Cyclohexylammonium picrate

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Key indicators

Single-crystal X-ray study
T = 293 K
Mean σ(C–C) = 0.005 Å
R factor = 0.062
wR factor = 0.176
Data-to-parameter ratio = 11.9

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

In the crystal structure of the title salt, $C_6H_{14}N^+ \cdot C_6H_2N_3O_7^-$, picrate anions lie parallel to one another with a relative orientation of nearly 120°. The protonated N atom of the cation makes one linear and two bifurcated hydrogen bonds with three neighbouring picrate ions. The centrosymmetrically related anions and cations form hydrogen-bonded graph-set motifs of $R_4^2(8)$ and $R_4^4(12)$ alternately along the [010] direction.

Comment

Picric acid forms salts with various protonated molecules that are convenient for the identification and qualitative analysis of relevant organic compounds (Takayanagi *et al.*, 1996). The formation of picrates is also a common method for the conversion of liquids into stable, tractable solid compounds, which, in many cases, leads to the formation of crystalline solids suitable for X-ray structure determination (Saleh *et al.*, 1997). Cyclohexylamine is used as a corrosion inhibitor in boiler feed water and has important applications as a chemical intermediate. Crystal structures of a number of cyclohexylammonium salts have been studied previously (Lis & Jerzykiewicz, 1995; Weichsel & Lis, 1989). Picric acid readily forms a crystalline salt with this amine, and in this study, the crystal structure was determined in order to understand the nature and directionality of the specific N—H···O hydrogen bond involving the protonated N atom (Muthamizhchelvan, Saminathan, Fraanje *et al.*, 2005*a*,*b*; Muthamizhchelvan, Saminathan, SethuSankar *et al.*, 2005*a*,*b*,*c*,*d*,*e*)
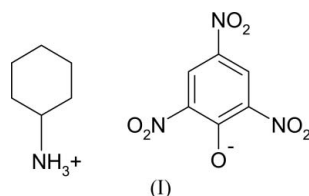

(I)

Fig. 1 shows a displacement ellipsoid plot of the title compound, (I). The bond lengths of the anion (Table 1) show characteristic values, with C1—O1 intermediate between single- and double-bond character, and C1—C2 and C1—C6 being longer and deviating from the standard aromatic C—C value of 1.395 Å (Walkinshaw, 1986). These bond lengths are similar to those of other picrate salts. The average N—O distance of the nitro groups is comparable to the literature C_{ar}—NO_2 value of 1.217 (11) Å (Allen *et al.*, 1987) and also agrees with the average value of 1.216 (7) Å reported by SethuSankar *et al.* (2003). The benzene plane of the picrate ion lies parallel to the (20$\bar{1}$) plane.
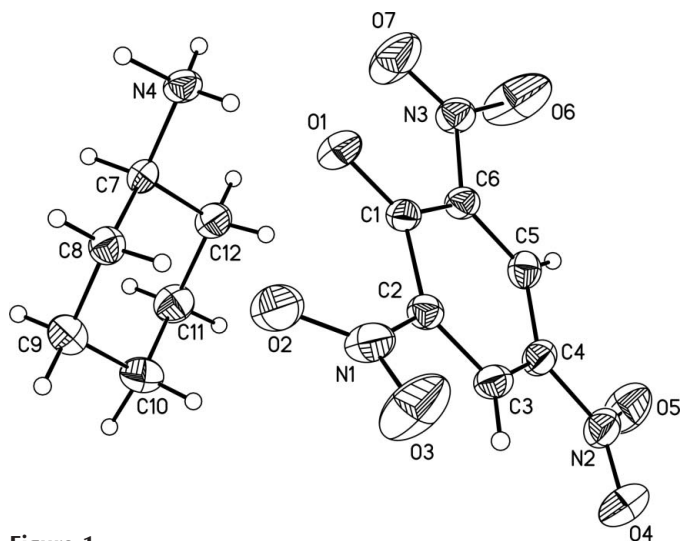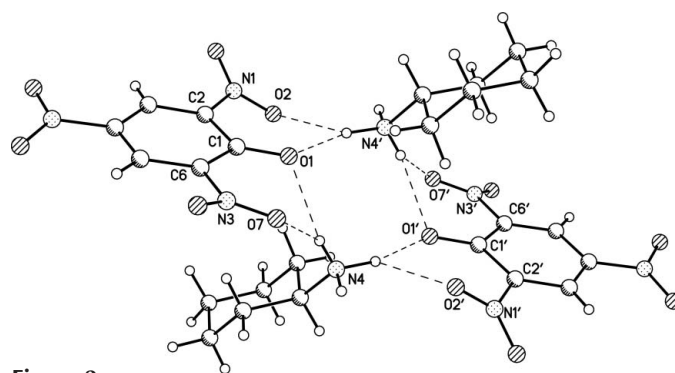
Figure 1
The title compound, showing 50% probability displacement ellipsoids for the non-H atoms, with the atom-numbering scheme.

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 29.6 (2) and 18.7 (4)°, respectively, and the *para* nitro group, O4/N2/O5, by 8.3 (4)°. These values exhibit a slight decrease in the tilt angle of O6/N3/O7 and show a slight increase in the tilt angle of the *para* nitro group compared with their characteristic tilting features. It is observed that in the crystal structure two picrate ions lie parallel to one another with a relative orientation of about 120° and separated by 3.555 Å. Their relative orientation makes the O4/N2/O5 group of one picrate ion lie over the O6/N3/O7 group of another picrate ion.

The C7—N4 bond length involving the protonated N atom of the cyclohexylammonium cation is 1.505 (5) Å, which is longer than those found in other structures and also the value (1.469 Å) given by Allen *et al.* (1987). The C—C distances in the cation range from 1.514 (6) Å to 1.523 (6) Å with an average value of 1.519 Å. The cyclohexane ring exists in its most stable chair conformation.

The protonated atom N4 makes five hydrogen bonds with three of its neighbouring picrate anions. We observe that, of the three H atoms of N4, two are involved in bifurcated hydrogen bonds and the other in a linear bond. The bifurcated hydrogen bonds are of varying strengths; in particular, those involving the phenolic O atoms (O1) are stronger than the others. Such cases have been observed in few structures and are in line with the discussions by Taylor *et al.* (1984).

The centrosymmetrically related cations and anions are linked through N—H···O hydrogen bonds. The hydrogen bonds in this structure were analysed by graph-set analysis (Bernstein *et al.*, 1995). A set of centrosymmetrically related anions and cations form a graph-set motif of $R_4^2(8)$ around the centre of symmetry involving N4—H4A···O1 (Table 2 and Fig. 2). Another set of inversion-related molecular ions have a graph-set motif of $R_4^4(12)$, involving N4—H4A···O7 and N4—H4C···O6[ii] (Table 2 and Fig. 3). These hydrogen-bond motifs alternate along the [010] direction as an infinite chain. Two

Figure 2
The hydrogen-bonded (dashed lines) graph-set motif $R_4^2(8)$ involving N4—H4A···O1. The prime corresponds to symmetry code (i) in Table 1

more hydrogen-bonded networks are also found in this structure: (i) with N4—H4A···O1 and N4—H4A···O7 combining together to form the graph-set motif $R_1^2(6)$, namely H4A···O1—C1—C6—N3—O7, and (ii) another motif $R_1^2(6)$, involving N4—H4B···O1[i] and N4—H4B···O2[i]. In addition, the structure contains three more hydrogen bonds of C—H···O type (Table 2). The packing of the salt, viewed down the crystallographic *b* axis, is shown in Fig. 4.

Experimental

The title salt was prepared by addition of cyclohexylamine (2.3 g) to a solution of picric acid (1.0 g) in ethanol (100 ml), followed by slow evaporation of the solvent to yield yellow needle-shaped single crystals suitable for X-ray diffraction studies.

Crystal data

$C_6H_{14}N^+ \cdot C_6H_2N_3O_7^-$	$D_x = 1.458$ Mg m^{-3}
$M_r = 328.29$	Mo $K\alpha$ radiation
Monoclinic, $C2/c$	Cell parameters from 25
$a = 23.543$ (1) Å	reflections
$b = 8.7177$ (10) Å	$\theta = 8–20°$
$c = 18.6177$ (14) Å	$\mu = 0.12$ mm^{-1}
$\beta = 128.484$ (10)°	$T = 293$ (2) K
$V = 2991.1$ (4) Å^3	Cut needle, yellow
$Z = 8$	$0.25 \times 0.20 \times 0.15$ mm

Data collection

Enraf–Nonius CAD-4 diffractometer	$R_{int} = 0.027$
ω–2θ scans	$\theta_{max} = 25.0°$
Absorption correction: ψ scan (North *et al.*, 1968)	$h = 0 \rightarrow 27$
	$k = -10 \rightarrow 0$
$T_{min} = 0.969$, $T_{max} = 0.998$	$l = -22 \rightarrow 17$
2686 measured reflections	2 standard reflections
2619 independent reflections	every 100 reflections
1489 reflections with $I > 2\sigma(I)$	intensity decay: 1%

Refinement

Refinement on F^2	$w = 1/[\sigma^2(F_o^2) + (0.0687P)^2$
$R[F^2 > 2\sigma(F^2)] = 0.062$	$+ 6.4872P]$
$wR(F^2) = 0.176$	where $P = (F_o^2 + 2F_c^2)/3$
$S = 1.01$	$(\Delta/\sigma)_{max} < 0.001$
2619 reflections	$\Delta\rho_{max} = 0.59$ e Å^{-3}
220 parameters	$\Delta\rho_{min} = -0.39$ e Å^{-3}
H atoms treated by a mixture of independent and constrained refinement	

Table 1
Selected geometric parameters (Å, °).

O1—C1	1.256 (4)	C1—C2	1.442 (5)
C1—C6	1.438 (5)		
O1—C1—C6	123.9 (3)	C6—C1—C2	111.7 (3)
O1—C1—C2	124.4 (3)		

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

D—H$\cdots A$	D—H	H$\cdots A$	$D\cdots A$	D—H$\cdots A$
N4—H4$A\cdots$O1	0.82 (5)	2.12 (5)	2.921 (5)	166 (4)
N4—H4$A\cdots$O7	0.82 (5)	2.48 (5)	3.011 (5)	124 (4)
N4—H4$B\cdots$O1^i	1.11 (6)	1.75 (6)	2.844 (4)	168 (4)
N4—H4$B\cdots$O2^i	1.11 (6)	2.40 (5)	2.955 (4)	109 (3)
N4—H4$C\cdots$O6^{ii}	0.91 (5)	2.07 (5)	2.942 (5)	162 (4)
C8—H8$A\cdots$O1^i	0.97	2.74	3.462 (5)	131
C7—H7$\cdots$O3^{iii}	0.98	2.53	3.410 (5)	150
C10—H10$B\cdots$O2^{iv}	0.97	2.71	3.417 (5)	130

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

Figure 3
The hydrogen-bonded graph-set motif $R_4^4(12)$ involving N4—H4$A\cdots$O7 and N4—H4$C\cdots$O6. The prime corresponds to symmetry code (ii) in Table 2.
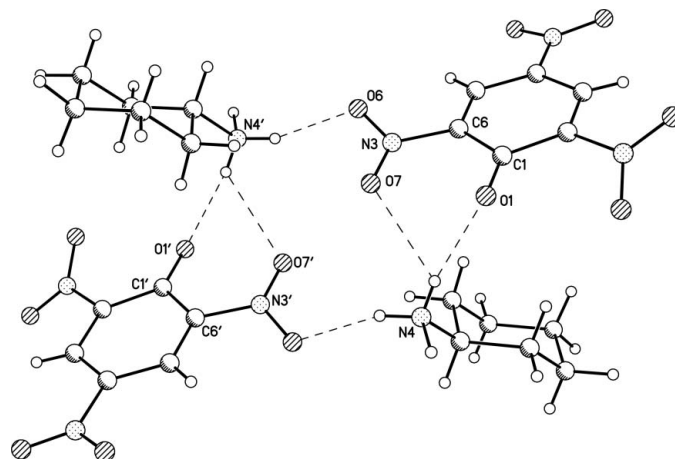
All H atoms were located in difference Fourier maps. The H atoms of the protonated N atom were refined isotropically. The C-bound H atoms were refined as riding on their parent atoms, with C—H = 0.93–0.98 Å and U_{iso}(H) = 1.2U_{eq}(C).

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: *ORTEP-3* (Farrugia, 1997) and *PLATON* (Spek, 2003); software used to prepare material for publication: *SHELXL97*.

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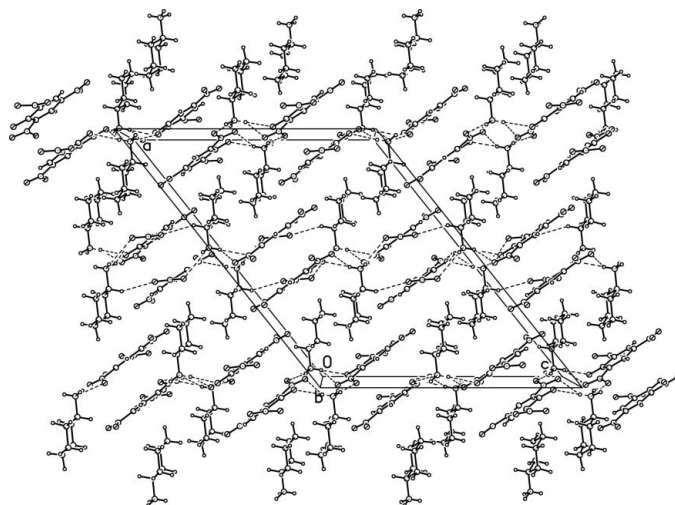
Figure 4
The packing of (I), viewed down the *b* axis. The hydrogen bonds are shown as dashed lines.

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