Acta Crystallographica Section E
Structure Reports
Online

ISSN 1600-5368

Bis(4-formyl-3-methyl-1-phenyl-1*H*-pyrazol-5-yl) sulfide

Li-Min Yang,[a] Hong-Qing Wang,[a] Zhao-Jie Liu[a]* and Hai-Bin Song[b]

[a]College of Chemistry, Central China Normal University, Wuhan, People's Republic of China, and [b]State Key Laboratory of Elemento-organic Chemistry, Nankai University, Tianjin 300071, People's Republic of China

Correspondence e-mail:
nimilyang@yahoo.com.cn

Received 26 August 2004
Accepted 24 September 2004
Online 30 September 2004

The molecule of the title compound, $C_{22}H_{18}N_4O_2S$, is non-planar and possesses no crystallographic symmetry. The crystal structure involves intermolecular C—H···O hydrogen bonds.

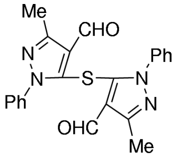
Key indicators

Single-crystal X-ray study
T = 293 K
Mean σ(C–C) = 0.003 Å
R factor = 0.041
wR factor = 0.103
Data-to-parameter ratio = 15.2

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

Comment

Pyrazole sulfide derivatives exhibit good fungicidal activity (Li *et al.*, 1997; Yu *et al.*, 1999). In an effort to obtain lead compounds, we have synthesized a series of such derivatives.



(I)

The crystal structure of (I) has been determined and the results are presented here. The molecular structure is shown in Fig. 1. The dihedral angle between the N1-pyrazole ring plane and its attached phenyl ring is 78.41 (7)°; that between the N3-pyrazole ring and its attached phenyl ring is 61.90 (9)°. The dihedral angle between the two pyrazole rings is 75.10 (8)°. Selected bond lengths and angles are listed in Table 1. These are in excellent agreement with the numerous literature reports of pyrazole derivatives (Allen *et al.*, 1987). The crystal structure involves intermolecular C—H···O hydrogen bonds (Table 2).

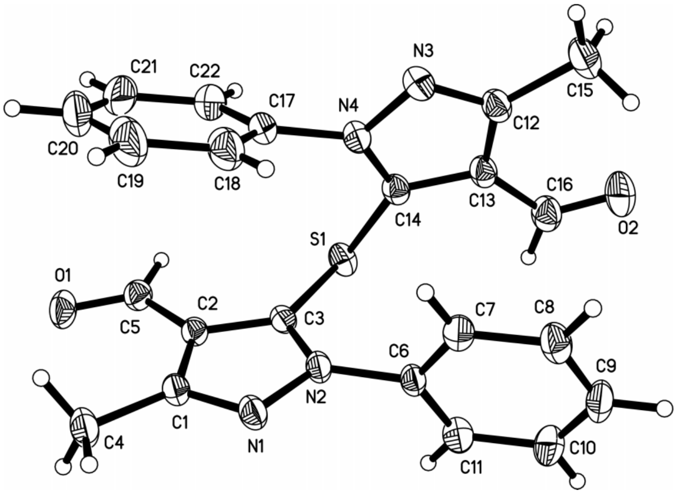


Figure 1
The molecular structure of (I), showing the atom-labellling scheme. Displacement ellipsoids are drawn at the 50% probability level.

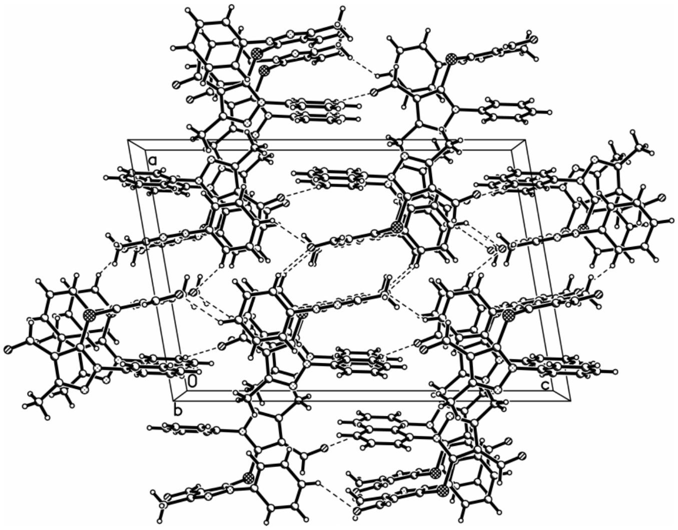


Figure 2
The molecular packing of (I), viewed along the *b* axis. Dashed lines indicate hydrogen bonds.

Experimental

To a 100 ml nitrogen-flushed three-neck round-bottomed flask, the catalyst NaH (10 mmol) in DMF was added. Thiourea (10 mmol) in DMF (10 ml) was added dropwise. After 30 min, 5-chloro-3-methyl-1-phenyl-pyrazol-4-yl carboxaldehyde was added dropwise and the solution was stirred for 24 h, under N_2 at 383 K. The reaction gave a mixture containing (I), which was separated by recrystallization from ethanol. Crystals suitable for X-ray analysis were obtained by evaporation of an ethanol solution (m.p. 468–469 K). ^{1}H NMR (DMSO, 400 MHz): δ 9.48 (*s*, 2H, CH=O), 7.31–7.43 (*m*, 10H, C_6H_5, C_6H_3), 2.19 (*s*, 6H, CH_3); L–MS (IS, 4500; TEM, 0.00; GS1, 14.00; GS2, 0.00) (*m*/*z*, relative intensity %): 425 (*M* + Na, 100.00), 403 (*M* + 1, 70.07), 402 (*M*, 1.75), 213 (1.94). Analysis calculated for $C_{22}H_{18}N_4O_2S$: C 65.60, H 4.47, N 13.91%; found: C 65.78, H 4.61, N 14.12%.

Crystal data

$C_{22}H_{18}N_4O_2S$
$M_r = 402.46$
Monoclinic, $P2_1/c$
$a = 13.853$ (4) Å
$b = 6.918$ (2) Å
$c = 20.723$ (6) Å
$\beta = 99.855$ (5)°
$V = 1956.6$ (10) Å^3
$Z = 4$

$D_x = 1.366$ Mg m^{-3}
Mo $K\alpha$ radiation
Cell parameters from 894 reflections
$\theta = 3.4$–24.6°
$\mu = 0.19$ mm^{-1}
$T = 293$ (2) K
Block, colorless
0.42 × 0.40 × 0.36 mm

Data collection

Siemens SMART CCD area-detector diffractometer
φ and ω scans
Absorption correction: multi-scan (*SADABS*; Sheldrick, 1996)
$T_{\min} = 0.918$, $T_{\max} = 0.933$
10 858 measured reflections

4015 independent reflections
2913 reflections with $I > 2\sigma(I)$
$R_{\rm int} = 0.029$
$\theta_{\max} = 26.5°$
$h = -17 \rightarrow 17$
$k = -4 \rightarrow 8$
$l = -25 \rightarrow 22$

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)] = 0.041$
$wR(F^2) = 0.103$
$S = 1.02$
4015 reflections
265 parameters
H-atom parameters constrained

$w = 1/[\sigma^2(F_o^2) + (0.045P)^2 + 0.5946P]$
where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{\max} = 0.001$
$\Delta\rho_{\max} = 0.21$ e Å^{-3}
$\Delta\rho_{\min} = -0.19$ e Å^{-3}
Extinction correction: *SHELXL*97
Extinction coefficient: 0.0124 (10)

Table 1
Selected geometric parameters (Å, °).

S1—C14	1.7555 (19)	N4—C14	1.355 (2)
S1—C3	1.7556 (18)	O1—C5	1.214 (2)
N1—C1	1.329 (2)	O2—C16	1.205 (2)
N1—N2	1.3724 (19)	C1—C2	1.416 (3)
N2—C3	1.344 (2)	C2—C3	1.384 (2)
N3—C12	1.324 (2)	C12—C13	1.411 (3)
N3—N4	1.374 (2)	C13—C14	1.382 (2)
C14—S1—C3	99.24 (8)	C3—C2—C1	104.63 (16)
C1—N1—N2	105.00 (15)	N2—C3—C2	107.31 (15)
C3—N2—N1	111.78 (14)	N3—C12—C13	111.64 (16)
C12—N3—N4	104.76 (16)	C14—C13—C12	105.03 (17)
C14—N4—N3	111.85 (15)	N4—C14—C13	106.68 (17)
N1—C1—C2	111.26 (15)		

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

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
C9—H9···O1$^{\rm i}$	0.93	2.49	3.244 (3)	138
C11—H11···O1$^{\rm ii}$	0.93	2.57	3.417 (3)	151
C21—H21···O2$^{\rm iii}$	0.93	2.53	3.385 (3)	153

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

H atoms were placed in calculated positions, with C—H distances of 0.93 and 0.96 Å. $U_{\rm iso}$(H) values were constrained to $1.5U_{\rm eq}$(carrier atom) for methyl H atoms and $1.2U_{\rm eq}$(carrier atom) for other H atoms.

Data collection: *SMART* (Bruker, 1997–2002); cell refinement: *SMART*; data reduction: *SAINT* (Bruker, 1997–2002); program(s) used to solve structure: *SHELXS*97 (Sheldrick, 1997); program(s) used to refine structure: *SHELXL*97 (Sheldrick, 1997); molecular graphics: *SHELXTL* (Bruker, 1997–2002); software used to prepare material for publication: *SHELXTL*.

References

Allen, F. H., Kennard, O., Watson, D. G., Brammer, L., Orpen, A. G. & Taylor, R. (1987). *J. Chem. Soc. Perkin Trans.* 2, pp. S1–19.
Bruker (1997–2002). *SMART* (Version 5.628), *SAINT* (Version 6.45) and *SHELXTL* (Version 6.14). Bruker AXS Inc., Madison, Wisconsin, USA.
Li, J. Z., Yu, W. J. & Du, X. Y. (1997). *Chin. J. Appl. Chem.* **14**, 98–100.
Sheldrick, G. M. (1996). *SADABS*. University of Göttingen, Germany.
Sheldrick, G. M. (1997). *SHELXS*97 and *SHELXL*97. University of Göttingen, Germany.
Yu, W. J., Li, J. Z. & Li, G. (1999). *Chin. J. Inorg. Chem.* **15**, 657–660.

Acta Cryst. (2004). E**60**, o1898–o1899 Li-Min Yang *et al.* • $C_{22}H_{18}N_4O_2S$ **o1899**