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Key indicators

Single-crystal X-ray study
 $T = 297$ K
Mean $\sigma(\text{C}-\text{C}) = 0.006$ Å
Disorder in main residue
 R factor = 0.081
 wR factor = 0.248
Data-to-parameter ratio = 16.2

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

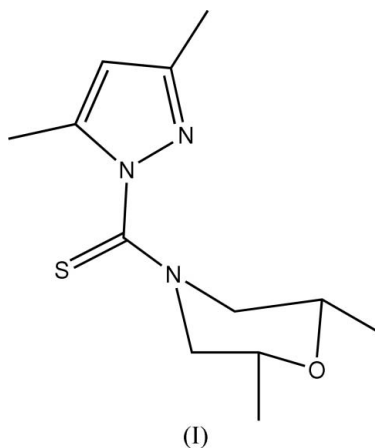
2,6-Dimethylmorpholin-4-yl 3,5-dimethyl-1H-pyrazole thio ketone

In the title compound, $\text{C}_{12}\text{H}_{19}\text{N}_3\text{OS}$, the 2,6-dimethylmorpholine ring, which is in a chair conformation, and the planar 3,5-dimethylpyrazole ring are linked at an angle of $114.2(3)^\circ$ by the methanethione group.

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Comment

This report is part of a general study devoted to the investigation of the coordination modes of thiosemicarbazones and bis(thiosemicarbazones) with organotin(IV) compounds, as well as to the chemistry and structures of five-, six- and seven-coordinate organotin(IV) complexes (de Sousa *et al.*, 2001, 2000). The title ligand, (I), was chosen because it has the potential of binding to a great number of transition metal ions, as well as to main group metal centres. Furthermore, metal complexes containing pyrazole ligands have attracted considerable interest, owing to their unusual coordination chemistry and their biological and biochemical importance (Evans *et al.*, 2004). Pyrazole ligands find applications in antipyretics, antirheumatics, herbicides, and fungicides, and in recent years, new developments have been made in the biocoordination chemistry of pyrazole and its derivatives (Bienvenue *et al.*, 1995).



A view of the molecule of (I), with the atom-labelling scheme, is shown in Fig. 1. Selected structural parameters are given in Table 1. The $\text{N}4-\text{C}8-\text{S}9$ bond angle is $126.8(3)^\circ$; its departure from the ideal sp^2 bond-angle value indicates repulsion between atoms $\text{S}9$ and $\text{N}4$. This effect can be explained by the induction of negative charge on atom $\text{S}9$ via resonance effects of the π electrons in the $\text{C}=\text{S}$ bond. A shortening of the $\text{C}8-\text{N}4$ bond to $1.322(5)$ Å, compared with a value of $1.422(4)$ Å for the $\text{C}8-\text{N}11$ bond, correlates with a degree of overlap between the $\text{N}4$ lone pair and the π system of the $\text{C}=\text{S}$ bond.

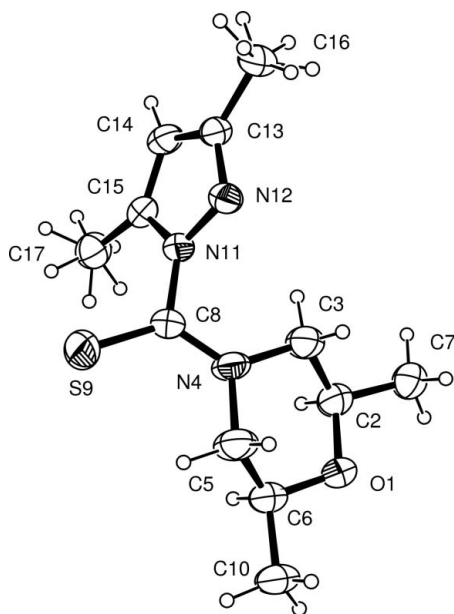


Figure 1
A view of (I), with the atom-numbering scheme. Displacement ellipsoids are drawn at the 30% probability level and H atoms are shown as spheres of arbitrary radii.

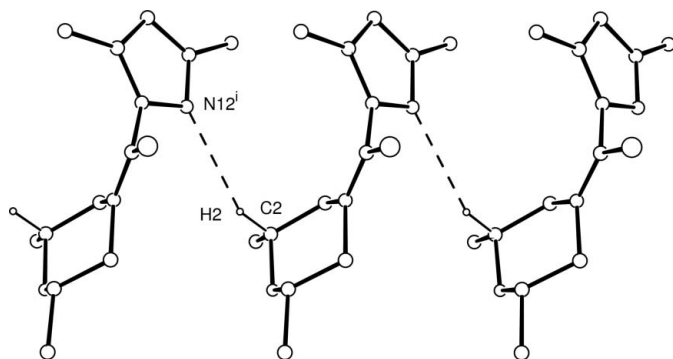


Figure 2
The formation of a chain along the *a* axis. C—H...N hydrogen bonds are shown. [Symmetry code: (i) $x - 1, y, z$.]

The dimethylpyrazole ring is planar, with atom C8 lying 0.172 (6) Å out of this plane, while methyl atoms C16 and C17 are 0.027 (7) and 0.022 (7) Å, respectively, from this plane, thus explaining the shortening of C13—C16 and C15—C17 by 0.03 Å from the expected bond length by resonance. The C13—N12 and C14—C15 bond lengths indicate that these are double bonds. The six-membered ring O1/C2/C3/N4/C5/C6 has puckering parameters (Cremer & Pople, 1975) of $Q = 0.526$ (5) Å, $\theta = 2.4$ (5)° and $\varphi = 320$ (14)°, showing a chair conformation.

The conformation of (I) is stabilized by three non-classical intramolecular H bonds, C3—H...N11, C3—H...N12 and C5—H...S9. These short contacts are responsible for the torsion angles N11—C8—N4—C3 and S9—C8—N4—C5 of -4.9 and -7.4 °, respectively. The crystal packing (Fig. 2) is mediated by a C—H...N hydrogen bond, which links neighbouring molecules into a linear chain along the *a* axis. Hydrogen-bond geometries are given in Table 2.

A search of the Cambridge Structural Database (CSD, Version 5.27; Allen, 2002) indicates that neither this ligand nor any of its metal complexes have been reported to date. However, further synthesis and structural determinations of metal complexes containing this ligand are necessary before drawing conclusions as to which coordination mode this ligand will adopt.

Experimental

A mixture of 2,5-pentanodione (1 g, 10 mmol) and 2,6-dimethylmorpholine-4-carbothiohydrazide (Swearingen & West, 2000) (1.9 g, 10 mmol) in methanol (15 ml) was refluxed for 1 h. After filtering to obtain a clear solution, slow evaporation of the solvent at room temperature led to the formation of a crystalline product, (I) (yield 50%; m.p. 404–406 K), as colourless prismatic crystals, suitable for X-ray diffraction. This ligand did not react with diorganotin(IV) compounds such as Me_2SnCl_2 and Ph_2SnCl_2 in methanol solution.

NMR spectra were recorded at room temperature on a Varian Mercury-Plus spectrometer (7.05 T), operating at 300 MHz for ^1H and 75.46 MHz for ^{13}C . The compound was dissolved in CDCl_3 containing TMS as internal reference. Chemical shifts were expressed in δ (p.p.m.) and coupling constants as J (Hz). The homonuclear and heteronuclear two-dimensional experiments (COSY, HMQC and HMBC) were carried out in the field gradient mode. IR spectra were recorded from KBr pellets on a Bomem BM100 FT-IR spectrometer in the 4000–400 cm^{-1} region. NMR (^1H , ^{13}C) spectra of the title compound in CDCl_3 solution confirmed the formation of a substituted pyrazoline ring. The methyl H atoms C17—H and C16—H appeared as singlets at $\delta = 2.23$ ($\delta_{\text{C}} = 13.1$ p.p.m.) and $\delta = 2.41$ ($\delta_{\text{C}} = 12$ p.p.m.), respectively. The resonance signal corresponding to an sp^2 methine H atom (C14—H) was also observed as a singlet at $\delta = 5.95$ ($\delta_{\text{C}} = 108.1$ p.p.m.). Nevertheless, the two-dimensional NMR spectra (COSY, HMQC and HMBC) correlated it clearly with the CH_3 groups of the pyrazoline ring.

The methyl H atoms C7—H or C10—H of the morpholine ring appeared as doublets at $\delta = 1.13$ ($\delta_{\text{C}} = 18.0$ p.p.m.) or $\delta = 1.29$ ($\delta_{\text{C}} = 18.4$ p.p.m.) and were correlated with the related C2—H and C6—H by COSY and HMQC techniques. The methylene H atoms C3—H gave two doublets at $\delta = 3.53$ ($\delta_{\text{C}} = 56.2$ p.p.m.) and $\delta = 5.11$ ($\delta_{\text{C}} = 56.2$ p.p.m.), attributed to H at the equatorial and axial positions, respectively. This behaviour was not noticed for the methylene H atoms C5—H, which absorbed at $\delta = 2.90$ ($\delta_{\text{C}} = 55.3$ p.p.m.) as a doublet of doublets.

The IR spectrum of the compound (I) showed strong bands characteristic for $\nu_{\text{as}}(\text{C—H})$ at 1969, $\nu_{\text{s}}(\text{CH}_3)$ at 2929 and $\nu_{\text{as}}(\text{CH}_3)$ at 2871 cm^{-1} . The strongest absorption bands were assigned to $\nu(\text{C=N})$ at 1560 cm^{-1} and $\nu(\text{C=C})$ at 1497 cm^{-1} . The absorptions at 1350 and at 1083 cm^{-1} were assigned to $\nu(\text{C—N})$ and $\nu_{\text{as}}(\text{C—O—C})$, respectively, and the absorptions at 1174, 840 and 784 cm^{-1} were attributed to $\nu(\text{C=S})$ (Rao & Vankataraghavan, 1962).

Crystal data

$\text{C}_{12}\text{H}_{19}\text{N}_3\text{OS}$	$V = 692.6$ (3) Å ³
$M_r = 253.37$	$Z = 2$
Triclinic, $P\bar{1}$	$D_x = 1.215$ Mg m ⁻³
$a = 5.242$ (2) Å	Cu $K\alpha$ radiation
$b = 11.209$ (2) Å	$\mu = 1.99$ mm ⁻¹
$c = 12.082$ (2) Å	$T = 297$ (2) K
$\alpha = 83.30$ (2)°	Prism, colourless
$\beta = 80.62$ (2)°	$0.30 \times 0.22 \times 0.08$ mm
$\gamma = 83.66$ (2)°	

Data collection

Enraf–Nonius CAD4 diffractometer	2507 independent reflections
$\omega/2\theta$ scans	1997 reflections with $I > 2\sigma(I)$
Absorption correction: ψ scan (North <i>et al.</i> , 1968)	$R_{\text{int}} = 0.016$
$T_{\text{min}} = 0.587$, $T_{\text{max}} = 0.857$	$\theta_{\text{max}} = 67.9^\circ$
2875 measured reflections	2 standard reflections
	frequency: 120 min
	intensity decay: 3%

Refinement

Refinement on F^2	$w = 1/[\sigma^2(F_o^2) + (0.1279P)^2 + 0.6447P]$
$R[F^2 > 2\sigma(F^2)] = 0.081$	where $P = (F_o^2 + 2F_c^2)/3$
$wR(F^2) = 0.248$	$(\Delta/\sigma)_{\text{max}} < 0.001$
$S = 1.04$	$\Delta\rho_{\text{max}} = 0.72 \text{ e } \text{Å}^{-3}$
2507 reflections	$\Delta\rho_{\text{min}} = -0.35 \text{ e } \text{Å}^{-3}$
155 parameters	Extinction correction: <i>SHELXL97</i>
H-atom parameters constrained	(Sheldrick, 1997)
	Extinction coefficient: 0.070 (7)

Table 1
Selected geometric parameters (Å, °).

S9–C8	1.634 (4)	N11–C8	1.422 (4)
N4–C8	1.322 (5)	N12–C13	1.322 (4)
N4–C5	1.477 (5)	C13–C16	1.493 (5)
N4–C3	1.481 (5)	C14–C15	1.357 (5)
N11–N12	1.383 (4)	C15–C17	1.487 (5)
C6–O1–C2	113.1 (3)	C8–N4–C3	126.2 (3)
C8–N4–C5	121.9 (3)		
C3–N4–C8–N11	–4.9 (6)	N12–N11–C8–N4	–66.8 (4)
C5–N4–C8–S9	–7.3 (6)		

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

$D-H \cdots A$	$D-H$	$H \cdots A$	$D \cdots A$	$D-H \cdots A$
C3–H3A \cdots N11	0.97	2.37	2.780 (5)	105
C3–H3A \cdots N12	0.97	2.57	3.013 (5)	108
C5–H5B \cdots S9	0.97	2.59	3.087 (5)	112
C2–H2 \cdots N12 ⁱ	0.98	2.74	3.560 (6)	142

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

All H atoms were placed in calculated positions and allowed to ride on their parent atoms, with C–H distances in the range 0.93–0.98 Å, and with $U_{\text{iso}}(\text{H}) = 1.5U_{\text{eq}}(\text{C})$ for methyl H atoms and $1.2U_{\text{eq}}(\text{C})$ for all other atoms. The methyl H atoms at C16 and C17 were modelled as torsionally disordered groups with an occupancy factor of 0.5 for each group. The displacement ellipsoids of the S atom and the dimethylmorpholine group are very anisotropic. This might be due to structural disorder indicated by the longer ellipsoid axis alignment, but this disorder could not be modelled reliably.

Data collection: *CAD-4 Software* (Enraf–Nonius, 1994); cell refinement: *CAD-4 Software*; data reduction: *XCAD4* (Harms & Wocadlo, 1995); program(s) used to solve structure: *SHELXS97* (Sheldrick, 1997); program(s) used to refine structure: *SHELXL97* (Sheldrick, 1997); molecular graphics: *ORTEP-3 for Windows* (Farrugia, 1997); software used to prepare material for publication: *WinGX* (Farrugia, 1999).

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