Acta Crystallographica Section E
Structure Reports
Online

ISSN 1600-5368

L-Asparaginium picrate

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Key indicators

Single-crystal X-ray study
T = 293 K
Mean σ(C–C) = 0.003 Å
R factor = 0.025
wR factor = 0.069
Data-to-parameter ratio = 6.1

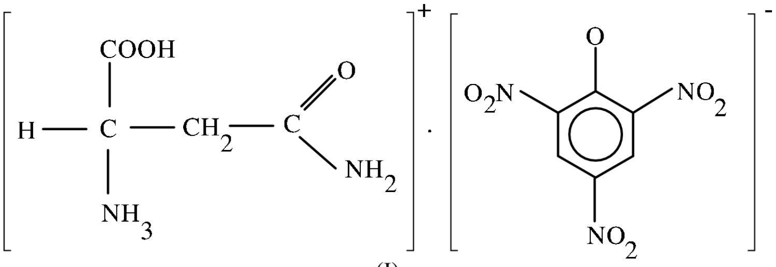
For details of how these key indicators were automatically derived from the article, see http://journals.iucr.org/e.

Received 7 February 2005
Accepted 18 April 2005
Online 27 April 2005

In the title compound, $C_4H_9N_2O_3^+\cdot C_6H_2N_3O_7^-$, the two ions are connected by strong asymmetric O—H···O hydrogen bonds. The cation is involved in a *Z*1 (zigzag) head-to-tail sequence along the *b* axis. The torsion angle χ^{21} corresponds to a *cis* conformation. Hydrophobic layers across $z = \frac{1}{2}$ are sandwiched between hydrophilic layers across the $z = 0$ plane.

Comment

Asparagine is a neutral amino acid with carboxamide as the side-chain functional group. The crystal structures of L-asparagine monohydrate (Ramanadham *et al.*, 1972; Verbist *et al.*, 1972), glycyl-L-asparagine (Pasternak *et al.*, 1954), *N*-(2,4-dinitrophenyl)-L-asparagine (Mauguen *et al.*, 1976) and L-asparagine-L-aspartic acid monohydrate (Wang *et al.*, 1985) have been reported previously. We present here the crystal structure of the title asparagine compound, (I).



(I)

The asymmetric unit of (I) contains an asparaginium cation and a picrate anion, as shown in Fig. 1. The asymmetric carboxyl bond distances and angles clearly indicate protonation of the carboxyl group. The deviation of amino atom N11 from the plane of the carboxyl group at C11 is 0.0451 (1) Å (Lakshminarayanan *et al.*, 1967). The backbone conformation angle ψ^1 is the *cis* form and ψ^2 is the *trans* form. The present molecule has a positive ψ^1 angle. As noted by Sundaralingam & Putkey (1970), a positive value for ψ^1 leads to a decrease in the intramolecular C13···O1*B* distance 2.827 (3) Å [2.9 Å in Ramanadham *et al.* (1972)]. The side-chain conformation angle χ^1 is *gauche* I, χ^{21} is *cis* and χ^{22} is *trans*. The conformations and configurations are similar to those in L-asparagine monohydrate.

The picrate anion plays a vital role in hydrogen bonding with the L-asparaginium residue, as shown in Fig. 2 and Table 2. Of the three nitro groups, two are more twisted from the plane of the ring than the third. This property does not depend upon the C—N bond distances (Soriano-Garcia *et al.*, 1978). The picrate anion forms strong asymmetric O—H···O and N—H···O hydrogen bonds with the asparaginium residue. One of

doi:10.1107/S1600536805012080

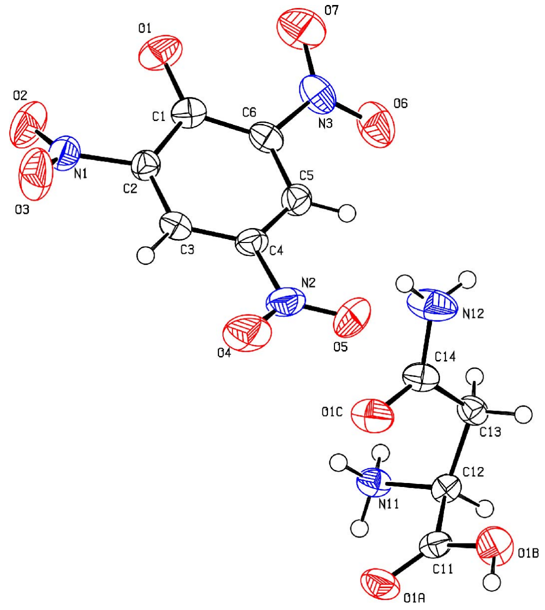


Figure 1
The molecular structure of (I), with the atom-numbering scheme and 50% probability displacement ellipsoids. H atoms are shown as open circles of arbitrary radii.

the O atoms of each nitro group (O2, O5 and O7) and atom O1 are involved in hydrogen bonds.

The backbone amino group forms one two-centred and two three-centred hydrogen bonds, leading to a class III hydrogen-bonding pattern (Jeffrey & Saenger, 1991). A zigzag (*Z*1) head-to-tail sequence along the *b* axis is observed in this residue, connecting two amino acids related by a 2_1 operation. An intramolecular hydrogen bond between the α-amino group and the γ-carbonyl group is also observed. The amino atom N11 forms, together with atom O1*C*, an infinite hydrogen-bonded chain along the *b* axis. The side-chain amino atom N12 forms one two-centred and one chelated three-centred hydrogen bond. This amino N atom forms an infinite chain along the *b* axis with atom O7 of the picrate anion. The same amino N atom connects two different picrate anions.

Hydrophobic layers across $z = \frac{1}{2}$ are sandwiched between hydrophilic layers across the $z = 0$ plane.

Experimental

The title compound was crystallized by slow evaporation at room temperature of a solution of L-asparagine and picric acid (1:1).

Crystal data

$C_4H_9N_2O_3^+ \cdot C_6H_2N_3O_7^-$
$M_r = 361.24$
Monoclinic, $P2_1$
$a = 10.367$ (4) Å
$b = 5.1611$ (7) Å
$c = 13.120$ (3) Å
$\beta = 93.20$ (2)°
$V = 700.9$ (3) Å^3
$Z = 2$
$D_x = 1.712$ Mg m^{-3}
$D_m = 1.710$ Mg m^{-3}
D_m measured by flotation, using a mixture of carbon tetrachloride and bromoform
Mo $K\alpha$ radiation
Cell parameters from 25 reflections
$\theta = 10.1$–14.3°
$\mu = 0.16$ mm^{-1}
$T = 293$ (2) K
Block, yellow
0.3 × 0.25 × 0.2 mm

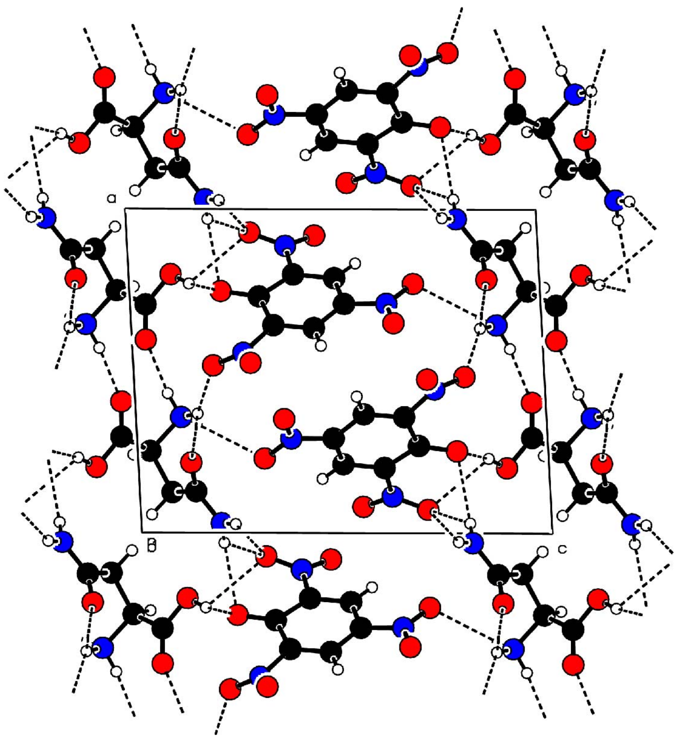


Figure 2
A packing diagram for (I), viewed along the *b* axis. Dashed lines indicate hydrogen bonds.

Data collection

Nonius MACH-3 diffractometer
$\omega/2\theta$ scans
Absorption correction: ψ scan (North *et al.*, 1968)
$T_{min} = 0.956$, $T_{max} = 0.967$
1769 measured reflections
1380 independent reflections
1300 reflections with $I > 2\sigma(I)$
$R_{int} = 0.010$
$\theta_{max} = 25.0$°
$h = 0 \rightarrow 12$
$k = -1 \rightarrow 6$
$l = -15 \rightarrow 15$
3 standard reflections frequency: 60 min intensity decay: 2%

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)] = 0.025$
$wR(F^2) = 0.070$
$S = 1.09$
1380 reflections
227 parameters
H-atom parameters constrained
$w = 1/[\sigma^2(F_o^2) + (0.0395P)^2 + 0.1431P]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max} < 0.001$
$\Delta\rho_{max} = 0.13$ e Å^{-3}
$\Delta\rho_{min} = -0.16$ e Å^{-3}

Table 1
Selected geometric parameters (Å, °).

O1*A*—C11	1.203 (2)	O1*B*—C11	1.309 (2)
O1*A*—C11—O1*B*	125.8 (2)	O1*B*—C11—C12	110.9 (2)
O1*A*—C11—C12	123.2 (2)		
O1*A*—C11—C12—N11	9.4 (3)	C3—C2—N1—O3	29.2 (3)
O1*B*—C11—C12—N11	−173.3 (2)	C3—C4—N2—O4	−3.9 (3)
N11—C12—C13—C14	67.7 (2)	C5—C4—N2—O5	−7.7 (3)
C12—C13—C14—O1*C*	11.0 (3)	C5—C6—N3—O6	18.7 (3)
C12—C13—C14—N12	−169.8 (2)	C1—C6—N3—O7	17.5 (3)
C1—C2—N1—O2	32.3 (3)		

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

D—H···A	D—H	H···A	D···A	D—H···A
O1B—H1B···O1$^{\rm i}$	0.82	1.79	2.572 (2)	160
N11—H11A···O1$A^{\rm ii}$	0.89	1.95	2.829 (2)	170
N11—H11B···O2$^{\rm iii}$	0.89	2.33	3.074 (3)	141
N11—H11B···O1C	0.89	2.49	3.032 (3)	120
N11—H11C···O1$C^{\rm iv}$	0.89	2.21	2.929 (3)	138
N11—H11C···O5$^{\rm v}$	0.89	2.44	3.024 (2)	123
N12—H12A···O7$^{\rm vi}$	0.86	2.28	3.077 (3)	155
N12—H12B···O1$^{\rm vii}$	0.86	2.38	3.135 (3)	147
N12—H12B···O7$^{\rm vii}$	0.86	2.50	3.189 (4)	138

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

All H atoms were placed in geometrically calculated positions, with C—H distances in the range 0.93–0.98 Å, N—H distances in the range 0.86–0.89 Å and an O—H distance of 0.82 Å, and included in the refinement in the riding-model approximation, with $U_{\rm iso}$(H) equal to 1.2$U_{\rm eq}$ of the carrier atom. In addition to the 1380 unique reflections, 291 Friedel pairs were measured but, due to the absence of atoms with significant anomalous dispersion effects, these data were merged.

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*.

The authors thank the Department of Science and Technology, Government of India, for establishing the Single-Crystal Diffractometer Facility at the School of Physics, Madurai Kamaraj University, Madurai, through the FIST programme.

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