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## Key indicators

Single-crystal X-ray study

T = 293 K

Mean  $\sigma(\text{C}-\text{C}) = 0.007 \text{ \AA}$ 

R factor = 0.041

wR factor = 0.118

Data-to-parameter ratio = 7.4

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

## L-Aspartic acid nitrate–L-aspartic acid (1/1)

In the title compound,  $\text{C}_4\text{H}_8\text{NO}_4^+ \cdot \text{C}_4\text{H}_7\text{NO}_4 \cdot \text{NO}_3^-$ , the cation and neutral molecule are connected by an asymmetric hydrogen bond. The cation, residue 1, exists in a *gauche* I conformation, whereas the neutral molecule, residue 2, exhibits a *gauche* II conformation. A *syn-syn* orientation is also observed in this structure and residue 1 is involved in a straight (S1) head-to-tail sequence. The structure is stabilized by both inter- and intramolecular N–H...O hydrogen bonding.

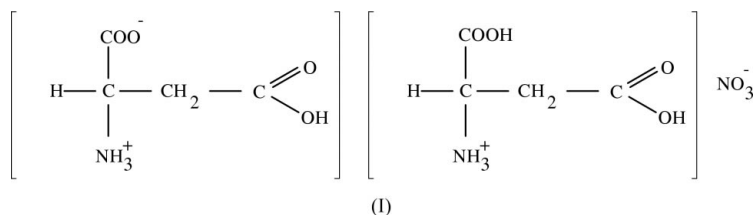
Received 31 October 2002

Accepted 6 November 2002

Online 15 November 2002

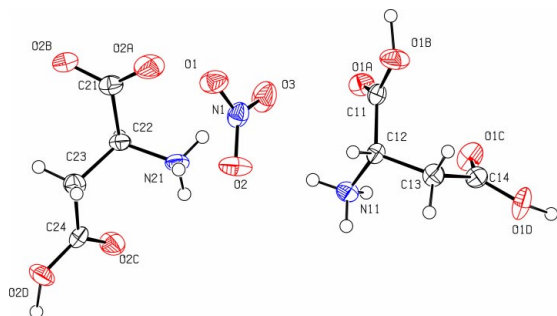
## Comment

Aspartic acid is a non-essential amino acid, widely distributed in proteins, which plays a major role in the energy cycle of the human body. The crystal structures of L-aspartic acid (Derissen *et al.*, 1968), DL-aspartic acid (Rao, 1973; Sequeira *et al.*, 1989), DL-aspartic acid nitrate monohydrate (Asath Bahadur & Rajaram, 1995) and bis(DL-aspartic acid) sulfate (Srinivasan *et al.*, 2001) have been reported. In the present paper, the crystal structure of the product, (I), of the reaction of L-aspartic acid with nitric acid is reported.

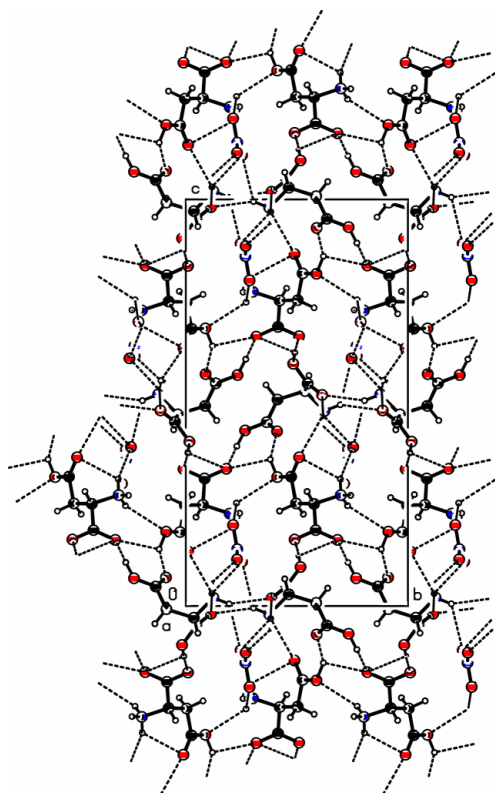


The asymmetric unit of (I) contains one protonated aspartic acid molecule (residue 1), one neutral aspartic acid molecule (residue 2) and one nitrate anion. Superposition of residue 1 on residue 2 results in an r.m.s. deviation of the constituent atoms of 1.088 Å. Examination of the coordinates suggests that the two residues might be related by a pseudo-inversion centre. The unsymmetrical carboxyl bond distances and angles [1.217 (7)/1.297(6) Å and 122.3 (5)/109.9(5)°] of residue 1 clearly indicate protonation of the carboxyl group, whilst, in the case of residue 2, the equality of C–O bond distances [1.240 (7)/1.250(6) Å] and O–C–C bond angles [117.4 (5)/115.5(5)°] represent the deprotonated carboxylate group (Table 1).

The backbone conformation angle  $\psi^1$  is the *cis* form for both residues [O1A–C11–C12–N1  $-7.0$  (7)° and O2A–C21–C22–N21  $-1.7$  (7)°]. The deviations of the amino atoms N11 and N21 from the planar carboxyl groups at C11 and C22 are 0.198 (8) and 0.044 (1) Å, respectively. This non-planarity of the amino nitrogen and carboxyl group is also found in other amino acids (Lakshminarayanan *et al.*, 1967).



**Figure 1**  
The molecular structure, with the atom-numbering scheme and 50% probability displacement ellipsoids (Johnson, 1976).



**Figure 2**  
Packing diagram of the title molecule, viewed down the *a* axis.

The side-chain conformation angle  $\chi^1$  is in a *gauche* I form [66.1 (6)°] for residue 1 and a *gauche* II form [−64.8 (6)°] for residue 2. The branched chain conformation angles,  $\chi^{11}$  and  $\chi^{21}$ , are in *cis* and *trans* forms [10.0 (8)/−5.5 (8) and −170.8 (5)/174.3(5)°] for both residues. In residue 1, the *C<sup>γ</sup>* atom C14 is in the *gauche* II [−58.1 (6)°] conformation with respect to C11, while, in the case of residue 2, the *C<sup>γ</sup>* atom C24 is *trans* [170.9 (5)°] with respect to C21.

The average N—O and O—N—O values are 1.248 Å and 120°, respectively, clearly showing the nearly ideal trigonal symmetry of the anion, which plays a vital role in hydrogen bonding and the resulting stabilization of the structure.

The aspartic acid cation and neutral aspartic acid molecule are linked, by strong O—H···O hydrogen bonding, to form dimers. This hydrogen bond may be termed an asymmetric

hydrogen bond, since the H atom is closer to one of the O atoms of the carboxyl group (Olovsson *et al.*, 2001). Atom H1B is in a *syn* orientation with respect to both donor carboxyl group and acceptor carboxylate group; the torsion angles H1B—O1B—C11—O1A and H1B—O2B<sup>i</sup>—C21<sup>i</sup>—O2A<sup>i</sup> [symmetry code: (i) 1 + *x*, *y*, *z*] are 13 (5) and 29 (3)°, respectively. This type of *syn-syn* orientation is also found in betaine betainium oxalate (Rodrigues *et al.*, 2001). The  $\beta$ -carboxyl group of residue 1 forms a strong O—H···O hydrogen bond with the  $\alpha$ -carboxylate group of residue 2. In the case of residue 2, the  $\beta$ -carboxyl group forms a rather strong O—H···O hydrogen bond with the carbonyl O atom of the  $\beta$ -carboxyl group of residue 1.

The amino N atom of both residues forms N—H···O hydrogen bonds with the nitrate anion, and the  $\alpha$ - and  $\beta$ -carboxyl groups. Three-centred hydrogen bonding is observed in both residues. Interestingly, in residue 1, three such three-centred bonds are observed, leading to a class IV hydrogen-bonding pattern (Jeffrey & Saenger, 1991). The frequency of such class IV hydrogen-bonding patterns is very low. A class II hydrogen-bonding pattern is observed in residue 2, having two two-centred and one three-centred hydrogen bonds. In both residues, intramolecular N—H···O hydrogen bonding is present, involving the amino nitrogen and the carbonyl oxygen of a carboxylic acid group. A straight (S1) head-to-tail sequence is observed in residue 1, connecting two amino acids separated by a unit translation (Vijayan, 1988). Each aspartic acid residue is linked by the nitrate anion through N—H···O hydrogen bonding, forming a chain running along the *a* axis: (a) O2(*x* − 1, *y*, *z*)··H11B—N11—H11A···O3(*x* − 2, *y*, *z*) and (b) O1(−½ − *x*, 2 − *y*, *z* − ½)··H21A—N21—H21B···O3(½ − *x*, 2 − *y*, *z* − ½).

## Experimental

The title compound was crystallized by slow evaporation of an aqueous solution of L-aspartic acid and nitric acid in a 2:1 stoichiometric ratio.

### Crystal data

$C_4H_8NO_4^+ \cdot C_4H_7NO_4 \cdot NO_3^-$   
 $M_r = 329.23$   
Orthorhombic,  $P2_12_12_1$   
 $a = 5.5840$  (7) Å  
 $b = 11.491$  (3) Å  
 $c = 21.043$  (5) Å  
 $V = 1350.2$  (5) Å<sup>3</sup>  
 $Z = 4$   
 $D_x = 1.620$  Mg m<sup>−3</sup>  
 $D_m = 1.58$  Mg m<sup>−3</sup>

$D_m$ , measured by flotation in a mixture of carbon tetrachloride and xylene  
Mo  $K\alpha$  radiation  
Cell parameters from 25 reflections  
 $\theta = 11.0$ –14.7°  
 $\mu = 0.15$  mm<sup>−1</sup>  
 $T = 293$  (2) K  
Needle, colourless  
0.5 × 0.2 × 0.2 mm

### Data collection

Enraf–Nonius CAD-4 diffractometer  
 $\omega$ – $2\theta$  scans  
Absorption correction:  $\psi$  scan (North *et al.*, 1968)  
 $T_{\min} = 0.932$ ,  $T_{\max} = 0.968$   
1640 measured reflections  
1578 independent reflections  
929 reflections with  $I > 2\sigma(I)$

$R_{\text{int}} = 0.020$   
 $\theta_{\text{max}} = 25.0^\circ$   
 $h = 0 \rightarrow 6$   
 $k = -1 \rightarrow 13$   
 $l = -1 \rightarrow 24$   
3 standard reflections  
frequency: 60 min  
intensity decay: none

Refinement

Refinement on $F^2$	$w = 1/[\sigma^2(F_o^2) + (0.058P)^2 + 0.0829P]$
$R[F^2 > 2\sigma(F^2)] = 0.041$	where $P = (F_o^2 + 2F_c^2)/3$
$wR(F^2) = 0.118$	$(\Delta/\sigma)_{\max} < 0.001$
$S = 1.02$	$\Delta\rho_{\max} = 0.24 \text{ e } \text{\AA}^{-3}$
1578 reflections	$\Delta\rho_{\min} = -0.30 \text{ e } \text{\AA}^{-3}$
212 parameters	Extinction correction: <i>SHELXL</i>
H atoms treated by a mixture of independent and constrained refinement	Extinction coefficient: 0.011 (3)

**Table 1**  
Selected geometric parameters ( $\text{\AA}$ ,  $^\circ$ ).

O1A—C11	1.217 (7)	O2A—C21	1.240 (7)
O1B—C11	1.297 (6)	O2B—C21	1.250 (6)
C14—O1C	1.215 (6)	C24—O2C	1.208 (6)
C14—O1D	1.306 (6)	C24—O2D	1.319 (7)
O1A—C11—C12	122.3 (5)	O2A—C21—C22	117.4 (5)
O1B—C11—C12	109.9 (5)	O2B—C21—C22	115.5 (5)
O1A—C11—C12—N11	-7.0 (7)	O2A—C21—C22—N21	-1.7 (7)
N11—C12—C13—C14	66.1 (6)	N21—C22—C23—C24	-64.8 (6)
C11—C12—C13—C14	-58.1 (6)	C21—C22—C23—C24	170.9 (5)
C12—C13—C14—O1C	10.0 (8)	C22—C23—C24—O2C	-5.5 (8)
C12—C13—C14—O1D	-170.8 (5)	C22—C23—C24—O2D	174.3 (5)

**Table 2**  
Hydrogen-bonding geometry ( $\text{\AA}$ ,  $^\circ$ ).

$D-H \cdots A$	$D-H$	$H \cdots A$	$D \cdots A$	$D-H \cdots A$
O1B—H1B <sup>i</sup> ···O2B <sup>i</sup>	1.05 (8)	1.47 (8)	2.512 (5)	175 (8)
N11—H11A <sup>ii</sup> ···O1A <sup>ii</sup>	0.89	2.39	3.126 (6)	140
N11—H11A <sup>iii</sup> ···O3 <sup>iii</sup>	0.89	2.50	3.050 (6)	121
N11—H11B <sup>iv</sup> ···O2 <sup>iv</sup>	0.89	2.12	2.793 (6)	131
N11—H11B <sup>v</sup> ···O1C	0.89	2.63	3.170 (6)	120
N11—H11C <sup>vi</sup> ···O1A <sup>v</sup>	0.89	2.25	3.018 (5)	145
N11—H11C <sup>vii</sup> ···O3 <sup>vii</sup>	0.89	2.58	3.192 (6)	127
O1D—H1D <sup>viii</sup> ···O2A <sup>viii</sup>	0.96 (6)	1.68 (6)	2.594 (5)	156 (6)
N21—H21A <sup>ix</sup> ···O1 <sup>ix</sup>	0.89	2.20	2.892 (6)	134
N21—H21B <sup>x</sup> ···O3 <sup>x</sup>	0.89	2.34	3.155 (6)	152
N21—H21B <sup>xi</sup> ···O2C	0.89	2.47	3.040 (5)	122
N21—H21C <sup>xii</sup> ···O2D <sup>xii</sup>	0.89	2.53	3.111 (6)	124
O2D—H2D <sup>xiii</sup> ···O1C <sup>xiii</sup>	1.06 (6)	1.74 (6)	2.699 (5)	148 (5)

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

The carboxyl H atoms were located in a difference Fourier synthesis and refined isotropically [O—H = 0.96 (6)–1.06 (6)  $\text{\AA}$ ]. All

other H atoms were placed in geometrically calculated positions and included in the refinement in a riding-model approximation, with  $U_{\text{iso}}$  equal to  $1.2U_{\text{eq}}$  of the carrier atom ( $1.5U_{\text{eq}}$  for methyl and H atoms attached to nitrogen).

Data collection: *CAD-4 Software* (Enraf–Nonius, 1989); cell refinement: *CAD-4 Software*; data reduction: *CAD-4 Software*; program(s) used to solve structure: *SHELXS97* (Sheldrick, 1997); program(s) used to refine structure: *SHELXL97* (Sheldrick, 1997); molecular graphics: *PLATON* (Spek, 1999); software used to prepare material for publication: *SHELXL97*.

One of the authors (BS) thanks the Council of Scientific & Industrial Research (CSIR), Government of India, for financial assistance and the author RKR thanks the Department of Science and Technology (DST), Government of India, for financial support. Financial support from the UGC is also gratefully acknowledged.

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