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# A comparative study of two polymorphs of L-aspartic acid hydrochloride

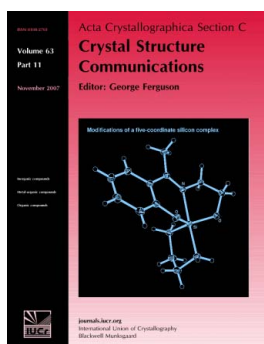
Rim Benali-Cherif, Radhwane Takouachet, El-Eulmi Bendeif and Nourredine Benali-Cherif

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## A comparative study of two polymorphs of L-aspartic acid hydrochloride

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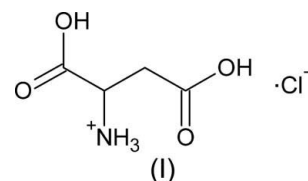
Two polymorphs of L-aspartic acid hydrochloride,  $C_4H_8NO_4^+ \cdot Cl^-$ , were obtained from the same aqueous solution. Their crystal structures have been determined from single-crystal data collected at 100 K. The crystal structures revealed three- and two-dimensional hydrogen-bonding networks for the triclinic and orthorhombic polymorphs, respectively. The cations and anions are connected to one another *via*  $N-H \cdots Cl$  and  $O-H \cdots Cl$  interactions and form alternating cation–anion layer-like structures. The two polymorphs share common structural features; however, the conformations of the L-aspartate cations and the crystal packings are different. Furthermore, the molecular packing of the orthorhombic polymorph contains more interesting interactions which seems to be a favourable factor for more efficient charge transfer within the crystal.

**Keywords:** crystal structure; amino acids; polymorphism; hydrogen bonding; L-aspartic acid hydrochloride; pharmaceutical compounds.

### 1. Introduction

Recently, extensive experimental and theoretical investigations have been devoted to polymorphism of amino-acid-based materials in view of their crucial role in various fundamental biological processes and also their use in drugs and the pharmaceutical industry (Byrn, 1982; Brittain, 1999; Bernstein, 2002; Kitamura, 2004; Herstein, 2004). The purpose of such studies is to define the relevant kinetic and thermodynamic factors that control this phenomenon, allowing for a better optimization of the physical properties of these fundamental biomolecules. Many amino acids display a rich polymorphism, for example, 4-aminobenzoic acid (PABA) (Killeen *et al.*, 1965; Alleaume *et al.*, 1966; Lai & Marsh, 1967; Benali-Cherif *et al.*, 2014) and glutamic acid,

asparagine and aspartic acid (Ono *et al.*, 2004; Ni *et al.*, 2004; Doki *et al.*, 2004; Bendeif & Jelsch, 2007). Aspartic and glutamic acid are probably the most important amino acids that are widely distributed within proteins associated with disease. They are also known for playing a major role in maintaining the solubility and ionic character of proteins which are involved in the energy cycle of the human body. For example, it has been shown that L-aspartic acid is implicated in the mutations of the chlorine channel that leads to Bartter's syndrome (Chapman & Bryce, 2007; Simon *et al.*, 1997). Aspartic acid has found extensive use as a medicine of cardiopathy (ammoniac detoxicating agent, hepar function accelerator and fatigue refresher). On the other hand, the potassium, magnesium or calcium salts of aspartic acid are also widely utilized for mineral nutrition supplement. Thus, the control of the polymorphism of potential organic–inorganic pharmaceutical agents based on aspartic acid salts is crucial to fully exploit their specific functions for future pharmaceutical development.



So far, only three crystal structures of aspartic acid hydrochloride have been deposited in the Cambridge Structural Database (CSD, *Mogul* Version 1.16 of 2013; Allen, 2002). In their preliminary crystallographic studies on some  $\alpha$ -amino acids, Dawson & Mathieson (1951) reported the unit-cell parameters of DL-aspartic acid hydrochloride hemihydrate. Later, Dawson (1977) reported the crystal structure of the anhydrous form (DL-aspartic acid hydrochloride). The two crystal forms are monoclinic (published with the alternate settings  $P2_1/n$  and  $P2_1/a$  of  $P2_1/c$ ). Chapman & Bryce (2007) studied the triclinic  $P1$  crystal structure of L-aspartic acid hydrochloride at 200 K. We were able to grow, from the same aqueous solution, single crystals of two different polymorphs of L-aspartic acid hydrochloride. Structural investigation (at 100 K) of these single crystals revealed that one polymorph, denoted (I), exhibits the same structural properties as those previously reported by Chapman & Bryce (2007). The second polymorph, denoted (II), is a new noncentrosymmetric polymorph of L-aspartic acid hydrochloride. Herein, we report the crystal structure at 100 K of this novel polymorph of L-aspartic acid hydrochloride, (II), and compare the results with our determination at 100 K of the known polymorph, (I).

### 2. Experimental

#### 2.1. Synthesis and crystallization

The title compounds were obtained from an aqueous solution containing a stoichiometric ratio of L-aspartic acid (99%) and hydrochloric acid (40%). The resulting aqueous solution was kept at room temperature. After a few weeks of

**Table 1**  
Experimental details.

	Polymorph (I)	Polymorph (II)
<b>Crystal data</b>		
Chemical formula	$C_4H_8NO_4^+ \cdot Cl^-$	$C_4H_8NO_4^+ \cdot Cl^-$
$M_r$	169.56	169.56
Crystal system, space group	Triclinic, $P1$	Orthorhombic, $P2_12_12$
Temperature (K)	100	100
$a, b, c$ (Å)	5.5888 (5), 5.6045 (6), 6.1697 (7)	9.7082 (2), 8.9123 (3), 8.4820 (2)
$\alpha, \beta, \gamma$ (°)	114.57 (1), 97.752 (9), 95.720 (8)	90, 90, 90
$V$ (Å <sup>3</sup> )	171.52 (3)	733.88 (3)
$Z$	1	4
Radiation type	Mo $K\alpha$	Mo $K\alpha$
$\mu$ (mm <sup>-1</sup> )	0.51	0.48
Crystal size (mm)	0.14 × 0.09 × 0.06	0.20 × 0.14 × 0.12
<b>Data collection</b>		
Diffractometer	Agilent SuperNova (Dual, Cu at zero, Atlas) diffractometer	Agilent SuperNova (Dual, Cu at zero, Atlas) diffractometer
Absorption correction	Analytical [ <i>CrysAlis PRO</i> (Agilent, 2012), using a multifaceted crystal model based on expressions derived by Clark & Reid (1995)]	Analytical [ <i>CrysAlis PRO</i> (Agilent, 2012), using a multifaceted crystal model based on expressions derived by Clark & Reid (1995)]
$T_{min}, T_{max}$	0.963, 0.981	0.936, 0.955
No. of measured, independent and observed [ $I > 2\sigma(I)$ ] reflections	4428, 2273, 2259	17470, 6012, 5353
$R_{int}$	0.020	0.027
$(\sin \theta/\lambda)_{max}$ (Å <sup>-1</sup> )	0.762	1.003
<b>Refinement</b>		
$R[F^2 > 2\sigma(F^2)], wR(F^2), S$	0.022, 0.054, 1.05	0.037, 0.090, 1.04
No. of reflections	2273	6012
No. of parameters	123	123
No. of restraints	3	0
H-atom treatment	All H-atom parameters refined	All H-atom parameters refined
$\Delta\rho_{max}, \Delta\rho_{min}$ (e Å <sup>-3</sup> )	0.30, -0.18	0.46, -0.57
Absolute structure	Flack $x$ determined using 1069 quotients (Parsons <i>et al.</i> , 2013)	Flack $x$ determined using 2029 quotients (Parsons <i>et al.</i> , 2013)
Absolute structure parameter	0.03 (3)	-0.031 (16)

Computer programs: *CrysAlis PRO* (Agilent, 2012), *SHELXS2014* (Sheldrick, 2008), *SHELXL2014* (Sheldrick, 2008), *WinGX* (Farrugia, 2012), *Mercury* (Macrae *et al.*, 2006), *PLATON* (Spek, 2009) and *enCIFer* (Allen *et al.*, 2004).

slow evaporation, colourless prismatic and plate-like single crystals appeared in the solution.

## 2.2. Refinement

Crystal data, data collection and structure refinement details are summarized in Table 1. The electron density of the H atoms was clearly identified in the difference density Fourier maps and their atomic coordinates and isotropic displacement parameters were refined.

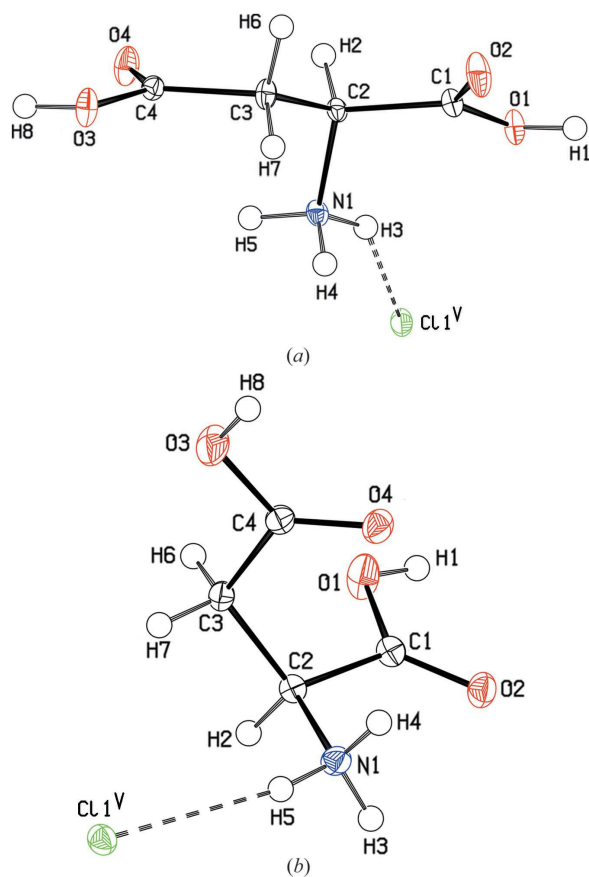
## 3. Results and discussion

The molecular structures of both polymorphs of L-aspartic acid hydrochloride are shown in Fig. 1. In both structures, the asymmetric unit contains one aspartate cation and one chloride anion linked together by weak N—H...Cl hydrogen bonds (Fig. 1), thereby showing the hybrid organic–inorganic character of these compounds. In both polymorphs, the two carboxylic acid groups remain protonated and have a typical environment of a slightly distorted  $sp^2$ -hybridization (see Table 2). It is worth noting that the O atoms of both carboxylic acid groups are displaced on either side of the mean plane of the C-atom skeleton, thereby showing that the carboxylic acid groups adopt a staggered conformation from the mean plane of the C-atom skeleton. This staggered conformation was also

found in a number of aspartic acid compounds (Dawson, 1977; Bahadur & Rajaram, 1995; Srinivasan *et al.*, 2001; Bendeif & Jelsch, 2007) and appears to be preferred over the eclipsed conformation.

Although the two polymorphs have similar features in terms of molecular dimensions (see Tables 2 and 3) and in their networks of inter-ion interactions, important differences should be noted. Firstly, polymorph (I) has a triclinic  $P1$  unit cell containing one hybrid anion–cation asymmetric unit. In contrast, polymorph (II) crystallizes in the higher symmetry orthorhombic space group  $P2_12_12$ , as do the majority of amino acid salts. This difference is a direct consequence of the different physical arrangement of molecules in the crystal, *i.e.* the crystal packing.

Another significant difference concerns the molecular conformation. In (I), the C-atom skeleton is practically extended, as shown by the C1—C2—C3—C4 torsion angle of 172.92 (13)°, whereas in (II) the four C atoms form a torsion angle of -62.11 (12)°, which allows the connection between the carboxylic acid and ammonium groups through an intracation interaction [N1—H4...O4: N1...O4 = 2.9696 (13) Å; Table 5]. This directly impacts the conformation of the carboxylic acid groups around the C2—C3 bridge bond. Indeed, in (II), the carboxylic acid groups adopt the *syn* conformation; however, they are in an *anti* conformation in (I).


**Figure 1**

The molecular structures of (a) polymorph (I) and (b) polymorph (II), showing the atom-labelling schemes. Displacement ellipsoids are drawn at the 50% probability level. The weak N—H...Cl hydrogen bonds are shown as dashed lines. For symmetry codes, see Tables 4 and 5, respectively.

The crystal structure of each of the salts can be described as a donor–acceptor adduct, in which the independent components are connected through an extensive hydrogen-bonding network (Tables 4 and 5, and Fig. 2). While these species form an alternating cation–anion layer-like structure along the *b* axis in (II), they are linked into a continuous ionic framework along the [011] direction in (I). A detailed examination of the molecular packing in both (I) and (II) reveals that the cations and anions are connected alternately by means of three N—H...Cl and O—H...Cl hydrogen bonds (Tables 4 and 5). Within the layers, each chloride anion is surrounded by three different L-aspartate cations and is consequently an acceptor of three hydrogen bonds. On the other hand, the ammonium group is involved in three inter-ion interactions, namely two N—H...O hydrogen bonds with two different carboxylic acid groups and one N—H...Cl interaction. The carboxylic acid groups act as proton acceptors and proton donors by the combination of two distinct types of inter-ion interactions and ensure therefore connection along the *b* and *c* axes (Fig. 2, and Tables 4 and 5).

In polymorph (I), the —OH groups (O1 and O3) interact with two chloride anions (Cl1<sup>iii</sup> and Cl1<sup>iv</sup>; Table 4), while the terminal O atoms (O2 and O4) act as hydrogen-bond accep-

**Table 2**

Selected geometric parameters (Å, °) for polymorph (I).

O1—C1	1.315 (2)	N1—C2	1.492 (2)
O2—C1	1.208 (2)	C1—C2	1.533 (2)
O3—C4	1.323 (2)	C2—C3	1.510 (3)
O4—C4	1.209 (2)	C3—C4	1.513 (2)
O2—C1—O1	126.37 (16)	N1—C2—C1	109.32 (13)
O2—C1—C2	121.88 (16)	O4—C4—O3	124.22 (14)
O1—C1—C2	111.72 (14)	O4—C4—C3	122.70 (14)
N1—C2—C3	111.06 (12)	O3—C4—C3	113.07 (14)
C1—C2—C3—C4	172.92 (13)		

**Table 3**

Selected geometric parameters (Å, °) for polymorph (II).

O1—C1	1.3215 (14)	N1—C2	1.4879 (14)
O2—C1	1.2079 (13)	C1—C2	1.5171 (14)
O3—C4	1.3204 (13)	C2—C3	1.5201 (14)
O4—C4	1.2165 (13)	C3—C4	1.5058 (14)
O2—C1—O1	125.47 (10)	N1—C2—C3	112.26 (8)
O2—C1—C2	122.64 (9)	O4—C4—O3	124.87 (10)
O1—C1—C2	111.84 (8)	O4—C4—C3	123.53 (9)
N1—C2—C1	107.08 (8)	O3—C4—C3	111.59 (9)
C1—C2—C3—C4	−62.11 (12)		

**Table 4**

Hydrogen-bond geometry (Å, °) for polymorph (I).

<i>D</i> —H... <i>A</i>	<i>D</i> —H	H... <i>A</i>	<i>D</i> ... <i>A</i>	<i>D</i> —H... <i>A</i>
N1—H5...O2 <sup>i</sup>	0.92 (3)	1.93 (3)	2.8030 (19)	158 (3)
N1—H4...O4 <sup>ii</sup>	0.89 (3)	2.14 (3)	2.817 (2)	132 (2)
O1—H1...Cl1 <sup>iii</sup>	0.81 (3)	2.26 (3)	3.0657 (13)	176 (3)
O3—H8...Cl1 <sup>iv</sup>	0.84 (3)	2.26 (3)	3.0909 (14)	173 (3)
N1—H5...O4	0.92 (3)	2.58 (3)	3.099 (2)	116 (2)
N1—H3...Cl1 <sup>v</sup>	0.95 (3)	2.33 (3)	3.1682 (15)	147 (2)
N1—H4...Cl1	0.89 (3)	2.66 (3)	3.3562 (15)	136 (2)
C2—H2...O3 <sup>v</sup>	0.99 (2)	2.56 (2)	3.305 (2)	132.1 (18)
C3—H7...O1 <sup>vi</sup>	0.95 (3)	2.57 (3)	3.357 (2)	141 (2)

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

**Table 5**

Hydrogen-bond geometry (Å, °) for polymorph (II).

<i>D</i> —H... <i>A</i>	<i>D</i> —H	H... <i>A</i>	<i>D</i> ... <i>A</i>	<i>D</i> —H... <i>A</i>
N1—H4...O2 <sup>i</sup>	0.876 (17)	2.400 (18)	2.8257 (13)	110.3 (14)
N1—H3...O4 <sup>ii</sup>	0.888 (18)	2.078 (18)	2.9354 (12)	162.0 (16)
N1—H4...O4	0.877 (17)	2.390 (17)	2.9696 (13)	123.9 (14)
O3—H8...Cl1 <sup>iii</sup>	0.84 (3)	2.21 (3)	3.0111 (10)	160 (2)
O1—H1...Cl1 <sup>iv</sup>	0.83 (3)	2.21 (3)	3.0320 (10)	172 (3)
N1—H5...Cl1 <sup>v</sup>	0.86 (2)	2.40 (2)	3.2487 (10)	167 (2)
N1—H4...Cl1 <sup>vi</sup>	0.876 (17)	2.766 (18)	3.5056 (10)	143.1 (14)
C2—H2...Cl1	0.963 (18)	2.650 (18)	3.4217 (10)	137.5 (15)

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

tors from two different ammonium groups (N1—H5...O2<sup>i</sup> and N1—H4...O4<sup>ii</sup>; Table 4). Interestingly, all these inter-ion interactions are also present in the hydrogen-bonding network of polymorph (II) (Table 5).

Besides these hydrogen bonds, the crystal packing in (II) is also characterized by short inter-ion contacts established between two neighbouring carboxylic acid groups [O2...O2<sup>iv</sup> = 3.0252 (14) Å; symmetry code: (iv)  $-x + 1$ ,

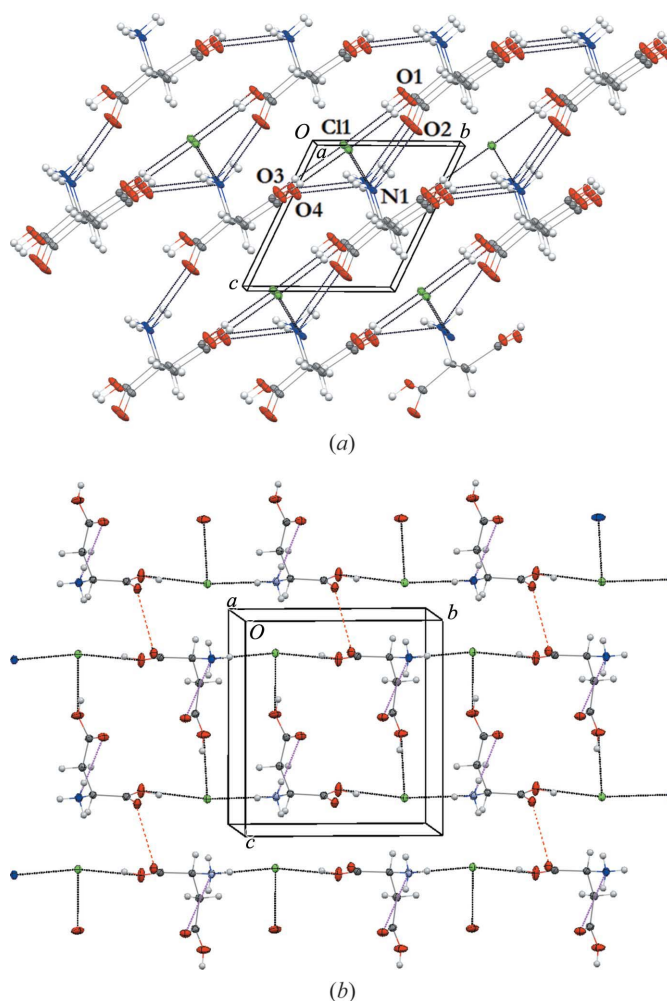
$-y + 1, z]$ . This is probably due to the conformation of the L-aspartate cation, as explained above.

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Supporting information for this paper is available from the IUCr electronic archives (Reference: SK3547).

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**Figure 2**

The molecular packing of (a) polymorph (I) and (b) polymorph (II), viewed along the *a* axis, showing the different intra- (pink) and inter-ion interactions (black). Additional O...O contacts in (II) are shown with red dashed lines. Displacement ellipsoids are drawn at the 50% probability level.

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## supporting information

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## A comparative study of two polymorphs of L-aspartic acid hydrochloride

Rim Benali-Cherif, Radhwane Takouachet, El-Eulmi Bendeif and Nourredine Benali-Cherif

### Computing details

For both compounds, data collection: *CrysAlis PRO* (Agilent, 2012); cell refinement: *CrysAlis PRO* (Agilent, 2012); data reduction: *CrysAlis PRO* (Agilent, 2012); program(s) used to solve structure: *SHELXS2014* (Sheldrick, 2008); program(s) used to refine structure: *SHELXL2014* (Sheldrick, 2008) and *WinGX* (Farrugia, 2012); molecular graphics: *Mercury* (Macrae *et al.*, 2006) and *PLATON* (Spek, 2003).; software used to prepare material for publication: *enCIFer* (Allen *et al.*, 2004).

### (I) L-Aspartic acid hydrochloride

#### Crystal data

$C_4H_8NO_4^+ \cdot Cl^-$

$M_r = 169.56$

Triclinic, *P1*

$a = 5.5888$  (5) Å

$b = 5.6045$  (6) Å

$c = 6.1697$  (7) Å

$\alpha = 114.57$  (1)°

$\beta = 97.752$  (9)°

$\gamma = 95.720$  (8)°

$V = 171.52$  (3) Å<sup>3</sup>

$Z = 1$

$F(000) = 88$

$D_x = 1.642$  Mg m<sup>-3</sup>

Mo *K* $\alpha$  radiation,  $\lambda = 0.71073$  Å

Cell parameters from 4428 reflections

$\theta = 3.7$ – $32.8$ °

$\mu = 0.51$  mm<sup>-1</sup>

$T = 100$  K

Prism, colourless

$0.14 \times 0.09 \times 0.06$  mm

#### Data collection

Agilent SuperNova (Dual, Cu at zero, Atlas) diffractometer

Radiation source: SuperNova (Mo) X-ray Source

Detector resolution: 10.4508 pixels mm<sup>-1</sup>

$\omega$  scans

Absorption correction: analytical  
[*CrysAlis PRO* (Agilent, 2012), using a multifaceted crystal model based on expressions derived by Clark & Reid (1995)]

$T_{\min} = 0.963$ ,  $T_{\max} = 0.981$

4428 measured reflections

2273 independent reflections

2259 reflections with  $I > 2\sigma(I)$

$R_{\text{int}} = 0.020$

$\theta_{\max} = 32.8$ °,  $\theta_{\min} = 3.7$ °

$h = -8 \rightarrow 8$

$k = -8 \rightarrow 8$

$l = -9 \rightarrow 9$

#### Refinement

Refinement on  $F^2$

Least-squares matrix: full

$R[F^2 > 2\sigma(F^2)] = 0.022$

$wR(F^2) = 0.054$

$S = 1.05$

2273 reflections

123 parameters

3 restraints

Primary atom site location: structure-invariant direct methods

Secondary atom site location: difference Fourier map

Hydrogen site location: difference Fourier map

All H-atom parameters refined

$$w = 1/[\sigma^2(F_o^2) + (0.033P)^2]$$

where  $P = (F_o^2 + 2F_c^2)/3$   
 $(\Delta/\sigma)_{\max} = 0.001$   
 $\Delta\rho_{\max} = 0.30 \text{ e } \text{\AA}^{-3}$   
 $\Delta\rho_{\min} = -0.18 \text{ e } \text{\AA}^{-3}$

Absolute structure: Flack  $x$  determined using  
 1069 quotients [(I+)-(I-)]/[(I+)+(I-)] (Parsons *et al.*, 2013)  
 Absolute structure parameter: 0.03 (3)

*Special details*

**Experimental.** Absorption correction: CrysAlisPro (2012), Agilent Technologies UK Ltd, Oxford, UK, Version 1.171.36.24 (release 03-12-2012 CrysAlis171 .NET) (compiled Dec 3 2012,18:21:49) Analytical numeric absorption correction using a multifaceted crystal model based on expressions derived by Clark & Reid, 1995.

**Geometry.** All e.s.d.'s (except the e.s.d. in the dihedral angle between two l.s. planes) are estimated using the full covariance matrix. The cell e.s.d.'s are taken into account individually in the estimation of e.s.d.'s in distances, angles and torsion angles; correlations between e.s.d.'s in cell parameters are only used when they are defined by crystal symmetry. An approximate (isotropic) treatment of cell e.s.d.'s is used for estimating e.s.d.'s involving l.s. planes.

**Refinement.** Refinement of  $F^2$  against ALL reflections. The weighted  $R$ -factor  $wR$  and goodness of fit  $S$  are based on  $F^2$ , conventional  $R$ -factors  $R$  are based on  $F$ , with  $F$  set to zero for negative  $F^2$ . The threshold expression of  $F^2 > 2\sigma(F^2)$  is used only for calculating  $R$ -factors(gt) *etc.* and is not relevant to the choice of reflections for refinement.  $R$ -factors based on  $F^2$  are statistically about twice as large as those based on  $F$ , and  $R$ -factors based on ALL data will be even larger.

*Fractional atomic coordinates and isotropic or equivalent isotropic displacement parameters ( $\text{\AA}^2$ )*

	$x$	$y$	$z$	$U_{\text{iso}}^*/U_{\text{eq}}$
C11	0.33694 (3)	0.19280 (4)	0.00641 (3)	0.01163 (9)
O1	1.1985 (2)	0.4542 (3)	0.6692 (2)	0.0134 (2)
O2	0.8786 (3)	0.5621 (3)	0.8553 (2)	0.0200 (3)
O3	0.3787 (2)	0.9020 (3)	0.3361 (2)	0.0156 (3)
O4	0.7723 (2)	1.0058 (3)	0.3238 (2)	0.0169 (3)
N1	0.9237 (3)	0.4702 (3)	0.2710 (2)	0.0096 (2)
C1	0.9953 (3)	0.5527 (4)	0.7016 (3)	0.0110 (3)
C2	0.9217 (3)	0.6696 (3)	0.5227 (3)	0.0087 (3)
C3	0.6740 (3)	0.7536 (3)	0.5416 (3)	0.0110 (3)
C4	0.6157 (3)	0.8998 (3)	0.3881 (3)	0.0100 (3)
H1	1.228 (6)	0.381 (7)	0.756 (6)	0.039 (9)*
H2	1.049 (4)	0.826 (5)	0.561 (4)	0.008 (5)*
H3	1.074 (5)	0.403 (6)	0.259 (5)	0.023 (7)*
H4	0.806 (5)	0.331 (6)	0.226 (5)	0.023 (6)*
H5	0.894 (5)	0.539 (6)	0.160 (5)	0.028 (7)*
H6	0.669 (5)	0.880 (5)	0.712 (4)	0.013 (6)*
H7	0.544 (5)	0.609 (6)	0.497 (5)	0.020 (6)*
H8	0.353 (5)	0.978 (6)	0.245 (5)	0.026 (7)*

*Atomic displacement parameters ( $\text{\AA}^2$ )*

	$U^{11}$	$U^{22}$	$U^{33}$	$U^{12}$	$U^{13}$	$U^{23}$
C11	0.01271 (15)	0.01316 (16)	0.01092 (14)	0.00439 (11)	0.00192 (11)	0.00671 (11)
O1	0.0120 (6)	0.0198 (6)	0.0144 (5)	0.0055 (5)	0.0030 (4)	0.0125 (5)
O2	0.0207 (6)	0.0352 (8)	0.0165 (6)	0.0132 (6)	0.0095 (5)	0.0195 (6)
O3	0.0114 (6)	0.0211 (6)	0.0223 (6)	0.0060 (5)	0.0041 (5)	0.0163 (5)
O4	0.0127 (5)	0.0209 (6)	0.0250 (6)	0.0030 (5)	0.0040 (5)	0.0176 (5)
N1	0.0110 (5)	0.0123 (6)	0.0078 (5)	0.0030 (5)	0.0031 (5)	0.0058 (5)



C1	0.0104 (7)	0.0139 (7)	0.0103 (6)	0.0028 (5)	0.0012 (5)	0.0069 (5)
C2	0.0099 (6)	0.0101 (7)	0.0072 (6)	0.0020 (5)	0.0017 (5)	0.0049 (5)
C3	0.0111 (7)	0.0144 (7)	0.0123 (7)	0.0050 (6)	0.0044 (5)	0.0091 (6)
C4	0.0103 (7)	0.0101 (7)	0.0100 (7)	0.0031 (5)	0.0019 (5)	0.0045 (6)

*Geometric parameters (Å, °)*

O1—C1	1.315 (2)	N1—H4	0.89 (3)
O1—H1	0.81 (3)	N1—H5	0.92 (3)
O2—C1	1.208 (2)	C1—C2	1.533 (2)
O3—C4	1.323 (2)	C2—C3	1.510 (3)
O3—H8	0.84 (3)	C2—H2	0.99 (2)
O4—C4	1.209 (2)	C3—C4	1.513 (2)
N1—C2	1.492 (2)	C3—H6	1.00 (3)
N1—H3	0.95 (3)	C3—H7	0.95 (3)
C1—O1—H1	111 (2)	C3—C2—C1	111.37 (13)
C4—O3—H8	110 (2)	N1—C2—H2	107.2 (13)
C2—N1—H3	112.2 (16)	C3—C2—H2	110.1 (14)
C2—N1—H4	109.9 (19)	C1—C2—H2	107.7 (13)
H3—N1—H4	106 (3)	C2—C3—C4	111.26 (13)
C2—N1—H5	112 (2)	C2—C3—H6	111.3 (15)
H3—N1—H5	109 (2)	C4—C3—H6	106.2 (15)
H4—N1—H5	107 (2)	C2—C3—H7	113.3 (17)
O2—C1—O1	126.37 (16)	C4—C3—H7	108.9 (16)
O2—C1—C2	121.88 (16)	H6—C3—H7	105 (2)
O1—C1—C2	111.72 (14)	O4—C4—O3	124.22 (14)
N1—C2—C3	111.06 (12)	O4—C4—C3	122.70 (14)
N1—C2—C1	109.32 (13)	O3—C4—C3	113.07 (14)
O2—C1—C2—N1	-131.63 (18)	N1—C2—C3—C4	-64.97 (17)
O1—C1—C2—N1	50.39 (19)	C1—C2—C3—C4	172.92 (13)
O2—C1—C2—C3	-8.5 (2)	C2—C3—C4—O4	-21.3 (2)
O1—C1—C2—C3	173.49 (14)	C2—C3—C4—O3	159.64 (14)

*Hydrogen-bond geometry (Å, °)*

<i>D</i> —H $\cdots$ <i>A</i>	<i>D</i> —H	H $\cdots$ <i>A</i>	<i>D</i> $\cdots$ <i>A</i>	<i>D</i> —H $\cdots$ <i>A</i>
N1—H5 $\cdots$ O2 <sup>i</sup>	0.92 (3)	1.93 (3)	2.8030 (19)	158 (3)
N1—H4 $\cdots$ O4 <sup>ii</sup>	0.89 (3)	2.14 (3)	2.817 (2)	132 (2)
O1—H1 $\cdots$ C11 <sup>iii</sup>	0.81 (3)	2.26 (3)	3.0657 (13)	176 (3)
O3—H8 $\cdots$ C11 <sup>iv</sup>	0.84 (3)	2.26 (3)	3.0909 (14)	173 (3)
N1—H5 $\cdots$ O4	0.92 (3)	2.58 (3)	3.099 (2)	116 (2)
N1—H3 $\cdots$ C11 <sup>v</sup>	0.95 (3)	2.33 (3)	3.1682 (15)	147 (2)
N1—H4 $\cdots$ C11	0.89 (3)	2.66 (3)	3.3562 (15)	136 (2)

C2—H2...O3 <sup>v</sup>	0.99 (2)	2.56 (2)	3.305 (2)	132.1 (18)
C3—H7...O1 <sup>vi</sup>	0.95 (3)	2.57 (3)	3.357 (2)	141 (2)

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

## (II) L-Aspartic acid hydrochloride

### Crystal data

$C_4H_8NO_4^+ \cdot Cl^-$

$M_r = 169.56$

Orthorhombic,  $P2_12_12$

$a = 9.7082$  (2) Å

$b = 8.9123$  (3) Å

$c = 8.4820$  (2) Å

$V = 733.88$  (3) Å<sup>3</sup>

$Z = 4$

$F(000) = 352$

$D_x = 1.535$  Mg m<sup>-3</sup>

Mo  $K\alpha$  radiation,  $\lambda = 0.71073$  Å

Cell parameters from 17470 reflections

$\theta = 3.2$ – $45.5^\circ$

$\mu = 0.48$  mm<sup>-1</sup>

$T = 100$  K

Prism, colourless

$0.20 \times 0.14 \times 0.12$  mm

### Data collection

Agilent SuperNova (Dual, Cu at zero, Atlas) diffractometer

Radiation source: SuperNova (Mo) X-ray Source

Detector resolution: 10.4508 pixels mm<sup>-1</sup>

$\omega$  scans

Absorption correction: analytical

[*CrysAlis PRO* (Agilent, 2012), using a multifaceted crystal model based on expressions derived by Clark & Reid (1995)]

$T_{\min} = 0.936$ ,  $T_{\max} = 0.955$

17470 measured reflections

6012 independent reflections

5353 reflections with  $I > 2\sigma(I)$

$R_{\text{int}} = 0.027$

$\theta_{\max} = 45.5^\circ$ ,  $\theta_{\min} = 3.2^\circ$

$h = -19 \rightarrow 19$

$k = -17 \rightarrow 12$

$l = -16 \rightarrow 17$

### Refinement

Refinement on  $F^2$

Least-squares matrix: full

$R[F^2 > 2\sigma(F^2)] = 0.037$

$wR(F^2) = 0.090$

$S = 1.04$

6012 reflections

123 parameters

0 restraints

Primary atom site location: structure-invariant direct methods

Secondary atom site location: difference Fourier map

Hydrogen site location: difference Fourier map

All H-atom parameters refined

$w = 1/[\sigma^2(F_o^2) + (0.0448P)^2 + 0.017P]$

where  $P = (F_o^2 + 2F_c^2)/3$

$(\Delta/\sigma)_{\max} = 0.003$

$\Delta\rho_{\max} = 0.46$  e Å<sup>-3</sup>

$\Delta\rho_{\min} = -0.57$  e Å<sup>-3</sup>

Absolute structure: Flack  $x$  determined using

2029 quotients [(I+)-(I-)]/[(I+)+(I-)] (Parsons *et al.*, 2013)

Absolute structure parameter:  $-0.031$  (16)

### Special details

**Experimental.** Absorption correction: *CrysAlisPro* (2012), Agilent Technologies UK Ltd, Oxford, UK, Version 1.171.36.24 (release 03-12-2012 *CrysAlis171 .NET*) (compiled Dec 3 2012, 18:21:49) Analytical numeric absorption correction using a multifaceted crystal model based on expressions derived by Clark & Reid, 1995.

**Geometry.** All e.s.d.'s (except the e.s.d. in the dihedral angle between two l.s. planes) are estimated using the full covariance matrix. The cell e.s.d.'s are taken into account individually in the estimation of e.s.d.'s in distances, angles and torsion angles; correlations between e.s.d.'s in cell parameters are only used when they are defined by crystal symmetry. An approximate (isotropic) treatment of cell e.s.d.'s is used for estimating e.s.d.'s involving l.s. planes.

**Refinement.** Refinement of  $F^2$  against ALL reflections. The weighted  $R$ -factor  $wR$  and goodness of fit  $S$  are based on  $F^2$ , conventional  $R$ -factors  $R$  are based on  $F$ , with  $F$  set to zero for negative  $F^2$ . The threshold expression of  $F^2 > 2\sigma(F^2)$  is used only for calculating  $R$ -factors(gt) *etc.* and is not relevant to the choice of reflections for refinement.  $R$ -factors based on  $F^2$  are statistically about twice as large as those based on  $F$ , and  $R$ -factors based on ALL data will be even larger.

Fractional atomic coordinates and isotropic or equivalent isotropic displacement parameters ( $\text{\AA}^2$ )

	$x$	$y$	$z$	$U_{\text{iso}}^*/U_{\text{eq}}$
C11	0.66179 (2)	0.17292 (3)	0.26316 (3)	0.01443 (5)
O1	0.30341 (12)	0.50000 (11)	0.17327 (10)	0.02335 (19)
O2	0.34892 (10)	0.45850 (9)	0.42956 (9)	0.01692 (14)
O3	-0.04610 (10)	0.18092 (13)	0.14412 (12)	0.0262 (2)
O4	0.04221 (9)	0.29182 (10)	0.35986 (10)	0.01801 (15)
N1	0.32151 (10)	0.16396 (11)	0.40818 (11)	0.01400 (13)
C1	0.32323 (10)	0.41414 (12)	0.29825 (12)	0.01320 (15)
C2	0.31630 (9)	0.24865 (11)	0.25713 (12)	0.01193 (13)
C3	0.19377 (10)	0.20373 (12)	0.15602 (12)	0.01299 (15)
C4	0.05605 (10)	0.23073 (11)	0.23259 (13)	0.01351 (15)
H1	0.322 (3)	0.587 (4)	0.200 (4)	0.070 (9)*
H2	0.3993 (18)	0.227 (2)	0.199 (2)	0.020 (4)*
H3	0.3987 (18)	0.184 (2)	0.460 (2)	0.020 (4)*
H4	0.2485 (17)	0.185 (2)	0.465 (2)	0.016 (4)*
H5	0.328 (3)	0.070 (3)	0.386 (3)	0.042 (6)*
H6	0.1978 (19)	0.255 (2)	0.061 (2)	0.020 (4)*
H7	0.201 (2)	0.103 (2)	0.127 (2)	0.019 (4)*
H8	-0.119 (3)	0.192 (3)	0.195 (3)	0.046 (6)*

Atomic displacement parameters ( $\text{\AA}^2$ )

	$U^{11}$	$U^{22}$	$U^{33}$	$U^{12}$	$U^{13}$	$U^{23}$
C11	0.01398 (8)	0.01229 (9)	0.01702 (9)	0.00002 (7)	0.00008 (7)	0.00187 (7)
O1	0.0429 (6)	0.0118 (3)	0.0153 (3)	-0.0024 (3)	-0.0019 (3)	0.0018 (3)
O2	0.0210 (4)	0.0143 (3)	0.0155 (3)	-0.0013 (3)	-0.0019 (3)	-0.0028 (2)
O3	0.0128 (3)	0.0382 (5)	0.0277 (5)	-0.0020 (3)	-0.0017 (3)	-0.0158 (4)
O4	0.0143 (3)	0.0265 (4)	0.0132 (3)	0.0004 (3)	0.0012 (2)	-0.0036 (3)
N1	0.0161 (3)	0.0119 (3)	0.0140 (3)	0.0002 (3)	-0.0025 (3)	0.0010 (3)
C1	0.0132 (3)	0.0121 (3)	0.0142 (3)	-0.0008 (3)	0.0012 (3)	-0.0001 (3)
C2	0.0121 (3)	0.0116 (3)	0.0121 (3)	0.0000 (2)	0.0006 (3)	-0.0003 (3)
C3	0.0136 (3)	0.0141 (4)	0.0113 (3)	0.0003 (3)	-0.0002 (3)	-0.0022 (3)
C4	0.0122 (3)	0.0142 (4)	0.0142 (4)	-0.0005 (3)	-0.0007 (3)	-0.0009 (3)

Geometric parameters ( $\text{\AA}$ ,  $^\circ$ )

O1—C1	1.3215 (14)	N1—H4	0.876 (17)
O1—H1	0.83 (3)	N1—H5	0.86 (2)
O2—C1	1.2079 (13)	C1—C2	1.5171 (14)
O3—C4	1.3204 (13)	C2—C3	1.5201 (14)
O3—H8	0.84 (3)	C2—H2	0.963 (18)

O4—C4	1.2165 (13)	C3—C4	1.5058 (14)
N1—C2	1.4879 (14)	C3—H6	0.929 (18)
N1—H3	0.888 (18)	C3—H7	0.937 (18)
C1—O1—H1	107 (2)	C1—C2—C3	114.86 (8)
C4—O3—H8	107.7 (18)	N1—C2—H2	108.0 (12)
C2—N1—H3	110.6 (12)	C1—C2—H2	105.9 (11)
C2—N1—H4	109.7 (12)	C3—C2—H2	108.3 (11)
H3—N1—H4	111.7 (15)	C4—C3—C2	114.17 (8)
C2—N1—H5	107.9 (16)	C4—C3—H6	109.5 (12)
H3—N1—H5	104 (2)	C2—C3—H6	109.2 (12)
H4—N1—H5	113 (2)	C4—C3—H7	109.7 (12)
O2—C1—O1	125.47 (10)	C2—C3—H7	110.0 (12)
O2—C1—C2	122.64 (9)	H6—C3—H7	103.8 (16)
O1—C1—C2	111.84 (8)	O4—C4—O3	124.87 (10)
N1—C2—C1	107.08 (8)	O4—C4—C3	123.53 (9)
N1—C2—C3	112.26 (8)	O3—C4—C3	111.59 (9)
O2—C1—C2—N1	9.71 (13)	N1—C2—C3—C4	60.53 (11)
O1—C1—C2—N1	-172.76 (9)	C1—C2—C3—C4	-62.11 (12)
O2—C1—C2—C3	135.10 (10)	C2—C3—C4—O4	4.49 (15)
O1—C1—C2—C3	-47.36 (13)	C2—C3—C4—O3	-175.92 (10)

Hydrogen-bond geometry (Å, °)

<i>D</i> —H... <i>A</i>	<i>D</i> —H	H... <i>A</i>	<i>D</i> ... <i>A</i>	<i>D</i> —H... <i>A</i>
N1—H4...O2 <sup>i</sup>	0.876 (17)	2.400 (18)	2.8257 (13)	110.3 (14)
N1—H3...O4 <sup>ii</sup>	0.888 (18)	2.078 (18)	2.9354 (12)	162.0 (16)
N1—H4...O4	0.877 (17)	2.390 (17)	2.9696 (13)	123.9 (14)
O3—H8...C11 <sup>iii</sup>	0.84 (3)	2.21 (3)	3.0111 (10)	160 (2)
O1—H1...C11 <sup>iv</sup>	0.83 (3)	2.21 (3)	3.0320 (10)	172 (3)
N1—H5...C11 <sup>v</sup>	0.86 (2)	2.40 (2)	3.2487 (10)	167 (2)
N1—H4...C11 <sup>vi</sup>	0.876 (17)	2.766 (18)	3.5056 (10)	143.1 (14)
C2—H2...C11	0.963 (18)	2.650 (18)	3.4217 (10)	137.5 (15)

Symmetry codes: (i)  $-x+1/2, y-1/2, -z+1$ ; (ii)  $x+1/2, -y+1/2, -z+1$ ; (iii)  $x-1, y, z$ ; (iv)  $-x+1, -y+1, z$ ; (v)  $-x+1, -y, z$ ; (vi)  $x-1/2, -y+1/2, -z+1$ .