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Pyridyl 1-Thio-β-D-glucopyranoside Monohydrate*

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Abstract. $C_{11}H_{15}NO_5S.H_2O$, $M_r = 291.3$, orthorhombic, $P2_12_12_1$, $a = 7.531$ (1), $b = 8.298$ (1), $c = 21.712$ (3) Å, $Z = 4$, $D_x = 1.426$ Mg m^{-3}. The structure was solved by *MULTAN* and refined to $R_w = 0.045$ for 1922 reflections. The glucopyranose ring is a normal $^4C_1$ chair, the pyridyl ring is planar, and the linkage bonds are O—C—S—C = −75°, C—S—C—N = −167°. Close intramolecular O···H and H···H separations of 2·64 and 2·47 Å between the two residues and some related valence-angle distortions suggest that the conformation of the glucosyl–pyridyl linkages is determined primarily by interactions between the ring oxygen and sulfur lone-pair electrons and the π electrons of the pyridyl group. The C—S bonds are short and unequal, 1·793 (3) and 1·759 (3) Å; the latter being adjacent to the pyridyl ring. The hydrogen bonding is complex and involves several bifurcated bonds and weak intramolecular interactions.

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Introduction. Crystals of (I) were provided by Professor Hanessian of the University of Montreal. The unit-cell dimensions were determined from a least-squares fit of 25 2θ values with $39° < 2\theta < 45°$ on a CAD-4 diffractometer with Zr-filtered Mo $K\alpha$ radiation ($\lambda = 0.71069$ Å). 6913 intensity data were collected for hkl, $h\bar{k}l$, and $\bar{h}\bar{k}\bar{l}$ with $2\theta < 60°$ using Mo $K\alpha$ radiation on a crystal of dimensions 0·48 × 0·36 × 0·13 mm. After correction for absorption with *ABSOR* (Templeton & Templeton, 1973), and for extinction using a Zachariasen isotropic extinction parameter (Coppens & Hamilton, 1970), these data were averaged to give 2267 symmetry-independent reflections, of which 1922 had $F_o^2 > \sigma(F_o^2)$. The maximum and minimum absorption corrections were 1·091 and 1·033 respectively, and the extinction parameter, g, was 4×10^{-6}. The agreement between symmetry-equivalent reflections was $R = 0.036$. The structure was solved by *MULTAN* (Germain, Main & Woolfson, 1971). Successive isotropic and anisotropic least-squares refinement of $\sum w_i(F_o - kF_c)^2$, where $w_i = (\{\sigma[F_o^2(\text{corr.})]/2F_o\} + 0.005F_o^2)^{-1}$, gave final agreement indices of $R = 0.045$, $R_w = 0.046$, $S = 1.53$. All the H atoms were located by a difference Fourier

Table 1. *Atomic coordinates for pyridyl* 1-*thio*-β-D-*glucopyranoside monohydrate* (*non-hydrogen atoms* $\times 10^4$, *hydrogen atoms* $\times 10^3$)

	x	y	z	B_{eq} (Å^2)
N	988 (4)	5573 (4)	9148 (1)	4·2
S	1943 (1)	5355 (1)	8013 (1)	3·1
C(1)	960 (3)	6131 (3)	7322 (1)	2·4
C(2)	2398 (3)	6187 (3)	6828 (1)	2·4
C(3)	1618 (3)	6699 (3)	6215 (1)	2·6
C(4)	0 (3)	5686 (3)	6053 (1)	2·5
C(5)	−1295 (3)	5687 (3)	6587 (1)	2·5
C(6)	−2898 (3)	4612 (4)	6492 (1)	3·3
C(7)	342 (4)	5785 (3)	8579 (1)	3·1
C(8)	−1401 (5)	6225 (4)	8465 (2)	3·8
C(9)	−2505 (6)	6466 (6)	8970 (2)	5·1
C(10)	−1849 (7)	6232 (6)	9549 (2)	5·9
C(11)	−114 (7)	5784 (5)	9623 (2)	5·6
O(2)	3752 (3)	7300 (3)	6997 (1)	3·2
O(3)	2883 (3)	6518 (3)	5736 (1)	3·9
O(4)	−905 (3)	6281 (3)	5523 (1)	3·5
O(5)	−412 (2)	5075 (2)	7125 (1)	2·6
O(6)	−4023 (3)	4659 (3)	7016 (1)	4·1
O(W)	1047 (3)	6651 (4)	4439 (1)	4·2

	x	y	z	B (Å^2)
H(C1)	52 (4)	722 (4)	740 (1)	3·2
H(C2)	293 (4)	511 (3)	680 (1)	2·0
H(C3)	122 (4)	785 (4)	626 (1)	2·9
H(C4)	34 (4)	459 (4)	602 (1)	3·6
H(C5)	−164 (4)	681 (3)	665 (1)	1·8
H1(C6)	−359 (4)	503 (4)	619 (1)	3·0
H2(C6)	−249 (5)	347 (5)	645 (2)	4·1
H(C8)	−183 (5)	639 (4)	813 (2)	3·4
H(C9)	−376 (8)	662 (7)	878 (2)	8·3
H(C10)	−253 (6)	631 (6)	981 (2)	6·3
H(C11)	53 (7)	554 (7)	1006 (2)	8·7
H(O2)	455 (5)	680 (4)	707 (1)	2·7
H(O3)	366 (8)	718 (7)	586 (3)	9·3
H(O4)	−11 (5)	631 (5)	523 (2)	4·3
H(O6)	−369 (7)	410 (6)	723 (2)	7·3
H1(OW)	179 (6)	596 (6)	425 (2)	6·1
H2(OW)	191 (8)	722 (6)	458 (2)	8·3

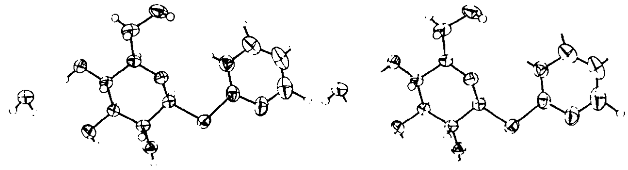
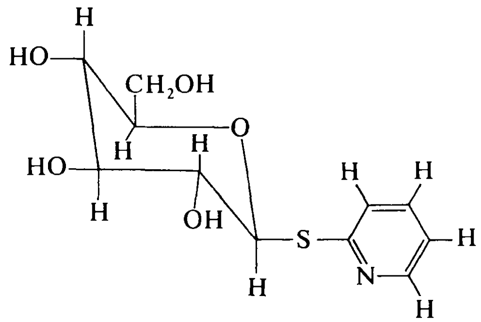


Fig. 1. Stereoview of pyridyl 1-thio-β-D-glucopyranoside monohydrate, with thermal ellipsoids at 50% probability (Johnson, 1976).

synthesis and refined with isotropic temperature factors. The atomic coordinates are given in Table 1.* The atomic notation and thermal ellipsoids are shown in Fig. 1.



(I)

A rigid-body thermal-motion analysis (Schomaker & Trueblood, 1968) was carried out using (i) the glucosyl ring atoms alone, (ii) the glycosyl ring atoms with the oxygen substituents, and (iii) all heavy atoms.* The r.m.s. ΔU_{ij}'s were 0·0006, 0·0011 and 0·0026 Å, respectively. The thermal-motion corrections to the C—C, C—O and C—S bond lengths were, for (i) 0·004, 0·003, 0·003 Å; for (ii) 0·007, 0·005, 0·006 Å; for (iii) 0·005, 0·004, 0·005 Å, respectively.

Discussion. The glucopyranose residue has the normal $^4C_1$-(D) conformation. The puckering parameters (Cremer & Pople, 1975) are θ = 6·6 (2)°, φ = 352 (2)°, Q = 0·586 (2) Å. These small departures from the ideal chair conformation (θ = 0°) are of the same magnitude as those observed in methyl β-D-glucopyranoside [*i.e.* θ = 6·9 (3)°, φ = 38 (2)°, Q = 0·597 (3) Å] (Jeffrey & Takagi, 1977), except that the distortion is more in the direction of a $^3B_0$ boat.

The pyridine ring is planar, with ring torsion angles between 0 and 1·5°, corresponding to deviations of less than 0·008 Å from the least-squares plane. The S—C(7) bond is bent out of the plane of the pyridine rings, so that the S atom is displaced 0·068 Å from the ring plane.

* Lists of structure factors and anisotropic thermal parameters, and thermal-analysis data have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 35014 (19 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

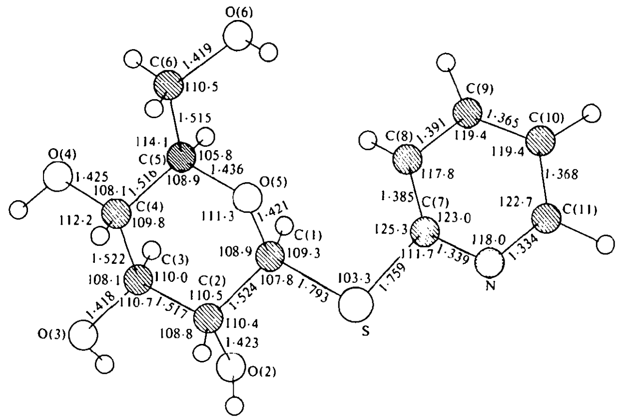


Fig. 2. Bond lengths (Å) and valence angles (°) in pyridyl 1-thio-β-D-glucopyranoside monohydrate. The standard deviations are C—S, 0·003 Å; C—C and C—O, 0·004 Å, except C(8)—C(9), 0·005 Å and C(9)—C(10) and C(10)—C(11), 0·007 Å; for angles, C—S—C, 0·1°; other angles 0·2°, except pyridyl-ring angles, 0·4°.

The bond lengths and valence angles are given in Fig. 2. The C(5)—O(5) bond is longer than O(5)—C(1) by 0·015 Å, in exact agreement with the theoretical predictions for a β-pyranoside (Jeffrey, Pople, Binkley & Vishveshwara, 1978). The two C—S bond lengths are short [relative to 1·807 Å in $(CH_3)_2S$ (Iijima, Tsuchiya & Kimuru, 1977)], and differ by 8σ, which is significant. The bond adjacent to the pyridyl ring is the shorter. The conformation about the C(1)—S and S—C(7) linkage bonds is not that of a minimum *steric* interaction between the two residues, since it brings the pyridyl H(C8) to 2·47 and 2·64 Å from H(C1) and the glucosidic ring oxygen O(5), respectively. Conformations with the O(5)—C(1)—S—C(7) and C(1)—S—C(7)—N torsion angles in the region of −120 and ±90° respectively would provide less crowded structures. Evidence that the intramolecular interactions involving H(C8) are repulsive rather than attractive is provided by the valence angles about C(7). The angle S—C(7)—C(8) is greater than 120° while S—C(7)—N is less. The C(1)—S—C(7) valence angle of 103·3° is also larger than the usual C—S—C values [*cf.* $(CH_3)_2S$, 99°], and the O(5)—C(1)—S angle is greater than the 107·4° observed in methyl β-pyranosides (Jeffrey, 1979).

The glycosidic conformation angle of −75° can be interpreted as a manifestation of the *exo-anomeric effect* (Lemieux, Koto & Voisin, 1979), which results in preferred values of −70 to −90° in methyl β-pyranosides and β-linked oligosaccharides (Jeffrey, Pople, Binkley & Vishveshwara, 1978; Jeffrey, 1979).

Table 2. *Hydrogen-bond geometry in pyridyl 1-thio-β-D-glucopyranoside monohydrate*

The values in parentheses are H···*X* distances, when the O—H covalent bond lengths have been normalized to the neutron diffraction value of 0·97 Å by extension along the direction of the covalent bond. The estimated standard deviations are 0·05 Å and 2°.

O—H···*X*	O—H	H···*X*	∠O—H···*X*	∠*X*···H···*X*′	Symmetry of acceptor atoms
O(2)—H···O(6)	0·75 Å	2·08 (1·89) Å	151°		1 + *x*, *y*, *z*
O(3)—H···O(*W*)	0·84	2·15 (2·09)	140	105°	½ + *x*, 3/2 − *y*, 1 − *z*
O(3)—H···O(2)*		2·47 (2·37)	112		*x*,*y*,*z*
O(4)—H···O(*W*)	0·87	1·95 (1·85)	162	89	*x*,*y*,*z*
O(4)—H···O(3)*		2·51 (2·50)	107		*x*,*y*,*z*
O(6)—H···O(2)	0·70	2·24 (2·02)	158	107	−*x*, ½ + *y*, 3/2 − *z*
O(6)—H···O(5)*		2·61 (2·57)	94		*x*,*y*,*z*
O(*W*)—H(2)···O(4)	0·86	2·07 (2·02)	153	91	½ + *x*, 3/2 − *y*, 1 − *z*
O(*W*)—H(2)···O(3)		2·68 (2·56)	115		*x*,*y*,*z*
O(*W*)—H(1)···N	0·90	2·11 (2·06)	157	56	½ + *x*, 1 − *y*, −½ + *z*
O(*W*)—H(1)···S		3·05 (2·97)	145		½ + *x*, 1 − *y*, −½ + *z*

* Intramolecular.

The electronic interactions which determine the rotational potential function of S—C(7) will be mainly of the $V_1(1-\cos\theta)$ and $V_2(1-\cos 2\theta)$ types (*cf.* Jeffrey, Pople & Radom, 1972). The former will arise from dipole–dipole interactions between the lone pairs on the N, S and O atoms. The latter will involve the potential between the C(1)—S bond and the vicinal C(7)—N, C(7)—C(8) bonds in the plane of the pyridine ring and between the pyridyl π-bond system and the S 2*p* orbitals. The shortening of the S—C(7) bond to 1·759 Å and the proximity of the torsion angle C(1)—S—C(7)—N to 180° suggests that the π bonding in the S—C(7) bond is the significant factor favoring the observed conformation. The H(C8)···O(5) distance of 2·64 Å could be regarded as indicative of a weak hydrogen bond which would also stabilize the observed conformation, but, as pointed out above, the valence-angle distortions suggest that this is not the case, since the interaction appears to be repulsive rather than attractive.

The hydrogen-bond geometry is given in Table 2. Of the six interactions, only one is a linear hydrogen bond, that from O(2)—H to O(6). The other five hydrogen bonds are unsymmetrical bifurcated interactions (Newton, Jeffrey & Takagi, 1979), in three of which the weaker component is intramolecular.

All the potential hydrogen-bond donor and acceptor atoms in the molecules are included in the hydrogen bonding. The ···O(2)—H···O(6) bonds and the major component of the ···O(6)—H···O(2) bonds form an infinite chain, as do the major components of the ···O(4)—H···O(*W*)—H(2) bonds. The major components of the O(3)—H···O(*W*)—H···N bonds form finite hydrogen-bond chains. These chains are then cross-linked by the minor components of the bifurcated bonds. The weak intramolecular interaction between the primary alcohol hydroxyl and ring oxygen of the glucose, O(6)—H···O(5), is unusual. It is rarely observed in carbohydrate crystal structures, since the hydroxyl bond is usually engaged only in intermolecular bonding which points away from the sugar ring.

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