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6-Acetamido-4-methoxy-2-methylthiopyrimidine

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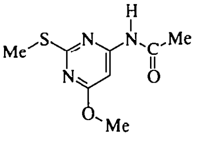
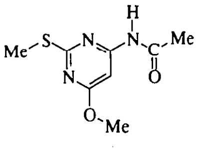
Abstract

Molecules of the title compound, 4-methoxy-2-methylthio-6-pyrimidinylacetamide, $C_8H_{11}N_3O_2S$, lie on crystallographic mirror planes and are linked by N—H···O hydrogen bonds to form zigzag ribbons running parallel to the *a* axis, with an N···O distance of 3.018 (2) Å.

Comment

Derivatives of 6-aminopyrimidines are of interest because of both their biological activity (Cobo, 1995) and their use as intermediates in the synthesis of other nucleoside derivatives (Low *et al.*, 1996). Our analysis of the title compound, (1), is part of a series of such studies.


(1*a*)


(1*b*)

Apart from the methyl H atoms, all the atoms of the molecule (Fig. 1) lie on a crystallographic mirror plane. Molecular dimensions (Table 2) are consistent with equal contributions from resonance forms (1*a*) and (1*b*), and are in agreement with dimensions reported for the parent compound 6-amino-4-methoxy-2-methylthiopyrimidine (Low *et al.*, 1996).

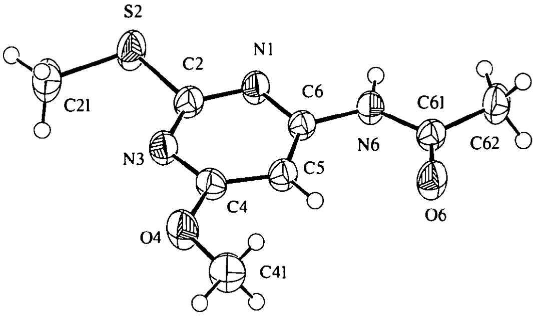


Fig. 1. A view of (1) with the atomic numbering scheme. Displacement ellipsoids are drawn at the 30% probability level. Only one orientation of the disordered H atoms on C62 is shown.

Molecules of (1) are linked into zigzag chains by N—H···O hydrogen bonds (Fig. 2 and Table 2) extending along the **a** direction. There is also a short C—H···O intramolecular contact between the H atom on the C5 atom and the adjacent carbonyl O6 atom. These links serve to keep the structure fairly rigid and explain why the data collection was able to obtain measurable reflections up to a θ value of 30° with Mo radiation.

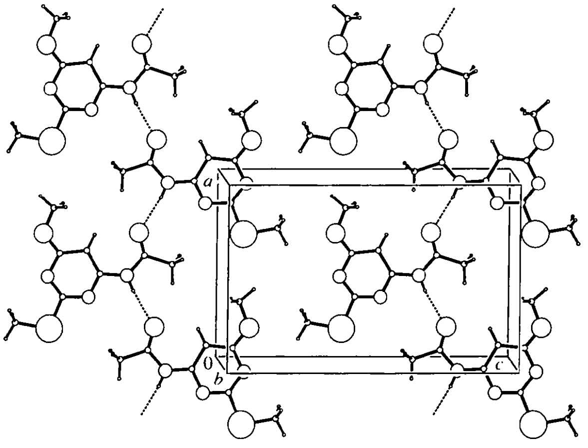


Fig. 2. A view of part of the the crystal structure of (1) showing the hydrogen-bonded chains.

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Experimental

Compound (1) was obtained by acetylation of 6-amino-4-methoxy-2-methylthiopyrimidine (Low *et al.*, 1996) (0.800 g, 5.16 mmol) in a mixture of acetic anhydride (8 ml) and pyridine (8 ml) heated at 333 K for 22 h. The solvent was evaporated under reduced pressure and the remaining residue co-evaporated three times with absolute ethanol. The resulting solid residue was recrystallized from ethanol (12 ml) to give 0.579 g (2.72 mmol, 53%) of crystalline 6-acetamido-4-methoxy-2-methylthiopyrimidine; m.p. 435 K (uncorrected); ^{1}H NMR ($CDCl_3$, 60 MHz, δ in p.p.m. from TMS): 2.19 (*s*, 3H, acetyl), 2.52 (*s*, 3H, methylthio), 3.97 (*s*, 3H, methoxy), 7.24 (*s*, 1H, C5H), 8.15 (broad *s*, 1H, D_2O exchangeable, 4-NH); IR (cm^{-1}, solid, KBr pellet): 3304, 3020, 2954, 2939, 1671, 1593, 1562, 1519, 1469, 1377, 1295, 1263, 1186, 1161; UV-Vis (MeOH, $c = 4.5 \times 10^{-5}$ M), λ (nm)(log *E*): 230(4.42), 247(4.12, shoulder), 272(3.77, shoulder). A subsequent recrystallization from methanol afforded large prisms suitable for X-ray diffraction. The IR spectrum was recorded with an FT-IR Perkin–Elmer 1760X spectrophotometer, the UV-Vis spectrum was obtained with a GBC-911 instrument, the melting point was measured in an Electrothermal 9300 device and the ^{1}H NMR spectra were recorded on a Hitachi–Perkin–Elmer R-600 system.

Crystal data

$C_8H_{11}N_3O_2S$
$M_r = 213.26$
Orthorhombic
Pnma
$a = 9.6850\ (6)$ Å
$b = 6.7980\ (7)$ Å
$c = 15.1829\ (13)$ Å
$V = 999.62\ (15)$ Å^3
$Z = 4$
$D_x = 1.417$ Mg m^{-3}
D_m not measured

Mo $K\alpha$ radiation
$\lambda = 0.7107$ Å
Cell parameters from 25 reflections
$\theta = 12.30$–$22.30°$
$\mu = 0.302$ mm^{-1}
$T = 294\ (1)$ K
Needle
$0.41 \times 0.24 \times 0.24$ mm
Colorless

Data collection

Enraf–Nonius CAD-4 diffractometer
$\theta/2\theta$ scans
Absorption correction: none
1565 measured reflections
1565 independent reflections
924 observed reflections $[I > 2\sigma(I)]$

$\theta_{max} = 30°$
$h = 0 \rightarrow 13$
$k = 0 \rightarrow 9$
$l = 0 \rightarrow 21$
3 standard reflections
frequency: 120 min
intensity variation: 1.6%

Refinement

Refinement on F^2
$R(F) = 0.0367$
$wR(F^2) = 0.1088$
$S = 0.996$
1565 reflections
86 parameters
H atoms riding (*SHELXL*93 defaults; C—H 0.93–0.98, N—H 0.86 Å)
$w = 1/[\sigma^2(F_o^2) + (0.0650P)^2]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max} = -0.019$

$\Delta\rho_{max} = 0.360$ e Å^{-3}
$\Delta\rho_{min} = -0.207$ e Å^{-3}
Extinction correction: *SHELXL*93
Extinction coefficient: 0.0069 (16)
Atomic scattering factors from *International Tables for Crystallography* (1992, Vol. C, Tables 4.2.6.8 and 6.1.1.4)

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	−0.1666 (2)	1/4	−0.05244 (10)	0.0369 (4)
C2	−0.1651 (2)	1/4	0.03566 (13)	0.0364 (4)
S2	−0.33175 (6)	1/4	0.08059 (3)	0.0499 (2)
C21	−0.2992 (3)	1/4	0.19692 (14)	0.0563 (7)
N3	−0.0563 (2)	1/4	0.08831 (9)	0.0393 (4)
C4	0.0659 (2)	1/4	0.04767 (12)	0.0370 (5)
O4	0.17188 (15)	1/4	0.10423 (10)	0.0517 (5)
C41	0.3088 (2)	1/4	0.0702 (2)	0.0540 (7)
C5	0.0808 (2)	1/4	−0.04359 (11)	0.0369 (5)
C6	−0.0418 (2)	1/4	−0.09083 (11)	0.0333 (4)
N6	−0.0503 (2)	1/4	−0.18243 (9)	0.0370 (4)
C61	0.0553 (2)	1/4	−0.24246 (12)	0.0361 (5)
C62	0.0083 (2)	1/4	−0.33674 (12)	0.0505 (6)
O6	0.17653 (14)	1/4	−0.22192 (9)	0.0508 (5)

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

N1—C6	1.342 (2)	O4—C41	1.423 (2)
C2—N3	1.323 (3)	C5—C6	1.387 (2)
C2—S2	1.752 (2)	C6—N6	1.393 (2)
S2—C21	1.794 (2)	N6—C61	1.370 (2)
N3—C4	1.335 (3)	C61—O6	1.215 (2)
C4—O4	1.338 (2)	C61—C62	1.502 (3)
C4—C5	1.393 (2)		
C2—N1—C6	115.1 (2)	C4—O4—C41	118.8 (2)
N3—C2—N1	127.8 (2)	C4—C5—C6	115.2 (2)
N3—C2—S2	119.91 (14)	N1—C6—C5	123.1 (2)
N1—C2—S2	112.31 (14)	N1—C6—N6	112.4 (2)
C2—S2—C21	102.78 (11)	C5—C6—N6	124.5 (2)
C2—N3—C4	115.3 (2)	C61—N6—C6	128.3 (2)
N3—C4—O4	112.5 (2)	O6—C61—N6	123.4 (2)
N3—C4—C5	123.5 (2)	O6—C61—C62	122.5 (2)
O4—C4—C5	124.0 (2)	N6—C61—C62	114.1 (2)

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
N6—H6···O6^{i}	0.86	2.17	3.018 (2)	171
C5—H5···O6	0.93	2.30	2.862 (2)	119

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

Examination of $\Delta\rho$ maps in the expected planes of the methyl H atoms showed that the C62 methyl H atoms were disordered. This was allowed for using the AFIX123 command in the *SHELXL*93 refinement (Sheldrick, 1993). The *ORTEP* diagram (Fig. 1) was prepared using *ORTEP*II (Johnson, 1976) as implemented in *PLATON* (Spek, 1995*a*). The packing diagram (Fig. 2) was produced using *PLUTON* (Spek, 1995*b*). 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: *SET*4 and *CELDIM* in *CAD*-4/*PC Software*. Data reduction: *DATRD*2 in *NRCVAX*94 (Gabe, Le Page, Charland, Lee & White, 1989). Program(s) used to solve structure: *SOLVER* in *NRCVAX*.

GF thanks NSERC (Canada) for Research Grants and JNL thanks Mr Richard Guy of the High School of Dundee for his enthusiastic contribution to the solution of this structure.

Lists of structure factors, anisotropic displacement parameters, H-atom coordinates, complete geometry and torsion angles have been deposited with the IUCr (Reference: AB1363). Copies may be obtained through The Managing Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

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17α-Benzyl-17β-hydroxy-16-hydroxyimino-3-methoxyestra-1,3,5(10)-triene

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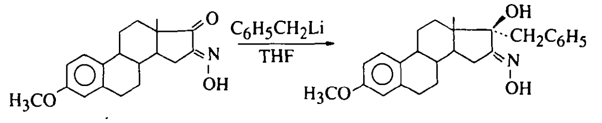
Abstract

The asymmetric unit of the title compound, 17α-benzyl-16-hydroxyimino-3-methoxyestra-1,3,5(10)-trien-17β-ol, $C_{26}H_{31}NO_3$, contains two molecules which differ in the orientations of the methoxy groups at C(3). The 17-hydroxy and 16-hydroxyimino moieties are involved in intramolecular N···O and intermolecular N···O and O···O hydrogen bonds. The hydrogen-bond network accounts for the differences in bond and torsion angles of the α-hydroxyimino moieties of the symmetry-independent molecules. This has been confirmed by molecular-mechanics calculations on the individual molecules which indicate that they have the same geometry in their energy minimum states.

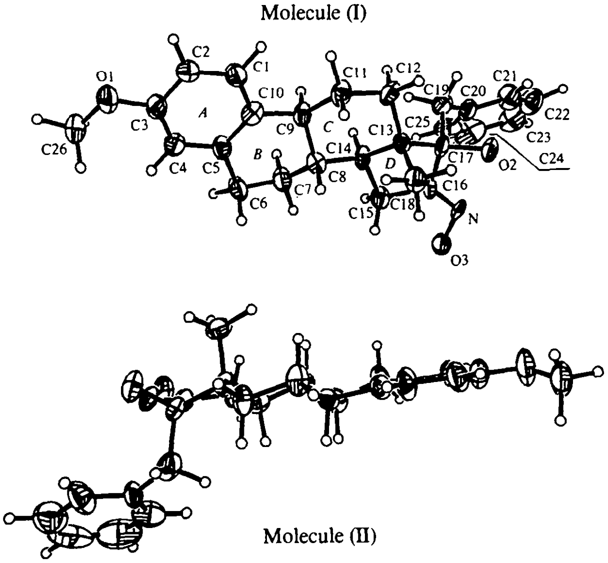
Comment

As a part of our study of the Beckmann fragmentation reaction in a series of steroidal tertiary α-hydroxyimino alcohols, the synthesis of 17α-benzyl-17β-hydroxy-16-hydroxyimino-3-methoxyestra-1,3,5(10)-triene, (2), was performed (Miljković, Gaši, Medić-Mijačević, Stanković & Lazar, 1995). Regioselective addition of benzyllithium to the 17-carbonyl group of 16-hydroxyimino-3-methoxyestra-1,3,5(1)-triene-17-one, (1), afforded the title compound, (2). Its structure, deduced from chemical spectroscopic evidence, was confirmed by X-ray diffraction analysis.



(1) (2)

Perspective views of the two symmetry-independent molecules, (I) and (II), of compound (2) are shown in Fig. 1. Selected geometric parameters are given in Table 2, together with corresponding values (in square brackets) obtained from molecular-mechanics calculations. The puckering (Cremer & Pople, 1975) and asymmetry parameters (Duax, Weeks & Rohrer, 1976) listed in Table 3 reveal usual ring conformations. Ring *B* has a 7α,8β-half-chair conformation; the distances of atoms C(7) and C(8) from the best plane of the remaining four atoms are −0.369 (7) and 0.413 (6) Å, respectively, for molecule (I), and −0.319 (7) and 0.437 (6) Å for molecule (II). Ring *C* has a chair conformation, while ring *D* exhibits a conformation between a 13β-envelope [the distance of atom C(13) from the best


Molecule (I)

Molecule (II)

Fig. 1. A perspective view of the two symmetry-independent molecules, (I) and (II), of the title compound. Displacement ellipsoids are plotted at the 40% probability level.