Data collection

Syntex $P4$ four-circle diffractometer
$\theta/2\theta$ scans
Absorption correction: none
2204 measured reflections
1554 independent reflections
512 observed reflections $[F > 4.0\sigma(F)]$

$R_{\rm int} = 0.066$
$\theta_{\rm max} = 27.5°$
$h = -18 \rightarrow 17$
$k = -5 \rightarrow 1$
$l = -1 \rightarrow 14$
3 standard reflections monitored every 97 reflections
intensity decay: 0.0001%

Refinement

Refinement on F
$R = 0.0470$
$wR = 0.0475$
$S = 1.06$
512 reflections
119 parameters
$w = 1/[\sigma^2(F) + 0.0008F^2]$
$(\Delta/\sigma)_{\rm max} = 0.001$

$\Delta\rho_{\rm max} = 0.26$ e Å^{-3}
$\Delta\rho_{\rm min} = -0.25$ e Å^{-3}
Extinction correction: none
Atomic scattering factors from *International Tables for Crystallography* (1992, Vol. C, Tables 4.2.6.8 and 6.1.1.4)

Table 1. *Fractional atomic coordinates and equivalent isotropic displacement parameters* (Å^2)

$$U_{\rm eq} = (1/3)\Sigma_i\Sigma_j U_{ij}a_i^*a_j^*\mathbf{a}_i.\mathbf{a}_j.$$

	x	y†	z	$U_{\rm eq}$
O1	0.5038 (3)	0.069 (1)	0.3570 (4)	0.043 (3)
N1	0.4001 (4)	0.294 (1)	0.4548 (5)	0.046 (4)
C2	0.3328 (5)	0.435 (2)	0.4922 (6)	0.039 (4)
N3	0.2928 (5)	0.623 (2)	0.3985 (5)	0.046 (4)
C4	0.3254 (5)	0.587 (2)	0.3056 (6)	0.039 (4)
N4	0.4442 (5)	0.278 (1)	0.2938 (5)	0.036 (3)
C5	0.3959 (5)	0.365 (2)	0.3516 (7)	0.032 (4)
C11	0.2214 (6)	0.793 (2)	0.3926 (7)	0.039 (4)
C12	0.1789 (6)	0.964 (2)	0.2987 (7)	0.051 (4)
C13	0.1084 (6)	1.140 (2)	0.2973 (8)	0.059 (5)
C14	0.0779 (7)	1.150 (2)	0.3877 (9)	0.059 (5)
C15	0.1167 (6)	0.976 (2)	0.4782 (9)	0.062 (5)
C16	0.1876 (6)	0.805 (2)	0.4829 (7)	0.046 (5)

† The small b cell dimension is reflected in high errors in the y atomic coordinates.

Table 2. *Selected geometric parameters* (Å, °)

C11—N3	1.37 (1)	N4—O1	1.421 (8)
C11—C12	1.40 (1)	C4—C5	1.51 (1)
C11—C16	1.41 (2)	C5—N1	1.32 (1)
C12—C13	1.39 (2)	C5—N4	1.29 (1)
C13—C14	1.38 (2)	N1—C2	1.47 (1)
C14—C15	1.37 (2)	N3—C2	1.45 (1)
C15—C16	1.37 (2)	N3—C4	1.44 (1)
C4—N3—C2	113.8 (7)	C12—C11—N3	122.5 (9)
N3—C4—C5	101.6 (7)	C16—C11—N3	120.8 (8)
C4—C5—N1	109.8 (8)	C11—C12—C13	120.8 (10)
C4—C5—N4	121.1 (8)	C12—C13—C14	121.1 (9)
N1—C5—N4	129.1 (7)	C13—C14—C15	118.6 (10)
C5—N1—C2	113.7 (7)	C14—C15—C16	121.5 (11)
N3—C2—N1	100.9 (7)	C11—C16—C15	121.1 (9)
C5—N4—O1	108.9 (6)	C11—N3—C4	123.3 (7)
C12—C11—C16	116.7 (9)	C11—N3—C2	122.3 (8)

The H atom associated with the oxime O1 atom was located from a difference Fourier synthesis and the remaining H atoms were placed in sites with idealized geometry. All H atoms were included in least-squares cycles with fixed positional and isotropic displacement parameters. A variable scan rate was used, with a scan width of 0.6° below $K\alpha_1$ and 0.6° above $K\alpha_2$ to a maximum 2θ value of 60°. Refinement was completed using full-matrix least-squares methods.

Data collection: *XSCANS* (Siemens, 1991). Cell refinement: *XSCANS*. Data reduction: *XSCANS*. Program(s) used to solve structure: *SHELXS86* (Sheldrick, 1990). Program(s) used to refine structure: *SHELXS86*. Molecular graphics: *XP* (Siemens, 1990).

Lists of structure factors, anisotropic displacement parameters, H-atom coordinates and complete geometry have been deposited with the IUCr (Reference: PA1215). Copies may be obtained through The Managing Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

References

Grimmett, M. R., Hua, S. T., Chang, K. C., Foley, S. A. & Simpson, J. (1989). *J. Aust. Chem.* **42**, 1281–1289.

Hutchins, R. D., Lamson, D. W., Rua, L., Milewski, C. & Maryanoff, B. (1971). *Heterocycles*, **36**, 803–806.

Kaplan, L. A. (1964). *J. Am. Chem. Soc.* **84**, 740–741.

Makosza, M. (1992). *Pol. J. Chem.* **66**, 3–23.

Moss, M. B., Paniucci, R., McClelland, R. A. & Rauth, A. M. (1988). *Biochem. Pharmacol.* **37**, 2588–2593.

Patai, S. (1970). *The Chemistry of the Carbon-Nitrogen Double Bond*, p. 24. London: Interscience.

Sheldrick, G. M. (1990). *Acta Cryst.* A**46**, 467–473.

Siemens (1990). *XP. Interactive Molecular Graphics Program*. Version 4.1. Siemens Analytical X-ray Instruments Inc., Madison, Wisconsin, USA.

Siemens (1991). *XSCANS Users Manual*. Siemens Analytical X-ray Instruments Inc., Madison, Wisconsin, USA.

Suwinski, J., Salwinska, E., Swierczek, K. & Pawlus, W. (1994). *Heterocycles*, **37**, 1511–1520.

Suwinski, J., Swierczek, K. & Glowiak, T. (1993). *Tetrahedron*, **49**, 5339–5350.

Suwinski, J. & Walczak, K. (1994). *Pol. J. Chem.* **68**, 675–681.

Acta Cryst. (1996). **C52**, 1464–1466

L-Isoleucine, Redetermination at 120 K

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Abstract

This redetermination of L-isoleucine, $C_6H_{13}NO_2$, forms part II in the series of crystal structures of hydrophobic amino acids. Standard deviations for bond lengths between heavy atoms are down to 0.002 Å. Detailed parameters for the hydrogen-bonding pattern are given.

Comment

The hydrophobic amino acids, except L-alanine, crystallize in monoclinic space groups with alternating hydro-

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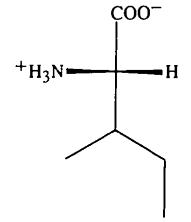
philic and hydrophobic layers, and almost identical hydrogen-bonding patterns. This makes them suitable as a database for multivariate analysis of hydrogen-bond parameters. We have undertaken a program to provide high-precision X-ray structures of these compounds. The first paper in the series describing the results of this investigation dealt with the structures of L-valine and L-methionine (Dalhus & Görbitz, 1996). The structure of L-isoleucine (L-Ile) was first determined by Torii & Iitaka (1971) with $R = 0.117$ and standard deviations for bond lengths between heavy atoms in the range 0.011–0.018 Å. The current low-temperature study is considerably more accurate with standard deviations of 0.002–0.003 Å.



L-Ile

The asymmetric unit of L-Ile, with two crystallographically independent molecules A and B, is shown in Fig. 1. All deviations between analogous bond lengths in the polar parts of the two molecules are ≤ 0.005 Å (Table 2). The most important difference, also observed for L-Val and L-Met, lies in the carboxylate group, which is symmetric in molecule A, but asymmetric in molecule B with C—O bond lengths differing by 0.014 Å (7σ) and bond angles C2B—C1B—O1B = 115.7 (2)° and C2B—C1B—O2B = 118.4 (2)°. The difference in the C2—C3 bonds observed by Torii & Iitaka (1971), 1.537 and 1.570 Å, was considered to be rather significant, but is not found at low temperature. As for the side chains, Fig. 1 reveals more extensive thermal motion in L-Ile(B), resulting in slightly shorter calculated bond lengths. This librational effect is particularly evident for the C3—C6 bond, which is 1.532 (3) Å for L-Ile(A) with $U_{\rm eq}$(C6A) = 0.022 Å^2 and 1.518 (3) Å for L-Ile(B) with $U_{\rm eq}$(C6B) = 0.052 Å^2.

The conformations of L-Ile(A) and L-Ile(B) are very similar to those of the corresponding molecules in L-Val (Dalhus & Görbitz, 1996). For the corresponding torsion angles there are no deviations larger than 1.4° between the two structures. As in L-Val(A), the side chain of L-Ile(A) is significantly twisted relative to the ideal staggered positions at the C^α—C^β bond, giving somewhat unusual values for the torsion angles with N1A—C2A—C3A—C4A = −155.0 (2)° and N1A—C2A—C3A—C6A = 79.4 (2)°.

Hydrogen-bond parameters are given in Table 3. The hydrogen-bond pattern and the crystal packing are strikingly similar to those observed previously for L-Met and L-Val (Dalhus & Görbitz, 1996).

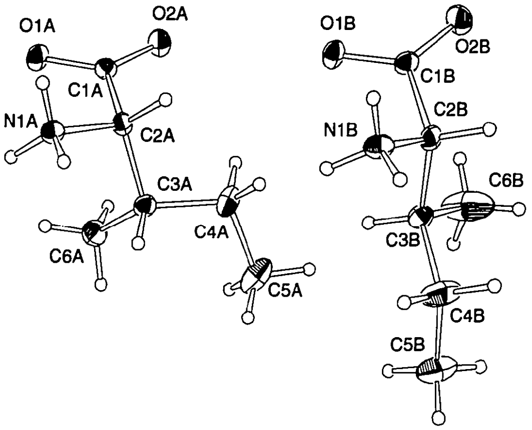


Fig. 1. The asymmetric unit with atomic numbering (*ORTEP*II; Johnson, 1976). Displacement ellipsoids are shown at the 50% probability level. H atoms are shown as spheres of arbitrary size.

Experimental

The title compound was obtained from Sigma Corporation and used without further refinement. Crystals were grown by slow cooling of a warm saturated aqueous solution.

Crystal data

$C_6H_{13}NO_2$
$M_r = 131.17$
Monoclinic
$P2_1$
$a = 9.681$ (5) Å
$b = 5.301$ (3) Å
$c = 13.956$ (6) Å
$\beta = 96.16$ (4)°
$V = 712.1$ (6) Å^3
$Z = 4$
$D_x = 1.224$ Mg m^{-3}
D_m not measured

Mo $K\alpha$ radiation
$\lambda = 0.71069$ Å
Cell parameters from 25 reflections
$\theta = 12.5$–17.5°
$\mu = 0.091$ mm^{-1}
$T = 120$ (2) K
Plate
1.00 × 0.50 × 0.05 mm
Colourless

Data collection

Nicolet $P3$ diffractometer
2θ scans
Absorption correction: none
3431 measured reflections
3431 independent reflections
2738 observed reflections [$I > 2\sigma(I)$]

$\theta_{\rm max} = 35.0$°
$h = -15 \rightarrow 15$
$k = 0 \rightarrow 8$
$l = 0 \rightarrow 22$
3 standard reflections monitored every 96 reflections
intensity decay: none

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)] = 0.0524$
$wR(F^2) = 0.1316$
$S = 1.009$
3430 reflections
205 parameters
All H-atom parameters refined
$w = 1/[\sigma^2(F_o^2) + (0.0809P)^2]$ where $P = (F_o^2 + 2F_c^2)/3$

$(\Delta/\sigma)_{\rm max} = 0.003$
$\Delta\rho_{\rm max} = 0.422$ e Å^{-3}
$\Delta\rho_{\rm min} = -0.270$ e Å^{-3}
Extinction correction: none
Atomic scattering factors from *International Tables for Crystallography* (1992, Vol. C, Tables 4.2.6.8 and 6.1.1.4)

Table 1. *Fractional atomic coordinates and equivalent isotropic displacement parameters (Å²)*

$U_{eq} = (1/3)\Sigma_i\Sigma_j U_{ij}a_i^*a_j^*\mathbf{a}_i.\mathbf{a}_j.$

	x	*y*	*z*	U_{eq}
O1*A*	0.11628 (11)	−0.0167 (3)	0.41256 (9)	0.0177 (3)
O2*A*	0.18514 (12)	0.3602 (3)	0.36350 (10)	0.0195 (3)
N1*A*	0.36618 (14)	−0.2275 (3)	0.41995 (11)	0.0149 (3)
C1*A*	0.2055 (2)	0.1312 (3)	0.38363 (12)	0.0139 (3)
C2*A*	0.34707 (15)	0.0176 (3)	0.36696 (11)	0.0133 (3)
C3*A*	0.3628 (2)	−0.0190 (4)	0.25875 (12)	0.0160 (3)
C4*A*	0.4075 (2)	0.2312 (5)	0.21567 (15)	0.0260 (4)
C5*A*	0.4308 (3)	0.2170 (6)	0.10901 (15)	0.0363 (6)
C6*A*	0.2304 (2)	−0.1279 (4)	0.20399 (13)	0.0222 (3)
O1*B*	0.62713 (12)	0.5636 (3)	0.40883 (9)	0.0175 (2)
O2*B*	0.70429 (15)	0.9557 (3)	0.38462 (11)	0.0241 (3)
N1*B*	0.88872 (15)	0.3764 (3)	0.39427 (11)	0.0182 (3)
C1*B*	0.7143 (2)	0.7198 (4)	0.38167 (12)	0.0156 (3)
C2*B*	0.8385 (2)	0.6041 (3)	0.33698 (12)	0.0158 (3)
C3*B*	0.7967 (2)	0.5281 (4)	0.23100 (12)	0.0179 (3)
C4*B*	0.9163 (2)	0.4018 (6)	0.18619 (14)	0.0338 (6)
C5*B*	0.8842 (2)	0.3372 (6)	0.07956 (15)	0.0369 (6)
C6*B*	0.7421 (4)	0.7567 (6)	0.17339 (15)	0.0536 (9)

Table 2. *Selected geometric parameters (Å, °)*

O1*A*—C1*A*	1.264 (2)	O1*B*—C1*B*	1.269 (2)
O2*A*—C1*A*	1.257 (2)	O2*B*—C1*B*	1.255 (2)
N1*A*—C2*A*	1.497 (2)	N1*B*—C2*B*	1.500 (2)
C1*A*—C2*A*	1.537 (2)	C1*B*—C2*B*	1.540 (2)
C2*A*—C3*A*	1.546 (2)	C2*B*—C3*B*	1.544 (2)
C3*A*—C6*A*	1.532 (3)	C3*B*—C6*B*	1.518 (3)
C3*A*—C4*A*	1.537 (3)	C3*B*—C4*B*	1.528 (3)
C4*A*—C5*A*	1.531 (3)	C4*B*—C5*B*	1.526 (3)
O2*A*—C1*A*—O1*A*	125.0 (2)	O2*B*—C1*B*—O1*B*	125.8 (2)
O2*A*—C1*A*—C2*A*	117.73 (15)	O2*B*—C1*B*—C2*B*	118.4 (2)
O1*A*—C1*A*—C2*A*	117.2 (2)	O1*B*—C1*B*—C2*B*	115.7 (2)
N1*A*—C2*A*—C1*A*	109.27 (13)	N1*B*—C2*B*—C1*B*	109.09 (14)
N1*A*—C2*A*—C3*A*	110.72 (14)	N1*B*—C2*B*—C3*B*	109.72 (15)
C1*A*—C2*A*—C3*A*	112.31 (13)	C1*B*—C2*B*—C3*B*	110.85 (13)
C6*A*—C3*A*—C4*A*	112.7 (2)	C6*B*—C3*B*—C4*B*	111.7 (2)
C6*A*—C3*A*—C2*A*	111.71 (14)	C6*B*—C3*B*—C2*B*	109.9 (2)
C4*A*—C3*A*—C2*A*	109.6 (2)	C4*B*—C3*B*—C2*B*	111.97 (14)
C5*A*—C4*A*—C3*A*	114.5 (2)	C5*B*—C4*B*—C3*B*	114.4 (2)
O1*A*—C1*A*—C2*A*—N1*A*	−19.0 (2)	O1*B*—C1*B*—C2*B*—N1*B*	−41.4 (2)
N1*A*—C2*A*—C3*A*—C6*A*	79.4 (2)	N1*B*—C2*B*—C3*B*—C6*B*	178.4 (2)
N1*A*—C2*A*—C3*A*—C4*A*	−154.95 (14)	N1*B*—C2*B*—C3*B*—C4*B*	−56.9 (2)
C2*A*—C3*A*—C4*A*—C5*A*	178.3 (2)	C2*B*—C3*B*—C4*B*—C5*B*	−176.4 (2)

Table 3. *Hydrogen-bonding geometry (Å, °)*

D—H···*A*	*D*—H	H···*A**	H···*A*†	*D*···*A*	*D*—H···*A**
N1*A*—H1*A*···O2*A*^{i}	0.92 (3)	1.95(3)	1.841	2.859 (2)	170 (2)
N1*A*—H2*A*···O1*B*^{i}	0.89 (3)	1.89(3)	1.751	2.778 (2)	175 (3)
N1*A*—H3*A*···O1*B*^{ii}	0.86 (2)	2.07(2)	1.931	2.839 (2)	148 (2)
N1*B*—H1*B*···O2*B*^{i}	0.93 (4)	1.94(4)	1.837	2.851 (3)	168 (3)
N1*B*—H2*B*···O2*A*^{iii}	0.85 (3)	2.13(3)	1.961	2.948 (2)	161 (4)
N1*B*—H2*B*···O1A^{iii}	0.85 (3)	2.35(4)	2.230	3.023 (2)	136 (3)
N1*B*—H3*B*···O1A^{iv}	0.85 (2)	1.91(3)	1.735	2.760 (2)	174 (2)

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

* Experimental H-atom positions. † Normalized (Taylor & Kennard, 1983) hydrogen bonds with *d*(N—H) = 1.030 Å.

Amino-group H atoms were refined isotropically, other H atoms were placed geometrically. Refinement then allowed the H atoms to move along the C—H bond direction with the C—H distance being kept constant for all H atoms on the same C atom. The U_{iso} values were fixed at 1.2 × U_{eq} of the bonded atom, except that a free variable for U_{iso} was refined for each of the four methyl groups.

Program(s) used to solve structure: *SIR*92 (Altomare *et al.*, 1994). Program(s) used to refine structure: *SHELXL*93 (Sheldrick, 1993). Molecular graphics: *ORTEP*II (Johnson, 1976).

Lists of structure factors, anisotropic displacement parameters, H-atom coordinates and complete geometry have been deposited with the IUCr (Reference: HA1156). Copies may be obtained through The Managing Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

References

Altomare, A., Cascarano, G., Giacovazzo, C., Guagliardi, A., Burla, M. C., Polidori, G. & Camalli, M. (1994). *J. Appl. Cryst.* **27**, 435.

Dalhus, B. & Görbitz, C. H. (1996). *Acta Chem. Scand.* **50**. In the press.

Johnson, C. K. (1976). *ORTEP*II. Report ORNL-5138. Oak Ridge National Laboratory, Tennessee, USA.

Sheldrick, G. M. (1993). *SHELXL*93. *Program for the Refinement of Crystal Structures*. University of Göttingen, Germany.

Taylor, R. & Kennard, O. (1983). *Acta Cryst.* B**39**, 133–138.

Torii, K. & Iitaka, Y. (1971). *Acta Cryst.* B**27**, 2237–2246.

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1,3-Adamantanedicarboxylic Acid and 1,3-Adamantanediacetic Acid

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Abstract

The structure of 1,3-adamantanedicarboxylic acid (tricyclo[3.3.1.1^{3,7}]decane-1,3-dicarboxylic acid), $C_{12}H_{16}O_4$, consists of hydrogen-bonded chains of molecules related by a glide plane. In 1,3-adamantanediacetic acid (tricyclo[3.3.1.1^{3,7}]decane-1,3-diacetic acid), $C_{14}H_{20}O_4$, the asymmetric unit comprises two hydrogen-bonded molecules and these bimolecular units are in turn linked by hydrogen bonds across centres of inversion to give chains.

Comment

The crystal structures of dicarboxylic acids in which the two acidic functions are at sites remote from one another on a rigid three-dimensional framework exhibit a range of hydrogen-bonding patterns. The structures of bicyclo[2.2.2]octane-1,4-dicarboxylic acid (Ermer &