organic compounds

Methyl 3-methyl-5-oxo-4-(phenylhydrazono)-4,5-dihydro-1H-pyrazole-1-carbodithioate

Xiao-Lan Liu,[a] Yue Zhao,[a] Zhi-Gang Li[b] and Yong-Hong Liu[a]*

[a]College of Chemistry and Chemical Engineering, Yangzhou University, Yangzhou, 225002, People's Republic of China, and [b]Tianshui Institute for Drug Control, Tianshui 741018, People's Republic of China
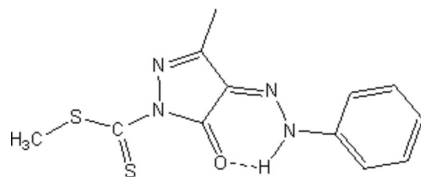Correspondence e-mail: yhliuyzu@yahoo.com.cn

The title compound, $C_{12}H_{11}N_4OS_2$, has been synthesized by the condensation reaction of 3-oxo-2-(phenylhydrazono)-butanate and S-methyldithiocarbazate. The hydrazine unit and the pyrazole ring are coplanar [dihedral angle 3.8 (4)°] due to extensive conjugation and the N—H···O=C intramolecular hydrogen bond. Two adjacent molecules form dimers due to short C—H···O=C [R_2^2 (18)] and C—H···S=C [R_2^2 (22)] intermolecular interactions. C—H···S—C [R_2^2 (14)] interactions link these dimers into ribbons in the [011] direction.

Related literature

For related literature, see: Bao *et al.* (2006); Bernstein *et al.* (1995); Bose *et al.* (2005); Brassy *et al.* (1974); Liu *et al.* (2007); Shi *et al.* (2005); Yang *et al.* (2003); Zelenak *et al.* (1999).

Experimental

Crystal data

C$_{12}$H$_{12}$N$_4$OS$_2$
$M_r = 292.40$
Triclinic, $P\bar{1}$
$a = 5.0915$ (8) Å
$b = 10.9705$ (16) Å
$c = 11.9398$ (18) Å
$\alpha = 93.770$ (2)°
$\beta = 97.947$ (2)°

$\gamma = 91.422$ (2)°
$V = 658.69$ (17) Å^3
$Z = 2$
Mo $K\alpha$ radiation
$\mu = 0.40$ mm^{-1}
$T = 293$ (2) K
$0.26 \times 0.23 \times 0.17$ mm

Data collection

Bruker SMART CCD area-detector diffractometer
Absorption correction: multi-scan (*SADABS*; Sheldrick, 2004)
$T_{min} = 0.816$, $T_{max} = 0.874$
(expected range = 0.872–0.934)

4799 measured reflections
2304 independent reflections
2035 reflections with $I > 2\sigma(I)$
$R_{int} = 0.033$

Refinement

$R[F^2 > 2\sigma(F^2)] = 0.031$
$wR(F^2) = 0.092$
$S = 1.02$
2304 reflections

174 parameters
H-atom parameters constrained
$\Delta\rho_{max} = 0.25$ e Å^{-3}
$\Delta\rho_{min} = -0.30$ e Å^{-3}

Table 1
Hydrogen-bond geometry (Å, °).

D—H···A	D—H	H···A	D···A	D—H···A
N1—H1···O1	0.86	2.06	2.751 (2)	137
C4—H4···O1^i	0.93	2.49	3.244 (3)	139
C4—H4···S2^i	0.93	2.99	3.842 (2)	152

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

Data collection: *SMART* (Bruker, 2001); cell refinement: *SAINT* (Bruker, 2001); data reduction: *SAINT*; program(s) used to solve structure: *SHELXS97* (Sheldrick, 1990); program(s) used to refine structure: *SHELXL97* (Sheldrick, 1997); molecular graphics: *PLATON* (Spek, 2003); software used to prepare material for publication: *SHELXTL* (Sheldrick, 2001).

References

Bao, F., Lu, X., Kang, B. & Wu, Q. (2006). *Eur. Polym. J.* **42**, 928–934.
Bernstein, J., Davis, R. E., Shimoni, L. & Chang, N.-L. (1995). *Angew. Chem. Int. Ed. Engl.* **34**, 1555–1573.
Bose, R., Murty, D. S. R. & Chakrapani, G. J. (2005). *Radioanal. Nucl. Chem.* **265**, 115–122.
Brassy, C., Renaud, A., Delettré, J. & Mornon, J.-P. (1974). *Acta Cryst.* B**30**, 2246–2248.
Bruker (2001). *SMART* and *SAINT*. Bruker AXS Inc., Madison, Wisconsin, USA.
Liu, Y.-H., Zhao, Y., Liu, X.-L., Tong, B.-W. & Ye, J. (2007). *Acta Cryst.* E**63**, o4072.
Sheldrick, G. M. (1990). *Acta Cryst.* A**46**, 467–473.
Sheldrick, G. M. (1997). *SHELXL97*. University of Göttingen, Germany.
Sheldrick, G. M. (2001). *SHELXTL*. Version 5.0. Bruker AXS Inc., Madison, Wisconsin, USA.
Sheldrick, G. M. (2004). *SADABS*. University of Göttingen, Germany.
Shi, M., Li, F., Yi, T., Zhang, D., Hu, H. & Huang, C. (2005). *Inorg. Chem.* **44**, 8929–8936.
Spek, A. L. (2003). *J. Appl. Cryst.* **36**, 7–13.
Yang, X.-P., Kang, B.-S., Wong, W.-K., Su, Ch.-Y. & Liu, H.-Q. (2003). *Inorg. Chem.* **42**, 169–174.
Zelenak, V., Gyoryova, K. & Vargova, S. (1999). *Main Group Met. Chem.* **22**, 179–184.

supplementary materials

Methyl 3-methyl-5-oxo-4-(phenylhydrazono)-4,5-dihydro-1*H*-pyrazole-1-carbodithioate

X.-L. Liu, Y. Zhao, Z.-G. Li and Y.-H. Liu

Comment

Pyrazolones compounds are finding increasing numbers of applications as ligands in coordination chemistry (Brassy *et al.*, 1974; Zelenak *et al.*, 1999; Yang *et al.*,2003). For example, they have been applied to the solvent extraction of metal ions (Bose *et al.*, 2005) as ligands in complexes with catalytic activity (Bao *et al.*, 2006) and in the synthesis of rare earth metal complexes with interesting photophysical properties (Shi *et al.* 2005). A related compound, (II), has already been studied (Liu *et al.*, 2007).

Similar to (II), the title compound, (I), has been shown by UV spectroscopy to have extensive conjugation involving four carbon atoms (C2—C5), four nitrogen atoms (N1—N4) and one oxygen (O1). And this has been further confirmed by the determination of its crystal structure (Fig. 1) The bond lengths and angles of the large conjugated system in (I) are similar to the corresponding values in (II). The dihedral angle between the conjugated system and with plane of C1–S1–C2=S2 in (I) is 3.8 (4)° while the value in (II) is 13.1 (3)°. The bond distances of C11—N4 is 1.392 (2) in (I), and the value in (II) is the same with (I), which is shorter than the range of C—N single bonds (1.47–1.40 Å) and might be attributed to a nonclassical sp^2-hybrid nitrogen atom and the conjugated system.

Two adjacent molecules form dimers due to short C—H⋯O=C [R^2_2 (18)] and C—H⋯S=C [R^2_2 (22)] (Bernstein *et al.*, 1995) intermolecular interactions. C—H⋯S—C [R^2_2 (14)] interactions link these dimers into ribbons in the (011) direction (Table 1).

Experimental

The title compound was synthesized by refluxing an ethanol solution of ethyl 3-oxo-2-(phenylhydrazono)butanate and *S*-methyldithiocarbazate (1:1) for 24 h. After 12 h at room temperature, the precipitate was collected by filtration and recrystallized from ethanol (yield 86.7%)·The yellow crystals suitable for X-ray analysis were obtained by slow evaporation of a dichloromethane solution at 293 K (m.p. 396.2–397.7 K). Analysis calculated for $C_{12}H_{11}N_4OS_2$: C49.47, H 3.81, N 19.23%; found: C 49.63, H 3.56, N 19.14%. IR (KBr,cm^{-1}): 3250(w, NH), 1630 (*vs*, O=C), 1520 (s, N=C), 1275(S=C). UV (λ_{max}, in CHCl$_3$, nm): 396 (K-band, 1.87× 10^4). ^{1}H NMR (600 MHz, CDCl$_3$, δ, p.p.m.): 9.64 (m, 5H, ArH), 6.91 (s, H, NH), 3.96 (s, 3H, SCH$_3$), 1.13 (s, 3H, CH$_3$).

Refinement

The H atoms were placed in calculated positions and refined as riding, with C—H=0.93–0.97 Å and N—H=0.91 Å, and refined using a riding model, with $U_{iso}(H) = 1.2U_{eq}(C, N)$ and $1.5U_{eq}$(methyl C).
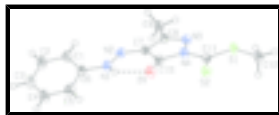
supplementary materials

Figures

Fig. 1. The molecular of (I) structure of the title compound, showing 50% probability ellipsoids. The C — H ··· N intramolecular hydrogen bond is shown dashed.
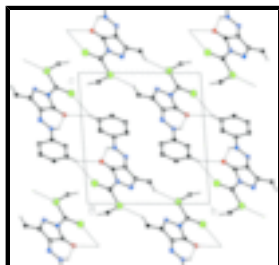

Fig. 2. Packing diagram of (I), showing the formation of R^2_2 (18), and R^2_2 (22) and R^2_2 (14) ring *via* the short intermolecular interaction of C—H···O=C and C—H···S=C, and C—H···S—C, respectively, viewed along *a* axis. H atoms not involved in hydrogen bonding have been omitted.

Fig. 3. The structures of (I) and (II).

Methyl 3-methyl-5-oxo-4-(phenylhydrazono)-4,5-dihydro-1*H*-pyrazole-1-carbodithioate

Crystal data

$C_{12}H_{12}N_4OS_2$	$Z = 2$
$M_r = 292.40$	$F_{000} = 304.0$
Triclinic, $P\overline{1}$	$D_x = 1.474$ Mg m^{-3}
Hall symbol: -P 1	Melting point: 397 K
$a = 5.0915$ (8) Å	Mo $K\alpha$ radiation $\lambda = 0.71073$ Å
$b = 10.9705$ (16) Å	Cell parameters from 3332 reflections
$c = 11.9398$ (18) Å	$\theta = 2.4$–28.2º
$\alpha = 93.770$ (2)º	$\mu = 0.40$ mm^{-1}
$\beta = 97.947$ (2)º	$T = 293$ (2) K
$\gamma = 91.422$ (2)º	Block, yellow
$V = 658.69$ (17) Å^3	$0.26 \times 0.23 \times 0.17$ mm

Data collection

Bruker SMART CCD area-detector diffractometer	2304 independent reflections
Radiation source: fine-focus sealed tube	2035 reflections with $I > 2\sigma(I)$
Monochromator: graphite	$R_{int} = 0.033$
$T = 293(2)$ K	$\theta_{max} = 25.0$º
phi and ω scans	$\theta_{min} = 1.9$º
Absorption correction: multi-scan (SADABS; Sheldrick, 2004)	$h = -5 \rightarrow 6$
$T_{min} = 0.816$, $T_{max} = 0.874$	$k = -12 \rightarrow 13$
4799 measured reflections	$l = -13 \rightarrow 14$

Refinement

Refinement on F^2	Secondary atom site location: difference Fourier map
Least-squares matrix: full	Hydrogen site location: inferred from neighbouring sites
$R[F^2 > 2\sigma(F^2)] = 0.031$	H-atom parameters constrained
$wR(F^2) = 0.092$	$w = 1/[\sigma^2(F_o^2) + (0.0578P)^2 + 0.115P]$ where $P = (F_o^2 + 2F_c^2)/3$
$S = 1.02$	$(\Delta/\sigma)_{max} < 0.001$
2304 reflections	$\Delta\rho_{max} = 0.25$ e Å^{-3}
174 parameters	$\Delta\rho_{min} = -0.30$ e Å^{-3}
Primary atom site location: structure-invariant direct methods	Extinction correction: none

Special details

Geometry. All e.s.d.'s (except the e.s.d. in the dihedral angle between two l.s. planes) are estimated using the full covariance matrix. The cell e.s.d.'s are taken into account individually in the estimation of e.s.d.'s in distances, angles and torsion angles; correlations between e.s.d.'s in cell parameters are only used when they are defined by crystal symmetry. An approximate (isotropic) treatment of cell e.s.d.'s is used for estimating e.s.d.'s involving l.s. planes.

Refinement. Refinement of F^2 against ALL reflections. The weighted R-factor wR and goodness of fit S are based on F^2, conventional R-factors R are based on F, with F set to zero for negative F^2. The threshold expression of $F^2 > 2sigma(F^2)$ is used only for calculating R-factors(gt) *etc*. and is not relevant to the choice of reflections for refinement. R-factors based on F^2 are statistically about twice as large as those based on F, and R– factors based on ALL data will be even larger.

Fractional atomic coordinates and isotropic or equivalent isotropic displacement parameters (Å^2)

	x	y	z	U_{iso}*/U_{eq}
S1	1.11220 (9)	0.25831 (4)	−0.01602 (4)	0.02887 (16)
S2	1.21824 (9)	0.06971 (4)	0.15622 (4)	0.03043 (16)
O1	0.8212 (2)	0.13832 (11)	0.32205 (10)	0.0297 (3)
N2	0.4418 (3)	0.33971 (12)	0.35801 (12)	0.0232 (3)
N1	0.4384 (3)	0.25235 (13)	0.42827 (12)	0.0257 (3)
H1	0.5430	0.1925	0.4233	0.031*
N3	0.7936 (3)	0.36637 (13)	0.12557 (13)	0.0248 (3)
N4	0.8960 (3)	0.25697 (13)	0.16941 (12)	0.0237 (3)
C8	0.6255 (3)	0.40665 (15)	0.19108 (14)	0.0230 (4)
C6	0.2679 (3)	0.25469 (15)	0.51098 (14)	0.0235 (4)
C10	0.7816 (3)	0.22690 (15)	0.26553 (14)	0.0229 (4)
C11	1.0712 (3)	0.19198 (15)	0.11056 (14)	0.0232 (4)
C5	0.2180 (4)	0.14648 (16)	0.56018 (16)	0.0310 (4)
H5	0.3012	0.0755	0.5397	0.037*
C7	0.6034 (3)	0.32719 (15)	0.28113 (14)	0.0225 (4)
C9	0.4760 (4)	0.51969 (16)	0.16867 (16)	0.0289 (4)
H9A	0.5274	0.5542	0.1028	0.043*
H9B	0.5153	0.5779	0.2328	0.043*

H9C	0.2891	0.4998	0.1560	0.043*
C1	0.1473 (4)	0.36136 (16)	0.54284 (15)	0.0283 (4)
H1A	0.1827	0.4341	0.5110	0.034*
C2	−0.0262 (4)	0.35827 (17)	0.62250 (16)	0.0325 (4)
H2	−0.1079	0.4293	0.6440	0.039*
C3	−0.0791 (4)	0.25008 (17)	0.67044 (15)	0.0315 (4)
H3	−0.1974	0.2485	0.7232	0.038*
C12	1.3501 (4)	0.15958 (18)	−0.06889 (16)	0.0328 (4)
H12A	1.5066	0.1599	−0.0139	0.049*
H12B	1.3958	0.1882	−0.1382	0.049*
H12C	1.2751	0.0779	−0.0829	0.049*
C4	0.0444 (4)	0.14470 (17)	0.63963 (16)	0.0326 (4)
H4	0.0107	0.0724	0.6724	0.039*

Atomic displacement parameters (Å^2)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
S1	0.0259 (3)	0.0330 (3)	0.0306 (3)	0.00503 (19)	0.01298 (19)	0.00305 (19)
S2	0.0270 (3)	0.0285 (3)	0.0381 (3)	0.00935 (19)	0.0109 (2)	0.0028 (2)
O1	0.0298 (7)	0.0309 (7)	0.0310 (7)	0.0109 (5)	0.0090 (5)	0.0079 (6)
N2	0.0242 (8)	0.0215 (7)	0.0241 (8)	0.0028 (6)	0.0040 (6)	0.0016 (6)
N1	0.0289 (8)	0.0239 (8)	0.0274 (8)	0.0102 (6)	0.0110 (6)	0.0060 (6)
N3	0.0239 (8)	0.0216 (7)	0.0305 (8)	0.0047 (6)	0.0081 (6)	0.0032 (6)
N4	0.0205 (8)	0.0248 (8)	0.0274 (8)	0.0068 (6)	0.0076 (6)	0.0028 (6)
C8	0.0211 (9)	0.0240 (9)	0.0245 (9)	0.0017 (7)	0.0058 (7)	0.0000 (7)
C6	0.0240 (9)	0.0262 (9)	0.0213 (8)	0.0053 (7)	0.0049 (7)	0.0029 (7)
C10	0.0186 (9)	0.0273 (9)	0.0230 (9)	0.0022 (7)	0.0033 (7)	0.0013 (7)
C11	0.0168 (9)	0.0251 (9)	0.0278 (9)	−0.0009 (7)	0.0058 (7)	−0.0034 (7)
C5	0.0372 (11)	0.0253 (9)	0.0334 (10)	0.0102 (8)	0.0113 (8)	0.0058 (8)
C7	0.0214 (9)	0.0238 (9)	0.0234 (9)	0.0022 (7)	0.0068 (7)	0.0013 (7)
C9	0.0334 (10)	0.0244 (9)	0.0316 (10)	0.0074 (8)	0.0124 (8)	0.0037 (7)
C1	0.0320 (10)	0.0273 (9)	0.0281 (9)	0.0062 (8)	0.0103 (8)	0.0060 (7)
C2	0.0358 (11)	0.0339 (10)	0.0310 (10)	0.0125 (8)	0.0134 (8)	0.0042 (8)
C3	0.0301 (10)	0.0410 (11)	0.0265 (10)	0.0069 (8)	0.0116 (8)	0.0077 (8)
C12	0.0268 (10)	0.0398 (11)	0.0339 (10)	0.0033 (8)	0.0136 (8)	−0.0034 (8)
C4	0.0370 (11)	0.0304 (10)	0.0333 (10)	0.0041 (8)	0.0113 (8)	0.0096 (8)

Geometric parameters (Å, °)

S1—C11	1.7555 (18)	C10—C7	1.462 (2)
S1—C12	1.7960 (18)	C5—C4	1.384 (3)
S2—C11	1.6403 (17)	C5—H5	0.9300
O1—C10	1.224 (2)	C9—H9A	0.9600
N2—N1	1.3159 (19)	C9—H9B	0.9600
N2—C7	1.318 (2)	C9—H9C	0.9600
N1—C6	1.401 (2)	C1—C2	1.386 (3)
N1—H1	0.8600	C1—H1A	0.9300
N3—C8	1.303 (2)	C2—C3	1.387 (3)
N3—N4	1.4227 (19)	C2—H2	0.9300

N4—C11	1.392 (2)	C3—C4	1.383 (3)
N4—C10	1.411 (2)	C3—H3	0.9300
C8—C7	1.442 (2)	C12—H12A	0.9600
C8—C9	1.491 (2)	C12—H12B	0.9600
C6—C1	1.390 (2)	C12—H12C	0.9600
C6—C5	1.392 (2)	C4—H4	0.9300
C11—S1—C12	100.91 (8)	C8—C7—C10	106.59 (15)
N1—N2—C7	116.78 (14)	C8—C9—H9A	109.5
N2—N1—C6	121.45 (14)	C8—C9—H9B	109.5
N2—N1—H1	119.3	H9A—C9—H9B	109.5
C6—N1—H1	119.3	C8—C9—H9C	109.5
C8—N3—N4	107.13 (14)	H9A—C9—H9C	109.5
C11—N4—C10	129.66 (14)	H9B—C9—H9C	109.5
C11—N4—N3	118.47 (14)	C2—C1—C6	119.35 (17)
C10—N4—N3	111.69 (13)	C2—C1—H1A	120.3
N3—C8—C7	111.47 (15)	C6—C1—H1A	120.3
N3—C8—C9	121.65 (16)	C1—C2—C3	120.54 (17)
C7—C8—C9	126.86 (15)	C1—C2—H2	119.7
C1—C6—C5	120.19 (17)	C3—C2—H2	119.7
C1—C6—N1	121.47 (16)	C4—C3—C2	119.84 (18)
C5—C6—N1	118.34 (15)	C4—C3—H3	120.1
O1—C10—N4	128.54 (16)	C2—C3—H3	120.1
O1—C10—C7	128.36 (16)	S1—C12—H12A	109.5
N4—C10—C7	103.10 (14)	S1—C12—H12B	109.5
N4—C11—S2	123.30 (13)	H12A—C12—H12B	109.5
N4—C11—S1	111.28 (12)	S1—C12—H12C	109.5
S2—C11—S1	125.42 (10)	H12A—C12—H12C	109.5
C4—C5—C6	119.86 (17)	H12B—C12—H12C	109.5
C4—C5—H5	120.1	C3—C4—C5	120.22 (17)
C6—C5—H5	120.1	C3—C4—H4	119.9
N2—C7—C8	126.19 (15)	C5—C4—H4	119.9
N2—C7—C10	127.11 (15)		
C7—N2—N1—C6	−178.00 (16)	N1—C6—C5—C4	−178.05 (17)
C8—N3—N4—C11	176.70 (14)	N1—N2—C7—C8	175.26 (16)
C8—N3—N4—C10	1.18 (19)	N1—N2—C7—C10	−0.4 (3)
N4—N3—C8—C7	−0.49 (19)	N3—C8—C7—N2	−176.75 (16)
N4—N3—C8—C9	−178.93 (15)	C9—C8—C7—N2	1.6 (3)
N2—N1—C6—C1	−17.1 (3)	N3—C8—C7—C10	−0.3 (2)
N2—N1—C6—C5	162.07 (16)	C9—C8—C7—C10	178.02 (17)
C11—N4—C10—O1	3.6 (3)	O1—C10—C7—N2	−2.5 (3)
N3—N4—C10—O1	178.51 (16)	N4—C10—C7—N2	177.36 (16)
C11—N4—C10—C7	−176.20 (16)	O1—C10—C7—C8	−178.85 (17)
N3—N4—C10—C7	−1.32 (18)	N4—C10—C7—C8	0.97 (18)
C10—N4—C11—S2	−9.6 (3)	C5—C6—C1—C2	−1.1 (3)
N3—N4—C11—S2	175.85 (12)	N1—C6—C1—C2	178.01 (17)
C10—N4—C11—S1	170.68 (14)	C6—C1—C2—C3	0.2 (3)
N3—N4—C11—S1	−3.90 (19)	C1—C2—C3—C4	0.8 (3)
C12—S1—C11—N4	178.32 (12)	C2—C3—C4—C5	−0.8 (3)

C12—S1—C11—S2	−1.43 (14)	C6—C5—C4—C3	−0.1 (3)
C1—C6—C5—C4	1.1 (3)		

Hydrogen-bond geometry (Å, °)

D—H⋯A	D—H	H⋯A	D⋯A	D—H⋯A
N1—H1⋯O1	0.86	2.06	2.751 (2)	137
C4—H4⋯O1[i]	0.93	2.49	3.244 (3)	139
C4—H4⋯S2[i]	0.93	2.99	3.842 (2)	152

Symmetry codes: (i) −x+1, −y, −z+1.

Fig. 1

Fig. 2

Fig. 3

(I)   (II)