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Crystal structure of (*S*)-2-amino-2-methylsuccinic acid

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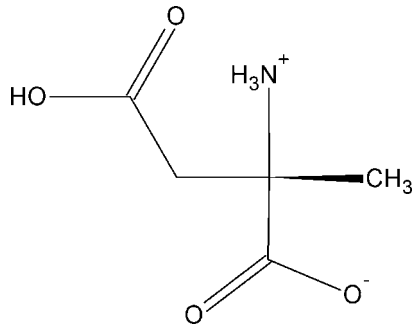
The title compound, $C_5H_9NO_4$, crystallized as a zwitterion. There is an intramolecular N—H···O hydrogen bond involving the *trans*-succinic acid and the ammonium group, forming an *S*(6) ring motif. In the crystal, molecules are linked by O—H···O hydrogen bonds, forming *C*(7) chains along the *c*-axis direction. The chains are linked by N—H···O and C—H···O hydrogen bonds, forming sheets parallel to the *bc* plane. Further N—H···O hydrogen bonds link the sheets to form a three-dimensional framework.

Keywords: crystal structure; succinic acid; zwitterion; hydrogen bonding; three-dimensional framework.

CCDC reference: 1422827

1. Related literature

For general background and biological properties of 2-methylaspartic acid (MeASP), see: Pfeiffer & Heinrich (1936); Delbaere *et al.* (1989); Nobe *et al.* (1998). For the absolute configuration and synthesis of the title compound, see: Terashima *et al.* (1966). For the crystal structure of related racemic compounds, see: Derricott *et al.* (1979); Brewer *et al.* (2013). For the crystal structure of DL-ASP, see: Flaig *et al.* (1998).



2. Experimental

2.1. Crystal data

$C_5H_9NO_4$
M_r = 147.13
Monoclinic, *C*2
a = 8.3398 (12) Å
b = 9.6725 (10) Å
c = 8.0671 (10) Å
β = 95.175 (5)°
V = 648.09 (14) Å^3
Z = 4
Cu *K*α radiation
μ = 1.14 mm^{-1}
T = 297 K
0.4 × 0.2 × 0.2 mm

2.2. Data collection

Enraf–Nonius CAD-4 diffractometer
Absorption correction: ψ scan (North *et al.*, 1968)
T_{min} = 0.76, T_{max} = 0.81
843 measured reflections
700 independent reflections
699 reflections with $I > 2\sigma(I)$
R_{int} = 0.019
3 standard reflections every 300 reflections
intensity decay: none

2.3. Refinement

$R[F^2 > 2\sigma(F^2)]$ = 0.034
$wR(F^2)$ = 0.096
S = 1.27
700 reflections
109 parameters
2 restraints
H atoms treated by a mixture of independent and constrained refinement
$\Delta\rho_{max}$ = 0.29 e Å^{-3}
$\Delta\rho_{min}$ = −0.21 e Å^{-3}

Table 1
Hydrogen-bond geometry (Å, °).

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
N1—H7···O4	0.79 (4)	2.23 (4)	2.798 (3)	130 (3)
O3—H6···O1^{i}	0.84 (4)	1.70 (4)	2.543 (2)	177 (5)
N1—H7···O3^{ii}	0.79 (4)	2.53 (4)	3.093 (3)	130 (3)
N1—H8···O2^{iii}	0.86 (3)	1.90 (4)	2.754 (3)	170 (3)
N1—H9···O1^{iv}	0.93 (3)	1.93 (4)	2.844 (3)	168 (4)
C3—H3*B*···O4^{v}	0.97	2.52	3.279 (4)	135

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

Data collection: *CAD-4 Software* (Enraf–Nonius, 1989); cell refinement: *CAD-4 Software*; data reduction: *XCAD4* (Harms & Wocadlo, 1995); program(s) used to solve structure: *SHELXS97* (Sheldrick, 2008); program(s) used to refine structure: *SHELXL2014* (Sheldrick, 2015); molecular graphics: *ORTEP-3* for Windows (Farrugia, 2012) and *Mercury* (Macrae *et al.*, 2008); software used to prepare material for publication: *PLATON* (Spek, 2003) and *WinGX* (Farrugia, 2012).

Acknowledgements

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Supporting information for this paper is available from the IUCr electronic archives (Reference: SU5203).

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supporting information

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Crystal structure of (*S*)-2-amino-2-methylsuccinic acid

Isao Fujii

S1. Comment

Solid-phase synthesis is now the accepted method to synthesis peptides, in which protected natural or non-natural amino acids are widely used; for example, 2-methylaspartic acid (MeASP) a non-natural amino acid. It has attracted attention as a substrate analog of aspartate aminotransferase (EC 2.6.1.1), and acts as a competitive inhibitor in the external aldimine (Delbaere *et al.*, 1989; Nobe *et al.*, 1998). Despite the biological and pharmaceutical interest, no crystal structures of MeASP derivatives have been reported except for the structure of DL-MeASP monohydrate (Brewer *et al.*, 2013).

In the title compound, Fig. 1, the succinic acid group has a *trans*-conformation [C1—C2—C3—C4 = -177.1 (2)°] *versus*. a *cis*-conformation [48.8 (4) °] in DL-MeASP. The carboxy group and the amino group make a hydrogen bonded half-chair S(6) ring motif (Table 1 and Fig. 1). The S(6) ring half-chair conformation and the *trans*-succinic acid arrangement are similar to the situation found in for DL-ASP (DLASPA03: Flaig *et al.* 1998).

In the crystal, molecules are linked by O—H···O hydrogen bonds, involving the succinic acid groups, to form C(7) chains along the *c* axis direction (Table 1 and Fig. 2). This is in contrast to the N—H···O hydrogen bonded C(5) chains observed in the crystal structure of DL-MeASP. The chains are linked by N—H···O and C—H···O hydrogen bonds forming sheets parallel to the *bc* plane. Further N—H···O hydrogen bonds link the sheets to form a three-dimensional framework (Table 1 and Fig. 3). The methyl groups are surrounded by the hydrophilic planes and make a columnar structure (Fig. 3).

S2. Synthesis and crystallization

The title compound was purchased from Nagase-Sangyo Co. Ltd. The absolute configuration could not be established by anomalous-dispersion effects. The (*S*) enantiomer has been chosen by referring the sign of known polarity in the synthetic procedure (Terashima *et al.*, 1966). Rod-like colourless crystals of the title compound were obtained by vapour-phase diffusion of an ethanol-chloroform mixture at room temperature.

S3. Refinement

Crystal data, data collection and structure refinement details are summarized in Table 2. All the H atoms were located in difference Fourier maps. The NH2 and OH H atoms were freely refined. The C-bound H atoms were included in calculated positions and treated as riding atoms: C–H = 0.96-0.97 Å with U_{iso}(H) = 1.5U_{eq}(C) for methyl H atoms and 1.2U_{eq}(C) for other H atoms.

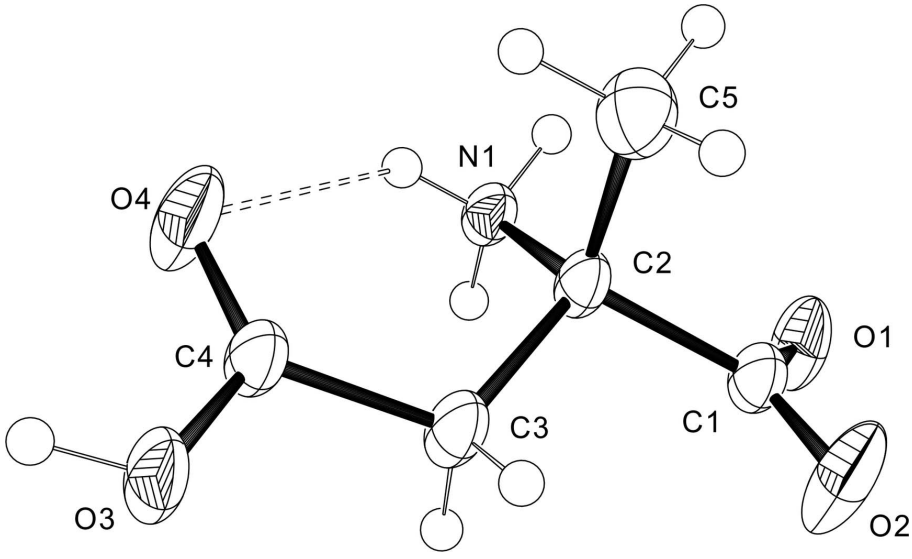

Figure 1

A view of the molecular structure of the title compound, with atom labelling. Displacement ellipsoids are drawn at the 50% probability level. The dashed line indicates the intramolecular N—H···O hydrogen bond (see Table 1).

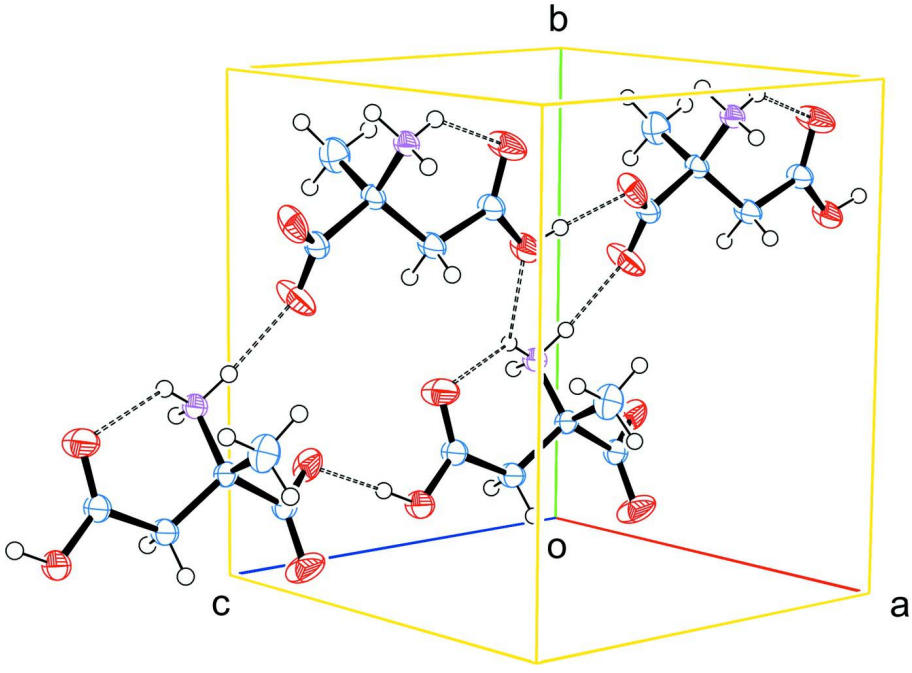

Figure 2

A partial view of the crystal packing of the title compound. Dashed lines indicate the O—H···O and N—H···O hydrogen bonds (see Table 1).

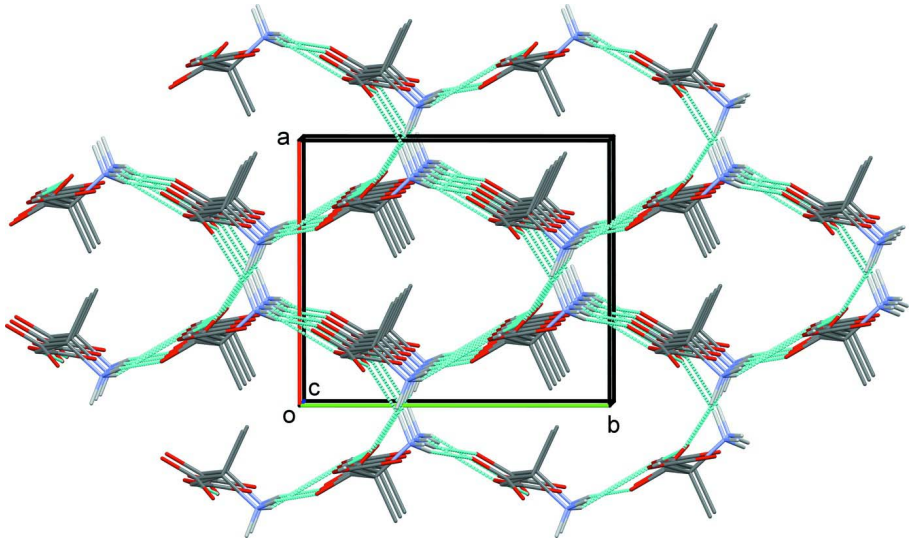

Figure 3

A view along the *c* axis of the crystal packing of the title compound. Dashed lines indicate the O—H···O and N—H···O hydrogen bonds (see Table 1), and C-bound H atoms have been omitted for clarity.

(*S*)-2-Amino-2-methylsuccinic acid

Crystal data

$C_5H_9NO_4$
M_r = 147.13
Monoclinic, *C*2
Hall symbol: C 2y
a = 8.3398 (12) Å
b = 9.6725 (10) Å
c = 8.0671 (10) Å
β = 95.175 (5)°
V = 648.09 (14) Å^3
Z = 4
F(000) = 312
D_x = 1.508 Mg m^{-3}
Cu *Kα* radiation, *λ* = 1.54178 Å
Cell parameters from 25 reflections
θ = 20–28°
μ = 1.14 mm^{-1}
T = 297 K
Rod, colorless
0.4 × 0.2 × 0.2 mm

Data collection

Enraf–Nonius CAD-4 diffractometer
Radiation source: sealed X-ray tube
Graphite monochromator
ω/2*θ* scans
Absorption correction: *ψ* scan (North *et al.*, 1968)
T_{min} = 0.76, T_{max} = 0.81
843 measured reflections
700 independent reflections
699 reflections with $I > 2\sigma(I)$
R_{int} = 0.019
θ_{max} = 74.0°, θ_{min} = 5.5°
h = −10→1
k = −12→0
l = −10→10
3 standard reflections every 300 reflections
intensity decay: none

Refinement

Refinement on F^2
Least-squares matrix: full
$R[F^2 > 2\sigma(F^2)]$ = 0.034
$wR(F^2)$ = 0.096
S = 1.27
700 reflections
109 parameters
2 restraints
Primary atom site location: structure-invariant direct methods
Secondary atom site location: difference Fourier map

Hydrogen site location: mixed
H atoms treated by a mixture of independent and constrained refinement
$w = 1/[\sigma^2(F_o^2) + (0.0559P)^2 + 0.2563P]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max} < 0.001$

$\Delta\rho_{max} = 0.29$ e Å^{-3}
$\Delta\rho_{min} = -0.21$ e Å^{-3}
Extinction correction: *SHELXL2014* (Sheldrick, 2014), $Fc^* = kFc[1+0.001xFc^2\lambda^3/\sin(2\theta)]^{-1/4}$
Extinction coefficient: 0.045 (4)

Special details

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.

Fractional atomic coordinates and isotropic or equivalent isotropic displacement parameters (Å²)

	x	*y*	*z*	U_{iso}*/U_{eq}
H8	0.155 (3)	0.434 (4)	0.122 (4)	0.026 (7)*
H7	0.126 (4)	0.416 (4)	0.275 (5)	0.040 (9)*
H6	0.207 (5)	0.170 (5)	0.725 (4)	0.071 (14)*
H9	0.022 (4)	0.340 (4)	0.164 (4)	0.040 (9)*
C1	0.2417 (3)	0.1802 (3)	0.0388 (3)	0.0273 (5)
C2	0.2485 (3)	0.2608 (2)	0.2046 (3)	0.0238 (5)
C3	0.2132 (3)	0.1603 (3)	0.3436 (3)	0.0305 (6)
H3A	0.1108	0.1156	0.3124	0.037*
H3B	0.2954	0.0891	0.3512	0.037*
C4	0.2069 (3)	0.2244 (3)	0.5137 (3)	0.0284 (6)
C5	0.4148 (3)	0.3267 (4)	0.2343 (4)	0.0386 (7)
H5A	0.4277	0.3947	0.1498	0.058*
H5B	0.4959	0.2567	0.2301	0.058*
H5C	0.4254	0.3702	0.3417	0.058*
N1	0.1250 (3)	0.3741 (2)	0.1916 (3)	0.0248 (5)
O1	0.1677 (2)	0.2358 (2)	−0.0871 (2)	0.0378 (5)
O2	0.3164 (3)	0.0705 (2)	0.0427 (3)	0.0525 (7)
O3	0.2242 (3)	0.1339 (2)	0.6334 (2)	0.0392 (6)
O4	0.1831 (4)	0.3463 (2)	0.5370 (2)	0.0554 (7)

Atomic displacement parameters (Å²)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
C1	0.0384 (11)	0.0263 (12)	0.0177 (10)	0.0010 (10)	0.0051 (8)	−0.0020 (9)
C2	0.0349 (10)	0.0220 (11)	0.0147 (10)	0.0029 (9)	0.0028 (8)	−0.0013 (8)
C3	0.0520 (14)	0.0239 (13)	0.0157 (10)	0.0039 (11)	0.0039 (9)	−0.0005 (9)
C4	0.0436 (13)	0.0252 (12)	0.0164 (10)	0.0015 (10)	0.0025 (9)	−0.0014 (9)
C5	0.0342 (12)	0.0476 (17)	0.0338 (13)	−0.0022 (12)	0.0020 (10)	−0.0065 (12)
N1	0.0368 (11)	0.0213 (10)	0.0164 (9)	0.0008 (8)	0.0036 (7)	−0.0007 (8)
O1	0.0510 (10)	0.0455 (11)	0.0167 (8)	0.0152 (9)	0.0011 (7)	−0.0039 (8)
O2	0.0930 (17)	0.0383 (13)	0.0257 (10)	0.0290 (13)	0.0023 (10)	−0.0082 (9)
O3	0.0721 (13)	0.0304 (10)	0.0162 (9)	0.0085 (9)	0.0096 (8)	0.0010 (8)
O4	0.118 (2)	0.0290 (12)	0.0200 (9)	0.0126 (12)	0.0102 (10)	−0.0024 (8)

Geometric parameters (Å, º)

C1—O2	1.229 (3)	C4—O4	1.213 (4)
C1—O1	1.261 (3)	C4—O3	1.301 (3)
C1—C2	1.545 (3)	C5—H5A	0.9600
C2—N1	1.502 (3)	C5—H5B	0.9600
C2—C5	1.525 (3)	C5—H5C	0.9600
C2—C3	1.532 (3)	N1—H8	0.86 (4)
C3—C4	1.511 (3)	N1—H7	0.78 (4)
C3—H3A	0.9700	N1—H9	0.93 (4)
C3—H3B	0.9700	O3—H6	0.84 (2)
O2—C1—O1	126.8 (2)	O4—C4—C3	124.0 (2)
O2—C1—C2	115.7 (2)	O3—C4—C3	112.8 (2)
O1—C1—C2	117.3 (2)	C2—C5—H5A	109.5
N1—C2—C5	108.3 (2)	C2—C5—H5B	109.5
N1—C2—C3	109.79 (18)	H5A—C5—H5B	109.5
C5—C2—C3	112.5 (2)	C2—C5—H5C	109.5
N1—C2—C1	109.67 (18)	H5A—C5—H5C	109.5
C5—C2—C1	107.98 (18)	H5B—C5—H5C	109.5
C3—C2—C1	108.60 (19)	C2—N1—H8	107 (2)
C4—C3—C2	115.4 (2)	C2—N1—H7	112 (3)
C4—C3—H3A	108.4	H8—N1—H7	104 (3)
C2—C3—H3A	108.4	C2—N1—H9	112 (3)
C4—C3—H3B	108.4	H8—N1—H9	113 (3)
C2—C3—H3B	108.4	H7—N1—H9	109 (3)
H3A—C3—H3B	107.5	C4—O3—H6	111 (4)
O4—C4—O3	123.2 (2)		

Hydrogen-bond geometry (Å, º)

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
N1—H7···O4	0.79 (4)	2.23 (4)	2.798 (3)	130 (3)
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