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Ethyl 1-phenyl-3-sulfanyl-5-(4*H*-1,2,4-triazol-4-yl)-pyrazole-4-carboxylate

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Key indicators

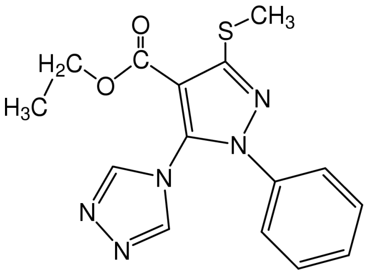
Single-crystal X-ray study
T = 298 K
Mean σ(C–C) = 0.004 Å
R factor = 0.038
wR factor = 0.111
Data-to-parameter ratio = 12.6

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

In the crystal structure of the title compound, $C_{15}H_{15}N_5O_2S$, the triazole ring forms a π_5^6 configuration in which the N between the two C atoms is sp^2 hybridized. A strong S···S($-x$, $-y$, $-z$) interaction exists between adjacent molecules producing a zigzag line along the c axis with an S···S distance of 3.123 (3) Å, and a three-dimensional network is formed through C—H···N and C—H···O hydrogen bonds.

Comment

In studies on new pharmaceuticals and agrochemicals, heterocycles are worthy of very important consideration. Pyrazoles and their derivatives have been reported to show a broad spectrum of biological activities (Liu *et al.*, 1998; Morimoto *et al.*, 1997). In our earlier study on this type of compounds, we have found that substituted arylpyrazoles exhibit good biological activity (Chen *et al.*, 2000); also, pesticidal properties were reported, analgesic and anti-inflammatory activities have been observed (Reddy *et al.*, 1999), and xanthine oxidase inhibition and central depressant activity have also been studied (Ishibuchi *et al.*, 1998; Darias *et al.*, 1998). Since knowledge of the stereochemistry is useful in the rational design of pharmaceuticals and agrochemicals, we here report the synthesis and X-ray crystal structure of the title compound, (I).



(I)

In the title compound, the N1—C1, N3—C6 and N3—C7 bond lengths are remarkably shorter than that of a single C—N (1.47 Å; Sasada, 1984) and close to the value of the C═N double-bond distance (1.28 Å; Wang *et al.*, 1998), which is indicative of significant double-bond character. The triazole ring forms a π_5^6 configuration in which the N3 atom is sp^2 hybridized. The C3—S1 bond length (1.689 Å) is slightly shorter than that of C4—S1 (1.747 Å), which may be due to the conjugation of S1 with the pyrazole ring. The C5—O2 bond length (1.294 Å) is longer than that of C5—O1 (1.175 Å) and remarkably shorter than C14—O2 (1.418 Å), which demonstrates the conjugation of O2 with C5—O1. The pyra-

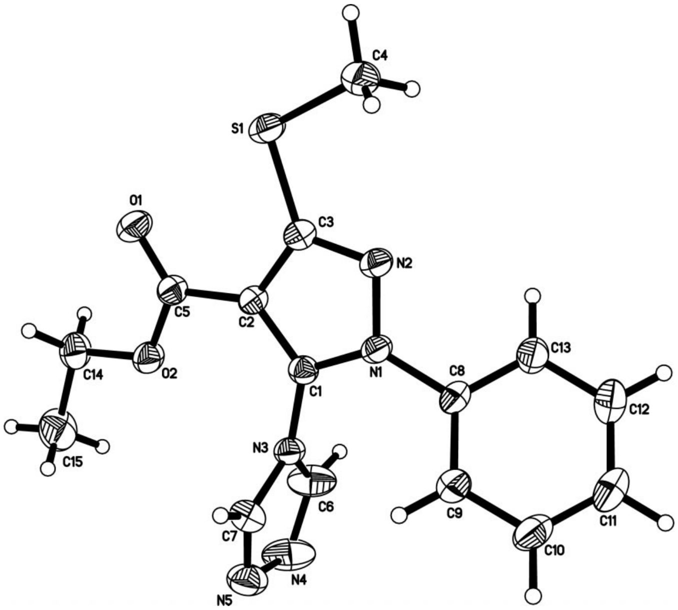


Figure 1
*ORTEP*II view (Johnson, 1976) of the title compound with 30% probability ellipsoids.

zole ring makes dihedral angles of 140.2 (3) and 86.5 (3)° with the phenyl and triazole planes, respectively, and the dihedral angle between them is 109.2 (4)°.

An important feature to note is that a strong S···S($-x$, $-y$, $-z$) interaction exists between adjacent molecules to yield a zigzag linear structure along the *c* axis with the S···S distance of 3.123 (3) Å. In addition, weak intermolecular interactions are found to exist for C6—H6*A*···O1($1-x$, $-y$, $-z$) and C11—H11···N5($-\frac{3}{2}-x$, $\frac{1}{2}+y$, z), forming a three-dimensional network as shown in Fig. 2.

Experimental

To a solution of 1.00 g (3 mmol) ethyl *N*-(1-phenyl-3-methylsulfanyl-4-ethoxycarbonyl-pyrazol-5-yl)formimidate in 15 ml anhydrous acetonitrile, 0.39 g (3 mmol) 2-hydroxybenzal hydrazine was added, then 2 drops of an ether solution of BF_3. After stirring for 2 h, the mixture was filtered. The solution was evaporated and purified by silica-gel column chromatography to give the title compound (yield: 23%). m.p.: 465–467 K. Analysis calculated for the title compound: C 54.69, H 4.59, N 21.27%; found: C 54.42, H 4.63, N 21.16%. FT–IR data (KBr pellet, cm^{-1}): 3115, 2997, 2930, 1695, 1594, 1576, 1496. ^{1}H NMR ($CDCl_3$, δ, p.p.m.): 1.16–1.24 (*t*, 3H), 2.60 (*s*, 3H), 4.10–4.36 (*q*, 2H), 7.18–7.50 (*m*, 5H), 8.30 (*s*, 2H). Crystals of (I) were obtained as blocks by recrystallization from a petroleum ether/ethyl acetate mixture.

Crystal data

$C_{15}H_{15}N_5O_2S$
$M_r = 329.38$
Orthorhombic, *Pbca*
$a = 9.669$ (5) Å
$b = 17.063$ (9) Å
$c = 17.875$ (10) Å
$V = 2949$ (3) Å^3
$Z = 8$
$D_x = 1.484$ Mg m^{-3}

Mo Kα radiation
Cell parameters from 11 458 reflections
$\theta = 2.3$–25.0°
$\mu = 0.24$ mm^{-1}
$T = 298$ (2) K
Prism, colorless
0.25 × 0.20 × 0.15 mm

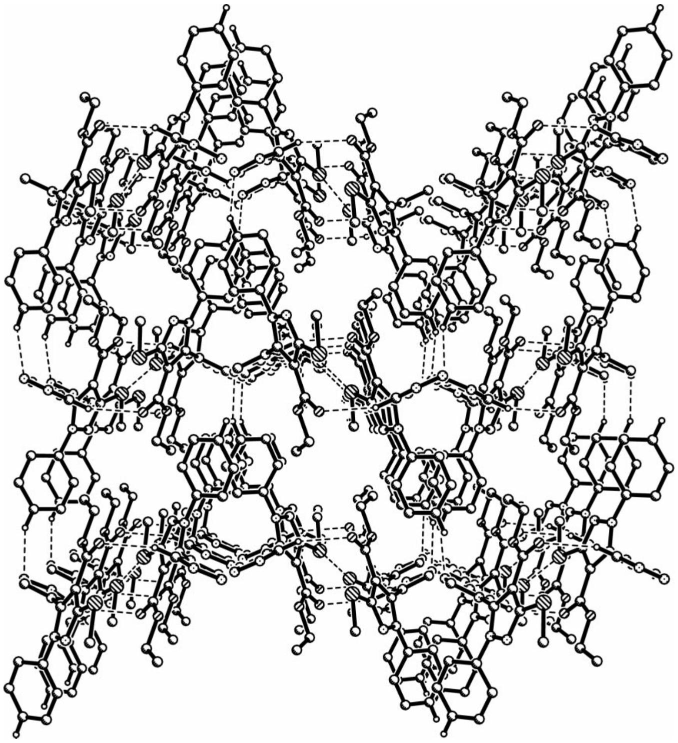


Figure 2
The molecular packing diagram of (I) (H atoms not mentioned in the text have been omitted for clarity).

Data collection

Bruker SMART 1000 diffractometer
ω scans
Absorption correction: multi-scan [*SAINT* (Bruker, 1998) and *SADABS* (Sheldrick, 1997)]
$T_{min} = 0.943$, $T_{max} = 0.965$
11 622 measured reflections

2614 independent reflections
1880 reflections with $I > 2\sigma(I)$
$R_{int} = 0.058$
$\theta_{max} = 25.0°$
$h = -11 \rightarrow 11$
$k = -20 \rightarrow 14$
$l = -18 \rightarrow 21$

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)] = 0.038$
$wR(F^2) = 0.111$
$S = 1.01$
2614 reflections
208 parameters
H-atom parameters constrained

$w = 1/[\sigma^2(F_o^2) + (0.0551P)^2 + 0.8570P]$
where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max} < 0.001$
$\Delta\rho_{max} = 0.19$ e Å^{-3}
$\Delta\rho_{min} = -0.27$ e Å^{-3}

Table 1
Selected geometric parameters (Å, °).

S1—C3	1.689 (2)	N3—C1	1.370 (3)
S1—C4	1.747 (3)	N4—C6	1.266 (3)
N1—C1	1.320 (3)	N4—N5	1.344 (3)
N1—N2	1.341 (2)	N5—C7	1.261 (3)
N1—C8	1.396 (3)	O1—C5	1.175 (3)
N2—C3	1.298 (3)	O2—C5	1.294 (3)
N3—C6	1.314 (3)	O2—C14	1.418 (3)
N3—C7	1.323 (3)		
C3—S1—C4	100.55 (12)	C6—N3—C1	128.8 (2)
C1—N1—N2	110.90 (16)	C7—N3—C1	127.0 (2)
C1—N1—C8	130.53 (18)	C6—N4—N5	106.9 (2)
N2—N1—C8	118.17 (17)	C7—N5—N4	107.0 (2)
C3—N2—N1	104.87 (17)	C5—O2—C14	116.01 (18)
C6—N3—C7	104.2 (2)		

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

D—H···A	D—H	H···A	D···A	D—H···A
C6—H6A···O1$^{\rm i}$	0.930	2.346	3.190 (4)	151
C11—H11A···N5$^{\rm ii}$	0.930	2.514	3.381 (3)	155

Symmetry codes: (i) $1 - x, -y, -z$; (ii) $\frac{3}{2} - x, \frac{1}{2} + y, z$.

The H atoms bonded to C atoms were placed in their geometrically calculated positions and included in the final refinement in the riding model approximation with displacement parameters derived from the atoms to which they were bonded.

Data collection: *SMART* (Bruker, 1998); cell refinement: *SMART*; data reduction: *SAINT* (Bruker, 1998); program(s) used to solve structure: *SHELXS*97 (Sheldrick, 1997); program(s) used to refine structure: *SHELXL*97 (Sheldrick, 1997); molecular graphics: *XP* (Bruker, 1998).

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