organic compounds

(S)-(+)-2-Formylamino-3-methylbutanoic acid

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The title compound, $C_6H_{11}NO_3$, a chiral source for ligands utilized in asymmetric catalysis, was synthesized from commercial (S)-(+)-valine. The stereochemistry is unchanged by the reaction and the structure consists of a single enantiomer. The structure displays O—H···O and N—H···O hydrogen bonding that links the molecules into a complex three-dimensional hydrogen-bonded network. The isopropyl group is disordered over two positions, with site-occupancy factors 0.819 (6) and 0.181 (6).

Related literature

For related literature, see: Boyle *et al.* (2004a,b, 2007); Muramatsu (1965).
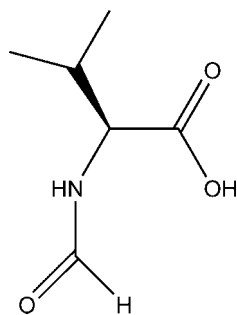
Experimental

Crystal data

$C_6H_{11}NO_3$	Orthorhombic, $P2_12_12_1$
M_r = 145.16	a = 7.0760 (6) Å
b = 9.5221 (8) Å	Mo $K\alpha$ radiation
c = 12.1934 (12) Å	μ = 0.09 mm^{-1}
V = 821.57 (13) Å^3	T = 291 (2) K
Z = 4	$0.20 \times 0.20 \times 0.05$ mm

Data collection

Oxford Diffraction Xcalibur2 diffractometer	7394 measured reflections
Absorption correction: multi-scan (*CrysAlis RED*; Oxford Diffraction, 2006)	1234 independent reflections
	780 reflections with $I > 2\sigma(I)$
T_{min} = 0.962, T_{max} = 0.995	R_{int} = 0.023

Refinement

$R[F^2 > 2\sigma(F^2)]$ = 0.045	H atoms treated by a mixture of independent and constrained refinement
$wR(F^2)$ = 0.132	
S = 0.98	
1234 reflections	$\Delta\rho_{max}$ = 0.16 e Å^{-3}
107 parameters	$\Delta\rho_{min}$ = −0.19 e Å^{-3}
17 restraints	

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

D—H···A	D—H	H···A	D···A	D—H···A
O2—H2A···O3^i	0.82	1.74	2.559 (2)	173
N1—H1···O1^{ii}	0.81 (4)	2.06 (4)	2.849 (3)	165 (4)

Symmetry codes: (i) $-x + \frac{3}{2}, -y + 1, z - \frac{1}{2}$; (ii) $-x + 2, y - \frac{1}{2}, -z + \frac{1}{2}$.

Data collection: *CrysAlis CCD* (Oxford Diffraction, 2006); cell refinement: *CrysAlis RED* (Oxford Diffraction, 2006); data reduction: *CrysAlis RED*; program(s) used to solve structure: *SHELXS97* (Sheldrick, 1997); program(s) used to refine structure: *SHELXL97* (Sheldrick, 1997); molecular graphics: *Mercury* (Macrae *et al.*, 2006); software used to prepare material for publication: *PLATON* (Spek, 2003) and *WinGX* (Farrugia, 1999).

Supplementary data and figures for this paper are available from the IUCr electronic archives (Reference: GK2094).

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supplementary materials

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Comment

The title compound (**I**) was used as a source of chirality for various pentacycloundecane ligands (Boyle *et al.*, 2004*a*) and macrocycles (Boyle *et al.*, 2004*b*) that were synthesized for applications in asymmetric catalysis. Here we report the crystal stucture of the title compound, (**I**). The compound was derived from commercially available (S)-(+)-valine and exists as a single enantiomer since the stereochemistry of the amino acid is unchanged during the reaction. The geometry and labelling scheme employed for the molecule is illustrated in Fig. 1.

In the molecule the iso-propyl moiety is disordered over two positions, with site occupancy factors of 0.82 and 0.18 for atoms C4A and C4B respectively. Atoms C1, C2, C3 and C5 are co-planar.

The molecules are involved in intermolecular O—H···O and N—H···O hydrogen bonding. The hydrogen bonding geometry is listed in Table 1. The molecular packing and hydrogen bonding interactions are illustrated in Fig. 2. The O2—H2A···O3^{i} ((i) $-x + 3/2$, $-y + 1$, $z - 1/2$) interaction links molecules in a head to tail fashion to form a corrugated, one-dimensional hydrogen bonded chain that extends along the *a*-direction. Neighbouring chains are connected *via* the N1—H1O···O1^{ii} ((ii)-$x + 2$, $y - 1/2$, $-z + 1/2$) interaction. It is interesting to note that each chain interacts with four other chains, two above it and two below it, when viewed down the *a* axis. In the interaction with the chains above, one of the neighbouring chains act as N—H···O hydrogen bond donor to the chain considered, while the second chain above acts as hydrogen bond acceptor to the chain under discussion. The same is true for the interactions to the hydrogen bonded chains below the chain. A three-dimensional hydrogen bonding network results, with the smallest hydrogen bonded ring described by the graph set notation $R^{6}_{6}(34)$.

Experimental

Acetic anhydride (30 mol equivalents) was added dropwise to a stirred solution of (*S*)-(+)-valine (1 mol equivalent) in formic acid (approximately 30 ml per 1.0 g of amino acid) at 0°C. After addition of the acetic anhydride, the external ice bath was removed and the solution stirred at room temperature during 24 h. The solution was treated with water (60 ml) and stirred for 1 hr. The solvent was removed under reduced pressure to yield a white residue. This residue was recrystallized from water to yield the pure product (Muramatsu, 1965). Yield 72%. Colourless crystals suitable for X-ray diffraction were obtained by evaporation of water at room temperature in a fume hood over a period of 2 days.

Refinement

Friedel pairs were merged before the final refinement. Hydrogen atoms H1 and H6 were placed as observed in the Fourier map and refined. All other hydrogen atoms were placed in calculated positions, with methyl C—H distances of 0.96 Å and methine C—H distances of 0.98 Å, and were refined using a riding model, with $U_{iso}(H)=1.2U_{eq}$ of the parent atom. The

supplementary materials

iso-propyl group is disordered over two positions, with site occupancy factors of 0.784 (5) and 0.216 (5) for atoms C4A and C4B respectively.
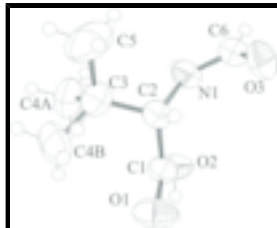
Figures

Fig. 1. The molecular structure of the title compound showing atomic numbering scheme and displacement ellipsoids drawn at the 50% probability level.
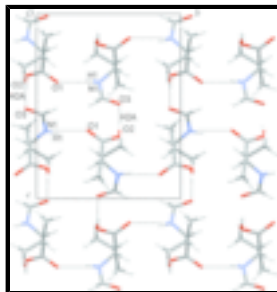

Fig. 2. The molecular packing, viewed down the *a* axis, showing intermolecular hydrogen bonding (dashed lines).

(*S*)-(+)-2-Formylamino-3-methylbutanoic acid

Crystal data

$C_6H_{11}NO_3$	$F_{000} = 312$
$M_r = 145.16$	$D_x = 1.174$ Mg m^{-3}
Orthorhombic, $P2_12_12_1$	Mo $K\alpha$ radiation $\lambda = 0.71073$ Å
Hall symbol: P 2ac 2ab	Cell parameters from 2582 reflections
$a = 7.0760$ (6) Å	$\theta = 4.0–32.0º$
$b = 9.5221$ (8) Å	$\mu = 0.09$ mm^{-1}
$c = 12.1934$ (12) Å	$T = 291$ (2) K
$V = 821.57$ (13) Å^3	Plate, colourless
$Z = 4$	$0.20 \times 0.20 \times 0.05$ mm

Data collection

Oxford Diffraction Xcalibur2 diffractometer	1234 independent reflections
Radiation source: fine-focus sealed tube	780 reflections with $I > 2\sigma(I)$
Monochromator: graphite	$R_{int} = 0.023$
$T = 291(2)$ K	$\theta_{max} = 28.7º$
ω scans	$\theta_{min} = 4.0º$
Absorption correction: multi-scan (CrysAlis RED; Oxford Diffraction, 2006)	$h = -9 \rightarrow 9$
$T_{min} = 0.962$, $T_{max} = 0.995$	$k = -12 \rightarrow 9$

7394 measured reflections	$l = -16 \rightarrow 16$

Refinement

Refinement on F^2	Hydrogen site location: inferred from neighbouring sites
Least-squares matrix: full	H atoms treated by a mixture of independent and constrained refinement
$R[F^2 > 2\sigma(F^2)] = 0.045$	$w = 1/[\sigma^2(F_o^2) + (0.1363P)^2]$ where $P = (F_o^2 + 2F_c^2)/3$
$wR(F^2) = 0.132$	$(\Delta/\sigma)_{max} < 0.001$
$S = 0.98$	$\Delta\rho_{max} = 0.16$ e Å^{-3}
1234 reflections	$\Delta\rho_{min} = -0.18$ e Å^{-3}
107 parameters	Extinction correction: none
17 restraints	
Primary atom site location: structure-invariant direct methods	
Secondary atom site location: difference Fourier map	

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 $F^2 > 2$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	$U_{iso}*/U_{eq}$	Occ. (<1)
O3	0.8283 (3)	0.57349 (19)	0.48653 (15)	0.0656 (6)	
O2	0.8665 (3)	0.42040 (17)	0.16325 (16)	0.0678 (6)	
H2A	0.8101	0.4268	0.1047	0.081*	
O1	0.9249 (3)	0.64337 (18)	0.13073 (16)	0.0779 (7)	
C6	0.8854 (4)	0.4570 (3)	0.45614 (19)	0.0528 (6)	
C2	1.0487 (3)	0.5464 (2)	0.29479 (19)	0.0494 (6)	
H2	1.0202	0.6363	0.3303	0.059*	
C3	1.2604 (4)	0.5434 (4)	0.2727 (3)	0.0826 (9)	
H3B	1.2864	0.6233	0.2242	0.099*	0.819 (6)
H3A	1.2872	0.4475	0.2541	0.099*	0.181 (6)
C5	1.3680 (6)	0.5682 (6)	0.3806 (4)	0.1294 (16)	
H5A	1.3225	0.5044	0.4355	0.155*	
H5B	1.3482	0.6631	0.4046	0.155*	
H5C	1.5006	0.5526	0.3689	0.155*	

C4A	1.3294 (6)	0.4166 (5)	0.2145 (4)	0.1077 (18)	0.819 (6)
H4A3	1.4634	0.4237	0.2036	0.129*	0.819 (6)
H4A1	1.2676	0.4092	0.1446	0.129*	0.819 (6)
H4A2	1.3018	0.3346	0.2575	0.129*	0.819 (6)
C4B	1.334 (3)	0.6303 (19)	0.1810 (11)	0.087 (6)	0.181 (6)
H4B1	1.4683	0.6182	0.1755	0.104*	0.181 (6)
H4B2	1.3058	0.7273	0.1947	0.104*	0.181 (6)
H4B3	1.2754	0.6015	0.1137	0.104*	0.181 (6)
H6	0.855 (6)	0.366 (4)	0.492 (3)	0.104*	
H1	1.013 (6)	0.354 (4)	0.357 (3)	0.104*	
N1	0.9895 (3)	0.4357 (2)	0.36939 (16)	0.0505 (5)	
C1	0.9393 (3)	0.5421 (2)	0.18868 (18)	0.0473 (6)	

Atomic displacement parameters ($Å^2$)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
O3	0.0753 (12)	0.0554 (10)	0.0662 (11)	0.0019 (9)	0.0235 (10)	−0.0055 (8)
O2	0.0863 (13)	0.0493 (10)	0.0677 (11)	−0.0118 (10)	−0.0304 (10)	0.0097 (8)
O1	0.1141 (17)	0.0465 (10)	0.0730 (12)	−0.0149 (11)	−0.0281 (13)	0.0134 (10)
C6	0.0603 (14)	0.0536 (15)	0.0443 (11)	−0.0022 (13)	0.0000 (11)	0.0018 (11)
C2	0.0581 (14)	0.0455 (12)	0.0445 (11)	−0.0007 (11)	0.0020 (11)	0.0003 (11)
C3	0.0542 (16)	0.116 (3)	0.0779 (18)	−0.011 (2)	−0.0072 (15)	0.015 (2)
C5	0.090 (3)	0.171 (4)	0.128 (3)	−0.027 (3)	−0.050 (3)	0.015 (3)
C4A	0.061 (2)	0.157 (4)	0.106 (3)	0.024 (3)	0.019 (2)	0.001 (3)
C4B	0.078 (11)	0.098 (13)	0.083 (12)	−0.037 (10)	0.017 (10)	0.003 (11)
N1	0.0673 (12)	0.0412 (10)	0.0431 (9)	0.0048 (10)	0.0042 (10)	−0.0006 (9)
C1	0.0544 (13)	0.0406 (11)	0.0468 (12)	−0.0028 (10)	0.0004 (11)	0.0017 (11)

Geometric parameters (Å, °)

O3—C6	1.238 (3)	C3—H3B	0.98
O2—C1	1.305 (3)	C3—H3A	0.96
O2—H2A	0.8200	C5—H5A	0.96
O1—C1	1.200 (3)	C5—H5B	0.96
C6—N1	1.305 (3)	C5—H5C	0.96
C6—H6	0.99 (4)	C4A—H4A3	0.96
C2—N1	1.454 (3)	C4A—H4A1	0.96
C2—C1	1.508 (3)	C4A—H4A2	0.96
C2—C3	1.522 (4)	C4B—H4B1	0.96
C2—H2	0.98	C4B—H4B2	0.96
C3—C4A	1.484 (4)	C4B—H4B3	0.96
C3—C4B	1.484 (5)	N1—H1	0.81 (4)
C3—C5	1.539 (5)		
C1—O2—H2A	109.5	H5A—C5—H5B	109.5
O3—C6—N1	124.5 (2)	C3—C5—H5C	109.5
O3—C6—H6	126 (2)	H5A—C5—H5C	109.5
N1—C6—H6	110 (2)	H5B—C5—H5C	109.5
N1—C2—C1	111.65 (18)	C3—C4A—H4A3	109.5

N1—C2—C3	112.4 (2)	C3—C4A—H4A1	109.5
C1—C2—C3	110.6 (2)	H4A3—C4A—H4A1	109.5
N1—C2—H2	107.3	C3—C4A—H4A2	109.5
C1—C2—H2	107.3	H4A3—C4A—H4A2	109.5
C3—C2—H2	107.3	H4A1—C4A—H4A2	109.5
C4A—C3—C2	115.1 (3)	C3—C4B—H4B1	109.5
C4B—C3—C2	117.9 (9)	C3—C4B—H4B2	109.5
C4A—C3—C5	111.8 (4)	H4B1—C4B—H4B2	109.5
C4B—C3—C5	112.6 (8)	C3—C4B—H4B3	109.5
C2—C3—C5	109.4 (3)	H4B1—C4B—H4B3	109.5
C4A—C3—H3B	106.4	H4B2—C4B—H4B3	109.5
C2—C3—H3B	106.1	C6—N1—C2	123.9 (2)
C5—C3—H3B	107.7	C6—N1—H1	115 (3)
C4B—C3—H3A	106.5	C2—N1—H1	121 (3)
C2—C3—H3A	104.7	O1—C1—O2	122.7 (2)
C5—C3—H3A	104.5	O1—C1—C2	121.8 (2)
C3—C5—H5A	109.5	O2—C1—C2	115.51 (18)
C3—C5—H5B	109.5		
N1—C2—C3—C4A	64.7 (4)	C1—C2—N1—C6	−105.3 (3)
C1—C2—C3—C4A	−60.8 (4)	C3—C2—N1—C6	129.6 (3)
N1—C2—C3—C4B	167.5 (9)	N1—C2—C1—O1	157.9 (2)
C1—C2—C3—C4B	41.9 (9)	C3—C2—C1—O1	−76.1 (3)
N1—C2—C3—C5	−62.1 (3)	N1—C2—C1—O2	−23.8 (3)
C1—C2—C3—C5	172.3 (3)	C3—C2—C1—O2	102.2 (3)
O3—C6—N1—C2	−1.6 (4)		

Hydrogen-bond geometry (Å, °)

D—H···A	D—H	H···A	D···A	D—H···A
O2—H2A···O3[i]	0.82	1.74	2.559 (2)	173
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Symmetry codes: (i) −x+3/2, −y+1, z−1/2; (ii) −x+2, y−1/2, −z+1/2.

Fig. 1

Fig. 2