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The X-ray crystal structure of *N*-(1-octyl)-D-talonamide and a consideration of its hydrogen-bonding scheme

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ABSTRACT

The crystal structure of *N*-(1-octyl)-D-talonamide [space group $P2_12_12_1$, $a = 914.0(2)$, $b = 581.4(1)$, $c = 6257(1)$ pm] shows two independent molecules in the asymmetric unit. The oligomethylene chains of both molecules are extended. The talonic acid moieties have a *gauche*-bend along C-1–C-2–C-3–C-4 thereby avoiding a 1,3-*syn* interaction (O‖O) between O-2 and O-4, whereas the resulting C‖O orientation between C-1 and O-4 is tolerated. The molecular packing is a symmetric tail-to-tail bilayer sheet comparable to that of the diastereomeric gulonamide analogue, but in contrast to the head-to-tail packing in the gluconamide analogue. This experimental result is explained by the occurrence of different hydrogen-bond patterns between hydroxyl groups (*i*) of adjacent crystal sheets (talon- and gulon-amide derivative) or (*ii*) within one crystal sheet (gluconamide derivative).

INTRODUCTION

The three diastereomeric *N*-octylaldonamides **1–3** derived from talose, gulose, and glucose all have in the extended conformation one pair of 1,3-*syn* and 1,3-*gauche* oriented hydroxyl groups. As indicated in Scheme 1 for the D-talonamide (**1**) and D-gluconamide (**3**) derivatives, the *syn*-interaction appears between OH-2 and OH-4, whereas in the D-gulonamide (**2**) it is between OH-3 and OH-5. The steric interactions in **1** and **3** should thus be very similar, but different from those in **2**. In micellar aqeous solution at 80°C, where all hydrogen bonds are broken, the aggregation is not affected by stereochemical differences[1] and thus all three amides give critical micelle concentrations around 2.8×10^{-2} M. Upon cooling, however, different aggregates are formed. The talonamide **1** produces ill-defined, short tubules having some helical twist which immediately rearrange into crystal sheets. The gulonamide **2** crystallizes directly from the micellar

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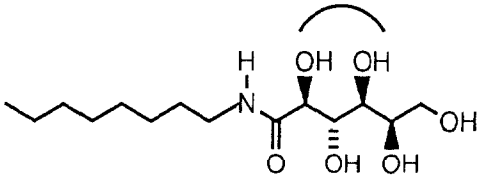
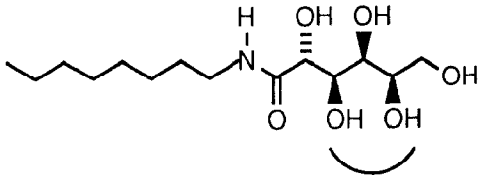


N-(1-Octyl)-D-talonamide (**1**)



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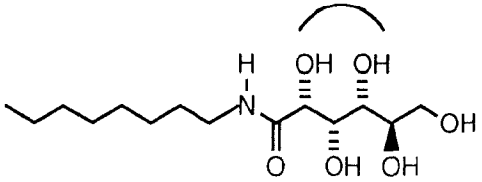


N-(1-Octyl)-D-gluconamide (**3**)

Scheme 1

solution in the form of platelets, whereas the gluconamide **3** gives very long, well-defined quadruple helices of bimolecular strands which are stable during several h[2–4]. Furthermore, the crystal structure of the gulonamide **2** shows the tail-to-tail bilayer packing[5] usually found in the crystals of amphiphiles[6–8]. The gluconamide **3** produces head-to-tail oriented (= enantiomer polar[9]) crystal sheets[10]. Both the stability of the fibers and the unusual crystallization behavior of **3** have been traced back to a homodromic hydrogen-bond cycle between hydroxyl groups within one crystal sheet[11,12].

Differential scanning calorimetry (DSC) measurements of the crystalline talonamide **1** shows three pretransition signals, at 80.5, 83.0 and 102.0°C (ΔH = 10.5 kJ mol^{-1}), and the melting peak at 132.0°C (ΔH = 32.3 kJ mol^{-1})[13]. The thermogram of the gulonamide **2** exhibits a small pretransition signal at 115°C (δH = 1.0 kJ mol^{-1}) and the melting peak at 124°C (ΔH = 30.5 kJ mol^{-1})[13], whereas for the gluconamide **3**, two pretransition signals at 72.0 and 87.4°C (ΔH = 12.6 kJ mol^{-1}) are accompanied by the melting peak at 158.2°C (ΔH = 43.1 kJ mol^{-1})[14]. The high pretransition enthalpy of **3** indicates the molecular reorientation from head-to-tail to the bilayer packing during the heating process, as detected also by X-ray diffraction measurements of *N*-(undecyl)gluconamide[12,15].

Despite the differences in fiber formation between the talonamide **1** and gluconamide **3**, the thermodynamic behavior suggests a similar head-to-tail packing within the crystals. As investigated thus far, this behavior has been found in only seven other amphiphilic *N*-alkyl aldonamides, namely the heptyl[16], decyl[16], undecyl[15], and tetradecane-6,8-diynyl[17]-D-gluconamides, in *N*-methyl nonamido-[18] and undecamido-[19] D-glucitol (but not in the octamido compound[19]), and in *N*-decyl-D-ribonamide[20]. These observations prompted us to investigate the crystal structure of *N*-(1-octyl)-D-talonamide (**1**). This is only the second published structure having an acyclic talose moiety, the other compound being the corresponding alditol, D-talitol[21].

EXPERIMENTAL

N-(1-Octyl)-D-talonamide (**1**) was prepared by electrolytic oxidation of D-talose[22], lactonization, and aminolysis of the resultant D-talonolactone with 1-aminooctane in MeOH[3]. The single crystals selected for the Weissenberg photographs and data collection were cut from a clear region of an otherwise opaque and flexible plexus that had been grown by very slow cooling of a hot solution of **1** in water. Single-crystal Weissenberg photographs of the *h*0*l* layer showed weak reflections at odd orders of *h*, indicative of a superlattice. Closer inspection, however, including Weissenberg photographs of the *h*1*l* and *h*2*l* layers, where the weak reflections were of even and odd orders in *h*, showed that they occurred at *hkl* with $h + k = 2n + 1$. This showed the structure to be pseudo-C-centered.

Precise lattice constants and the intensity data for an octant were measured on a Stoe four-circle diffractometer with Ni-filtered Cu$K\alpha$ radiation in the ω-2θ-scan mode. Due to the large lattice constant of $c = 6257$ pm resulting in narrow distances of reflections in the c^*-direction, overlap of neighboring reflections could not be avoided in several cases. To correct for errors due to overlap, all reflection profiles were measured and were subsequently edited to give correct intensities using the computer program RECOR[23].

The 42 largest peaks in the structure solution using[24] SHELXS-86 provided all nonhydrogen atoms of both molecules in the asymmetric unit.

After the anisotropic refinement of the nonhydrogen atoms with the XTAL 2.2 computer program[25], hydrogen atoms positions were calculated for the carbon atoms of the talonic acid moieties, the nitrogen atoms of the amide bonds, and for both octyl chains. They were given isotropic thermal parameters by adding ~ 10% to the values of their corresponding heavy atoms. The model was refined with the

* A complete atom list with the hydrogen atom parameters and the displacement parameters included, and the list of observed and calculated structure factors as well as the list of bond lengths and bond and torsion angles for **1** (32 pp) can be obtained on request from the Elsevier Science Publishers, B.V., BBA Data Deposition, P.O. Box 1527, Amsterdam, Netherlands. Reference should be made to No. BBA/DD/518/*Carbohydr. Res.*, 240 (1993) 47–56.

TABLE I

Crystal and refinement data [a] for *N*-(1-octyl)-D-talonamide (**1**)

Formula	$C_{14}H_{29}NO_5$
Space group	$P2_12_12_1$
Lattice constants	$a = 914.0(2)$
(pm)	$b = 581.4(1)$
	$c = 6257(1)$
Cell volume (pm^3)	3.32497×10^9
Crystal size (mm)	$0.6 \times 0.3 \times 0.04$
Z	8
ρ_x (g/cm^3)	1.228
μ (Cu $K\alpha$, cm^{-1})	7.96
Reflections	2955
unobserved ($F < 2\sigma$)	706
R_F	9.9%
wR_F	7.1%
S	4.27
Function minimized	$\Sigma[1/\sigma_{F_o}^2(\lvert F_o \rvert - \lvert F_c \rvert)^2]$

[a] Numbers in parentheses are esd values

calculated hydrogen atoms kept fixed. Attempts to localize hydrogen atoms of hydroxyl groups, in order to obtain information for the interpretation of the hydrogen-bonding scheme, yielded only four stereochemically reasonable positions that also fitted into a hydrogen-bonding geometry. They were treated like the calculated hydrogen atoms. The remaining six hydroxyl hydrogen atoms were not visible in the difference Fourier map and their positions could consequently not be determined.

Table I displays the crystal and refinement data for **1**, the atomic parameters are listed in Table II, and relevant torsion angles are given in Table III. The hydrogen-bond geometry, with the amide group and located hydrogen atoms involved and oxygen–oxygen distances indicating possible hydrogen bonds, are shown in Table IV.

RESULTS AND DISCUSSION

Molecular structure and packing.—The molecular geometry and the numbering scheme of the two independent molecules in the asymmetric unit are given in Fig. 1. Both molecules are essentially extended from C-2 to C-14, and C-2A to C-14A, respectively. The C–C and C–O bond lengths vary from 148(1) to 157(2) pm and 139(1) to 148(1) pm, respectively. Their mean values of 151(2) and 144(3) pm are comparable to the corresponding values in alditols[27]. The bond lengths of the amide unit are 135(2) and 130(1) pm for the C–N and 122(1) and 124(1) pm for the C–O bonds. The talonamide moieties of both molecules exhibit a *gauche*-bend along C-1–C-2–C-3–C-4 avoiding a 1,3-*syn* interaction between O-2 and O-4, whereas the resulting C‖O interaction between C-1 and O-4 is tolerated. The

TABLE II

Atomic parameters and U_{eq}- and U-values for **1** [a]

Atom	x	y	z	U_{eq} / U
C-1	−0.731(1)	−0.467(2)	0.1086(2)	5.4(4)
O-1	−0.8607(8)	−0.434(2)	0.1120(1)	7.4(4)
C-2	−0.655(1)	−0.305(2)	0.0935(2)	5.8(5)
O-2	−0.4999(7)	−0.356(1)	0.0918(1)	6.5(3)
C-3	−0.717(1)	−0.300(2)	0.0713(2)	4.5(4)
O-3	−0.6643(8)	−0.115(1)	0.0595(1)	5.3(3)
C-4	−0.699(1)	−0.524(2)	0.0578(2)	4.1(4)
O-4	−0.7657(7)	−0.708(1)	0.0695(1)	4.8(3)
C-5	−0.750(1)	−0.498(2)	0.0351(2)	4.5(4)
O-5	−0.9094(7)	−0.465(1)	0.0357(1)	5.9(3)
C-6	−0.719(1)	−0.716(2)	0.0211(2)	4.8(4)
O-6	−0.5634(8)	−0.711(1)	0.0159(1)	6.7(3)
N-1	−0.6571(9)	−0.639(2)	0.1184(1)	5.6(4)
C-7	−0.727(1)	−0.791(2)	0.1331(2)	5.9(5)
C-8	−0.624(1)	−0.937(2)	0.1454(2)	5.2(4)
C-9	−0.702(1)	−1.104(2)	0.1609(2)	5.6(4)
C-10	−0.603(1)	−1.257(2)	0.1729(2)	6.5(5)
C-11	−0.684(1)	−1.402(2)	0.1896(2)	7.5(5)
C-12	−0.585(1)	−1.567(2)	0.2016(2)	7.2(5)
C-13	−0.663(2)	−1.712(3)	0.2183(2)	10.1(7)
C-14	−0.563(2)	−1.876(2)	0.2304(2)	10.4(7)
C-1A	−0.215(1)	−0.018(2)	0.1079(2)	4.2(4)
O-1A	−0.3482(7)	0.021(1)	0.1096(1)	5.6(3)
C-2A	−0.131(1)	0.143(2)	0.0932(2)	4.2(4)
O-2A	0.0184(6)	0.072(1)	0.0917(1)	5.3(3)
C-3A	−0.197(1)	0.171(2)	0.0714(2)	4.5(4)
O-3A	−0.1262(8)	0.349(1)	0.0600(1)	5.5(3)
C-4A	−0.188(1)	−0.047(2)	0.0572(2)	3.7(4)
O-4A	−0.2404(7)	−0.244(1)	0.0685(1)	4.3(2)
C-5A	−0.257(1)	−0.022(2)	0.0360(2)	3.5(4)
O-5A	−0.4164(7)	−0.019(1)	0.0394(1)	6.2(3)
C-6A	−0.221(1)	−0.214(2)	0.0199(2)	4.7(4)
O-6A	−0.0724(8)	−0.181(1)	0.0117(1)	6.9(3)
N-1A	−0.1465(8)	−0.180(2)	0.1181(1)	5.1(4)
C-7A	−0.225(1)	−0.329(2)	0.1325(2)	5.4(4)
C-8A	−0.123(1)	−0.466(2)	0.1463(2)	4.7(4)
C-9A	−0.205(1)	−0.634(2)	0.1611(2)	6.0(5)
C-10A	−0.106(1)	−0.784(2)	0.1746(2)	6.8(5)
C-11A	−0.186(1)	−0.940(2)	0.1903(2)	6.8(5)
C-12A	−0.085(1)	−1.093(2)	0.2035(2)	7.1(5)
C-13A	−0.168(2)	−1.241(3)	0.2194(2)	10.5(7)
C-14A	−0.069(2)	−1.409(2)	0.2314(2)	10.4(7)
H-N	−0.56(−)	−0.67(−)	0.116(−)	6.0(−)
H-NA	−0.05(−)	−0.21(−)	0.117(−)	6.7(−)
H-O2	−0.46(−)	−0.15(−)	0.096(−)	7.9(−)
H-O3	−0.70(−)	0.06(−)	0.064(−)	5.7(−)
H-O5	−0.99(−)	−0.57(−)	0.044(−)	6.9(−)
H-O4A	−0.21(−)	−0.46(−)	0.069(−)	5.6(−)

[a] Numbers in parentheses are esd values.

TABLE III

Selected torsion angles of **1**[a]

Sequence	Angle (°)	Sequence	Angle (°)
C-1–C-2–C-3–C-4	−67(1)	C-1A–C-2A–C-3A–C-4A	−69(1)
C-2–C-3–C-4–C-5	173(1)	C-2A–C-3A–C-4A–C-5A	178(1)
C-3–C-4–C-5–C-6	175(1)	C-3A–C-4A–C-5A–C-6A	167(1)
C-4–C-5–C-6–O-6	−77(1)	C-4A–C-5A–C-6A–O-6A	−76(1)
N-1–C-1–C-2–C-3	122(1)	N-1A–C-1A–C-2A–C-3A	131(1)
C-2–C-1–N-1–C-7	179(1)	C-2A–C-1A–N-1A–C-7A	178(1)
C-1–N-1–C-7–C-8	−169(1)	C-1A–N-1A–C-7A–C-8A	−167(1)
N-1–C-7–C-8–C-9	−179(1)	N-1A–C-7A–C-8A–C-9A	−177(1)
O-1–C-1–C-2–O-2	177(1)	O-1A–C-1A–C-2A–O-2A	−177(1)
O-2–C-2–C-3–O-3	−67(1)	O-2A–C-2A–C-3A–O-3A	−64(1)
O-3–C-3–C-4–O-4	−175(1)	O-3A–C-3A–C-4A–O-4A	173(1)
O-4–C-4–C-5–O-5	57(1)	O-4A–C-4A–C-5A–O-5A	55(1)
O-5–C-5–C-6–O-6	165(1)	O-5A–C-5A–C-6A–O-6A	164(1)

[a] Esds in parentheses.

orientation of the terminal oxygen atoms (O-6 and O-6A) is *gauche* to the carbon chain, with torsion angles of −77 and −76°, thus producing an apolar edge within the head group similar to that of the gluconamide **3**.

TABLE IV

Summary of hydrogen-bonding data in **1** [a,b]

(*a*) At the amide nitrogen and involving located hydroxyl hydrogen atoms

D-H···A	D-H	H···A	D···A	D-H···A	Symmetry operator for Atom A
N–H-N···O-2	92	242	275(1)	101	x, y, z
N–H-N···O-1A	92	267	349(1)	147	$x, -1+y, z$
NA–H-NA···O-2A	92	235	267(1)	101	x, y, z
NA–H-NA···O-1	92	217	303(1)	156	$1+x, y, z$
O-2–H-O-2···O-1A	125	170	282(1)	147	x, y, z
O-3–H-O-3···O-4	112	150	261.8(9)	176	$x, 1+y, z$
O-5–H-O-5···O-3A	110	165	272(1)	163	$-1+x, -1+y, z$
O-4A–H-O-4A···O-3A	128	146	264.0(9)	150	$x, -1+y, z$

(*b*) Oxygen–oxygen distances [a]

Atom 1	Atom 2	D [b]	Symmetry operator for Atom 2
O-2	O-3	288(1)	x, y, z
O-2	O-4A	285.6(9)	x, y, z
O-3	O-5A	265(1)	x, y, z
O-4	O-5	286(1)	x, y, z
O-4	O-2A	273.3(9)	$-1+x, -1+y, z$
O-5	O-6A	268(1)	$-1+x, y, z$
O-6	O-5A	268(1)	$x, -1+y, z$
O-6	O-6A	286(1)	$-1/2+x, -1/2-y, -z$
O-2A	O-3A	288(1)	x, y, z
O-4A	O-5A	276.2(9)	x, y, z

[a] Distances in pm. [b] Esds in parentheses.

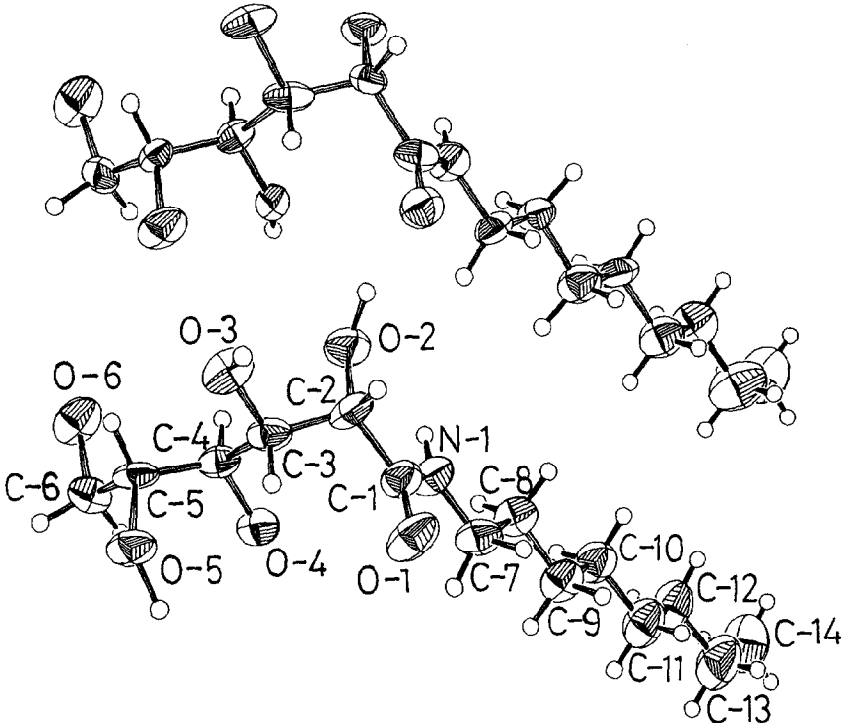


Fig. 1. ORTEP Plot[26] of the conformation and atomic numbering scheme of the two independent molecules in the asymmetric unit of **1**. The atoms of the second molecule (above) carry the suffix 'A' in their atom number (see Table II).

Despite this structural relationship, the talonamide **1** crystallizes in tail-to-tail packing (Fig. 2). This crystallization behavior indicates that the *gauche* orientation of the terminal hydroxyl group does not necessarily lead, as assumed previously[5], to head-to-tail monolayers. Table II shows that the corresponding atoms of the two molecules have similar *z*-coordinates. They differ in *x* and *y* by ~0.5. This

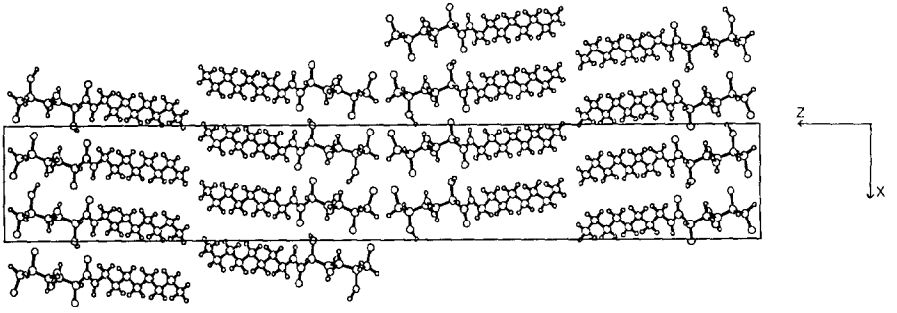
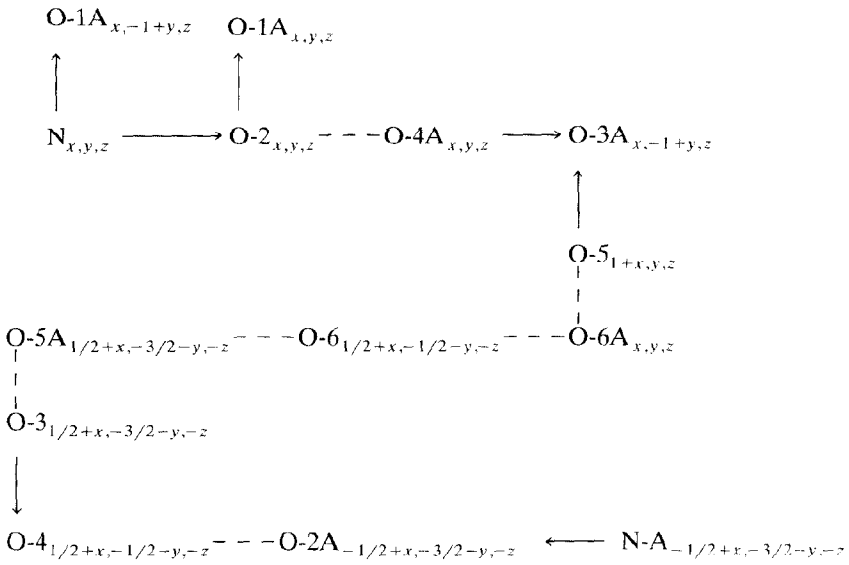


Fig. 2. Tail-to-tail crystal packing of **1**, viewed in the negative *c*-axis direction. Atoms H, C, N, and O are indicated with increasing radii (SCHAKAL-88b[28]).



Scheme 2. Possible hydrogen-bonding scheme of **1** derived from intermolecular oxygen–oxygen distances below 300 pm. Donor → acceptor directions derived from localized hydroxyl hydrogen and calculated amide hydrogen atoms suggest that the hydrogen-bonding scheme consists of chains running in opposite directions.

agreement is, however, rather poor especially for the head groups, so that a C-centered lattice is not precisely realized. The two molecules in the asymmetric unit of **1** show similar conformations, as is often the case with crystallographically independent molecules[29]. The torsion angles (Table III) differ at most by 10° in the region of the amide group. This small structural difference causes the hydrogen-bonding schemes at the amide groups to be different, as discussed later. Moreover, the IR spectrum of **1** shows two discernible amide I signals[13] at 1653 and 1614 cm^{-1}. *N*-(1-Octyl)-D-talonamide is, therefore, the first aldonamide found to exhibit conformational isomorphism[30] in its crystal structure. Independent molecules also occur in the asymmetric unit of related α-monoglycerides of fatty acids. The two molecules of optically active glycerides[8,31] as well as the four molecules of the racemate[32] differ slightly in the conformation of their glycerol head groups.

The hydrogen-bonding scheme.—The subtle difference of the torsion angles in the talonamide moieties is accompanied by drastic changes in the environment of the amide groups: NA is involved in a hydrogen bond with O-1 with an N ··· O distance of 303 pm, whereas the interaction (if any) of N with O-1A is very weak (N ··· O 349 pm). Without a knowledge of all hydroxyl hydrogen atom positions, it is impossible to derive the complete hydrogen-bonding scheme of the talonamide **1**. However, regarding the patterns found in other open-chain sugars[33], a possible hydrogen-bonding scheme may be deduced by using only intermolecular oxygen–

oxygen distances below 300 pm and the calculated amide hydrogen-atom positions (Scheme 2). Additional arrows indicate the direction of hydrogen bonds as derived from localized hydroxyl hydrogen atoms.

In contrast to the similar thermodynamic behavior, the hydrogen-bonding scheme of the talonamide **1** shows no analogy when compared to the crystal structures of the diastereomeric gluconamide **3** and the homologous amides and odd numbered glucitols already mentioned. The monolayer head-to-tail packing of all of these compounds is associated with a homodromic, four-bond cycle within one crystal sheet[12] that is not present in **1**. The formation of such a cycle requires a special spatial arrangement of the four interacting hydroxyl groups, namely a MAP-orientation[34] (following the nomenclature of Mills[35]). This arrangement is realized in the gluconic and glucitol compounds along the extended-chain segment between C-3 and C-6. As a consequence of this packing condition[34], two unit-cell constants have a length of ~ 500 pm, which are not observed in the talonamide **1** (Table I). This is a rather unexpected observation because the related D-talitol * shows a hydrogen-bond system consisting of two infinite chains at O-1 and O-6 and the quadrilateral homodromic cycle, which was not mentioned in the original paper[21]. The MAP-orientation is accomplished in D-talitol by a rotation of 120° around the C-2–C-3 bond, resulting in a *gauche*-bend and a 1,3-*syn* disposition of C-1 and O-4. The destabilization of the molecule is overcome by the described cooperative hydrogen-bond pattern, which is known to be very stable[36]. Thus, it remains an open question as to why the title compound **1** occurs in a conformation analogous to talitol, but exhibits a crystal packing having a divergent hydrogen-bond scheme.

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* D-Talitol is the alternative (non-preferred) name for D-altritol[21], and the atomic-numbering scheme is opposite: C-*n* of D-altritol matches C-(7-*n*) in D-talitol. Herein, the numbering scheme of D-talitol is used to allow direct comparison with the conformation of **1**.

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