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Synthesis and structural studies of anomeric 2,3,4,6-tetra-*O*-acetyl-5-thio-D-glucopyranosyl azides

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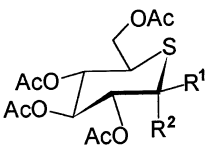
Abstract

Two methods are presented for the preparation of the α and β anomers of 2,3,4,6-tetra-*O*-acetyl-5-thio-D-glucopyranosyl azide. These methods are comparable in yield, but the one that converts a glucopyranosyl bromide into the azide is preferable because of easier purification. After chromatographic separation, the α and β anomers were analysed by NMR spectroscopy. The crystal and molecular structure of the β anomer was determined by X-ray diffraction. It crystallises in space group $P2_1$ [$a = 11.729(3)$, $b = 7.305(3)$, $c = 11.363(3)$Å, $\beta = 107.63(5)°$, $Z = 2$]. The hexopyranose ring of the β anomer assumes a $^4C_1$ conformation and the orientation of the azido group is compatible with the requirements of the exo-anomeric effect. This geometry is compared to that of other similar structures.

Keywords: 5-Thio-D-glucopyranose; Anomeric azides; NMR; X-ray crystal structure

1. Introduction

Because glycosyl azides are versatile synthetic intermediates, their efficient stereoselective syntheses (such as those of their 1,2-cis and trans isomers) are of continuing interest [1–3]. Furthermore, 5-thio-D-glucose [4] exhibits interesting biological activities, such as inhibition of D-glucose transport across membranes (inhibition of spermatogenesis) and of carbohydrate-metabolising enzymes [5]. Glycosides of 1,5-dithio-D-xylopyranose proved to be venous antithrombotics [6]. Here we wish to report the stereoselective syntheses and NMR analysis of both anomers of 2,3,4,6-tetra-*O*-acetyl-5-thio-D-glucopyranosyl azide and the crystal structure determination of the β anomer **4**.



	R^1	R^2
1	Ac	H
2	Br	H
3	H	Br
4	N_3	H
5	H	N_3

The geometrical data of **4,** obtained by single-crystal X-ray analysis, are compared with a glycopyranosyl azide and with different thiopyranosyl rings. The study tests whether the β anomer shows the exo-anomeric effect. This anomeric effect was first formulated by Lemieux [7] for acetals to describe the partial extra bonding that occurs between an oxygen and a carbon atom in certain orientations of the

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acetal, namely, when lone-pair electrons of an oxygen line up with an antibonding orbital of a carbon atom. These effects are observed experimentally and supported by theoretical calculations for electronegative atoms other than oxygen as well. For pyranose rings the anomeric effect manifests itself by the preference of an electronegative substituent on the anomeric carbon atom (C-1) to be axial. The partial extra bond is then formed between the ring oxygen (O-5) and the anomeric carbon atom (C-1).

The exo-anomeric effect, an important determining factor for the conformation of glycosidic linkages, describes partial extra bonding between C-1 and the electronegative substituent O-1 (or a halogen or an azide). This bond can be formed only if O-5–C-1 is gauche to the aglyconic bond O-1–C-1′, which means the torsional angle O-5–C-1–O-1–C-1′ is near $\pm 60°$. In the present case the analogous torsional angle to be inspected for the presence of the exo-anomeric effect is S–C-1–N-1–N-2.

2. Results and discussion

Acylated glycosyl halides are known to react readily with alkali azides in hexamethylphosphoric triamide (HMPA) at room temperature (1–2 h reaction time) to furnish the corresponding glycosyl azides by a S_N2 displacement [3].

In order to avoid losses during chromatographic separation of anomeric 2,3,4,6-tetra-*O*-acetyl-5-thio-D-glucopyranosyl bromides, **2** and **3** [8,9], the crude mixture of **2** + **3** was allowed to react with sodium azide in HMPA. This reaction proceeded smoothly and a mixture of the β- and α-azido derivatives (**4** and **5**) was obtained in good overall yield. However, chromatographic separation of **4** and **5** proved to be difficult due to similar R_f values in various solvent systems. Furthermore, it was noticed that **5** slowly isomerises to **4** on standing. Similar phenomena were observed by Szarek et al. on glycosyl azides [10].

Alternatively, we attempted to utilise our method, which previously gave good results in analogous cases [1,3], by reacting the easily available pentaacetyl derivative **1** with Me_3SiN_3 in the presence of $SnCl_4$ as a Lewis acid catalyst [4]. This catalyst had also proved to be useful for the synthesis of the pure β-anomeric form of methyl (5-acetamido-4,7,8,9-tetra-*O*-acetyl-3,5-dideoxy-D-*glycero*-*β*-D-*galacto*-non-2-ulopyranosyl)onate azide from the appropriate O-acetylated educt [11]. A synthesis of the analogue with sulfur in the ring using our method was also published [12].

The ring sulfur atom decreases the reactivity at the anomeric centre, so in order to achieve satisfactory conversion in the present case, the usual reaction time of 1–3 h employed for acylated hexopyranosyl analogues [3] had to be increased to 16–18 h.

Longer reaction times were also needed for significant conversion during preparation of methyl (glycopyranosyl azide) uronates from the corresponding acetates [13]. This reaction could, however, be accelerated by using a large excess of Me_3SiN_3 [14].

The sluggishness of the reaction in the present case resulted in the formation of the two anomeric azides in comparable amounts (**4**:**5** ≈ 1.3). Although **4** and **5** can be separated by extensive column chromatography, the procedure based on **2** as the starting material seems to be preferable because of the absence of side products in the reaction mixture. The β anomer **4** can be readily crystallised.

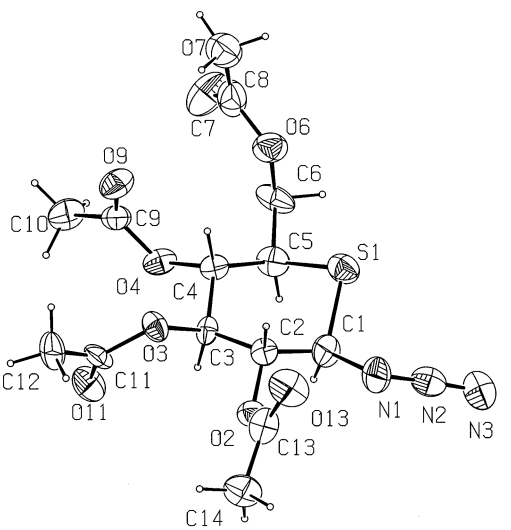


Fig. 1. ORTEP [20] picture of molecule **4**. Ellipsoids drawn at 50% probability.

Table 1
Crystal data and structure refinement

Empirical formula	$C_{14}H_{19}N_3O_8S$
Formula weight	389.38
Temperature (K)	193(0.5)
Radiation	Cu–K_α (Ni filter)
Wavelength	1.54180 Å
Crystal system	Monoclinic
Space group	$P2_1$
Unit cell dimensions	
a	11.729(3) Å
b	7.305(3) Å
c	11.363(3) Å
α	90°
β	107.63(5)°
γ	90°
Volume	927.9(5) Å^3
Z	2
Density (calculated) (Mg m^{-3})	1.394
Crystal size	0.33 mm × 0.13 mm × 0.05 mm
Theta range for data collection	3.95–42.00°
Independent reflections	709
μ (absorption coefficient) (cm^{-1})	19.4
Refinement method	Full-matrix least-squares on F^2
Final R indices [$I>2\sigma(I)$]	$R_1 = 0.0264$, $wR_2 = 0.0467$
R indices (all data)	$R_1 = 0.0551$, $wR_2 = 0.0545$

Fig. 1 shows molecule **4** with atom numbering and thermal ellipsoids. Table 1 lists unit cell information and Table 2 contains positional parameters for the non-hydrogen atoms. Table 3 is a listing of selected bond lengths and angles and Table 4 of torsional angles for the pyranosyl ring and the azide group. Anisotropic temperature factors and a complete listing of the molecular geometry are deposited[1]. Fig. 2 shows the crystal packing in the unit cell.

The thiopyranosyl ring adopts a $^4C_1$ chair conformation and all substituents are equatorial. This conformation is conserved in solution as attested by the $^3J_{HH}$ values (see Section 3). Structure **4** can be compared to a previously solved pyranosyl analogue, 2,3,4-tri-*O*-acetyl-β-D-xylopyranosyl azide **6** [2b], where the CH_2COAc group on ring atom C-5 is replaced by a hydrogen. Fig. 3 shows the fit between the two molecules. In the ring containing the sulfur atom the ring atoms C-1 and C-5 are 'pushed apart' (compared with the pyranosyl analogue) to accommodate the heavy sulfur atom, resulting in longer bonds (C–O ~ 1.4, C–S ~ 1.8 Å) and a smaller bond angle (C–O–C ~ 110°; C–S–C ~ 95°). Exact values for the two structures are listed in Table 5. The remaining parts of the two structures are very similar, especially with respect to the orientations of the substituent groups. It was interesting to find out whether the exo-anomeric effect applies to the title compound. In the xylopyranosyl azide, where two independent molecules are present in the asymmetric unit, the torsional angles O-1–C-1–N-1–N-2 are −51.4(7)° and −67.9(9)°. For the title compound the analogous torsional angle S-1–C-1–N-1–N-2 is −67.3(12)° (see Table 5). These values correspond to a

[1] The deposited material can be obtained from Fachinformationszentrum Karlsruhe, D-16344 Eggenstein-Leopoldshafen under the CSD-Number 406961.

Table 2
Atomic coordinates and equivalent isotropic displacement parameters (Å$^2 \times 10^3$) [a]

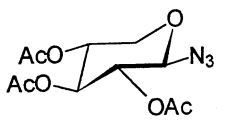
	x	y	z	U_{eq}
S-1	0.1047(2)	0.6901(5)	0.1622(2)	56(1)
C-1	0.258(1)	0.620(2)	0.178(1)	59(4)
N-1	0.2615(8)	0.513(2)	0.071(1)	70(3)
N-2	0.2101(9)	0.362(2)	0.0634(8)	55(3)
N-3	0.1665(9)	0.219(2)	0.0447(9)	76(3)
C-2	0.335(1)	0.789(2)	0.182(1)	41(3)
O-2	0.4528(6)	0.742(1)	0.1820(5)	45(2)
C-3	0.343(1)	0.907(2)	0.2950(9)	34(3)
O-3	0.4050(6)	1.070(1)	0.2751(6)	45(2)
C-4	0.225(1)	0.961(2)	0.311(1)	38(3)
O-4	0.2538(5)	1.045(1)	0.4322(6)	46(2)
C-5	0.143(1)	0.804(2)	0.3127(9)	51(3)
C-6	0.029(1)	0.863(2)	0.341(1)	60(4)
O-6	−0.0285(6)	1.000(1)	0.2546(6)	64(2)
C-7	−0.073(1)	1.145(2)	0.296(1)	69(4)
O-7	−0.0751(7)	1.155(1)	0.4016(9)	95(3)
C-8	−0.1195(9)	1.291(2)	0.2010(9)	75(3)
C-9	0.2324(9)	1.222(2)	0.439(1)	46(3)
O-9	0.1971(6)	1.321(1)	0.3501(7)	63(2)
C-10	0.2566(8)	1.285(1)	0.5697(8)	66(4)
C-11	0.5015(9)	1.131(2)	0.368(1)	50(4)
O-11	0.5348(6)	1.060(1)	0.4678(6)	63(2)
C-12	0.5583(9)	1.293(1)	0.3284(8)	57(3)
C-13	0.483(1)	0.757(2)	0.077(1)	54(4)
O-13	0.4130(7)	0.798(1)	−0.0196(7)	74(3)
C-14	0.6124(8)	0.717(2)	0.0972(8)	64(3)

[a] U_{eq} is defined as one third of the trace of the orthogonalized U_{ij} tensor.

Table 3
Bond lengths (Å) and angles (°)

S-1–C-5	1.832(10)
S-1–C-1	1.827(12)
C-1–N-1	1.456(13)
C-1–C-2	1.524(14)
N-1–N-2	1.249(12)
N-2–N-3	1.155(12)
C-2–O-2	1.426(12)
C-2–C-3	1.521(13)
C-3–O-3	1.449(10)
C-3–C-4	1.501(13)
C-4–O-4	1.452(10)
C-4–C-5	1.507(13)
O-4–C-9	1.322(13)
C-5–C-6	1.53(2)
C-6–O-6	1.423(13)
C-5–S-1–C-1	94.6(5)
N-1–C-1–C-2	107.1(11)
N-1–C-1–S-1	110.0(8)
C-2–C-1–S-1	109.2(8)
N-2–N-1–C-1	113.3(11)
N-3–N-2–N-1	172.2(12)
O-2–C-2–C-3	108.8(9)
O-2–C-2–C-1	111.7(9)
C-3–C-2–C-1	111.8(10)
O-3–C-3–C-4	108.9(9)
O-3–C-3–C-2	104.0(8)
C-4–C-3–C-2	115.1(9)
O-4–C-4–C-5	105.9(9)
O-4–C-4–C-3	105.7(9)
C-5–C-4–C-3	114.6(9)
C-9–O-4–C-4	118.3(9)
C-4–C-5–C-6	113.2(10)
C-4–C-5–S-1	108.1(8)
C–6–C-5–S-1	110.1(8)
O-6–C-6–C-5	107.9(10)

gauche arrangement along the C-1–N-1 bonds and indicate the operation of the exo-anomeric effect [7].



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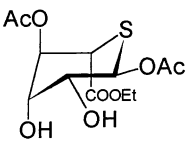

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The geometry of the thiopyranosyl ring can also be compared to the $^4C_1$ thiopyranosyl ring in ethyl 3-c, 6-c-diacetoxy-4-t,5-t-dihydroxythiacyclohexane-2-r-carboxylate (**7**) [15]. In spite of the different substituents, the geometries of the two rings are very similar. For the sake of consistency, the numbering of all compared compounds in Table 5 follows the numbering used in Fig. 1. This Table also contains data on thio-α-D-glucopyranose for which only averaged values of the C–S bonds are available [16]. We did not find any thiopyranosyl azides in the Cambridge data file.

We may conclude that there is a clear evidence for the operation of the exo-anomeric effect in thiopyranosyl azide **4**, which is a close structural analogue of a pyranosyl azide **6**. Furthermore, the conformation of thiopyranosyl rings does not seem to depend much on the nature of the substituents.

3. Experimental

General methods.—Distilled solvents, CH_2Cl_2 and pyridine were dried by storage over 3 and 4 Å molecular sieves, respectively. Melting points were measured on a Kofler hot-stage apparatus and are uncorrected. Optical rotations were measured in chloroform solution on a Schmidt–Haënsch type polarimeter. Column chromatography was carried out using columns packed with E. Merck Sil-

Table 4
Torsion angles (°)

C-5–S-1–C-1–N-1	177.7(9)
C-5–S-1–C-1–C-2	−64.9(10)
C-2–C-1–N-1–N-2	174.2(10)
S-1–C-1–N-1–N-2	−67.3(12)
C-1–N-1–N-2–N-3	−178(8)
N-1–C-1–C-2–O-2	−54.9(14)
S-1–C-1–C-2–O-2	−174.0(7)
N-1–C-1–C-2–C-3	−177.1(10)
S-1–C-1–C-2–C-3	63.8(13)
O-2–C-2–C-3–O-3	63.3(11)
C-1–C-2–C-3–O-3	−172.9(10)
O-2–C-2–C-3–C-4	−177.7(9)
C-1–C-2–C-3–C-4	−53.9(13)
O-3–C-3–C-4–O-4	−72.7(10)
C-2–C-3–C-4–O-4	171.0(9)
O-3–C-3–C-4–C-5	171.0(9)
C-2–C-3–C-4–C-5	54.8(13)
O-4–C-4–C-5–C-6	58.4(13)
C-3–C-4–C-5–C-6	174.5(10)
O-4–C-4–C-5–S-1	−179.4(7)
C-3–C-4–C-5–S-1	−63.3(12)
C-1–S-1–C-5–C-4	63.4(9)
C-1–S-1–C-5–C-6	−172.5(9)
C-4–C-5–C-6–O-6	55.2(14)
S-1–C-5–C-6–O-6	−65.8(12)

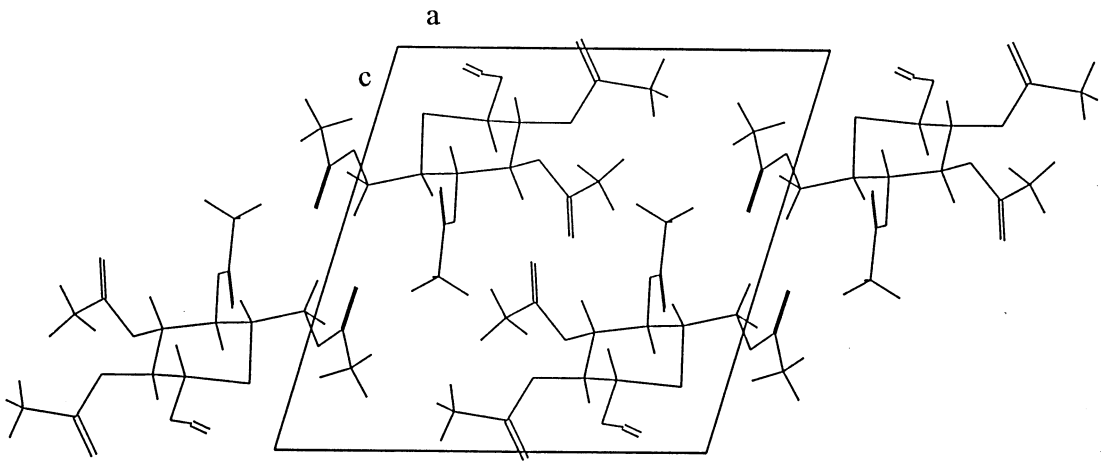

Fig. 2. The unit cell of compound **4** viewed along the **b** axis.

ica Gel 60 (230–400 mesh). TLC was performed on precoated silica gel plates (E. Merck, Silica Gel 60 F_{245}) with 1:3 hexane–diethyl ether; detection was carried out by spraying the plates with 5% alcoholic H_2SO_4 followed by heating.

NMR spectra were recorded for solutions in $CDCl_3$ using Bruker WP 200SY (200/50 MHz for $^1H/^{13}C$) or Avance DRX500 (500/125 MHz) spectrometers. Chemical shifts are referenced to Me_4Si (^1H) or to the residual solvent signal (^{13}C: 77.00 ppm for $CDCl_3$). ^{13}C assignments were based on, and $^1J_{CH}$ values determined from, ^1H-coupled HMQC spectra recorded at 500/125 MHz.

2,3,4,6-Tetra-O-*acetyl-5-thio-β-* (**4**) *and -α-*D-*glucopyranosyl azide* (**5**)

Method A. 1,2,3,4,6-Penta-*O*-acetyl-5-thio-α,β-D-glucopyranosyl bromide (**2** + **3**) [7,8] (0.55 g, 1.29 mmol) was dissolved in HMPA (4 mL), and LiN_3 (0.11 g, 2.2 mmol) was added under stirring at room temperature. After 80 min the clear solution was diluted with water (60 mL) and extracted with diethyl ether (3 × 70 mL). After washing with water (15 mL), the organic phase was evaporated and the residue (0.388 g, 77.3%) was chromatographed to give 0.08 g syrupy **5**; $[\alpha]_D^{24}$ + 309° (*c* 0.8, $CHCl_3$); IR (KBr) *ν* 2108 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$): *δ* 3.58 (dd, 1 H, $J_{5,6a}$ 4.9, $J_{5,6b}$ 3.1 Hz, H-5), 4.10 (dd, 1 H, $J_{6a,6b}$ 12.2 Hz, H-6b), 4.39 (dd, 1 H, H-6a), 5.04 (d, 1 H, $J_{1,2}$ 3.5 Hz, H-1), 5.11 (dd, 1 H, $J_{2,3}$ 10.0 Hz, H-2), 5.25 (dd, 1 H, $J_{4,5}$ 10.7 Hz, H-4), 5.37 (t, $J_{3,4}$ 9.8 Hz, H-3); ^{13}C NMR (50 MHz, $CDCl_3$): *δ* 170.36, 169.76, 169.41, and 169.32 (4 × CO), 62.46 (C-1, $J_{C1,H1}$ 158.5 Hz), 73.59 (C-2, $J_{C2,H2}$ 154.5 Hz), 70.20 (C-3, $J_{C3,H3}$ 152.6 Hz), 71.51 (C-4, $J_{C4,H4}$ 156.5 Hz), 39.59 (C-5, $J_{C5,H5}$ 142.8 Hz), 60.75 (C-6, $J_{C6,H6}$ 146.5 Hz) 20.55, 20.48 (2 ×) and 20.38 (Me). Anal. Calcd for $C_{14}H_{19}N_3O_8S$ (389.4): C, 43.18; H, 4.92; N, 10.79; S, 8.24. Found: C, 42.96; H, 4.79; N, 10.85; S, 8.12.

Further elution gave 0.15 g of anomeric mixture. We pooled the fractions containing pure **4** (0.08 g), which crystallised upon standing; mp 72–74 °C (EtOH); $[\alpha]_D^{24}$ + 14 (*c* 0.27, $CHCl_3$); ^1H NMR (500 MHz, $CDCl_3$): *δ* 3.23 (ddd, 1 H, $J_{5,6a}$ 5.6, $J_{5,6b}$ 3.4 Hz, H-5), 4.09 (dd, 1 H, $J_{6a,6b}$ 12.1 Hz, H-6b), 4.21 (dd, 1 H, H-6a), 4.49 (d, 1 H, $J_{1,2}$ 9.6 Hz, H-1), 5.00 (dd, 1 H, $J_{2,3}$ 9.6 Hz, H-3), 5.11 (t, 1 H, H-2), 5.19 (dd, 1 H, $J_{4,5}$ 10.6 Hz, H-4); ^{13}C NMR (50 MHz, $CDCl_3$): *δ* 170.20, 169.37, 169.04, and

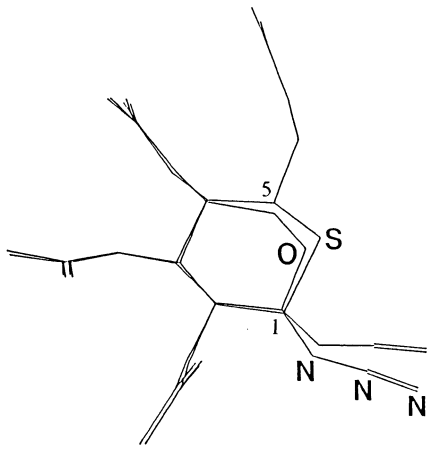

Fig. 3. Fitting molecule **4** to molecule **6**.

Table 5
Comparison of the β-pyranosyl azide to related structures

	Xylopyranosilazide [2]		Thiopyranosyl azide **4**	Thiopyran-diol [15]	Thio-α-D-glucose [16]
Geometry	Molecule 1	Molecule 2			
C-1…C-5	2.33 Å	2.35 Å	2.69 Å	2.68 Å	~2.7 Å
C-5–S-1(or O-1)	1.428(8) Å	1.436(9) Å	1.832(10) Å	1.807 Å	av. 1.820 Å
S-1(or O-1)–C-1	1.421(6) Å	1.438(8) Å	1.827(12) Å	1.810 Å	av. 1.820 Å
C-5–S-1(O-1)–C-1	110(4)°	110.2(5)°	94.6(5)°	95.5°	98.0(3)°
S-1(O-1)–C-1–N-1–N-2	−51.4(7)°	−67.9(9)°	−67.3(12)°		
N-1–N-2–N-3	171.5(6)°	171.4(8)°	172.2(12)°		

168.96 (4 × CO), 62.33 (C-1, $J_{C1,H1}$ 158.5 Hz), 73.69 (C-2, $J_{C2,H2}$ 158.5 Hz), 72.85 (C-3, $J_{C3,H3}$ 150.6 Hz), 71.19 (C-4, $J_{C4,H4}$ 154.5 Hz), 42.14 (C-5, $J_{C5,H5}$ 141.0 Hz), 60.98 (C-6, $J_{C6,H6}$ 150.6 Hz) 20.27 (4 × Me).

Although in pyranoid sugars the coupling constants $J_{C1,H1}$ are usually sufficiently different for axial and equatorial hydrogen atoms to be useful measures for deducing the anomeric configuration at C-1, this is not the case for thiapyranoses. It has been observed before that the replacement of the ring oxygen by sulfur reduces the difference between these coupling constants to such an extent that they are no longer useful for determining the anomeric configuration [17]. In this case $J_{C1,H1}$ has coincidentally exactly the same value for the α and β anomers.

Method B. The pentaacetyl compound **1** (2.03 g, 5 mmol) was dissolved in CH_2Cl_2 (50 mL), and trimethylsilyl azide (1.1 mL) and $SnCl_4$ (0.55 mL) were added. After 16 h the mixture was diluted with CH_2Cl_2 (40 mL), then washed with saturated aq $NaHCO_3$ and water. The dried ($MgSO_4$) organic phase contained the anomers **4** and **5** and some impurity. Concentration yielded the crude azide mixture (1.52 g, 77.9%), which was separated by column chromatography as above.

Colourless crystals of **4** were obtained by recrystallisation from EtOH. The crystal structure was determined by X-ray diffraction. Data were collected on a STOE four-circle diffractometer with Cu–K_α radiation. The crystals were very thin and therefore diffracted rather poorly. Data could not be collected for $\theta > 45°$, but structure solution and refinement proceeded without difficulty. Only the rather large standard deviations of the parameters indicate that the reflections to parameter ratio is low (2.7). Conditions of measurement and cell parameters are listed in Table 1. The structure was solved with direct methods using the program system SIR92 [18]. Refinement was carried out with the program SHELXL [19]. Some hydrogen atoms were found from difference Fourier syntheses, while others, mostly the methyl hydrogens were calculated and not refined. The final agreement factor $R_1 = 0.026$ for 511 observed reflections.

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