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Structure of L-Leucine: a Redetermination

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Abstract. $C_6H_{13}NO_2$, $M_r = 131.2$, monoclinic, $P2_1$, $a = 14.666$ (2), $b = 5.324$ (7), $c = 9.606$ (3) Å, $\beta = 94.06$ (3)°, $V = 748$ (1) Å^3, $Z = 4$, $D_x = 1.16$ Mg m^{-3}, $\lambda(\text{Mo } K\alpha) = 0.71069$ Å, $\mu = 0.087$ mm^{-1}, $F(000) = 288$, room temperature, $R = 0.058$ for 686 observed reflections. The crystals studied and the conformation obtained are similar to those reported by Harding & Howieson [Acta Cryst. (1976), B32, 633–634], but the present structure is more accurately determined. The crystal studied and the conformation obtained are similar to those reported by Harding & Howieson but the present structure is more accurately determined, and the hydrogen-bonding scheme is clearly defined. The crystal structure contains hydrophobic layers intercalated with hydrophilic ones.

Introduction. The zwitterionic structure of L-Leu has been described by Harding & Howieson (1976). These authors refined the structure to $R = 0.13$. They reported that the atom positions had not been accurately determined because of the poor quality of their crystals. Here we present a redetermination of the structure.

Experimental. Thin colorless plates obtained by vapor diffusion of acetone into acetone–aqueous solution of amino acid. Crystal $0.05 \times 0.7 \times 1.5$ mm mounted in capillary. Philips PW 1100 diffractometer, Mo $K\alpha$ radiation, graphite monochromator. h, k, l range $= \pm 14$, 6, 11. Cell parameters from 25 reflections $(4 \leq \theta \leq 9°)$, ω-scan technique. Three reflections measured every 2 h as intensity control, no significant differences. 1170 independent reflections $(\theta \leq 25°)$, 686 with $I > 2.5\sigma(I)$; Lp correction, absorption ignored. Structure determined by direct methods (MULTAN80; Main, Fiske, Hull, Lessinger, Germain, Declercq & Woolfson, 1980). Anisotropic full-matrix least-squares refinement on F with SHELX76 (Sheldrick, 1976). f, f'

and f'' for all atoms from *International Tables for X-ray Crystallography* (1974). Almost all H atoms visible in difference Fourier maps, included at calculated positions, overall isotropic temperature factor refined to $U = 0.091$ (8) Å^2. Final $R = 0.058$, $wR = 0.058$, $w = [\sigma^2(F) + 0.001221\sigma|F|^2]^{-1}$, max. shift/e.s.d. $= 0.43$, max. and min. heights in final difference Fourier synthesis 0.26 and -0.28 e Å^{-3}. IBM 4341 and VAX 750 computers.

Discussion. The final atomic parameters are given in Table 1* and the molecular dimensions are shown in Fig. 1. In Table 2* the torsion angles of the present structure are compared with those found in previously determined L-Leu structures (Harding & Howieson, 1976; Subramanian, 1967; Chaney, Seely & Steinrauf, 1971; Di Blasio, Pedone & Sirigu, 1975). All adopt extended conformations where the methyl groups are at a maximum distance from the polar groups. This feature is also found in the packing arrangement of the present structure (Fig. 2). The molecules on both sides of the unit cell shown in Fig. 2 are organized in layers parallel to the *bc* face of the crystal. These layers interact through hydrogen bonds on one side, as shown at the center of Fig. 2. On the other side, the interaction involves the methyl groups of the leucine side chains. The organization of the crystal thus resembles that found in alternating polypeptides, such as poly(Lys-Leu), in which *β*-sheets are formed with the basic groups on one side and the leucine side chains on the other. In this way the structure contains hydrophobic layers which are intercalated with hydrophilic layers, as shown by Brack & Orgel (1975) and by Vives, Azorin, Subirana, Brack & Mayer (1985).

Every amino N atom forms H bonds with three different molecules and not two (see Fig. 2 and Table 3). There are other N(amino)···O(carboxylic) intramolecular distances shorter than 3 Å, but we do not consider these to be H bonds since no H atom was found between these atoms, in spite of the fact that the H atoms, even though they were placed and refined with geometrical restrictions, were free to rotate with the N atom. One of the H atoms linked to N(*B*) forms a bifurcated H bond with O(1*A*) and O(2*A*). In this respect our hydrogen-bonding scheme differs from that of Harding & Howieson (1976). As a result, the H-bond distances are increased in this case, as shown in Table 3.

Table 1. *Fractional atomic coordinates with e.s.d.'s in parentheses and equivalent isotropic thermal parameters (Å^2)*

	x	y	z	B_{eq}*
N(*A*)	0.5746 (4)	0.1644 (22)	0.8874 (6)	2.51
O(1*A*)	0.5870 (4)	0.3815 (21)	0.6389 (6)	3.28
O(2*A*)	0.6363 (4)	0.7426	0.7305 (6)	3.59
C(1*A*)	0.6184 (6)	0.5122 (19)	0.7379 (9)	2.32
C(2*A*)	0.6363 (5)	0.3888 (25)	0.8800 (8)	2.53
C(3*A*)	0.7361 (5)	0.2829 (26)	0.8979 (9)	3.43
C(4*A*)	0.8100 (6)	0.4853 (27)	0.9049 (10)	3.87
C(5*A*)	0.8073 (8)	0.6485 (30)	1.0299 (12)	6.37
C(6*A*)	0.9032 (6)	0.3446 (37)	0.9079 (13)	7.11
N(*B*)	0.4050 (5)	0.2545 (20)	0.5873 (7)	3.34
O(1*B*)	0.4136 (3)	0.4496 (18)	0.8471 (6)	2.85
O(2*B*)	0.3820 (5)	0.8350 (22)	0.7645 (7)	3.91
C(1*B*)	0.3861 (6)	0.6036 (28)	0.7547 (9)	2.75
C(2*B*)	0.3526 (5)	0.4893 (21)	0.6130 (8)	2.48
C(3*B*)	0.2507 (6)	0.4123 (28)	0.6130 (9)	3.98
C(4*B*)	0.1841 (6)	0.6283 (36)	0.6114 (11)	5.65
C(5*B*)	0.1781 (8)	0.7725 (36)	0.4792 (13)	7.08
C(6*B*)	0.0894 (6)	0.5242 (45)	0.6405 (15)	10.03

$$* B_{eq} = \tfrac{8}{3}\pi^2 \sum_i \sum_j U_{ij} a_i^* a_j^* \mathbf{a}_i . \mathbf{a}_j .$$
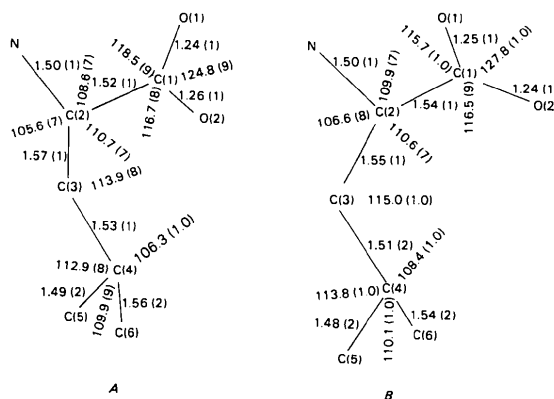

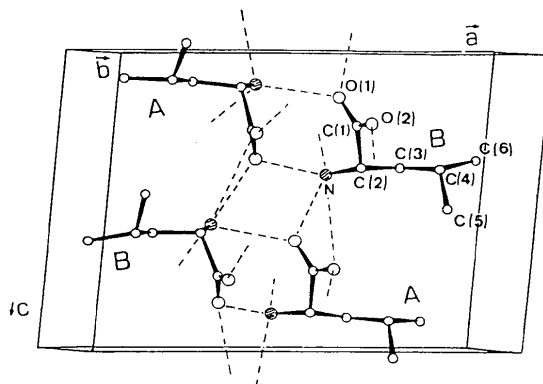Fig. 1. Bond distances (Å) and angles (°) with e.s.d.'s in parentheses.

Fig. 2. The unit cell. N atoms are indicated by hatched circles, H bonds by broken lines.

Table 3. *Hydrogen-bond lengths* (Å)

$A-H\cdots B$	$A\cdots B$	$H\cdots B$
N(A)—H$\cdots$O(1B)	2·811 (9)	1·753 (9)
N(A)—H$\cdots$O(2A^i)	2·885 (11)	1·887 (11)
N(A)—H$\cdots$O(1B^{ii})	2·789 (9)	1·721 (9)
N(B)—H$\cdots$O(1A)	2·764 (9)	1·689 (9)
N(B)—H$\cdots$O(1A^{iii})	2·952 (9)	2·104 (9)*
N(B)—H$\cdots$O(2A^{iii})	3·070 (10)	2·027 (10)*
N(B)—H$\cdots$O(2B^i)	2·842 (11)	1·765 (11)

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

* Bifurcated hydrogen bond.

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Structure of 9-{2-[(4-Imidazolyl)methylthio]ethyl}adenine

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Abstract. $C_{11}H_{13}N_7S$, $M_r = 275\cdot33$, monoclinic, $P2_1/c$, $a = 15\cdot495$ (1), $b = 8\cdot345$ (1), $c = 9\cdot926$ (1) Å, $\beta = 97\cdot205$ (5)°, $V = 1273\cdot4$ (2) Å^3, $Z = 4$, $D_m = 1\cdot44$, $D_x = 1\cdot436$ g cm^{-3}, Cu $K\alpha$, $\lambda = 1\cdot54184$ Å, $\mu = 21\cdot9$ cm^{-1}, $F(000) = 576$, room temperature, $R = 0\cdot069$ for 1496 reflexions. The adenine moieties are arranged so as to form ribbons along the twofold screw axes through N(6)H$\cdots$N(7) and N(6)H$\cdots$N(1) hydrogen bonds. The imidazolyl groups are connected to each other along the c axis by N(1′)H$\cdots$N(3′) hydrogen bonds. There are no direct interactions between the neutral imidazolyl group and the adenine moiety. This is in contrast with the stacking interactions between the protonated imidazolyl group and the adenine moiety in the crystal of 3-(9-adeninyl)-propionhistamide hydrochloride (9-{2-[(4-imidazolyl)-methylthio]ethyl}adenine hydrochloride).

Introduction. As a model of the interaction between histidine and adenine, we have determined the structure of 3-(9-adeninyl)propionhistamide hydrochloride by X-ray analysis and found that the imidazolium group stacks with the adenine moiety in the crystal (Takenaka, Takimoto & Sasada, 1984). Changes in UV and NMR spectra on mixing histamine and adenine derivatives are different between acidic and neutral solutions (Takenaka, Takimoto & Sasada, 1984). In order to reveal the structural basis of the difference, we have determined the crystal structure of the title compound in which the imidazolyl group is not protonated.

Experimental. The title compound was synthesized by one of the authors (MO, unpublished work). Prism-like crystals from ethanol solution; D_m by flotation in a mixture of cyclohexane and carbon tetrachloride; crystal size $0\cdot48 \times 0\cdot15 \times 0\cdot01$ mm; Rigaku four-circle diffractometer; graphite-monochromated Cu $K\alpha$ radiation; unit-cell dimensions determined by least squares with 34 high-angle reflexions; intensities measured for $5° < 2\theta < 125°$; h −18~18, k 0~10, l 0~12; ω-scan mode; scan rate 4° min^{-1}; scan width 2°; five reference reflexions monitored every 50 reflexions, no significant intensity deterioration; corrections for Lorentz, polarization and absorption; 2028 independent reflexions, 485 reflexions with no net