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Ethyl 6-methylsulfanyl-2-phenyl-1*H*-imidazo[1,2-*b*]pyrazole-7-carboxylate monohydrate

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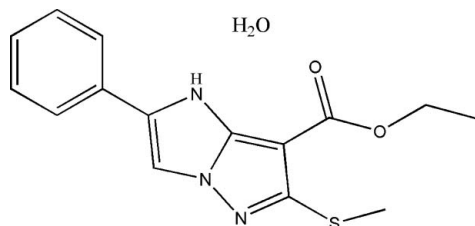
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Key indicators: single-crystal X-ray study; $T = 273$ K; mean $\sigma(\text{C}-\text{C}) = 0.005$ Å; R factor = 0.044; wR factor = 0.094; data-to-parameter ratio = 16.1.

The title compound, $\text{C}_{15}\text{H}_{15}\text{N}_3\text{O}_2\text{S}\cdot\text{H}_2\text{O}$, has been obtained in a search for new imidazo[1,2-*b*]pyrazole derivatives with better biological activity. The 1*H*-imidazo[1,2-*b*]pyrazole plane forms a dihedral angle of $16.90(3)^\circ$ with the benzene ring. π - π interactions are indicated by the short distance of $3.643(2)$ Å between the centroids of the benzene and imidazole rings. The crystal structure also involves intermolecular $\text{O}-\text{H}\cdots\text{N}$ hydrogen bonds.

Related literature

For the biological activity of imidazo[1,2-*b*]pyrazole derivatives, see: Vanotti *et al.* (1994); Kinnamon *et al.* (2000); Li *et al.* (2005). For bond-length data, see: Allen *et al.*, 1987.



Experimental

Crystal data

 $\text{C}_{15}\text{H}_{15}\text{N}_3\text{O}_2\text{S}\cdot\text{H}_2\text{O}$ $M_r = 319.38$ Orthorhombic, $Pna2_1$ $a = 19.017(2)$ Å $b = 5.4854(7)$ Å $c = 15.2314(18)$ Å $V = 1588.9(3)$ Å³ $Z = 4$ Mo $K\alpha$ radiation $\mu = 0.22$ mm⁻¹ $T = 273$ K $0.20 \times 0.10 \times 0.10$ mm

Data collection

Bruker SMART CCD area-detector diffractometer

Absorption correction: multi-scan

(SADABS; Sheldrick, 1996)

 $T_{\min} = 0.957$, $T_{\max} = 0.978$

8763 measured reflections

3326 independent reflections

1877 reflections with $I > 2\sigma(I)$ $R_{\text{int}} = 0.051$

Refinement

 $R[F^2 > 2\sigma(F^2)] = 0.044$ $wR(F^2) = 0.094$ $S = 0.97$

3326 reflections

207 parameters

1 restraint

H atoms treated by a mixture of independent and constrained refinement

 $\Delta\rho_{\text{max}} = 0.15$ e Å⁻³ $\Delta\rho_{\text{min}} = -0.14$ e Å⁻³

Absolute structure: Flack (1983),

1442 Friedel pairs

Flack parameter: $-0.01(9)$

Table 1

Hydrogen-bond geometry (Å, °).

$D-H\cdots A$	$D-H$	$H\cdots A$	$D\cdots A$	$D-H\cdots A$
$\text{O3}-\text{H3A}\cdots\text{N3}^i$	0.99 (6)	1.86 (6)	2.809 (4)	160 (5)

Symmetry code: (i) $-x + \frac{1}{2}, y + \frac{1}{2}, z - \frac{1}{2}$.

Data collection: SMART (Bruker, 1998); cell refinement: SAINT (Bruker, 1999); data reduction: SAINT; program(s) used to solve structure: SHELXTL (Sheldrick, 2008); program(s) used to refine structure: SHELXTL; molecular graphics: SHELXTL; software used to prepare material for publication: SHELXTL.

Supplementary data and figures for this paper are available from the IUCr electronic archives (Reference: HG2495).

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supplementary materials

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Ethyl 6-methylsulfanyl-2-phenyl-1*H*-imidazo[1,2-*b*]pyrazole-7-carboxylate monohydrate

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Comment

Imidazo[1,2-*b*]pyrazole derivatives have been reported to show various biological activities [Vanotti *et al.*, 1994; Kinnamon *et al.*, 2000], in continuation of our research interest in this field [Li *et al.*, 2005], the new title compound has been synthesized in a search for new compounds with better biological activity, and its crystal structure was determined by X-ray diffraction method.

The title compound crystallizes as a monohydrate (Fig. 1), all bond lengths are normal and in a good agreement with those reported previously (Allen *et al.*, 1987). Atoms S1/O1/O2/C12/C13/C14 lie in 1*H*-imidazo[1,2-*b*]pyrazole (C7—C11/N1/N2/N3) plane with maximum least squares plane deviation for C14 0.070 (3) Å. The 1*H*-imidazo[1,2-*b*]pyrazole plane forms dihedral angles of 16.90 (3)° with the benzene ring (C1—C6). π - π stacking interactions (Table 1) are present in the structure. The crystal structure involves intermolecular are O—H \cdots N hydrogen bonds.

Experimental

A suspended solution in 30 ml of acetonitrile containing 5 mmol (1.01 g) of ethyl 5-amino-3-methylthio-1*H*-pyrazole-4-carboxylate, 5 mmol (1.00) of α -bromoacetophenone and 10 mmol (1.38 g) of sodium carbonate was refluxed for about 10 h until the starting materials were consumed completely, as indicated by TLC. On cooling, the solid was removed through filtration, and the filtrate was evaporated to afford a residue, which was dissolved in 30 ml of absolute ethanol, followed by the addition of several drops of concentrated hydrochloric acid. The resulting solution was then refluxed for about 3 h, and cooled to room temperature. The solution was then evaporated in vacuo to afford the crude product, which was purified by column chromatography using ethyl acetate/petroleum ether (1:5) to give 0.87 g of pure title compound. Crystals suitable for X-ray diffraction were obtained from slow evaporation of a solution of the title compound in dichloromethane/ethyl acetate/petroleum ether (1/2/1) at room temperature.

Refinement

All H atoms were found on difference maps. The water H atoms were refined freely, giving 0.85 (6) and 0.99 (6)Å, and included in the final cycles of refinement using a riding model, with $U_{\text{iso}}(\text{H}) = 1.2U_{\text{eq}}(\text{C}, \text{N})$ and $1.5U_{\text{eq}}(\text{C})$ for the methyl H atoms.

Figures

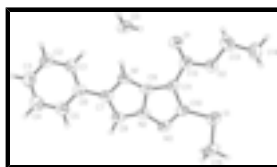


Fig. 1. View of the title compound, with displacement ellipsoids drawn at the 40% probability level.

Ethyl 6-methylsulfanyl-2-phenyl-1*H*-imidazo[1,2-*b*]pyrazole-7-carboxylate monohydrate

Crystal data

C₁₅H₁₅N₃O₂S·H₂O

M_r = 319.38

Orthorhombic, *Pna*2₁

Hall symbol: P 2c -2n

a = 19.017 (2) Å

b = 5.4854 (7) Å

c = 15.2314 (18) Å

V = 1588.9 (3) Å³

Z = 4

*F*₀₀₀ = 672

D_x = 1.335 Mg m⁻³

Mo *K*α radiation

λ = 0.71073 Å

Cell parameters from 1077 reflections

θ = 2.5–18.0°

μ = 0.22 mm⁻¹

T = 273 K

Block, colorless

0.20 × 0.10 × 0.10 mm

Data collection

Bruker SMART CCD area-detector
diffractometer

Radiation source: fine-focus sealed tube

Monochromator: graphite

T = 273 K

φ and ω scans

Absorption correction: multi-scan
(SADABS; Sheldrick, 1996)

*T*_{min} = 0.957, *T*_{max} = 0.978

8763 measured reflections

3326 independent reflections

1877 reflections with *I* > 2σ(*I*)

*R*_{int} = 0.051

θ_{max} = 27.5°

θ_{min} = 2.1°

h = -24→17

k = -7→6

l = -19→19

Refinement

Refinement on *F*²

Least-squares matrix: full

R [*F*² > 2σ(*F*²)] = 0.044

wR (*F*²) = 0.094

S = 0.97

3326 reflections

207 parameters

1 restraint

Primary atom site location: structure-invariant direct
methods

Secondary atom site location: difference Fourier map

Hydrogen site location: inferred from neighbouring
sites

H atoms treated by a mixture of
independent and constrained refinement

$$w = 1/[\sigma^2(F_o^2) + (0.0345P)^2]$$

where *P* = (*F_o*² + 2*F_c*²)/3

(Δ/σ)_{max} = 0.001

Δρ_{max} = 0.15 e Å⁻³

Δρ_{min} = -0.14 e Å⁻³

Extinction correction: none

Absolute structure: Flack (1983), 1442 Friedel pairs

Flack parameter: -0.01 (9)

Special details

Geometry. All e.s.d.'s (except the e.s.d. in the dihedral angle between two l.s. planes) are estimated using the full covariance matrix. The cell e.s.d.'s are taken into account individually in the estimation of e.s.d.'s in distances, angles and torsion angles; correlations between e.s.d.'s in cell parameters are only used when they are defined by crystal symmetry. An approximate (isotropic) treatment of cell e.s.d.'s is used for estimating e.s.d.'s involving l.s. planes.

Refinement. Refinement of F^2 against ALL reflections. The weighted R -factor wR and goodness of fit S are based on F^2 , conventional R -factors R are based on F , with F set to zero for negative F^2 . The threshold expression of $F^2 > \sigma(F^2)$ is used only for calculating R -factors(gt) *etc.* and is not relevant to the choice of reflections for refinement. R -factors based on F^2 are statistically about twice as large as those based on F , and R -factors based on ALL data will be even larger.

Fractional atomic coordinates and isotropic or equivalent isotropic displacement parameters (\AA^2)

	<i>x</i>	<i>y</i>	<i>z</i>	$U_{\text{iso}}^*/U_{\text{eq}}$
S1	0.09788 (5)	-0.14517 (15)	0.84062 (6)	0.0691 (3)
O1	0.15780 (12)	0.2624 (4)	0.58697 (15)	0.0736 (7)
O2	0.09476 (11)	-0.0245 (4)	0.65679 (14)	0.0650 (6)
O3	0.2436 (2)	0.6611 (6)	0.55376 (16)	0.0945 (10)
H3A	0.275 (3)	0.647 (9)	0.502 (4)	0.16 (2)*
H3C	0.223 (3)	0.523 (10)	0.551 (3)	0.15 (2)*
N1	0.25532 (13)	0.5824 (4)	0.73178 (16)	0.0526 (7)
H1A	0.2568	0.6315	0.6782	0.063*
N2	0.22812 (12)	0.3832 (5)	0.84912 (16)	0.0525 (6)
N3	0.19001 (14)	0.2003 (5)	0.88960 (15)	0.0577 (7)
C1	0.34450 (18)	1.0192 (6)	0.7130 (2)	0.0603 (9)
H1B	0.3120	0.9869	0.6689	0.072*
C2	0.3920 (2)	1.2072 (6)	0.7024 (2)	0.0719 (11)
H2A	0.3909	1.3011	0.6516	0.086*
C3	0.4406 (2)	1.2562 (7)	0.7662 (3)	0.0738 (10)
H3B	0.4727	1.3824	0.7588	0.089*
C4	0.4416 (2)	1.1188 (7)	0.8405 (3)	0.0839 (10)
H4A	0.4748	1.1508	0.8838	0.101*
C5	0.39376 (19)	0.9320 (6)	0.8522 (3)	0.0759 (10)
H5A	0.3947	0.8413	0.9038	0.091*
C6	0.34440 (16)	0.8779 (6)	0.7882 (2)	0.0512 (8)
C7	0.29409 (17)	0.6804 (5)	0.8010 (2)	0.0527 (8)
C8	0.27674 (16)	0.5545 (6)	0.8748 (2)	0.0544 (9)
H8A	0.2942	0.5792	0.9312	0.065*
C9	0.21516 (17)	0.3985 (6)	0.76236 (19)	0.0490 (8)
C10	0.15369 (15)	0.1013 (5)	0.8233 (2)	0.0511 (8)
C11	0.16699 (17)	0.2151 (5)	0.7410 (2)	0.0502 (8)
C12	0.14107 (16)	0.1594 (6)	0.6547 (2)	0.0542 (8)
C13	0.0647 (2)	-0.1008 (7)	0.5744 (2)	0.0850 (12)
H13A	0.1009	-0.1654	0.5360	0.102*
H13B	0.0422	0.0358	0.5452	0.102*
C14	0.0120 (2)	-0.2929 (7)	0.5953 (3)	0.0986 (13)
H14A	-0.0095	-0.3494	0.5421	0.148*

supplementary materials

H14B	-0.0235	-0.2265	0.6333	0.148*
H14C	0.0349	-0.4267	0.6242	0.148*
C15	0.1101 (2)	-0.1931 (7)	0.9562 (3)	0.0873 (13)
H15A	0.0816	-0.3276	0.9751	0.131*
H15B	0.0966	-0.0488	0.9876	0.131*
H15C	0.1587	-0.2285	0.9677	0.131*

Atomic displacement parameters (\AA^2)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
S1	0.0711 (6)	0.0678 (5)	0.0682 (6)	-0.0051 (5)	0.0093 (5)	0.0161 (5)
O1	0.0939 (19)	0.0829 (16)	0.0440 (12)	-0.0255 (15)	-0.0010 (14)	0.0096 (12)
O2	0.0703 (14)	0.0722 (15)	0.0526 (14)	-0.0146 (14)	-0.0035 (12)	0.0025 (12)
O3	0.131 (3)	0.107 (3)	0.0453 (15)	-0.041 (2)	0.0042 (15)	0.0143 (15)
N1	0.0628 (17)	0.0571 (16)	0.0377 (15)	0.0017 (14)	-0.0024 (13)	0.0054 (14)
N2	0.0642 (17)	0.0573 (16)	0.0359 (15)	0.0048 (13)	-0.0019 (14)	0.0087 (13)
N3	0.0700 (19)	0.0583 (16)	0.0448 (16)	-0.0010 (15)	0.0068 (15)	0.0150 (14)
C1	0.057 (2)	0.067 (2)	0.056 (2)	-0.0041 (19)	-0.0011 (16)	0.0014 (18)
C2	0.082 (3)	0.074 (3)	0.060 (2)	-0.006 (2)	0.013 (2)	0.007 (2)
C3	0.070 (2)	0.076 (2)	0.076 (3)	-0.015 (2)	0.010 (2)	-0.010 (2)
C4	0.089 (3)	0.088 (3)	0.075 (3)	-0.019 (2)	-0.015 (3)	-0.003 (3)
C5	0.088 (3)	0.077 (2)	0.062 (2)	-0.011 (2)	-0.018 (2)	0.006 (2)
C6	0.054 (2)	0.0534 (18)	0.046 (2)	0.0094 (16)	0.0014 (15)	-0.0006 (15)
C7	0.060 (2)	0.0549 (19)	0.0435 (19)	0.0042 (17)	-0.0012 (17)	0.0009 (17)
C8	0.062 (2)	0.060 (2)	0.0403 (18)	0.0040 (18)	-0.0048 (15)	0.0020 (16)
C9	0.0551 (19)	0.056 (2)	0.0365 (18)	0.0079 (17)	0.0028 (15)	0.0095 (16)
C10	0.0534 (19)	0.0508 (18)	0.049 (2)	0.0074 (15)	0.0022 (15)	0.0050 (16)
C11	0.057 (2)	0.054 (2)	0.0405 (17)	0.0023 (17)	0.0057 (16)	0.0049 (16)
C12	0.055 (2)	0.055 (2)	0.053 (2)	0.0005 (17)	0.0055 (17)	0.0062 (18)
C13	0.087 (3)	0.101 (3)	0.066 (3)	-0.026 (2)	-0.005 (2)	-0.011 (2)
C14	0.108 (3)	0.094 (3)	0.095 (3)	-0.043 (3)	0.001 (3)	-0.013 (2)
C15	0.107 (3)	0.089 (3)	0.067 (3)	-0.005 (2)	0.026 (2)	0.027 (2)

Geometric parameters (\AA , $^\circ$)

S1—C10	1.739 (3)	C3—H3B	0.9300
S1—C15	1.795 (4)	C4—C5	1.382 (4)
O1—C12	1.219 (4)	C4—H4A	0.9300
O2—C12	1.339 (3)	C5—C6	1.385 (4)
O2—C13	1.442 (4)	C5—H5A	0.9300
O3—H3A	0.99 (6)	C6—C7	1.459 (4)
O3—H3C	0.85 (6)	C7—C8	1.359 (4)
N1—C9	1.348 (3)	C8—H8A	0.9300
N1—C7	1.395 (4)	C9—C11	1.399 (4)
N1—H1A	0.8600	C10—C11	1.423 (4)
N2—C9	1.347 (4)	C11—C12	1.436 (4)
N2—C8	1.375 (4)	C13—C14	1.489 (5)
N2—N3	1.383 (3)	C13—H13A	0.9700
N3—C10	1.339 (4)	C13—H13B	0.9700

C1—C2	1.380 (4)	C14—H14A	0.9600
C1—C6	1.383 (4)	C14—H14B	0.9600
C1—H1B	0.9300	C14—H14C	0.9600
C2—C3	1.368 (5)	C15—H15A	0.9600
C2—H2A	0.9300	C15—H15B	0.9600
C3—C4	1.360 (5)	C15—H15C	0.9600
Cg1...Cg2 ⁱ	3.643 (2)		
C10—S1—C15	100.60 (17)	C7—C8—H8A	127.0
C12—O2—C13	117.3 (3)	N2—C8—H8A	127.0
H3A—O3—H3C	99 (4)	N2—C9—N1	106.4 (3)
C9—N1—C7	109.0 (3)	N2—C9—C11	107.7 (3)
C9—N1—H1A	125.5	N1—C9—C11	146.0 (3)
C7—N1—H1A	125.5	N3—C10—C11	113.3 (3)
C9—N2—C8	111.1 (3)	N3—C10—S1	121.0 (2)
C9—N2—N3	112.8 (3)	C11—C10—S1	125.7 (2)
C8—N2—N3	136.2 (3)	C9—C11—C10	103.1 (3)
C10—N3—N2	103.2 (2)	C9—C11—C12	126.2 (3)
C2—C1—C6	121.1 (3)	C10—C11—C12	130.6 (3)
C2—C1—H1B	119.4	O1—C12—O2	122.7 (3)
C6—C1—H1B	119.4	O1—C12—C11	125.9 (3)
C3—C2—C1	120.4 (3)	O2—C12—C11	111.4 (3)
C3—C2—H2A	119.8	O2—C13—C14	106.6 (3)
C1—C2—H2A	119.8	O2—C13—H13A	110.4
C4—C3—C2	119.5 (4)	C14—C13—H13A	110.4
C4—C3—H3B	120.3	O2—C13—H13B	110.4
C2—C3—H3B	120.3	C14—C13—H13B	110.4
C3—C4—C5	120.6 (4)	H13A—C13—H13B	108.6
C3—C4—H4A	119.7	C13—C14—H14A	109.5
C5—C4—H4A	119.7	C13—C14—H14B	109.5
C4—C5—C6	120.9 (4)	H14A—C14—H14B	109.5
C4—C5—H5A	119.5	C13—C14—H14C	109.5
C6—C5—H5A	119.5	H14A—C14—H14C	109.5
C1—C6—C5	117.5 (3)	H14B—C14—H14C	109.5
C1—C6—C7	121.9 (3)	S1—C15—H15A	109.5
C5—C6—C7	120.6 (3)	S1—C15—H15B	109.5
C8—C7—N1	107.5 (3)	H15A—C15—H15B	109.5
C8—C7—C6	130.3 (3)	S1—C15—H15C	109.5
N1—C7—C6	122.1 (3)	H15A—C15—H15C	109.5
C7—C8—N2	106.0 (3)	H15B—C15—H15C	109.5
C9—N2—N3—C10	0.9 (3)	N3—N2—C9—C11	-1.2 (3)
C8—N2—N3—C10	-178.6 (3)	C7—N1—C9—N2	0.5 (3)
C6—C1—C2—C3	0.6 (5)	C7—N1—C9—C11	-177.5 (4)
C1—C2—C3—C4	-0.3 (5)	N2—N3—C10—C11	-0.2 (3)
C2—C3—C4—C5	-0.5 (6)	N2—N3—C10—S1	178.80 (19)
C3—C4—C5—C6	1.0 (6)	C15—S1—C10—N3	-0.8 (3)
C2—C1—C6—C5	-0.1 (5)	C15—S1—C10—C11	178.0 (3)
C2—C1—C6—C7	179.2 (3)	N2—C9—C11—C10	1.0 (3)
C4—C5—C6—C1	-0.7 (5)	N1—C9—C11—C10	179.0 (4)

supplementary materials

C4—C5—C6—C7	179.9 (3)	N2—C9—C11—C12	-177.1 (3)
C9—N1—C7—C8	-0.4 (3)	N1—C9—C11—C12	0.9 (7)
C9—N1—C7—C6	178.0 (2)	N3—C10—C11—C9	-0.5 (3)
C1—C6—C7—C8	-165.9 (3)	S1—C10—C11—C9	-179.5 (2)
C5—C6—C7—C8	13.5 (5)	N3—C10—C11—C12	177.5 (3)
C1—C6—C7—N1	16.2 (4)	S1—C10—C11—C12	-1.4 (5)
C5—C6—C7—N1	-164.4 (3)	C13—O2—C12—O1	0.4 (4)
N1—C7—C8—N2	0.1 (3)	C13—O2—C12—C11	-179.7 (3)
C6—C7—C8—N2	-178.1 (3)	C9—C11—C12—O1	0.8 (5)
C9—N2—C8—C7	0.2 (3)	C10—C11—C12—O1	-176.9 (3)
N3—N2—C8—C7	179.7 (3)	C9—C11—C12—O2	-179.1 (3)
C8—N2—C9—N1	-0.5 (3)	C10—C11—C12—O2	3.2 (4)
N3—N2—C9—N1	179.9 (2)	C12—O2—C13—C14	-176.1 (3)
C8—N2—C9—C11	178.4 (2)		

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

Hydrogen-bond geometry (\AA , $^\circ$)

$D-H\cdots A$	$D-H$	$H\cdots A$	$D\cdots A$	$D-H\cdots A$
O3—H3A \cdots N3 ⁱⁱ	0.99 (6)	1.86 (6)	2.809 (4)	160 (5)

Symmetry codes: (ii) $-x+1/2, y+1/2, z-1/2$.

Fig. 1

