, 47.99; H, 8.05; N, 5.60. Found: C, 47.89; H, 7.86; N, 5.29.

Crystallisation of the material in the mother liquor gave **7** (1.2 g, 37%); mp 125°C. The elemental analysis of this hygroscopic amine, which oxidises readily, was not satisfactory.

A solution of **7** (500 mg, 1.4 mmol) and L-glucono-1,5-lactone (250 mg, 1.4 mmol) in MeOH (30 mL) was boiled under reflux for 2 h, then cooled to room temperature to give **6** (220 mg, 31%); mp 165°C. A satisfactory analysis for the *meso* compound **6** was not obtained.

Compounds **5**–**7** crystallised as thin platelets from MeOH, but only the crystals of **5** gave diffraction patterns that could be analysed.

Crystallography.—Crystals of **5** were grown from solutions in MeOH, but most were either too thin for X-ray investigations or intergrown. One crystal with dimensions $0.4 \times 0.4 \times 0.1$ mm^3 was used for data collection on a STOE four-circle diffractometer with Ni-filtered CuKα radiation. Intensity data (4613) were measured up to $2\theta = 120°$ in the $2\theta/\omega$ step-scan mode. Of these, 319 intensity data were below the 2σ level and 187 had an unbalanced background. The data were corrected for Lorentz and polarisation effects, but not for absorption.

The structure was determined by a combination of direct methods[8] and Fourier techniques. Convergence during the least-squares refinement[9] was slow, and several atoms belonging to the aliphatic part of the molecule had to be held fixed in the early stages of the refinement process because of excessive co-ordinate shifts. Refinement was anisotropic for all non-hydrogen atoms, and standard deviations $\sigma(F_o)$ were based on counting statistics. The positions of C–H hydrogen atoms were calculated. Most of the positions of the O–H and N–H hydrogen atoms could not be determined because of the poor quality of the intensity data. The final R factor was 0.107.

The crystals belong to the monoclinic space group $P2_1$ with $a = 8.375(5)$, $b = 51.52(2)$, and $c = 5.647(3)$ Å, and $\beta = 89.64(4)°$. There are two molecules in the asymmetric unit.

RESULTS AND DISCUSSION

The determination of the space group was complicated by the fact that there are two molecules in the asymmetric unit and that the monoclinic angle β is close to 90°. This angle was derived independently from the angular positions of 25 reflections with $15° \leqslant 2\theta \leqslant 35°$ for several crystals. All structure factors F_{hkl} are close to $F_{\bar{h}kl}$. The merging R value for these pairs of reflections is 0.162, showing clearly that F_{hkl} and $F_{\bar{h}kl}$ are not identical and that the space group is monoclinic.

The positional and thermal atomic parameters for **5** are given in Table I * and O · · · O contacts of $\leqslant 3.5$ Å, indicative of hydrogen bonding, are listed in Table II. In order to facilitate comparison with the other *N*-alkyl-D-gluconamides, each of the two bola-amphiphiles in the asymmetric unit was dissected in two as illustrated in the formulae to give fragments **A** and **B** from molecule **I**, and fragments **C** and **D** from molecule **II**.

Molecules **I** and **II** have nearly identical conformations with a mean difference in torsion angles of 3.1° and a maximum difference of 6.5° (Table II and Fig. 1). There is correspondence between fragments **A** and **C** and between fragments **B** and **D**, but a difference in the torsion angle N-1–C-7–C-8–C-9 between **A** and **B** and between **C** and **D**.

The torsion angles (Table III) in fragments **B** and **D** are similar to those in *N*-heptyl- (**1**) and *N*-undecyl-D-gluconamide (**4**), and those in fragments **A** and **C** are comparable to those in *N*-octyl- (**2**) and *N*-decyl-D-gluconamide (**3**) except for a difference of 50° in the torsion angle N-1–C-7–C-8–C-9 that is assumed to be due to crystal packing effects.

The *N*-CH_2-D-gluconamide moiety has a strongly preferred conformation which is nearly identical in **1–5**, although there are many degrees of rotational freedom about the 5 C–C bonds. The carbon-backbone torsion angles and C-7–N-1–C-1–C-2 are in the all-*anti* form (Table III and Fig. 2). The torsion angle N-1–C-1–C-2–C-3 is stabilised in the −anticlinal range (−111° to −118°) by the intramolecular N–H · · · O-2 hydrogen bond (Table II). The torsion angle C-4–C-5–C-6–O-6 is in the synclinal range (55°–59°) for **1–4**, but in **5** there are ~ 50% each of synclinal and *anti* forms.

The alkyl chains are bent at the amide link. Fragments **A** and **C** are conformationally different from fragments **B** and D (Fig. 3). The C-1–N-1 amide group is fixed in the *anti* form due to its double-bond character. The attached C_8 (**2**) and C_{10} (**3**) alkyl chains are in the all-*anti* conformation. However, for the C_7 (**1**) and

* Lists of bond angles and distances (which are comparable within the 3σ limit to those[3,4] for **1–4**), anisotropic temperature factors, and observed and calculated structure amplitudes are deposited with, and can be obtained from, Elsevier Science Publishers BV, BBA Data Deposition, P.O. Box 1527, Amsterdam, The Netherlands. Reference should be made to No. BBA/DD/522 *Carbohydr. Res.*, 242 (1993) 11–20.

C_{11} (**4**) alkyl chains and those in fragments **A**–**D** of **5**, the torsion angle C-1–N-1–C-7–C-8 is twisted to the anticlinal range (101°–125°). In addition, in **1**, **4**, and fragments **B** and **D**, the torsion angle N-1–C-7–C-8–C-9 is in the −synclinal range (−64° to −66°) but *anti* in **2**, **3**, and fragments **A** and **C**. All the other alkyl CH_2–CH_2 bonds in **5** are *anti* (Fig. 1).

The crystal packing and hydrogen bonding of the D-gluconamide moieties in the crystal structures of **1**–**5** are comparable. Although the space groups and cell constants for **1**–**5** differ widely, the D-gluconamide moieties have the same conformation and the packing and the hydrogen bonds are similar. The *N*-CH_2-D-gluconamide moiety packs in a systematic, preferred pattern which is probably initiated by the strong N-1–H · · · O-1 hydrogen bond. Because CONH and OH groups are both hydrogen-bond donors and acceptors, the hydrogen bonds form infinite chains and are cooperative, i.e., ~30% stronger than isolated, individual N–H · · · O and O–H · · · O hydrogen bonds[10,11].

All the N–H and O–H hydrogen atoms in **2** and **4** were located from difference Fourier maps. In **3**, the O-5–H hydrogen was not located, and in **1**, O-4–H and O-5–H hydrogens could not be determined. In the bola-amphiphile **5**, only few of the O–H hydrogen atoms were located and their positions are to some extent ambiguous as the final *R* factor is only 10.7%. In consequence, the discussion must be restricted to N · · · O and O · · · O distances.

The hydrogen-bonding interactions observed in **1**–**5** include a three-center (bifurcated) hydrogen bond involving N-1–H as the donor, and O-1 and O-2 as the inter- and intra-molecular acceptors, respectively, and cyclic hydrogen bond systems which connect four different molecules through · · · O-3–H · · · O-5–H · · · O-6–H · · · O-4–H · · · O-3–H · · · (see Table II).

This scheme was observed also in **5** with some distortions so that O-3 is not only close to O-4 and O-5 of symmetry-related molecules, but is also as near to O-2 in the same molecule as O-4, and O-4 is also close to O-5 of an adjacent molecule. Since O–H hydrogen atoms could not be located, it is not clear whether these contacts are of the van der Waals or hydrogen-bonding type. The interactions of O-6–H in **5** cannot occur in **1**–**4** because the N-alkyl-D-gluconamides are each packed in a head-to-tail mode[4,5].

The only difference in hydrogen bonding in structures **1**–**5** appears to reside in O-2–H. In **4**, O-2–H donates a three-centre bond with a major component to O-4 and a minor component to O-3. In **1**–**3**, O-2–H was thought not to have a hydrogen-bond partner[4,5], but a reinvestigation showed that weak three-centre bonds exist to O-3 and O-1 with long H · · · O distances of ~2.6 Å and O-2–H · · · O angles close to 90°. In **5**, O-2–H hydrogens could be located only for fragments **B** and **D**; they form three-centre bonds with O-3 and O-1 with H · · · O distances in the range 2.03–2.56 Å and O-H · · · O angles in the range 114°–146°. It appears that the hydrogen bonding of O-2–H is sensitive to local molecular packing, whereas that of the peptide bond and the formation of the homodromic quadrilateral bonds are a common feature of these crystal structures.

Final Atomic Parameters [a] for *N*-[8-(D-gluconamido)octyl]-D-gluconamide (**5**) [a]

Atom	Molecule I				Molecule II			
	x / a	*y / b*	*z / c*	U_{eq}	*x / a*	*y / b*	*z / c*	U_{eq}
C-6(A)	0.568(1)	0.5690(-)	0.344(1)	0.112(2)	0.054(1)	0.5694(4)	0.865(1)	0.136(2)
O-61(A)	0.5762(9)	0.5748(3)	0.578(1)	0.066(2)	−0.056(1)	0.5478(4)	0.840(1)	0.055(2)
O-62(A)	0.453(1)	0.5494(5)	0.316(1)	0.084(2)	0.058(1)	0.5753(5)	1.076(1)	0.107(2)
C-5(A)	0.5006(9)	0.5942(3)	0.195(1)	0.060(2)	0.0046(9)	0.5944(3)	0.703(1)	0.076(2)
O-5(A)	0.3424(8)	0.5984(2)	0.255(1)	0.095(2)	−0.1719(8)	0.5998(2)	0.753(1)	0.117(2)
C-4(A)	0.6002(9)	0.6184(3)	0.257(1)	0.080(2)	0.0955(9)	0.6192(3)	0.755(1)	0.067(2)
O-4(A)	0.7672(8)	0.6101(2)	0.210(1)	0.095(2)	0.2669(8)	0.6109(2)	0.709(1)	0.090(2)
C-3(A)	0.549(1)	0.6395(4)	0.107(1)	0.088(2)	0.0536(8)	0.6400(3)	0.612(1)	0.071(2)
O-3(A)	0.5632(9)	0.6341(2)	−0.1528(9)	0.092(2)	0.0599(8)	0.6327(2)	0.3495(9)	0.078(2)
C-2(A)	0.642(1)	0.6680(3)	0.166(1)	0.082(2)	0.144(1)	0.6667(3)	0.661(1)	0.092(2)
O-2(A)	0.8020(8)	0.6642(2)	0.105(1)	0.112(2)	0.3047(8)	0.6635(3)	0.589(1)	0.122(2)
C-1(A)	0.553(1)	0.6887(4)	0.011(1)	0.127(2)	0.066(1)	0.6872(4)	0.540(1)	0.121(2)
O-1(A)	0.4172(7)	0.6912(3)	0.041(1)	0.118(2)	−0.0841(7)	0.6910(2)	0.553(1)	0.100(2)
N-1(A)	0.6500(9)	0.6992(3)	−0.138(1)	0.098(2)	0.1493(9)	0.6992(3)	0.363(1)	0.103(2)
C-7(A)	0.5922(9)	0.7180(4)	−0.304(1)	0.120(2)	0.091(1)	0.7197(4)	0.206(1)	0.101(2)
C-8(A)	0.6910(9)	0.7470(3)	−0.299(1)	0.079(2)	0.189(1)	0.7466(4)	0.223(1)	0.097(2)
C-9(A)	0.649(1)	0.7615(4)	−0.496(1)	0.125(2)	0.154(1)	0.7610(4)	0.019(1)	0.151(2)
C-10(A)	0.7529(9)	0.7862(4)	−0.497(1)	0.123(2)	0.250(1)	0.7864(4)	−0.008(1)	0.100(2)
C-10(B)	0.733(1)	0.8031(4)	−0.724(1)	0.132(2)	0.245(1)	0.8025(4)	−0.235(1)	0.139(2)
C-9(B)	0.836(1)	0.8296(3)	−0.723(1)	0.092(2)	0.342(1)	0.8292(3)	−0.250(1)	0.107(2)
C-8(B)	0.8197(9)	0.8425(3)	−0.947(1)	0.070(2)	0.317(1)	0.8424(3)	−0.456(1)	0.080(2)
C-7(B)	0.9092(9)	0.8671(3)	−0.969(1)	0.072(2)	0.406(1)	0.8672(3)	−0.467(1)	0.097(2)
N-1(B)	0.8554(9)	0.8866(3)	−0.806(1)	0.113(2)	0.3509(9)	0.8884(3)	−0.309(1)	0.106(2)
C-1(B)	0.9376(9)	0.8962(4)	−0.658(1)	0.079(2)	0.4359(9)	0.8983(3)	−0.161(1)	0.069(2)
O-1(B)	1.084(1)	0.8923(4)	−0.604(1)	0.126(2)	0.5812(9)	0.8916(3)	−0.100(1)	0.149(2)
C-2(B)	0.865(1)	0.9214(3)	−0.515(1)	0.114(2)	0.368(1)	0.9214(4)	−0.016(1)	0.118(2)
O-2(B)	0.6986(9)	0.9217(4)	−0.576(1)	0.119(2)	0.1949(8)	0.9216(2)	−0.063(1)	0.109(2)
C-3(B)	0.948(1)	0.9455(3)	−0.579(1)	0.082(2)	0.4442(8)	0.9440(3)	−0.0727(9)	0.053(2)
O-3(B)	0.9288(8)	0.9500(3)	−0.813(1)	0.105(2)	0.4337(7)	0.9502(2)	−0.3096(9)	0.088(2)
C-4(B)	0.8958(9)	0.9692(4)	−0.420(1)	0.090(2)	0.3966(9)	0.9665(4)	0.076(1)	0.089(2)
O-4(B)	0.7331(9)	0.9738(3)	−0.462(1)	0.133(2)	0.2354(8)	0.9755(3)	0.040(1)	0.113(2)
C-5(B)	0.999(1)	0.9938(4)	−0.474(1)	0.094(2)	0.504(1)	0.9931(5)	0.030(1)	0.058(2)
O-5(B)	1.1586(7)	0.9859(2)	−0.427(1)	0.100(2)	0.659(1)	0.9852(3)	0.081(1)	0.098(2)
C-6(B)	0.955(1)	1.0147(4)	−0.312(1)	0.113(2)	0.453(1)	1.0168(4)	0.190(1)	0.117(2)
O-61(B)	1.063(1)	1.0363(4)	−0.356(1)	0.086(2)	0.415(1)	1.0150(3)	0.418(1)	0.097(2)
O-62(B)	0.9322(9)	1.0126(3)	−0.084(1)	0.079(2)	0.5566(1)	1.0361(4)	0.154(1)	0.057(2)

[a] Atomic co-ordinates are fractional. Standard deviations obtained from the least-squares correlation matrix are given in parentheses.

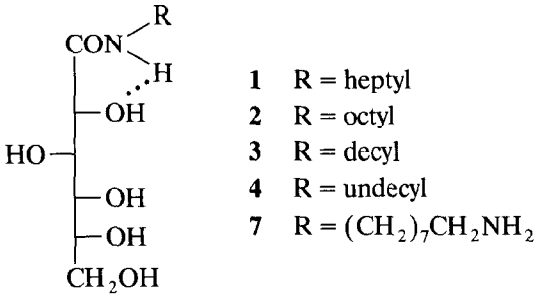
TABLE II

Short intermolecular O···O contacts < 3.5 Å which are indicative of hydrogen bonding [a]

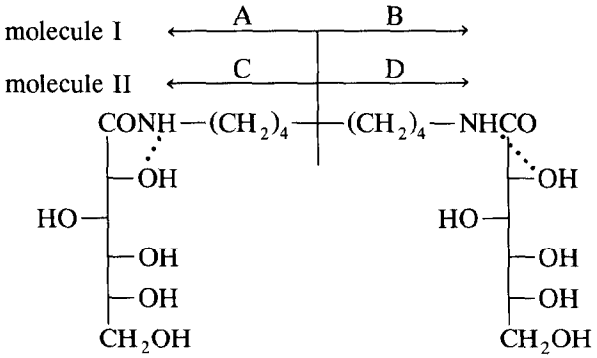
Atom	A		B		C		D	
O-61	O-61(D)	3.06	O-61(C)	2.82	O-61(B)	2.82	O-61(A)	2.80
	O-62(D)	2.80	O-61(C)	2.94	O-61(B)	2.94	O-62(A)	2.78
	O-4(C)	3.25	O-62(C)	2.80	O-62(B)	2.50	O-62(A)	3.07
	O-5(C)	2.64	O-61(D)	3.35			O-5(D)	2.75
	O-3(A)	3.36						
O-62	O-61(D)	2.54	O-61(C)	2.50	O-61(B)	2.80	O-61(A)	3.06
	O-62(D)	2.78	O-62(C)	3.23	O-62(B)	3.23	O-62(A)	2.54
	O-62(D)	3.07	O-4(D)	3.28	O-5(A)	2.83	O-5(B)	2.79
			O-5(D)	2.86	O-4(A)	3.12	O-5(D)	3.35
					O-3(C)	3.30	O-61(B)	
O-5	O-4(C)	2.70	O-4(D)	2.77	O-4(A)	2.67	O-4(B)	2.74
	O-62(C)	2.83	O-4(D)	3.11	O-4(A)	3.17	O-4(B)	3.16
	O-3(C)	2.96	O-3(D)	3.00	O-3(A)	2.88	O-3(B)	2.96
	O-4(C)	3.22	O-61(D)	2.79	O-61(A)	2.64	O-62(B)	2.86
					O-3(C)	3.44		
O-4	O-3(C)	2.84	O-3(D)	2.89	O-3(A)	2.86	O-3(B)	3.01
	O-5(C)	2.67	O-5(D)	3.16	O-5(A)	2.70	O-5(B)	2.77
	O-5(C)	3.17	O-5(D)	2.74	O-5(A)	3.22	O-5(B)	3.11
	O-62(C)	3.12			O-61(A)	3.25	O-62(B)	3.28
O-3	O-2(C)	3.03	O-2(D)	3.01	O-2(A)	3.03	O-2(B)	3.05
	O-4(C)	2.86	O-4(D)	3.01	O-4(A)	2.84	O-4(B)	2.89
	O-5(C)	2.88	O-5(D)	2.96	O-5(A)	3.96	O-5(B)	3.00
	O-61(A)	3.36			O-62(C)	3.30		
O-2	O-1(C)	3.06	O-1(D)	3.25	O-1(A)	3.09	O-1(B)	3.16
	O-3(C)	3.03	O-3(D)	3.05	O-3(A)	3.03	O-3(B)	3.01
	N-1(A) *	2.61	N-1(B) *	2.59	N-1(C) *	2.60	N-1(D) *	2.54
O-1	N-1(C)	2.92	N-1(D)	2.77	N-1(A)	2.86	N-1(B)	2.87
	O-2(C)	3.09	O-2(D)	3.16	O-2(A)	3.06	O-2(B)	3.25
N-1	O-2(A) *	2.61	O-2(B) *	2.59	O-2(C) *	2.60	O-2(D) *	2.54
	O-1(C)	2.86	O-1(D)	2.87	O-1(A)	2.92	O-1(B)	2.77

[a] Distances (Å) from atoms O,N (left column) in molecular fragments **A–D** to other atoms. Standard deviations for the distances are ~ 0.01 Å; * denotes an intramolecular hydrogen bond.

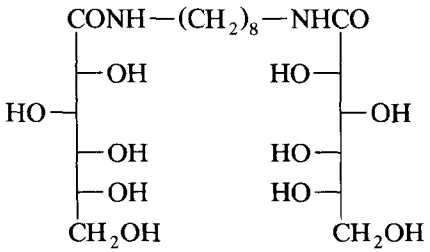
The alkyl groups are spacers with a flexible hinge at the amide link. As observed in a comparison of **1–3**, the interface between the molecules in the head-to-tail arrangement is nearly identical, with the $-CH_2CH_3$ terminus in similar van der Waals contact with the gluconamide C-6–H_2–O-6–H terminus[5]. In the octyl (**2**) and decyl (**3**) derivatives, this arrangement requires only a lengthening of one unit-cell axis, whereas, in the heptyl (**1**) and undecyl (**4**) derivatives, a change in the conformation of the alkyl chain is required in order to bring the termini into the same relative orientation as in **2** and **3**. It appears that the locus of greatest flexibility of the alkyl chain is at the amide link, because the torsion angles



1 R = heptyl
2 R = octyl
3 R = decyl
4 R = undecyl
7 R = $(CH_2)_7CH_2NH_2$



5



6

C-1–N-1–C-7–C-8 and N-1–C-7–C-8–C-9 deviate from *anti*, being anticlinal in the former and −synclinal in the latter.

There is an analogy with the fatty acids where synclinal conformations of the alkyl chains next to sp^2-hybridised carbons[12] or to carboxyl groups in esters[13] have been observed frequently. Most noteworthy is the value −68° for the torsion angle C-1–C-2–C-3–C-4 in the B-form stearic acid[12] which may be considered the standard amphiphile. This twist in an otherwise all-*anti* molecule brings the H atoms of C-4 close to the terminal oxygens and introduces a tilt of the alkyl chains with respect to the plane defined by the head groups. The low temperature crystals (A forms) of fatty acids contain no synclinal conformers, and the chains are not tilted, and tight packing is achieved by an antiparallel arrangement of the molecules which compensates for the space requirements of the bulky end groups.

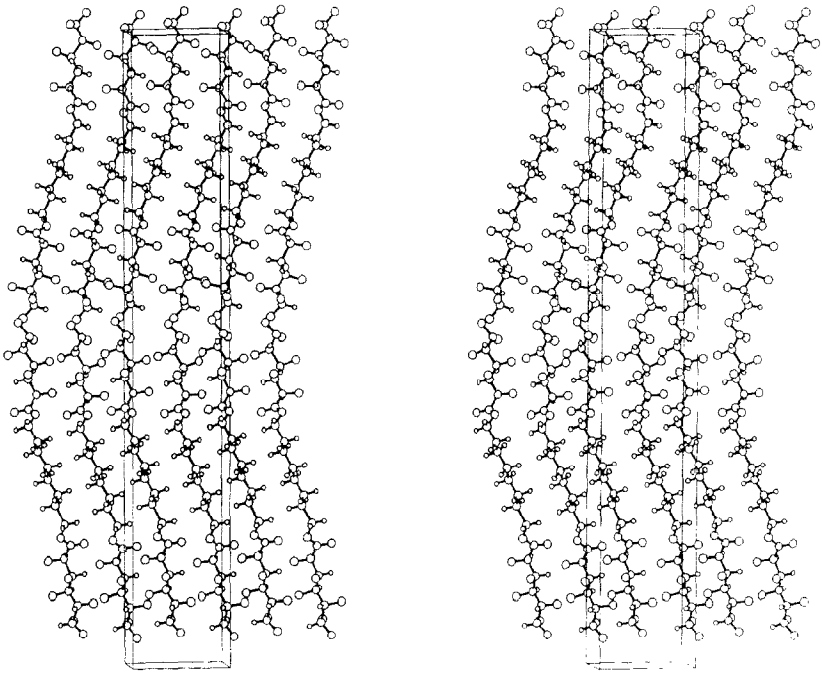


Fig. 1. Packing scheme of **5** in the crystal lattice viewed along the *c* direction.

TABLE III

Relevant torsion angles (°) for *N*-heptyl- (**1**), *N*-octyl- (**2**), and *N*-decyl-D-gluconamide (**3**), and for the bola-amphiphile **5** (molecules **I** and **II**) (see Fig. 3)

Torsion angle	1	2	3	5(I)	5(II)
C-6(A)–C-5(A)–C-4(A)–C-3(A)		−179.2	−178.2	174.6	178.8
C-5(A)–C-4(A)–C-3(A)–C-2(A)		177.5	179.9	177.1	179.1
C-4(A)–C-3(A)–C-2(A)–C-1(A)		−166.1	−159.0	−172.2	−167.6
C-3(A)–C-2(A)–C-1(A)–N-1(A) [a]		−111.6	−114.3	−118.0	−114.4
C-2(A)–C-1(A)–N-1(A)–C-7(A)		177.9	177.8	177.9	176.6
C-1(A)–N-1(A)–C-7(A)–C-8(A)		**−172.5**	**−175.1**	**124.5**	**118.7**
N-1(A)–C-7(A)–C-8(A)–C-9(A)		**−175.7**	**−177.0**	**167.6**	**162.2**
C-7(A)–C-8(A)–C-9(A)–C-10(A)		176.7	179.4	−174.6	−174.4
C-8(A)–C-9(A)–C-10(A)–C-10(B)	173.0	−178.0	−177.2	173.5	170.9
C-9(A)–C-10(A)–C-10(B)–C-9(B)	−179.6	177.6	177.3	176.9	177.3
C-10(A)–C-10(B)–C-9(B)–C-8(B)	174.9	−179.8	179.1	174.8	175.7
C-10(B)–C-9(B)–C-8(B)–C-7(B)	−179.4	178.2	177.9	−179.4	179.8
C-9(B)–C-8(B)–C-7(B)–N-1(B)	**−64.7**			**−63.5**	**−70.0**
C-8(B)–C-7(B)–N-1(B)–C-1(B)	**101.3**			**119.2**	**120.3**
C-7(B)–N-1(B)–C-1(B)–C-2(B)	176.6			170.6	176.0
N-1(B)–C-1(B)–C-2(B)–C-3(B) [a]	−114.2			−109.7	−110.6
C-1(B)–C-2(B)–C-3(B)–C-4(B)	−167.0			−172.4	−173.8
C-2(B)–C-3(B)–C-4(B)–C-5(B)	178.4			173.5	172.8
C-3(B)–C-4(B)–C-5(B)–C-6(B)	−179.9			−176.4	179.8

[a] Constrained to −111 to −118° due to the intramolecular N–H ··· O-2 hydrogen bond.

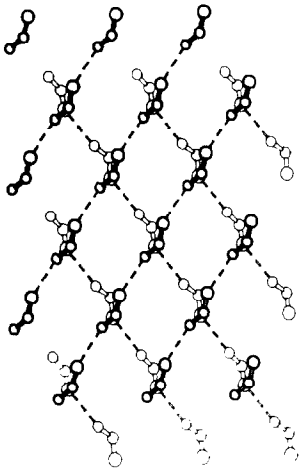


Fig. 2. A view of the *a*, *c* plane to show N-1–H · · · O-1 hydrogen bonding. Top layer (thick lines) includes fragments **A** (see formulae) and **C**, and the bottom layer (thin lines) includes fragments **B** and **D**. For clarity, only atoms N-1–C-1=O-1 are shown.

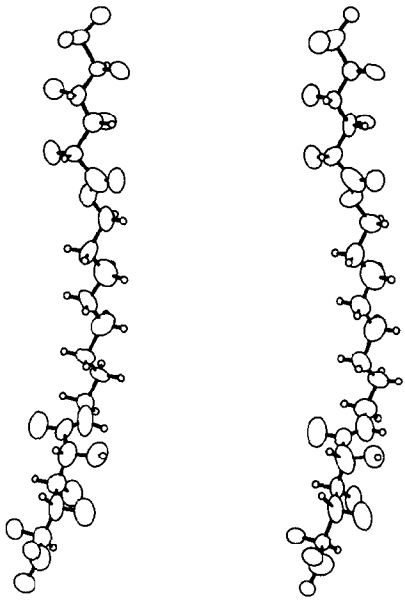


Fig. 3. ORTEP-drawing of molecules **I** (left) and **II** (right) of **5**. The molecules are oriented with fragments **A** and **C** in the upper part, and fragments **B** and **D** in the lower part. Thermal ellipsoids are drawn at a 50% probability level.

ACKNOWLEDGMENTS

This work was supported by the Deutsche Forschungsgemeinschaft (Sonderforschungsbereich 312, Teilprojekte C1 and D1) and the Fonds der Chemischen Industrie.

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