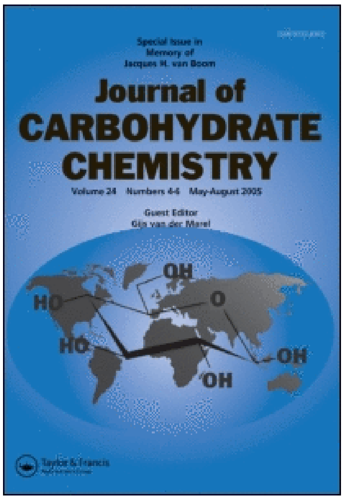

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CRYSTAL AND MOLECULAR STRUCTURES OF TWO AZA-HETEROCYCLIC DERIVATIVES OF 6-THIO-D-GALACTOPYRANOSE.

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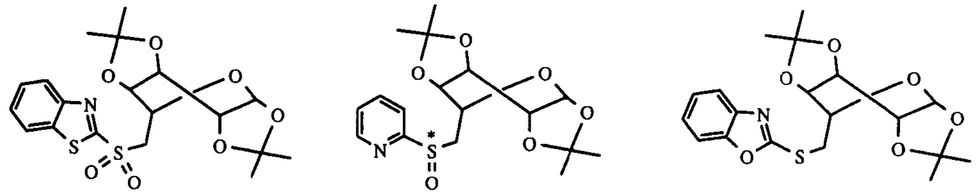
ABSTRACT

The conformations of crystalline 6-*C*-(benzothiazol-2-yl)sulfonyl-6-deoxy-1,2:3,4-di-*O*-isopropylidene-α-D-galactopyranose (**1**) and S_R-6-deoxy-1,2:3,4-di-*O*-isopropylidene-6-*C*-(2-pyridyl)sulfinyl-α-D-galactopyranose (**2**) have been determined by X-ray diffraction. The crystal structure of **1** belongs to the monoclinic $P2_1$ space group with a = 10.779(4), b = 10.431(6), c = 10.258(6) Å) and β =113.51(2) °. The crystal structure of **2** belongs to the tetragonal space $P4_12_12$ with a = 10.652(2) and c = 33.037(4) Å. The molecular features of these two compounds are compared with those of the related 6-*S*-(benzoxazol-2-yl)-1,2 :3,4-di-*O*-isopropylidene-6-thio-α-D-galactopyranose (**3**).

INTRODUCTION

For more than 150 years, the association of the sulfur element with sugars has opened many fertile investigation fields in chemistry and biology. In the plant kingdom, glucosinolates[2] have been and still remain a major topic for multidisciplinary research. In



1 2 3

Scheme 1

other respects, the chemistry of sulfur-containing sugars developed considerably within the 1960-1980 period[3] and more recently, promising advances were made in using thio functions for the activation of an anomeric carbon.[4-6]

For several years, we have been involved in investigating the chemistry of new classes of thiosugars with a twofold interest in methodological and biological applications: in particular, our efforts have been centered largely on original aza-heterocycle/thiosugar hybrids,[7-9] in which the oxidation number of the sulfur atom can be 2, 4 or 6. In the course of our studies on the reactivity of hexose-derived heteroaryl sulfides, the discovery and establishement of an aza-thia assistance concept[10] has prompted us to undertake thorough structural analyses of such hybrids.[11] We now report a complete stereochemical study of two aza-heterocyclic hybrids derived from 6-thio-D-galactose: the benzothiazol-2-yl sulfone **1**, which was developed as a versatile synthetic precursor,[8] and the 2-pyridyl sulfoxide **2**, in which the determination of the configuration at the S-center was essential.[9]

The present work describes the crystal and molecular structure of 6-*C*-(benzothiazol-2-yl)sulfonyl-6-deoxy-1,2:3,4-di-*O*-isopropylidene-α-D-galactopyranose (**1**), and S_R-6-deoxy-1,2:3,4-di-*O*-isopropylidene-6-*C*-(2-pyridyl)sulfinyl-α-D-galactopyr-anose (**2**) as determined by X-ray diffraction. The molecular features of these two compounds are also compared with those of the related 6-*S*-(benzoxazol-2-yl)-1,2:3,4-di-*O*-isopropylidene-6-thio-α-D-galactopyranose (**3**).[11]

RESULTS AND DISCUSSION

Crystal Structure of Sulfone 1. The atomic coordinates of the non-hydrogen atoms of **1** are listed in Table 1. A view of the molecule, along with the numbering of

Table 1. Fractional atomic coordinates and equivalent isotropic temperature factors (Å^2) for **1** (with e.s.d.s in parentheses).

atom	x	y	z	Ueq
S-6	-0.2926(2)	-0.3423(2)	-0.3148(2)	0.0395(6)
S-13	-0.4009(2)	-0.0695(2)	-0.3685(2)	0.0440(6)
O-1	-0.3330(5)	-0.1940(6)	-0.7218(6)	0.049(2)
O-2	-0.1907(5)	-0.2922(6)	-0.8019(6)	0.050(2)
O-3	0.1018(5)	-0.1868(5)	-0.4982(6)	0.050(2)
O-4	0.0959(5)	-0.3592(5)	-0.3660(5)	0.046(2)
O-5	-0.1724(5)	-0.2080(5)	-0.4912(6)	0.039(2)
O-61	-0.2837(6)	-0.4046(6)	-0.1856(7)	0.062(2)
O-62	-0.4117(5)	-0.3593(5)	-0.4416(6)	0.052(2)
N-13	-0.1615(6)	-0.1319(6)	-0.1842(7)	0.039(2)
C-1	-0.2009(8)	-0.1567(7)	-0.6274(8)	0.041(3)
C-2	-0.1078(8)	-0.2051(8)	-0.6964(8)	0.043(3)
C-3	0.0131(8)	-0.2775(8)	-0.5956(9)	0.046(3)
C-4	-0.0165(7)	-0.3736(7)	-0.4981(9)	0.042(3)
C-5	-0.1495(7)	-0.3457(8)	-0.4862(7)	0.035(2)
C-6	-0.1481(7)	-0.3902(8)	-0.3445(8)	0.043(3)
C-7	-0.3256(8)	-0.2436(9)	-0.8484(9)	0.050(3)
C-8	-0.3530(10)	-0.1400(10)	-0.9570(10)	0.073(4)
C-9	-0.4203(8)	-0.3570(10)	-0.9020(10)	0.068(4)
C-10	0.1763(8)	-0.2510(9)	-0.3670(10)	0.054(3)
C-11	0.3107(8)	-0.2940(10)	-0.3600(10)	0.087(4)
C-12	0.1820(10)	-0.1631(9)	-0.2470(10)	0.082(4)
C-13	-0.2709(6)	-0.1754(7)	-0.2777(7)	0.033(3)
C-14	-0.2989(7)	0.0494(7)	-0.2646(9)	0.040(3)
C-15	-0.1729(7)	0.0001(8)	-0.1741(8)	0.040(3)
C-16	-0.0737(8)	0.0791(8)	-0.0830(9)	0.052(3)
C-17	-0.1040(10)	0.2080(10)	-0.0840(10)	0.063(3)
C-18	-0.2290(10)	0.2582(9)	-0.1700(10)	0.063(4)
C-19	-0.3298(9)	0.1811(8)	-0.2643(9)	0.055(3)

atoms and the thermal ellipsoids, is given in Figure 1. Bond lengths and valence angles are reported in Table 2 and Table 3. The stereochemistry around the sulfur atom is discussed below. The other bond lengths and bond angles all lie within the expected ranges. Due to the constraint of the isopropylidene groups, the C-1—O-1 bond distance of 1.42 Å is slightly larger than the standard value of 1.41 Å adopted by α-glycosides[12] but still smaller than the other C-O bonds, except for the O-5—C-1 bond which is shortened to a value or 1.41 Å.

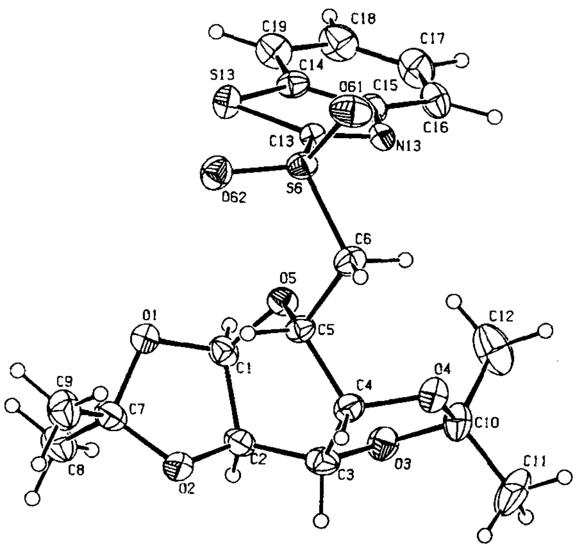


Figure 1. ORTEP drawing of **1**. Ellipsoids are drawn at the 30% probability level.

All intracyclic and exocyclic torsion angles are listed in Table 3. The pyranose ring displays the following puckering parameters, $Q = 0.66Å$, $\Theta = 81.1$ ° and $\Phi = 333.0°$, corresponding to a conformation that lies between a skew-boat and a twist-boat form. The adopted conformation results in an axial aspect for the isopropylidene oxygen atoms. The nine-membered benzothiazole system is effectively planar with a maximum deviation of 0.037 Å from the mean plane. The orientation of the benzothiazol-2-yl group at C-5 depends on rotation about three bonds; the one around C-5—C-6 is described as *gauche-trans* (referred to O-5 and C-4) whereas the orientation around C-6—S-6 is *gauche.*

Two orthogonal views of the molecular packing of the crystal are shown in Figure 2 illustrating the strong packing anisotropy which results from van der Waals interactions in chains parallel to the *b* axis. This strong interaction is created by the screw axis symmetry, so that the molecules are held together by van der Waals forces only.

Crystal Structure of Sulfoxide (**2**). The atomic coordinates of the non-hydrogen atoms of **2** are listed in Table 4. A view of the molecule, along with the numbering of atoms and the thermal ellipsoids is given in Figure 3. The present work provides configurational assignment of the chiral sulfur atom. It supports the correctness of the (*R*)

Table 2. Bond lengths (Å) and bond angles (°) for **1** (with e.s.d.s in parentheses)

S-6—O-61	1.445(7)	O-3—C-10	1.429(11)	C-5—C-6	1.520(10)
S-6—O-62	1.428(6)	O-4—C-4	1.420(10)	C-7—C-8	1.495(13)
S-6—C-6	1.774(9)	O-4—C-10	1.426(11)	C-7—C-9	1.515(14)
S-6—C-13	1.777(8)	O-5—C-1	1.411(9)	C-10—C-11	1.491(14)
S-13—C-13	1.735(7)	O-5—C-5	1.455(10)	C-10—C-12	1.516(13)
S-13—C-14	1.717(8)	N-13—C-13	1.270(10)	C-14—C-15	1.402(12)
O-1—C-1	1.420(10)	N-13—C-15	1.390(10)	C-14—C-19	1.414(11)
O-1—C-7	1.429(11)	C-1—C-2	1.526(12)	C-15—C-16	1.378(12)
O-2—C-2	1.423(10)	C-2—C-3	1.504(12)	C-16—C-17	1.383(13)
O-2—C-7	1.430(11)	C-3—C-4	1.537(12)	C-17—C-18	1.385(15)
O-3—C-3	1.430(10)	C-4—C-5	1.515(12)	C-18—C-19	1.387(13)

O-61—S-6—O-62	119.1(4)	C-1—C-2—C-3	113.4(7)	O-3—C-10—C-11	110.9(8)
O-61—S-6—C-6	106.8(4)	O-3—C-3—C-2	107.6(7)	O-3—C-10—C-12	107.9(7)
O-61—S-6—C-13	106.8(3)	O-3—C-3—C-4	103.4(6)	O-4—C-10—C-11	110.1(8)
O-62—S-6—C-6	109.9(4)	C-2—C-3—C-4	115.3(8)	O-4—C-10—C-12	107.5(7)
O-62—S-6—C-13	108.1(3)	O-4—C-4—C-3	103.4(6)	C-11—C-10—C-12	114.8(8)
C-6—S-6—C-13	105.3(4)	O-4—C-4—C-5	112.2(6)	S-6—C-13—S-13	120.0(4)
C-13—S-13—C-14	86.9(4)	C-3—C-4—C-5	112.1(7)	S-6—C-13—N-13	121.0(6)
C-1—O-1—C-7	108.3(6)	O-5—C-5—C-4	109.9(6)	S-13—C-13—N-13	119.0(6)
C-2—O-2—C-7	105.9(6)	O-5—C-5—C-6	105.8(6)	S-13—C-14—C-15	110.9(6)
C-3—O-3—C-10	108.4(6)	C-4—C-5—C-6	111.7(6)	S-13—C-14—C-19	127.6(7)
C-4—O-4—C-10	111.5(6)	S-6—C-6—C-5	113.8(6)	C-15—C-14—C-19	121.5(8)
C-1—O-5—C-5	112.1(5)	O-1—C-7—O-2	104.1(6)	N-13—C-15—C-14	113.9(7)
C-13—N-13—C-15	109.1(7)	O-1—C-7—C-8	110.5(8)	N-13—C-15—C-16	125.1(7)
O-1—C-1—O-5	109.5(7)	O-1—C-7—C-9	109.8(7)	C-14—C-15—C-16	121.0(8)
O-1—C-1—C-2	105.0(6)	O-2—C-7—C-8	112.2(8)	C-15—C-16—C-17	117.3(8)
O-5—C-1—C-2	114.2(7)	O-2—C-7—C-9	107.0(7)	C-16—C-17—C-18	122.6(9)
O-2—C-2—C-1	103.6(7)	C-8—C-7—C-9	112.9(8)	C-17—C-18—C-19	121.1(9)
O-2—C-2—C-3	108.1(7)	O-3—C-10—O-4	105.2(7)	C-14—C-19—C-18	116.4(8)

assignment obtained using (*S*)-α-methoxyphenylacetic acid as a chiral NMR shift reagent.[13] Bond lengths and valence angles are reported in Table 5. The stereochemistry around the sulfur atom is discussed below. The other bond lengths and bond angles all lie within the expected ranges, but note should be taken of the short O-5—C-1 distance of 1.397(3) Å.

Table 3. Torsion angles (°) for **1** (with e.s.d.s in parentheses)

S-6—C-6—C-5—O-5	53.0(7)	N-13—C-13—S-6—C-6	-51.1(7)
S-6—C-6—C-5—C-4	172.5(5)	C-1—O-1—C-7—C-8	-93.0(8)
S-6—C-13—S-13—C-14	177.3(5)	C-1—O-1—C-7—C-9	141.8(7)
S-6—C-13—N-13—C-15	-178.4(5)	C-1—O-5—C-5—C-4	70.2(8)
S-13—C-13—S-6—O-61	-117.1(5)	C-1—O-5—C-5—C-6	-169.1(6)
S-13—C-13—S-6—O-62	12.1(6)	C-1—C-2—O-2—C-7	31.7(8)
S-13—C-13—S-6—C-6	129.5(4)	C-1—C-2—C-3—C-4	43.6(10)
S-13—C-13—N-13—C-15	0.9(9)	C-2—O-2—C-7—C-8	82.2(8)
S-13—C-14—C-15—N-13	-2.7(9)	C-2—O-2—C-7—C-9	-153.4(7)
S-13—C-14—C-15—C-16	178.7(7)	C-2—C-1—O-1—C-7	-8.0(8)
S-13—C-14—C-19—C-18	-179.7(7)	C-2—C-1—O-5—C-5	-44.9(9)
O-1—C-1—O-5—C-5	72.5(8)	C-2—C-3—O-3—C-10	151.4(7)
O-1—C-1—C-2—O-2	-14.5(7)	C-2—C-3—C-4—C-5	-19.5(10)
O-1—C-1—C-2—C-3	-131.4(7)	C-3—O-3—C-10—C-11	95.7(9)
O-1—C-7—O-2—C-2	-37.2(8)	C-3—O-3—C-10—C-12	-137.9(8)
O-2—C-2—C-1—O-5	105.5(7)	C-3—C-2—O-2—C-7	152.2(7)
O-2—C-2—C-3—O-3	174.6(6)	C-3—C-4—O-4—C-10	10.1(8)
O-2—C-2—C-3—C-4	-70.6(9)	C-3—C-4—C-5—O-5	-34.5(8)
O-2—C-7—O-1—C-1	27.6(8)	C-3—C-4—C-5—C-6	-151.6(7)
O-3—C-3—C-2—C-1	-71.1(9)	C-4—O-4—C-10—C-11	-112.3(8)
O-3—C-3—C-4—O-4	-23.4(8)	C-4—O-4—C-10—C-12	122.1(7)
O-3—C-3—C-4—C-5	97.7(8)	C-4—C-3—O-3—C-10	29.0(8)
O-3—C-10—O-4—C-4	7.3(9)	C-5—C-4—O-4—C-10	-110.9(7)
O-4—C-4—C-3—C-2	-140.5(7)	C-5—C-6—S-6—C-13	-73.5(6)
O-4—C-4—C-5—O-5	81.4(7)	C-13—S-13—C-14—C-15	2.5(6)
O-4—C-4—C-5—C-6	-35.7(9)	C-13—S-13—C-14—C-19	-177.8(8)
O-4—C-10—O-3—C-3	-23.3(9)	C-13—N-13—C-15—C-14	1.2(10)
O-5—C-1—O-1—C-7	-131.1(7)	C-13—N-13—C-15—C-16	179.7(9)
O-5—C-1—C-2—C-3	-11.4(10)	C-14—C-15—C-16—C-17	0.5(13)
O-5—C-5—C-4—C-3	-34.5(8)	C-14—C-19—C-18—C-17	1.6(15)
O-61—S-6—C-6—C-5	173.2(6)	C-15—C-14—C-19—C-18	0(4)
O-61—S-6—C-13—N-13	62.2(7)	C-15—C-16—C-17—C-18	1.2(15)
O-62—S-6—C-6—C-5	42.6(7)	C-16—C-15—C-14—C-19	-1.1(13)
O-62—S-6—C-13—N-13	-168.5(6)	C-16—C-17—C-18—C-19	-2.3(16)

All torsion angles are listed in Table 6. The following puckering parameters, Q = 0.58 Å, Θ = 76.3 ° and Φ = 320.1°, indicate a conformation that lies between a skew-boat and a twist-boat form for the pyranose ring. The isopropylidene groups display an orientation similar to that observed in the crystalline conformation of **1**. The orientation of

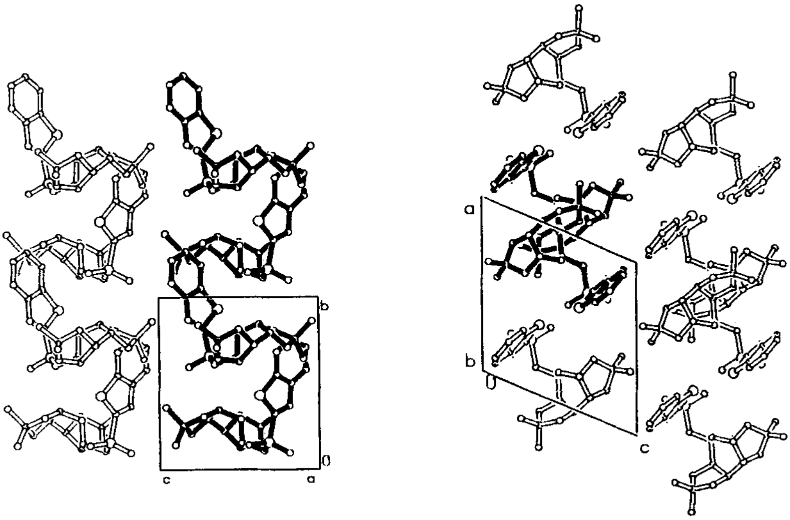


Figure 2. Molecular packing of the crystal of **1** viewed along the *a* and *b* axes.

Table 4. Fractional atomic coordinates and equivalent thermal parameters ($Å^2$) for **2** (with e.s.d.s in parentheses).

atom	x	y	z	B
S-6	0.07740(9)	0.44183(8)	0.05086(2)	4.44(2)
O-1	-0.1959(2)	0.2317(2)	0.12331(5)	4.43(5)
O-2	-0.0750(2)	0.1112(2)	0.16361(5)	4.36(5)
O-3	0.0197(2)	-0.1112(2)	0.08838(5)	3.91(5)
O-4	0.1435(2)	0.0200(2)	0.05378(5)	4.37(5)
O-5	-0.0685(2)	0.1866(2)	0.06908(5)	3.41(5)
O-7	0.1552(3)	0.4978(2)	0.08369(6)	7.00(7)
N-13	0.0778(3)	0.4533(2)	-0.02787(7)	5.76(8)
C-1	-0.1487(3)	0.1351(3)	0.09810(8)	3.49(8)
C-2	-0.0889(3)	0.0415(3)	0.12709(8)	3.30(7)
C-3	0.0377(3)	-0.0084(3)	0.11494(8)	3.36(8)
C-4	0.1213(3)	0.0828(3)	0.09093(9)	3.35(8)
C-5	0.0564(3)	0.2063(3)	0.08255(8)	3.11(7)
C-6	0.1212(3)	0.2790(3)	0.04882(9)	3.72(8)
C-7	-0.1756(3)	0.1977(3)	0.16456(9)	4.63(9)
C-8	-0.2934(4)	0.1383(4)	0.1811(1)	7.4(1)
C-9	-0.1366(4)	0.3115(4)	0.1879(1)	7.7(1)
C-10	0.1220(3)	-0.1096(3)	0.06055(8)	3.77(8)
C-11	0.2366(4)	-0.1718(3)	0.0785(1)	5.6(1)
C-12	0.0809(4)	-0.1698(3)	0.0216(1)	5.4(1)
C-13	0.1515(3)	0.4817(3)	0.00353(9)	4.23(8)
C-14	0.2662(3)	0.5359(3)	0.0017(1)	6.4(1)
C-15	0.3125(4)	0.5626(4)	-0.0373(1)	7.5(1)
C-16	0.2392(4)	0.5319(4)	-0.0694(1)	7.5(1)
C-17	0.1248(4)	0.4782(4)	-0.0649(1)	7.0(1)

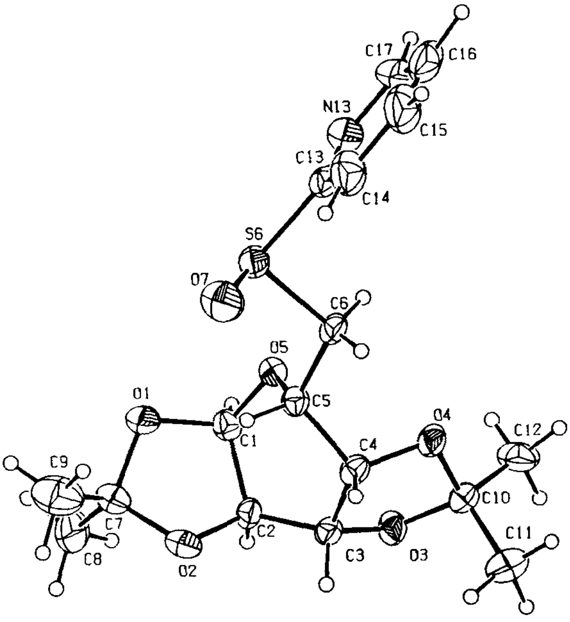


Figure 3. ORTEP drawing of **2**. Ellipsoids are drawn at the 30% probability level.

Table 5. Bond lengths (Å) and Bond angles (°) for **2** (with e.s.d.s in parentheses).

S-6—O-7	1.489(2)	O-4—C-10	1.418(3)	C-7—C-8	1.508(5)
S-6—C-6	1.797(3)	O-5—C-1	1.397(3)	C-7—C-9	1.496(5)
S-6—C-13	1.803(3)	O-5—C-5	1.418(3)	C-10 —C-11	1.509(4)
O-1—C-1	1.416(3)	N-13—C-13	1.336(4)	C-10—C-12	1.501(4)
O-1—C-7	1.427(3)	N-13—C-17	1.350(4)	C-13—C-14	1.353(4)
O-2—C-2	1.424(3)	C-1—C-2	1.523(4)	C-14—C-15	1.408(4)
O-2—C-7	1.414(3)	C-2—C-3	1.503(4)	C-15—C-16	1.358(5)
O-3—C-3	1.416(3)	C-3—C-4	1.539(4)	C-16—C-17	1.354(5)
O-3—C-10	1.425(3)	C-4—C-5	1.512(4)		
O-4—C-4	1.418(3)	C-5—C-6	1.523(4)		

Table 5 (continued).

O-7—S-6—C-6	105.6(1)	O-3—C-3—C-2	108.5(2)	C-8—C-7—C-9	112.6(3)
O-7—S-6—C-13	107.1(1)	O-3—C-3—C-4	104.3(2)	O-3—C-10—O-4	103.7(2)
C-6—S-6—C-13	94.6(1)	O-4—C-4—C-3	104.2(2)	O-3—C-10—C-11	111.1(2)
C-1—O-1—C-7	108.8(2)	O-4—C-4—C-5	109.2(2)	O-3—C-10—C-12	109.0(3)
C-2—O-2—C-7	106.2(2)	C-3—C-4—C-5	112.3(2)	O-4—C-10—C-11	111.0(3)
C-3—O-3—C-10	106.7(2)	O-5—C-5—C-4	110.9(2)	O-4—C-10—C-12	109.1(2)
C-4—O-4—C-10	107.2(2)	O-5—C-5—C-6	105.7(2)	C-11—C-10—C-12	112.6(3)
C-1—O-5—C-5	114.6(2)	C-4—C-5—C-6	111.7(2)	S-6—C-13—N-13	111.2(2)
C-13—N-13—C-17	116.2(3)	S-6—C-6—C-5	110.2(2)	S-6—C-13—C-14	122.3(3)
O-1—C-1—O-5	109.6(2)	O-1—C-7—O-2	105.1(2)	N-13—C-13—C-14	126.4(3)
O-1—C-1—C-2	104.8(2)	O-1—C-7—C-8	109.1(3)	C-13—C-14—C-15	116.3(4)
O-5—C-1—C-2	115.6(2)	O-1—C-7—C-9	109.2(3)	C-14—C-15—C-16	117.8(4)
O-2—C-2—C-1	103.6(2)	O-2—C-7—C-8	111.4(3)	C-15—C-16—C-17	122.2(4)
O-2—C-2—C-3	108.5(2)	C-2—C-3—C-4	115.7(2)	N-13—C-17—C-16	121.1(4)
C-1—C-2—C-3	116.1(2)	O-2—C-7—C-9	109.2(3)		

Table 6. Torsion angles (°) for **2** (with e.s.d.s in parentheses)

S-6—C-6—C-5—O-5	78.4(2)	C-1—O-1—C-7—C-8	-96.3(3)
S-6—C-6—C-5—C-4	-160.9(2)	C-1—O-1—C-7—C-9	140.3(3)
S-6—C-13—N-13—C-17	-179.3(2)	C-1—O-5—C-5—C-4	66.7(3)
S-6—C-13—C-14—C-15	-179.6(3)	C-1—O-5—C-5—C-6	-172.1(2)
O-1—C-1—O-5—C-5	83.3(3)	C-1—C-2—O-2—C-7	31.4(3)
O-1—C-1—C-2—O-2	-16.8(3)	C-1—C-2—C-3—C-3	31.9(3)
O-1—C-1—C-2—C-3	-135.6(2)	C-2—O-2—C-7—C-8	83.6(3)
O-1—C-7—O-2—C-2	-34.4(3)	C-2—O-2—C-7—C-9	-151.4(3
O-2—C-2—C-1—O-5	104.0(3)	C-2—C-1—O-1—C-7	-3.8(3)
O-2—C-2—C-3—O-3	159.3(2)	C-2—C-1—O-5—C-5	-34.8(3)
O-2—C-2—C-3—C-4	-84.0(3)	C-2—C-3—O-3—C-10	147.0(2)
O-2—C-7—O-1—C-1	23.3(3)	C-2—C-3—C-4—C-5	-2.3(3)
O-3—C-3—C-2—C-1	-84.6(3)	C-3—O-3—C-10—C-11	82.5(3)
O-3—C-3—C-4—O-4	-1.3(3)	C-3—O-3—C-10—C-12	-152.9(2)
O-3—C-3—C-4—C-5	116.8(2)	C-3—C-2—O-2—C-7	155.3(2)
O-3—C-10—O-4—C-4	36.0(3)	C-3—C-4—O-4—C-10	-21.3(3)
O-4—C-4—C-3—C-2	-120.3(2)	C-3—C-4—C-5—O-5	-45.3(3)
O-4—C-4—C-5—O-5	70.0(3)	C-3—C-4—C-5—C-6	-162.7(2)
O-4—C-4—C-5—C-6	-47.7(3)	C-4—O-4—C-10—C-11	-83.3(3)
O-4—C-10—O-3—C-3	-36.8(3)	C-4—O-4—C-10—C-12	152.0(3)
O-5—C-1—O-1—C-7	-128.5(2)	C-4—C-3—O-3—C-10	23.2(3)
O-5—C-1—C-2—C-3	-14.8(4)	C-5—C-4—O-4—C-10	-141.4(2)
O-5—C-5—C-4—C-3	-45.1(3)	C-5—C-6—S-6—C-13	-171.7(2)
O-7—S-6—C-6—C-5	79.1(2)	C-6—S-6—C-13—C-14	-99.0(3)
O-7—S-6—C-13—N-13	-169.8(2)	C-13—N-13—C-17—C-16	-1.7(5)
O-7—S-6—C-13—C-14	8.9(3)	C-13—C-14—C-15—C-16	-0.2(6)
N-13—C-13—S-6—C-6	82.3(2)	C-14—C-13—N-13—C-17	2.1(5)
N-13—C-13—C-14—C-15	-1.2(5)	C-14—C-15—C-16—C-17	0.6(6)
N-13—C-17—C-16—C-15	0.4(6)		

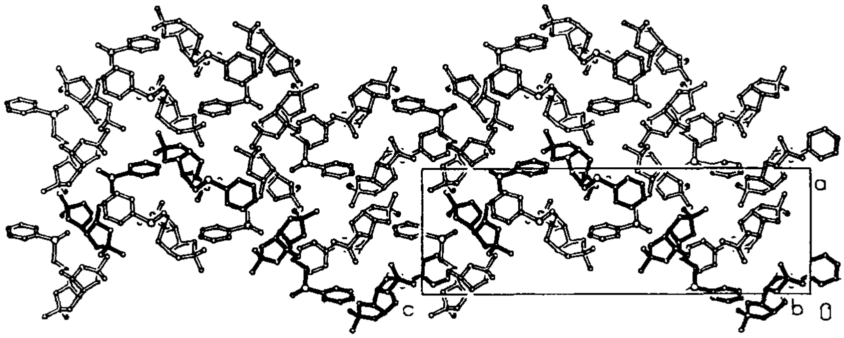


Figure 4. Molecular packing of the crystal of **2** viewed along the *b* axes.

the pyridyl group at C-5 is *gauche-trans* (referred to O-5 and C-4) about C-5—C6 whereas the orientation of the pyridyl group around C-6—S-6 is *trans.*

The projection of the crystalline packing along the *b* axis is given in Figure 4. The anisotropy of intermolecular interaction is less pronounced than in compound **1**. The molecules are held together by van der Waals forces only.

Comparison of the Stereochemistry of Three Aza-heterocycylic Hybrids Derived from 6-Thio-D-galactopyranose. The galactose ring has been used for fitting molecules **1**, **2** and **3** and the corresponding superimposition is displayed in Figure 5. The conformational similarities of the di-*O*-isopropylidene-α-D-galactopyranose scaffold are clearly seen. In contrast, large differences are displayed by the 6-thio groups (Table 7). The length of the S—O bond varies from 1.43 Å in the sulfone (**1**) to 1.49 Å for the S=O in the sulfoxide (**2**) while the C—S—C bond angle varies from 105.2° to 94.4°, respectively. The corresponding values found in DMSO for S—O bond length and C—S—C bond angle were 1.47 Å and 107° by X-rays[14] and 1.485 Å and 96.6° by microwave spectroscopy.[15]

It is noteworthy that the sulfoxide group of **2** in the present study has a smaller value than that reported for DMSO. In the three compounds studied here, the C—S bond lengths vary between 1.73Å and 1.80Å. As established previously the C—S bond lengths vary accordingly to carbon valence states but sulfones and sulfoxides are less sensitive than sulfides in this respect.[16]

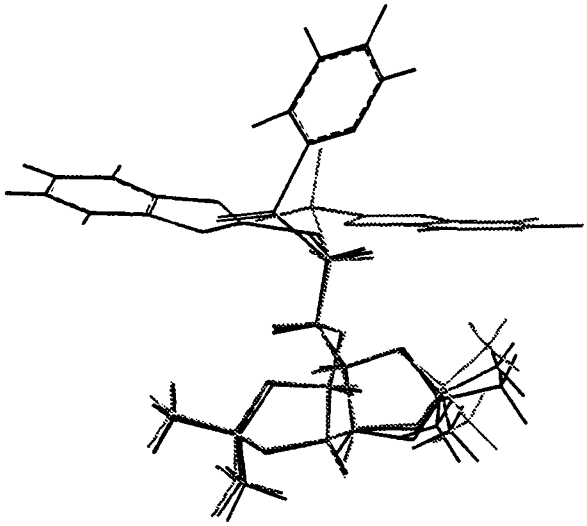


Figure 5. Superimposition of the crystalline conformation of the three compounds.

Table 7. Comparison of the sulfur atom stereochemistry for the three compounds.

Compound	1	2	3
Distances (Å)			
C-6—S-6	1.774(9)	1.797(2)	1.806(3)
S-6—C-13	1.777(8)	1.803(3)	1.734(3)
S-6—O	1.445(7), 1.428(6)	1.489(2)	
Valence angles (°)			
C-6—S-6—C-13	105.3(4)	94.6(1)	100.9(1)
C-6—S-6—O	106.8(4), 109.9(4)	105.6(1)	
C-13—S-6—O	108.1(3), 106.8(3)	107.1(1)	
Torsion angles (°)			
O-5—C-5—C-6—S-6	53.0(7)	78.4(2)	-168.6(2)
C-4—C-5—C-6—S-6	172.5(5)	-160.9(2)	-48.1(3)
C-5—C-6—S-6—C-13	-73.5(6)	-171.7(2)	-79.7(2)
C-5—C-6—S-6—O	173.2(6), 42.6(7)	79.1(2)	
C-6—S-6—C-13—N	-51.1(7)	82.3(2)	2.8(3)

The torsion angles that drive the orientation of the exocyclic group connected to the sulfur atom display a large range of values (Figure 5). The orientation adopted by each molecule could depend on the valence of the sulfur atom but also on packing effect.

EXPERIMENTAL

Crystal Structure Determination of 1. Crystal data for C_{19} H_{23} N O_7 S_2, Mr = 441.53, monoclinic, P2$_1$, a = 10.779(4), b = 10.431(6), c = 10.258(6) Å, β =113.51(2)°, Z = 2, V = 1057.6(10) Å^3 Dc = 1.386 g cm^{-3}, T= 290 K . The diffraction patterns were obtained from a single crystal of approximately 0.2 x 0.2 x 1.7 mm mounted on a glass fiber using a PHILIPS PW1100 diffractometer. Accurate unit-cell dimensions were determined by a least-squares fit of the setting angles at high 2θ values. Lorentz and polarization corrections were applied, but no correction was made for absorption. The intensities of 1887 independent reflections were measured inside the sphere limited by 2θ < 110° at the Cu wavelength using the ω-2θ technique. The average of three reference reflections monitored each hour decreased by about 0.2% during the collection time. All the intensities were corrected for the background noise. From the 1887 measured reflections, 1566 such as $I/\sigma(I) > 2\sigma$ were considered as observed. No absorption correction has been made given the crystal dimensions and the small value of the absorption coefficient at the wavelength used. Scattering factors were taken from the International Tables of Crystallography.[17] The structure was solved by direct methods[18] allowing the location of all C, O, S and N atoms. The H atoms were located by successive difference Fourier maps. The last cycles were performed using an anisotropic thermal temperature factor for non-hydrogen atoms, whereas the hydrogen atoms were assigned an isotropic temperature factor. The final R-value was 0.044. During the refinement, each reflection was assigned a weight $w = 1/\sigma(F_o)^2$ derived from σ(I) and the function minimized was $\Sigma w(Fo\text{-}Fc)^2$. A final electron density map showed no significant residual density. Geometrical calculations and ORTEP representations were obtained with PLATON.[19]

Crystal Structure Determination of 2. Crystal data for C_{17} H_{23} N O_6 S, Mr = 369.43, tetragonal, P4$_1$2$_1$2, a = 10.652(2), c = 33.037(4) Å, Z = 8, V = 3748.4(1) Å^3, Dc = 1.309 g cm^{-3}, μ = 2.04 (Mo$K\alpha$) cm^{-1}) T= 290 K. The diffraction patterns were obtained from a single crystal of approximately 0.2 x 0.2 x 0.5 mm mounted on a glass fiber using a Nonius CAD4 diffractometer. Accurate unit-cell dimensions were determined by a least-squares fit of the setting angles at high 2θ values. Lorentz and polarization corrections were applied, but no correction was made for absorption. The intensities of 2321 independent reflections were measured inside the sphere limited by $2\theta < 60°$ at the Mo wavelength. The average of three reference reflections monitored each hour decreased by about 0.2% during the collection time. All the intensities were corrected from the background noise. From the 2321 measured reflections, 1153 such as $I/\sigma(I) > 3\sigma$ were considered as observed. No absorption correction has been made given the crystal dimensions and the small value of the absorption coefficient at the wavelength used. Scattering factors were taken from the International Tables of Crystallography.[17] The structure was solved by direct methods[18] allowing the location of all C, O, S and N atoms. The H atoms were located by successive difference Fourier maps, and isotropic refinement, leading to R-value of 0.029. The last cycles were performed using an anisotropic thermal temperature factor for non-hydrogen atoms, whereas the hydrogen atoms were assigned an isotropic temperature factor. The final R-value was 0.019. During the refinement, each reflection was assigned a weight $w = 1/\sigma(F_o)^2$ derived from $\sigma(I)$ and the function minimized was $\Sigma w(Fo-Fc)^2$. A final electron density map showed no significant residual density.

Deposition of Data. Tables of atomic coordinates, bond lengths, and bond angles have been deposited with the Cambridge Crystallographic Data Centre. These tables may be obtained on request from the Director, Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 IEZ, UK.

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