

Crystal and molecular structure of DL-aspartic acid nitrate monohydrate

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Received September 29, 1993; accepted April 25, 1994

Crystal structure / DL-aspartic acid nitrate

Abstract. DL-aspartic acid nitrate monohydrate, $(C_4H_8NO_4)^+(NO_3)^- \cdot H_2O$, $M = 214.128$, triclinic, $P\bar{1}$, $a = 5.680(1) \text{ \AA}$, $b = 7.331(2) \text{ \AA}$, $c = 10.812(1) \text{ \AA}$, $\alpha = 76.74(1)^\circ$, $\beta = 105.33(1)^\circ$, $\gamma = 96.41(1)^\circ$, $V = 422.0 \text{ \AA}^3$, $D_m = 1.66 \text{ g cm}^{-3}$ (floatation), $D_c = 1.685 \text{ g cm}^{-3}$, $Z = 2$, $\mu = 1.561 \text{ cm}^{-1}$, $\lambda(\text{MoK}\alpha) = 0.70926 \text{ \AA}$.

The crystal structure was solved by direct, Fourier and difference-Fourier methods and refined by full-matrix least-squares technique to an $R = 0.041$ and $wR = 0.049$ for 1249 unique reflections. The aspartic acid molecule exists in cationic form by the protonation of the α -carboxylic group. All the hydrogen atoms were located by difference-Fourier-syntheses.

Introduction

The crystal structure of L-aspartic acid (Derissen, Endeman, Peerdeman, 1968), DL-aspartic acid (Rao, 1973) and DL-aspartic acid hydrochloride (Dawson, 1977) were solved earlier. The addition of an inorganic acid to the acidic aminoacid has resulted in slight change of the aminoacid residue. However, the conformation of the DL-aspartic acid has not been affected very much. In order to study the changes in the geometry and the conformation of the aminoacid, the crystal structure of DL-aspartic acid nitrate monohydrate was investigated.

Experimental

The title compound was crystallized in aqueous solution from 1:1 stoichiometric ratio of DL-aspartic acid and nitric acid. The crystals are plate shaped, elongated along the a -axis. The density of the sample was measured by the flotation technique using a liquid mixture of bromoform and xylene. The unit-cell parameters were obtained by least-squares refinement of 25 strong reflections in the range $10^\circ < \theta < 14^\circ$, confirming our earlier estimation by oscillation and Weissenberg patterns. The three-

dimensional intensity data were collected for 1476 reflections in the range $1^\circ \leq \theta \leq 25^\circ$ on an Enraf-Nonius CAD-4 diffractometer with graphite monochromatized $\text{MoK}\alpha$ radiation by a $w - 2\theta$ scan mode. Reflections in the hemisphere with $-6 \leq h \leq 6$, $-8 \leq k \leq 8$ and $0 \leq l \leq 12$ were measured. Three reflections ($\bar{1}26$); $(0\bar{4}2)$; (300) were monitored for every 85 reflections. No significant variation was observed. The crystal size was $0.1 \times 0.15 \times 0.1 \text{ mm}$. Lorentz, polarization and absorption corrections were applied.

Structure determination

The structure determination was carried out by direct methods (SHELX-86, Sheldrick, 1986). The best E map gave the position of all the non-hydrogen atoms. After refining the positional and anisotropic thermal parameters of all the non-hydrogen atoms, all hydrogen atoms were located using the weighted difference-Fourier-synthesis. During the final stages, the positional and isotropic thermal parameters of all hydrogen atoms were refined. The convergence was achieved at $R = 0.041$ and $wR = 0.049$ for 1279 unique reflections and 167 parameters. The function minimized was $w(\Delta F)^2$ with $\Delta F = |F_o| - |F_c|$ and $w = 1.00/[\sigma^2(F) + 0.003330 |F|^2]$. The maximum shift to e.s.d. ratio was 0.007. Atomic scattering factors were taken from the International Tables for X-ray crystallography (1974).

Results and Discussion

The positional and the anisotropic thermal parameters for the non-hydrogen atoms are presented in Table 1. The positional and isotropic thermal parameters of the hydrogen atoms are presented in Table 2. The crystal structure and packing of the title compound is shown in Fig. 1 and Fig. 2, respectively.¹

¹ Additional material to this paper can be ordered referring to the no. CSD 57582, names of the authors and citation of the paper at the Fachinformationszentrum Karlsruhe, Gesellschaft für wissenschaftlich-technische Information mbH, D-76344 Eggenstein-Leopoldshafen, Germany.

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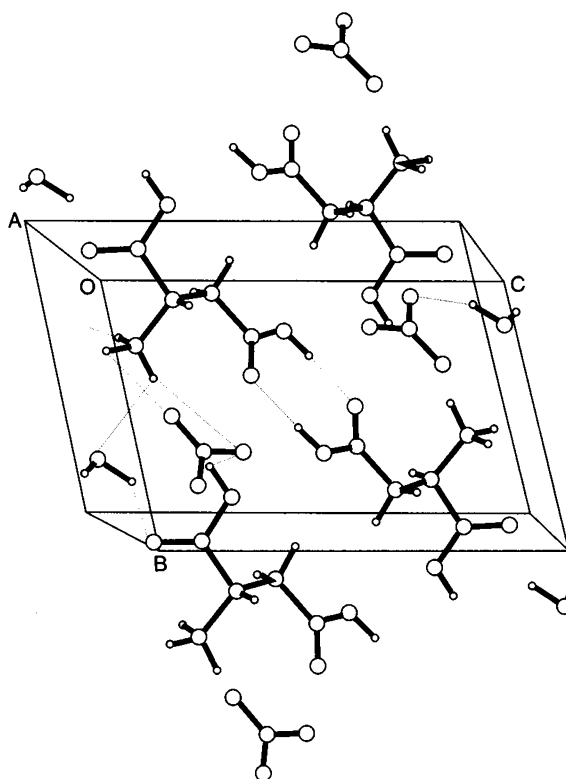
Table 1. Fractional atomic coordinates and equivalent isotropic thermal parameters ($\times 10^4$) of non-H atoms in DL-aspartic acid nitrate monohydrate.

$$U_{eq} = \frac{1}{3} \sum_i \sum_j \{U_{ij}(a_i^* \cdot a_j^*) (a_i \cdot a_j)\}$$

Atom	x	y	z	U_{eq} (\AA^2)
N(11)	2617(2)	6764(2)	1980(1)	300(3)
O(11)	1192(2)	6569(2)	2725(1)	390(3)
O(12)	2586(3)	5487(2)	1380(1)	427(3)
O(13)	4007(3)	8167(2)	1870(1)	481(3)
O(1)	0023(3)	0554(2)	6631(1)	403(3)
O(2)	0653(3)	-0921(2)	8730(1)	431(3)
O(3)	5955(2)	-2671(2)	5251(1)	366(3)
O(4)	3182(2)	-4772(2)	5940(1)	359(3)
C(1)	0746(3)	-0838(2)	7622(2)	281(3)
C(2)	1666(3)	-2416(2)	7215(1)	262(3)
C(3)	3669(3)	-1759(2)	6501(2)	299(4)
C(4)	4246(3)	-3218(2)	5869(1)	260(3)
N(1)	2493(3)	-3881(2)	8409(1)	318(3)
OW	3427(3)	2319(2)	9996(1)	449(3)

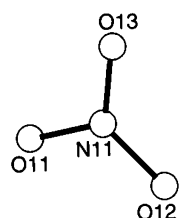
Table 2. Fractional atomic coordinates and isotropic temperature factors ($\times 10^3$) of hydrogen atoms.

Atom	Bonded to	x	y	z	U_{iso} (\AA^2)
H(1)	O(1)	950(5)	147(4)	688(2)	51(6)
H(2)	O(3)	626(6)	-350(5)	481(3)	65(1)
H(3)	C(2)	024(4)	-290(3)	666(2)	24(4)
H(4)	C(3)	504(5)	-143(4)	710(3)	56(7)
H(5)	C(3)	320(4)	-070(3)	583(2)	37(5)
H(6)	N(1)	286(5)	-498(4)	822(3)	58(7)
H(7)	N(1)	138(7)	-427(5)	896(4)	94(11)
H(8)	N(1)	390(6)	-335(4)	896(3)	61(7)
H(9)	OW	228(6)	166(5)	1019(3)	67(9)
H(10)	OW	372(8)	163(7)	937(4)	106(12)

**Fig. 2.** Crystal packing of DL-aspartic acid nitrate monohydrate viewed along the *a*-axis.

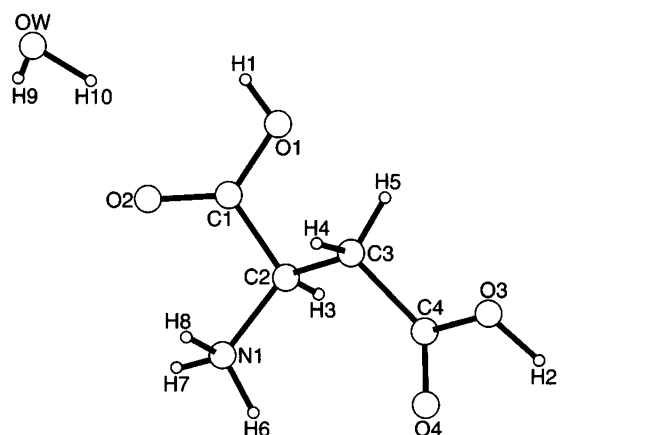
The nitrate anion is planar and the geometry is as expected in similar compounds. The oxygen of the α -carboxyl group is protonated by the hydrogen of the nitric acid, exhibiting cationic form for the aspartic acid group as observed in DL-aspartic acid hydrochloride (Dawson, 1977). The dimension of the aspartic acid group compares well with related compounds.

The aspartic acid molecule has extended trans conformation ($C1-C2-C3-C4 = -168.8^\circ$) as in other compounds. However, the amino nitrogen N(1) is in *gauche* position with respect to C(4). The internal rotation angles defining the conformation of the aspartic acid molecule are presented in Table 3 with similar com-

**Table 3.** Torsion Angles ($^\circ$).

	I	II	III	IV
O(1)-C(1)-C(2)-C(3)	54.7	165.7	-94.2	-64.0
O(2)-C(1)-C(2)-C(3)	-127.1	-12.3	83.2	117.6
O(1)-C(1)-C(2)-N(1)	178.1	41.5	144.8	171.3
O(2)-C(1)-C(2)-N(1)	-3.4	-136.5	-37.8	-7.3
C(1)-C(2)-C(3)-C(4)	-168.8	172.1	178.2	174.2
N(1)-C(2)-C(3)-C(4)	69.6	-64.0	-61.9	-61.9
C(2)-C(3)-C(4)-O(3)	179.8	174.1	-51.3	-175.8
C(2)-C(3)-C(4)-O(4)	-0.1	-7.5	131.4	3.1
H(6)-N(1)-C(2)-C(1)	171.1	-175.2	-173.0	-177.0
H(7)-N(1)-C(2)-C(1)	49.1	61.8	-50.0	-59.0
H(8)-N(1)-C(2)-C(1)	-66.4	-55.2	75.0	61.0
C(3)-C(4)-O(3)-H(2)	-175.5	161.9	179.0	177.0
O(4)-C(4)-O(3)-H(2)	4.4	-16.5	-4.0	-2.0

- I DL-aspartic acid nitrate monohydrate (present work)
 II DL-aspartic acid hydrochloride
 III L-aspartic acid
 IV DL-aspartic acid

**Fig. 1.** Numbering Scheme in DL-aspartic acid nitrate monohydrate.

pounds for comparison. The average C–H, N–H and O–H distances are 0.94(3) Å, 0.95(3) Å and 0.90(3) Å, respectively.

Hydrogen bonding

The hydrogen bonding is extensive (Table 4). All the potential donors are involved in hydrogen bonding. The nitrate group N(11) connects two different aspartic acid

Table 4. Hydrogen bond distances (Å) and angles (°) in DL-aspartic acid nitrate monohydrate.

D	H	A	D–H	H–A	D–A	D–H–A
O(1)	H(1)	O(11) ⁱ	0.88	1.703	2.581	175.2
O(3)	H(2)	O(4) ⁱⁱ	0.91	1.747	2.657	180.0
N(1)	N(6)	*O(11) ⁱⁱⁱ	0.93	2.530	2.933	106.5
N(1)	H(6)	*OW ^{iv}	0.93	2.407	2.940	116.3
N(1)	H(7)	O(12) ^{vii}	0.96	2.298	3.038	133.6
N(1)	H(8)	OW ^v	0.96	1.840	2.802	180.0
OW	H(9)	O(2) ^{vi}	0.81	2.227	2.970	152.7
OW	H(10)	O(13) ^{viii}	0.99	2.063	2.886	139.2

i. $-x, 1-y, 1-z$

ii. $1-x, -1-y, 1-z$

iii. $-x, -y, 1-z$

iv. $x, -1+y, z$

v. $1-x, -y, 2-z$

vi. $-x, -y, 2-z$

vii. $1-x, 1-y, 1-z$

* bifurcated hydrogen bond.

molecules through carboxylic oxygen, O(1), and amino nitrogen, N(1), along *a*- and *c*-directions respectively. Two different, but symmetry-related water oxygen atoms, OW, form a hydrogen bond with amino nitrogen, N(1), of the same molecule in the *bc*-plane. The hydrogen bonds N(1)–H(6) ... O(11) and N(1)–H(6) ... OW seem to be bifurcated. The only intermolecular hydrogen bond between two aspartic acid molecule is O(3)–H(2) ... O(4). This hydrogen bond connects two different symmetry-related aspartic acid molecule as a dimer in the *bc*-plane.

Acknowledgements. The authors thank Prof. K. S. Chandrasekaran for his help and encouragement and Prof. T. S. Cameron, for his kind help in data collection. One of the authors (SAB) thanks Madurai Kamaraj University for financial assistance.

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