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3-Methyl-2-propionamidobutanoic acid

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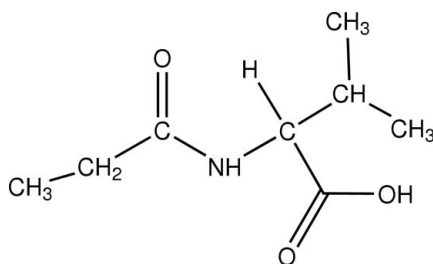
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Key indicators: single-crystal X-ray study; $T = 298$ K; mean $\sigma(\text{C}-\text{C}) = 0.004$ Å; R factor = 0.059; wR factor = 0.167; data-to-parameter ratio = 16.1.

The reaction of propionyl isothiocyanate with valine was found to give the title compound, $\text{C}_8\text{H}_{15}\text{NO}_3$, instead of the expected thiourea product. The whole molecule is non-planar and the carbonyl group is *cis* to the methylbutanoic acid group across the C–N bond. Intermolecular O–H...O and N–H...O hydrogen bonds build up a two-dimensional network developing parallel to (100).

Related literature

For the crystal structure of *N*-propionylthiourea, see: Yamin & Othman (2008). For bond-length data, see: Allen *et al.* (1987).



Experimental

Crystal data

$\text{C}_8\text{H}_{15}\text{NO}_3$
 $M_r = 173.21$
 Monoclinic, $P2_1/c$
 $a = 9.477$ (3) Å
 $b = 8.633$ (2) Å
 $c = 12.766$ (3) Å
 $\beta = 103.123$ (6)°

$V = 1017.2$ (5) Å³
 $Z = 4$
 Mo $K\alpha$ radiation
 $\mu = 0.09$ mm⁻¹
 $T = 298$ K
 $0.49 \times 0.33 \times 0.18$ mm

Data collection

Bruker SMART APEX CCD area-detector diffractometer
 Absorption correction: multi-scan (SADABS; Bruker, 2000)
 $T_{\min} = 0.959$, $T_{\max} = 0.984$

5313 measured reflections
 1887 independent reflections
 1262 reflections with $I > 2\sigma(I)$
 $R_{\text{int}} = 0.024$

Refinement

$R[F^2 > 2\sigma(F^2)] = 0.059$
 $wR(F^2) = 0.167$
 $S = 1.04$
 1887 reflections
 117 parameters
 2 restraints

H atoms treated by a mixture of independent and constrained refinement
 $\Delta\rho_{\max} = 0.24$ e Å⁻³
 $\Delta\rho_{\min} = -0.15$ e Å⁻³

Table 1

Hydrogen-bond geometry (Å, °).

$D-H\cdots A$	$D-H$	$H\cdots A$	$D\cdots A$	$D-H\cdots A$
$\text{N1}-\text{H1D}\cdots\text{O1}^{\text{i}}$	0.855 (18)	2.125 (18)	2.978 (3)	176.6 (16)
$\text{O2}-\text{H2C}\cdots\text{O3}^{\text{ii}}$	0.82 (2)	1.78 (2)	2.598 (3)	176 (2)

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

Data collection: *SMART* (Bruker, 2000); cell refinement: *SAINT* (Bruker, 2000); data reduction: *SAINT*; program(s) used to solve structure: *SHELXS97* (Sheldrick, 2008); program(s) used to refine structure: *SHELXL97* (Sheldrick, 2008); molecular graphics: *ORTEP-III* (Burnett & Johnson, 1996), *ORTEP-3 for Windows* (Farrugia, 1997) and *PLATON* (Spek, 2009); software used to prepare material for publication: *SHELXL97*, *PARST* (Nardelli, 1995) and *PLATON*.

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Supplementary data and figures for this paper are available from the IUCr electronic archives (Reference: DN2429).

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3-Methyl-2-propionamidobutanoic acid

Bohari M. Yamin and Eliyanti A. Othman

S1. Comment

The carbonyl isothiocyanate is a well known intermediate for the synthesis of carbonylthiourea derivatives. However, some carbonyl isothiocyanates such as propionyl isothiocyanate was reactive enough to give *N*-propionylthiourea (Yamin & Othman, 2008) after sitting for about 1 h. In the present study, the reaction of propionyl isothiocyanate with valine did not give the expected thiourea derivative but instead the 3-methyl-2-propionamidobutanoic acid (I), thus indicating a nucleophilic substitution of the isothiocyanato group by the amino group of the amino acid.

The molecule adopts *cis* configuration with respect to the position of the 3-methylbutanoic acid group relative to the carbonyl O3 atom across the C3—N1 bond. The bond lengths and angles are within normal ranges (Allen *et al.*, 1987). The acetamide [O3/N1/C2/C3/C4 (A)] and acetate [O1/O2/C4/C8 (B)] fragments are essentially planar with maximum deviation of 0.011 (2) Å for atom N1. The compound has a stereogenic center at C4 but the space group is centrosymmetric so the molecule exists as a racemate (R/S).

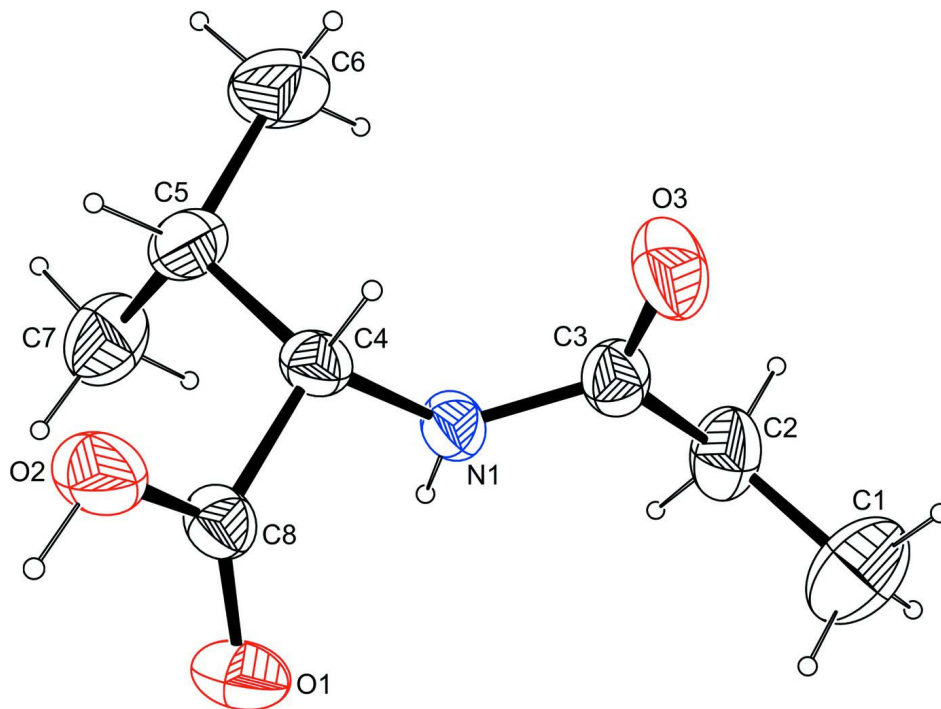
O—H \cdots O and N—H \cdots O intermolecular hydrogen bonds build up a two dimensional network with a corrugated iron shape developing parallel to the (1 0 0) plane.

S2. Experimental

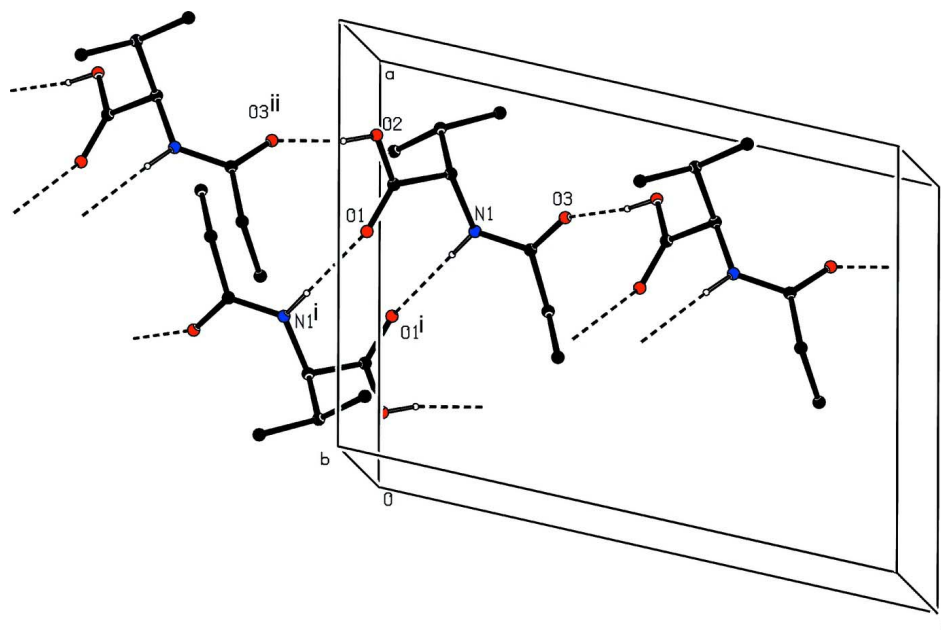
A solution of propionylisothiocyanate (1.15 g, 0.01 mol) in 30 ml acetone was added into a flask containing 30 ml acetone solution of valine (1.17 g, 0.01 mol). The mixture was refluxed for 5 h. The solution was filtered and left to evaporate at room temperature. The colourless solid were obtained after one day of evaporation (yield 85%, m.p 475.1–476.3 K)

S3. Refinement

H atoms attached to carbon atoms were positioned geometrically and treated as riding on their parent atoms with C—H = 0.96–0.98 Å and $U_{\text{iso}}(\text{H}) = xU_{\text{eq}}(\text{C})$ where $x = 1.5$ for CH₃ group and 1.2 for CH₂ and CH groups. The hydrogen atoms attached to nitrogen and oxygen atoms were located from Fourier difference map and refined isotropically,

**Figure 1**

The molecular structure of (I) with the atom-labeling scheme. Ellipsoids are drawn at the 30% probability level. H atoms are represented as small spheres of arbitrary radii. The enantiomer represented has S configuration.

**Figure 2**

Partial packing view of I showing the H bonds network. Hydrogen bonds are shown as dashed lines. [Symmetry codes: (i) $-x+1, -y, -z$; (ii) $x, -y+1/2, z-1/2$]

3-Methyl-2-propionamidobutanoic acid

Crystal data

C₈H₁₅NO₃ $M_r = 173.21$ Monoclinic, $P2_1/c$

Hall symbol: -P 2ybc

 $a = 9.477 (3) \text{ \AA}$ $b = 8.633 (2) \text{ \AA}$ $c = 12.766 (3) \text{ \AA}$ $\beta = 103.123 (6)^\circ$ $V = 1017.2 (5) \text{ \AA}^3$ $Z = 4$ $F(000) = 376$ $D_x = 1.131 \text{ Mg m}^{-3}$

Melting point: 475.5 K

Mo $K\alpha$ radiation, $\lambda = 0.71073 \text{ \AA}$

Cell parameters from 1183 reflections

 $\theta = 2.2\text{--}25.5^\circ$ $\mu = 0.09 \text{ mm}^{-1}$ $T = 298 \text{ K}$

Block, colourless

 $0.49 \times 0.33 \times 0.18 \text{ mm}$

Data collection

Bruker SMART APEX CCD area-detector
diffractometer

Radiation source: fine-focus sealed tube

Graphite monochromator

Detector resolution: 83.66 pixels mm^{-1} ω scansAbsorption correction: multi-scan
(SADABS; Bruker, 2000) $T_{\min} = 0.959$, $T_{\max} = 0.984$

5313 measured reflections

1887 independent reflections

1262 reflections with $I > 2\sigma(I)$ $R_{\text{int}} = 0.024$ $\theta_{\max} = 25.5^\circ$, $\theta_{\min} = 2.2^\circ$ $h = -10 \rightarrow 11$ $k = -10 \rightarrow 10$ $l = -15 \rightarrow 8$

Refinement

Refinement on F^2

Least-squares matrix: full

 $R[F^2 > 2\sigma(F^2)] = 0.059$ $wR(F^2) = 0.167$ $S = 1.04$

1887 reflections

117 parameters

2 restraints

Primary atom site location: structure-invariant
direct methodsSecondary atom site location: difference Fourier
mapHydrogen site location: inferred from
neighbouring sitesH atoms treated by a mixture of independent
and constrained refinement $w = 1/[\sigma^2(F_o^2) + (0.0815P)^2 + 0.2058P]$ where $P = (F_o^2 + 2F_c^2)/3$ $(\Delta/\sigma)_{\max} = 0.001$ $\Delta\rho_{\max} = 0.24 \text{ e \AA}^{-3}$ $\Delta\rho_{\min} = -0.15 \text{ e \AA}^{-3}$

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.

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 (\AA^2)

	x	y	z	$U_{\text{iso}}^*/U_{\text{eq}}$
O1	0.58011 (17)	0.1690 (2)	-0.01032 (13)	0.0706 (6)
O2	0.80400 (19)	0.2599 (2)	0.01281 (15)	0.0808 (6)
H2C	0.775 (3)	0.309 (3)	-0.0430 (16)	0.115 (12)*

O3	0.7243 (2)	0.0786 (2)	0.33764 (14)	0.0835 (6)
N1	0.6507 (2)	-0.0073 (2)	0.17012 (15)	0.0523 (5)
H1D	0.5834 (18)	-0.050 (2)	0.1230 (15)	0.058 (7)*
C1	0.3968 (4)	0.0265 (4)	0.3214 (3)	0.1079 (12)
H1A	0.3188	-0.0340	0.3366	0.162*
H1B	0.3602	0.0928	0.2610	0.162*
H1C	0.4390	0.0884	0.3830	0.162*
C2	0.5071 (3)	-0.0769 (3)	0.2963 (2)	0.0776 (8)
H2A	0.4623	-0.1411	0.2354	0.093*
H2B	0.5414	-0.1449	0.3572	0.093*
C3	0.6357 (3)	0.0049 (3)	0.27028 (19)	0.0573 (6)
C4	0.7670 (2)	0.0664 (3)	0.13158 (16)	0.0509 (6)
H4A	0.8199	0.1331	0.1894	0.061*
C5	0.8765 (3)	-0.0509 (3)	0.1042 (2)	0.0684 (7)
H5A	0.9512	0.0083	0.0797	0.082*
C6	0.9513 (3)	-0.1423 (4)	0.2037 (3)	0.1062 (11)
H6A	1.0190	-0.2138	0.1847	0.159*
H6B	0.8802	-0.1983	0.2313	0.159*
H6C	1.0020	-0.0721	0.2576	0.159*
C7	0.8066 (3)	-0.1595 (4)	0.0136 (3)	0.0905 (9)
H7A	0.8782	-0.2296	-0.0012	0.136*
H7B	0.7664	-0.1002	-0.0498	0.136*
H7C	0.7309	-0.2173	0.0345	0.136*
C8	0.7047 (2)	0.1683 (2)	0.03739 (16)	0.0517 (6)

Atomic displacement parameters (Å²)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
O1	0.0574 (11)	0.0732 (12)	0.0697 (11)	-0.0047 (8)	-0.0100 (8)	0.0117 (8)
O2	0.0616 (11)	0.1039 (14)	0.0740 (13)	-0.0103 (10)	0.0094 (9)	0.0375 (11)
O3	0.1026 (15)	0.0943 (14)	0.0564 (11)	-0.0129 (11)	0.0237 (10)	-0.0233 (10)
N1	0.0491 (11)	0.0648 (12)	0.0422 (10)	-0.0072 (9)	0.0087 (8)	-0.0021 (9)
C1	0.088 (2)	0.088 (2)	0.162 (4)	-0.0066 (18)	0.057 (2)	0.001 (2)
C2	0.097 (2)	0.0680 (17)	0.0806 (18)	0.0026 (15)	0.0463 (16)	0.0076 (13)
C3	0.0682 (15)	0.0526 (13)	0.0538 (14)	0.0077 (12)	0.0194 (12)	-0.0015 (11)
C4	0.0442 (12)	0.0609 (13)	0.0444 (12)	-0.0073 (10)	0.0035 (9)	0.0038 (10)
C5	0.0495 (13)	0.0817 (17)	0.0755 (17)	0.0093 (12)	0.0172 (12)	0.0186 (14)
C6	0.082 (2)	0.123 (3)	0.110 (2)	0.036 (2)	0.0132 (17)	0.040 (2)
C7	0.091 (2)	0.087 (2)	0.101 (2)	0.0129 (17)	0.0370 (17)	-0.0154 (17)
C8	0.0533 (13)	0.0564 (13)	0.0438 (12)	-0.0049 (11)	0.0077 (10)	-0.0016 (10)

Geometric parameters (Å, °)

O1—C8	1.200 (2)	C2—H2B	0.9700
O2—C8	1.320 (3)	C4—C8	1.499 (3)
O2—H2C	0.821 (10)	C4—C5	1.546 (3)
O3—C3	1.233 (3)	C4—H4A	0.9800
N1—C3	1.322 (3)	C5—C7	1.519 (4)

N1—C4	1.453 (3)	C5—C6	1.526 (4)
N1—H1D	0.855 (10)	C5—H5A	0.9800
C1—C2	1.464 (4)	C6—H6A	0.9600
C1—H1A	0.9600	C6—H6B	0.9600
C1—H1B	0.9600	C6—H6C	0.9600
C1—H1C	0.9600	C7—H7A	0.9600
C2—C3	1.509 (3)	C7—H7B	0.9600
C2—H2A	0.9700	C7—H7C	0.9600
C8—O2—H2C	114 (2)	C8—C4—H4A	107.5
C3—N1—C4	123.30 (19)	C5—C4—H4A	107.5
C3—N1—H1D	119.2 (16)	C7—C5—C6	110.8 (3)
C4—N1—H1D	117.0 (16)	C7—C5—C4	112.18 (19)
C2—C1—H1A	109.5	C6—C5—C4	111.1 (2)
C2—C1—H1B	109.5	C7—C5—H5A	107.5
H1A—C1—H1B	109.5	C6—C5—H5A	107.5
C2—C1—H1C	109.5	C4—C5—H5A	107.5
H1A—C1—H1C	109.5	C5—C6—H6A	109.5
H1B—C1—H1C	109.5	C5—C6—H6B	109.5
C1—C2—C3	114.5 (2)	H6A—C6—H6B	109.5
C1—C2—H2A	108.6	C5—C6—H6C	109.5
C3—C2—H2A	108.6	H6A—C6—H6C	109.5
C1—C2—H2B	108.6	H6B—C6—H6C	109.5
C3—C2—H2B	108.6	C5—C7—H7A	109.5
H2A—C2—H2B	107.6	C5—C7—H7B	109.5
O3—C3—N1	120.7 (2)	H7A—C7—H7B	109.5
O3—C3—C2	122.9 (2)	C5—C7—H7C	109.5
N1—C3—C2	116.4 (2)	H7A—C7—H7C	109.5
N1—C4—C8	109.76 (17)	H7B—C7—H7C	109.5
N1—C4—C5	112.93 (19)	O1—C8—O2	123.3 (2)
C8—C4—C5	111.44 (18)	O1—C8—C4	125.0 (2)
N1—C4—H4A	107.5	O2—C8—C4	111.72 (19)
C4—N1—C3—O3	-1.7 (3)	C8—C4—C5—C7	-61.5 (3)
C4—N1—C3—C2	179.0 (2)	N1—C4—C5—C6	-62.0 (3)
C1—C2—C3—O3	68.0 (4)	C8—C4—C5—C6	173.9 (2)
C1—C2—C3—N1	-112.7 (3)	N1—C4—C8—O1	-11.6 (3)
C3—N1—C4—C8	-123.5 (2)	C5—C4—C8—O1	114.2 (3)
C3—N1—C4—C5	111.5 (2)	N1—C4—C8—O2	167.87 (19)
N1—C4—C5—C7	62.6 (3)	C5—C4—C8—O2	-66.3 (2)

Hydrogen-bond geometry (\AA , $^\circ$)

$D-H\cdots A$	$D-H$	$H\cdots A$	$D\cdots A$	$D-H\cdots A$
N1—H1D \cdots O1 ⁱ	0.86 (2)	2.13 (2)	2.978 (3)	177 (2)
O2—H2C \cdots O3 ⁱⁱ	0.82 (2)	1.78 (2)	2.598 (3)	176 (2)

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