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Ethylaminium picrate

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Key indicators

Single-crystal X-ray study
T = 293 K
Mean σ(C–C) = 0.005 Å
R factor = 0.079
wR factor = 0.226
Data-to-parameter ratio = 12.0

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

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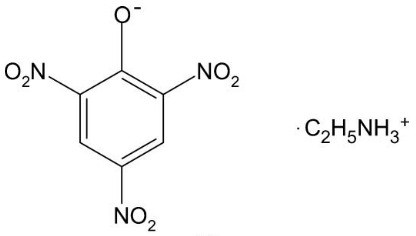
In the title salt, $C_2H_8N^+\cdot C_6H_2N_3O_7^-$, there is complete transfer of the OH proton from picric acid to the amine. The picrate anions lie almost parallel to the monoclinic (101) plane and are connected by O$\cdots$O short contacts. The ethylaminium and picrate ions are linked through N—H$\cdots$O and C—H$\cdots$O hydrogen bonds along the crystallographic *b* axis. In the picrate anion, tilting of the *para*-nitro group is a consequence of C—H$\cdots$O hydrogen bonding between the ions.

Comment

Picric acid (2,4,6-trinitrophenol) is used primarily to manufacture explosives and as an intermediate in dye manufacturing. It is well known that picric acid forms salts or charge-transfer complexes with many organic compounds, particularly with aromatic and aliphatic amines. Picric acid acts not only as an acceptor to form various π-stacking arrangements but also as an acidic ligand to form salts through electrostatic or hydrogen-bonding interactions (In *et al.*, 1997). The crystal structures of a large number of picrate salts and picric acid complexes, including those of biological base molecules, have been studied in the past (Nagata *et al.*, 1995; Smith *et al.*, 2004; Goto *et al.*, 2004). Our studies aimed to look at the nature and directionality of the specific N—H$\cdots$O hydrogen bonding between the ions involving the phenolate O and protonated N atom and the packing mode in the crystal structure.



(I)

In the title compound, (I), the bond lengths and angles of the picrate anion show characteristic values, with C1—C2 and C1—C6 distances that are longer than regular aromatic values and a C1—O1 distance that shows possible double-bond character. These differences are due to the loss of a hydroxyl proton at O1, leading to conversion from the neutral to the anionic state. The observed values are comparable to those of many such picrates. Other bond lengths and angles are found to be normal. The nitro groups in the picrate anion tend to have different orientations with respect to the benzene plane, as observed in other molecular complexes. In general, the

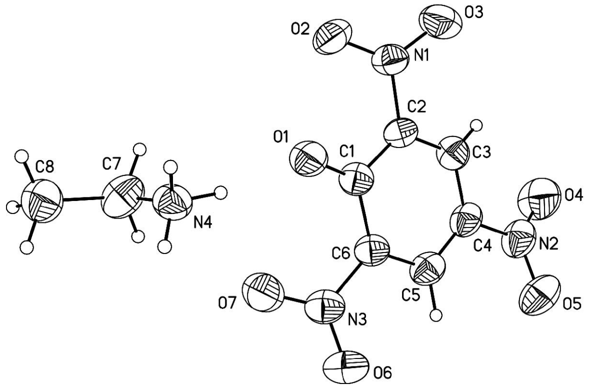


Figure 1
A 50% displacement ellipsoid plot of the title complex with the numbering scheme.

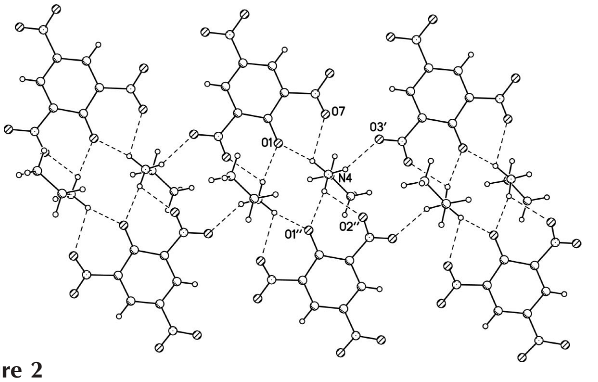


Figure 2
N—H$\cdots$O hydrogen-bonding scheme (dashed lines) involving the cations and anions.

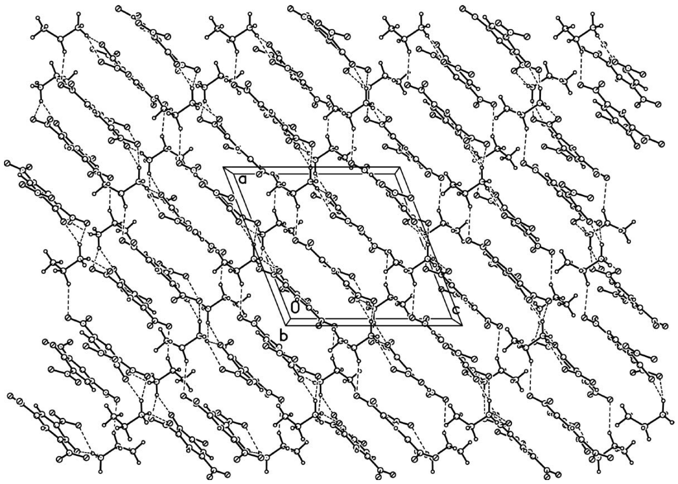


Figure 3
Packing of the ions, viewed down the *b* axis; dashed lines indicate the C—H$\cdots$O hydrogen bonds.

ortho nitro groups deviate more, while the *para*-nitro group lies almost in the benzene plane (Muthamizhchelvan, Saminathan, Fraanje *et al.*, 2005). The deviation of *para*-nitro groups may be attributed to the steric effects of the nearby phenolate group. In this structure, we observe that, while the *ortho*-nitro groups deviate in a regular fashion, the *para*-nitro group shows a significant difference. The twist angles between planes through the benzene ring and the nitro groups are 29.1 (2)° (N1), 17.5 (2)° (N2) and 24.4 (2)° (N3). We have observed such tilting of the *para*-nitro group, in the structure of 1-(4-methylpiperidinemethyl)-2-(4-bromophenyl)-6-methyl-8-(trifluoromethyl)imidazo[1,2-*a*][1,8]naphthyridinium picrate, due to the formation of N—H$\cdots$O bonding between the ions (Muthamizhchelvan, Saminathan, Sethu-Sankar *et al.*, 2005). In the present complex, deviation of the *para*-nitro group from the benzene plane is caused by the C—H$\cdots$O hydrogen-bond formation between C7 of the cation and O5 of the anion (Table 2). Therefore, the tilting of the *para*-nitro group is a consequence of the hydrogen bonding between the ions.

The aliphatic cation positions itself in an interesting way, having the C—C bond in the [101] direction and N4 lying almost in the plane of the picrate ion, the deviation being 0.168 (3) Å. This position of N4 favours hydrogen-bond formation with all three of its nearest neighbour cations. Of the five N—H$\cdots$O bonds, the strongest is a linear bond between N4 and O1. We also observe that there are two sets of bifurcated N—H$\cdots$O bonds (Table 2). The N4—H3N$\cdots$O1^{i} and N4—H3N$\cdots$O2^{i} hydrogen bonds form a ring pattern with a graph-set descriptor of $R_1^2(6)$ (Bernstein *et al.*, 1995). In the same fashion, N4—H1N$\cdots$O1 and N4—H1N$\cdots$O7 hydrogen bonds also form a ring pattern of $R_1^2(6)$. The N4—H1N$\cdots$O1 and N4—H3N$\cdots$O1^{i} hydrogen bonds of the symmetry-related molecules link the anions and cations and form a ring pattern of $R_4^2(8)$. The intermolecular N4—H2N$\cdots$O3^{ii} and N4—H3N$\cdots$O2^{i} hydrogen bonds of the symmetry-related molecules link the anions and cations to form a ring pattern of $R_4^4(12)$. The graph sets $R_4^2(8)$ and $R_4^4(12)$ alternate along the *b* axis.

The picrate anions lie parallel to the (101) plane and are connected by an O$\cdots$O short contact O7$\cdots$O3^{ii} [2.927 (4) Å]. The cations lie between two such antiparallel picrate chains and link them through N—H$\cdots$O hydrogen bonds (Fig. 2). The linkage extends infinitely along the *b* axis. In addition to N—H$\cdots$O hydrogen bonds, we observe two C—H$\cdots$O hydrogen bonds involving both the C atoms of the cation (Table 2). Of these, C7—H7*A*$\cdots$O^{iii} influences the *para*-nitro group of the picrate ion, causing it to tilt from its normal position to accommodate the hydrogen bonding.

Experimental

Crystals of the title salt were prepared from an ethanol solution containing equimolar amounts of picric acid and ethylamine by slow evaporation at room temperature.

Crystal data

$C_2H_8N^+\cdot C_6H_2N_3O_7^-$
$M_r = 274.20$
Monoclinic, $P2_1/n$
$a = 11.616$ (1) Å
$b = 8.663$ (1) Å
$c = 12.046$ (1) Å
$\beta = 111.52$ (1)°
$V = 1127.70$ (19) Å^3
$Z = 4$

$D_x = 1.615$ Mg m^{-3}
Cu *Kα* radiation
Cell parameters from 25 reflections
$\theta = 25$–45°
$\mu = 1.26$ mm^{-1}
$T = 293$ (2) K
Block, red
0.58 × 0.38 × 0.32 mm

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Data collection

Enraf–Nonius CAD-4 diffractometer
ω–2θ scans
Absorption correction: ψ scan (North *et al.* 1968)
$T_{min} = 0.404$, $T_{max} = 0.671$
2646 measured reflections
2325 independent reflections
2006 reflections with $I > 2\sigma(I)$

$R_{int} = 0.063$
$\theta_{max} = 75.0°$
$h = -14 \rightarrow 13$
$k = -10 \rightarrow 4$
$l = -6 \rightarrow 15$
2 standard reflections every 100 reflections intensity decay: 1%

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)] = 0.079$
$wR(F^2) = 0.226$
$S = 1.08$
2325 reflections
194 parameters
H atoms treated by a mixture of independent and constrained refinement

$w = 1/[\sigma^2(F_o^2) + (0.1181P)^2 + 1.0073P]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max} < 0.001$
$\Delta\rho_{max} = 0.68$ e Å^{-3}
$\Delta\rho_{min} = -0.36$ e Å^{-3}
Extinction correction: *SHELXL*97
Extinction coefficient: 0.025 (3)

Table 1
Selected geometric parameters (Å, °).

O1—C1	1.251 (3)	N4—C7	1.470 (4)
C1—C6	1.442 (4)	C7—C8	1.504 (5)
C1—C2	1.445 (4)		
O1—C1—C6	124.4 (3)	C6—C1—C2	111.9 (2)
O1—C1—C2	123.7 (2)	N4—C7—C8	111.4 (3)

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

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
N4—H1N···O1	0.97 (5)	1.86 (5)	2.828 (3)	173 (4)
N4—H1N···O7	0.97 (5)	2.39 (5)	2.866 (4)	109 (3)
N4—H3N···O1^{i}	0.85 (5)	2.10 (5)	2.881 (3)	153 (4)
N4—H3N···O2^{i}	0.85 (5)	2.43 (4)	2.984 (4)	123 (3)
N4—H2N···O3^{ii}	0.90 (4)	2.14 (4)	2.975 (4)	154 (3)
C7—H7*A*···O5^{iii}	0.97	2.45	3.389 (4)	164
C8—H8*C*···O6^{iv}	0.96	2.68	3.470 (5)	140

Symmetry codes: (i) $2 - x, 1 - y, 1 - z$; (ii) $x, 1 + y, z$; (iii) $1 - x, 1 - y, 1 - z$; (iv) $\frac{1}{2} + x, \frac{3}{2} - y, z - \frac{1}{2}$.

All H atoms were located in difference Fourier maps. While the H atoms of the amine group were refined isotropically, the H atoms of the cation were made to ride on their respective C atoms. The U_{iso}(H) values were set equal to $1.2U_{eq}$(C) for CH_2 and $1.5U_{eq}$ for the methyl group.

Data collection: *CAD-4 EXPRESS* (Enraf–Nonius, 1994); cell refinement: *CAD-4 EXPRESS*; data reduction: *XCAD4* (Harms & Wocadlo, 1995); program(s) used to solve structure: *SHELXS97* (Sheldrick, 1997); program(s) used to refine structure: *SHELXL97* (Sheldrick, 1997); molecular graphics: *ORTEP-3* (Farrugia, 1997) and *PLATON* (Spek, 2003); software used to prepare material for publication: *SHELXL97*.

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