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Note

Crystal and molecular structure of 2,3,4-tri-*O*-acetyl-β-D-arabinopyranosyl azide

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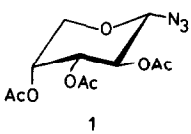
The known tendency of halogen or alkoxyl groups on C-1 in a pyranose system to adopt an axial conformation is generally designated as the anomeric effect. This effect plays an important and frequently discussed role in the field of conformational analysis of carbohydrates and related acetals [1]. The essential consequence of this phenomenon manifests itself not only in a relative stability but also in the reactivity of the anomeric centre and in such structural characteristics as bond lengths and bond angles. The origin of the anomeric effect has been discussed in terms of electrostatic interactions, n–n (and n–σ^*) interactions, double bond–no bond resonance, and polar–polar bond interactions[1–3].

In our previous study[4] of glycopyranosyl compounds with nitrogen-containing moieties on C-1, we proposed a sequence of groups with decreasing anomeric effect where the azido group falls between the OAc and $NHCOCF_3$ groups. An X-ray structure analysis of 2,3,4-tri-*O*-acetyl-α-D-arabinopyranosyl azide (**1**) showed[5] that the equatorial azido group was oriented *gauche* with respect to the ring oxygen with a torsion angle O-5–C-1–N-1–N-2 of 75.6°. This value is comparable with a bending of the $O–CH_3$ bond in methyl β-pyranosides (ca. 70–76°), which demonstrates that the *exo*-anomeric effect of the azido group is of the same magnitude as the effect of a methoxyl group. These findings were supported by a further X-ray analysis of 2,3,4-tri-*O*-acetyl-β-D-xylopyranosyl azide (**2**), where a *gauche* arrangement with respect to the ring oxygen was also found for the equatorial azido group[6].



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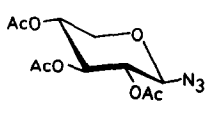

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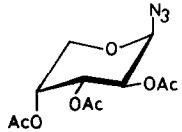

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TABLE I

Unit cell and atomic parameters of **3** (U_{eq} in 10^2 Å^2) [a]. Lattice constants $a = 949.0(5)$, $b = 870.1(3)$, $c = 889.4(5)$ pm; $\beta = 104.40(4)°$; Cell volume $V = 7.199 \times 10^8$ pm^3; Space group monoclinic, $P2_1$, $Z = 2$; R, R_w based on 1273 independent observed reflections: 0.044, 0.042.

Atom	x	y	z	U_{eq}
C-1	0.5820(5)	0.08827(–)	0.9934(5)	5.5(2)
C-2	0.6262(5)	0.0657(9)	0.8400(6)	4.7(2)
C-3	0.7857(4)	0.0384(8)	0.8625(5)	4.1(1)
C-4	0.8261(4)	−0.0967(8)	0.9703(5)	4.5(1)
C-5	0.7723(5)	−0.076(1)	1.1157(5)	5.1(2)
O-5	0.6209(3)	−0.0411(8)	1.0874(4)	5.6(1)
N-1	0.6523(5)	0.2314(8)	1.0611(5)	6.4(2)
N-2	0.6579(6)	0.2393(9)	1.1984(6)	8.3(2)
N-3	0.6711(9)	0.254(1)	1.3265(7)	13.4(3)
O-2	0.5920(3)	0.1975(7)	0.7434(3)	5.2(1)
C-21	0.4561(5)	0.2045(9)	0.6567(5)	5.9(2)
O-21	0.3680(4)	0.1094(9)	0.6639(5)	9.3(2)
C-22	0.4368(6)	0.346(1)	0.5633(6)	7.5(2)
O-3	0.8238(3)	0.0091(7)	0.7176(3)	4.65(9)
C-31	0.9476(6)	0.063(1)	0.6950(6)	7.3(2)
O-31	1.0231(6)	0.138(1)	0.7885(6)	17.5(3)
C-32	0.9824(6)	0.017(1)	0.5483(6)	8.3(2)
O-4	0.7639(3)	−0.2361(7)	0.8972(4)	5.0(1)
O-41	0.9723(4)	−0.3013(8)	0.8304(4)	7.2(1)
C-41	0.8505(6)	−0.3303(9)	0.8355(5)	5.9(2)
C-42	0.7717(7)	−0.474(1)	0.7775(8)	9.0(3)

[a] Esd's in parentheses, U_{eq} values after Hamilton[14].

In a further publication[7], we reported calculations on the anomeric and *exo*-anomeric effects for 2,3,4-tri-*O*-acetyl-α- (**1**) and -β-D-arabinopyranosyl azide (**3**), and the results were compared in the case of α-anomer **1** with the data of the previous X-ray investigation.

Having elaborated a method for the preparation of 1,2-*cis*-glycopyranosyl azides[8] (to which compound **3** also belongs) through S_N2-type conversion of acylated glycopyranosyl halides (mainly chlorides) with alkali metal azides in hexamethylphosphoric triamide, we have now performed the X-ray structure determination of the β anomer **3** crystallized from ethanol[8d]. Relevant crystallographic data are given in Table I; experimental crystallographic work, structure determination[9], and refinement[10] were straightforward *.

* A detailed list of crystal data, a complete atom list, including the hydrogen atom and displacement parameters, together with the list of observed and calculated structure factors, bond angles, and a choice of torsion angles for **3** 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/540/*Carbohydr. Res.*, 247 (1993) 305–308.

TABLE II

Bond lengths (in pm) for 3 [a]

C-1–C-2	151.7(7)	C-1–O-5	140.8(6)
C-1–N-1	148.4(7)	C-2–C-3	150.6(6)
C-2–O-2	143.2(9)	C-3–C-4	151.8(9)
C-3–O-3	142.8(6)	C-4–C-5	149.3(7)
C-4–O-4	144.6(8)	C-5–O-5	144.1(6)
N-1–N-2	121.3(7)	N-2–N-3	112.9(8)
O-2–C-21	136.7(5)	C-21–O-21	118.6(9)
C-21–C-22	148(1)	O-3–C-31	131.7(7)
C-31–O-31	118.2(9)	C-31–C-32	146.5(8)
C-4–C-41	135.2(8)	O-41–C-41	119.3(7)
C-41–C-42	150(1)		

[a] Esd's in parentheses.

The results of the X-ray analysis (Tables I and II, Fig. 1) can be summarized as follows: the pyranoid ring adopts a nearly ideal $^1C_4$(D) chair form with the azido group and the acetyl group on C-4 in axial positions while the other two acetyl groups (on C-2 and C-3) are linked equatorially.

The Cremer–Pople puckering parameters[12] are Q = 55.1(6) pm, Θ = 175.8(6)°, and Φ = 293(8)°. In contrast to the crystalline state, **3** adopts practically the $^4C_1$(D) conformation in solution (both in C_6D_6 and $CDCl_3$) as derived from NMR data[8d].

The bond length O-5–C-1 140.8(6) pm seems to be somewhat shorter than the average 142.7(10) pm of the two equatorially substituted α-D-*arabino*[5] and β-D-*xylo*[6] derivatives. More pronounced is the difference in the C-1–N-1 bond which is significantly longer in the axial case [148.4(7) pm] compared to the averaged equatorial bonds of **1** and **2** [144.6(3) pm]. The torsion angle O-5–C-1–N-1–N-2 is −39.8(6)°, remarkably smaller than the corresponding value (75.6°) for **1**. In the

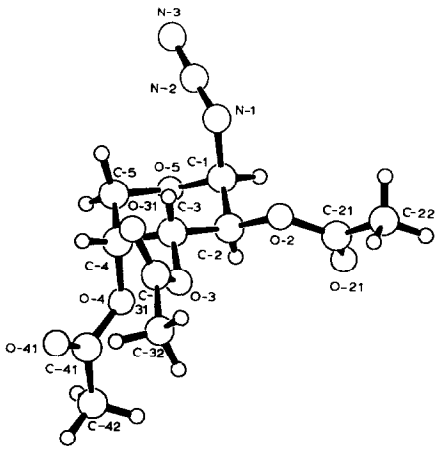

Fig. 1. SCHAKAL drawing[11] of the molecular structure of **3** in the crystal, also showing the atom numbering scheme.

β-D-*xylo* derivative **2**, one of the two independent molecules showed a smaller value (−51.4°); the second one was −67.9°.

In conclusion, the crystal structure determination of 2,3,4-tri-*O*-acetyl-β-D-arabinopyranosyl azide (**3**) shows that the *exo*-anomeric effect is also valid for the existing group of 1,2-*cis*-glycopyranosyl azides (cf. the claim of ref 13).

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