organic compounds

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

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The title compound, $C_6H_{10}N_2O$, is a zwitterionic pyrazole derivative. The crystal packing is predominantly governed by a three-center iminium–amine N^+—H$\cdots$O$^-\cdots$H—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).
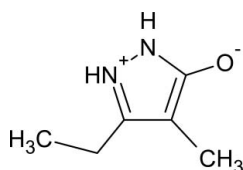
Experimental

Crystal data

$C_6H_{10}N_2O$
M_r = 126.16
Monoclinic, $P2_1/c$
a = 9.1299 (15) Å
b = 7.1600 (11) Å
c = 11.374 (2) Å
β = 113.232 (9)°

V = 683.2 (2) Å^3
Z = 4
Mo $K\alpha$ radiation
μ = 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_{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
$\Delta\rho_{max}$ = 0.17 e Å^{-3}
$\Delta\rho_{min}$ = −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$\cdots A$
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) $x, -y+\frac{1}{2}, z+\frac{1}{2}$.

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).

References

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supporting information

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

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S1. 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, lieing paralallel to (100), is formed (Fig. 2).

S2. 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.

S3. 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 CH_3 H-atoms, respectively, with $U_{iso}(H) = k \times U_{eq}(C,)$ where k = 1.5 for CH_3 H-atoms and 1.2 for the CH H-atoms.
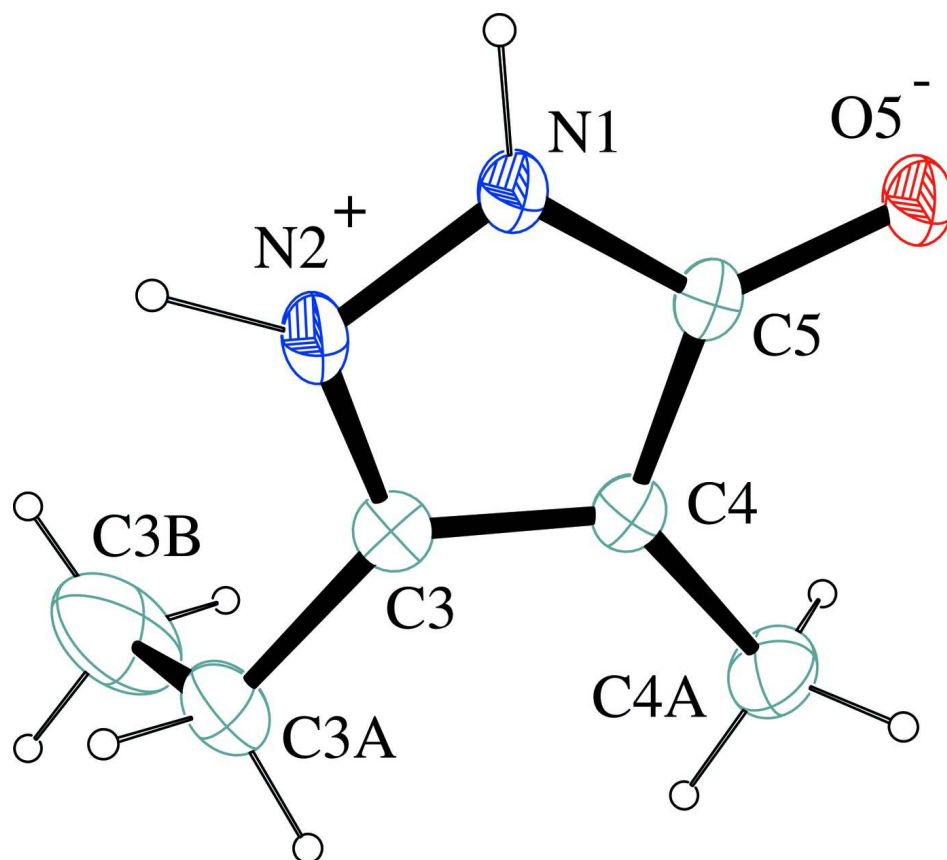
Figure 1

A view of the molecular structure of the title molecule, with labelling scheme and displacement ellipsoids drawn at the 30% probability level.
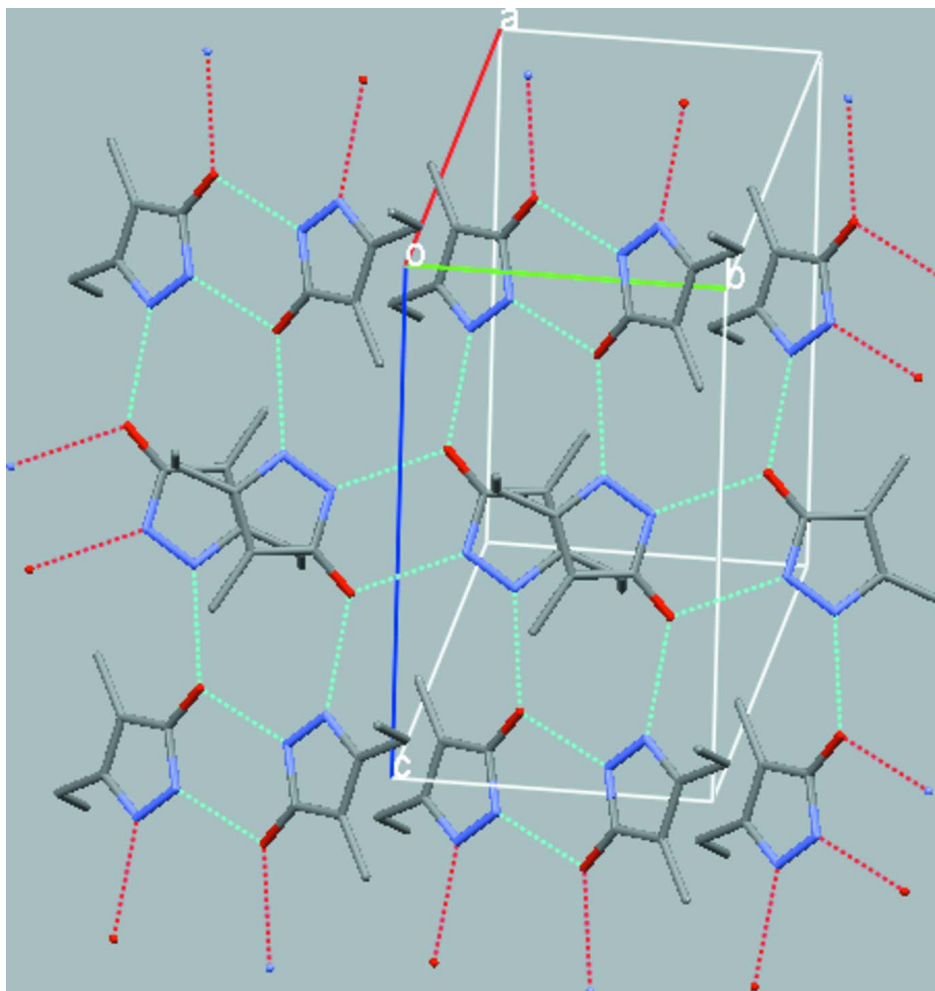
Figure 2
A view of the N—H⋯O hydrogen bonded (dashed cyan lines) sheet structure in the crystal structure of the title compound (see Table 1 for details).

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

Crystal data

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

Data collection

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

Refinement

Refinement on F^2	Secondary atom site location: difference Fourier map
Least-squares matrix: full	
$R[F^2 > 2\sigma(F^2)] = 0.049$	Hydrogen site location: inferred from neighbouring sites
$wR(F^2) = 0.136$	
$S = 1.03$	H atoms treated by a mixture of independent and constrained refinement
1332 reflections	
92 parameters	$w = 1/[\sigma^2(F_o^2) + (0.0674P)^2 + 0.2195P]$
0 restraints	where $P = (F_o^2 + 2F_c^2)/3$
Primary atom site location: structure-invariant direct methods	$(\Delta/\sigma)_{max} < 0.001$
	$\Delta\rho_{max} = 0.17$ e Å^{-3}
	$\Delta\rho_{min} = -0.21$ e Å^{-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 (Å²)

	x	y	z	U_{iso}*/U_{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 (Å²)

	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)
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 (Å, º)

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 (Å, º)

D—H···A	D—H	H···A	D···A	D—H···A
N1—H1···O5[i]	0.91 (2)	1.82 (2)	2.730 (2)	175 (2)
N2—H2···O5[ii]	0.96 (2)	1.75 (2)	2.693 (2)	168 (2)

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