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5-Amino-1-methyl-4*H*-tetrazolium picrate

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Key indicators

Single-crystal X-ray study
T = 292 K
Mean σ(C–C) = 0.002 Å
R factor = 0.044
wR factor = 0.133
Data-to-parameter ratio = 16.7

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

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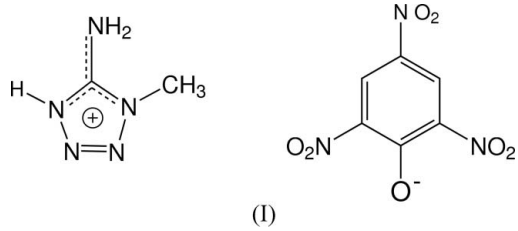
The title compound, $C_2H_6N_5^+\cdot C_6H_2N_3O_7^-$, was prepared by the equimolar reaction of 5-amino-1-methyltetrazole with picric acid. In the salt, the N^4 atom of the tetrazole ring is protonated. Cations and anions in (I) are linked together by a complex set of hydrogen bonds, forming polymeric chains extending along the *a* axis, with van der Waals interactions between the chains.

Comment

Previous studies have shown that *C*- and *N*-aminotetrazolium salts are useful as gas-generating propellants (Ma *et al.*, 2004) and energetic compounds (Denffer *et al.*, 2005; Xue *et al.*, 2004), but only a few salts have been characterized crystallographically, in particular, 5-aminotetrazolium nitrate (Ma *et al.*, 2004; Denffer *et al.*, 2005) and a series of salts obtained by protonation and alkylation of 1,5-diaminotetrazole (Matulis *et al.*, 2003, Drake *et al.*, 2005; Galvez-Ruiz *et al.*, 2005). Structural investigations of these compounds are also interesting with respect to amino–imine tautomerism, which is characteristic of 5-aminotetrazole derivatives (Matulis *et al.*, 2003; Drake *et al.*, 2005). We report here the crystal structure of the title compound, (I), obtained by reaction of 1-methyl-5-aminotetrazole with picric acid (Fig. 1).



(I)

Atom N4 of the tetrazole ring is protonated and the ring is planar to within 0.0026 (8) Å. The N1—C5 and N4—C5 bonds (Table 1) are the same within 2σ. The C5—N7 bond is rather short [1.3163 (16) Å] and the dihedral angle between the amino group and tetrazolium ring is 8(3)°, indicating strong π-delocalization across the N1—C5—N4—N7 fragment of the cation. The bond lengths (Table 1) across the N1—N2—N3—N4 fragment of the tetrazole ring lie in the range found for normal single and double bonds.

The structure of (I) compares well with that found for other similar tetrazolium salts (Ma *et al.*, 2004; Denffer *et al.*, 2005; Matulis *et al.*, 2003; Drake *et al.*, 2005; Galvez-Ruiz *et al.*, 2005). In (I), as well as in the other structures, the 5-amino group influences the tetrazole ring geometry due to π-conjugation of the amino group and the tetrazole ring. Additional 1-amino or 1-methyl substituents do not cause any meaningful changes in

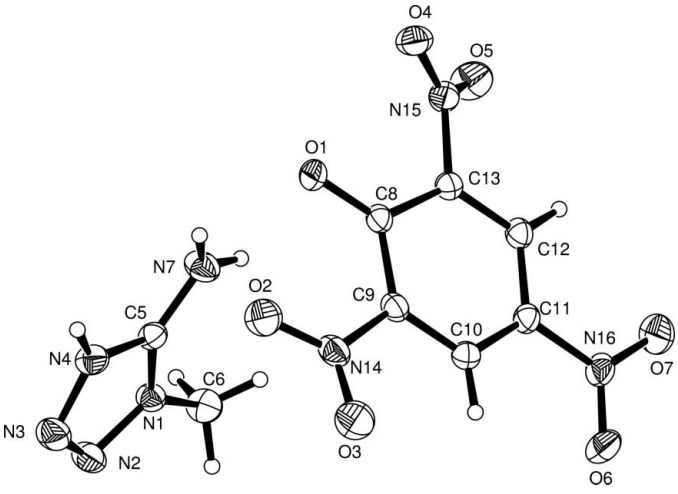


Figure 1
ORTEP3 plot (Farrugia, 1997) of the asymmetric unit of (I). Displacement ellipsoids are drawn at the 30% probability level and H atoms are shown as spheres of arbitrary radii.

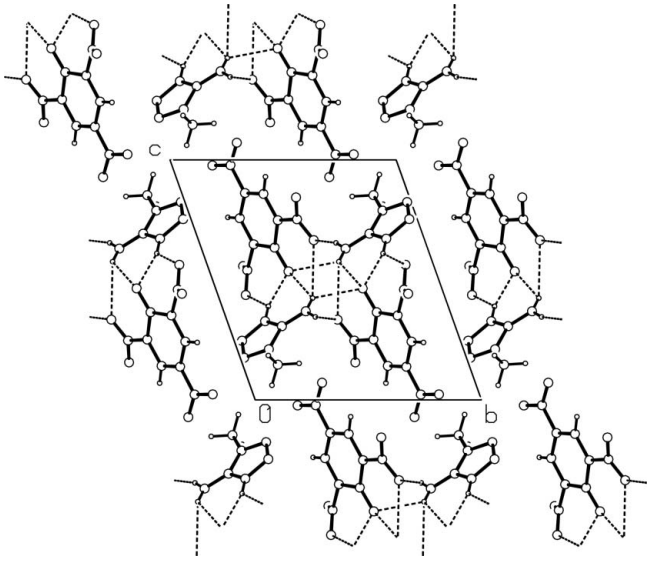


Figure 2
The crystal structure of (I), viwed along the *a* axis. Dashed lines indicate hydrogen bonds.

the tetrazolium ring compared with the H—N[1] form. Moreover, N_4 protonated tetrazolium rings or the rings with a 4-methyl substituent reveal practically the same geometry.

In the picrate anion, the benzene ring is planar to within 0.0128 (8) Å. The dihedral angles between the planes of the NO_2 groups and the benzene ring are 11.1 (2), 35.4 (9) and 5.12 (18)° for nitro groups N14, N15 and N16, respectively.

Cations and anions in the structure of (I) are linked together by a complex set of multicentred hydrogen bonds (Table 2), forming polymeric chains extending along the *a* axis, with van der Waals interactions between the chains.

Experimental

Single crystals of (I) were prepared by slow evaporation of an ethyl alcohol solution of an equimolar mixture of 5-amino-1-methyltetrazole and picric acid at room temperature (m.p. 433–435 K). ^{1}H NMR (100 MHz, CD_3CN): δ 3.80 (s, 3H, CH_3), 8.12 (*s*, 2H, NH_2), 9.04 (*s*, 2H, Ar).

Crystal data

$C_2H_6N_5^+\cdot C_6H_2N_3O_7^-$
M_r = 328.22
Triclinic, $P\overline{1}$
a = 5.9278 (11) Å
b = 10.234 (2) Å
c = 11.6013 (18) Å
α = 107.311 (14)°
β = 100.662 (14)°
γ = 98.548 (15)°
V = 644.6 (2) Å^3
Z = 2
D_x = 1.691 Mg m^{-3}
Mo $K\alpha$ radiation
Cell parameters from 25 reflections
θ = 16.4–22.0°
μ = 0.15 mm^{-1}
T = 292 (2) K
Prism, yellow
0.42 × 0.40 × 0.24 mm

Data collection

Nicolet *R3m* four-circle diffractometer
$\omega/2\theta$ scans
Absorption correction: none
4267 measured reflections
3796 independent reflections
3152 reflections with $I > 2\sigma(I)$
R_{int} = 0.009
θ_{max} = 30.1°
$h = 0 \rightarrow 8$
$k = -14 \rightarrow 14$
$l = -16 \rightarrow 16$
3 standard reflections every 100 reflections
intensity decay: none

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)]$ = 0.044
$wR(F^2)$ = 0.134
S = 1.06
3796 reflections
227 parameters
H atoms treated by a mixture of independent and constrained refinement
$w = 1/[\sigma^2(F_o^2) + (0.075P)^2 + 0.1158P]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max}$ = 0.001
$\Delta\rho_{max}$ = 0.27 e Å^{-3}
$\Delta\rho_{min}$ = −0.28 e Å^{-3}

Table 1
Selected bond lengths (Å).

N1—C5	1.3344 (14)	N3—N4	1.3543 (17)
N1—N2	1.3641 (15)	N4—C5	1.3295 (15)
N1—C6	1.4516 (16)	C5—N7	1.3163 (16)
N2—N3	1.2678 (18)		

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

D—H···A	D—H	H···A	D···A	D—H···A
N4—H4···O1^{i}	0.92 (2)	1.83 (2)	2.6249 (15)	143 (2)
N4—H4···O4^{i}	0.92 (2)	2.22 (2)	2.9242 (16)	133 (2)
N7—H7*A*···O1	0.85 (1)	2.42 (2)	3.0496 (16)	131 (2)
N7—H7*A*···O1^{i}	0.85 (1)	2.44 (2)	3.0621 (16)	131 (2)
N7—H7*A*···O2^{i}	0.85 (1)	2.60 (1)	3.2303 (19)	132 (2)
N7—H7*B*···O2^{ii}	0.86 (1)	2.21 (1)	3.0472 (18)	165 (2)

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

The H atoms of the methyl group were included in geometrically calculated positions, with C—H = 0.96 Å, and refined using a riding model, with U_{iso}(H) = 1.5U_{eq}(C). The positions of the remaining H atoms were found in a difference Fourier map. The H atoms of the amino group were refined with a restrained N—H distance of 0.86 (1) Å, and U_{iso}(H) = 1.2U_{eq}(N). The other H atoms were refined isotropically.

Data collection: *R3m Software* (Nicolet, 1980); cell refinement: *R3m Software*; data reduction: *R3m Software*; program(s) used to

solve structure: *SIR97* (Altomare *et al.*, 1999); program(s) used to refine structure: *SHELXL97* (Sheldrick, 1997); molecular graphics: *ORTEP3 for Windows* (Farrugia, 1997) and *PLATON* (Spek, 2003); software used to prepare material for publication: *SHELXL97*.

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