O52	0.0520 (5)	0.7630 (3)	−0.0497 (3)	0.0879 (11)
C52	−0.0103 (9)	0.6881 (5)	−0.1238 (6)	0.119 (3)
C6	0.2435 (5)	0.8402 (3)	0.1972 (4)	0.0489 (9)
S61	0.3733 (2)	0.75373 (8)	0.16581 (11)	0.0662 (3)
C61	0.5625 (6)	0.7720 (3)	0.2744 (5)	0.0695 (13)
C21	0.4714 (5)	1.0224 (3)	0.4379 (4)	0.0519 (10)
O2	0.4722 (4)	0.9864 (2)	0.5643 (3)	0.0621 (8)
C22	0.5573 (5)	1.1088 (3)	0.4555 (4)	0.0458 (9)
O221	0.5657 (4)	1.1471 (2)	0.3311 (2)	0.0582 (8)
C221	0.4875 (6)	1.2222 (3)	0.3073 (4)	0.0623 (12)
O222	0.4027 (5)	1.2543 (3)	0.3797 (4)	0.0957 (12)
C222	0.5212 (7)	1.2561 (5)	0.1780 (5)	0.108 (2)
C23	0.7391 (5)	1.0976 (2)	0.5173 (4)	0.0445 (9)
O231	0.8100 (3)	1.1806 (2)	0.5420 (2)	0.0491 (6)
C231	0.9579 (6)	1.1991 (3)	0.4978 (4)	0.0539 (11)
O232	1.0377 (4)	1.1490 (2)	0.4426 (4)	0.0819 (10)
C232	1.0066 (8)	1.2895 (4)	0.5223 (6)	0.085 (2)
C24	0.7457 (5)	1.0491 (3)	0.6435 (4)	0.0519 (10)
O241	0.9238 (4)	1.0278 (2)	0.6810 (3)	0.0680 (9)
C241	0.9775 (6)	1.0251 (4)	0.8085 (6)	0.0753 (15)
O242	0.8848 (5)	1.0384 (4)	0.8884 (4)	0.1063 (14)
C242	1.1610 (7)	1.0024 (5)	0.8330 (7)	0.122 (3)
C25	0.6431 (6)	0.9677 (3)	0.6206 (5)	0.0659 (13)

Table 4. *Selected geometric parameters (Å, °) for* (IV)

N1—C2	1.323 (5)	C4—C5	1.391 (6)
N1—C6	1.353 (5)	C4—C41	1.540 (6)
N2—C2	1.396 (5)	C5—C6	1.408 (6)
C2—C3	1.418 (6)	C5—C51	1.525 (6)
N2—C21	1.448 (5)	S61—C6	1.752 (4)
C3—C4	1.393 (6)	S61—C61	1.823 (5)
C2—N1—C6	117.6 (3)	C3—C4—C41	122.1 (4)
N1—C2—N2	115.8 (3)	C4—C5—C6	117.2 (3)
N1—C2—C3	122.5 (3)	C4—C5—C51	120.4 (4)
N2—C2—C3	121.7 (3)	C6—C5—C51	122.3 (4)
C2—N2—C21	124.3 (3)	N1—C6—C5	124.4 (4)
C2—C3—C4	119.3 (4)	N1—C6—S61	116.4 (3)
C3—C4—C5	119.0 (4)	S61—C6—C5	119.2 (3)
C5—C4—C41	118.9 (4)	C6—S61—C61	102.8 (2)
C5—C4—C41—O41	−11.7 (7)	C22—O221—C221—O222	−6.0 (7)
C4—C5—C51—O51	−76.9 (6)	C23—O231—C231—O232	−2.9 (6)
N1—C6—S61—C61	7.1 (4)	C24—O241—C241—O242	0.9 (8)

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
N2—H2···O232^{i}	0.86	2.11	2.913 (5)	157

Symmetry code: (i) $x-1, y, z$.

It was not possible to determine the absolute configuration of molecules (III) and (IV) from the X-ray data, but the absolute configuration of the β-D-xylopyranosyl moiety was known from the synthetic work and the coordinates were chosen to have this known configuration. The diagram of (IV) (Fig. 1) was prepared using *ORTEP*II (Johnson, 1976) as implemented in *PLATON* (Spek, 1995*a*). The packing diagram (deposited figure) of (III) was prepared using *PLUTON* (Spek, 1995*b*). Examination of the structures with *PLATON* showed that there were no solvent-accessible voids in the crystal lattices.

For both compounds, data collection: *CAD*-4/*PC Software* (Enraf–Nonius, 1992); cell refinement: Enraf–Nonius *SET*4 (de Boer & Duisenberg, 1984) and *CELDIM*; data reduction: *DATRD*2 in *NRCVAX*94 (Gabe, Le Page, Charland, Lee & White, 1989); program(s) used to solve structures: *SOLVER* in *NRCVAX*; program(s) used to refine structures: *NRCVAX*94 and *SHELXL*93 (Sheldrick, 1993); molecular graphics: *NRCVAX*94, *PLATON* and *PLUTON*; software used to prepare material for publication: *NRCVAX*94, *SHELXL*93 and WordPerfect.

GF thanks NSERC (Canada) for Research Grants.

Lists of structure factors, anisotropic displacement parameters, H-atom coordinates, complete geometry and torsion angles, together with a displacement ellipsoid plot (30% probability) and a packing diagram for compound (III), have been deposited with the IUCr (Reference: AB1310). Copies may be obtained through The Managing Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

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2-Methylthio-5-nitroso-6-*N*-(2,3,4-tri-*O*-acetyl-β-D-xylopyranosyl)amino-4(3*H*)-pyrimidinone

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Abstract

The title compound, $C_{16}H_{20}N_4O_9S$, has a strong intramolecular N—H···O hydrogen bond between the nitrosyl O atom and an adjacent N—H moiety [N···O 2.516 (8) Å]. The β-D-xylopyranosyl ring has a $^4C_1$ conformation, with all non-H substituents in equatorial positions. Molecules are linked about 2_1 axes *via* intermolecular N—H···O hydrogen bonds [N···O 2.892 (8) Å].

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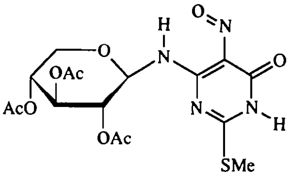
Comment

5-Nitroso-6-glycosylaminopyrimidine derivatives are of interest both because of their biological activity and their use as intermediates in the synthesis of other nucleoside derivatives derived from purine, such as 8-azapurine (Nogueras, Quijano, Sánchez & Melgarejo, 1989), pteridine and 8-aminopurine (Melguizo, Nogueras & Sánchez, 1992). We report here on the structure of 2-methylthio-5-nitroso-6-*N*-(2,3,4-tri-*O*-acetyl-β-D-xylopyranosyl)amino-4(3*H*)-pyrimidinone, (I).



(I)

A view of the molecule of (I) is shown in Fig. 1. The pyrimidine ring is planar to within 3σ and the conformation of the xylopyranoside ring is the usual $^4C_1$; the β configuration at the anomeric centre was known from the synthesis. The 5-nitroso and 2-methylthio groups are close to being coplanar with the pyrimidine ring (torsion angles are given in Table 2) and in the β-D-xylopyranosyl ring, the conformation of the acetyl side groups is as is usually found, with the carbonyl group *cis* to a C—H group of an adjacent ring. The nitroso geometry [N—O 1.288 (9) Å and C—N—O 116.2 (6)°] is very similar to that reported for 6-amino-1,3-dimethyl-5-nitrosouracil [N—O 1.281 (4) Å and C—N—O 119.1 (3)°; Low, Howie, Hueso-Ureña & Moreno-Carretero, 1992].

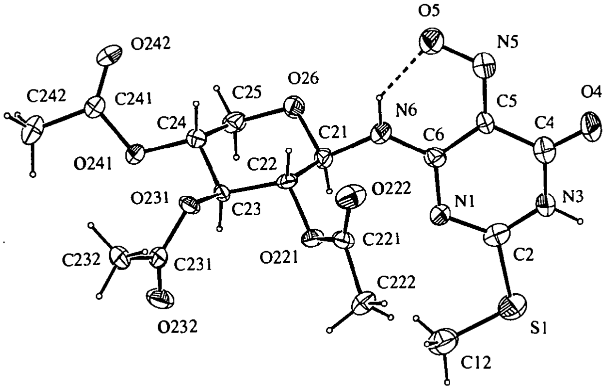


Fig. 1. The molecular structure of (I) with the atomic numbering scheme. Displacement ellipsoids are drawn at the 30% probability level.

The molecular conformation is determined by a strong intramolecular N—H···O hydrogen bond (Table 2) between the H atom on the amino N6 atom and the nitrosyl O5 atom; the H atom on N6 was unambiguously located from a $\Delta\rho$ in the relevant plane. Molecules are also linked into infinite spirals about a 2_1 screw axis by N—H···O hydrogen bonds between N3—H3 and the carbonyl O222 atom of an adjacent molecule (Table 2).

Experimental

The title compound was prepared according to Nogueras, López, Gutiérrez & Sánchez (1988). Recrystallization from ethanol gave blue needles.

Crystal data

$C_{16}H_{20}N_4O_9S$
$M_r = 444.42$
Orthorhombic
$P2_12_12_1$
$a = 6.9874$ (4) Å
$b = 10.647$ (2) Å
$c = 27.0341$ (16) Å
$V = 2011.1$ (4) Å^3
$Z = 4$
$D_x = 1.468$ Mg m^{-3}
D_m not measured

Mo $K\alpha$ radiation
$\lambda = 0.7107$ Å
Cell parameters from 25 reflections
$\theta = 6.15$–12.15°
$\mu = 0.219$ mm^{-1}
$T = 294$ (1) K
Needle
0.43 × 0.28 × 0.10 mm
Blue

Data collection

Enraf–Nonius CAD-4 diffractometer
$\theta/2\theta$ scans
Absorption correction: none
2520 measured reflections
2520 independent reflections
1099 observed reflections [$I > 2\sigma(I)$]

$\theta_{max} = 26.9°$
$h = 0 \rightarrow 8$
$k = 0 \rightarrow 13$
$l = 0 \rightarrow 34$
3 standard reflections
frequency: 120 min
intensity decay: 2.7%

Refinement

Refinement on F^2
$R(F) = 0.0575$
$wR(F^2) = 0.1967$
$S = 0.913$
2520 reflections
273 parameters
H atoms riding (*SHELXL*93 defaults, C—H 0.96–0.98, N—H 0.86 Å)
$w = 1/[\sigma^2(F_o^2) + (0.1176P)^2]$ where $P = (F_o^2 + 2F_c^2)/3$

$(\Delta/\sigma)_{max} = 0.001$
$\Delta\rho_{max} = 0.475$ e Å^{-3}
$\Delta\rho_{min} = -0.388$ e Å^{-3}
Atomic scattering factors from *International Tables for Crystallography* (1992, Vol. C, Tables 4.2.6.8 and 6.1.1.4)
Absolute configuration: Flack (1983) parameter = 0.3 (3)

Table 1. *Fractional atomic coordinates and equivalent isotropic displacement parameters* (Å^2)

$$U_{eq} = (1/3)\Sigma_i\Sigma_j U_{ij}a_i^*a_j^*\mathbf{a}_i.\mathbf{a}_j.$$

	x	y	z	U_{eq}
N1	0.7834 (9)	0.6249 (5)	0.2038 (2)	0.041 (2)
C2	0.7865 (11)	0.5280 (7)	0.2354 (3)	0.046 (2)
S1	0.8423 (4)	0.3778 (2)	0.21509 (10)	0.0654 (7)
C12	0.8306 (18)	0.3906 (8)	0.1517 (4)	0.077 (3)
N3	0.7478 (11)	0.5338 (6)	0.2833 (2)	0.050 (2)
C4	0.6912 (13)	0.6387 (8)	0.3068 (3)	0.052 (2)
O4	0.6446 (12)	0.6356 (5)	0.3503 (2)	0.075 (2)
C5	0.6887 (12)	0.7512 (7)	0.2761 (2)	0.038 (2)
N5	0.6458 (11)	0.8596 (7)	0.3003 (3)	0.056 (2)

O5	0.6418 (10)	0.9600 (5)	0.2737 (2)	0.063 (2)
C6	0.7380 (11)	0.7380 (6)	0.2253 (3)	0.037 (2)
N6	0.7360 (10)	0.8397 (5)	0.1974 (2)	0.042 (2)
C21	0.7855 (11)	0.8507 (6)	0.1453 (2)	0.034 (2)
C22	0.6034 (10)	0.8676 (6)	0.1141 (2)	0.031 (2)
O221	0.5107 (8)	0.7472 (4)	0.1101 (2)	0.0382 (12)
C221	0.3451 (13)	0.7280 (6)	0.1347 (3)	0.041 (2)
O222	0.2721 (9)	0.8043 (5)	0.1597 (2)	0.063 (2)
C222	0.2668 (14)	0.6011 (6)	0.1243 (3)	0.056 (2)
C23	0.6530 (11)	0.9100 (6)	0.0620 (2)	0.028 (2)
O231	0.4745 (7)	0.9412 (4)	0.0380 (2)	0.0362 (12)
C231	0.4327 (12)	0.8847 (7)	−0.0049 (3)	0.039 (2)
O232	0.5260 (10)	0.8002 (5)	−0.0226 (2)	0.057 (2)
C232	0.2608 (13)	0.9428 (8)	−0.0282 (3)	0.051 (2)
C24	0.7753 (11)	1.0225 (6)	0.0643 (2)	0.035 (2)
O241	0.8220 (8)	1.0550 (4)	0.0138 (2)	0.0396 (13)
C241	0.8555 (13)	1.1788 (7)	0.0042 (3)	0.043 (2)
O242	0.8753 (11)	1.2541 (5)	0.0360 (2)	0.070 (2)
C242	0.8732 (14)	1.2017 (8)	−0.0494 (3)	0.057 (2)
C25	0.9526 (12)	0.9925 (7)	0.0937 (3)	0.046 (2)
O26	0.8952 (8)	0.9627 (5)	0.1434 (2)	0.0444 (14)

Table 2. *Selected geometric parameters (Å, °)*

N1—C2	1.338 (10)	C4—C5	1.456 (11)
N1—C6	1.374 (9)	C5—N5	1.360 (10)
C2—N3	1.325 (10)	C5—C6	1.422 (10)
C2—S1	1.735 (8)	N5—O5	1.288 (9)
S1—C12	1.722 (10)	C6—N6	1.319 (9)
N3—C4	1.345 (10)	N6—C21	1.455 (9)
C4—O4	1.222 (9)		
C2—N1—C6	114.3 (6)	N5—C5—C6	127.0 (7)
N3—C2—N1	125.7 (7)	N5—C5—C4	115.2 (6)
N3—C2—S1	113.4 (6)	C6—C5—C4	117.8 (7)
N1—C2—S1	120.9 (6)	O5—N5—C5	116.2 (6)
C12—S1—C2	103.4 (4)	N6—C6—N1	118.8 (6)
C2—N3—C4	124.1 (7)	N6—C6—C5	117.9 (7)
O4—C4—N3	120.7 (8)	N1—C6—C5	123.3 (6)
O4—C4—C5	124.6 (8)	C6—N6—C21	128.0 (6)
N3—C4—C5	114.7 (7)		

N1—C2—S1—C12	−12.8 (9)
C6—C5—N5—O5	3.1 (13)
C22—O221—C221—O222	−0.5 (10)
C23—O231—C231—O232	7.4 (10)
C24—O241—C241—O242	11.4 (13)

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
N3—H3···O222^{i}	0.86	2.05	2.892 (8)	168
N6—H6···O5	0.86	1.81	2.516 (8)	138

Symmetry codes: (i) $1 - x, y - \frac{1}{2}, \frac{1}{2} - z$.

It was not possible to determine the absolute configuration of the title molecule from the X-ray data, but the absolute configuration of the β-D-xylopyranosyl moiety was known from the synthetic work and the coordinates were chosen to have this known configuration. Difference maps showed that the methyl H atoms at C12 and C242 were disordered. This was allowed for by placing six 0.5 occupancy H atoms in appropriate positions at each atom. The diagram (Fig. 1) was prepared using *ORTEP*II (Johnson, 1976) as implemented in *PLATON* (Spek, 1995*a*). Examination of the structure with *PLATON* showed that there were no solvent accessible voids in the crystal lattice.

Data collection: *CAD*-4/*PC Software* (Enraf–Nonius, 1992). Cell refinement: Enraf–Nonius *SET*4 (de Boer & Duisenberg, 1984) and *CELDIM*. Data reduction: *DATRD*2 *NRCVAX*94 (Gabe, Le Page, Charland, Lee & White, 1989). Program(s) used to solve structure: *SOLVER NRCVAX*. Program(s) used to refine structure: *NRCVAX*94; *SHELXL*93 (Sheldrick, 1993). Molecular graphics: *NRCVAX*94; *PLATON*; *PLUTON* (Spek 1995*b*). Software used to prepare material for publication: *NRCVAX*94; *SHELXL*93 and WordPerfect.

GF thanks NSERC (Canada) for Research Grants.

Lists of structure factors, anisotropic displacement parameters, H-atom coordinates, complete geometry and torsion angles, together with a view of (I) in the (100) projection, have been deposited with the IUCr (Reference: AB1309). Copies may be obtained through The Managing Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

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5-Hexylamino-1,2-benzoquinone 2-Oxime Monohydrate

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Abstract

In $C_{12}H_{18}N_2O_2.H_2O$, the oximic OH group is *anti* (*trans*) to the quinoid carbonyl group, thus there are no intramolecular hydrogen bonds in the molecule. Extensive intermolecular interactions between neighbouring quinone oxime molecules and associated water molecules are observed. Bond distances are intermediate between those predicted for the 1,2-quinone oxime and 2,5-oxime imino forms.

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