Acta Crystallographica Section E
Structure Reports Online
ISSN 1600-5368

1-Ethyl-5-methyl-3-methylsulfanyl-1*H*-pyrazole-4-carboxylic acid

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Key indicators

Single-crystal X-ray study
T = 293 K
Mean σ(C–C) = 0.005 Å
Disorder in main residue
R factor = 0.054
wR factor = 0.152
Data-to-parameter ratio = 12.4

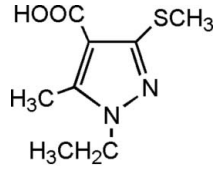
For details of how these key indicators were automatically derived from the article, see http://journals.iucr.org/e.

Received 27 October 2005
Accepted 21 November 2005
Online 16 December 2005

In the crystal structure of the title compound, $C_8H_{12}N_2O_2S$, the molecules are linked into centrosymmetric dimers by a pair of strong O—H···O hydrogen bonds. Intermolecular S···S contacts between adjacent dimers generate a sheet-like structure running parallel to the (211) plane.

Comment

Pyrazole and its derivatives represent one of the most important classes of compounds, possessing a wide spectrum of biological activities (Iovu *et al.*, 2003), such as antibacterial, fungicidal, herbicidal and insecticidal. In the course of our systematic studies aimed at the synthesis of new bioactive compounds, we synthesized the title compound, (I), the structure of which is reported here.



(I)

The pyrazole ring is planar, the largest deviation from planarity being 0.009 (4) Å for atom C1. Bond distances and angles (Table 1) are as expected for this type of compound. In the crystal structure, centrosymmetrically related molecules are linked into dimers by intermolecular O—H···O hydrogen bonds (Table 2 and Fig. 2), thus generating rings of graph-set motifs $R_2^2(8)$ (Bernstein *et al.*, 1995). Intermolecular contacts between S atoms of adjacent dimers [S1···S1^{ii} = 3.5374 (17) Å; symmetry code: (ii) $1-x, -y, -z$] are observed, generating a sheet-like structure running parallel to the (211) plane.

Experimental

To a solution of ketene *S*,*S*-acetal (23.43 g, 0.1 mol) in ethanol (50 ml), 80% hydrazine hydrate (6.3 g,0.1 mol) was added slowly. The mixture was stirred for 3 h at room temperature to give ethyl 3-methyl-5-methylthio-1*H*-pyrazol-4-carboxylate, (1). NaOH (1 g) and and Et_2SO_4 (0.77 g, 5 mmol) in chloroform (50 ml) were added slowly to the mixture of (1) (1.0 g, 5 mmol) with stirring for 5 h at room temperature to give ethyl 1-ethyl-5-methyl-3-methylthiopyrazole-4-carboxylate, (2). Compound (2) was hydrolysed under reflux for 3 h and after cooling acidified to pH 3.0, to give (I). Single crystals suitable for X-ray diffraction studies were isolated by recrystallization from ethanol and MeCN (m.p. 466.5 K).

Crystal data

$C_8H_{12}N_2O_2S$
M_r = 200.27
Triclinic, $P\overline{1}$
a = 7.949 (2) Å
b = 8.330 (2) Å
c = 8.368 (2) Å
α = 71.267 (4)°
β = 80.761 (5)°
γ = 74.291 (5)°
V = 503.5 (2) Å^3
Z = 2
D_x = 1.321 Mg m^{-3}
Mo $K\alpha$ radiation
Cell parameters from 1010 reflections
θ = 2.6–25.0°
μ = 0.29 mm^{-1}
T = 293 (2) K
Prism, colourless
0.22 × 0.18 × 0.12 mm

Data collection

Bruker SMART 1000 CCD area-detector diffractometer
φ and ω scans
Absorption correction: multi-scan (*SADABS*; Sheldrick, 1996)
T_{min} = 0.939, T_{max} = 0.966
2645 measured reflections
1765 independent reflections
1253 reflections with $I > 2\sigma(I)$
R_{int} = 0.022
θ_{max} = 25.0°
$h = -9 \rightarrow 7$
$k = -9 \rightarrow 7$
$l = -9 \rightarrow 9$

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)]$ = 0.054
$wR(F^2)$ = 0.152
S = 1.04
1765 reflections
142 parameters
H-atom parameters constrained
$w = 1/[\sigma^2(F_o^2) + (0.0597P)^2 + 0.4305P]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max}$ = 0.002
$\Delta\rho_{max}$ = 0.35 e Å^{-3}
$\Delta\rho_{min}$ = −0.42 e Å^{-3}

Table 1
Selected geometric parameters (Å, °).

N1—C1	1.330 (5)	C1—C3	1.390 (4)
N1—N2	1.375 (4)	C3—C5	1.415 (5)
N2—C5	1.321 (5)		
C1—N1—N2	113.4 (3)	C1—C3—C5	104.9 (3)
C5—N2—N1	104.0 (3)	N2—C5—C3	111.5 (3)
N1—C1—C3	106.1 (3)		

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

D—H···A	D—H	H···A	D···A	D—H···A
O2—H2···O1^{i}	0.82	1.79	2.599 (4)	169

Symmetry code: (i) $-x+1, -y-1, -z+1$.

All H atoms were placed in calculated positions, with C—H = 0.96 or 0.97 Å and O—H = 0.82 Å, and included in the final cycles of refinement using a riding model, with U_{iso}(H) values of 1.2 or 1.5 times U_{eq} of the parent atoms. The ethyl group is disordered; atoms C7 and C8 and related H atoms were refined over two positions with occupancies of 0.751 (10) and 0.249 (10) for the major and minor components, respectively.

Data collection: *SMART* (Bruker, 1998); cell refinement: *SAINT* (Bruker, 1999); data reduction: *SAINT*; program(s) used to solve structure: *SHELXS97* (Sheldrick, 1997); program(s) used to refine structure: *SHELXL97* (Sheldrick, 1997); molecular graphics: *SHELXTL* (Bruker, 1999); software used to prepare material for publication: *SHELXTL*.

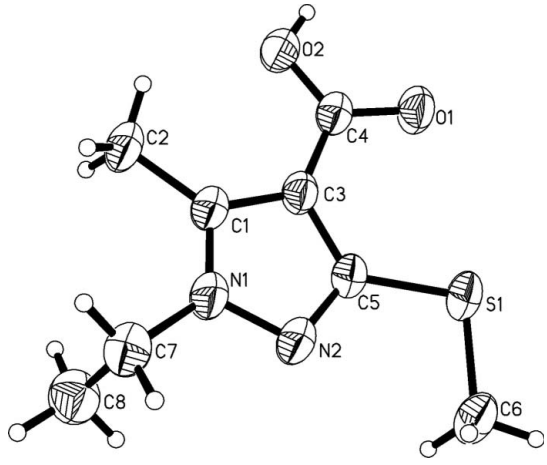


Figure 1
View of the title compound, with 35% probability displacement ellipsoids. Only the major component of the disordered C7/C8 ethyl group is shown.

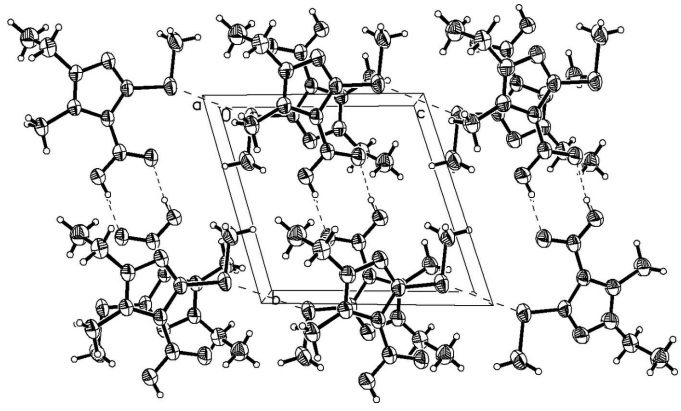


Figure 2
Molecular packing of the title compound, viewed along the *a* axis. Hydrogen bonds and S···S contacts are shown as dashed lines. Only the major component of the disordered C7/C8 ethyl group is shown.

This project was supported by the National Natural Science Foundation of China (No. 20572057).

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