Acta Crystallographica Section E
Structure Reports
Online

ISSN 1600-5368

Nicotinium picrate

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Received 4 July 2005
Accepted 11 July 2005
Online 16 July 2005

Key indicators

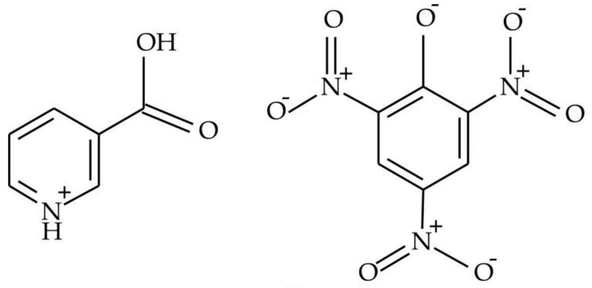
Single-crystal X-ray study
T = 293 K
Mean σ(C–C) = 0.004 Å
R factor = 0.045
wR factor = 0.136
Data-to-parameter ratio = 11.0

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

The title compound, $C_6H_6NO_2^+\cdot C_6H_2N_3O_7^-$, is the picrate salt of the nicotinium cation. In the picrate anion, the *ortho* nitro groups are twisted out of the plane of the ring, whereas the *para* nitro group lies approximately in the ring plane. Hydrogen bonds from the nicotinate cation link two different picrate anions, forming a straight chain along the *b* axis. The picrate anions are stacked in columns along [010].

Comment

Nicotinic acid (3-pyridine carboxylic acid) is a B vitamin known as niacin. The crystal structures of nicotinic acid (Wright & King, 1953; Kutoglu & Scheringer, 1983), nicotinamide (Wright & King, 1954), isonicotinic acid hydrazide (Bhat *et al.*, 1974), 1-methyl nicotinamide iodide, chloride and picrate (Freeman & Bugg, 1974), isonicotinic acid (Takusagawa & Shimada, 1976), nicotinoylglycine (Krishnaswamy *et al.*, 1987), 6-aminonicotinic acid hydrochloride (Giantsidis & Turnbull, 2000), and dinicotinamidium squarate (Bulut *et al.*, 2003) have been reported. The structure of the title compound, (I), is reported here.



(I)

In (I) (Fig. 1), the H atom of the hydroxy group of picric acid has been transferred to the N atom of nicotinic acid, leading to the formation of a molecular complex. The bond lengths and bond angles in the pyridine ring of the nicotinium cation are comparable to the average values of 1.38 Å for the C—C bonds and 1.33 Å for the C—N bonds found in dinicotinamidium squarate (Bulut *et al.*, 2003) and nicotinoylglycine (Krishnaswamy *et al.*, 1987). The C11—C12 bond length is similar to that observed in dinicotinamidium squarate (Bulut *et al.*, 2003), while atom O1*B* is identified as the hydroxy O atom by comparison of the C11—O1*A* and C11—O1*B* distances. A comparison of equivalent bond distances involving the pyridine ring atoms of (I) with the values found in nicotinic acid (Wright & King, 1953) shows that the positive charge is localized on the pyridine N atom and does not have much effect on the ring structure. These distances also

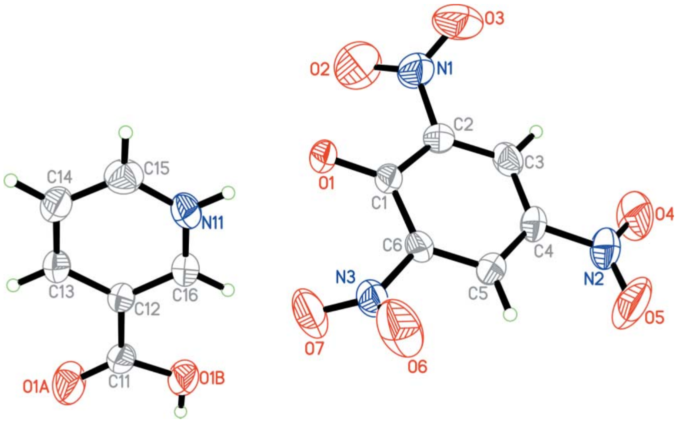


Figure 1
The molecular structure of (I), with the atom-numbering scheme and 50% probability displacement ellipsoids.

compare well with those for 6-aminonicotinic acid hydrochloride (Giantsidis & Turnbull, 2000) and dinicotinamidium squarate (Bulut *et al.*, 2003). The nicotinium cation is planar, and the planes of the nicotinium cation and the ring of the picrate anion are inclined to one another at 62.9 (1)°. In the picrate anion, removal of the phenol H atom leads to a shortening of the C1—O1 bond, while the C1—C2 and C1—C6 distances increase as observed previously (Anitha *et al.*, 2004; Muthamizhchelvan *et al.*, 2005). The torsion angles involving the *ortho*-related nitro groups in the picrate anion (C1—C6—N3—O6,O7 and C1—C2—N1—O2,O3) are 144.0 (3), 139.6 (3), −131.5 (3) and −132.1 (3)°, respectively (Table 1). It has been found that in most picrates the *ortho*-related nitro groups, which are commonly involved in hydrogen-bonding interactions, are more likely to be rotated out of the molecular plane than the *para* nitro substituent (Anitha *et al.*, 2004; Kai *et al.*, 1994; Smith *et al.*, 2004; Gartland *et al.*, 1974). Here, even though one of the *ortho* nitro groups is not involved in hydrogen bonding, it is still twisted from the plane of the ring, while the *para* nitro group lies approximately in the ring plane. It is also found that the twisting of these nitro groups is independent of C—N bond distances (Soriano-Garcia *et al.*, 1978; Srikrishnan *et al.*, 1980). The nitro O atoms not involved in hydrogen bonding have large U_{eq} values. In the crystal structure, the cations and anions are linked by strong N11—H111···O1 and O1*B*—H11*B*···O1 hydrogen bonds (Table 2). The structure is also stabilized by C—H···O hydrogen bonding. These hydrogen bonds link the layers of cations with the layers of anions, with each nicotinium cation linking two different picrate anions to form a straight chain along the *b* axis (Fig. 2). The picrate anions are stacked in columns along [010].

Experimental

The title compound was crystallized from a nicotonic acid and picric acid mixture in the stoichiometric ratio of 1:1 at room temperature by slow evaporation.

Crystal data

$C_6H_6NO_2^+\cdot C_6H_2N_3O_7^-$
$M_r = 352.22$
Triclinic, $P\overline{1}$
$a = 8.063$ (3) Å
$b = 8.080$ (3) Å
$c = 12.030$ (5) Å
$\alpha = 93.27$ (3)°
$\beta = 95.87$ (4)°
$\gamma = 113.46$ (3)°
$V = 711.1$ (5) Å^3
$Z = 2$
$D_x = 1.645$ Mg m^{-3}
$D_m = 1.639$ Mg m^{-3}
D_m measured by flotation in $CHBr_3$ and CCl_4
Mo *Kα* radiation
Cell parameters from 25 reflections
$\theta = 10.2$–14.3°
$\mu = 0.14$ mm^{-1}
$T = 293$ (2) K
Block, yellow
0.19 × 0.17 × 0.15 mm

Data collection

Nonius MACH3 four-circle diffractometer
ω–2θ scans
Absorption correction: ψ scan (North *et al.*, 1968)
$T_{min} = 0.973$, $T_{max} = 0.978$
3091 measured reflections
2509 independent reflections
1765 reflections with $I > 2\sigma(I)$
$R_{int} = 0.012$
$\theta_{max} = 25°$
$h = -1 \rightarrow 9$
$k = -9 \rightarrow 9$
$l = -14 \rightarrow 14$
3 standard reflections
frequency: 60 min
intensity decay: none

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)] = 0.045$
$wR(F^2) = 0.136$
$S = 1.02$
2509 reflections
228 parameters
H-atom parameters constrained
$w = 1/[\sigma^2(F_o^2) + (0.0601P)^2 + 0.5668P]$
where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max} < 0.001$
$\Delta\rho_{max} = 0.50$ e Å^{-3}
$\Delta\rho_{min} = -0.26$ e Å^{-3}
Extinction correction: *SHELXTL/PC*
Extinction coefficient: 0.029 (5)

Table 1
Selected geometric parameters (Å, °).

O1*A*—C11	1.196 (3)	O1—C1	1.279 (3)
O1*B*—C11	1.308 (3)	C1—C6	1.423 (3)
N11—C15	1.332 (4)	C1—C2	1.431 (3)
N11—C16	1.332 (3)		
C15—N11—C16	122.7 (2)	N11—C16—C12	119.7 (2)
O1*A*—C11—O1*B*	125.6 (3)	O1—C1—C6	123.0 (2)
O1*A*—C11—C12	122.2 (2)	O1—C1—C2	124.4 (2)
O1*B*—C11—C12	112.3 (2)	C6—C1—C2	112.5 (2)
N11—C15—C14	119.8 (3)		
O2—N1—C2—C3	144.0 (3)	O5—N2—C4—C3	171.0 (3)
O3—N1—C2—C1	139.6 (3)	O7—N3—C6—C5	−131.5 (3)
O4—N2—C4—C5	170.2 (3)	O6—N3—C6—C1	−132.1 (3)

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

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
N11—H11···O1	0.86	1.85	2.711 (3)	174
O1*B*—H11*B*···O1^i	0.82	1.75	2.563 (3)	170
C16—H16···O7	0.93	2.55	2.962 (4)	107

Symmetry code: (i) $x, y - 1, z$.

All H atoms were placed in geometrically calculated positions, with C—H distances of 0.93 Å, an N—H distance of 0.86 Å and an O—H distance of 0.82 Å, and allowed to ride on the carrier atom with U_{iso}(H) equal to 1.2U_{eq}(C,N) and 1.5U_{eq}(O).

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*

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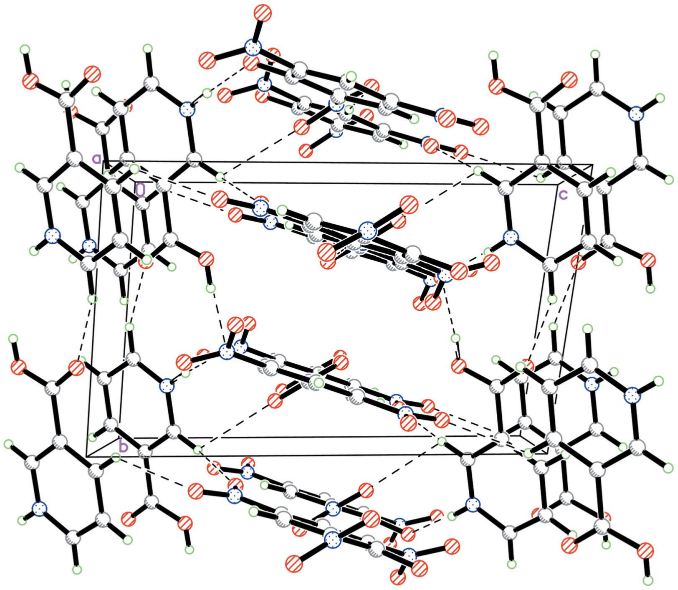

Figure 2
Packing diagram for (I), viewed down the *a* axis. Hydrogen bonds are drawn as dashed lines.

(Bruker, 2000); program(s) used to refine structure: *SHELXTL*/*PC*; molecular graphics: *SHELXTL*/*PC*; software used to prepare material for publication: *SHELXTL*/*PC*.

The authors thank the Department of Science and Technology, Government of India, for establishing a single-crystal diffractometer facility at the School of Physics, Madurai Kamaraj University, Madurai, through the FIST programme.

References

Anitha, K., Sridhar, B. & Rajaram, R. K. (2004). *Acta Cryst.* E**60**, o1530–o1532.

Bhat, T. N., Singh, T. P. & Vijayan, M. (1974). *Acta Cryst.* B**30**, 2921–2922.

Bruker (2000). *SHELXTL*/*PC*. Version 6.10. Bruker AXS Inc., Madison, Wisconsin, USA.

Bulut, A., Yesilel, O. Z., Dege, N., Icbudak, H., Olmaz, H. & Bujukgungor, O. (2003). *Acta Cryst.* C**59**, o727–o729.

Enraf–Nonius (1994). *CAD-4 EXPRESS*. Version 5.1/1.2. Enraf–Nonius, Delft, The Netherlands.

Freeman, G. R. & Bugg, C. E. (1974). *Acta Cryst.* B**30**, 431–443.

Gartland, G. L., Freeman, G. R. & Bugg, C. E. (1974). *Acta Cryst.* B**30**, 1841–1849.

Giantsidis, J. & Turnbull, M. M. (2000). *Acta Cryst.* C**56**, 334–335.

Harms, K. & Wocadlo, S. (1995). *XCAD4*. University of Marburg, Germany.

Kai, T., Goto, M., Furuhata, K. & Takayanagi, H. (1994). *Anal. Sci.* **10**, 359–360.

Krishnaswamy, S., Pattabhi, V. & Guru Row, T. N. (1987). *Acta Cryst.* C**43**, 728–729.

Kutoglu, A. & Scheringer, C. (1983). *Acta Cryst.* C**39**, 232–234.

Muthamizhchelvan, C., Saminathan, K., Fraanje, J., Pescher, R. & Sivakumar, K. (2005). *Acta Cryst.* E**61**, o1153–o1155.

North, A. C. T., Phillips, D. C. & Mathews, F. S. (1968). *Acta Cryst.* A**24**, 351–359.

Smith, G., Wermuth, U. D. & Healy, P. C. (2004). *Acta Cryst.* E**60**, o1800–o1803.

Soriano-Garcia, M., Srikrishnan, T. & Parthasarathy, R. (1978). *Acta Cryst.* A**34**, s114.

Srikrishnan, T., Soriano-Garcia, M. & Parthasarathy, R. (1980). *Z. Kristallogr.* **151**, 317–323.

Takusagawa, F. & Shimada, A. (1976). *Acta Cryst.* B**32**, 1925–1927.

Wright, W. B. & King, G. S. D. (1953). *Acta Cryst.* **6**, 305–310.

Wright, W. B. & King, G. S. D. (1954). *Acta Cryst.* **7**, 283–288.

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