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Note

Crystal and molecular structure of 4,8-anhydro-3-deoxy-3-nitro-D-*lyxo*-D-*gluco*-nonitol

Peter Köll*
Department of Chemistry (Organic Chemistry), The University, Carl-von-Ossietzky-Str. 9–11, D-W 2900 Oldenburg (Germany)

Jürgen Kopf*, Martina Morf, Bärbel Zimmer
Institute of Inorganic and Applied Chemistry, The University, Martin-Luther-King-Platz 6, D-W 2000 Hamburg 13 (Germany)

Mária Petrušová, and Ladislav Petruš*
Institute of Chemistry, Slovak Academy of Sciences, CS-84238 Bratislava (Czechoslovakia)

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Addition of 2,6-anhydro-7-deoxy-7-nitro-L-*glycero*-L-*galacto*-heptitol (2,6-anhydro-1-deoxy-1-nitro-D-*glycero*-L-*manno*-heptitol, β-D-galactopyranosylnitromethane)[1] to glycolaldehyde in methanol in the presence of 4 equiv. of sodium methoxide yielded a mixture of four diastereomers[2], from which, after partial fractionation by chromatography, one isomer (**1**) could be crystallised from moist ethanol. Because of ambiguities in the configurational assignments by ^{1}H- and ^{13}C-n.m.r. spectroscopy, **1** was subjected to X-ray analysis.

The relevant crystallographic data of **1** are given in Table I. The structure was solved by direct methods in the usual way with the help of the programs SHELXS-90[3] and SHELX-76[4].

All atoms, hydrogens included, were refined. The final fractional co-ordinates of C, N, and O with equivalent isotropic thermal parameters are listed in Table II**. Selected torsion angles are given in Table III, and a perspective view (Schakal plot[5]) of **1** is presented in Fig. 1, which clearly shows that the structure is 4,8-anhydro-3-deoxy-3-nitro-D-*lyxo*-D-*gluco*-nonitol. The six-membered ring adopts a chair conformation [puckering parameters[6]: $Q = 59.5(5)$ pm, $\theta = 6.5(5)°$, $\Phi = 26.5(4)°$] with C-3 and C-9 equatorial, and C-2 *trans* to C-5 and *gauche* to O-4. This is the geometry generally observed[7] in "*C*-glycosides". The nitro group is *gauche* to O-4, C-5, and O-2 in

* To whom correspondence should be addressed.

** 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 from, Elsevier Science Publishers B.V., BBA Data Deposition, P.O. Box 1527, Amsterdam, The Netherlands. Reference should be made to No. BBA/DD/486/*Carbohydr. Res.*, 224 (1992) 273–276.

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TABLE I

Crystallographic data for **1**[a]

Formula	$C_9H_{17}NO_9$	Density (calc.) ($g.cm^{-3}$)	1.556
Mol. wt.	283.23	λ (Mo-K_α) (pm)	71.073
M.p. (degrees)	> 180 (dec.)	μ (cm^{-1})	1.3
Crystal size (mm)	0.2 × 0.2 × 0.1	2θ range (degrees)	55
Space group	$P2_1$	Reflections measured	1660
Cell parameters (pm, degrees)		Symmetry independent reflections	1361
a	576.7(2)	Symmetry independent	
b	1338.8(6)	reflections with $F_o > 3\sigma(F_o)$	944
c	793.6(3)	Number of refined parameters	239
β	99.46(3)	Final residual factors	
Volume (pm^3)	604.4(4) × 10^6	*R*	0.051
Z	2	R_w	0.043
F(000)	300	Diffractometer	SYNTEX $P2_1$

[a] Standard deviations in parentheses.

TABLE II

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

Atom	x	y	z	U_{eq}[b]
O-1	9973(6)	9086(3)	3824(5)	39(1)
O-2	7632(6)	8873(3)	6778(4)	35(1)
O-4	3786(5)	7455(3)	2463(4)	22(1)
O-5	8310(6)	5499(4)	3585(4)	32(1)
O-6	4986(6)	4585	798(4)	27(1)
O-7	1016(6)	5747(3)	927(4)	27(1)
O-9	1116(6)	8906(3)	528(4)	28(1)
O-31	6979(8)	6307(4)	7122(5)	68(1)
O-32	3724(7)	7076(4)	6250(6)	68(1)
N-3	5803(8)	6910(4)	6201(5)	37(1)
C-1	7488(9)	9239(4)	3786(7)	29(1)
C-2	6518(8)	8596(4)	5078(6)	27(1)
C-3	6950(8)	7469(4)	4885(6)	25(1)
C-4	6088(8)	7064(4)	3070(6)	25(1)
C-5	6061(8)	5926(4)	2907(6)	23(1)
C-6	5272(8)	5660(4)	1000(5)	22(1)
C-7	2969(8)	6171(4)	242(6)	22(1)
C-8	3135(7)	7292(4)	639(5)	22(1)
C-9	898(8)	7859(5)	68(7)	27(1)

[a] Standard deviations in parentheses.
[b] $U_{eq} = 1/3\,(U_{11} + U_{22} + U_{33}) \times 10^3$.

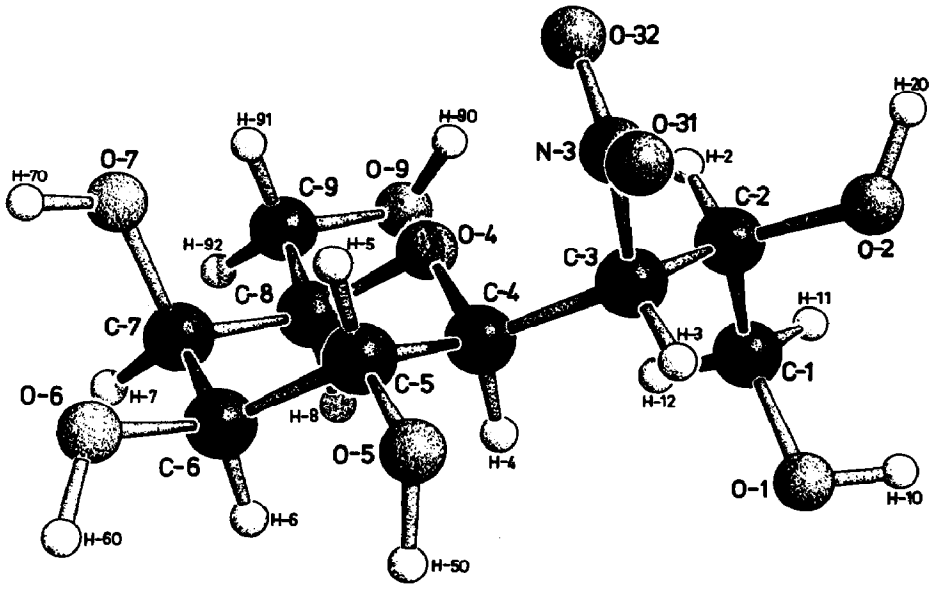

Fig. 1. A Schakal[5] drawing of a molecule of **1** showing atom numbering.

TABLE III

Selected torsion angles (°) in **1**[a]

Angles in the carbon chain		*Angles around the nitro group*	
C-1–C-2–C-3–C-4	−53.4(5)	N-3–C-3–C-4–O-4	77.7(5)
C-2–C-3–C-4–C-5	−169.0(4)	O-31–N-3–C-3–H-3	−10.0(14)
C-3–C-4–C-5–C-6	−177.3(4)	O-32–N-3–C-3–C-4	−72.9(6)
C-4–C-5–C-6–C-7	−552.6(5)	C-2–C-3–C-4–O-4	−45.1(5)
C-5–C-6–C-7–C-8	50.7(5)	O-2–C-2–C-3–N-3	61.7(5)
C-6–C-7–C-8–C-9	175.6(4)		
Angles between vicinal oxygens		*Angles between vicinal hydrogens*	
O-1–C-1–C-2–O-2	63.0(5)	H-11–C-1–C-2–H-2	63(2)
O-4–C-4–C-5–O-5	−177.0(3)	H-12–C-1–C-2–H-2	−57(2)
O-5–C-5–C-6–O-6	62.4(5)	H-2–C-2–C-3–H-3	−177(1)
O-6–C-6–C-7–O-7	52.0(5)	H-3–C-3–C-4–H-4	−47(2)
O-7–C-7–C-8–O-4	67.2(4)	H-4–C-4–C-5–H-5	−179(1)
O-4–C-8–C-9–O-9	55.2(5)	H-5–C-5–C-6–H-6	−174(2)
		H-6–C-6–C-7–H-7	50(2)
		H-7–C-7–C-8–H-8	−54(1)
		H-8–C-8–C-9–H-91	176(2)
		H-8–C-8–C-9–H-92	54(2)

[a] Standard deviations in parentheses.

TABLE IV

Pattern of hydrogen bonds in **1**[a]

Distances (pm) *D-H···A*	*Symmetry operation on A*	*Distance (pm)* *O···O*	*Angle (°)* *O–H···O*
O-1$^{91(2)}$H-10$^{195(2)}$: O-5	$-x + 2, 1/2 + y, -z + 1$	284.9(6)	169(2)
O-2$^{95(1)}$H-20$^{186(2)}$: O-6	$-x + 1, 1/2 + y, -z + 1$	280.1(5)	176(2)
O-5$^{103(1)}$H-50$^{182(1)}$: O-7	$x + 1, y, z$	284.2(5)	169(1)
O-6$^{100(2)}$H-60$^{180(1)}$: O-9	$-x + 1, 1/2 + y - 1, -z$	278.6(5)	168(2)
O-7$^{92(2)}$H-70$^{202(2)}$: O-9	$-x, 1/2 + y - 1, -z$	290.7(6)	159(1)
O-9$^{95(1)}$H-90$^{187(1)}$: O-1	$x - 1, y, z$	281.1(5)	166(2)

[a] Standard deviations in parentheses.

accordance with the general "gauche effect"[8], but adopts a position that is not observed in simple "glycosylnitromethanes". In these compounds, the nitro group is also *gauche* to the ring oxygen, but *trans* to the β-carbon of the ring[9], a position which is occupied in **1** by C-2. C-1 and O-2 are located in positions which are free of 1,3-parallel interactions with heavy atoms.

The oxygens of the nitro group are in a position which has been reported for many examples[9,10]: one oxygen is 1,2-*syn*-periplanar to an α- and the other 1,3-parallel to a β-hydrogen atom. Furthermore, O-32 is 1,3-*syn*-periplanar to O-4. The reasons for such an orientation have been discussed[9,10].

The molecules of **1** are interlinked in the crystal by a complex network of hydrogen bonds (Table IV), which involves all hydroxyl groups as donors: O-9 is an acceptor for two such bonds, whereas O-2 and O-4 are not acceptors.

REFERENCES

1 L. Hough and S. H. Shute, *J. Chem. Soc.*, (1962) 4633–4637; A. Förtsch, H. Kogelberg, and P. Köll, *Carbohydr. Res.*, 164 (1987) 391–402.
2 M. Petrušová, M. Matulová, and L. Petruš, *Abstr. Bratislava Symposium on Saccharides, 5th*, 1990, p. 17.
3 G. M. Sheldrick, *Acta Crystallogr., Sect. A*, 46 (1990) 467–473.
4 G. M. Sheldrick, SHELX-76, Programs for Crystal Structure Determination, Cambridge, 1976.
5 E. Keller, *Chem. Unserer Zeit*, 14 (1980) 56–60.
6 D. Cremer and J. A. Pople, *J. Am. Chem. Soc.*, 97 (1975) 1354–1358.
7 T.-C. Wu, P. G. Goekjian, and Y. Kishi, *J. Org. Chem.*, 52 (1987) 4819–4823; P. G. Goekjian, T.-C. Wu, H.-Y. Kang, and Y. Kishi, *ibid.*, 52 (1987) 4823–4825; S. A. Babirad, Y. Wang, P. G. Goekjian, and Y. Kishi, *ibid.*, 52 (1987) 4825–4827.
8 S. Wolfe, *Acc. Chem. Res.*, 5 (1972) 102–111; A. J. Kirby, *The Anomeric Effect and Related Stereoelectronic Effects at Oxygen*, Springer, Berlin, 1983.
9 J. Kopf, C. Topf, and P. Köll, *Carbohydr. Res.*, 186 (1989) 1–28; P. Köll, J. Kopf, D. Wess, and H. Brandenburg, *Liebigs Ann. Chem.*, (1988) 685–693; J. Kopf, M. Morf, B. Zimmer, O. Jarchow, H. Brandenburg, and P. Köll, *Carbohydr. Res.*, 208 (1990) 1–13.
10 J. Kopf, H. Brandenburg, W. Seelhorst, and P. Köll, *Carbohydr. Res.*, 200 (1990) 339–354; P. Köll, B. Malzahn, and J. Kopf, *ibid.*, 205 (1990) 1–17.