

3-Methylanilinium picrate

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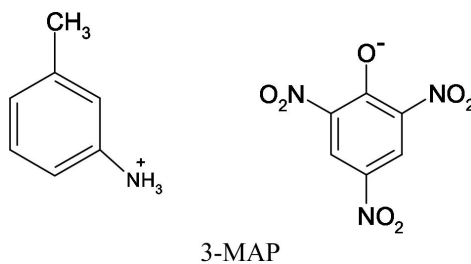
Key indicators

Single-crystal X-ray study
 $T = 293$ K
Mean $\sigma(\text{C}-\text{C}) = 0.004$ Å
Disorder in main residue
 R factor = 0.055
 wR factor = 0.170
Data-to-parameter ratio = 11.9For details of how these key indicators were automatically derived from the article, see <http://journals.iucr.org/e>.

In 3-methylanilinium picrate (3-MAP), $\text{C}_7\text{H}_{10}\text{N}^+\cdot\text{C}_6\text{H}_2\text{N}_3\text{O}_7^-$, one of the nitro groups in the picrate ion is rotationally disordered with site occupancy factors of 0.80 and 0.20. The expected proton transfer took place between picric acid and 3-methylaniline, and the amine group is hydrogen bonded to two of the phenolate O atoms. The *ortho*-nitro groups deviate greatly from the benzene plane of the picrate ion, facilitating hydrogen-bond formation. While the cations are stacked as columns along the [001] direction, the anions are stacked in an offset fashion.

Comment

Picric acid forms crystalline picrates with various organic molecules through well defined hydrogen bonds and π -bonding, and such picrates are useful for the identification and qualitative analysis of the corresponding organic compounds. The π - π interactions in picrate salts of aromatic compounds lead to the columnar stacking of the cations and anions either individually or in a mixed fashion (Botoshansky *et al.*, 1994; Goto *et al.*, 1992). Our studies aim to identify the nature of proton transfer, the direction of the specific N—H...O hydrogen bond between the amine and phenol groups, and also the type of stacking in the solid state. We have prepared and determined the crystal structure of 3-methylanilinium picrate (3-MAP). The present complex is found to be isomorphous with one of the two polymorphs of anilinium picrate, as the molecular structures of 3-methylaniline and aniline are very close to each other (Takayanagi *et al.*, 1996). However, we have not observed any other polymorphic forms of 3-MAP.



A displacement ellipsoid plot of the 3-MAP molecular complex along with the atom-numbering scheme is shown in Fig. 1. In 3-MAP, the proton of the hydroxyl group of picric acid has been transferred to the N atom of the 3-methylaniline molecule, leading to the formation of the molecular complex. The removal of the phenolic H atom leads to a shortening of the C1—O1 bond length, showing a partial double-bond character. This behaviour is similar to that observed in many picrate salts; it is attributed to the loss of the hydroxyl proton

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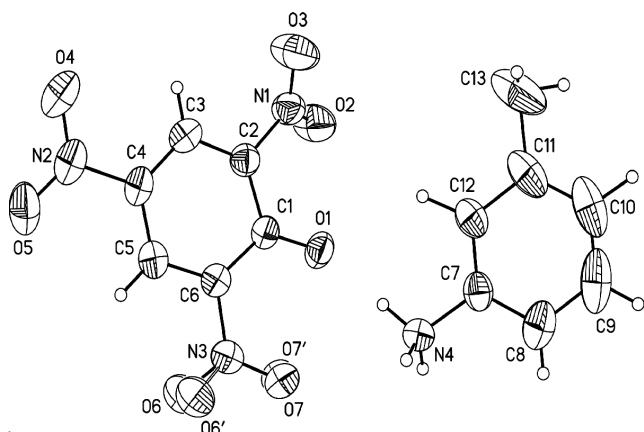


Figure 1
A displacement ellipsoid plot of 3-MAP, with the atom-numbering scheme.

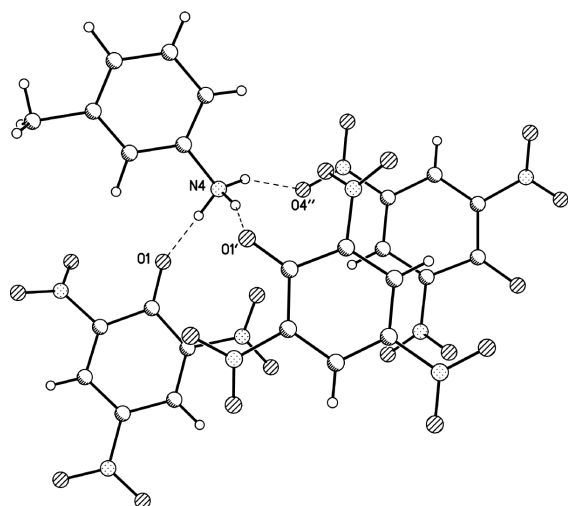


Figure 2
The N—H...O hydrogen bonding (dashed lines) between the cation and neighbouring anions. The prime and double prime in the atom labels correspond to symmetry codes (i) and (ii), respectively, in Table 2.

at O1, leading to the conversion of the neutral to an anionic state of the molecule. This leads to lengthening of the C1—C2 and C1—C6 bonds compared to the rest of the aromatic C—C distances in the picrate ion, *i.e.* a specific delocalization around atom C1, and this has been observed in almost all picrate salts. An analysis of related C—O and C—C (C1—C2 or C1—C6) distances among the picrates shows that as the C—O distance increases, the C—C distance decreases (Anitha *et al.*, 2004; Takayanagi *et al.*, 1996; Kaftory *et al.*, 1998; Tanaka *et al.*, 1994; Vembu *et al.*, 2003). Neither of the *ortho*-nitro groups lies in the benzene plane; while dihedral angle for O2...O3 is 43.9 (1)°, the other nitro group has two possible orientations having dihedral angles of 36.6 (2) and 27.0 (4)°. This is evident from the positional disorder observed in this group, with site occupancy factors of 0.80 and 0.20. The *para*-nitro group is less tilted from the benzene plane, with a dihedral angle of 12.6 (2)°. The 3-methylanilinium ion is planar and has normal geometrical parameters and lies in the (001) plane, whereas the picrate ion lies in the (10 $\bar{1}$) plane; the dihedral angle between the two planes is 33.5 (1)°.

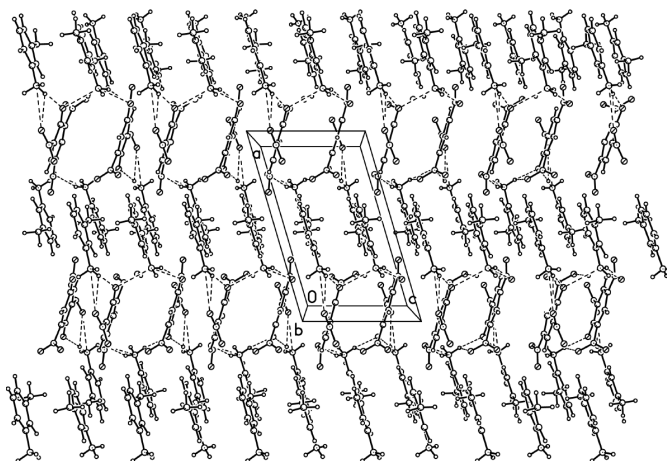


Figure 3
Packing of 3-MAP, viewed down the *b* axis, showing the ionic layer formation. Dashed lines indicate the hydrogen bonds.

The orientation of the anion and cation facilitates the formation of the expected strong N—H...O hydrogen bonds between amino atom N4 and the phenolate O atom; N4 hydrogen bonds to two phenolate O atoms of adjacent molecules. Hydrogen bonds are also observed between the amino group and an O atom of the *para*-nitro group (N4—H3N...O4ⁱⁱ; symmetry code as in Table 2).

The anilinium cations are stacked in columns along the [001] direction and have possible weak π — π interactions between them as they are separated by a perpendicular distance of 3.589 (1) Å. The anions (picrates), however, are stacked in an offset manner. This arrangement in the crystal structure produces separate layers of the anions and cations, linked by hydrogen bonds, as shown in Fig. 3.

Experimental

3-Methylammonium picrate (3-MAP) was prepared from ethanol solutions containing equimolar amounts of picric acid and 3-methylaniline at room temperature. Red block-shaped single crystals were obtained by slow evaporation of the ethanol solution.

Crystal data

C₇H₁₀N⁺·C₆H₂N₃O₇[−]
M_r = 336.27
 Monoclinic, *P*2₁/*c*
a = 12.439 (4) Å
b = 16.9472 (18) Å
c = 7.4504 (8) Å
 β = 106.437 (18)°
V = 1506.5 (5) Å³
Z = 4

D_x = 1.483 Mg m^{−3}
 Cu *K* α radiation
 Cell parameters from 25 reflections
 θ = 15–30°
 μ = 1.06 mm^{−1}
T = 293 (2) K
 Block, red
 0.50 × 0.30 × 0.30 mm

Data collection

Enraf–Nonius CAD-4 diffractometer
 ω –2 θ scans
 Absorption correction: ψ scan (North *et al.*, 1968)
T_{min} = 0.671, *T_{max}* = 0.727
 3596 measured reflections
 3096 independent reflections
 2574 reflections with *I* > 2 σ (*I*)

R_{int} = 0.029
 θ_{max} = 74.9°
h = −6 → 15
k = −21 → 8
l = −9 → 8
 2 standard reflections every 100 reflections
 intensity decay: 1%

Refinement

Refinement on F^2	$w = 1/[\sigma^2(F_o^2) + (0.0957P)^2 + 0.4692P]$
$R[F^2 > 2\sigma(F^2)] = 0.055$	where $P = (F_o^2 + 2F_c^2)/3$
$wR(F^2) = 0.170$	$(\Delta/\sigma)_{\max} < 0.001$
$S = 1.07$	$\Delta\rho_{\max} = 0.42 \text{ e } \text{Å}^{-3}$
3096 reflections	$\Delta\rho_{\min} = -0.34 \text{ e } \text{Å}^{-3}$
261 parameters	Extinction correction: <i>SHELXL97</i>
H atoms treated by a mixture of independent and constrained refinement	Extinction coefficient: 0.0050 (7)

Table 1

Selected geometric parameters (Å, °).

O1–C1	1.266 (2)	C1–C2	1.440 (3)
C1–C6	1.431 (3)		
O1–C1–C2	122.63 (17)	C3–C2–C1	125.03 (17)
C6–C1–C2	112.17 (15)		

Table 2

Hydrogen-bonding geometry (Å, °).

$D-H \cdots A$	$D-H$	$H \cdots A$	$D \cdots A$	$D-H \cdots A$
N4–H1N \cdots O1	0.95 (3)	1.82 (3)	2.767 (2)	175 (2)
N4–H2N \cdots O1 ⁱ	0.92 (3)	1.86 (3)	2.750 (2)	162 (3)
N4–H3N \cdots O4 ⁱⁱ	0.90 (3)	2.05 (3)	2.898 (2)	155 (2)

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

Disorder in one of the nitro groups (N3, O6 and O7) was manifest during refinement as very large ellipsoids. The positions were split and their occupancies were refined initially and later fixed at at 0.80 and 0.20. The disordered atoms were given the same displacement parameters. The H atoms were located from difference Fourier maps. All H atoms, except those belonging to the methyl group, were refined isotropically. The methyl H atoms were made to ride on atom C13 with C–H distances of 0.98 Å and $U_{\text{iso}}(\text{H}) = 1.5U_{\text{eq}}(\text{C13})$.

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: *ORTEPII* (Johnson, 1976) and *PLATON* (Spek, 2003); software used to prepare material for publication: *SHELXL97*.

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