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1,3-Parallel C//O interactions in acyclic carbohydrates: the crystal and molecular structure of 1-deoxy-1-nitro-D-altritol

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Abstract

The crystal structure of 1-deoxy-1-nitro-D-altritol (**1**; $C_7H_{13}NO_7$; space group $P2_1$) was resolved to a final conventional residual factor of R 0.081. The molecules showed a sickle conformation in which a 1,3-parallel interaction (C//O) between C-6 and O-3 is tolerated, thus avoiding a 1,3-parallel interaction (O//O) between O-3 and O-5 in a planar zigzag conformation. Interestingly, the bent conformation, which avoids all such interactions, was not adopted. The observed conformation resembles that of D-altritol and D-altritol hexaacetate. A systematic search for the occurrence of such C//O interactions in the solid state conformations of acyclic carbohydrate derivatives revealed that this is the conformation which usually is observed in those cases where compounds or part of compounds are of *ribo* configuration, but with a few remarkable exceptions such as ribitol itself.

Key words: X-ray structures; Conformation; 1,3-Parallel interactions; Alditols; Nitroalditols

1. Introduction

In 1986, Angyal et al. [1] reported the X-ray structure of D-*glycero*-L-*allo*-heptitol, which exhibited a 1,3-parallel interaction C//O in a bent conformation, and suggested that the assumed negative influence of such an interaction in determining the conformation of acyclic carbohydrates probably had been overestimated before. They also suggested that the negative steric effect of a 1,3-parallel arrangement of oxygens (O//O) in a planar zigzag chain in such compounds could be less influential than had been proposed and almost generally accepted at that time.

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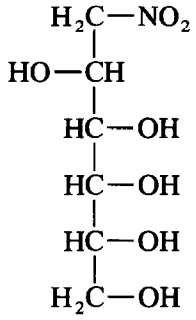
These ideas are supported nowadays by a considerable amount of new evidence [2–13]. Nevertheless, it seemed necessary to broaden this still small basis of data in order to gain new general insights into the conformational behaviour of acyclic carbohydrate derivatives. Therefore, the title compound was subjected to X-ray analysis. The parent compound, D-altritol, adopts in the solid state a sickle conformation tolerating a C//O interaction between O-3 and C-6 [4]. In contrast to the situation for the above-mentioned heptitol [1], in this case such an interaction could easily be avoided by a $-120°$ rotation around the C-4–C-5 bond. The topology of D-altritol hexaacetate is similar [7].

2. Results and discussion

Suitable crystals of 1-deoxy-1-nitro-D-altritol (**1**) [14] were obtained from a syrupy matrix and could not be recrystallised; they were not of the very high quality which is in many cases observed for unprotected alditols. The relevant crystallographic data are given in Table 1.



1

The structure was solved by direct methods with the help of the programs SHELXS-86 [15] (solution) and SHELXL-93 [16] (refinement). The refinement was done on F^2 for all reflections. The validated threshold $I > 2\sigma(I)$ was used for calculating R_{obsd} only.

All atoms, with hydrogens introduced at theoretical positions using the AFIX option [16], were refined. The final fractional co-ordinates of C, N, and O atoms with equivalent isotropic thermal parameters are listed in Table 2 [1]. A perspective view of compound **1** (SCHAKAL-92 plot [17]) is presented in Fig. 1 which shows the atom numbering scheme as well. As in all carbohydrates with free hydroxyl

[1] Lists of observed and calculated structure amplitudes, anisotropic thermal parameters, fractional co-ordinates of hydrogen atoms with isotropic thermal parameters, tables of bond distances and angles, and further information have been deposited with and can be obtained, on request, from the Director, Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge, CB2 1EZ, United Kingdom.

Table 1
Crystallographic data for 1 [a]

Formula	$C_6H_{13}NO_7$
Mol wt	211.17
Crystal dimension (mm)	0.4×0.3×0.3
Space group	$P2_1$
Cell parameters (pm, degrees)	
a	501.2(1)
b	877.9(1)
c	988.8(1)
β	93.42(1)
Volume V (pm^3)	434.3(1)×10^6
Z	2
$F(000)$	224
Calculated density, D_x (g cm^{-3})	1.615
λ (Cu$K\alpha_1$) (pm)	154.178
μ (mm^{-1})	1.31
2θ range (degrees)	4.5–153
Reflections measured	1366
Symmetry independent reflections	1080
Reflections with $I > 2\sigma(I)$	1021
Number of refined parameters	145
Final conventional residual factor	
R_{obsd}	0.081
Goodness of fit S_{obsd}	1.069
Diffractometer	Enraf–Nonius CAD4

[a] Standard deviations in parentheses.

Table 2
Fractional positional parameters of C, N, and O atoms (×10^4) and the temperature factors U_{eq} [a] (×10^3) for 1 [b]

Atom	x	y	z	U_{eq}
O-11	541(7)	7409(4)	−3681(3)	279(8)
O-12	618(8)	9853(5)	−3535(3)	345(9)
O-2	−778(6)	7505(4)	−702(3)	228(7)
O-3	4643(7)	7134(4)	712(3)	244(8)
O-4	−389(6)	9750(4)	1708(3)	224(7)
O-5	5111(7)	9907(4)	3155(3)	228(7)
O-6	5467(7)	7380(5)	5120(3)	299(9)
N-1	1294(8)	8595(5)	−3130(3)	230(8)
C-1	3046(9)	8469(6)	−1865(4)	225(9)
C-2	1333(9)	8600(6)	−642(4)	189(9)
C-3	3121(9)	8506(6)	657(4)	195(9)
C-4	1482(8)	8542(5)	1916(4)	185(8)
C-5	3164(9)	8747(5)	3258(4)	197(9)
C-6	4519(10)	7272(6)	3735(4)	265(10)

[a] $U_{eq} = 1/3\Sigma_i\Sigma_j U_{ij} a_i^* a_j^* \mathbf{a}_i \mathbf{a}_j$
[b] Standard deviations in parentheses.

Fig. 1. SCHAKAL-92 [17] plot of a molecule of **1**, showing atom numbering.

groups, individual molecules of **1** are members of a complex pattern of hydrogen bonds, which is given in Table 3. All hydroxyl groups act as donors and the corresponding oxygens, except O-3, are acceptors. A very complicated situation is observed for the primary hydroxyl group at C-6, which is involved in a trifurcated scheme of hydrogen bonds. In this case, one of the oxygens and the nitrogen of the nitro group at C-1 act as acceptors, a situation which is rare and, so far as the involvement of N is concerned, has never previously been observed [2,3,18]; this is most certainly an artefact. The position of H-6O shows an extremely high temperature factor and the esd for the *y* coordinate of this atom is a magnitude higher than for all others. Therefore, the exact position of H-6O remains unclear, but all attempts to locate it in more obvious positions resulted in lower *R* values. This situation is far from satisfactory, but fortunately does not influence the general positions of the other atoms appreciably.

Table 3
Hydrogen-bond pattern [a] in **1** (bond lengths in pm, angles in degrees) [b]

Distances D–H···A	Symmetry operation on A	Distance D···A	Distance H···A	Angle D–H···A	Angles of trifurcation
O-2 $\underline{\underline{82(1)}}$ H-2O···O-4	$-x, 1/2+y-1, -z$	269.3(5)	188(3)	169(2)	
O-3 $\underline{\underline{82(1)}}$ H-3O···O-2	$x+1, y, z$	277.7(5)	197(4)	170(5)	
O-4 $\underline{\underline{82(1)}}$ H-4O···O-5	$x-1, y, z$	274.6(5)	195(3)	162(3)	
O-5 $\underline{\underline{82(1)}}$ H-5O···O-6	$-x+1, 1/2+y, -z+1$	278.7(5)	197(4)	172(4)	
O-6 $\underline{\underline{82(1)}}$ H-6O···O-11	$x, y, z+1$	280.2(5)	200(1)	165(2)	
O-6 $\underline{\underline{82(1)}}$ H-6O···N-1	$x, y, z+1$	299.0(5)	224(8)	153(10)	33(1)
O-6 $\underline{\underline{82(1)}}$ H-6O···O-5	$-x+1, 1/2+y-z, -z+1$	278.7(5)	252(10)	100(10)	86(4); 102(2)

[a] A, Acceptor oxygen; D, Donor oxygen.
[b] Standard deviations in parentheses.

The molecules of **1** adopt a bent conformation which is very similar to that already reported for D-altritol [4] and D-altritol hexaacetate [7]; it is a sickle conformation which avoids an O//O interaction between O-3 and O-5 in the planar zigzag conformation, but with C-6 found in a 1,3-parallel relationship to O-3. This situation could easily have been avoided by a $-120°$ rotation around the C-4–C-5 bond (see above).

In a very recent paper [11], we made the first attempts to document and try to understand such apparently anomalous conformations. We claimed that, in the case of three contiguous stereogenic centres of the same configuration ("*ribo*") in an acyclic sugar, there is a very high probability of finding the same conformation as is observed for **1**. However, a thorough search based on the Cambridge Crystallographic Data File revealed that our previous compilation [11] of relevant structure determinations, although extensive, was incomplete. Therefore, we give in Table 4 a comprehensive summary of all these structures [1,4,5,7,13,19–32] in the order of their appearance in the literature, and include geometric data of distances and 1,3 torsion angles for observed C//O interactions, as calculated by the relevant options of the SCHAKAL-92 program [17]. In most cases, the C//O distance is shorter than the sum of the van der Waals radii (322 pm). Of the 23 substances (including **1**) covered in Table 4, 20 are of *ribo* configuration in the region of flexing, three of *arabino*, but none of *xylo* configuration (as far as four contiguous steric centres are involved, it is the *allo* and/or *altro* situation which is relevant). Another thorough check of X-ray structure determinations of compounds which also contain this element of three contiguous stereogenic centres of *ribo* configuration, but are not bent into a C//O interaction, revealed only six examples, four of them of importance. These are ribitol itself [33] and its pentaacetate [8], allitol [34], and D-*glycero*-D-*gluco*-heptitol [5]. The other two are riboflavin derivatives [35,36], in addition to single independent molecules of some riboflavin derivatives [21,29] given in Table 4.

Therefore, we conclude that the situation as observed for **1** is the favoured one and is the situation usually encountered for "*ribo* compounds" for reasons which we do not understand at present. Special patterns of hydrogen bonds, as discussed by Luger et al. [29], cannot explain this fact, because acetylated derivatives do not, generally, behave differently.

3. Experimental

The X-ray structure determination of **1** was performed at 293 K.

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Table 4
Acyclic carbohydrates adopting in the solid state a sickle conformation involving a C//O interaction, listed in the order of appearance in the literature

Compound	Code [a]	Configuration [b]	Interaction	Distance C//O (pm)	1,3-Dihedral angle (degrees)
Ribose *p*-bromophenylhydrazone [19]	RIBBRP [f]	*ribo*	C-5//O-2	333.8	17.5
Riboflavin hydrobromide–quinol complex dihydrate [20] [c]	RIBHQN [f]	*ribo*	C-5//O-2	301.0	12.2
			C-5//O-2	297.3	22.8
Adenine–riboflavin complex trihydrate [21] [c,d]	ADRBFT [f]	*ribo*	C-1//O-4	269.4	9.1
D-Ribose diethyl dithioacetal [22]	DRETAC	*ribo*	C-1//O-4	305.5	6.5
D-Ribose diphenyl dithioacetal [22]	RIBPTA	*ribo*	C-1//O-4	297.1	9.0
Cellobiitol [23]	BDGPGL	*arabino (gluco)*	C-6′//O-3′	301.6	3.6
Maltitol [24,25]	BIZHIB [24]	*arabino (gluco)*	C-3′//O-6′	308.7	14.2
	(JEXLON [25]			310.3	15.3)
Ethylthio-D-ribonate tetraacetate [26] [c]	BUWNEM	*ribo*	C-1//O-4	284.2	13.4
			C-1//O-4	288.5	13.8
N-Decyl-D-ribonamide [27]	DOHHIR	*ribo*	C-1//O-4	292.8	6.4
Lactitol monohydrate [28]	JEXZER	*arabino (gluco)*	C-3′//O-6′	311.9	9.4
D-*glycero*-L-*allo*-Heptitol [1]	FAJLOR	*ribo (allo / altro)*	C-2//O-5	306.5	12.5
D-Altritol [4]	JOJZOX	*ribo (altro)*	C-6//O-3	297.5	3.0
D-*glycero*-D-*manno*-Heptitol [5]	VOXXOV	*ribo (altro)*	C-7//O-4	294.2	6.5
Hexa-*O*-acetylallitol [7] [e]	VUPVIL	*ribo (allo)*	C-1//O-4=C-6//O-3	281.8	1.7
Hexa-*O*-acetyl-DL-altritol [7]	VUPXEJ	*ribo (altro)*	C-6//O-3	284.9	6.2
Riboflavin tetraacetate, acetone solvate, hemihydrate [29] [c,d,f]	JUKMUX	*ribo*	C-5//O-2	283.6	15.4
Riboflavin tetrabutyrate [29] [g]	VEFHUJ	*ribo*	C-5//O-2	302.6	33.1
			C-1//O-4	318.6	32.4
			C-1//O-4	323.7	29.5
meso-glycero-allo-Heptitol [13]		*ribo (allo)*	C-5//O-2	303.9	4.4
meso-glycero-allo-Heptitol heptaacetate [13]		*ribo (allo)*	C-6//O-3	316.7	5.2
			C-7//O-4	299.7	30.6
N-(1-Octyl)-D-talonamide [30] [c]	HAHXOD	*ribo (altro)*	C-1//O-4	283.7	4.4
			C-1′//O-4′	280.3	13.6

1(*S*)-2-*C*-[(*R*)-acetoxy(phenyl)methyl]-1,3,4,5,6-penta-*O*-acetyl-2-deoxy-1-*C*-phenyl-L-gulitol [31]	*ribo (altro)*	C-4//O-1	288.2	11.9
D-*glycero*-L-*altro*-Heptitol heptaacetate [32]	*ribo (altro)*	C-6//O-3	295.0	6.2
1-Deoxy-1-nitro-D-altritol (**1**)	*ribo (altro)*	C-6//O-3	299.5	5.4

[a] Code of the Cambridge Crystallographic Data File. [b] Configuration of the three (in brackets: four) contiguous stereogenic centres at which bending occurs. [c] Two independent molecules in the asymmetric unit. [d] In this case only one of the individual molecules showed the mentioned interaction. [e] In this case, by symmetry reasons, two equivalent C//O interactions are observed. [f] The reported coordinates are not those for the investigated sample, but those for the enantiomer. [g] Four independent molecules in the asymmetric unit; three show a 1,3-parallel interaction.

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