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Triethylaminium picrate

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Key indicators

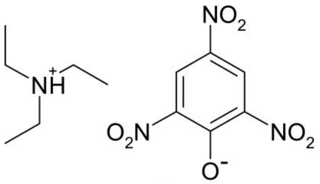
Single-crystal X-ray study
T = 293 K
Mean σ(C–C) = 0.009 Å
R factor = 0.052
wR factor = 0.165
Data-to-parameter ratio = 7.6

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

The title salt, $C_6H_{16}N^+\cdot C_6H_2N_3O_7^-$, crystallizes with two pairs of cations and anions in the asymmetric unit. Anions *A* and *B* are stacked alternately in the (020) plane to form anionic columns having an *ABABAB*... sequence, with possible π–π interactions between them. The cationic columns surround these columns in an almost hexagonal fashion, with each column of the same type of cation, *A* or *B*. The anions and cations are connected through lone N—H···O and by other C—H···O hydrogen bonds. N—H···O and C—H···O hydrogen bonds involving *A*-and *B*- type ions form a cyclic pattern with a graph-set descriptor $R_2^2(10)$.

Comment

Picric acid forms crystalline picrates with various organic molecules and such picrates are convenient for identification and qualitative analysis of organic compounds. The formation of picrates is a common method for the conversion of liquids into stable, tractable solid compounds (Takayanagi *et al.*, 1996). Crystal structures of a large number of picrate salts and picric acid complexes, including the biological base molecules, have been studied in the past (Nagata *et al.*, 1995; Smith *et al.*, 2004; Goto *et al.*, 2004). In many cases, the bonding of these electron-donor picric acid complexes depends stronglyon the nature of the partner. The linkage could involve not only electrostatic attraction, but also the formation of molecular complexes (Zaderenko *et al.*, 1997). The title salt, (I), was prepared to study the nature and directionality of the specific N—H···O hydrogen bond involving the protonated N atom and factors influencing the tilting of the nitro groups of the picrate ion in the solid state.



(I)

The asymmetric unit of (I) contains two sets of picrate anions and triethylaminium cations. The picrate anions lie almost parallel to each other, with a dihedral angle of 8.3 (1)°, but have different orientations. These ions lie on (020) planes in an alternate fashion. The triethylaminium cations take up suitable orientations to produce N—H···O hydrogen bonds between the ions (Fig. 1).

The partial double-bond character of C1—O1 and lengthening of the C1—C2 and C1—C6 bonds from the regular aromatic values around C1 may be attributed to the loss of the

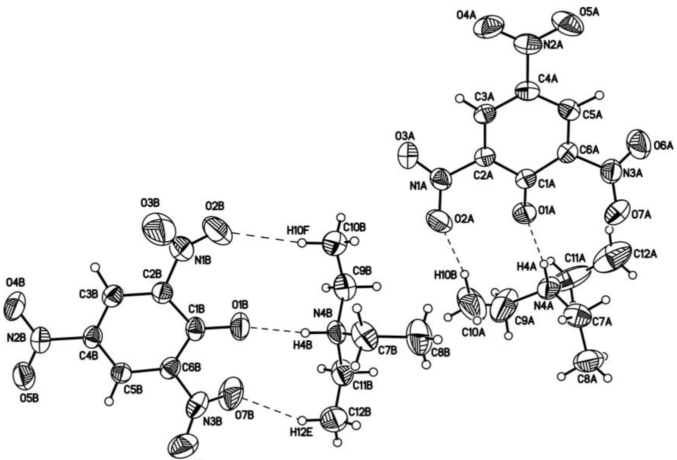


Figure 1
A 30% displacement ellipsoid plot of the title salt, showing the atom-numbering scheme. Both sets of cations and anions present in the asymmetric unit are shown. Dashed lines indicate the hydrogen bonds within each set of ions.

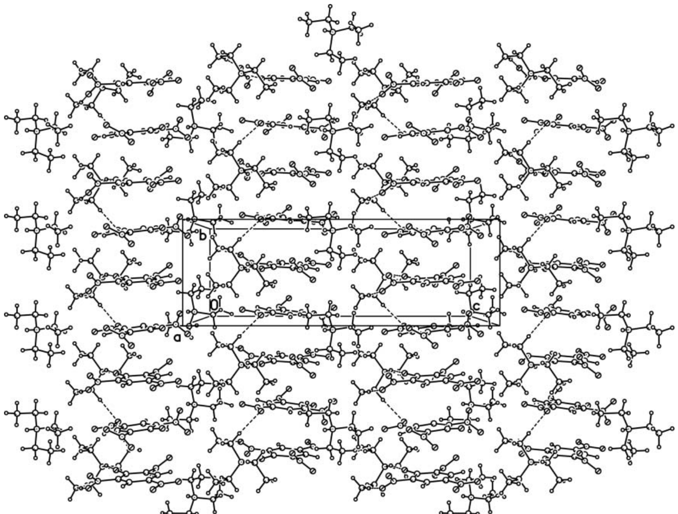


Figure 2
The packing of the molecules, viewed down the *a* axis.

hydroxyl proton at O1 for anions *A* and *B*, leading to the conversion from the neutral to the anionic state of the picrate molecules, as observed in other picrate salts (Muthamizhchelvan *et al.*, 2005, 2005*a*). This also suggests charge delocalization around atom C1.

The twist angles of the three nitro groups from the benzene plane of the picrate ion are 37.0 (3) (O2—N1—O3), 3.1 (4) (O4—N2—O5) and 37.7 (3)° (O6—N3—O7) for picrate anion *A*, and 37.9 (4), 3.0 (4) and 40.4 (4)° for anion *B*. An analysis of the tilting of the nitro groups in picrate ions shows that the *ortho*-nitro groups, in general, deviate away from the benzene plane due to steric interactions with the phenol group at C1, but the *para*-nitro groups lie in the benzene plane. Deviations from this normal tilting behaviour arise in many structures as a result of crystal packing criteria which involve N—H···O and C—H···O hydrogen bonds or short contacts with the nitro group O atoms (Muthamizhchelvan *et al.*, 2005*b*). In the present structure, however, the nitro-group orientations are normal in nature.

Anions *A* and *B* are stacked alternately in a plane parallel to the crystallographic (020) plane. The stacking leads to the formation of anionic columns having an *ABABAB*... sequence, with possible π–π interactions, as the anions are separated by 3.486 Å. The cationic columns surround these columns in an almost hexagonal manner, with each column of the same type of cation, *A* or *B*. This columnar stacking of the anions along the *b* axis is shown in Fig. 2. The intermolecular contacts between the anion and cation include the characteristic N—H···O and extensive C—H···O hydrogen bonds (Table 2). The positioning of cations facilitates the formation of N4—H4···O1, which is stronger and linear, as expected. Apart from this, the linear alignment of two of the three ethyl groups of the cation leads to the formation of C10—H10···O2 and C12—H12···O7 hydrogen bonds in ionic pair *B*, but only C10—H10···O2 between the *A* ions; C12*A*—H12*A*···O7*A* has longer H···*A* (3.406 Å) and C···O (3.976 Å) distances, and hence could not be classified as a C—H···O hydrogen bond. Cation *B* connects the two anions by N4*B*—H4*B*···O1*B* and C9*B*—H9*D*···O4*A* hydrogen bonds, with the C—H···O bond making the link along the *b* axis. C12*B*—H12*D*···O4*B* connects the *B* type anions and cations, and this link is nearly parallel to the *a* axis. No such linking is found among the ions of type *A*. The N—H···O and C—H···O hydrogen bonds involving *A*-type ions form a cyclic pattern with a graph-set descriptor $R_2^2(10)$, *viz.* N4*A*—H4*A*···O1*A*—C1*A*—C2*A*—N1*A*—O2*A*···H10*B*—C10*A*—C9*A*, whereas ions of type *B* form two such cyclic patterns with motifs N4*B*—H4*B*···O1*B*—C1*B*—C2*B*—N1*B*—O2*B*···H10*F*—C10*B*—C9*B* and N4*B*—H4*B*···O1*B*—C1*B*—C6*B*—N3*B*—O7*B*···H12*E*—C12*B*—C11*B* (Fig. 1) (Bernstein *et al.*, 1995).

Experimental

Crystals of (I) were prepared from an ethanol solution containing equimolar amounts of picric acid and triethylamine at room temperature. Yellow pyramid-shaped single crystals were obtained by slow evaporation of the ethanol solution.

Crystal data

$C_6H_{16}N^+\cdot C_6H_2N_3O_7^-$
M_r = 330.30
Orthorhombic, $Pca2_1$
a = 21.9799 (15) Å
b = 6.9727 (4) Å
c = 20.7700 (13) Å
V = 3183.2 (3) Å^3
Z = 8
D_x = 1.378 Mg m^{-3}

Cu *Kα* radiation
Cell parameters from 25 reflections
θ = 15–50°
μ = 0.98 mm^{-1}
T = 293 (2) K
Pyramid, yellow
0.5 × 0.4 × 0.3 mm

Data collection

Enraf–Nonius CAD-4 diffractometer
ω–2θ scans
Absorption correction: ψ scan (North *et al.*, 1968)
$T_{\min}$ = 0.682, $T_{\max}$ = 0.745
3634 measured reflections
3363 independent reflections
2403 reflections with $I > 2\sigma(I)$

$R_{\rm int}$ = 0.057
$\theta_{\max}$ = 74.7°
$h = -8 \rightarrow 27$
$k = -3 \rightarrow 8$
$l = -8 \rightarrow 25$
2 standard reflections every 100 reflections intensity decay: 1%

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Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)] = 0.052$
$wR(F^2) = 0.165$
$S = 1.02$
3363 reflections
440 parameters
H atoms treated by a mixture of independent and constrained refinement

$w = 1/[\sigma^2(F_o^2) + (0.1004P)^2 + 0.2349P]$
where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max} < 0.001$
$\Delta\rho_{max} = 0.27$ e Å^{-3}
$\Delta\rho_{min} = -0.18$ e Å^{-3}
Extinction correction: *SHELXL97*
Extinction coefficient: 0.0009 (2)

Table 1
Selected geometric parameters (Å, °).

O1A—C1A	1.234 (5)	O1B—C1B	1.250 (5)
C1A—C2A	1.450 (5)	C1B—C6B	1.431 (7)
C1A—C6A	1.454 (6)	C1B—C2B	1.441 (6)
N4A—C9A	1.444 (8)	N4B—C11B	1.495 (6)
N4A—C7A	1.477 (8)	N4B—C7B	1.502 (7)
N4A—C11A	1.487 (13)	N4B—C9B	1.519 (7)
O1A—C1A—C2A	123.5 (4)	O1B—C1B—C6B	125.0 (4)
O1A—C1A—C6A	124.8 (4)	O1B—C1B—C2B	123.4 (4)
C2A—C1A—C6A	111.5 (3)	C6B—C1B—C2B	111.5 (3)
C11A—N4A—C9A—C10A	−166.1 (11)	C11B—N4B—C9B—C10B	173.2 (5)
C9A—N4A—C11A—C12A	171.9 (7)	C9B—N4B—C11B—C12B	−179.3 (5)

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

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
N4A—H4A···O1A	1.01 (7)	1.76 (7)	2.767 (5)	172 (5)
N4B—H4B···O1B	1.00 (8)	1.82 (8)	2.781 (5)	160 (7)
C10A—H10B···O2A	0.96	2.42	3.307 (13)	154
C10B—H10F···O2B	0.96	2.53	3.483 (9)	170
C12B—H12E···O7B	0.96	2.64	3.258 (10)	123
C7A—H7A···O5B^{i}	0.97	2.65	3.584 (7)	162
C8A—H8C···O5A^{ii}	0.96	2.68	3.448 (10)	137
C10A—H10A···O6A^{ii}	0.96	2.61	3.547 (14)	166
C11A—H11B···O4B^{iii}	0.97	2.62	3.265 (9)	124
C12A—H12A···O6B^{iv}	0.96	2.62	3.553 (11)	163
C7B—H7C···O4A^{v}	0.97	2.60	3.454 (7)	147
C9B—H9D···O4A^{vi}	0.97	2.44	3.336 (8)	154
C12B—H12D···O4B^{vii}	0.96	2.58	3.496 (8)	160

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

The H atoms were located in difference maps. While the H atoms of the three ethyl group were made to ride (C—H = 0.93–0.96 Å) on their respective C atoms, the other H atoms were refined isotropically. For CH_2 H atoms, U_{iso}(H) values were set equal to $1.2U_{eq}$(C) and for the methyl H atoms they were set at $1.5U_{eq}$(C). In the absence of significant anomalous dispersion effects, Friedel pairs were averaged.

Data collection: *CAD-4 EXPRESS* (Enraf–Nonius, 1997); 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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