Acta Crystallographica Section E
Structure Reports Online
ISSN 1600-5368

Ethyl 1-[5-amino-1-*tert*-butyl-3-(methylsulfanyl)-1*H*-pyrazole-4-carbonyl]-5-methyl-3-(methylsulfanyl)-1*H*-pyrazole-4-carboxylate

Jun-Fei Li, Hai-Bin Song, You-Quan Zhu and Hua-Zheng Yang*

State Key Laboratory and Institute of Elemento-Organic Chemistry, Nankai University, Weijin Road No. 94, Tianjin, People's Republic of China

Correspondence e-mail: lijunfei@mail.nankai.edu.cn

Key indicators

Single-crystal X-ray study
T = 294 K
Mean σ(C–C) = 0.003 Å
Disorder in main residue
R factor = 0.043
wR factor = 0.117
Data-to-parameter ratio = 16.4

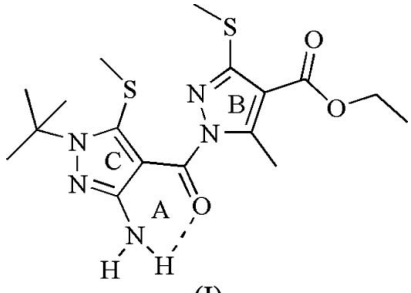
For details of how these key indicators were automatically derived from the article, see http://journals.iucr.org/e.

Received 6 March 2006
Accepted 29 March 2006

The title molecule, $C_{17}H_{25}N_5O_3S_2$, belongs to the family of bis-heterocycles. In the crystal structure, there are one intra- and two intermolecular hydrogen bonds. One of the two pyrazole rings and the six-membered ring formed by the intramolecular hydrogen bond are approximately coplanar.

Comment

4-Hydroxyphenylpyruvate dioxygenase (4-HPPD, EC1.1 3.11.27) is an important enzyme involved in the catabolism of tyrosine in most organisms and a relatively new target for herbicides. Due to their herbicidal activity and the fact that they belong to the inhibitor of this enzyme, many benzoylpyrazole derivatives have received much more attention, for example pyrazolate (Yamaoka *et al.*, 1987, 1988), pyroxyfen (Kimura, 1984) and benzofenap (Kaoru & Atsushi, 1991). All the compounds are prodrugs for a shared active entity, the free hydroxypyrazole destosylpryazolate. It has also been noticed that NH and OH possess a similar capability for forming hydrogen bonds and both pyrazole and benzene rings are aromatic. However, pyrazole derivatives containing two pyrazole rings have rarely been reported to act as herbicides. Here we describe the crystal structure of the title compound, (I).



(I)

In (I), an intramolecular hydrogen bond is formed between N1 and O1 (Fig. 1 and Table 2). Atom O1 lies 0.135 (4)Å from the plane defined by atoms C5, C6, C9 and N1; the largest deviation from plane A is 0.041 (1) Å for atom C5. The dihedral angles between this plane and planes *B* and *C* are 59.63 (8) and 5.95 (15)°, respectively. Thus, planes *A* and *C* are practically coplanar (Table 1). Adjacent molecules are linked *via* N1—H1*B*···O1^{ii} hydrogen bonds, forming rings along the *b* axis [symmetry code: (ii) $-x+1, -y+1, -z$] and glide-related molecules are linked *via* N1—H1*B*···O3^{iii} hydrogen bonds, forming chains along the *c* axis [symmetry code: (iii) $x-1, y, z-1$]. Part of the chain structure is shown in Fig. 2 (Table 2).

Experimental

To a solution of ethyl 2-[bis(methylsulfanyl)methylene]-3-oxobutanoate (5.0 mmol) in ethanol (15 ml) was added 1-*tert*-butyl-5-amino-3-(methylsulfanyl)-1*H*-pyrazole-4-carbohydrazide (5.5 mmol). The mixture was refluxed for 8 h and cooled to room temperature, then poured into water (30 ml). The white precipitate was purified by recrystallization from ethanol/water (3:1 *v*/*v*). Crystals of (I) suitable for single-crystal X-ray diffraction were selected directly from the sample as prepared.

Crystal data

$C_{17}H_{25}N_5O_3S_2$
M_r = 411.54
Monoclinic, $P2_1/c$
a = 9.3972 (14) Å
b = 22.870 (3) Å
c = 10.4065 (16) Å
β = 105.976 (2)°
V = 2150.1 (6) Å^3
Z = 4
D_x = 1.271 Mg m^{-3}
Mo $K\alpha$ radiation
μ = 0.27 mm^{-1}
T = 294 (2) K
Block, colorless
0.20 × 0.16 × 0.12 mm

Data collection

Bruker SMART CCD area-detector diffractometer
φ and ω scans
Absorption correction: multi-scan (*SADABS*; Sheldrick, 1996)
T_{min} = 0.940, T_{max} = 0.968
12099 measured reflections
4426 independent reflections
3188 reflections with $I > 2\sigma(I)$
R_{int} = 0.033
θ_{max} = 26.5°

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)]$ = 0.043
$wR(F^2)$ = 0.117
S = 1.03
4426 reflections
270 parameters
H atoms treated by a mixture of independent and constrained refinement
$w = 1/[\sigma^2(F_o^2) + (0.0506P)^2 + 0.8773P]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max}$ = 0.001
$\Delta\rho_{max}$ = 0.27 e Å^{-3}
$\Delta\rho_{min}$ = −0.25 e Å^{-3}
Extinction correction: *SHELXL97*
Extinction coefficient: 0.0097 (11)

Table 1
Selected geometric parameters (Å, °).

O1—C9	1.221 (2)	C5—C6	1.419 (3)
N1—C5	1.344 (3)	C6—C9	1.407 (3)
N1—C5—C6	126.78 (19)	O1—C9—C6	125.98 (17)
C9—C6—C5	122.55 (17)		
N1—C5—C6—C9	−4.8 (3)	C5—C6—C9—O1	−4.2 (3)
N2—C5—C6—C9	174.66 (18)	C7—C6—C9—O1	169.5 (2)
N1—C5—C6—C7	179.9 (2)	C5—C6—C9—N4	177.32 (17)
N2—C5—C6—C7	−0.6 (2)	C7—C6—C9—N4	−9.0 (3)

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

D—H···A	D—H	H···A	D···A	D—H···A
N1—H1A···O3^{i}	0.84 (3)	2.25 (3)	3.045 (2)	158 (2)
N1—H1B···O1	0.87 (3)	2.20 (3)	2.830 (3)	129 (2)
N1—H1B···O1^{ii}	0.87 (3)	2.35 (3)	3.091 (3)	143 (2)

Symmetry codes: (i) $x-1, y, z-1$; (ii) $-x+1, -y+1, -z$.

The C8 methyl group is disordered over two sites, with refined occupancies of 0.61 (3) and 0.39 (3). H atoms attached to the C atoms were included in calculated positions and treated as riding atoms using *SHELXL97* (Sheldrick, 1997) default parameters: C—H = 0.96 (CH_3) or 0.97 Å (CH_2), and U_{iso}(H) = 1.5U_{eq} and 1.2U_{eq}, respectively. H atoms of the amino group were located in difference Fourier maps and refined isotropically with no restraints.

Data collection: *SMART* (Bruker, 1999); 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*.

This work was supported by the National Key Project for Basic Research (No. 2003CB114400), the National Natural Science Foundation of China (No. 20572054), and the Research Foundation for the Doctoral Program of Higher Education.

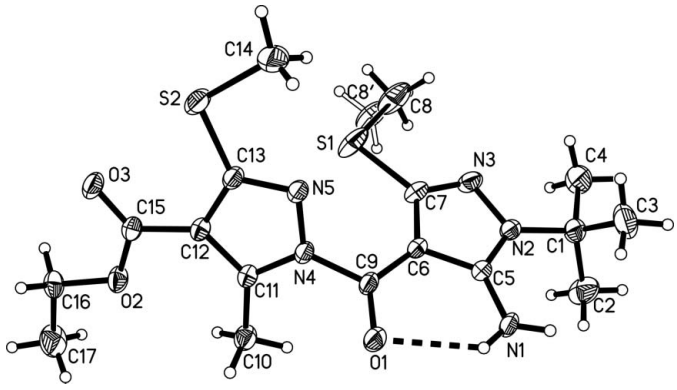


Figure 1
View of (I), showing the atom-labeling scheme. Displacement ellipsoids are drawn at the 30% probability level. The dashed line indicates a hydrogen bond.

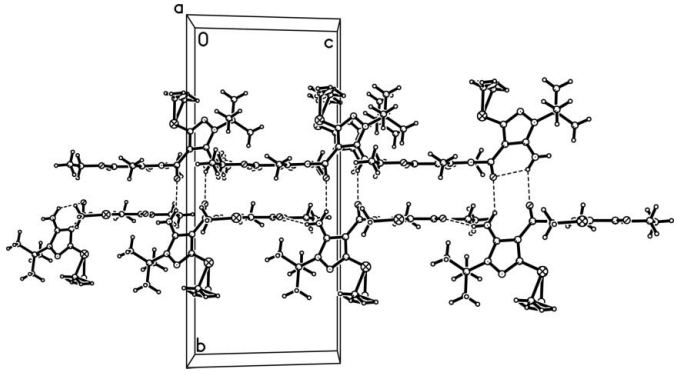


Figure 2
Packing diagram of (I), showing the intra- and intermolecular hydrogen bonds as dashed lines.

References

Bruker (1999). *SMART* (Version 5.618), *SAINT* (Version 6.45) and *SHELXTL* (Version 6.1). Bruker AXS Inc., Madison, Wisconsin, USA.
Kaoru, I. & Atsushi, G. (1991). *Jpn Pestic. Inf.* **59**, 16–18.
Kimura, F. P. (1984). *Jpn Pestic. Inf.* **45**, 24–27.

Sheldrick, G. M. (1996). *SADABS*. Version 4.202. University of Göttingen, Germany.
Sheldrick, G. M. (1997). *SHELXS97* and *SHELXL97*. University of Göttingen, Germany.
Yamaoka, K., Nakagawa, M. & Ishida, M. (1987). *J. Pestic. Sci.* **12**, 209–212.
Yamaoka, K., Tohjigamori, M., Tsujino, Y., Nakagawa, M. & Ishida, M. J. (1988). *Pestic. Sci.* **13**, 261–268.