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2,5-Dihydro-3,4-dimethyl-5-oxo-1*H*-pyrazole-1-carbothioamide

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Key indicators

Single-crystal X-ray study
T = 293 K
Mean σ(C–C) = 0.003 Å
R factor = 0.046
wR factor = 0.132
Data-to-parameter ratio = 18.1

For details of how these key indicators were automatically derived from the article, see http://journals.iucr.org/e.

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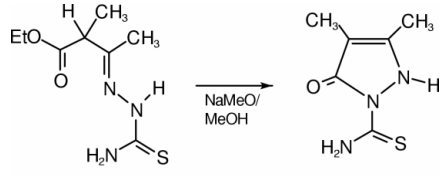
The title compound, $C_6H_9N_3OS$, was obtained by cyclization of ethyl 2-methylacetoacetate thiosemicarbazone with sodium methanolate in methanol. Single crystals suitable for X-ray analysis were obtained by slow evaporation of the mother liquor. The pyrazolone moiety is essentially planar. The S atom is *cis* with respect to the protonated endocyclic N^2 atom, probably because the intramolecular hydrogen bonds allowed by this arrangement afford greater stability than those allowed when S is *trans* to N-2. Intermolecular hydrogen bonds link the molecules in interlocking pleated sheets, stacked along the *c* axis.

Comment

The pyrazolones include a number of widely used analgesics and non-steroidal anti-inflammatory drugs (NSAIDS) (Insel, 1996), and the use of some members of this family to extract copper from ore has also recently been reported (Emeleus *et al.*, 2001). Synthesis of pyrazolones by cyclization of the thiosemicarbazones of β-ketomides or β-ketoesters endows them with a carbothioamide group that increases their versatility as coordinating ligands, and this synthetic approach appears also to be fast when mediated by metals (Casas *et al.*, 2000, 2002). In the course of an evaluation of several metals for this purpose, we recently prepared 2,5-dihydro-3,4-dimethyl-5-oxo-1*H*-pyrazole-1-carbothioamide, (I), by a method slightly different from that used previously (Casas *et al.*, 2002). We report here its structure, which has not previously been published.



H_2EMTSC (I)

Pyrazolone (I) was synthesized by reaction of ethyl 2-methylacetoacetate thiosemicarbazone (H_2EMTSC) with sodium methanolate in methanol (see Scheme). Single crystals of (I) were obtained by slow evaporation of the mother liquor, and its structure was determined by X-ray diffractometry.

The molecular structure of (I) is shown in Fig. 1. Selected geometric parameters of the molecule are listed in Table 1, and the hydrogen-bond geometry is given in Table 2. The molecule is essentially planar, the r.m.s. deviation of atoms N2, N3, C2, C3, C4, S, C1 and N1 from the least-squares plane they define being only 0.013 (12) Å, with an angle of only 2.0 (2)°

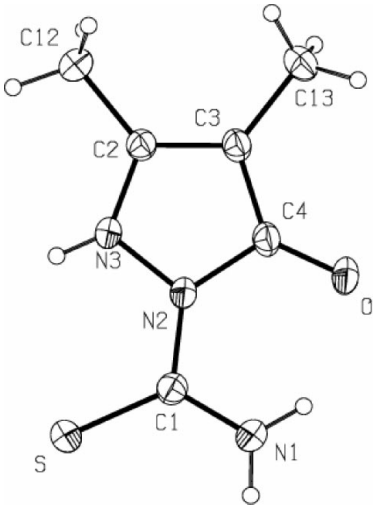


Figure 1
PLATON (Spek, 2002) diagram of (I), showing the atom-numbering system. Atoms are represented as displacement ellipsoids drawn at the 30% probability level.

between the carbothioamide plane and the pyrazole ring plane [r.m.s. = 0.0092 (10) Å].

The main structural parameters of the molecule are similar to those found in 2,5-dihydro-3-methyl-5-oxo-1*H*-pyrazole-1-carbothioamide [(II); Casas *et al.*, 2000]; in particular, the S atom of the carbothioamide group is *cis* to N3, probably because the intramolecular N1···O and N3···S hydrogen bonds allowed by this arrangement afford greater stability than the N1···S and N3···O bonds allowed when S is *trans* to N3. However, the intermolecular N3—H···O bond is longer in (I) than in (II) [2.840 (2) Å *versus* 2.778 (2) Å]. In the molecular chains formed along the *b* axis by these N3—H···O bonds in (I), successive pyrazole rings make an angle of 56.64 (5)° with each other (Fig. 2), whereas there is no such twist in the corresponding chains in (II). This difference is probably due to the steric requirements of the extra methyl group in (I). An additional intermolecular N1—H···S bond associates the molecules of neighbouring chains in centrosymmetric dimers, so linking the chains in pleated sheets that lie perpendicular to the *c* axis, with deep interlocking between successive sheets (Fig. 3).

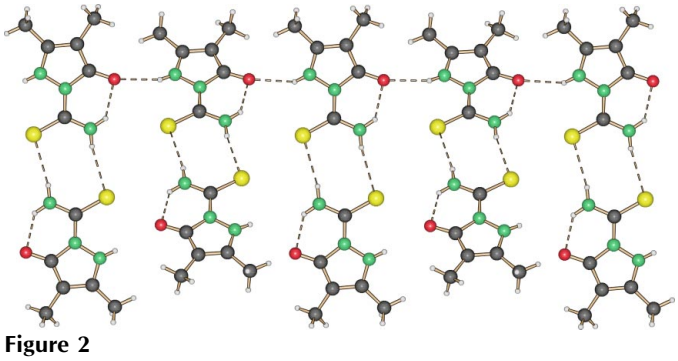


Figure 2
SCHAKAL (Keller, 1988) diagram, showing the hydrogen bonding in (I).

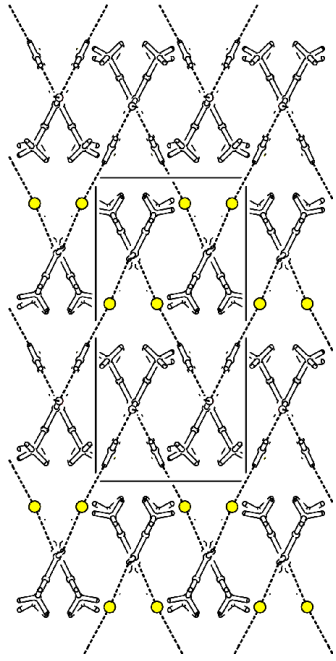


Figure 3
PLATON (Spekr, 2002) diagram showing the packing in (I). **[Quality very poor; can a better original be provided.**

Experimental

H_2EMTSC (203 mg, 0.93 mmol) and sodium methanolate (54 mg, 0.99 mmol) were dissolved in methanol (15 ml) and the mixture was refluxed for 30 min. The colourless solid which formed was filtered off, washed with diethyl ether, and vacuum dried. Yield: 130 mg (15%). Analysis found: C 42.0, H 5.0, N 24.3%; $C_6H_9N_3OS$ requires: C 42.1, H 5.3, N 24.5%. Mass (EI) and IR (KBr) spectra are in agreement with those reported previously (Casas *et al.*, 2002). Slow evaporation of the mother liquor gave colourless crystals suitable for X-ray analysis.

Crystal data

$C_6H_9N_3OS$
M_r = 171.22
Orthorhombic, *Pbcn*
a = 7.9246 (13) Å
b = 12.543 (2) Å
c = 16.015 (3) Å
V = 1591.9 (4) Å^3
Z = 8
D_x = 1.429 Mg m^{-3}
Mo $K\alpha$ radiation
Cell parameters from 4044 reflections
θ = 2.5–28.0°
μ = 0.35 mm^{-1}
T = 293 (2) K
Prism, colourless
0.37 × 0.27 × 0.20 mm

Data collection

Bruker SMART CCD 1000 diffractometer
φ and ω scans
Absorption correction: multi-scan (*SADABS*; Sheldrick, 1996)
T_{min} = 0.875, T_{max} = 0.932
8987 measured reflections
1904 independent reflections
1559 reflections with $I > 2\sigma(I)$
R_{int} = 0.062
θ_{max} = 28.0°
$h = -10 \rightarrow 10$
$k = -9 \rightarrow 16$
$l = -21 \rightarrow 20$

Refinement

Refinement on F^2	$w = 1/[\sigma^2(F_o^2) + (0.0809P)^2 + 0.2527P]$ where $P = (F_o^2 + 2F_c^2)/3$
$R[F^2 > 2\sigma(F^2)] = 0.046$	$(\Delta/\sigma)_{max} < 0.001$
$wR(F^2) = 0.132$	$\Delta\rho_{max} = 0.37$ e Å^{-3}
$S = 1.03$	$\Delta\rho_{min} = -0.31$ e Å^{-3}
1904 reflections	Extinction correction: *SHELXL*97
105 parameters	Extinction coefficient: 0.0133 (18)
H atoms treated by a mixture of independent and constrained refinement	

Table 1
Selected geometric parameters (Å, °).

S—C1	1.6682 (17)	N3—C2	1.350 (2)
N1—C1	1.321 (2)	O—C4	1.2468 (19)
N2—N3	1.3801 (18)	C2—C3	1.367 (2)
N2—C1	1.385 (2)	C3—C4	1.414 (2)
N2—C4	1.420 (2)		
N3—N2—C1	122.01 (12)	N2—C1—S	120.84 (11)
N3—N2—C4	108.19 (13)	N3—C2—C3	110.24 (14)
C1—N2—C4	129.68 (13)	C2—C3—C4	107.83 (13)
C2—N3—N2	108.22 (13)	O—C4—C3	132.52 (15)
N1—C1—N2	113.93 (15)	O—C4—N2	122.01 (16)
N1—C1—S	125.23 (14)	C3—C4—N2	105.47 (13)

Table 2
Hydrogen-bonding geometry (Å, °).

D—H···A	D—H	H···A	D···A	D—H···A
N1—H1*A*···O	0.86	1.97	2.661 (2)	137
N3—H3···S	0.82 (3)	2.60 (3)	2.9834 (16)	110 (2)
N1—H1*B*···S^{i}	0.86	2.60	3.4495 (17)	169
N3—H3···O^{ii}	0.82 (3)	2.15 (3)	2.840 (2)	142 (2)

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

The H atom bound to N3 (H3) was located and refined isotropically. All other H atoms were treated using riding models (Sheldrick, 1997).

Data collection: *SMART* (Bruker, 1998); cell refinement: *SAINT* (Bruker, 1998); data reduction: *SAINT*; program(s) used to solve structure: *SHELXS*97 (Sheldrick, 1990); program(s) used to refine structure: *SHELXL*97 (Sheldrick, 1997); molecular graphics: *PLATON* (Spek, 2002) and *SCHAKAL* (Keller, 1988); software used to prepare material for publication: *SHELXL*97.

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