organic compounds

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L-Prolinium picrate and 2-methyl-pyridinium picrate

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In the structure of L-prolinium picrate, $C_5H_{10}NO_2^+ \cdot C_6H_2N_3O_7^-$, the C^γ atom of the pyrrolidine ring has conformational disorder. Both the major and minor conformers of the pyrrolidine ring adopt conformations intermediate between a half-chair and an envelope. Both the cation and anion are packed through chelated three-centred N—H···O hydrogen bonds. The prolinium cation connects two different picrate anions, leading to an infinite chain running along the b axis. In 2-methylpyridinium picrate, $C_6H_8N^+ \cdot C_6H_2N_3O_7^-$, the cations and anions are packed separately along the a axis and are interconnected by N—H···O hydrogen bonds. Intramolecular contacts between phenolate O atoms and adjacent nitro groups are identified in both structures. A graph-set motif of $R_1^2(6)$ is observed in both structures.

Comment

Picric acid forms charge-transfer complexes with organic compounds. Crystalline picrates have commonly been used in the preparation of amine derivatives in qualitative organic chemistry (Shriner *et al.*, 1980). The crystal structure elucidation of L-prolinium picrate, (I), and 2-methylpyridinium picrate, (II), was undertaken to study the nature of hydrogen bonding between the molecular ions, involving phenolate O atoms and the protonated N atoms, and the crystal packing in the different environments.
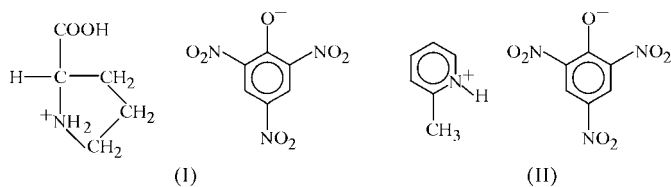
In the structure of (I), the asymmetric part of the unit cell contains a prolinium cation and a picrate anion (Fig. 1). An orthorhombic form of L-prolinium picrate has already been reported (Jin *et al.*, 2003). The backbone conformation angles ψ^1 (O1A—C1—C2—N1) and ψ^2 (O1B—C1—C2—N1) are *cis* and *trans*, respectively. The side-chain conformation angles χ^1 (N1—C2—C3—C4), χ^2 (C2—C3—C4—C5), χ^3 (C4—C5—

N1—C2), χ^4 (C3—C4—C5—N1) and θ (C4—C5—N1—C5) are 8.3, −27.2, −29.6, 34.7 and 13.2, respectively (Prasad & Vijayan, 1993) (Table 1). The C^γ atom (C4) of the pyrrolidine ring has conformational disorder, as observed in bis(L-proline) hydrogen perchlorate (Pandiarajan *et al.*, 2002). Atoms C4 and C41 deviate from the plane formed by atoms N1, C2, C3 and C5, whereas atoms N1, C2, C3 and C5 are nearly coplanar. Both the major and minor conformers of the pyrrolidine ring adopt conformations intermediate between a half-chair and an envelope (Cremer & Pople, 1975; Nardelli, 1983). The angle between the rings of the anion and cation is 44.4 (2)°.

Both the cation and anion of (I) are packed through chelated three-centred N—H···O hydrogen bonds, as observed in other picrate complexes (Jin *et al.*, 2003; Kai *et al.*, 1994). The prolinium cation connects two different picrate anions, leading to an infinite chain running along the b axis
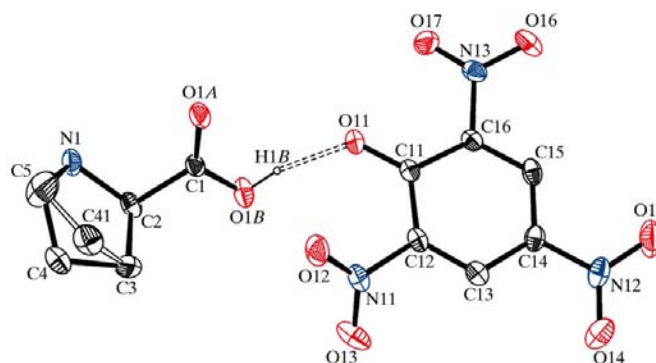

Figure 1
The molecular structure of compound (I), showing the atom-numbering scheme. Displacement ellipsoids are drawn at the 50% probability level. The hydrogen bond is indicated by dashed lines. H atoms not involved in this interaction have been omitted.
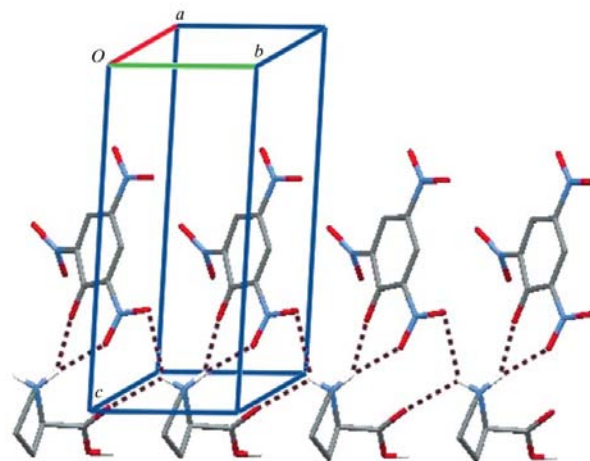

Figure 2
The infinite chain formed in the crystal structure of (I), connecting two picrate anions with cations, running along the a axis. Hydrogen bonds are shown as dashed lines and H atoms not involved in hydrogen bonding have been omitted for clarity.

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(Fig. 2). Weak three-centred C—H···O hydrogen bonds also stabilize the structure. The prolinium cation forms an infinite chain along the *b* axis through a C—H···O hydrogen bond (Table 2). The anion and cation form a hydrogen-bonded network with a graph-set motif of $R_1^2(6)$ (Etter *et al.*, 1990) (Fig. 2).

The crystal structures of pyridine and pyridine trihydrate (Mootz & Wussow, 1981), pyridine picrate (Talukdar & Chaudhuri, 1976) and pyridinium picrate (Takayanagi *et al.*, 1990) have already been reported. The asymmetric part of the unit cell of (II) contains two 2-methylpyridinium cations and two picrate anions (Fig. 4). The protonation of the N atom of
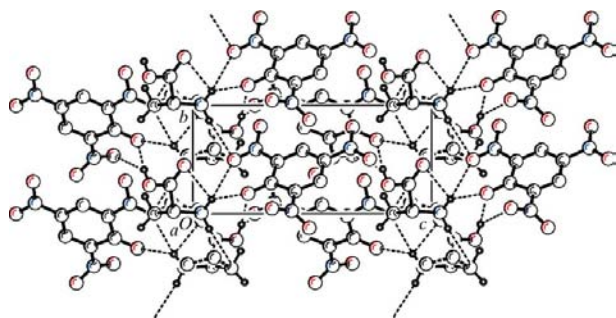

Figure 5
A packing diagram of the molecules in the structure of (II), viewed down the *a* axis. Hydrogen bonds are shown as dashed lines. H atoms not involved in hydrogen bonding have been omitted for clarity.

Figure 3
A packing diagram of the molecules in the structure of (I), viewed down the *b* axis. Hydrogen bonds are shown as dashed lines and H atoms not involved in hydrogen bonding have been omitted for clarity.
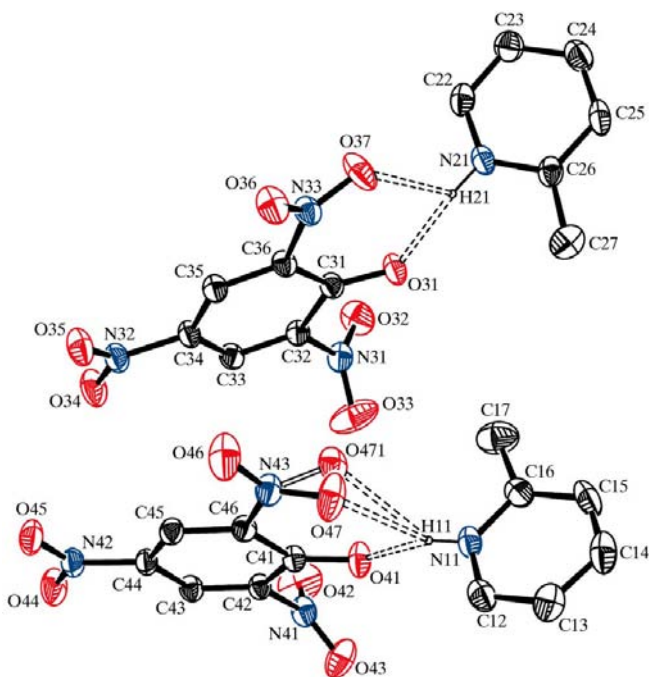

Figure 4
The molecular structure of compound (II), showing the atom-numbering scheme. Displacement ellipsoids are drawn at the 50% probability level. Hydrogen bonds are indicated by dashed lines and H atoms not involved in these interactions have been omitted.
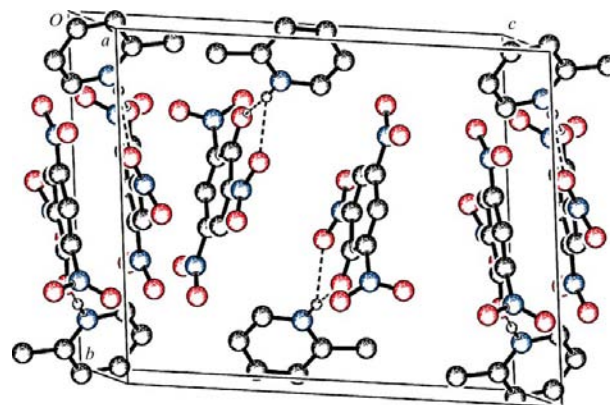
the pyridine ring is confirmed from the values of the C—N bond distances (Table 3), which agree well with those in pyridinum picrate. The angles between the rings of both anions and those of the cations are 74.4 (1) (between rings N11/C12–C16 and C31–C36) and 79.4 (1)° (between rings N11/C12–C16 and C41–C46), and 76.5 (1) (between rings N21/C22–C26 and C31–C36) and 80.7 (1)° (between rings N21/C22–C26 and C41–C46). The pyridine ring is almost normal to the benzene ring. This fact supports the absence of π bonding in this complex, as observed in *p*-phenylenediamine picrate and *o*-phenylenediamine picrate (Takayanagi *et al.*, 1996). Both cations form bifurcated N—H···O hydrogen bonds with inversely related anions, thus forming a graph-set motif of $R_1^2(6)$ (Fig. 5). This type of bifurcated hydrogen bonding (Table 4) is also observed in the crystal structure of (I).

In the picrate anions of (I) and (II), the bond distances and angles indicate the deprotonation of the phenol group, and the geometry is similar to that in other picrate complexes (Takayanagi *et al.*, 1996). The picrate anions are sandwiched between layers of prolinium cations along the *c* axis in (I) (Fig. 3), whereas in (II) the picrate anions are packed between layers of pyridinium cations (Fig. 5). In the structure of (II), the anions are arranged nearly parallel to each other, making angles of 9.02 (1) and 11.4 (1)° with the [001] plane. Intramolecular contacts between the phenolate O atoms and adjacent nitro groups are observed in both structures. In (I) and (II), one of the *ortho*-nitro groups is twisted more from the plane of the ring, while the *para*-nitro group is nearly coplanar. In the structure of (II), the angle between the rings of the picrate anions is 20.6 (1)°, and the angle between the rings of the pyridinium cations is 25.1 (1)°.

Experimental

Compound (I) was crystallized from an aqueous solution containing L-proline and picric acid in a 1:1 stoichiometric ratio at room

temperature by slow evaporation. Similarly, compound (II) was crystallized from an aqueous solution containing pyridoxine and picric acid in a 1:1 stoichiometric ratio at room temperature by slow evaporation. Instead of the expected picric acid complex with pyridoxine, crystals of 2-methylpyridinum picrate were obtained.

Compound (I)

Crystal data

$C_5H_{10}NO_2^+ \cdot C_6H_2N_3O_7^-$	D_m measured by flotation using a
$M_r = 344.25$	mixture of carbon tetrachloride
Monoclinic, $P2_1$	and bromoform
$a = 10.909 (4)$ Å	Mo $K\alpha$ radiation
$b = 5.352 (3)$ Å	$\mu = 0.15$ mm^{-1}
$c = 12.474 (5)$ Å	$T = 293 (2)$ K
$\beta = 109.142 (5)°$	Needle, yellow
$V = 688.0 (5)$ Å^3	$0.3 \times 0.2 \times 0.12$ mm
$Z = 2$	
$D_x = 1.662$ Mg m^{-3}	
$D_m = 1.66$ Mg m^{-3}	

Data collection

Nonius MACH3 sealed-tube diffractometer	1590 reflections with $I > 2\sigma(I)$
$\omega/2\theta$ scans	$R_{int} = 0.100$
Absorption correction: ψ scan	$\theta_{max} = 30.0°$
(North et al., 1968)	3 standard reflections
$T_{min} = 0.967$, $T_{max} = 0.981$	frequency: 60 min
3719 measured reflections	intensity decay: none
2205 independent reflections	

Refinement

Refinement on F^2	$w = 1/[\sigma^2(F_o^2) + (0.1016P)^2]$
$R[F^2 > 2\sigma(F^2)] = 0.058$	where $P = (F_o^2 + 2F_c^2)/3$
$wR(F^2) = 0.169$	$(\Delta/\sigma)_{max} = 0.001$
$S = 1.07$	$\Delta\rho_{max} = 0.49$ e Å^{-3}
2205 reflections	$\Delta\rho_{min} = -0.27$ e Å^{-3}
226 parameters	
H-atom parameters constrained	

Table 1
Selected geometric parameters (Å, °) for (I).

O1A—C1	1.202 (4)	C5—N1	1.497 (5)
O1B—C1	1.308 (4)	O11—C11	1.255 (4)
C2—N1	1.493 (4)		
C2—N1—C5	107.1 (3)		
O1A—C1—C2—N1	19.1 (5)	O13—N11—C12—C13	−42.6 (4)
O1B—C1—C2—N1	−163.0 (3)	O12—N11—C12—C11	−41.3 (4)
N1—C2—C3—C4	8.2 (6)	O15—N12—C14—C15	8.1 (5)
C2—C3—C4—C5	−27.1 (8)	O14—N12—C14—C13	11.5 (5)
C3—C4—C5—N1	34.7 (9)	O16—N13—C16—C15	−16.1 (4)
C3—C2—N1—C5	11.8 (5)	O17—N13—C16—C11	−16.6 (5)
C4—C5—N1—C2	−29.5 (8)		

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

D—H···A	D—H	H···A	D···A	D—H···A
O1B—H1B···O11	0.82	1.71	2.515 (4)	165
N1—H1C···O11^i	0.90	2.20	2.952 (4)	141
N1—H1A···O17^{ii}	0.90	2.38	3.202 (5)	153
N1—H1C···O17^i	0.90	2.37	3.106 (5)	139

Symmetry codes: (i) $-x + 1, y - \frac{1}{2}, -z + 2$; (ii) $-x + 1, y - \frac{3}{2}, -z + 2$.

Compound (II)

Crystal data

$C_6H_8N^+ \cdot C_6H_2N_3O_7^-$	$D_x = 1.575$ Mg m^{-3}
$M_r = 322.24$	$D_m = 1.57$ Mg m^{-3}
Triclinic, $P\bar{1}$	D_m measured by flotation using a
$a = 8.211 (3)$ Å	mixture of xylene and carbon
$b = 11.806 (4)$ Å	tetrachloride
$c = 14.388 (4)$ Å	Mo $K\alpha$ radiation
$\alpha = 85.428 (5)°$	$\mu = 0.13$ mm^{-1}
$\beta = 82.863 (5)°$	$T = 293 (2)$ K
$\gamma = 79.726 (4)°$	Block, yellow
$V = 1359.4 (8)$ Å^3	$0.25 \times 0.2 \times 0.15$ mm
$Z = 4$	

Data collection

Nonius MACH3 sealed-tube diffractometer	4762 independent reflections
$\omega/2\theta$ scans	3255 reflections with $I > 2\sigma(I)$
Absorption correction: ψ scan	$R_{int} = 0.015$
(North et al., 1968)	$\theta_{max} = 25.0°$
$T_{min} = 0.970$, $T_{max} = 0.980$	3 standard reflections
5848 measured reflections	frequency: 60 min
	intensity decay: none

Refinement

Refinement on F^2	$w = 1/[\sigma^2(F_o^2) + (0.0564P)^2$
$R[F^2 > 2\sigma(F^2)] = 0.042$	$+ 0.5564P]$
$wR(F^2) = 0.124$	where $P = (F_o^2 + 2F_c^2)/3$
$S = 1.04$	$(\Delta/\sigma)_{max} < 0.001$
4762 reflections	$\Delta\rho_{max} = 0.32$ e Å^{-3}
426 parameters	$\Delta\rho_{min} = -0.27$ e Å^{-3}
H-atom parameters constrained	

Table 3
Selected geometric parameters (Å, °) for (II).

N11—C12	1.324 (3)	O31—C31	1.252 (3)
N11—C16	1.335 (3)	O41—C41	1.253 (3)
C12—N11—C16	123.3 (2)	C22—N21—C26	123.1 (2)

Table 4
Hydrogen-bond geometry (Å, °) for (II).

D—H···A	D—H	H···A	D···A	D—H···A
N11—H11···O41	0.86	1.83	2.656 (3)	160
N11—H11···O47	0.86	2.28	2.771 (5)	117
N11—H11···O471	0.86	2.35	2.906 (11)	123
N21—H21···O31	0.86	1.85	2.680 (3)	160
N21—H21···O37	0.86	2.30	2.783 (3)	116

All H atoms were placed in geometrically calculated positions and included in the refinement in the riding-model approximation, with N—H = 0.90 Å and C—H = 0.93–0.98 Å in compound (I), and with N—H = 0.86 Å and C—H = 0.93–0.96 Å in compound (II). For both compounds, $U_{iso}(H) = 1.2$–$1.5U_{eq}(C,N)$. In compound (I), the C^γ atom (C4) of the pyrrolidine ring has conformational disorder, with site-occupancy factors of 0.52 and 0.48. In compound (II), one of the O atoms of the picrate anion is disordered, with occupancy factors of 0.71 and 0.29 for atoms O47 and O471. In compound (I), owing to the absence of atoms heavier than Si, the absolute configuration could not be reliably determined and Friedel pairs were merged.

For both compounds, 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: *SHELXTL/PC* (Bruker, 2000); program(s) used to refine

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Supplementary data for this paper are available from the IUCr electronic archives (Reference: DN3021). Services for accessing these data are described at the back of the journal.

References

Bruker (2000). *SHELXTL*. Version 6.10. Bruker AXS Inc., Madison, Wisconsin, USA.
Cremer, D. & Pople, J. A. (1975). *J. Am. Chem. Soc.* **97**, 1354–1358.
Enraf–Nonius (1994). *CAD-4 EXPRESS*. Version 5.0. Enraf–Nonius, Delft, The Netherlands.
Etter, M. C., MacDonald, J. C. & Bernstein, J. (1990). *Acta Cryst.* B**46**, 256–262.
Farrugia, L. J. (1997). *J. Appl. Cryst.* **30**, 565.
Harms, K. & Wocadlo, S. (1995). *XCAD4*. University of Marburg, Germany.
Jin, Z. M., Pan, Y. J., Hu, M. L., Shen, L. & Li, M. C. (2003). *Cryst. Res. Technol.* **38**, 1009–1012.
Kai, T., Goto, M., Furuhata, K. & Takayanagi, H. (1994). *Anal. Sci.* **10**, 359–360.
Macrae, C. F., Edgington, P. R., McCabe, P., Pidcock, E., Shields, G. P., Taylor, R., Towler, M. & van de Streek, J. (2006). *J. Appl. Cryst.* **39**, 453–457.
Mootz, D. & Wussow, H. G. (1981). *J. Chem. Phys.* **75**, 1517–1522.
Nardelli, M. (1983). *Acta Cryst.* C**39**, 1141–1142.
North, A. C. T., Phillips, D. C. & Mathews, F. S. (1968). *Acta Cryst.* A**24**, 351–359.
Pandiarajan, S., Sridhar, B. & Rajaram, R. K. (2002). *Acta Cryst.* E**58**, o862–o864.
Prasad, G. S. & Vijayan, M. (1993). *Acta Cryst.* B**49**, 348–356.
Shriner, R. L., Fuson, R. C., Curtin, D. Y. & Morrill, T. C. (1980). *Qualitative Identification of Organic Compounds*, 6th ed., pp. 236–237. New York: Wiley.
Spek, A. L. (2003). *J. Appl. Cryst.* **36**, 7–13.
Takayanagi, H., Kai, T., Yamaguchi, S., Takeda, K. & Goto, M. (1996). *Chem. Pharm. Bull.* **44**, 2199–2204.
Takayanagi, H., Kawaoka, R., Chin, K., Goto, M., Yamaguchi, S. & Ogura, H. (1990). *Anal. Sci.* **6**, 321–322.
Talukdar, A. N. & Chaudhuri, B. (1976). *Acta Cryst.* B**32**, 803–808.