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Lists of structure factors, anisotropic displacement parameters, H-atom coordinates and complete geometry have been deposited with the IUCr (Reference: AL566). Copies may be obtained through The Managing Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

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5-Acetyl-4-methyl-2-pyrimidinylhydrazine and 5-(1-Hydrazonoethyl)-4-methyl-2-pyrimidinylhydrazine, $C_7H_{10}N_4O$ and $C_7H_{12}N_6$

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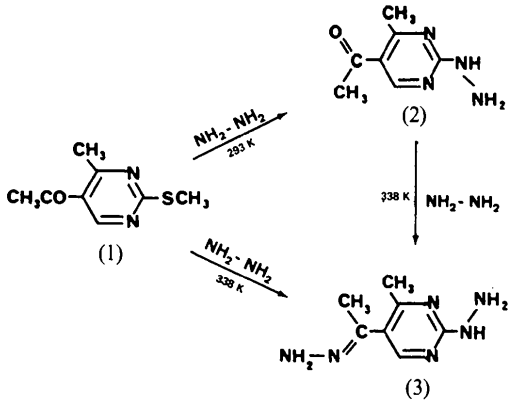
Abstract

5-Acetyl-4-methyl-2-pyrimidinylhydrazine is planar but its hydrazone is not. Distortions observed in the hydrazone are due to the presence of two methyl groups on the same side of the molecule.

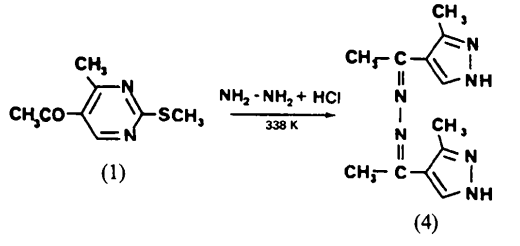
Comment

5-Acetyl-4-methyl-2-methylthiopyrimidine (1) reacted with an excess of hydrazine in methanolic solution at room temperature to form 5-acetyl-4-methyl-2-pyrimidinylhydrazine (2). This is insoluble in methanol at this temperature and therefore cannot be transformed directly into its hydrazone, 5-(1-hydrazonoethyl)-4-methyl-2-pyrimidinylhydrazine (3). However, the reaction of (1) with hydrazine at 338 K led directly to (3); this could also be prepared

by dissolving (2) in boiling methanol and reacting with hydrazine (Menichi, Boutar, Kokel, Takagi & Hubert-Habart, 1986).



Compounds (2) and (3) are the likely intermediates in the formation of 4-acetyl-3-methylpyrazole azine (4) which is readily obtained from a mixture of (1) and an excess of hydrazine kept in boiling acidic methanol solution for several hours (Menichi *et al.*, 1986).



The above hypothesis is based on experimental evidence from similar transformations of 5-acylpyrimidines into 4-acylpyrazoles by reaction with various hydrazine derivatives; formation of the corresponding 5-acylpyrimidine hydrazones has proved to be the intermediate step of this ring contraction (Bajnati & Hubert-Habart, 1988; Bajnati, Hubert-Habart, Takagi & Terada, 1989; Takagi, Bajnati, Hubert-Habart & Terada, 1990; Takagi, Bajnati & Hubert-Habart, 1990; Cousson, Nectoux, Bachet, Kokel & Hubert-Habart, 1994).

Compound (3) can also be considered as a 'stiffened' analogue of 1,7-diamino-3-azaheptane, a norspermidine-like molecule. In view of this and following our previous work on analogues of polyamines and mitoguazone, an anticancer drug (Cousson, Robert & Hubert-Habart, 1991; Cousson, Bachet, Kokel & Hubert-Habart, 1991, 1993), we determined the structures of the pyrimidines (2) and (3).

In molecules (2) and (3), the N(4)—N(5) and C(1)—C(2) bonds are located on the same side of the C(1)–N(4) axis. However, in (2) the C(4)—C(5) bond is on the opposite side of this axis, while in (3) all three bonds are on the same side. In (3) the N(2)—C(1) bond [1.279 (1) Å] has almost pure double-bond character with a *trans* (*E*) environment. The corresponding O(1)—C(1) bond [1.219 (2) Å] in (2) is typical of a carbonyl double bond.

Molecule (2) is planar while (3) is not; the C(4)—C(3)—C(1)—C(2) torsion angle is −175.6 (2) in (2) and 45.9 (5)° in (3), while C(4)—C(3)—C(1)—O(1) is 3.2 (3)° in (2) and the corresponding angle in (3), C(4)—C(3)—C(1)—N(2), is −135.4 (4)°. In molecule (3) the largest deviations from the best plane through the non-H atoms are −0.844 and −0.424 Å for C(2) and N(5), respectively. Even when these atoms are excluded, the rest of the molecule is far from planar with most of the atoms deviating from the best plane

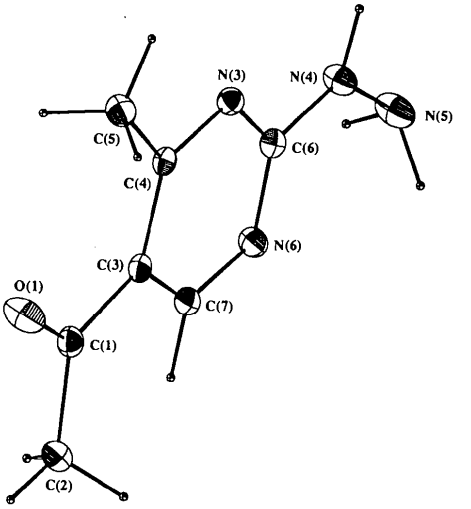


Fig. 1. *ORTEP* (Johnson, 1965) plot of (2). Displacement ellipsoids are drawn at the 50% probability level.

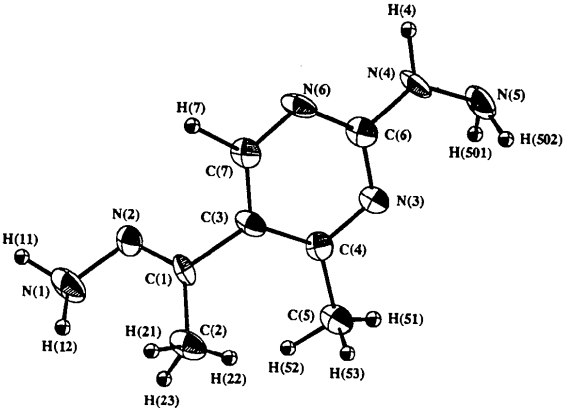


Fig. 2. *ORTEP* (Johnson, 1965) plot of (3). Displacement ellipsoids are drawn at the 50% probability level.

by 0.35 Å. These distortions could be due to steric effects caused by the presence of two methyl groups on the same side of the molecule. In (2) the largest deviation from the mean plane is 0.08 Å. The H atoms at N(5) are located on either side of and at equal distances (0.7 Å) from the mean plane of the molecule.

The structures of the compounds are composed of stacks of parallel planes of molecules and crystalline cohesion is due mainly to van der Waals contacts. In (2) the shortest distances between adjacent molecules are N(3)···N(4)($1-x$, $1-y$, $2-z$) = 3.041 (2) Å, where a hydrogen bond may be assumed [N(4)—H(4) 1.001 (2), N(3)···H(4) 2.042 (2) Å, N(3)—H(4)···N(4) 176.07 (11)°], N(5)···O(1)(x, $-y$, $z+\frac{1}{2}$) = 3.110 (2) and C(6)···N(4)(x, $y-1$, z) = 3.431 (3) Å. In (3) the shortest distances are N(4)···N(6)($1-x$, $2-y$, $1-z$) = 3.041 (4) Å [N(4)—H(4) 1.094 (3), N(6)···H(4) 1.977 (3) Å, N(4)—H(4)···N(6) 163.13 (18)°], N(1)···N(3)(x, $y-1$, z) = 3.215 (4) Å [N(1)—H(12) 0.985 (3), N(3)···H(12) 2.271 (3) Å, N(1)—H(12)···N(3) 172.86 (19)°], N(1)···N(5)(x, $y-1$, z) = 3.607 (4), N(1)···N(5)($2-x$, $2-y$, $2-z$) = 3.331 (5) and N(2)···N(3)($2-x$, $2-y$, $2=z$) = 3.457 (4) Å.

Experimental

Pyrimidines (2) and (3) were prepared using the method of Menichi, Boutar, Kokel, Takagi & Hubert-Habart (1986) and were recrystallized from methanol.

Compound (2)

Crystal data

$C_7H_{10}N_4O$
M_r = 166.18
Monoclinic
$C2/c$
a = 22.391 (9) Å
b = 3.876 (3) Å
c = 17.683 (7) Å
β = 90.12 (3)°
V = 1534 (3) Å^3
Z = 8
D_x = 1.439 Mg m^{-3}
Cu $K\alpha$ radiation
λ = 1.5418 Å
Cell parameters from 25 reflections
θ = 18–20°
μ = 0.810 mm^{-1}
T = 293 K
Prism
0.3 × 0.25 × 0.2 mm
Colourless

Data collection

Philips PW1100 diffractometer
ω–2θ scans
Absorption correction: empirical
T_{min} = 0.777, T_{max} = 0.965
3202 measured reflections
2758 independent reflections
1172 observed reflections [$I \geq 3\sigma(I)$]
R_{int} = 0.032
θ_{max} = 67°
$h = -26 \rightarrow 26$
$k = 0 \rightarrow 4$
$l = 0 \rightarrow 20$
3 standard reflections
frequency: 60 min
intensity variation: <0.02%

Refinement

Refinement on F
R = 0.038
wR = 0.039
S = 1.5
1172 reflections
111 parameters
Only H-atom U's refined
Unit weights applied
$(\Delta/\sigma)_{max}$ = 0.003
$\Delta\rho_{max}$ = 0.1 e Å^{-3}
$\Delta\rho_{min}$ = −0.2 e Å^{-3}
Extinction correction: Larson (1970)
Extinction coefficient: 27 (1)
Atomic scattering factors from *International Tables for X-ray Crystallography* (1974, Vol. IV)

Compound (3)

Crystal data

$C_7H_{12}N_6$
M_r = 180.21
Triclinic
$P\bar{1}$
a = 7.944 (5) Å
b = 8.485 (6) Å
c = 6.829 (3) Å
α = 87.11 (2)°
β = 93.65 (3)°
γ = 111.58 (2)°
V = 427 (1) Å^3
Z = 2
D_x = 1.402 Mg m^{-3}
Cu $K\alpha$ radiation
λ = 1.5418 Å
Cell parameters from 25 reflections
θ = 17.5–28.7°
μ = 0.746 mm^{-1}
T = 293 K
Prism
0.25 × 0.2 × 0.1 mm
Colourless

Data collection

Philips PW1100 diffractometer
ω–2θ scans
Absorption correction: empirical
T_{min} = 0.754, T_{max} = 0.950
1444 measured reflections
1444 independent reflections
1158 observed reflections [$I \geq 3\sigma(I)$]
θ_{max} = 67°
$h = -9 \rightarrow 9$
$k = -9 \rightarrow 10$
$l = 0 \rightarrow 8$
3 standard reflections
frequency: 60 min
intensity variation: <0.02%

Refinement

Refinement on F
R = 0.057
wR = 0.058
S = 2.2
1158 reflections
120 parameters
Only H-atom U's refined
Unit weights applied
$(\Delta/\sigma)_{max}$ = 0.02
$\Delta\rho_{max}$ = 0.2 e Å^{-3}
$\Delta\rho_{min}$ = −0.2 e Å^{-3}
Extinction correction: Larson (1970)
Extinction coefficient: 8.2 (9)
Atomic scattering factors from *International Tables for X-ray Crystallography* (1974, Vol. IV)

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}
Compound (2)				
C(1)	0.31854 (9)	−0.1830 (6)	0.8357 (1)	0.0325
C(2)	0.25308 (9)	−0.2555 (7)	0.8466 (1)	0.0398
C(3)	0.35170 (8)	−0.0136 (5)	0.8976 (1)	0.0275

C(4)	0.41246 (9)	0.0897 (5)	0.8925 (1)	0.0270
C(5)	0.45048 (9)	0.0313 (6)	0.8242 (1)	0.0365
C(6)	0.40629 (9)	0.3088 (6)	1.0132 (1)	0.0298
C(7)	0.32392 (9)	0.0590 (6)	0.9657 (1)	0.0317
N(3)	0.43879 (7)	0.2502 (5)	0.94972 (9)	0.0295
N(4)	0.43475 (8)	0.4759 (6)	1.06836 (9)	0.0366
N(5)	0.40831 (9)	0.5722 (6)	1.1375 (1)	0.0449
N(6)	0.34892 (7)	0.2158 (5)	1.02451 (9)	0.0338
O(1)	0.34194 (7)	−0.2608 (5)	0.77594 (9)	0.0496
Compound (3)				
C(1)	0.7559 (4)	0.7053 (4)	1.1558 (5)	0.0295
C(2)	0.7444 (6)	0.6990 (5)	1.3757 (5)	0.0439
C(3)	0.7203 (4)	0.8379 (4)	1.0322 (4)	0.0271
C(4)	0.7904 (4)	1.0112 (4)	1.0718 (5)	0.0265
C(5)	0.9074 (5)	1.0835 (4)	1.2512 (5)	0.0378
C(6)	0.6661 (4)	1.0713 (4)	0.7808 (5)	0.0284
C(7)	0.6186 (4)	0.7965 (4)	0.8553 (5)	0.0318
N(1)	0.8383 (4)	0.4739 (4)	1.1802 (5)	0.0425
N(2)	0.7933 (4)	0.5946 (3)	1.0657 (4)	0.0342
N(3)	0.7621 (4)	1.1268 (3)	0.9492 (4)	0.0294
N(4)	0.6444 (4)	1.1863 (4)	0.6489 (4)	0.0394
N(5)	0.7256 (5)	1.3625 (4)	0.6728 (5)	0.0475
N(6)	0.5883 (4)	0.9079 (4)	0.7296 (4)	0.0329

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

Compound (2)			
C(1)—C(2)	1.505 (3)	C(4)—N(3)	1.325 (2)
C(1)—C(3)	1.475 (3)	C(6)—N(3)	1.358 (2)
C(1)—O(1)	1.219 (2)	C(6)—N(4)	1.332 (3)
C(3)—C(4)	1.421 (3)	C(6)—N(6)	1.350 (2)
C(3)—C(7)	1.387 (3)	C(7)—N(6)	1.327 (3)
C(4)—C(5)	1.497 (3)	N(4)—N(5)	1.410 (2)
C(3)—C(1)—C(2)	118.5 (2)	N(3)—C(4)—C(5)	115.7 (2)
O(1)—C(1)—C(2)	119.0 (2)	N(4)—C(6)—N(3)	115.5 (2)
O(1)—C(1)—C(3)	122.4 (2)	N(6)—C(6)—N(3)	126.2 (2)
C(4)—C(3)—C(1)	124.0 (2)	N(6)—C(6)—N(4)	118.4 (2)
C(7)—C(3)—C(1)	120.6 (2)	N(6)—C(7)—C(3)	125.8 (2)
C(7)—C(3)—C(4)	115.4 (2)	C(6)—N(3)—C(4)	118.1 (2)
C(5)—C(4)—C(3)	123.7 (2)	N(5)—N(4)—C(6)	124.2 (2)
N(3)—C(4)—C(3)	120.6 (2)	C(7)—N(6)—C(6)	114.0 (2)
Compound (3)			
C(1)—C(2)	1.508 (5)	C(6)—N(3)	1.344 (4)
C(1)—C(3)	1.472 (4)	C(6)—N(4)	1.345 (4)
C(1)—N(2)	1.279 (4)	C(6)—N(6)	1.348 (4)
C(3)—C(4)	1.402 (4)	C(7)—N(6)	1.323 (4)
C(3)—C(7)	1.394 (4)	N(1)—N(2)	1.392 (4)
C(4)—C(5)	1.501 (4)	N(4)—N(5)	1.407 (4)
C(4)—N(3)	1.330 (4)		
C(3)—C(1)—C(2)	121.5 (3)	N(4)—C(6)—N(3)	118.4 (3)
N(2)—C(1)—C(2)	122.2 (3)	N(6)—C(6)—N(3)	125.7 (3)
N(2)—C(1)—C(3)	116.2 (3)	N(6)—C(6)—N(4)	115.9 (3)
C(4)—C(3)—C(1)	124.9 (3)	N(6)—C(7)—C(3)	124.5 (3)
C(7)—C(3)—C(1)	120.2 (3)	N(1)—N(2)—C(1)	117.3 (3)
C(7)—C(3)—C(4)	114.9 (3)	C(6)—N(3)—C(4)	117.1 (3)
C(5)—C(4)—C(3)	123.6 (3)	N(5)—N(4)—C(6)	123.4 (3)
N(3)—C(4)—C(3)	122.3 (3)	C(7)—N(6)—C(6)	115.4 (3)
N(3)—C(4)—C(5)	114.1 (3)		

The structure was solved using direct methods and successive Fourier maps (*SHELXS*86; Sheldrick, 1985), and refined using *CRYSTALS* (Watkin, Carruthers & Betteridge, 1985). H atoms were located from difference syntheses.

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Lists of structure factors, anisotropic displacement parameters, H-atom coordinates and complete geometry have been deposited with the IUCr (Reference: KA1062). Copies may be obtained through The Managing Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

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2-Acetyl-3-methyl-4*H*-1,4-benzothiazine 1-Oxide

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Abstract

Crystals of the title compound 2-acetyl-3-methyl-4*H*-1,4-benzothiazine 1-oxide (2), $C_{11}H_{11}NO_2S$, crystallize in the monoclinic space group $P2_1/n$. The cell parameters are almost identical to those of the unoxidized precursor 2-acetyl-3-methyl-4*H*-1,4-benzothiazine (1). The change in molecular geometry of the acetyl group with respect to the ring moiety in (2) from that in (1) is a consequence of hydrogen bonding involving the sulfoxide O atom.