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3-(Dimethylammonio)propanaminium dipicrate

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In the title complex, $C_5H_{16}N_2^{2+}\cdot 2C_6H_2N_3O_7^-$, the two picrate anions lie almost parallel to each other and have possible π–π interactions between them. One of the anions is involved in limited N—H···O bonds, whereas the other engages in extensive N—H···O and C—H···O hydrogen bonds. Tilting of one of the *ortho* nitro groups in the picrate anion is influenced by the N—H···O hydrogen bond. The dimethylaminopropylammonium and picrate ions are linked through N—H···O and C—H···O hydrogen bonds, forming chains along the crystallographic *b* axis. The anions form near-helical columns along the *b* axis owing to the presence of a 2_1 screw and are separated by nearly linear cationic chains.

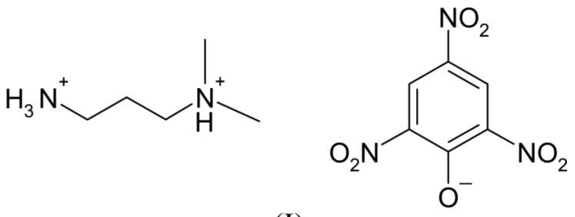
Key indicators

Single-crystal X-ray study
T = 293 K
Mean σ(C–C) = 0.003 Å
R factor = 0.060
wR factor = 0.171
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.

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 acid to form salts through electrostatic or hydrogen-bonding interactions (In *et al.*, 1997). Crystalline picrates have commonly been used in the preparation of amine derivatives in qualitative organic chemistry (Shriner *et al.*, 1980). The crystal structures of a number of picrate complexes with organic compounds and biological base molecules such as serotonin, guanine and β-alanine have been studied (Takayanagi *et al.*, 1996; Thewalt & Bugg, 1972; Bugg & Thewalt, 1975; Anitha *et al.*, 2004). The preparation of dipicrates with suitable cationic compounds have also been carried out by other workers (Lin & Lu 2004; Ma *et al.*, 2005). Our aim is to study the nature and directionality of the specific N—H···O hydrogen bonding between the molecular ions involving the phenolate O and the protonated N atom and the crystal packing mode. As part of our investigations, we have prepared and determined the crystal structure of the title molecular complex, (I) (Muthamizhchelvan *et al.*, 2005, 2005*a*, 2005*b*).



(I)

The title complex has two anions and one cation, as the cation has been protonated at the two possible amine sites,

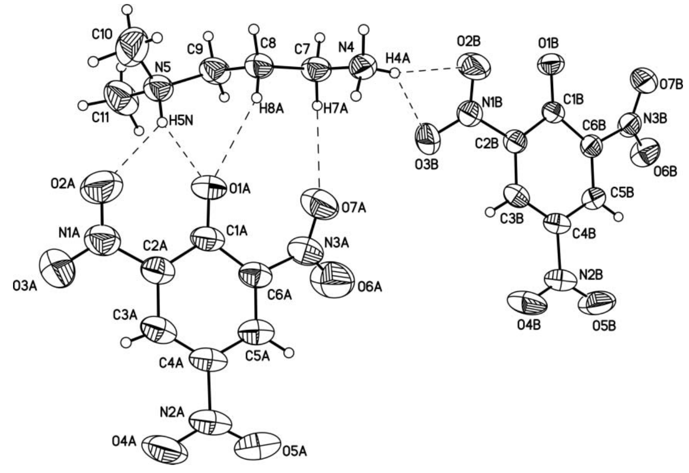


Figure 1
A 50% probability displacement ellipsoid plot of the title complex, with the atomic numbering scheme. Dashed lines indicate hydrogen bonds.

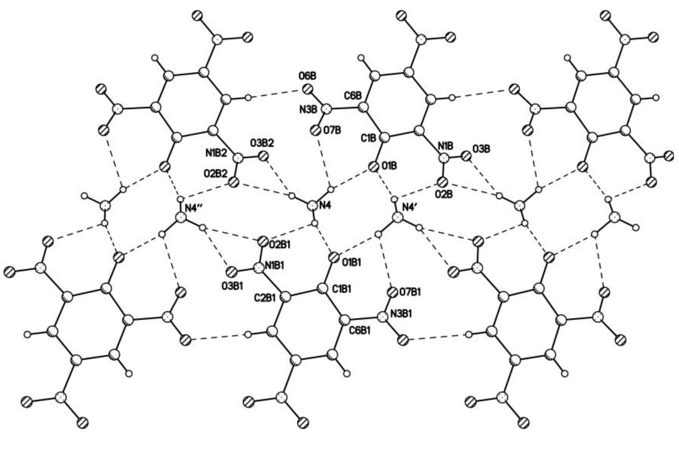


Figure 2
The N—H···O hydrogen-bond network formed by the terminal N atom N4 with *B*-type anions. Other atoms of the cation have been omitted for clarity. Dashed lines indicate hydrogen bonds.

forming the dipicrate. A displacement ellipsoid plot of this salt is shown in Fig. 1. The bond lengths of the two anions show characteristic values, with C1—O1 = 1.238 (3) Å for anion *A* and 1.253 (3) Å for anion *B*; these values are intermediate between typical single- and double-bond values. In addition, the bond distances C1—C2 = 1.448 (4) Å and C1—C6 = 1.448 (4) Å for *A*, and C1—C2 = 1.445 (3) Å and C1—C6 = 1.441 (3) Å for *B*, are longer and deviate from the standard aromatic C—C value of 1.395 Å (Walkinshaw, 1986). Obviously, these differences are due to the loss of a hydroxyl H atom at O1, leading to conversion from neutral picric acid to anionic picrate. The N—O distances of the nitro groups range from 1.203 (3) to 1.233 (4) Å, and the average value, 1.217 (4) Å, is comparable to the N—O value for C_{ar}—NO_2 groups, 1.217 Å, given by Allen *et al.* (1987), and also agrees with the average value of 1.216 (7) Å reported by Sethu-Sankar *et al.* (2003). C—N distances in the picrates have values from 1.449 (3) Å to 1.458 (4) Å.

The three nitro groups of the picrate anion *A* deviate from the benzene plane by 9.72 (2)° (N1*A*), 8.67 (2)° (N2*A*) and 31.23 (2)° (N3*A*), and in anion *B* the twist angles are 28.89 (1)° (N1*B*), 3.95 (2)° (N2*B*) and 28.18 (1)° (N3*B*). These tilt angles show that in anion *A* one of the *ortho* nitro groups (N1*A*) tends to align with the benzene plane, whereas the other (N3*A*) is at the normal orientation. In general, *ortho* nitro groups deviate significantly from the benzene plane, while *para* nitro groups lie in the plane. The abnormal behaviour of the nitro group N1*A* can be attributed to the N—H···O hydrogen bond between one of its nitro O atoms (O2*A*) and N5 of the cation. Analysis of such situations in picrate complexes reveals that, if any one of the two O atoms (not both) of the nitro group takes part in hydrogen-bond or short contact interactions, the nitro group is pushed towards or away from the benzene plane from its normal position. In this dipicrate complex, the nitro groups of anion *B* show regular tilting features, with the *ortho* nitro groups deviating more from the benzene plane and the *para* nitro group lying in the benzene plane. The two picrate anions lie almost parallel to each other, the dihedral angle between their planes being 5.46 (1)°, and are separated by 3.447 Å, suggesting a possible π–π interaction between them.

The cation is linear, as shown by the torsion angles N4—C7—C8—C9 = −177.6 (2)° and C7—C8—C9—N5 = 159.9 (2)°. The C—N bond length, C7—N4 = 1.490 (4) Å, of the cation is found to be normal and is in agreement with the reported value, 1.487 (2) Å, found in related literature (Anitha *et al.*, 2005). The other C—N bonds involving the other protonated N atom of the dimethylamine group, N5, are N5—C11 = 1.484 (4) Å, N5—C10 = 1.468 (4) Å and N5—C9 = 1.499 (4) Å. The bond lengths C7—C8 [1.511 (4) Å] and C8—C9 [1.516 (4) Å] in the cation have normal values observed for such molecules.

The crystal packing is stabilized by N—H···O and C—H···O hydrogen bonds. Of the two picrate anions, *B* is involved in extensive hydrogen bonds, whereas *A* is involved in only two N—H···O bonds, which are components of a bifurcated bond with the N5 atom of the cation, and also two C—H···O hydrogen bonds (Fig. 1). The strengths of the bifurcated N—H···O bonds of N5 (N5—H5*N*···O1*A* and N5—H5*N*···O2*A*) are very similar and completely different from the other cases observed. Anion *B* is involved in an N—H···O hydrogen bond with the terminal amine atom, N4, of the cation. This protonated terminal amine group forms extensive hydrogen bonds exclusively with *B*-type anions. All the three H atoms of atom N4 are involved in bifurcated hydrogen bonds (Fig. 2). In addition to these extensive N—H···O hydrogen bonds, the structure also contains C—H···O hydrogen bonds of varying strengths (Table 2). The N5—H5···O1*A* and N5—H5···O2*A* hydrogen bonds form a graph set descriptor of $R^2_1(6)$. The C—H···O hydrogen bonds (C8—H8*A*···O1*A* and C7—H7*A*···O7*A*) connect anion *A* and the cation and form a graph set descriptor $R^2_2(9)$ (Bernstein *et al.*, 1995). The hydrogen-bond networks created by the N4 atoms and the *B*-type picrate anions were analysed by graph set analysis. We find that networks of alternating graph sets of different $R^2_4(8)$ types extend along the *a*-axis direction. The

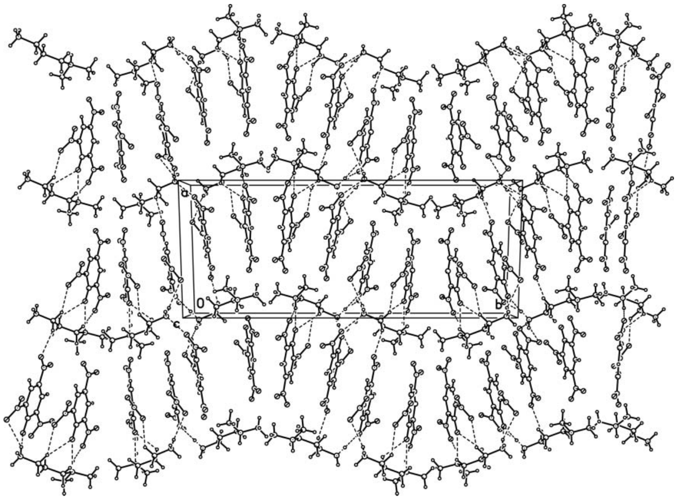


Figure 3
Packing of the title molecular complex, viewed down the *c* axis. Dashed lines indicate hydrogen bonds.

packing of this dipicrate complex viewed down the *c* axis is shown in Fig. 3. The anions form near-helical columns along the *b* axis owing to the presence of a 2_1 screw, separated by nearly linear cationic chains.

Experimental

Compound (I) was prepared from ethanol solutions containing equimolar amounts of picric acid and dimethylaminopropylamine at room temperature. Red single crystals of (I) were obtained by slow evaporation of the ethanol solution.

Crystal data

$C_5H_{16}N_2^{2+}\cdot 2C_6H_2N_3O_7^-$
$M_r = 560.41$
Monoclinic, $P2_1/c$
$a = 11.3271$ (14) Å
$b = 26.9657$ (12) Å
$c = 8.0667$ (6) Å
$\beta = 104.764(10)°$
$V = 2382.6$ (4) Å^3
$Z = 4$
$D_x = 1.562$ Mg m^{-3}
Cu $K\alpha$ radiation
Cell parameters from 25 reflections
$\theta = 15$–$50°$
$\mu = 1.21$ mm^{-1}
$T = 293$ (2) K
Block, red
0.25 × 0.20 × 0.15 mm

Data collection

Enraf–Nonius CAD-4 diffractometer
ω–2θ scans
Absorption correction: ψ scan (North *et al.*, 1968)
$T_{min} = 0.760$, $T_{max} = 0.835$
5478 measured reflections
4900 independent reflections
3473 reflections with $I > 2\sigma(I)$
$R_{int} = 0.040$
$\theta_{max} = 74.9°$
$h = -14 \rightarrow 5$
$k = -33 \rightarrow 10$
$l = -9 \rightarrow 10$
2 standard reflections every 100 reflections intensity decay: 1%

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)] = 0.060$
$wR(F^2) = 0.171$
$S = 1.05$
4900 reflections
408 parameters
H atoms treated by a mixture of independent and constrained refinement
$w = 1/[\sigma^2(F_o^2) + (0.092P)^2 + 0.6389P]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max} < 0.001$
$\Delta\rho_{max} = 0.42$ e Å^{-3}
$\Delta\rho_{min} = -0.32$ e Å^{-3}

Table 1
Selected geometric parameters (Å, °).

O1*A*—C1*A*	1.238 (3)	C1*B*—C2*B*	1.445 (3)
C1*A*—C2*A*	1.448 (4)	N4—C7	1.490 (4)
C1*A*—C6*A*	1.448 (4)	N5—C10	1.468 (4)
O1*B*—C1*B*	1.253 (3)	N5—C11	1.484 (4)
C1*B*—C6*B*	1.441 (3)	N5—C9	1.499 (4)
O1*A*—C1*A*—C2*A*	125.6 (3)	C6*B*—C1*B*—C2*B*	111.36 (18)
O1*A*—C1*A*—C6*A*	122.1 (3)	C10—N5—C11	111.3 (3)
C2*A*—C1*A*—C6*A*	112.2 (2)	C10—N5—C9	112.9 (2)
O1*B*—C1*B*—C6*B*	124.48 (19)	C11—N5—C9	110.2 (2)
O1*B*—C1*B*—C2*B*	124.1 (2)		
N4—C7—C8—C9	−177.6 (2)	C7—C8—C9—N5	159.9 (2)

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

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
N5—H5*N*···O1*A*	0.88 (3)	1.89 (3)	2.655 (3)	143 (3)
N5—H5*N*···O2*A*	0.88 (3)	2.26 (3)	2.968 (3)	137 (3)
N4—H4*A*···O2*B*	0.88 (4)	2.33 (4)	3.188 (3)	166 (3)
N4—H4*A*···O3*B*	0.88 (4)	2.31 (4)	3.023 (3)	138 (3)
N4—H4*B*···O1*B*^{i}	0.96 (4)	1.90 (4)	2.846 (3)	167 (3)
N4—H4*B*···O7*B*^{i}	0.96 (4)	2.53 (3)	3.089 (3)	118 (3)
N4—H4*C*···O1*B*^{ii}	0.95 (3)	1.89 (3)	2.814 (3)	164 (3)
N4—H4*C*···O2*B*^{ii}	0.95 (3)	2.34 (3)	2.905 (3)	117 (2)
C7—H7*A*···O7*A*	1.05 (3)	2.48 (3)	3.243 (4)	129 (2)
C8—H8*A*···O1*A*	0.94 (3)	2.52 (3)	3.117 (3)	122 (2)
C8—H8*A*···O1*B*^{i}	0.94 (3)	2.66 (3)	3.384 (3)	135 (2)
C3*B*—H3*B*···O6*B*^{i}	0.90 (3)	2.49 (3)	3.290 (3)	148 (3)
C3*A*—H3*A*···O6*A*^{i}	0.83 (3)	2.65 (3)	3.385 (4)	147 (3)
C7—H7*B*···O5*B*^{iii}	1.02 (4)	2.48 (4)	3.419 (3)	153 (3)
C11—H11*C*···O4*A*^{iv}	0.96	2.55	3.469 (4)	161

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

All H atoms were located in difference Fourier maps. While the H atoms of the methyl groups were made to ride on their respective C atoms, with C—H = 0.96 Å, all other H atoms were refined isotropically. The U_{iso}(H) values were set equal to $1.5U_{eq}$(C) for the methyl groups.

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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