Acta Crystallographica Section E
Structure Reports
Online
ISSN 1600-5368

L-Asparaginium nitrate

A. Aarthy,[a] K. Anitha,[a] S. Athimoolam,[a] S. Asath Bahadur[b] and R.K. Rajaram[a]*

[a]Department of Physics, Madurai Kamaraj University, Madurai 625 021, India, and [b]Arulmigu Kalasalingam College of Engineering, Anand Nagar, Krishnankoil 626190, India

Correspondence e-mail:
rkrsopmku@yahoo.co.in

The title compound, $C_4H_9N_2O_3^+\cdot NO_3^-$, crystallizes with two asparaginium cations and two nitrate anions in the asymmetric unit. In both asparaginium residues, protonation take place at the carboxyl O atom *cis* to the amine group. Cation I exists in a *trans* conformation, whereas cation II exhibits a *gauche* I conformation. A straight head-to-tail sequence is observed for one of the asparaginium cations. The crystal structure is stabilized by inter- and intramolecular hydrogen bonding.

Received 12 May 2005
Accepted 2 June 2005
Online 10 June 2005

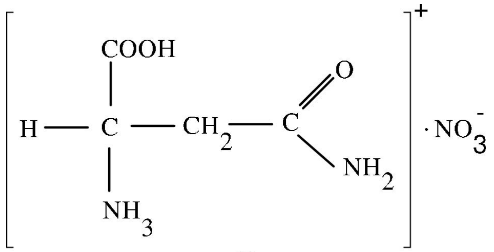
Key indicators

Single-crystal X-ray study
T = 293 K
Mean σ(C–C) = 0.008 Å
R factor = 0.058
wR factor = 0.189
Data-to-parameter ratio = 6.2

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

Comment

Asparagine, one of the non-essential amino acids, is the product of amidation of aspartate in the body. Asparagine stabilizes and balances the central nervous system by preventing a person from becoming too nervous or too calm. The crystal structure of the dipeptides glycyl-L-asparagine (Pasternak *et al.*, 1954), L-asparagine-L-asparatic acid monohydrate (Wang *et al.*, 1985), L-asparaginyl-L-valine 1.33-hydrate (Bonge *et al.*, 2005) and *N*-(2,4-dinitrophenyl)-L-asparagine (Mauguen *et al.*, 1976) have been reported. The crystal structure of asparagine itself has been studied extensively (Kartha & De Vries, 1961; Verbist *et al.*, 1972; Ramanadham *et al.*, 1972; Wang *et al.*, 1985; Arnold *et al.*, 2000). L-Asparagine complexed with picric acid has been reported recently from our laboratory (Anitha *et al.*, 2005). In the present investigation, the crystal structure of protonated asparagine with a nitrate anion is reported.



(I)

The asymmetric unit of the title compound, (I), contains two asparaginium cations and two nitrate anions (Fig. 1). The unsymmetrical C—O bond distances and the O—C—C bond angles clearly confirm the protonation of the carboxyl group in both cations. The difference between the asparaginium cations is the conformation of the NH_3—C—C—C chain, which is *trans* in one cation but *gauche* in the other. The deviation of the amine N atom from the plane of the carboxyl group is 0.076 (10) Å for cation I and 0.185 (9) Å for cation II. In both cations, the backbone conformation is the same. The torsion angles ψ^1 and ψ^2 correspond to *trans* and *cis* arrangements, respectively. As noted by Sundaralingam & Putkey (1970), a

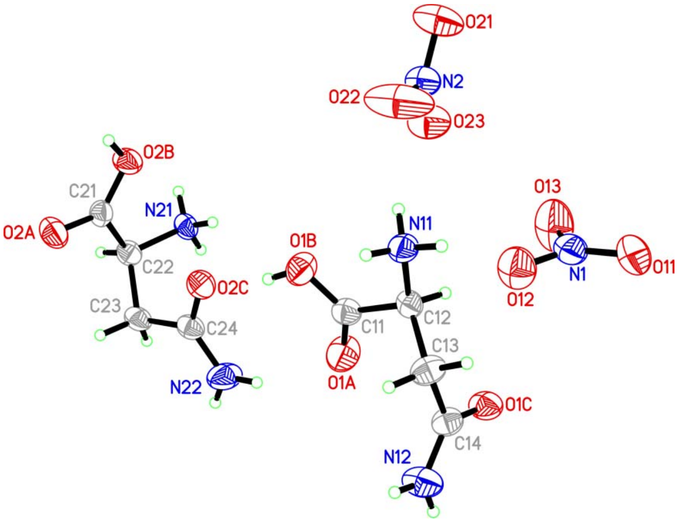


Figure 1
The asymmetric unit of the title compound, with the atom-numbering scheme and 50% probability displacement ellipsoids (Bruker, 2000).

positive value for ψ^2 leads to a decrease in the intramolecular C3$\cdots$O*A* distances, which are 2.9312 (6) Å for cation I and 2.9028 (6) Å for cation II [2.9 Å reported by Ramanadham *et al.* (1972) and 2.827 (3) Å by Anitha *et al.* (2005)]. Protonation at the O atom *cis* to the amine group seems to be unique. From the Cambridge Structural Database, it is found that protonation at the *cis* O atom has not previously been observed in asparagine complexes (Version 5.26 of November 2004; Allen, 2002). The side-chain rotamers are observed as *trans*/*gauche* I/*trans* and *gauche* I/*gauche* I/*trans* ($\chi^1/\chi^{21}/\chi^{22}$) for the asparaginium cations.

The nitrate anion plays a vital role in hydrogen bonding to stabilize the crystal structure. Hydrogen bonding is observed between the amine N atom and the nitrate anions. Both carboxyl O atoms form an intermolecular hydrogen bond with the O^{γ} atom of another cation. The amide N atoms form hydrogen bonds with the carbonyl atom of another cation (Table 2). This forms an infinite double chain spiralling parallel to the *b* axis

Experimental

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

Crystal data

$C_4H_9NO_3^+\cdot NO_3^-$
$M_r = 195.14$
Triclinic, $P1$
$a = 5.357$ (2) Å
$b = 8.232$ (3) Å
$c = 10.172$ (4) Å
$\alpha = 96.88$ (3)°
$\beta = 104.47$ (3)°
$\gamma = 102.11$ (3)°
$V = 417.5$ (3) Å^3
$Z = 2$
$D_x = 1.552$ Mg m^{-3}
$D_m = 1.545$ Mg m^{-3}
D_m measured by flotation using a liquid mixture of xylene and CCl_4
Mo $K\alpha$ radiation
Cell parameters from 25 reflections
$\theta = 9.8$–14.0°
$\mu = 0.15$ mm^{-1}
$T = 293$ (2) K
Block, colourless
0.24 × 0.21 × 0.19 mm

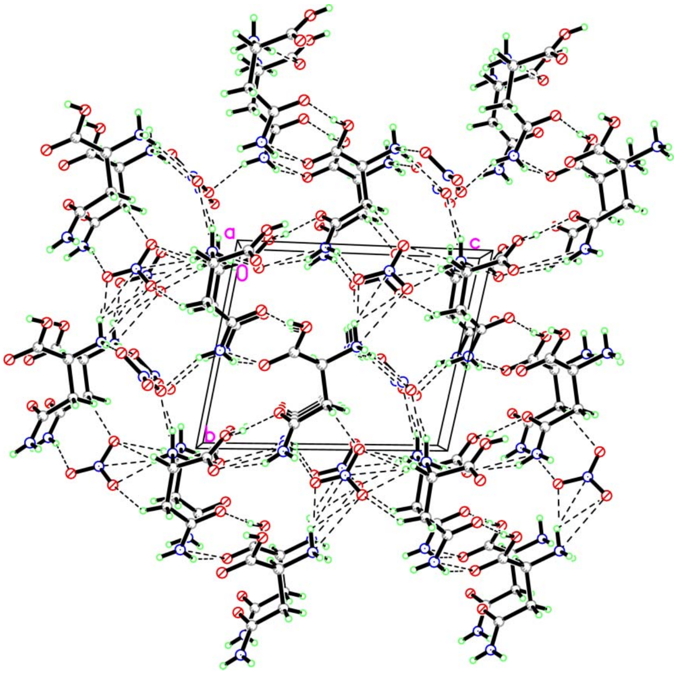


Figure 2
A packing diagram of the structure, viewed down the *a* axis (Bruker, 2000). Dashed lines indicate hydrogen bonds.

Data collection

Nonius MACH3 four-circle diffractometer
ω–2θ scans
Absorption correction: ψ scan (North *et al.*, 1968)
$T_{\min} = 0.846$, $T_{\max} = 0.993$
1988 measured reflections
1474 independent reflections
1358 reflections with $I > 2\sigma(I)$
$R_{\rm int} = 0.057$
$\theta_{\max} = 25.0°$
$h = -1 \rightarrow 6$
$k = -9 \rightarrow 9$
$l = -12 \rightarrow 12$
3 standard reflections
frequency: 60 min
intensity decay: none

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)] = 0.058$
$wR(F^2) = 0.189$
$S = 1.13$
1474 reflections
239 parameters
H-atom parameters constrained
$w = 1/[\sigma^2(F_o^2) + (0.1565P)^2 + 0.0806P]$
where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{\max} < 0.001$
$\Delta\rho_{\max} = 0.39$ e Å^{-3}
$\Delta\rho_{\min} = -0.42$ e Å^{-3}

Table 1
Selected geometric parameters (Å, °).

O1*A*—C11	1.205 (8)	O2*A*—C21	1.230 (7)
O1*B*—C11	1.298 (8)	O2*B*—C21	1.275 (7)
O1*A*—C11—C12	120.0 (5)	O2*A*—C21—C22	118.5 (5)
O1*B*—C11—C12	114.1 (5)	O2*B*—C21—C22	115.4 (4)
O1*A*—C11—C12—N11	−176.9 (6)	O2*A*—C21—C22—N21	−173.3 (5)
O1*B*—C11—C12—N11	3.2 (7)	O2*B*—C21—C22—N21	9.0 (6)
N11—C12—C13—C14	−168.9 (5)	N21—C22—C23—C24	53.5 (6)
C12—C13—C14—O1*C*	46.8 (8)	C22—C23—C24—O2*C*	32.7 (7)
C12—C13—C14—N12	−135.1 (6)	C22—C23—C24—N22	−145.6 (6)

Acta Cryst. (2005). E**61**, o2042–o2044 Aarthy *et al.* • $C_4H_9NO_3^+\cdot NO_3^-$ **o2043**

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

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
O1*B*—H1*B*···O2*C*	0.82	1.76	2.570 (6)	169
N11—H11*A*···O23	0.89	2.03	2.858 (7)	155
N11—H11*A*···O22	0.89	2.39	2.908 (8)	117
N11—H11*B*···O12	0.89	2.14	2.994 (7)	159
N11—H11*B*···O13	0.89	2.21	2.951 (8)	140
N11—H11*C*···O13$^{\rm i}$	0.89	1.97	2.855 (8)	175
N12—H12*A*···O2*A*$^{\rm ii}$	0.86	2.09	2.903 (8)	156
N12—H12*B*···O23$^{\rm iii}$	0.86	2.17	2.998 (7)	162
O2*B*—H2*B*···O1*C*$^{\rm iv}$	0.82	1.69	2.490 (6)	166
N21—H21*A*···O12$^{\rm v}$	0.89	1.96	2.815 (7)	161
N21—H21*B*···O22$^{\rm vi}$	0.89	1.97	2.832 (8)	162
N21—H21*B*···O21$^{\rm vi}$	0.89	2.43	3.176 (8)	141
N21—H21*C*···O2*A*$^{\rm vii}$	0.89	2.07	2.887 (6)	153
N21—H21*C*···O2*C*	0.89	2.45	2.988 (6)	120
N22—H22*A*···O1*A*	0.86	2.13	2.921 (7)	154
N22—H22*B*···O11$^{\rm viii}$	0.86	2.23	3.014 (8)	151

Symmetry codes: (i) $x + 1, y, z$; (ii) $x - 1, y + 1, z$; (iii) $x + 1, y + 1, z$; (iv) $x + 1, y - 1, z$; (v) $x, y - 1, z - 1$; (vi) $x, y, z - 1$; (vii) $x - 1, y, z$; (viii) $x + 1, y, z - 1$.

All H atoms were placed in geometrically calculated positions, with C—H distances of 0.97 and 0.98 Å, N—H distances of 0.86 and 0.89 Å, and O—H distances of 0.82 Å, and allowed to ride on their carrier atoms, with $U_{\rm iso}$(H) equal to $1.2U_{\rm eq}$ and $1.5U_{\rm eq}$ of the carrier C and N/O atoms, respectively. In addition to the 1474 unique reflections, 513 Friedel pairs were measured. However, owing 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: *SHELXTL*/*PC* (Bruker, 2000); 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.

References

Allen, F. H. (2002). *Acta Cryst.* B**58**, 380–388.

Anitha, K., Athimoolam, S. & Rajaram, R. K. (2005). *Acta Cryst.* E**61**, o1463–o1465.

Arnold, W. D., Sanders, L. K., McMahon, M. T., Volkov, A. V., Wu, G., Coppens, P., Wilson, S. R., Godbout, N. & Oldfield, E. (2000). *J. Am. Chem. Soc.* **122**, 4708–4717.

Bonge, H. T., Rosenberg, M. L., Riktor, M. & Görbitz, C. H. (2005). *Acta Cryst.* E**61**, o524–o527.

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

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

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

Kartha, G. & De Vries, A. (1961). *Nature* (*London*), **192**, 862.

Mauguen, Y., Brunie, S., Tsoucaris, G. & Knossow, M. (1976). *Cryst. Struct. Commun.* **5**, 723–726.

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

Pasternak, R. A., Katz, L. & Corey, R. B. (1954). *Acta Cryst.* **7**, 225–236.

Ramanadham, M., Sikka, S. K. & Chidambaram, R. (1972). *Acta Cryst.* B**28**, 3000–3005.

Sheldrick, G. M. (1997). *SHELXL97* and *SHELXS97*. University of Göttingen, Germany.

Sundaralingam, M. & Putkey, F. F. (1970). *Acta Cryst.* B**26**, 790–800.

Verbist, J. J., Lehmann, M. S., Koetzle, T. F. & Hamilton, W. C. (1972). *Acta Cryst.* B**28**, 3006–3013.

Wang, J. L., Berkovitch-Yellin, Z. & Leiserowitz, L. (1985). *Acta Cryst.* B**41**, 341–348.

o2044 Aarthy *et al.* • $C_4H_9NO_3^+ \cdot NO_3^-$ *Acta Cryst.* (2005). E**61**, o2042–o2044