1-Azaniumylcyclobutane-1-carboxylate monohydrate

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1-Azaniumycyclobutane-1-carboxylate monohydrate

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Key indicators: single-crystal X-ray study; T = 123 K; mean σ(C–C) = 0.002 Å; disorder in main residue; R factor = 0.038; wR factor = 0.103; data-to-parameter ratio = 11.8.

In the title compound, C₅H₉NO₂·H₂O, the amino acid is in the usual zwitterionic form involving the α-carboxylate group. The cyclobutane backbone of the amino acid is disordered over two conformations, with occupancies of 0.882 (7) and 0.118 (7). In the crystal, N—H·O and O—H·O hydrogen bonds link the zwitterions [with the water molecule involved as both acceptor (with the NH₃⁺) and donor (through a single carboxylate O from two different aminocyclobutane carboxylate moieties)], resulting in a two-dimensional layered structure lying parallel to (100).

Related literature

For the eighty amino acids that have been detected in meteorites or comets, see: Burdon et al. (2012); Pizzarello et al. (2004), (2006). For the role of the H atom on the α-C atom in enhancing the rate of racemization, see: Yamada et al. (1983). For the mechanism of racemization of amino acids lacking an α-H atom, see: Pizzarello & Groy (2011). For the role that crystallization can play in the enrichment of l-isovaline and its structure, see: Butcher et al. (2013). For normal bond lengths and angles, see: Orpen (1993). For the hydrochloride salt of the title compound and related non-proteinogenic amino acids, see: Chacko & Zand (1975); Butcher et al. (2012); Brewer et al. (2013). For conformational studies on model proteins with 1-aminocyclobutane-1-carboxylic acid residues, see: Balaji et al. (1995). For involvement of the title compound in ethylene production that leads to the ripening and spoilage of fruit, see: Nakatsuka et al. (1998); Bulantseva et al. (2003).

Data collection

Agilent Xcalibur (Ruby, Gemini) diffractometer

Absorption correction: multi-scan

(CrysAlis PRO; Agilent, 2012)

Tmin = 0.784, Tmax = 1.000

Refinement

H atoms treated by a mixture of independent and constrained refinement

Δρmax = 0.36 e Å⁻³

Δρmin = −0.19 e Å⁻³

Symmetry codes: (i) x, −y + 1, z + ½; (ii) −x, y − ½, −z + ½; (iii) −x, −y + 1, −z; (iv) x, y, z + ½.

Data collection: CrysAlis PRO (Agilent, 2012); cell refinement: CrysAlis PRO; data reduction: CrysAlis PRO; program(s) used to solve structure: SHELXS97 (Sheldrick, 2008); program(s) used to refine structure: SHELXL97 (Sheldrick, 2008); molecular graphics: SHELXTL (Sheldrick, 2008); software used to prepare material for publication: SHELXTL.

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Supplementary data and figures for this paper are available from the IUCr electronic archives (Reference: ZS2282).
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1. Comment

The alpha amino acids are essential for life as they are the building blocks of all proteins and enzymes. Nature uses almost exclusively the L form of the nineteen common chiral amino acids. The title compound is achiral due to the symmetry of the alpha carbon atom. It also lacks a hydrogen atom on the alpha carbon atom, which is critical in the racemization of the proteinogenic amino acids (Yamada et al., 1983). Little is known about the mechanism of racemization of amino acids lacking an alpha hydrogen atom (Pizzarello & Groy, 2011). Mechanistic investigation of racemization pathways of appropriate derivatives of the title compound may shed light on the racemization of this class of amino acids. Over eighty amino acids that have been identified in meteorites (Burton et al., 2012; Pizzarello et al., 2006). The title compound has not been detected to date in extraterrestrial sources but a higher analog, cycloleucine, has been reported (Pizzarello et al., 2004). The title compound has been incorporated into peptides for conformational studies on model proteins with 1-aminocyclobutane-1-carboxylic acid residues (Balaji et al., 1995). In addition the title compound has been shown to inhibit the enzyme 1-aminocyclopropane-1-carboxylate synthase, part of the pathway for ethylene production that leads to the ripening and spoilage of fruit (Nakatsuka et al., 1998; Bulantseva et al., 2003). The structures of some related non-proteinogenic amino acids have recently been reported (Butcher et al., 2013; Brewer et al., 2013).

The structure of the title compound has not been reported to the CCDC but there is a report of its hydrochloride salt as a monohydrate (Chacko & Zand, 1975). In the structure of the title compound the amino acid is in the usual zwitterionic form involving the α carboxylate group and all the the bond lengths and angles are in the normal range for such compounds (Orpen, 1993). The metrical parameters of the title compound and its hydrochloride salt do not differ significantly apart from the C—O bond lengths which are equivalent in the title compound but differ significantly in the hydrochloride salt. The cyclobutane backbone of the amino-acid is disordered over two conformations with occupancies of 0.882 (7) and 0.118 (7). There is extensive N—H···O and O—H···O hydrogen bonding (Table 1) linking the zwitterions into a two-dimensional layered structure lying parallel to (100) (Fig. 2).

2. Experimental

1-Aminocyclobutane carboxylic acid was purchased from Sigma Aldrich. Crystals of the title compound were grown by evaporation from an aqueous solution of the achiral amino acid.

3. Refinement

H atoms were placed in geometrically idealized positions and constrained to ride on their parent atoms with a C—H distances of 0.98 and 0.99 Å. The protons on the N and O were refined isotropically with the O—H distances for the water H's constrained to be 0.82 Å and the H—O—H angle close to 104.5°. The cyclobutane backbone of the amino-acid was disordered over two conformations with occupancies of 0.882 (7) and 0.118 (7).
Computing details
Data collection: CrysAlis PRO (Agilent, 2012); cell refinement: CrysAlis PRO (Agilent, 2012); data reduction: CrysAlis PRO (Agilent, 2012); program(s) used to solve structure: SHELXS97 (Sheldrick, 2008); program(s) used to refine structure: SHELXL97 (Sheldrick, 2008); molecular graphics: SHELXTL (Sheldrick, 2008); software used to prepare material for publication: SHELXTL (Sheldrick, 2008).

Figure 1
Fif. 1. Diagram of the title compound showing atom labeling. Atomic displacement parameters are at the 30% probability level. The disorder in the backbone is shown with atoms in the the minor component connected with unfilled bonds. Hydrogen bonds are shown as dashed lines.
Figure 2
Packing diagram of the title compound (major component only) viewed along the $b$ axis showing the N—H···O and O—H···O hydrogen bonds as dashed lines.

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Crystal data

$\text{C}_5\text{H}_9\text{NO}_2\cdot\text{H}_2\text{O}$

$M_r = 133.15$

Monoclinic, $P2_1/c$

Hall symbol: $-P 2ybc$

$a = 10.25082$ (19) Å

$b = 6.13117$ (9) Å

$c = 10.9209$ (2) Å

$\beta = 100.8735$ (18)°

$V = 674.05$ (2) Å$^3$

$Z = 4$

$F(000) = 288$

$D_x = 1.312$ Mg m$^{-3}$

Cu $K\alpha$ radiation, $\lambda = 1.54184$ Å

Cell parameters from 4146 reflections

$\theta = 4.1^-{77.2}^\circ$

$\mu = 0.92$ mm$^{-1}$

$T = 123$ K

0.41 × 0.34 × 0.16 mm

Data collection

Agilent Xcalibur (Ruby, Gemini)

diffractometer

Radiation source: Enhance (Cu) X-ray source

Graphite monochromator

Detector resolution: 10.5081 pixels mm$^{-1}$

$\omega$ scans

Absorption correction: multi-scan

(Crystalis PRO; Agilent, 2012)

$T_{\text{min}} = 0.784, T_{\text{max}} = 1.000$

Refinement

Refinement on $F^2$

Least-squares matrix: full

$R[F^2 > 2\sigma(F^2)] = 0.038$

$wR(F^2) = 0.103$

$S = 1.06$

1400 reflections

119 parameters

0 restraints

Primary atom site location: structure-invariant direct methods

Secondary atom site location: difference Fourier map

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Hydrogen site location: inferred from neighbouring sites
H atoms treated by a mixture of independent and constrained refinement
\[ \sigma = \frac{1}{\sigma^2(F^2) + 0.0616P^2 + 0.2169P} \]
where \( P = (F^2 + 2F^2)/3 \)

\( \Delta / \sigma \) _max_ ≤ 0.001
\( \Delta \rho \) _max_ = 0.36 e Å\(^{-3}\)
\( \Delta \rho \) _min_ = −0.19 e Å\(^{-3}\)

**Special details**

**Experimental.** Absorption correction: CrysAlisPro (Agilent, 2012) Empirical absorption correction using spherical harmonics, implemented in SCALE3 ABSPACK scaling algorithm.

**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 \( F^2 > \sigma(F^2) \) 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 (Å\(^2\))

|     | x       | y       | z       | \( U_{eq} \) * \( U_{eq} \) | Occ. (<1) |
|-----|---------|---------|---------|-----------------------------|-----------|
| O1W | 0.11907 (10) | 0.30045 (14) | 0.47599 (9) | 0.0268 (3) |
| H1W1 | 0.1576 (18) | 0.203 (3) | 0.5293 (18) | 0.037 (4)* |
| H1W2 | 0.0713 (19) | 0.231 (3) | 0.4210 (19) | 0.039 (5)* |
| O2  | 0.04488 (8) | 0.54177 (13) | 0.20493 (7) | 0.0218 (3) |
| O1  | 0.23745 (8) | 0.52875 (13) | 0.13611 (7) | 0.0213 (3) |
| N1  | 0.13993 (9) | 0.73526 (15) | 0.41449 (8) | 0.0159 (3) |
| H1N | 0.0661 (18) | 0.809 (3) | 0.3735 (16) | 0.032 (4)* |
| H2N | 0.1799 (15) | 0.815 (3) | 0.4840 (15) | 0.023 (4)* |
| H3N | 0.1179 (16) | 0.603 (3) | 0.4404 (15) | 0.026 (4)* |
| C1  | 0.16664 (10) | 0.57917 (16) | 0.21410 (9) | 0.0155 (3) |
| C2  | 0.23577 (10) | 0.70405 (17) | 0.32992 (9) | 0.0151 (3) |
| C3  | 0.30893 (12) | 0.9136 (2) | 0.30010 (12) | 0.0247 (3) |
| H3A | 0.2845 (16) | 0.967 (3) | 0.2165 (16) | 0.030* |
| H3B | 0.3019 (16) | 1.021 (3) | 0.3606 (16) | 0.030* |
| C4A | 0.44072 (14) | 0.7839 (3) | 0.32757 (17) | 0.0353 (6) |
| H4AA | 0.4706 | 0.7309 | 0.2518 | 0.042* |
| H4AB | 0.5134 | 0.8607 | 0.3837 | 0.042* |
| C4B | 0.4308 (11) | 0.845 (2) | 0.3984 (14) | 0.0353 (6) |
| H4BA | 0.4366 | 0.9176 | 0.4802 | 0.042* |
| H4BB | 0.5162 | 0.8543 | 0.3689 | 0.042* |
| C5  | 0.37127 (10) | 0.6082 (2) | 0.39333 (11) | 0.0228 (3) |
| H5A | 0.3873 (16) | 0.464 (3) | 0.3693 (15) | 0.027* |
| H5B | 0.3840 (16) | 0.615 (3) | 0.4822 (16) | 0.027* |

Atomic displacement parameters (Å\(^2\))

|     | \( U_{11} \) | \( U_{22} \) | \( U_{33} \) | \( U_{12} \) | \( U_{13} \) | \( U_{23} \) |
|-----|---------------|---------------|---------------|---------------|---------------|---------------|
| O1W | 0.0356 (5)    | 0.0181 (4)    | 0.0236 (5)    | −0.0006 (3)   | −0.0028 (4)   | 0.0030 (3)    |
| O2  | 0.0172 (4)    | 0.0236 (5)    | 0.0229 (4)    | −0.0017 (3)   | −0.0010 (3)   | −0.0053 (3)   |

*supplementary materials*
|          | U<sub>11</sub> (Å<sup>2</sup>) | U<sub>22</sub> (Å<sup>2</sup>) | U<sub>33</sub> (Å<sup>2</sup>) | U<sub>12</sub> (Å<sup>2</sup>) | U<sub>13</sub> (Å<sup>2</sup>) | U<sub>23</sub> (Å<sup>2</sup>) |
|----------|-------------------------------|-------------------------------|-------------------------------|-------------------------------|-------------------------------|-------------------------------|
| O1       | 0.0237 (4)                    | 0.0252 (5)                    | 0.0150 (4)                    | 0.0027 (3)                    | 0.0035 (3)                    | −0.0017 (3)                   |
| N1       | 0.0166 (5)                    | 0.0170 (5)                    | 0.0139 (5)                    | 0.0002 (3)                    | 0.0023 (3)                    | −0.0002 (3)                   |
| C1       | 0.0186 (5)                    | 0.0131 (5)                    | 0.0134 (5)                    | 0.0021 (4)                    | −0.0006 (4)                   | 0.0021 (4)                    |
| C2       | 0.0143 (5)                    | 0.0163 (5)                    | 0.0141 (5)                    | 0.0002 (4)                    | 0.0017 (4)                    | 0.0004 (4)                    |
| C3       | 0.0271 (6)                    | 0.0214 (6)                    | 0.0273 (6)                    | −0.0085 (4)                   | 0.0098 (5)                    | −0.0027 (5)                   |
| C4A      | 0.0195 (8)                    | 0.0404 (10)                   | 0.0476 (11)                   | −0.0086 (6)                   | 0.0105 (7)                    | −0.0069 (7)                   |
| C4B      | 0.0195 (8)                    | 0.0404 (10)                   | 0.0476 (11)                   | −0.0086 (6)                   | 0.0105 (7)                    | −0.0069 (7)                   |
| C5       | 0.0148 (5)                    | 0.0313 (7)                    | 0.0204 (6)                    | 0.0039 (4)                    | −0.0018 (4)                   | −0.0033 (4)                   |

**Geometric parameters (Å, °)**

| Bond          | Length (Å) | Angle (°) |
|---------------|------------|-----------|
| O1W—H1W1      | 0.87 (2)   | C3—C4A    | 1.547 (2) |
| O1W—H1W2      | 0.82 (2)   | C3—H3A    | 0.958 (17) |
| O2—C1         | 1.2543 (13)| C3—H3B    | 0.943 (18) |
| O1—C1         | 1.2574 (13)| C4A—C5    | 1.542 (2)  |
| N1—C2         | 1.4823 (13)| C4A—H4AA  | 0.9900     |
| N1—H1N        | 0.922 (18) | C4A—H4AB  | 0.9900     |
| N1—H2N        | 0.930 (17) | C4B—C5    | 1.570 (12) |
| N1—H3N        | 0.902 (17) | C4B—H4BA  | 0.9900     |
| C1—C2         | 1.5330 (14)| C4B—H4BB  | 0.9900     |
| C2—C5         | 1.5465 (14)| C5—H5A    | 0.942 (17) |
| C2—C3         | 1.5527 (15)| C5—H5B    | 0.956 (17) |
| C3—C4B        | 1.545 (13) |           |            |

| Bond          | Length (Å) | Angle (°) |
|---------------|------------|-----------|
| H1W1—O1W      | 105.5 (18) | C2—C3—H3B| 108.9 (10) |
| C2—N1—H1N     | 109.9 (11) | H3A—C3—H3B| 112.9 (14) |
| C2—N1—H2N     | 109.5 (9)  | C5—C4A—C3 | 89.22 (9)  |
| H1N—N1—H2N    | 109.6 (14) | C5—C4A—H4AA| 113.8     |
| C2—N1—H3N     | 108.3 (10) | C3—C4A—H4AA| 113.8     |
| H1N—N1—H3N    | 111.2 (15) | C5—C4A—H4AB| 113.8     |
| H2N—N1—H3N    | 108.2 (14) | C3—C4A—H4AB| 113.8     |
| O2—C1—O1      | 126.43 (10)| H4AA—C4A—H4AB| 111.0     |
| O2—C1—C2      | 117.09 (9) | C3—C4B—C5 | 88.3 (6)   |
| O1—C1—C2      | 116.46 (9) | C3—C4B—H4BA| 113.9     |
| N1—C2—C1      | 108.72 (8) | C5—C4B—H4BA| 113.9     |
| N1—C2—C5      | 114.52 (8) | C3—C4B—H4BB| 113.9     |
| C1—C2—C5      | 114.58 (9) | C5—C4B—H4BB| 113.9     |
| N1—C2—C3      | 115.28 (9) | H4BA—C4B—H4BB| 111.1     |
| C1—C2—C3      | 113.99 (9) | C4A—C5—C2 | 88.88 (9)  |
| C5—C2—C3      | 88.84 (8)  | C2—C5—C4B | 88.6 (4)   |
| C4B—C3—C2     | 89.3 (4)   | C4A—C5—H5A| 113.8 (10) |
| C4A—C3—C2     | 88.44 (9)  | C2—C5—H5A | 114.8 (10) |
| C4B—C3—H3A    | 142.0 (11) | C4B—C5—H5A| 141.8 (11) |
| C4A—C3—H3A    | 115.0 (10) | C4A—C5—H5B| 117.2 (9)  |
| C2—C3—H3A     | 115.6 (10) | C2—C5—H5B | 112.2 (10) |
| C4B—C3—H3B    | 82.1 (12)  | C4B—C5—H5B| 86.9 (11)  |
| C4A—C3—H3B    | 113.6 (10) | H5A—C5—H5B| 109.0 (14) |
| O2—C1—C2—N1   | 5.49 (13)  | C2—C3—C4A—C5| −16.15 (9) |
| O1—C1—C2—N1   | −176.10 (9)| C4A—C3—C4B—C5| −71.5 (8)  |
supplementary materials

| Bond | Distance (Å) | Bond | Distance (Å) |
|------|--------------|------|--------------|
| O2—C1—C2—C5 | 135.05 (10) | C2—C3—C4B—C5 | 16.8 (5) |
| O1—C1—C2—C5 | −46.54 (13) | C3—C4A—C5—C2 | 16.21 (10) |
| O2—C1—C2—C3 | −124.62 (10) | C3—C4A—C5—C4B | −72.9 (8) |
| O1—C1—C2—C3 | 53.79 (13) | N1—C2—C5—C4A | −133.55 (10) |
| N1—C2—C3—C4B | 99.7 (6) | C1—C2—C5—C4A | 99.82 (11) |
| C1—C2—C3—C4B | −133.6 (6) | C3—C2—C5—C4A | −16.16 (10) |
| C5—C2—C3—C4B | −17.0 (6) | N1—C2—C5—C4B | −100.6 (6) |
| N1—C2—C3—C4A | 132.80 (10) | C1—C2—C5—C4B | 132.7 (6) |
| C1—C2—C3—C4A | −100.42 (11) | C3—C2—C5—C4B | 16.8 (6) |
| C5—C2—C3—C4A | 16.10 (10) | C3—C4B—C5—C4A | 73.3 (8) |
| C4B—C3—C4A—C5 | 74.9 (8) | C3—C4B—C5—C2 | −16.9 (5) |

Hydrogen-bond geometry (Å, °)

| D—H···A | D—H | H···A | D···A | D—H···A |
|---------|------|------|-------|---------|
| O1W—H1W1···O1i | 0.87 (2) | 1.92 (2) | 2.7935 (12) | 175.2 (18) |
| O1W—H1W2···O2ii | 0.82 (2) | 2.01 (2) | 2.8268 (12) | 175.7 (19) |
| N1—H1N···O2iii | 0.922 (18) | 1.923 (18) | 2.8087 (12) | 160.6 (15) |
| N1—H2N···O1iv | 0.930 (17) | 1.913 (17) | 2.8351 (12) | 171.2 (14) |
| N1—H3N···O1W | 0.902 (17) | 1.895 (17) | 2.7673 (13) | 162.3 (15) |

Symmetry codes: (i) x, −y+1/2, z+1/2; (ii) −x, y−1/2, −z+1/2; (iii) −x, y+1/2, −z+1/2; (iv) x, −y+3/2, z+1/2.