# Redetermined structure of β-DL-methionine at 105 K: an example of the importance of freely refining the positions of the amino-group H atoms

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Diffraction data were taken from the contribution named 'β-DL-Methionine at 105 K' by Alagar *et al.* [*Acta Cryst.* (2005). E**61**, o1165–o1167]. Refinement of the coordinates of the three amino H atoms, previously constrained to an idealized geometry, shows that the amino group is in fact rotated 13.5° from the perfectly staggered orientation. This apparently modest change has a profound impact on the calculated hydrogen-bond geometries.

## 1. Chemical context

Upon comparing the hydrogen-bond geometries of the high-temperature α-phase of the amino acid racemate DL-methionine (Görbitz *et al.*, 2014) with the best published structure of the β-phase [Alagar *et al.*, 2005; refcode DLMETA05 in the Cambridge Structural Database (CSD), Version 5.35; Allen, 2002], we noted that H···O distances surprisingly appeared to get shorter at 340 K than at 105 K. This was judged to be an artefact resulting from different ways of handling the amino H atoms. Alagar *et al.* (2005) used an idealized geometry and a perfectly staggered orientation for this group in their refinement; while we found a 14° counterclockwise rotation (for the L-enantiomer) that served to give three shorter and more linear interactions. The experimental and structural data of Alagar *et al.* (2005), with coordinates for the D-enantiomer as the asymmetric unit, were subsequently downloaded and refined again with free amino H atoms, thus increasing the number of parameters from 82 (nine parameters for nine atoms + scale factor) to 91. In the improved structural model displayed in Fig. 1 [$R(F) = 0.0377$ versus 0.411 and $wR(F^2) = 0.0918$ versus 0.1001], the amino group is shifted slightly away from the staggered orientation through a 13.5° clockwise rotation (for the D-enantiomer), Table 1.
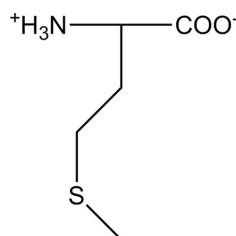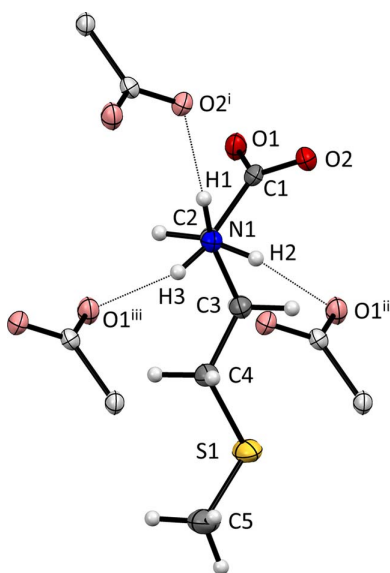


Figure 1



## 2. Supramolecular features

The hydrogen-bond geometries listed in Table 2 show that the free refinement of amino-group H atoms gives close to linear
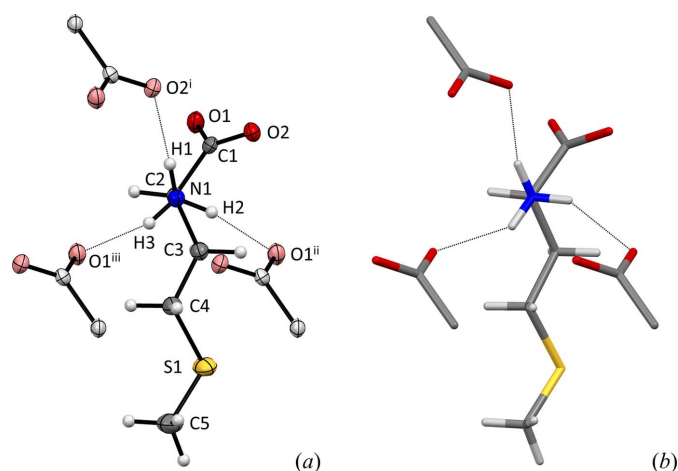
**Figure 1**
(*a*) The structure of DL-methionine, (I), viewed approximately along the N1—C2 bond vector, with 50% probability thermal displacement ellipsoids. The racemate contains molecules of both hands; the one depicted here is the D-enantiomer. Carboxylate groups of three neighboring amino acids accepting hydrogen bonds are shown in a lighter tone. O2$^{i}$ is at ($-x$, $y + \frac{1}{2}$, $-z + \frac{1}{2}$), O2$^{ii}$ at ($x + \frac{1}{2}$, $-y$, $z$) and O$^{iii}$ at ($x + \frac{1}{2}$, $-y + 1$, $z$), see Table 2. Compared to the previously published structure shown in capped sticks representation in (*b*) (Alagar *et al.*, 2005), the amino group has been rotated clockwise by about 13.5° to give shorter and more linear hydrogen bonds.

N—H···O interactions with substantially shorter H···O distances. There are no significant changes for geometric parameters involving only C, N and O atoms. This example demonstrates that in order not to unduly bias the statistics of hydrogen-bond geometries in the CSD, it is imperative that H atoms of amino groups and other hydrogen-bond donating

**Table 1**
Selected torsion angles (°).

| | | | |
|---|---|---|---|
| N1—C2—C3—C4 | 54.4 (2) | C1—C2—N1—H1 | 46.5 (17) |
| C1—C2—C3—C4 | 173.53 (15) | C1—C2—N1—H2 | −75.3 (15) |
| C2—C3—C4—S1 | 179.23 (12) | C1—C2—N1—H3 | 167.4 (15) |
| C3—C4—S1—C5 | 175.03 (14) | | |

**Table 2**
Hydrogen-bond geometry (Å, °).

| $D$—H···$A$ | Parameter | DLMETA05$^{a}$ | (I)-rigid$^{b}$ | (I) |
|---|---|---|---|---|
| N1—H1···O2$^{i}$ | N—H | 0.89 | 0.91 | 0.88 (3) |
| | H···O | 1.93 | 1.88 | 1.91 (3) |
| | N···O | 2.788 (2) | 2.787 (2) | 2.788 (2) |
| | N—H···O | 162 | 173 | 174 (2) |
| N1—H2···O1$^{ii}$ | N—H | 0.89 | 0.91 | 0.94 (3) |
| | H···O | 2.02 | 1.92 | 1.89 (3) |
| | N···O | 2.814 (2) | 2.815 (2) | 2.815 (2) |
| | N—H···O | 148 | 167 | 169 (2) |
| N1—H3···O1$^{iii}$ | N—H | 0.89 | 0.91 | 0.92 (3) |
| | H···O | 2.02 | 1.91 | 1.91 (3) |
| | N···O | 2.794 (2) | 2.795 (2) | 2.795 (2) |
| | N—H···O | 144 | 163 | 161 (2) |

Symmetry codes: (i) $-x$, $y + \frac{1}{2}$, $-z + \frac{1}{2}$; (ii) $x + \frac{1}{2}$, $-y$, $z$; (iii) $x + \frac{1}{2}$, $-y + 1$, $z$. Notes: (*a*) Alagar *et al.* (2005), 82 parameters; atoms H1, H2 and H3 were called H1A, H1B and H1C, respectively, by the original authors; the labels used in the CSD entry DLMETA05 have been retained here. (*b*) Rigid rotation refinement of (I), 83 parameters. 0.91 Å is the standard N—H bond length in *SHELXL* (Sheldrick, 2008) at 105 K.

**Table 3**
Experimental details.

| | |
|---|---|
| Crystal data | |
| Chemical formula | $C_5H_{11}NO_2S$ |
| $M_r$ | 149.21 |
| Crystal system, space group | Monoclinic, $I2/a$ |
| Temperature (K) | 105 |
| $a$, $b$, $c$ (Å) | 9.877 (2), 4.6915 (10), 32.603 (6) |
| $\beta$ (°) | 106.25 (1) |
| $V$ (Å$^3$) | 1450.4 (5) |
| $Z$ | 8 |
| Radiation type | Mo $K\alpha$ |
| $\mu$ (mm$^{-1}$) | 0.38 |
| Crystal size (mm) | 0.32 × 0.24 × 0.22 |
| | |
| Data collection | |
| Diffractometer | Bruker SMART CCD area detector |
| Absorption correction | Multi-scan (*SADABS*; Bruker, 1998) |
| $T_{min}$, $T_{max}$ | 0.85, 0.92 |
| No. of measured, independent and observed [$I > 2\sigma(I)$] reflections | 6469, 1436, 1373 |
| $R_{int}$ | 0.023 |
| $(\sin\theta/\lambda)_{max}$ (Å$^{-1}$) | 0.623 |
| | |
| Refinement | |
| $R[F^2 > 2\sigma(F^2)]$, $wR(F^2)$, $S$ | 0.038, 0.092, 1.26 |
| No. of reflections | 1436 |
| No. of parameters | 91 |
| H-atom treatment | H atoms treated by a mixture of independent and constrained refinement |
| $\Delta\rho_{max}$, $\Delta\rho_{min}$ (e Å$^{-3}$) | 0.35, −0.23 |

Computer programs: *SMART-NT* and *SAINT-NT* (Bruker, 1999), *SHELXS97*, *SHELXL2013* (Sheldrick, 2008) and *SHELXTL* (Sheldrick, 2008).

functional groups whenever possible are refined in a normal manner and not constrained to theoretical positions. The data set used here (Alagar *et al.*, 2005) is of good, but not excellent quality. Nevertheless, H atoms can be refined with decent accuracy [standard uncertainties (s.u.'s) = 0.03 Å for N—H distances], allowing experimental determination of hydrogen-bond geometries. In the event that s.u.'s get much higher and/or N—H distances are clearly unreasonably short or long, a rigid rotation refinement of the group (*e.g.* by an AFIX 37 command in *SHELXL*; Sheldrick, 2008) should be performed. The results of such a refinement for (I), which adds just a single refinement parameter compared to DLMETA05, but reaches the same *R* factor as for (I), are included in Table 2. The listed values are very close to those of the unconstrained refinement, but are obviously devoid of s.u.'s for geometric parameters involving H atoms.

Under other circumstances restraints on covalent geometry may be employed. Accordingly, we have found that it is often useful to restrain O—H bond distances and H—O—H bond angles (through the 1–3 distances) during refinement of water molecules in crystal hydrates. For a single molecule with atom labels H1W—O1W—H2W, the appropriate *SHELXL* commands would be DFIX 0.85 0.02 O1W H1W O1W H2W and DFIX 1.35 0.03 H1W H2W (the s.u.'s of 0.02 and 0.03 Å being subject to discussion). Similar approaches may be used for groups like –OH and –NH$_2$ for which AFIX 37 commands (or equivalent) are not applicable.

## 3. Experimental

For crystallization details, see Alagar *et al.* (2005). Crystal data, data collection and structure refinement details are summarized in Table 3.

Coordinates were refined for amino H atoms; other H atoms were positioned with idealized geometry, with fixed C—H = 0.98 (methyl), 0.99 (methylene) or 1.00 Å (methine). $U_{iso}(H)$ values were set at $1.2U_{eq}$ of the carrier atom or at $1.5U_{eq}$ for methyl and amino groups.

## References

Alagar, M., Krishnakumar, R. V., Mostad, A. & Natarajan, S. (2005). *Acta Cryst.* E**61**, o1165–o1167.

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Bruker (1998). *SADABS*. Bruker AXS Inc., Madison, Wisconsin, USA.

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Sheldrick, G. M. (2008). *Acta Cryst.* A**64**, 112–122.

# supporting information

## Redetermined structure of *β*-DL-methionine at 105 K: an example of the importance of freely refining the positions of the amino-group H atoms

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### Computing details

Data collection: *SMART-NT* (Bruker, 1999); cell refinement: *SAINT-NT* (Bruker, 1999); data reduction: *SAINT-NT* (Bruker, 1999); program(s) used to solve structure: *SHELXS97* (Sheldrick, 2008); program(s) used to refine structure: *SHELXL2013* (Sheldrick, 2008); molecular graphics: *SHELXTL* (Sheldrick, 2008); software used to prepare material for publication: *SHELXL2013* (Sheldrick, 2008).

**2-Amino-4-(methylsulfanyl)butanoic acid**

*Crystal data*

| | |
|---|---|
| $C_5H_{11}NO_2S$ | $F(000) = 640$ |
| $M_r = 149.21$ | $D_x = 1.367$ Mg m$^{-3}$ |
| Monoclinic, $I2/a$ | Mo $K\alpha$ radiation, $\lambda = 0.71073$ Å |
| $a = 9.877$ (2) Å | Cell parameters from 1012 reflections |
| $b = 4.6915$ (10) Å | $\theta = 2.6$–26.1° |
| $c = 32.603$ (6) Å | $\mu = 0.38$ mm$^{-1}$ |
| $\beta = 106.25$ (1)° | $T = 105$ K |
| $V = 1450.4$ (5) Å$^3$ | Block, colourless |
| $Z = 8$ | $0.32 \times 0.24 \times 0.22$ mm |

*Data collection*

| | |
|---|---|
| Bruker SMART CCD area-detector diffractometer | $T_{min} = 0.85$, $T_{max} = 0.92$ |
| | 6469 measured reflections |
| Radiation source: fine-focus sealed tube | 1436 independent reflections |
| Graphite monochromator | 1373 reflections with $I > 2\sigma(I)$ |
| Detector resolution: 8.3 pixels mm$^{-1}$ | $R_{int} = 0.023$ |
| Sets of exposures each taken over 0.5° $\omega$ rotation scans | $\theta_{max} = 26.3°$, $\theta_{min} = 2.6°$ |
| | $h = -12 \rightarrow 11$ |
| Absorption correction: multi-scan (*SADABS*; Bruker, 1998) | $k = 0 \rightarrow 5$ |
| | $l = 0 \rightarrow 40$ |

*Refinement*

| | |
|---|---|
| Refinement on $F^2$ | Hydrogen site location: inferred from neighbouring sites |
| Least-squares matrix: full | |
| $R[F^2 > 2\sigma(F^2)] = 0.038$ | H atoms treated by a mixture of independent and constrained refinement |
| $wR(F^2) = 0.092$ | $w = 1/[\sigma^2(F_o^2) + (0.0233P)^2 + 2.4782P]$ |
| $S = 1.26$ | where $P = (F_o^2 + 2F_c^2)/3$ |
| 1436 reflections | $(\Delta/\sigma)_{max} = 0.001$ |
| 91 parameters | $\Delta\rho_{max} = 0.35$ e Å$^{-3}$ |
| 0 restraints | $\Delta\rho_{min} = -0.23$ e Å$^{-3}$ |

*Special details*

**Experimental**. Diffraction data and experimental conditions are taken from Alagar *et al.* (2005), CSD refcode DLMETA05.

**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 amino H atom coordinates.

*Fractional atomic coordinates and isotropic or equivalent isotropic displacement parameters (Å$^2$)*

|  | *x* | *y* | *z* | $U_{iso}$*/$U_{eq}$ |
|---|---|---|---|---|
| S1 | 0.39652 (6) | 0.15681 (12) | 0.44292 (2) | 0.03291 (18) |
| O1 | −0.14523 (13) | 0.2025 (3) | 0.31403 (4) | 0.0240 (3) |
| O2 | −0.01841 (13) | −0.0810 (3) | 0.28411 (4) | 0.0216 (3) |
| N1 | 0.19296 (17) | 0.3000 (3) | 0.29733 (5) | 0.0193 (3) |
| H1 | 0.142 (3) | 0.332 (5) | 0.2710 (8) | 0.029* |
| H2 | 0.238 (2) | 0.122 (6) | 0.2999 (7) | 0.029* |
| H3 | 0.263 (2) | 0.436 (5) | 0.3054 (7) | 0.029* |
| C1 | −0.03289 (18) | 0.1301 (4) | 0.30562 (5) | 0.0185 (4) |
| C2 | 0.09967 (18) | 0.3087 (4) | 0.32589 (5) | 0.0183 (4) |
| H4 | 0.0719 | 0.5103 | 0.3294 | 0.022* |
| C3 | 0.17639 (19) | 0.1831 (4) | 0.36982 (5) | 0.0214 (4) |
| H5 | 0.1148 | 0.2038 | 0.3889 | 0.026* |
| H6 | 0.1911 | −0.0232 | 0.3664 | 0.026* |
| C4 | 0.3196 (2) | 0.3214 (4) | 0.39143 (6) | 0.0246 (4) |
| H7 | 0.3068 | 0.5281 | 0.3952 | 0.030* |
| H8 | 0.3837 | 0.2973 | 0.3731 | 0.030* |
| C5 | 0.5659 (2) | 0.3326 (5) | 0.45830 (7) | 0.0350 (5) |
| H9 | 0.6208 | 0.2627 | 0.4864 | 0.053* |
| H10 | 0.6169 | 0.2916 | 0.4371 | 0.053* |
| H11 | 0.5521 | 0.5388 | 0.4597 | 0.053* |

*Atomic displacement parameters (Å$^2$)*

|  | $U^{11}$ | $U^{22}$ | $U^{33}$ | $U^{12}$ | $U^{13}$ | $U^{23}$ |
|---|---|---|---|---|---|---|
| S1 | 0.0351 (3) | 0.0337 (3) | 0.0231 (3) | −0.0067 (2) | −0.0031 (2) | 0.0074 (2) |
| O1 | 0.0225 (7) | 0.0168 (6) | 0.0333 (7) | 0.0012 (5) | 0.0089 (5) | −0.0003 (5) |
| O2 | 0.0253 (7) | 0.0156 (6) | 0.0222 (6) | −0.0010 (5) | 0.0037 (5) | −0.0028 (5) |
| N1 | 0.0207 (7) | 0.0169 (8) | 0.0190 (7) | −0.0010 (6) | 0.0035 (6) | 0.0008 (6) |
| C1 | 0.0213 (8) | 0.0138 (8) | 0.0181 (8) | 0.0006 (7) | 0.0019 (7) | 0.0034 (6) |
| C2 | 0.0212 (8) | 0.0128 (8) | 0.0208 (8) | 0.0005 (7) | 0.0059 (7) | −0.0008 (7) |
| C3 | 0.0248 (9) | 0.0186 (9) | 0.0197 (8) | −0.0008 (7) | 0.0043 (7) | −0.0002 (7) |
| C4 | 0.0273 (10) | 0.0216 (9) | 0.0213 (9) | −0.0016 (8) | 0.0007 (7) | 0.0017 (7) |
| C5 | 0.0309 (11) | 0.0416 (13) | 0.0272 (10) | −0.0024 (9) | −0.0008 (8) | 0.0012 (9) |

*Geometric parameters (Å, º)*

| | | | |
|---|---|---|---|
| S1—C5 | 1.806 (2) | C2—H4 | 1.0000 |
| S1—C4 | 1.8104 (19) | C3—C4 | 1.536 (2) |
| O1—C1 | 1.262 (2) | C3—H5 | 0.9900 |
| O2—C1 | 1.245 (2) | C3—H6 | 0.9900 |
| N1—C2 | 1.483 (2) | C4—H7 | 0.9900 |
| N1—H1 | 0.88 (3) | C4—H8 | 0.9900 |
| N1—H2 | 0.94 (3) | C5—H9 | 0.9800 |
| N1—H3 | 0.92 (3) | C5—H10 | 0.9800 |
| C1—C2 | 1.539 (2) | C5—H11 | 0.9800 |
| C2—C3 | 1.538 (2) | | |
| | | | |
| C5—S1—C4 | 100.27 (10) | C4—C3—H5 | 108.6 |
| C2—N1—H1 | 108.9 (15) | C2—C3—H5 | 108.6 |
| C2—N1—H2 | 109.2 (14) | C4—C3—H6 | 108.6 |
| H1—N1—H2 | 111 (2) | C2—C3—H6 | 108.6 |
| C2—N1—H3 | 110.5 (14) | H5—C3—H6 | 107.6 |
| H1—N1—H3 | 110 (2) | C3—C4—S1 | 109.80 (13) |
| H2—N1—H3 | 107 (2) | C3—C4—H7 | 109.7 |
| O2—C1—O1 | 125.67 (17) | S1—C4—H7 | 109.7 |
| O2—C1—C2 | 117.19 (15) | C3—C4—H8 | 109.7 |
| O1—C1—C2 | 117.03 (15) | S1—C4—H8 | 109.7 |
| N1—C2—C3 | 110.09 (14) | H7—C4—H8 | 108.2 |
| N1—C2—C1 | 108.59 (14) | S1—C5—H9 | 109.5 |
| C3—C2—C1 | 109.25 (14) | S1—C5—H10 | 109.5 |
| N1—C2—H4 | 109.6 | H9—C5—H10 | 109.5 |
| C3—C2—H4 | 109.6 | S1—C5—H11 | 109.5 |
| C1—C2—H4 | 109.6 | H9—C5—H11 | 109.5 |
| C4—C3—C2 | 114.57 (15) | H10—C5—H11 | 109.5 |
| | | | |
| N1—C2—C3—C4 | 54.4 (2) | O2—C1—C2—C3 | −87.60 (18) |
| C1—C2—C3—C4 | 173.53 (15) | O1—C1—C2—C3 | 88.98 (18) |
| C2—C3—C4—S1 | 179.23 (12) | C1—C2—N1—H1 | 46.5 (17) |
| C3—C4—S1—C5 | 175.03 (14) | C1—C2—N1—H2 | −75.3 (15) |
| O2—C1—C2—N1 | 32.5 (2) | C1—C2—N1—H3 | 167.4 (15) |
| O1—C1—C2—N1 | −150.93 (15) | | |

*Hydrogen-bond geometry (Å, º)*

| D—H···A | D—H | H···A | D···A | D—H···A |
|---|---|---|---|---|
| N1—H1···O2[i] | 0.88 (3) | 1.91 (3) | 2.788 (2) | 175 (3) |
| N1—H2···O1[ii] | 0.94 (3) | 1.89 (3) | 2.815 (2) | 169 (2) |
| N1—H3···O1[iii] | 0.92 (2) | 1.91 (2) | 2.795 (2) | 161 (2) |
| C2—H4···O2[iv] | 1.00 | 2.43 | 3.244 (2) | 138 |

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