Bis[3-ethyl-1-methyl-5-(2-oxothiazolidin-3-ylcarbonyl)pyrazol-4-yl] disulfide

Cheng-Xia Tan,[a]* **Jian-Ming Gu,**[b] **De-Long Shen,**[a] **Jian-Quan Weng**[a] **and De-Fang Fan**[c]

[a]College of Chemical Engineering, Zhejiang University of Technology, Hangzhou 310014, People's Republic of China, [b]Analysis Center, Zhejiang University, Hangzhou 310028, People's Republic of China, and [c]College of Agriculture and Biotechnology, Zhejiang University, Hangzhou 310029, People's Republic of China

Correspondence e-mail: tanchengxia@hzcnc.com

The title compound, $C_{20}H_{24}N_6O_4S_4$, has non-crystallographic twofold symmetry about the mid-point of the disulphide bond.

Comment

Derivatives of pyrazolyl-heterocycles have high potential for biological activity and, as such, these derivatives have been widely used as pesticides and fungicides (Grenda *et al.*, 1965). As a continuation of our work on the structure–activity relationship of pyrazolyl-heterocycle derivatives, we have obtained a colourless crystalline compound that was the product of the condensation reaction of 3-ethyl-1-methyl-5-(formoxyl chloride)pyrazol-4-yl disulfide and 2-thiazolidinone.

The structural identity of the product, (I) (Fig. 1 and Table 1), has been established crystallographically. The molecule has non-crystallographic twofold symmetry about the mid-point of the disulphide bond, so the residues lie on the same side of the central bond.

(I)
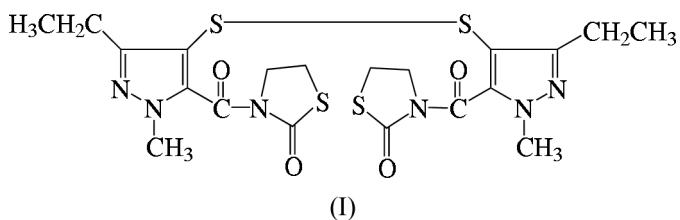
Experimental

To a chloroform solution (30 ml) containing 2-thiazolidinone (1.05 g, 10 mmol), prepared according to the procedure of Crawhall & Elliott (1952), and thiethylamine (1.2 g, 12 mmol) was added, dropwise, 3-ethyl-1-methyl-5-(formoxyl chloride)pyrazol-4-yl disulfide (3.0 g, 5.5 mmol; Miller *et al.*, 1942). The mixture was stirred for 10 h, poured into ice-water and extracted with chloroform. The chloroform layer was washed with an aqueous solution of sodium carbonate, water and a saturated aqueous solution of sodium chloride. After drying over anhydrous sodium sulfate, the solution was concentrated under reduced pressure. The residue was then recrystallized from ethyl acetate to give colourless blocks (m.p. 384–385 K).

Crystal data

$C_{20}H_{24}N_6O_4S_4$	$D_x = 1.444$ Mg m^{-3}
$M_r = 540.69$	Mo $K\alpha$ radiation
Monoclinic, $P2_1/c$	Cell parameters from 15829
$a = 13.342$ (1) Å	reflections
$b = 15.552$ (1) Å	$\theta = 1.3$–27.4°
$c = 12.0130$ (8) Å	$\mu = 0.42$ mm^{-1}
$\beta = 94.076$ (2)°	$T = 295$ (1) K
$V = 2486.4$ (3) Å^3	Block, colourless
$Z = 4$	$0.32 \times 0.26 \times 0.17$ mm

Data collection

Rigaku R-AXIS RAPID diffractometer	5666 independent reflections
ω scans	3436 reflections with $F^2 > 2\sigma(F^2)$
Absorption correction: multi-scan (*ABSCOR*; Higashi, 1995)	$R_{int} = 0.039$
$T_{min} = 0.809$, $T_{max} = 0.931$	$\theta_{max} = 27.4°$
23 803 measured reflections	$h = -16 \rightarrow 17$
	$k = -20 \rightarrow 20$
	$l = -15 \rightarrow 15$

Refinement

Refinement on F^2	H-atom parameters constrained
$R[F^2 > 2\sigma(F)] = 0.037$	$w = 1/[0.0013F_o{}^2 + \sigma(F_o{}^2)]/(4F_o{}^2)$
$wR(F^2) = 0.097$	$(\Delta/\sigma)_{max} < 0.001$
$S = 1.01$	$\Delta\rho_{max} = 0.31$ e Å^{-3}
3436 reflections	$\Delta\rho_{min} = -0.22$ e Å^{-3}
331 parameters	

Table 1
Selected geometric parameters (Å, °).

|			
S1—S3	2.0962 (9)	N4—C13	1.327 (3)
S1—C4	1.741 (2)	N5—C15	1.335 (3)
S2—C9	1.787 (3)	N5—C16	1.452 (4)
S2—C10	1.756 (3)	N6—C17	1.381 (3)
S3—C14	1.736 (2)	N6—C18	1.464 (3)
S4—C19	1.803 (3)	N6—C20	1.399 (3)
S4—C20	1.751 (3)	C1—C2	1.437 (5)
O1—C7	1.203 (3)	C2—C3	1.496 (4)
O2—C10	1.197 (3)	C3—C4	1.399 (3)
O3—C17	1.214 (3)	C4—C5	1.385 (3)
O4—C20	1.201 (4)	C5—C7	1.471 (3)
N1—N2	1.341 (3)	C8—C9	1.499 (4)
N1—C3	1.329 (3)	C11—C12	1.504 (5)
N2—C5	1.350 (3)	C12—C13	1.496 (4)
N2—C6	1.463 (3)	C13—C14	1.402 (3)
N3—C7	1.388 (3)	C14—C15	1.389 (3)
N3—C8	1.455 (3)	C15—C17	1.482 (3)
N3—C10	1.394 (3)	C18—C19	1.505 (5)
N4—N5	1.361 (3)		
C4—S1—S3	101.83 (8)	C6—N2—C5	128.3 (2)
S1—S3—C14	100.95 (8)	N3—C7—C5	117.5 (2)
S1—C4—C3	128.6 (2)	C10—N3—C7	125.0 (2)
S1—C4—C5	126.4 (2)	C8—N3—C7	118.1 (2)
C10—S2—C9	93.1 (1)	C10—N3—C8	115.0 (2)
S2—C9—C8	106.7 (2)	N3—C8—C9	106.6 (2)
S2—C10—O2	124.0 (2)	C13—N4—N5	105.8 (2)
S2—C10—N3	109.5 (2)	N4—N5—C15	111.8 (2)
S3—C14—C13	128.5 (2)	N4—N5—C16	119.0 (2)
S3—C14—C15	126.2 (2)	N4—C13—C14	110.4 (2)
C20—S4—C19	93.0 (2)	N4—C13—C12	122.4 (2)
S4—C19—C18	105.5 (2)	N5—C15—C14	106.8 (2)
S4—C20—O4	123.5 (2)	N5—C15—C17	121.3 (2)
S4—C20—N6	109.7 (2)	C16—N5—C15	129.3 (2)
O1—C7—N3	120.2 (2)	N6—C17—C15	118.9 (2)
O1—C7—C5	122.2 (2)	C20—N6—C17	124.9 (2)
O2—C10—N3	126.5 (2)	C18—N6—C17	117.7 (2)
O3—C17—N6	119.7 (2)	C20—N6—C18	114.9 (2)
O3—C17—C15	121.3 (2)	N6—C18—C19	106.5 (2)
O4—C20—N6	126.7 (3)	C1—C2—C3	115.6 (3)
C3—N1—N2	105.6 (2)	C2—C3—C4	127.6 (2)
N1—N2—C5	112.2 (2)	C3—C4—C5	105.0 (2)
N1—N2—C6	119.6 (2)	C4—C5—C7	132.4 (2)
N1—C3—C2	121.5 (2)	C11—C12—C13	115.3 (3)
N1—C3—C4	110.9 (2)	C12—C13—C14	127.2 (2)
N2—C5—C4	106.3 (2)	C13—C14—C15	105.2 (2)
N2—C5—C7	121.0 (2)	C14—C15—C17	131.5 (2)
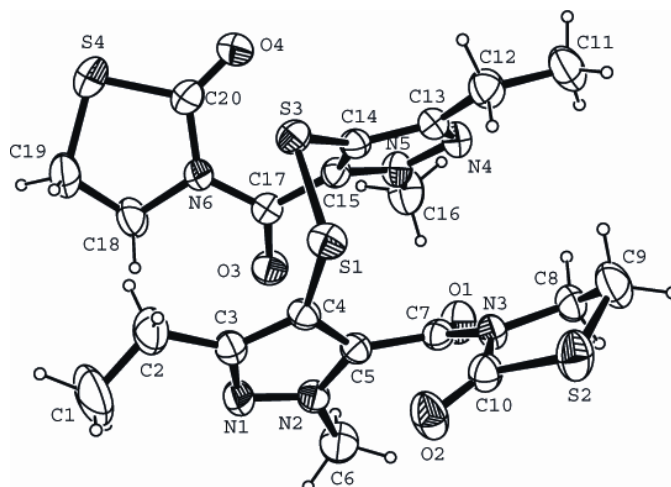
Figure 1
The structure of (I), showing 50% probability displacement ellipsoids.

H atoms were included in the final cycles of refinement in the riding-model approximation, with C—H = 0.96 and 0.97 Å for methyl and methylene H atoms, respectively, and with $U_{iso}(H) = 1.2U_{eq}(C)$.

Data collection: *PROCESS-AUTO* (Rigaku, 1998); cell refinement: *PROCESS-AUTO*; data reduction: *CrystalStructure* (Rigaku and Rigaku/MSC, 2000–2004); program(s) used to solve structure: *SIR*97 (Altomare *et al.*, 1999); program(s) used to refine structure: *CRYSTALS* (Watkin *et al.*, 1996); molecular graphics: *ORTEP*-3 (Farrugia, 1997); software used to prepare material for publication: *CrystalStructure*.

References

Altomare, A., Burla, M., Camalli, M., Cascarano, G., Giacovazzo, C., Guagliardi, A., Moliterni, A., Polidori, G. & Spagna, R. (1999). *J. Appl. Cryst.* **32**, 115–119.
Crawhall, J. C. & Elliott, D. F. (1952). *J. Chem. Soc.* pp. 3094–3102.
Farrugia, L. J. (1997). *J. Appl. Cryst.* **30**, 565.
Grenda, V. J., Jones, R. E. & Gel, G. (1965). *J. Org. Chem.* **30**, 259–261.
Higashi, T. (1995). *ABSCOR*. Rigaku Corporation, 3-9-12 Akishima, Tokyo 196-8666, Japan.
Miller, E., Crossley, F. S. & Moore, M. L. (1942). *J. Am. Chem. Soc.* **64**, 2322–2323.
Rigaku (1998). *PROCESS-AUTO*. Rigaku Corporation, 3-9-12 Akishima, Tokyo 196-8666, Japan.
Rigaku & Rigaku/MSC (2000–2004). CrystalStructure. Verion 3.6.0. Rigaku Corporation, 3-9-12 Akishima, Tokyo 196-8666, Japan, and Rigaku/MSC, 9009 New Trails Drive, The Woodlands, TX 77381–5209, USA.
Watkin, D. J., Prout, C. K., Carruthers, J. R. & Betteridge, P. W. (1996). *CRYSTALS*. Issue 10. Chemical Crystallography Laboratory, Oxford, England.