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Ethyl 3-methyl-1-(3-methylbenzoyl)-5-(methylsulfanyl)-1*H*-pyrazole-4-carboxylate

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Key indicators

Single-crystal X-ray study
T = 293 K
Mean σ(C–C) = 0.003 Å
R factor = 0.043
wR factor = 0.109
Data-to-parameter ratio = 13.7

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

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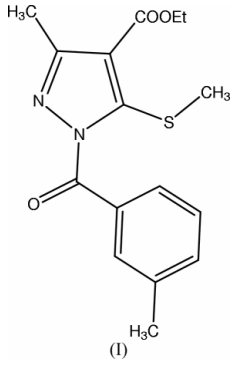
In the title compound, $C_{16}H_{18}N_2O_3S$, the pyrazole and ester fragments are almost coplanar and the dihedral angle between the pyrazole and benzene rings is 46.08 (13)°. There are three intramolecular interactions in the structure, forming three six-membered rings. The crystal packing is stabilized by C—H···O and C—H···π interactions.

Comment

Pyrazole and its derivatives represent one of the most active classes of compounds, possessing a wide spectrum of biological activities, including antibacterial, antifungal (Chen & Li, 2000), insecticidal (Huang *et al.*, 1996) and other biological activities (Kopp *et al.*, 2001). Until now, a great variety of such compounds have been synthesized, among which some commercial pesticides have been developed including ET-751 (Miura *et al.*, 1993) and pyrazosulfuron–ethyl (NC-311). For these reasons and as a continuation of our research for new and better biologically active agents, we have synthesized the title compound, (I). An X-ray analysis of (I) was undertaken to establish its molecular structure.



(I)

The bond lengths and angles in (I) are within normal ranges (Allen *et al.*, 1987) and are comparable with those observed in a related structure, ethyl 5-amino-1-[(5-methyl-1-phenyl-1*H*-pyrazol-4-yl)carbonyl]-3-(methylsulfanyl)-1*H*-pyrazole-4-carboxylate (Li *et al.*, 2004). The bonds in the pyrazole ring show a character intermediate between single and double bonds (Table 1). The S1—C11 [1.7448 (19) Å] bond is shorter than S1—C12 [1.792 (2) Å] because of the π-conjugation effects of the pyrazole ring.

The methylsulfanyl–pyrazole and ester fragments are almost coplanar, with a deviation of 0.227 (4) Å for atom C16 from the O1/O2/N1/N2/C9–C11/C14/C15 mean plane. The C15—O1—C14—O2, C15—O1—C14—C10, C12—S1—C11—N2 and C12—S1—C11—C10 torsion angles are −0.6 (3), 179.36 (19), −1.2 (2) and 177.55 (19)°, respectively. The mol-

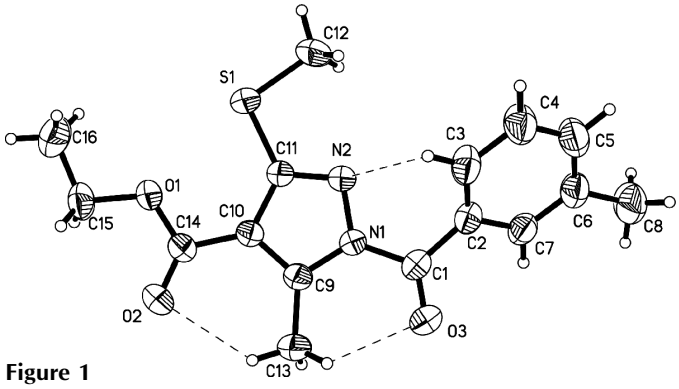


Figure 1
View of (I), showing 50% probability displacement ellipsoids and the atom-numbering scheme. Dashed lines indicate intramolecular interactions.

ecule as a whole is not planar, as the tolyl ring is twisted away from the remainder of the molecule; the dihedral angle between the benzene and pyrazole rings is 46.08 (13)°

There are three intramolecular interactions in the molecular structure of (I) (Table 2), forming three six-membered rings (Fig. 1). In the crystal structure, there is a weak C12—H12$B\cdots$O2(x, $y-1$, z) intermolecular interaction. The molecular packing is further stabilized by C—H$\cdots\pi$ interactions involving the benzene ring (see Table 2 for details).

Experimental

In a 50 ml three-necked round-bottomed flask was placed a solution of ethyl 3-methyl-5-methylsulfanyl-1*H*-pyrazole-4-carboxylate (1.000 g, 5 mmol) in chloroform (20 ml). After cooling in an ice–water bath to 273–278 K, 3-methylbenzoyl chloride (0.773 g, 5 mmol) in chloroform (10 ml) was added dropwise with stirring, and the resulting solution was stirred for another 2 h. The solution was filtered through a Hirsch funnel and evaporated. Crystallization from acetonitrile afforded 1.35 g of the pure final product as colourless needle-like crystals in a yield of 85%. Around 0.1 g of the pure title compound was dissolved in about 5 ml 1,4-dioxane, and the resulting solution was refluxed for 1 h, cooled to room temperature, filtered through a Hirsch funnel and then allowed to stand at room temperature in a 10 ml beaker. Single crystals suitable for X-ray diffraction study were obtained from this solution.

Crystal data

$C_{16}H_{18}N_2O_3S$
M_r = 318.38
Triclinic, $P\overline{1}$
a = 7.677 (3) Å
b = 9.228 (3) Å
c = 12.271 (4) Å
α = 81.745 (5)°
β = 73.352 (5)°
γ = 73.583 (5)°
V = 797.1 (5) Å^3
Z = 2
D_x = 1.327 Mg m^{-3}
Mo $K\alpha$ radiation
Cell parameters from 4133 reflections
θ = 2.8–25.0°
μ = 0.22 mm^{-1}
T = 293 (2) K
Block, colourless
0.30 × 0.24 × 0.16 mm

Data collection

Simens SMART 1000 CCD area-detector diffractometer
ω scans
Absorption correction: multi-scan (*SADABS*; Sheldrick, 1996)
T_{min} = 0.938, T_{max} = 0.966
4133 measured reflections
2789 independent reflections
2224 reflections with $I > 2\sigma(I)$
R_{int} = 0.021
θ_{max} = 25.0°
$h = -9 \rightarrow 8$
$k = -8 \rightarrow 10$
$l = -14 \rightarrow 12$

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)]$ = 0.043
$wR(F^2)$ = 0.109
S = 1.06
2789 reflections
203 parameters
H-atom parameters constrained
$w = 1/[\sigma^2(F_o^2) + (0.049P)^2 + 0.2362P]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max}$ = 0.002
$\Delta\rho_{max}$ = 0.21 e Å^{-3}
$\Delta\rho_{min}$ = −0.32 e Å^{-3}

Table 1
Selected geometric parameters (Å, °).

S1—C11	1.7448 (19)	N1—N2	1.385 (2)
S1—C12	1.792 (2)	N1—C1	1.420 (3)
O2—C14	1.202 (2)	N2—C11	1.314 (3)
O3—C1	1.205 (3)	C9—C10	1.376 (3)
N1—C9	1.369 (2)	C10—C11	1.429 (3)
C12—S1—C11—N2	−1.2 (2)	C15—O1—C14—O2	−0.6 (3)
C12—S1—C11—C10	177.55 (19)	C15—O1—C14—C10	179.36 (19)

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

D—H$\cdots A$	D—H	H$\cdots A$	$D\cdots A$	D—H$\cdots A$
C3—H3$\cdots$N2	0.93	2.48	2.853 (3)	104
C12—H12$B\cdots$O2^{i}	0.96	2.58	3.508 (3)	162
C13—H13$A\cdots$O2	0.96	2.42	3.047 (3)	123
C13—H13$B\cdots$O3	0.96	2.45	2.850 (3)	105
C8—H8$A\cdots CgP^{ii}$	0.96	2.84	3.735 (4)	155

Symmetry codes: (i) $x, y-1, z$; (ii) $-x, -y, 2-z$. *CgP* denotes the centroid of the benzene ring.

All H atoms were placed at idealized positions and allowed to ride on their parent C atom, with C—H = 0.93–0.97 Å and U_{iso}(H) = 1.2U_{eq}(C) [for methyl H atoms, U_{iso}(H) = 1.5U_{eq}(C)]. Owing to the large fraction of weak data at higher angles, the 2θ maximum was limited to 50.0°.

Data collection: *SMART* (Siemens, 1996); cell refinement: *SAINT* (Siemens, 1996); data reduction: *SAINT*; program(s) used to solve structure: *SHELXTL* (Sheldrick, 1997); program(s) used to refine structure: *SHELXTL*; molecular graphics: *SHELXTL*; software used to prepare material for publication: *SHELXTL, PARST* (Nardelli, 1995) and *PLATON* (Spek, 1990).

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