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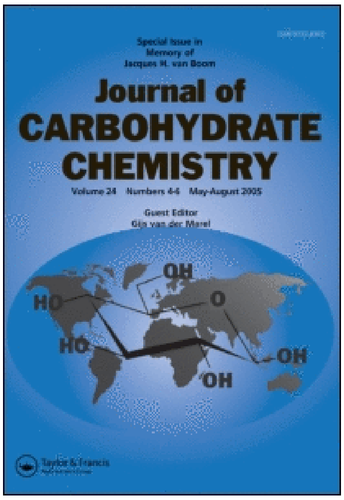

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COMPARATIVE X-RAY SINGLE CRYSTAL STUDY OF ACETYLATED-β-D-GALACTOPYRANOSYLS AZIDE AND ISOTHIOCYANATE

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ABSTRACT

The structures of two peracetylated β-D-galactopyranosides substituted at the anomeric C atom with either an isothiocyanate or an azide group, have been determined by single crystal X-ray diffraction analysis. The two compounds show very similar molecular conformation, except for the substituent groups at the anomeric C atom and for the acetyl groups of the O6 atoms. They crystallize in different infinite chain-type structures. While the isothiocyanate group extends in a large intermolecular space, the azide group is placed in a more crowded environment.

INTRODUCTION

Glycosyl isothiocyanates and glycosyl azides have been recognized as important families of carbohydrate derivatives. They have been widely used as key intermediates in the chemical synthesis of *N*-glycopeptides[1] and *N*-glycoconjugates.[2] The corresponding *N*-glycosidic linkage is obtained by easy conversion of glycosyl isothiocyanate into amide in the presence of an acid derivative and triethylamine, or by conventional reduction methods of an azide group into amine.[2]

In the present study, we have determined the crystal structures of the 2,3,4,6-tetra-*O*-acetyl-β-D-galactopyranosyl isothiocyanate (**1**) and of the 2,3,4,6-tetra-*O*-acetyl-β-D-galactopyranosyl azide (**2**). The structure determination of compound **1**, is the first structural characterization of a pyranosyl isothiocyanate. The only reported crystal structure of a β-D-pyranosyl azide is that of peracetylated β-D-xylopyranosyl azide.[3] It has been shown that the azide group adopts a *gauche-trans* conformation relative to the anomeric C1-N1 bond, therefore it is directed towards the ring O atom. This conformation has been ascribed to an important contribution of the *exo*-anomeric effect. Interestingly, the structure of the peracetylated 1-methyl-β-D-glucopyranosyl azide[4] has demonstrated that in the presence of the axial 1-*O*-methyl, the conformation of the azide group is *trans-gauche*, probably as a result of steric restraints. In that case, the azide group is oriented towards the C2 ring atom.

For acetylated monosaccharides, the cohesion of their structures is ensured by van der Waals contacts and, possibly, by weak interactions such as C-H···O hydrogen bonds, as a consequence of the total absence of free hydroxyl groups. In this study, the location of the H atoms was not accurate enough to allow a precise analysis of such interactions. Nevertheless, it is worth noticing that, in both structures, intermolecular contacts are seen between donor groups and acceptor atoms.

RESULTS AND DISCUSSION

For the two compounds, the molecular conformation and the atom-labelling scheme are presented in Figure 1. The geometrical data describing the molecular conformation of **1** and **2** are listed in Tables 1-3. The crystal structures exhibit different molecular packings, illustrated in Figures 2-4.

Molecular Conformation

The pyranose ring has a regular ${}^1C_4$ chair conformation, as follows from the endocyclic torsion angles, and does not significantly differ from that observed in the previously reported structure of β-D-galactose.[5,6] The average bond lengths and valence angles are in the expected ranges for pyranosyl residues.[7] In both compounds, the

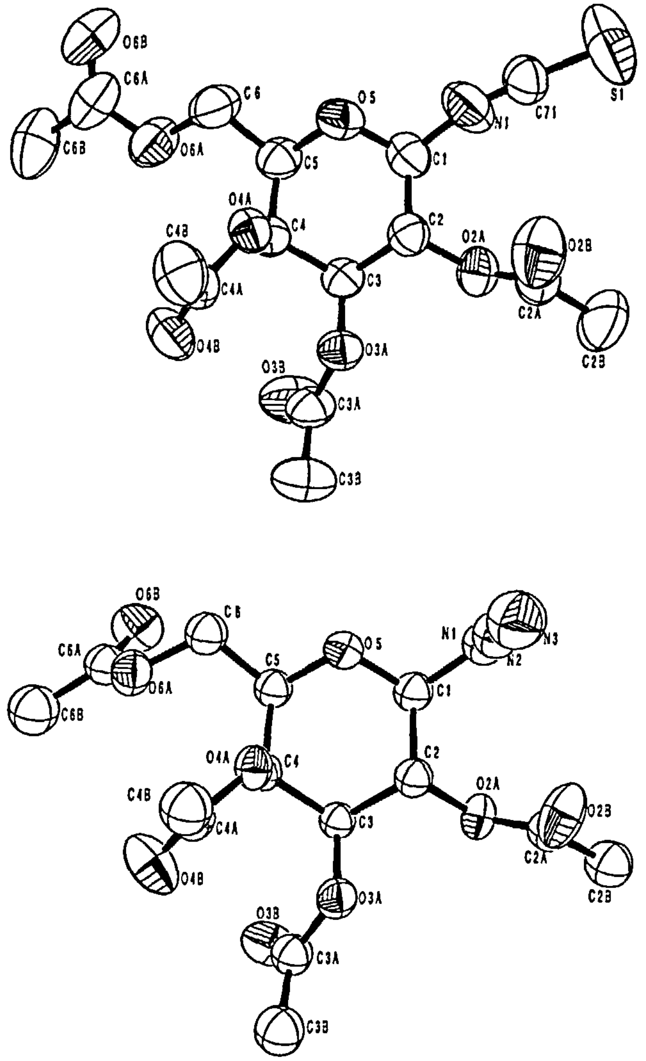


Figure 1. Molecular structure and atomic numbering scheme of **1** (top) and **2** (bottom). The displacement ellipsoids are drawn at the 50% probability level. For clarity, only the major components of C7 and S atoms are represented for **1**.

torsion angles concerning the orientation of the C6-O6 bond show a *trans-gauche* conformation, with for **2**, a deviation of the C4-C5-C6-O6A torsion angle from the standard value (-60°) of approximately 11°, Table 3.

For **1**, the torsion angle ψ = [C5-C6-O6A-C6A] of -170.1(3)° is consistent with those found for structures of 6-*O*-acetyl-, 2,3,4,6-tetra-*O*-acetyl- and 1,3,4,6-tetra-*O*-

Table 1. Selected bond lengths (Å) for **1** and **2**

Atoms	1	2	Atoms	1	2
C1-C2	1.526 (4)	1.541 (8)	C3A-C3B	1.479 (5)	1.489 (9)
C2-C3	1.504 (3)	1.506 (8)	C3A-O3B	1.184 (4)	1.179 (8)
C3-C4	1.523 (3)	1.533 (8)	O4A-C4A	1.350 (3)	1.351 (8)
C4-C5	1.511 (4)	1.512 (8)	C4A-C4B	1.485 (5)	1.480 (9)
C5-O5	1.420 (3)	1.423 (7)	C4A-O4B	1.188 (3)	1.192 (7)
O5-C1	1.402 (4)	1.427 (7)	O6A-C6A	1.322 (4)	1.346 (8)
C2-O2A	1.432 (3)	1.443 (7)	C6A-C6B	1.488 (6)	1.486 (9)
C3-O3A	1.424 (3)	1.450 (7)	C6A-O6B	1.191 (5)	1.185 (8)
C4-O4A	1.445 (3)	1.446 (7)	C1-N1	1.415 (4)	1.455 (8)
C5-C6	1.502 (4)	1.505 (8)	N1-C71	1.105 (4)	
C6-O6A	1.433 (4)	1.446 (7)	C71-S1	1.543 (4)	
O2A-C2A	1.362 (4)	1.347 (7)	N1-C72	1.108(13)	
C2A-C2B	1.492 (6)	1.484 (9)	C72-S2	1.519(13)	
C2A-O2B	1.208 (5)	1.183 (8)	N1-N2		1.250 (7)
O3A-C3A	1.349 (3)	1.366 (8)	N2-N3		1.117 (7)

Table 2. Bond angles (°) for **1** and **2**

Atoms	1	2	Atoms	1	2
C1-C2-C3	109.7 (2)	110.2 (5)	O3A-C3A-C3B	111.2 (3)	111.1 (6)
C2-C3-C4	110.5 (2)	111.1 (5)	O3A-C3A-O3B	123.1 (3)	123.1 (7)
C3-C4-C5	109.5 (2)	109.7 (5)	C3B-C3A-O3B	125.7 (3)	125.8 (7)
C4-C5-O5	110.5 (2)	111.3 (5)	C4-O4A-C4A	117.1 (2)	117.2 (5)
C5-O5-C1	112.3 (2)	112.6 (4)	O4A-C4A-C4B	110.6 (2)	111.1 (6)
O5-C1-C2	109.7 (2)	110.3 (5)	O4A-C4A-O4B	123.6 (3)	122.8 (6)
C1-C2-O2A	108.9 (2)	106.4 (5)	C4B-C4A-O4B	125.8 (3)	126.1 (7)
C3-C2-O2A	108.2 (2)	108.0 (5)	C6-O6A-C6A	115.9 (3)	117.3 (5)
C2-C3-O3A	106.9 (2)	106.5 (5)	O6A-C6A-C6B	111.3 (4)	110.8 (6)
C4-C3-O3A	110.7 (2)	109.3 (5)	O6A-C6A-O6B	121.9 (4)	123.5 (7)
C3-C4-O4A	108.8 (2)	108.9 (5)	C6B-C6A-O6B	126.9 (4)	125.7 (7)
C5-C4-O4A	107.7 (2)	107.7 (5)	O5-C1-N1	106.2 (3)	107.9 (5)
C4-C5-C6	115.1 (3)	113.3 (5)	C2-C1-N1	111.5 (2)	113.9 (5)
O5-C5-C6	104.1 (2)	105.4 (5)	C1-N1-C71	163.4 (4)	
C5-C6-O6A	107.2 (2)	109.9 (5)	N1-C71-S1	177.3 (4)	
C2-O2A-C2A	117.8 (3)	117.4 (5)	C1-N1-C72	163.7 (7)	
O2A-C2A-C2B	110.0 (4)	110.8 (6)	N1-C72-S2	178.1(11)	
O2A-C2A-O2B	123.1 (3)	124.1 (7)	C1-N1-N2		112.2 (5)
C2B-C2A-O2B	126.8 (4)	125.0 (7)	N1-N2-N3		171.9 (7)
C3-O3A-C3A	118.3 (2)	115.6 (5)			

Table 3. Selected torsion angles (°) for **1** and **2**

Atoms	1	2	Atoms	1	2
C1-C2-C3-C4	-53.2 (3)	-52.1 (7)	C4-C5-O5-C1	62.9 (3)	61.5 (6)
C2-C3-C4-C5	52.6 (3)	52.3 (7)	C5-O5-C1-C2	-63.0 (3)	-60.5 (6)
C3-C4-C5-O5	-56.1 (3)	-55.9 (7)	O5-C1-C2-C3	57.7 (3)	55.5 (7)
C4-C5-C6-O6A	-60.0 (4)	-49.0 (7)	C3-C2-C1-N1	175.1 (3)	177.0 (5)
O5-C5-C6-O6A	178.9 (3)	-171.0 (5)	C5-O5-C1-N1	176.3 (3)	174.5 (5)
O5-C1-N1-C71	-167.5(13)		O5-C1-N1-N2		65.1 (7)
C2-C1-N1-C71	73.0(14)		C2-C1-N1-N2		-57.8 (7)

acetyl-β-D-galactopyranosides, which describe a *trans* conformation (mean ψ value of -172°)[8,9,10] or an approximately *trans* conformation (ψ values of -154° and 147°).[11,12] In contrast for **2**, the acetyl group adopts an unexpected conformation around the C6-O6A bond with a ψ torsion angle of -89.9(7)°. The conformational differences between **1** and **2** about the other acetyl groups are slight. For all the acetyl groups, the carbonyl group is close to eclipsing the parent pyranose C-O bond, as generally observed.

The rigid linear NCS group is equatorially attached to the anomeric C1 atom by the N atom so that it is directed away from the ring. The C and S atoms are disordered over two sites, with respective occupancies of 0.75 and 0.25. Nevertheless, for both major and minor components, the C1-N-C and N-C-S angle values agree well with those seen in crystal structures of organic molecules containing the isothiocyanate group.[13] The N-C bond lengths are in the usual range while the C-S bond lengths are slightly shorter than would be expected, but this could be explained by the effects of the disorder.

The conformation of the azide group is *gauche-gauche* relative to the pyranose ring. The N-N bond lengths and the N-N-N angle value are in the normal range and similar to those found in a series of structures of β-D-galactopyranosides with an azide group attached to the C2 ring atom.[14,15,16] The central nitrogen atom (N2) is placed nearly at equal distances from C2 and from the endocyclic O atom (C2···N2 and O5···N2 distances of 2.846(8) and 2.730(7)Å, respectively). This orientation of the azide group is different from that described for the structure of the peracetylated β-D-xylopyranosyl azide.[3]

Crystal Packing

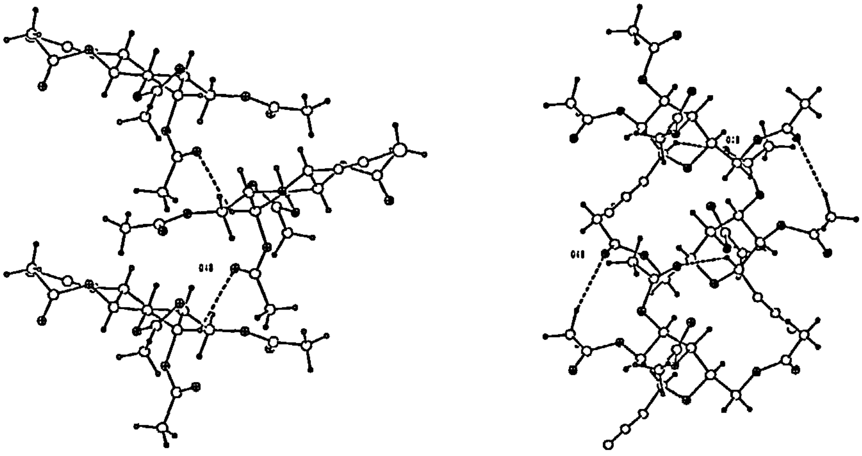
The crystal structures reveal two different arrangements of the molecules which are stacked in infinite chain-like patterns built up by crystallographic 2_1 symmetry, as illustrated in Figure 2. The topologies of the chains mainly depend on the orientations of the pyranose rings with respect to the plane perpendicular to the chain axis (**ac** plane and **bc** plane for **1** and **2**, respectively).

For **1**, the molecules are stacked along the twofold screw *b*-axis, with the pyranose rings nearly parallel to the **ac** plane (inclination of the least squares plane through C2, C3, C5 and O5, at 4°). Therefore, the axial C4-O4A bond directs its corresponding acetyl group along the chain axis, towards the adjacent molecule, Figure 2a. The chains are aligned parallel to the **ab** plane forming sheets which are packed along the *c*-axis, Figure 3.

The situation is quite different for **2**. The pyranose rings are steeply inclined at the **bc** plane (inclination of the least squares plane through C2, C3, C5 and O5, at 75°), Figure 2b. Now, the acetyl group bonded to O4A points away from the chain. Two chains with the opposite direction (antiparallel) run along the twofold screw axes parallel to the *a*-axis. Each chain is stacked parallel to the *b*-axis to form sheets. There are two antiparallel sheets alternately packed along the *c*-axis, at the levels 0 and 1/2, respectively, Figure 4.

As a consequence of the topological differences between the chains, the N_3 group is disposed at the interior of the chain while the NCS group protudes away from the chains; it is placed in a large intermolecular space between the sheets. This is the reason why the NCS group can adopt two slightly different positions without perturbations of its environment.

In both structures, intermolecular contacts between donor groups and *O*-acceptors are seen. Although most of the hydrogen atoms were clearly visible in a final electron density map, their positions could not be refined. Therefore, a precise analysis of hydrogen bonding patterns is not possible. Nevertheless, a number of contacts might be suggestive of significant interactions, as they are typical of those described for carbohydrate structures from analysis of neutron diffraction and crystal correlation studies[17,18,19,20] (C···O distances < 3.50Å, calculated H···O separations ranging from 2.37 to 2.77Å and calculated angles at H > 120°).



(a) (b)

Figure 2. Comparison between the structural organization of the molecular chains, which run vertically: a) structure 1; b) structure 2. Donor-acceptor contacts are showed in dashed lines.

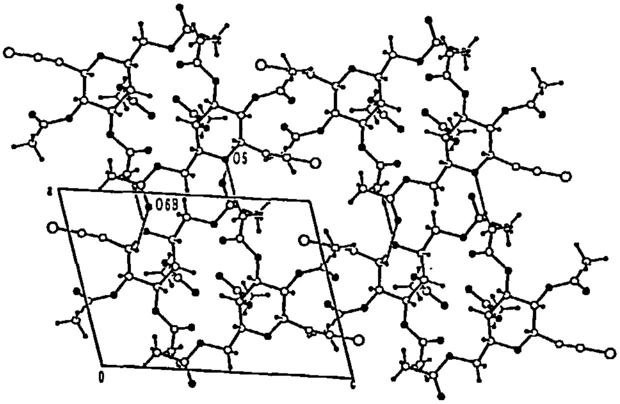


Figure 3. Packing view down the *b*-axis of the structure **1**, showing the stacking of the sheets of parallel chains along the *c*-axis. Donor-acceptor contacts are indicated in dashed lines.

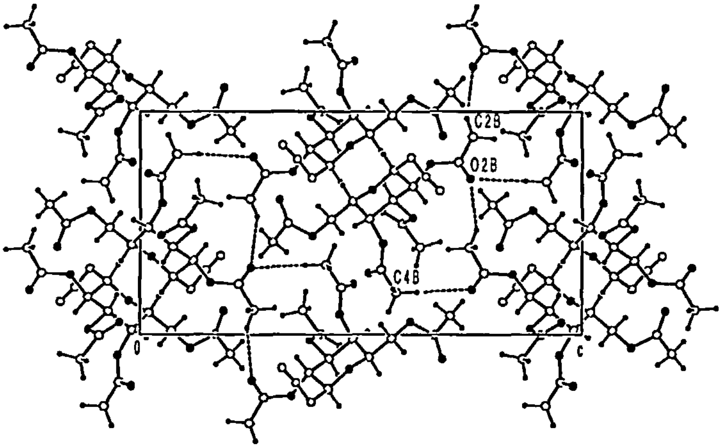


Figure 4. Packing view down the *a*-axis of the structure **2**, illustrating the stacking of the antiparallel chains along the *c*-axis. Donor-acceptor contacts are shown in dashed lines.

For **1**, three intermolecular donor-acceptor contacts are observed between donors ring C-H groups and *O*-carbonyl atoms. Two contacts are seen between neighbouring molecules within a chain and the third between two molecules from adjacent chains inside a sheet (Table 4). There are no donor-acceptor contacts between molecules lying in adjacent sheets.

A specific feature of structure **2** is the large contribution of the acetyl groups to the intermolecular donor-acceptor contacts (Table 5). Only one *O*-carbonyl atom is in contact with a ring C-H group. The other three *O*-carbonyl atoms are in contact with methyl groups of neighbouring molecules lying within a chain, inside a sheet or in adjacent sheets.

EXPERIMENTAL

Previous syntheses of β-D-galactopyranosyl isothiocyanate[21] and β-D-galactopyranosyl azide[22] from α-D-galactopyranosyl bromide were accomplished under phase transfer catalysis (PTC) conditions. This treatment of 2,3,4,6-tetra-*O*-acetyl-α-D-galactopyranosyl bromide with tetrabutylammonium bromide (TBAB) and KSCN or tetrabutylammonium hydrogen sulfate (TBAHS) and sodium azide in a liquid two-phase

Table 4. Intermolecular donor-acceptor contacts (<3.5Å) for **1**

	Donor	Acceptor	C...O	Symmetry codes
(2)	C1	O6B^{a}	3.142 (5)	a: -x, y+1/2, -z+1
(1)	C4	O4B^{b}	3.223 (3)	b: -x+1, y+1/2, -z+1
(1)	C5	O4B^{b}	3.357 (3)	
(2)	C3B	O5^{c}	3.422 (4)	c: x+1, y, z

(1) and (2) indicate contacts between molecules lying within a chain and inside a sheet, respectively. Calculated H···O separations range from 2.47 to 2.77Å, the calculated angles at H are close to 120°, except for the fourth contact (169°).

Table 5. Intermolecular donor-acceptor contacts (<3.5Å) for **2**

	Donor	Acceptor	C...O	Symmetry codes
(1)	C1	O3B^{a}	3.183 (8)	a: x-1/2, -y+3/2, -z+1
(1)	C2B	O6B^{b}	3.424 (9)	b: x+1/2, -y+3/2, -z+1
(3)	C2B	O2B^{c}	3.384 (8)	c: -x+1, y+1/2, -z+3/2
(2)	C3B	O6A^{d}	3.440 (8)	d: x+1/2, -y+1/2, -z+1/2
(2)	C4B	O4B^{e}	3.356 (9)	e: x-1/2, -y+1/2, -z+1
(3)	C4B	O2B^{f}	3.460 (8)	f: -x+1, y-1/2, -z+3/2

(1), (2) and (3) indicate contacts between molecules lying within a chain, inside a sheet and in adjacent sheets, respectively. Calculated H···O separations range from 2.48 to 2.68Å, except for the first contact (2.37Å); the calculated angles at H are greater than 136°.

system give their corresponding β-D-galactopyranosyl isothiocyanate and β-D-galactopyranosyl azide. These reactions occurred with complete anomeric inversion. No mixture of anomers could be detected by ^{1}H NMR spectroscopy; the stereochemistry at the C1 atom is β from the observed coupling constant 8.6 Hz.

Colourless crystals were grown by slow evaporation of a methanolic solution. They were sealed in the presence of the mother liquor in thin glass capillaries and mounted on an Enraf-Nonius CAD-4 diffractometer. Absorption effects were corrected by the ψ scan procedure.[23] Crystal data, data collection and structure refinement parameters are summarized in Table 6.[24]

Table 6. Crystal data from compounds **1** and **2**

	1	**2**
Molecular formula	$C_{15}H_{19}N\,O_9S$	$C_{14}H_{19}N_3\,O_9$
Molecular weight	389.4	373.3
Crystal system	Monoclinic	Orthorhombic
Space group	$P2_1$	$P2_12_12_1$
a (Å)	9.208 (2)	9.082 (2)
b (Å)	8.729 (2)	10.135(2)
c (Å)	12.652 (3)	20.001(5)
β°	107.00 (3)	
V (Å^3)	972.5 (4)	1840.9(7)
Z (molecules/cell)	2	4
Density (calculated, Mg.m^{-3})	1.330	1.347
Wavelength (Å)	0.71073	0.71073
Absorption coefficient (mm^{-1})	0.21	0.11
Temperature (K)	291	291
Crystal size (mm)	0.4 x 0.4 x 0.2	0.5 x 0.4 x 0.25
θmax(°)	27.25	22.5
Octants collected	-11,11; -11,11; 0,13	0,10; -11,0; 0,22
Reflections collected	4158	1404
Unique reflections	3973	1404
Observed reflections [I>2σ(I)]	3130	970
Refinement on	F^2	F^2
Final R_1 [I>2σ(I)]	0.051	0.048
R_1 (all data)	0.068	0.098
wR_2 (all data)	0.152	0.135
Goodness of fit on F^2	1.04	1.03
Data / Parameters	3968 / 263	1398 / 160
$\Delta\rho_{max}$, $\Delta\rho_{min}$ (e Å^{-3})	0.19, -0.20	0.24, -0.22

The two structures were solved by direct methods using the *SHELXS86* program package.[25] The absolute configuration was assigned to agree with the known chirality. The positions of the H atoms were first determined from successive difference syntheses. Then, the H atoms were included in further refinement calculations with idealized geometry and constrained to ride on their parent C atom; the C-H distances of ring and methylene C-H groups, and the torsion angles of the methyl groups were allowed to refine. The H atoms were assigned isotropic displacement parameters fixed at

Table 7. Fractional coordinates and equivalent isotropic displacement parameters (Å^2) for non-H atoms of compound **1** (Ueq is defined as one third of the trace of the orthogonalized Uq tensor).

Atoms	x	y	z	Ueq
C1	0.3242 (3)	0.6478 (4)	0.7779 (2)	0.066 (1)
C2	0.4804 (3)	0.5724 (3)	0.8076 (2)	0.057 (1)
C3	0.5313 (2)	0.5560 (3)	0.7055 (2)	0.053 (1)
C4	0.4107 (2)	0.4739 (3)	0.6147 (2)	0.054 (1)
C5	0.2596 (3)	0.5533 (4)	0.5967 (2)	0.063 (1)
C6	0.1267 (3)	0.4742 (5)	0.5180 (2)	0.082 (1)
O5	0.2204 (2)	0.5607 (2)	0.6971 (2)	0.069 (1)
N1	0.2665 (3)	0.6537 (4)	0.8699 (3)	0.093 (1)
C71	0.2468 (5)	0.6843 (5)	0.9494 (3)	0.070 (1)
S1	0.2240 (3)	0.7338 (3)	1.0605 (1)	0.154 (1)
O2A	0.5869 (2)	0.6686 (2)	0.8841 (2)	0.073 (1)
C2A	0.6303 (4)	0.6270 (5)	0.9926 (3)	0.086 (1)
C2B	0.7425 (5)	0.7394 (7)	1.0588 (4)	0.136 (2)
O2B	0.5776 (4)	0.5179 (4)	1.0273 (2)	0.117 (1)
O3A	0.6688 (2)	0.4702 (2)	0.7363 (1)	0.057 (1)
C3A	0.7690 (3)	0.4914 (4)	0.6784 (2)	0.070 (1)
C3B	0.8967 (4)	0.3819 (5)	0.7129 (4)	0.097 (1)
O3B	0.7527 (3)	0.5849 (4)	0.6080 (2)	0.105 (1)
O4A	0.3950 (2)	0.3191 (2)	0.6504 (1)	0.058 (1)
C4A	0.4726 (3)	0.2084 (3)	0.6156 (2)	0.064 (1)
C4B	0.4461 (5)	0.0569 (4)	0.6601 (3)	0.088 (1)
O4B	0.5505 (3)	0.2319 (3)	0.5572 (2)	0.084 (1)
O6A	0.1572 (2)	0.4652 (3)	0.4134 (2)	0.086 (1)
C6A	0.0429 (4)	0.4198 (4)	0.3291 (3)	0.093 (1)
C6B	0.0897 (7)	0.4066 (7)	0.2264 (3)	0.126 (2)
O6B	0.0790 (3)	0.3919 (5)	0.3392 (3)	0.139 (1)
C72	0.1923 (15)	0.6448 (14)	0.9246 (10)	0.073 (3)
S2	0.0947 (11)	0.6352 (11)	1.0026 (7)	0.193 (4)

1.2xUeq of their respective C atom. For **1**, all the non-H atoms were refined anisotropically. For **2**, due to the large number of parameters to be refined with respect to the number of observed structure factors, only O atoms were given anisotropic displacement parameters.

For **1**, during the course of the refinement, a significant peak (> 1eÅ^{-3}) was found on the difference synthesis map near the NCS group, at 1.48Å from the S atom

Table 8. Fractional coordinates and isotropic or equivalent isotropic displacement parameters (Å^2) for non-H atoms of compound **2** (Uiso for starred atoms, Ueq for others).

Atoms	x	y	z	U(iso/eq)
C1	0.4231 (7)	0.7389 (7)	0.5732 (3)	0.046 (2)*
C2	0.5393 (7)	0.6675 (6)	0.6161 (3)	0.043 (2)*
C3	0.6548 (7)	0.6059 (6)	0.5719 (3)	0.039 (2)*
C4	0.5842 (7)	0.5198 (6)	0.5176 (3)	0.041 (2)*
C5	0.4683 (7)	0.5984 (6)	0.4807 (3)	0.044 (2)*
C6	0.3829 (8)	0.5176 (7)	0.4308 (3)	0.053 (2)*
O5	0.3611 (4)	0.6503 (4)	0.5254 (2)	0.047 (1)
N1	0.3027 (6)	0.7956 (5)	0.6117 (3)	0.055 (1)*
N2	0.2367 (6)	0.7109 (6)	0.6458 (3)	0.060 (2)*
N3	0.1676 (8)	0.6470 (7)	0.6787 (3)	0.085 (2)*
O2A	0.6098 (5)	0.7677 (4)	0.6561 (2)	0.048 (1)
C2A	0.5718 (8)	0.7750 (7)	0.7211 (3)	0.050 (2)*
C2B	0.6439 (8)	0.8895 (7)	0.7539 (3)	0.064 (2)*
O2B	0.4896 (7)	0.7013 (5)	0.7478 (2)	0.077 (2)
O3A	0.7451 (5)	0.5239 (4)	0.6149 (2)	0.048 (1)
C3A	0.8836 (8)	0.4978 (7)	0.5918 (3)	0.050 (2)*
C3B	0.9556 (8)	0.3926 (7)	0.6322 (3)	0.067 (2)*
O3B	0.9367 (5)	0.5536 (5)	0.5461 (3)	0.073 (2)
O4A	0.5115 (5)	0.4091 (4)	0.5491 (2)	0.043 (1)
C4A	0.5792 (8)	0.2907 (7)	0.5454 (3)	0.049 (2)*
C4B	0.4922 (8)	0.1873 (7)	0.5796 (3)	0.064 (2)*
O4B	0.6944 (6)	0.2753 (5)	0.5179 (3)	0.077 (2)
O6A	0.4833 (6)	0.4432 (4)	0.3893 (2)	0.057 (1)
C6A	0.5309 (8)	0.5011 (7)	0.3327 (3)	0.053 (2)*
C6B	0.6393 (9)	0.4158 (8)	0.2976 (4)	0.081 (2)*
O6B	0.4898 (6)	0.6059 (5)	0.3142 (2)	0.072 (1)

(S1). This peak was interpreted as a result of a positional disorder of the S atom; therefore it was assigned to a second (S2) S atom site. Further refinement with fixed site occupancy factors, estimated from the relative heights of the electron density at 0.75 and 0.25 for S1 and S2, respectively, gave acceptable results for S1 and two close alternative positions could be discernable for the C atom (C71 and C72). For the final step, the major and minor sites of C and S atoms were refined anisotropically, in separate blocks, and the enlarged displacement ellipsoid for S2 reflects the "smeared-out" of the electron density resulting from the disorder, which did not affect the rest of the structure. Final difference synthesis map was featureless.

Final atomic coordinates and displacement parameters of the non-H atoms are given in Tables 7 and 8 for **1** and **2**, respectively. Refinement was carried out with the *SHELXL93* program.[26] Molecular graphics were performed by the *ORTEP-III* program.[27] The data of the referenced structures were retrieved from the *Cambridge Structural Database.*[28]

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