

Acta Crystallographica Section E

Structure Reports

Online

ISSN 1600-5368

3-Ethyl-4-methyl-1*H*-pyrazol-2-ium-5-olate

 R. S. Rathore,^{a*} T. Narasimhamurthy,^b R. Venkat Ragavan,^c V. Vijayakumar^c and S. Sarveswari^c

^aBioinformatics Infrastructure Facility, School of Life Science, University of Hyderabad, Hyderabad 500 046, India, ^bMaterials Research Center, Indian Institute of Science, Bangalore 560 012, India, and ^cOrganic Chemistry Division, School of Advanced Sciences, VIT University, Vellore 632 014, India

Correspondence e-mail: rrsrl@uohyd.ernet.in

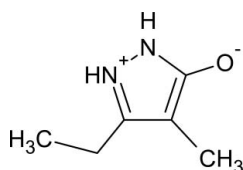
Received 24 June 2011; accepted 13 July 2011

Key indicators: single-crystal X-ray study; $T = 296$ K; mean $\sigma(\text{C}-\text{C}) = 0.003$ Å; R factor = 0.049; wR factor = 0.136; data-to-parameter ratio = 14.5.

The title compound, $\text{C}_6\text{H}_{10}\text{N}_2\text{O}$, is a zwitterionic pyrazole derivative. The crystal packing is predominantly governed by a three-center iminium–amine $\text{N}^+-\text{H}\cdots\text{O}^-\cdots\text{H}-\text{N}$ interaction, leading to an undulating sheet-like structure lying parallel to (100).

Related literature

For related structures and the preparation of similar compounds, see: Ragavan *et al.* (2009, 2010) and references therein. For related salt-bridge-mediated sheet structures, see: Shylaja *et al.* (2008).



Experimental

Crystal data

$\text{C}_6\text{H}_{10}\text{N}_2\text{O}$
 $M_r = 126.16$
 Monoclinic, $P2_1/c$
 $a = 9.1299$ (15) Å
 $b = 7.1600$ (11) Å
 $c = 11.374$ (2) Å
 $\beta = 113.232$ (9)°

$V = 683.2$ (2) Å³
 $Z = 4$
 Mo $K\alpha$ radiation
 $\mu = 0.09$ mm⁻¹
 $T = 296$ K
 $0.21 \times 0.19 \times 0.11$ mm

Data collection

Bruker APEXII CCD diffractometer
 Absorption correction: multi-scan (SADABS; Bruker, 2001)
 $T_{\min} = 0.64$, $T_{\max} = 0.83$

12120 measured reflections
 1332 independent reflections
 961 reflections with $I > 2\sigma(I)$
 $R_{\text{int}} = 0.034$

Refinement

$R[F^2 > 2\sigma(F^2)] = 0.049$
 $wR(F^2) = 0.136$
 $S = 1.03$
 1332 reflections
 92 parameters

H atoms treated by a mixture of independent and constrained refinement
 $\Delta\rho_{\text{max}} = 0.17$ e Å⁻³
 $\Delta\rho_{\text{min}} = -0.21$ e Å⁻³

Table 1
 Hydrogen-bond geometry (Å, °).

$D-H\cdots A$	$D-H$	$H\cdots A$	$D\cdots A$	$D-H\cdots A$
$\text{N1}-\text{H1}\cdots\text{O5}^{\text{i}}$	0.91 (2)	1.82 (2)	2.730 (2)	175 (2)
$\text{N2}-\text{H2}\cdots\text{O5}^{\text{ii}}$	0.96 (2)	1.75 (2)	2.693 (2)	168 (2)

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

Data collection: APEX2 (Bruker, 2007); cell refinement: SAINT-Plus (Bruker, 2007); data reduction: SAINT-Plus; program(s) used to solve structure: SHELXS97 (Sheldrick, 2008); program(s) used to refine structure: SHELXL97 (Sheldrick, 2008); molecular graphics: ORTEP-3 (Farrugia, 1997) and PLATON (Spek, 2009); software used to prepare material for publication: SHELXL97 and PLATON (Spek, 2009).

We acknowledge the CCD facility, set up under the IRHPA–DST program at the IISc, Bangalore. VV thanks the DST for financial assistance under the Fast-Track young scientist scheme, and RSR acknowledges the CSIR for funding under the scientist's pool scheme.

Supplementary data and figures for this paper are available from the IUCr electronic archives (Reference: SU2287).

References

- Bruker (2001). SADABS. Bruker AXS Inc., Madison, Wisconsin, USA.
 Bruker (2007). APEX2 and SAINT-Plus. Bruker AXS Inc., Madison, Wisconsin, USA.
 Farrugia, L. J. (1997). *J. Appl. Cryst.* **30**, 565.
 Ragavan, R. V., Vijayakumar, V. & Kumari, N. S. (2009). *Eur. J. Med. Chem.* **44**, 3852–3857.
 Ragavan, R. V., Vijayakumar, V. & Kumari, N. S. (2010). *Eur. J. Med. Chem.* **45**, 1173–1180.
 Sheldrick, G. M. (2008). *Acta Cryst.* **A64**, 112–122.
 Shylaja, S., Mahendra, K. N., Varma, K. B. R., Narasimhamurthy, T. & Rathore, R. S. (2008). *Acta Cryst.* **C64**, o361–o363.
 Spek, A. L. (2009). *Acta Cryst.* **D65**, 148–155.

supplementary materials

Acta Cryst. (2011). E67, o2129 [doi:10.1107/S160053681102808X]

3-Ethyl-4-methyl-1*H*-pyrazol-2-ium-5-olate

R. S. Rathore, T. Narasimhamurthy, R. V. Ragavan, V. Vijayakumar and S. Sarveswari

Comment

As a part of our interest in antimicrobial compounds, we have synthesized the title pyrazole derivative using the procedure described earlier by (Ragavan *et al.*, 2009, and references therein; 2010, and references therein).

The molecular structure of the title molecule is shown in Fig 1. The methyl atom (C3B) of the 3-ethyl substituent lies out of the mean plane of the pyrazole moiety (N1,N2,C3-C5) by 1.366 (4) Å.

The crystal packing is a fine balance of strong N—H···O hydrogen bonds (Table 1) and salt bridges, which normally tend to promote the formation of a planar structure and compact packing (Shylaja *et al.*, 2008). In the title compound all the hydrogen bonding donors, iminium N⁺H (N1) and amine NH (N2), and the O⁻(O1) acceptor, are in the plane of the pyrazole moiety, which would normally yield a planar hydrogen-bonded structure. However, in order to accommodate the out-of-plane methyl group, (C3B), an undulating hydrogen bonded sheet-like structure, lying parallel to (100), is formed (Fig. 2).

Experimental

The title compound was synthesized using the method described earlier by (Ragavan *et al.*, 2009, 2010). It was crystallized using an ethanol-chloroform (1:1) mixture. Yield, 74%; m.p. 779-780 K.

Refinement

The NH atoms were located in a difference Fourier map and were freely refined: N2—H2 = 0.92 (2) Å and N1⁺—H1 = 0.95 (3) Å. The methylene and methyl hydrogen atoms were placed in calculated positions and refined as riding atoms: C—H = 0.97 and 0.96 Å, for CH and CH₃ H-atoms, respectively, with $U_{\text{iso}}(\text{H}) = k \times U_{\text{eq}}(\text{C})$ where $k = 1.5$ for CH₃ H-atoms and 1.2 for the CH H-atoms.

Figures

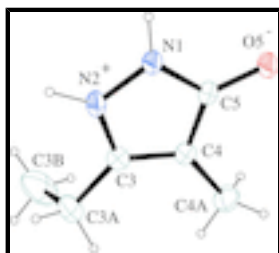


Fig. 1. A view of the molecular structure of the title molecule, with labelling scheme and displacement ellipsoids drawn at the 30% probability level.

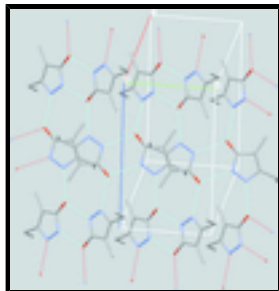


Fig. 2. A view of the N—H...O hydrogen bonded (dashed cyan lines) sheet structure in the crystal structure of the title compound (see Table 1 for details).

3-Ethyl-4-methyl-1*H*-pyrazol-2-ium-5-olate

Crystal data

$C_6H_{10}N_2O$	$F(000) = 272$
$M_r = 126.16$	$D_x = 1.227 \text{ Mg m}^{-3}$
Monoclinic, $P2_1/c$	Mo $K\alpha$ radiation, $\lambda = 0.71073 \text{ \AA}$
Hall symbol: -P 2ybc	Cell parameters from 3015 reflections
$a = 9.1299 (15) \text{ \AA}$	$\theta = 2.4\text{--}22.9^\circ$
$b = 7.1600 (11) \text{ \AA}$	$\mu = 0.09 \text{ mm}^{-1}$
$c = 11.374 (2) \text{ \AA}$	$T = 296 \text{ K}$
$\beta = 113.232 (9)^\circ$	Plate, colourless
$V = 683.2 (2) \text{ \AA}^3$	$0.21 \times 0.19 \times 0.11 \text{ mm}$
$Z = 4$	

Data collection

Bruker APEXII CCD diffractometer	1332 independent reflections
Radiation source: fine-focus sealed tube graphite	961 reflections with $I > 2\sigma(I)$
φ and ω scans	$R_{\text{int}} = 0.034$
Absorption correction: multi-scan (SADABS; Bruker, 2001)	$\theta_{\text{max}} = 26.0^\circ$, $\theta_{\text{min}} = 2.4^\circ$
$T_{\text{min}} = 0.64$, $T_{\text{max}} = 0.83$	$h = -11 \rightarrow 11$
12120 measured reflections	$k = -8 \rightarrow 8$
	$l = -13 \rightarrow 13$

Refinement

Refinement on F^2	Primary atom site location: structure-invariant direct methods
Least-squares matrix: full	Secondary atom site location: difference Fourier map
$R[F^2 > 2\sigma(F^2)] = 0.049$	Hydrogen site location: inferred from neighbouring sites
$wR(F^2) = 0.136$	H atoms treated by a mixture of independent and constrained refinement
$S = 1.03$	$w = 1/[\sigma^2(F_o^2) + (0.0674P)^2 + 0.2195P]$
1332 reflections	where $P = (F_o^2 + 2F_c^2)/3$
	$(\Delta/\sigma)_{\text{max}} < 0.001$

92 parameters

$$\Delta\rho_{\max} = 0.17 \text{ e } \text{\AA}^{-3}$$

0 restraints

$$\Delta\rho_{\min} = -0.21 \text{ e } \text{\AA}^{-3}$$

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>	$U_{\text{iso}}^*/U_{\text{eq}}$
N1	0.0756 (2)	0.1929 (2)	0.58699 (14)	0.0427 (5)
H1	0.029 (3)	0.087 (3)	0.601 (2)	0.051 (6)*
N2	0.1373 (2)	0.3275 (2)	0.67795 (15)	0.0462 (5)
H2	0.116 (3)	0.326 (3)	0.754 (2)	0.062 (6)*
O5	0.07244 (17)	0.12652 (19)	0.38750 (11)	0.0489 (4)
C3	0.2107 (2)	0.4552 (3)	0.63369 (17)	0.0402 (5)
C3A	0.2903 (3)	0.6189 (3)	0.7141 (2)	0.0573 (6)
H3A1	0.2994	0.7177	0.6591	0.069*
H3A2	0.2238	0.6648	0.7566	0.069*
C3B	0.4512 (4)	0.5766 (4)	0.8123 (3)	0.1014 (12)
H3B1	0.4424	0.4859	0.8714	0.152*
H3B2	0.4982	0.6889	0.8577	0.152*
H3B3	0.5171	0.5277	0.7714	0.152*
C4	0.1999 (2)	0.4015 (2)	0.51474 (17)	0.0367 (5)
C4A	0.2643 (3)	0.4995 (3)	0.4291 (2)	0.0544 (6)
H41	0.3131	0.6149	0.4681	0.082*
H42	0.1789	0.5248	0.3482	0.082*
H43	0.3422	0.4216	0.4162	0.082*
C5	0.1135 (2)	0.2330 (3)	0.48611 (16)	0.0359 (5)

Atomic displacement parameters (\AA^2)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
N1	0.0661 (11)	0.0389 (9)	0.0308 (8)	-0.0145 (8)	0.0275 (8)	-0.0061 (7)
N2	0.0698 (12)	0.0444 (10)	0.0313 (9)	-0.0109 (8)	0.0275 (8)	-0.0098 (7)
O5	0.0759 (10)	0.0484 (8)	0.0304 (7)	-0.0197 (7)	0.0295 (7)	-0.0092 (6)
C3	0.0470 (11)	0.0362 (10)	0.0369 (10)	-0.0008 (8)	0.0162 (9)	-0.0008 (8)
C3A	0.0725 (15)	0.0467 (12)	0.0519 (13)	-0.0103 (11)	0.0237 (12)	-0.0149 (10)
C3B	0.084 (2)	0.082 (2)	0.097 (2)	-0.0121 (16)	-0.0077 (17)	-0.0341 (18)
C4	0.0428 (10)	0.0361 (10)	0.0322 (9)	-0.0018 (8)	0.0159 (8)	0.0016 (8)

supplementary materials

C4A	0.0632 (14)	0.0566 (13)	0.0485 (12)	-0.0143 (11)	0.0274 (11)	0.0035 (10)
C5	0.0455 (10)	0.0378 (10)	0.0266 (9)	-0.0018 (8)	0.0165 (8)	0.0003 (8)

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

N1—C5	1.354 (2)	C3A—H3A2	0.9700
N1—N2	1.363 (2)	C3B—H3B1	0.9600
N1—H1	0.92 (2)	C3B—H3B2	0.9600
N2—C3	1.343 (3)	C3B—H3B3	0.9600
N2—H2	0.95 (3)	C4—C5	1.408 (3)
O5—C5	1.284 (2)	C4—C4A	1.495 (3)
C3—C4	1.372 (3)	C4A—H41	0.9600
C3—C3A	1.488 (3)	C4A—H42	0.9600
C3A—C3B	1.484 (4)	C4A—H43	0.9600
C3A—H3A1	0.9700		
C5—N1—N2	109.01 (16)	H3B1—C3B—H3B2	109.5
C5—N1—H1	128.2 (13)	C3A—C3B—H3B3	109.5
N2—N1—H1	122.3 (13)	H3B1—C3B—H3B3	109.5
C3—N2—N1	108.38 (16)	H3B2—C3B—H3B3	109.5
C3—N2—H2	130.8 (14)	C3—C4—C5	106.50 (16)
N1—N2—H2	120.5 (14)	C3—C4—C4A	128.08 (17)
N2—C3—C4	109.04 (16)	C5—C4—C4A	125.42 (17)
N2—C3—C3A	120.03 (18)	C4—C4A—H41	109.5
C4—C3—C3A	130.90 (18)	C4—C4A—H42	109.5
C3B—C3A—C3	113.6 (2)	H41—C4A—H42	109.5
C3B—C3A—H3A1	108.8	C4—C4A—H43	109.5
C3—C3A—H3A1	108.8	H41—C4A—H43	109.5
C3B—C3A—H3A2	108.8	H42—C4A—H43	109.5
C3—C3A—H3A2	108.8	O5—C5—N1	122.03 (16)
H3A1—C3A—H3A2	107.7	O5—C5—C4	130.92 (17)
C3A—C3B—H3B1	109.5	N1—C5—C4	107.05 (15)
C3A—C3B—H3B2	109.5		
C5—N1—N2—C3	1.6 (2)	C3A—C3—C4—C4A	-1.7 (3)
N1—N2—C3—C4	-1.4 (2)	N2—N1—C5—O5	178.68 (17)
N1—N2—C3—C3A	-179.69 (17)	N2—N1—C5—C4	-1.2 (2)
N2—C3—C3A—C3B	80.6 (3)	C3—C4—C5—O5	-179.5 (2)
C4—C3—C3A—C3B	-97.3 (3)	C4A—C4—C5—O5	0.9 (3)
N2—C3—C4—C5	0.7 (2)	C3—C4—C5—N1	0.3 (2)
C3A—C3—C4—C5	178.7 (2)	C4A—C4—C5—N1	-179.25 (18)
N2—C3—C4—C4A	-179.80 (19)		

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

$D-H\cdots A$	$D-H$	$H\cdots A$	$D\cdots A$	$D-H\cdots A$
N1—H1 \cdots O5 ⁱ	0.91 (2)	1.82 (2)	2.730 (2)	175 (2)
N2—H2 \cdots O5 ⁱⁱ	0.96 (2)	1.75 (2)	2.693 (2)	168 (2)

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

Fig. 1

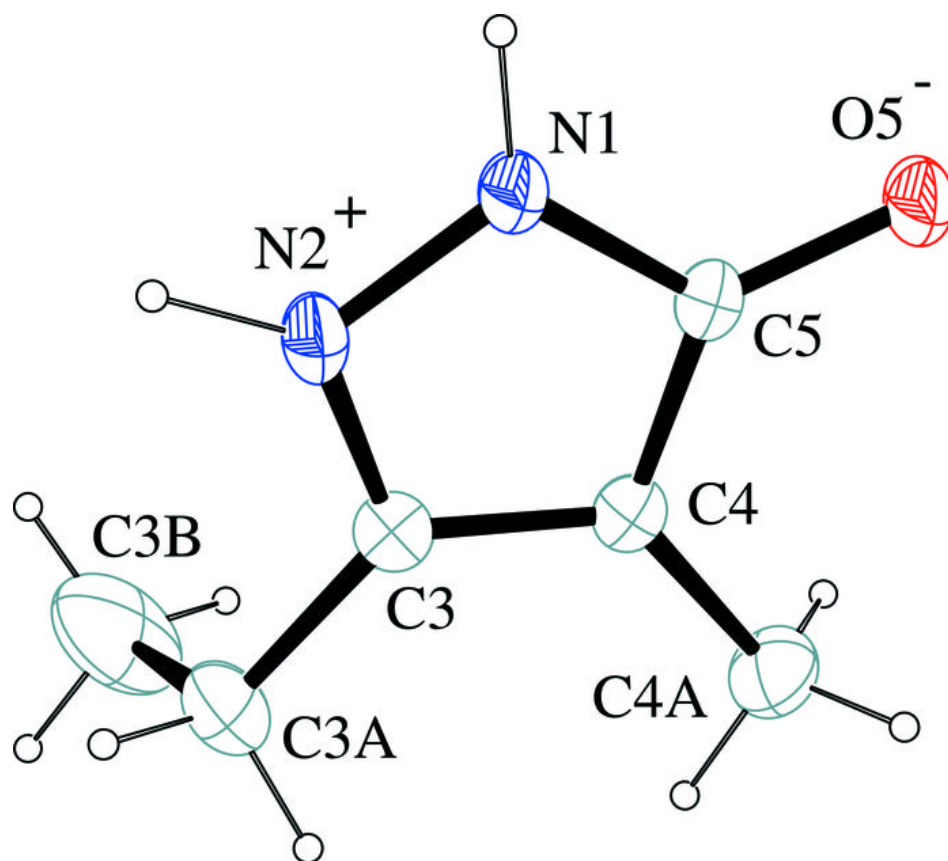
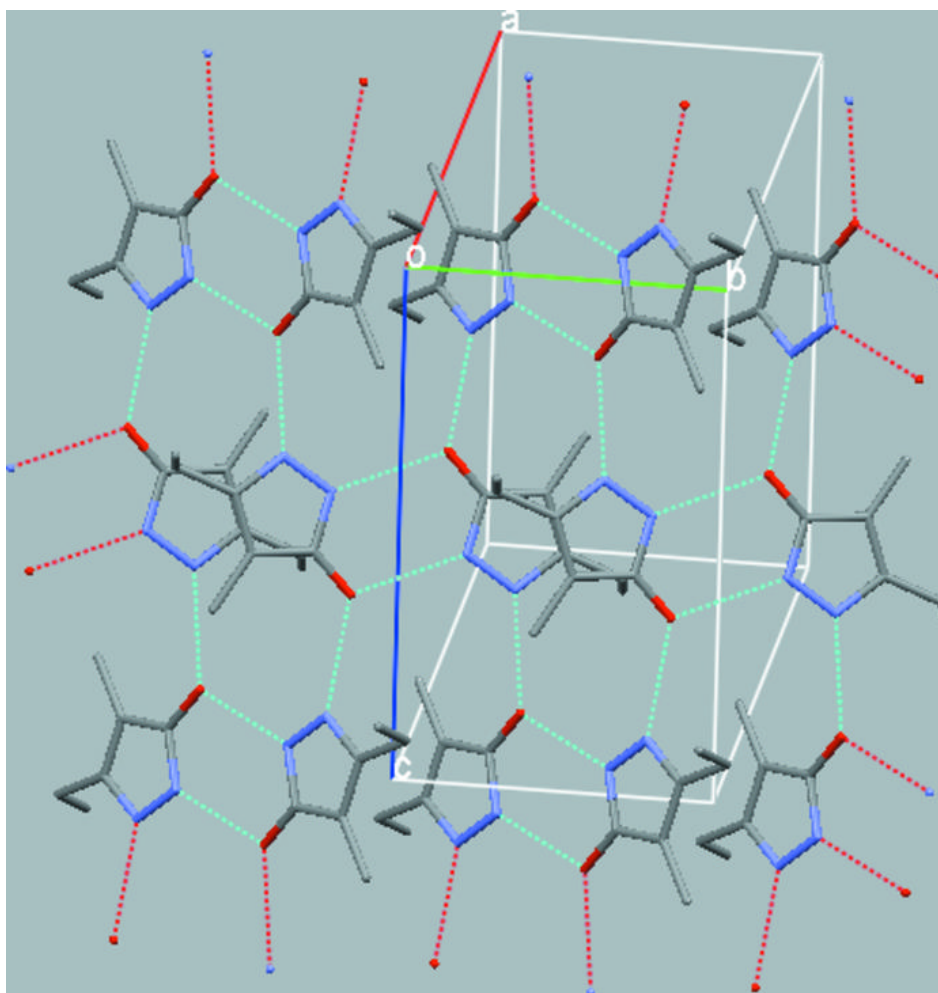


Fig. 2



Copyright of Acta Crystallographica: Section E (International Union of Crystallography - IUCr) is the property of International Union of Crystallography - IUCr and its content may not be copied or emailed to multiple sites or posted to a listserv without the copyright holder's express written permission. However, users may print, download, or email articles for individual use.