Acta Crystallographica Section E
Structure Reports Online
ISSN 1600-5368

Piperidinium picrate

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Key indicators

Single-crystal X-ray study
T = 293 K
Mean σ(C–C) = 0.003 Å
R factor = 0.040
wR factor = 0.121
Data-to-parameter ratio = 11.5

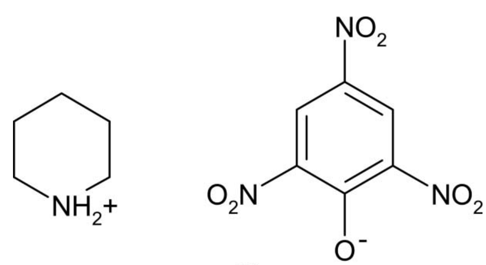
For details of how these key indicators were automatically derived from the article, see http://journals.iucr.org/e.

Received 21 November 2005
Accepted 25 November 2005
Online 30 November 2005

In the title compound, $C_5H_{12}N^+\cdot C_6H_2N_3O_7^-$, the protonated N atom of the cation makes one linear and two bifucated hydrogen bonds with two neighbouring picrate anions. Centrosymmetrically related anions and cations form a hydrogen-bonded network with a graph-set motif $R_4^4(12)$. The picrate ions are parallel to one another and governed by π–π interactions; they form columns along the b axis.

Comment

Picric acid forms salts or charge-transfer complexes with many organic compounds, particularly with aromatic and aliphatic amines. Crystalline picrates have commonly been used in the preparation of amine derivatives in qualitative organic chemistry (Shriner *et al.*, 1980). 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 in the past (Takayanagi *et al.*, 1996; Thewalt & Bugg, 1972; Anitha *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 piperidinium picrate, (I) (Muthamizhchelvan, Saminathan, Fraanje *et al.*, 2005*a*,*b*; Muthamizhchelvan, Saminathan, SethuSankar *et al.*, 2005*a*,*b*,*c*,*d*,*e*).



(I)

The bond lengths of the anion show characteristic values, with C1—O1 [1.242 (2) Å] intermediate between single- and double-bond character; C1—C2 [1.450 (3) Å] and C1—C6 [1.452 (2) Å] deviate from the standard aromatic C—C value of 1.375 Å, as observed in other picrate salts (Muthamizhchelvan, Saminathan, SethuSankar *et al.*, 2005*a*,*b*,*c*,*d*,*e*). These differences are attributed to the loss of a hydroxyl proton at O1, leading to conversion from neutral to the anionic state of the picrate molecule, where the negative charge is constrained to lie in the ring (Ferguson *et al.*, 1984).

The twist angles of the three nitro groups of the picrate ions show that the *ortho* nitro groups O2—N1—O3 and O6—N3—O7 deviate from the benzene plane by 16.0 (2) and 50.5 (1)°,

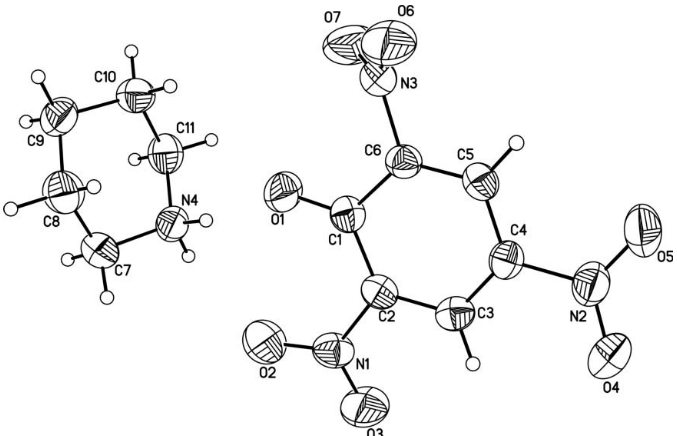


Figure 1
The title complex, showing 50% probability displacement ellipsoids and the atom-numbering scheme.

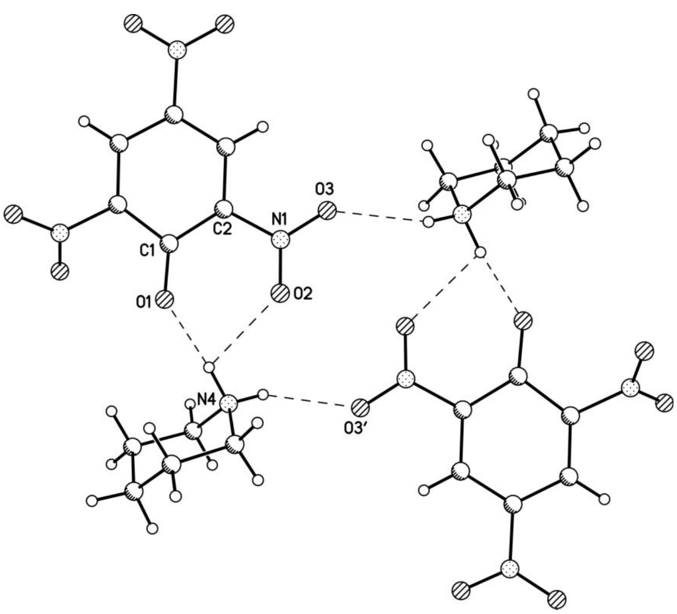


Figure 2
Plot showing the hydrogen-bonded (dashed lines) graph-set motifs: $R_4^4(12)$ involving N4—H4*A*···O2 and N4—H4*B*····O3', and $R_1^2(6)$ involving N4—H4*A*···O1 and N4—H4*A*···O2.

respectively, and the *para* nitro group (O4/N2/O5) by 8.7 (2)°. The tilting of the nitro groups facilitates C—H···O hydrogen bonding with the neighbouring cations (Table 2).

In the piperidinium cation, bond lengths involving protonated atom N4 are 1.495 (2) (N4—C7) and 1.488 (2) Å (N4—C11), which are longer than those found in other structures and the value 1.469 Å given by Allen *et al.* (1987). Moreover, the average value of the C—C bond, 1.507 Å, is also found to be less than the normal C—C distance. The cation exists in its most stable chair conformation.

Protonated atom N4 makes three hydrogen bonds with two of its neighbouring picrate anions. Of the two H atoms of N4, one is involved in bifurcated hydrogen bonds and the other one in a linear bond (Table 2). The bifurcated hydrogen bonds are of different strengths; the one involving the phenolic O atom (O1) is stronger than the other. Such cases have been

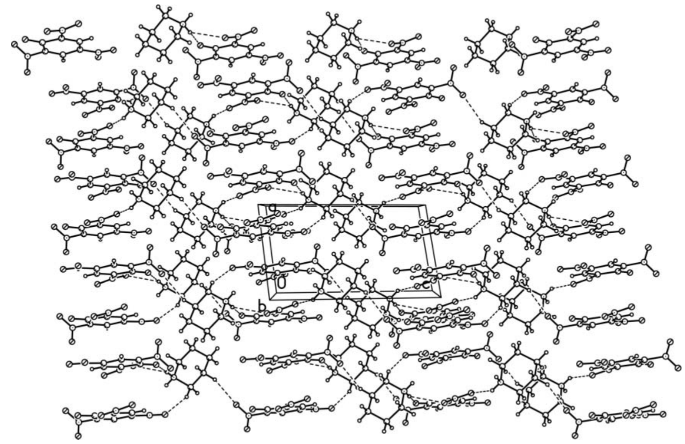


Figure 3
Packing of the molecular complex, viewed down the crystallographic *b* axis. Hydrogen bonds are shown as dashed lines.

observed in other picrate structures and are in line with the discussions of Taylor *et al.* (1984).

A set of centrosymmetrically related anions and cations form a graph-set motif of $R_4^4(12)$ involving N4—H4*A*···O2 and N4—H4*B*···O3', as shown in Fig. 2 (Bernstein *et al.*, 1995). One more hydrogen-bond network is found in this structure, with N4—H4*A*···O1 and N4—H4*A*···O2 combining together to form a graph-set of motif $R_1^2(6)$.

The picrate ions stack parallel to one another in an offset fashion, with possible π–π interactions as they are separated by 3.438 Å This leads to columnar stacking of the picrate ions, with the columns running along *a* axis. These anionic columns are separaed by cationic layers, as shown in Fig. 3.

Experimental

The title compound was prepared by taking equimolar amounts (1:1) of picric acid and piperidine and dissolving them in ethanol. Slow evaporation of the solution resulted in the formation of transparent yellow prism-shaped single crystals.

Crystal data

$C_5H_{12}N^+\cdot C_6H_2N_3O_7^-$	$Z = 2$
$M_r = 314.26$	$D_x = 1.533$ Mg m^{-3}
Triclinic, $P\overline{1}$	Mo $K\alpha$ radiation
$a = 6.8750$ (15) Å	Cell parameters from 25 reflections
$b = 9.3471$ (17) Å	$\theta = 8$–15°
$c = 11.9198$ (11) Å	$\mu = 0.13$ mm^{-1}
$\alpha = 105.393$ (12)°	$T = 293$ (2) K
$\beta = 91.856$ (11)°	Prism, yellow
$\gamma = 111.341$ (18)°	0.54 × 0.52 × 0.38 mm
$V = 680.7$ (2) Å^3	

Data collection

Enraf–Nonius CAD-4 diffractometer	$R_{int} = 0.014$
ω–2θ scans	$\theta_{max} = 25.0$°
Absorption correction: ψ scan (North *et al.*, 1968)	$h = -2 \rightarrow 8$
$T_{min} = 0.873$, $T_{max} = 0.961$	$k = -11 \rightarrow 10$
2606 measured reflections	$l = -14 \rightarrow 14$
2382 independent reflections	2 standard reflections every 100 reflections
1830 reflections with $I > 2\sigma(I)$	intensity decay: 1%

Refinement

Refinement on F^2	$w = 1/[\sigma^2(F_o^2) + (0.0615P)^2 + 0.2412P]$ where $P = (F_o^2 + 2F_c^2)/3$
$R[F^2 > 2\sigma(F^2)] = 0.040$	$(\Delta/\sigma)_{max} < 0.001$
$wR(F^2) = 0.121$	$\Delta\rho_{max} = 0.43$ e Å^{-3}
$S = 1.03$	$\Delta\rho_{min} = -0.28$ e Å^{-3}
2382 reflections	Extinction correction: *SHELXL97*
208 parameters	Extinction coefficient: 0.015 (4)
H atoms treated by a mixture of independent and constrained refinement	

Table 1
Selected geometric parameters (Å, °).

O1—C1	1.242 (2)	N4—C11	1.488 (3)
C1—C2	1.450 (3)	N4—C7	1.494 (3)
C1—C6	1.452 (2)		
O1—C1—C2	126.65 (16)	C2—C1—C6	111.30 (15)
O1—C1—C6	122.04 (17)	C11—N4—C7	112.42 (16)

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

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
N4—H4*A*···O1	0.96 (2)	1.82 (2)	2.767 (2)	171 (2)
N4—H4*A*···O2	0.96 (2)	2.50 (2)	2.996 (3)	112 (2)
N4—H4*B*···O3^{i}	0.86 (3)	2.28 (3)	2.970 (2)	138 (2)
C8—H8*A*···O4^{ii}	0.97	2.58	3.399 (3)	142
C10—H10*A*···O7^{iii}	0.97	2.53	3.290 (3)	135
C11—H11*B*···O4^{iv}	0.97	2.44	3.361 (3)	157

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

All H atoms were located in difference Fourier maps. While the H atoms of the protonated N atom were refined isotropically, the C-bound H atoms were refined as riding on their parent atoms, with C—H = 0.93–0.98 Å and $U_{iso}(H) = 1.2U_{eq}(C)$.

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: *ORTEP3* (Farrugia, 1997) and *PLATON* (Spek, 2003); software used to prepare material for publication: *SHELXL97*.

The authors thank Dr Babu Varghese, SAIF, Indian Institute of Technology, Chennai, for collecting the single-crystal data.

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