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The Crystal Structure of L-Isoleucine

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The crystal structure of L-isoleucine has been determined by X-ray analysis. L-Isoleucine crystallizes in the monoclinic space group $P2_1$, $Z=4$, with lattice constants $a=9{\cdot}75$, $b=5{\cdot}32$, $c=14{\cdot}12$ Å, $\beta=95{\cdot}8°$. Final refinement was carried out for 1387 observed structure factors by the full-matrix least-squares method including anisotropic thermal parameters. The R value was 0·117. Two crystallographically independent molecules have different rotational angles about the C^α–C^β bond. The crystal structure is formed by hydrogen-bonded double layers of molecules stacked in such a way that their terminal groups of the side chain face each other. The molecular and crystal structures are closely related to those in L-valine. Crystal data for other L-α-amino acids having similar hydrocarbon side chains are given indicating that they also have closely related crystal structures.

Introduction

On the basis of infrared spectroscopic study, the crystal of L-isoleucine was assumed to belong to a rather unusual type in which the molecules take two kinds of conformation (Tsuboi, Takenishi & Iitaka, 1959). L-Valine also crystallizes into the same type of crystal. The crystal structure of L-valine was investigated by X-ray diffraction methods; it contains two crystallographically independent molecules having different rotational angles about the C^α–C^β bond: *trans* and *gauche* I forms (Torii & Iitaka, 1970). The present study of the crystal structure of L-isoleucine was undertaken to compare its structure with that of L-valine and to establish a typical structure of L-α-amino acids having hydrophobic side chains.

Experimental

Crystals of L-isoleucine were grown from a warm saturated aqueous solution by slow cooling. They are colourless thin plates elongated along the b axis with well developed {001} faces.

Unit-cell dimensions were measured on $0kl$ and $h0l$ precession photographs. The crystal density was measured by the flotation method using benzene-carbon tetrachloride mixture. Crystal data are as follows:

L-Isoleucine, $C_6H_{13}O_2N$, M.W. 131·2
Monoclinic
$a=9{\cdot}75\pm0{\cdot}02$, $b=5{\cdot}32\pm0{\cdot}02$, $c=14{\cdot}12\pm0{\cdot}02$ Å
$\beta=95{\cdot}8\pm0{\cdot}2°$
$U=723{\cdot}0$ Å^3
$D_m=1{\cdot}202$ g.cm^{-3}, $D_x=1{\cdot}196$ g.cm^{-3}
$Z=4$
Systematic absences, $0k0$ when $k\neq2n$
Space group, $P2_1$.

Three-dimensional intensity data were collected from multiple-film equi-inclination Weissenberg photographs. For both the a and b axes, five layers from zero to the 4th layer were taken with Cu $K\alpha$ radiation.

The size of the crystal was about $0{\cdot}13 \times 0{\cdot}35 \times 0{\cdot}50$ mm for the *a* axis and about $0{\cdot}2 \times 0{\cdot}4 \times 0{\cdot}9$ mm for the *b* axis; in both cases the longest edge was parallel to the *b* axis. Intensities were measured by the use of a microdensitometer and partly by visual estimation. Values were corrected for Lorentz, polarization and spot-shape factors but not for absorption factors. These values were then scaled to a common base by correlating various layers. The mean-temperature factor was calculated to be 2·1 Å^2 by Wilson's method. The total number of observed non-zero structure factors was 1387 which corresponds to 87% of the possible reflexions within the sphere of $\theta \le 80°$.

Statistical values of the normalized structure factors are:

	Observed	Theoretical (non-centric)
$\langle \lvert E\rvert^2 \rangle$	0·996	1·000
$\langle \lvert E\rvert \rangle$	0·839	0·886
$\langle \lvert \lvert E\rvert^2-1 \rvert \rangle$	0·795	0·736

X-ray diffraction photographs showed weak diffuse scattering extending in the **c*** direction along the row lines in reciprocal space.

Determination and refinement of the structure

The crystal structure of L-isoleucine was solved on the basis of that of L-valine (Torii & Iitaka, 1970). Both of these crystals belong to the same space group and have similar lattice constants; hence, the fractional coordinates of all atoms except γ and δ carbon atoms of the two crystallographically independent L-isoleucine molecules were assumed to be the same as those in L-valine. (Following the convention of selecting axes in monoclinic crystals, the directions of the *a* and *b* axes are reversed to those in L-valine.) A three-dimensional electron density map, based on the 12 atoms revealed six carbon atoms at γ and δ positions. Calculated structure factors for the whole 18 atoms gave an *R* value of 0·24.

Refinement of the structural parameters was carried out by successive use of least-squares methods. The final result was obtained by full-matrix least-squares calculations using the *ORFLS* program of Busing, Martin & Levy (1962). Atomic scattering factors used for carbon, nitrogen and oxygen atoms were those of Berghuis, Haanappel, Potters, Loopstra, MacGillavry & Veenendaal (1955). The final *R* value was 0·117 for 1387 observed structure factors. The weight function was chosen as:

$$\sqrt{w}=F_o/8{\cdot}0\,, \quad \text{if} \quad F_o \le 8{\cdot}0\,,$$
$$\sqrt{w}=8{\cdot}0/F_o\,, \quad \text{if} \quad 8{\cdot}0 < F_o \le 40{\cdot}0\,,$$
$$\sqrt{w}=8{\cdot}0\times 40{\cdot}0/F_o^2\,, \quad \text{if} \quad 40{\cdot}0 < F_o\,.$$

Parameter shifts obtained in the final cycle were less than $\frac{1}{3}$ of the estimated standard deviations of the corresponding parameters. Final values are listed in

Table 1. *Final atomic parameters and their e.s.d.'s*

For L molecules the coordinates refer to the right-handed system. Temperature factors are in the form: $T=\exp\,[-(\beta_{11}h^2+\beta_{22}k^2+\beta_{33}l^2+2\beta_{12}hk+2\beta_{13}hl+2\beta_{23}kl)]$

Molecule *A*	x	y	z	β_{11}	β_{22}	β_{33}	β_{12}	β_{13}	β_{23}
O(1)	0·1188 (5)	−0·0167 (0)	0·4126 (4)	0·0035 (4)	0·0244 (26)	0·0041 (3)	0·0006 (9)	0·0009 (3)	0·0016 (7)
O(2)	0·1892 (6)	0·3526 (17)	0·3643 (4)	0·0075 (6)	0·0143 (23)	0·0045 (3)	0·0027 (10)	−0·0001 (4)	0·0007 (7)
N(1)	0·3669 (5)	−0·2316 (17)	0·4194 (4)	0·0029 (5)	0·0154 (25)	0·0034 (3)	0·0028 (9)	−0·0004 (3)	0·0002 (7)
C(1)	0·2082 (6)	0·1266 (19)	0·3841 (5)	0·0032 (6)	0·0174 (30)	0·0018 (3)	0·0023 (11)	−0·0000 (3)	−0·0002 (8)
C(2)	0·3474 (6)	0·0131 (19)	0·3670 (5)	0·0034 (6)	0·0172 (31)	0·0035 (4)	−0·0007 (12)	−0·0007 (4)	0·0014 (9)
C(3)	0·3611 (7)	−0·0283 (19)	0·2582 (5)	0·0061 (7)	0·0188 (31)	0·0027 (4)	0·0008 (13)	0·0002 (4)	0·0005 (8)
C(4)	0·4043 (10)	0·2216 (26)	0·2134 (7)	0·0111 (11)	0·0412 (49)	0·0045 (5)	−0·0057 (20)	0·0021 (6)	0·0014 (14)
C(5)	0·4344 (12)	0·1990 (32)	0·1078 (7)	0·0144 (13)	0·0681 (76)	0·0035 (5)	−0·0037 (27)	0·0015 (6)	0·0057 (16)
C(6)	0·2285 (9)	−0·1389 (24)	0·2042 (6)	0·0098 (10)	0·0325 (41)	0·0033 (4)	−0·0004 (18)	−0·0006 (5)	−0·0022 (11)
Molecule *B*									
O(11)	0·6268 (4)	0·5471 (15)	0·4083 (4)	0·0035 (4)	0·0192 (22)	0·0039 (3)	0·0050 (8)	0·0012 (3)	0·0025 (6)
O(12)	0·7050 (7)	0·9342 (16)	0·3830 (5)	0·0096 (7)	0·0161 (26)	0·0061 (4)	0·0020 (10)	0·0017 (4)	−0·0001 (8)
N(11)	0·8867 (6)	0·3542 (17)	0·3960 (5)	0·0046 (6)	0·0179 (27)	0·0037 (3)	0·0051 (11)	−0·0002 (4)	−0·0017 (8)
C(11)	0·7148 (7)	0·6962 (19)	0·3818 (6)	0·0047 (7)	0·0139 (31)	0·0034 (4)	0·0041 (12)	0·0004 (4)	0·0013 (8)
C(12)	0·8384 (7)	0·5808 (19)	0·3375 (6)	0·0040 (6)	0·0192 (32)	0·0036 (4)	0·0000 (12)	−0·0001 (4)	−0·0008 (9)
C(13)	0·7983 (7)	0·5049 (20)	0·2334 (5)	0·0043 (6)	0·0243 (32)	0·0030 (4)	−0·0004 (13)	0·0001 (4)	0·0006 (9)
C(14)	0·9237 (10)	0·3867 (30)	0·1879 (7)	0·0092 (10)	0·0775 (77)	0·0034 (5)	0·0028 (24)	0·0008 (5)	−0·0089 (16)
C(15)	0·8916 (14)	0·3183 (32)	0·0824 (8)	0·0203 (18)	0·0621 (77)	0·0041 (6)	0·0030 (34)	0·0020 (8)	−0·0035 (19)
C(16)	0·7416 (18)	0·7328 (33)	0·1760 (8)	0·0320 (27)	0·0527 (65)	0·0039 (6)	0·0186 (39)	0·0009 (10)	0·0040 (17)

Table 2. *Observed and calculated structure factors*

H	K	L	|F(OBS)|	|F(CAL)|
0	0	2	26.40	27.88
0	0	3	12.97	18.22
0	0	4	54.22	72.02
0	0	5	63.15	78.34
0	0	6	39.48	37.08
0	0	7	26.32	21.27
0	0	8	17.00	14.25
0	0	9	11.98	12.57
0	0	10	18.68	17.58
0	0	14	6.85	4.48
0	1	1	5.34	3.84
0	1	2	21.37	20.49
0	1	3	9.73	7.22
0	1	4	22.83	18.78
0	1	5	4.31	6.01
0	1	6	8.08	3.86
0	1	7	15.82	14.10
0	1	8	16.80	14.92
0	1	9	4.67	4.78
0	1	10	8.40	6.64
0	1	11	9.11	9.00
0	1	12	3.67	3.29
0	1	13	5.27	4.63
0	1	14	4.51	3.66
0	1	17	3.23	2.64
0	2	0	19.35	21.00
0	2	1	23.22	22.57
0	2	2	8.48	6.40
0	2	3	19.01	17.84
0	2	4	4.26	2.56
0	2	5	15.68	14.62
0	2	6	8.29	8.76
0	2	7	8.04	7.62
0	2	8	8.39	9.31
0	2	9	5.61	6.50
0	2	10	7.03	6.47
0	2	11	4.81	5.93
0	2	12	4.45	5.17
0	2	15	2.54	2.56
0	2	17	1.78	1.95
0	3	1	12.84	12.20
0	3	2	21.86	20.53
0	3	3	15.53	16.27
0	3	4	7.60	6.45
0	3	5	10.96	9.91
0	3	6	7.48	7.34
0	3	7	7.87	7.01
0	3	8	7.22	7.75
0	3	9	4.79	5.25
0	3	10	10.90	13.06
0	3	11	2.55	2.13
0	3	12	1.40	3.07
0	3	14	5.67	4.18
0	3	15	3.58	3.31
0	3	16	2.06	2.08
0	4	0	5.72	5.66
0	4	1	4.62	3.79
0	4	2	5.12	3.31
0	4	3	6.46	6.06
0	4	4	6.53	5.93
0	4	5	1.15	2.07
0	4	6	9.65	9.42
0	4	7	8.22	7.58
0	4	8	5.38	5.33
0	4	9	5.73	5.29
0	4	10	2.49	2.14
0	4	11	5.88	5.41
0	4	12	7.63	6.98
0	4	13	4.20	3.68
0	4	14	3.16	4.04
0	5	1	13.15	11.99
0	5	2	14.59	16.43
0	5	3	13.23	13.11
0	5	4	4.74	3.86
0	5	6	8.94	7.02
0	5	7	9.99	9.37
0	5	8	7.19	6.79
0	5	10	4.59	4.21
0	5	11	3.42	4.01
0	5	12	4.65	4.76
0	6	0	6.02	4.81
0	6	4	2.95	3.09
0	6	5	3.26	3.62
0	6	6	4.93	3.26
0	6	7	4.41	4.54
0	6	8	2.99	4.45
1	0	-17	4.68	3.74
1	0	-15	5.62	5.17
1	0	-14	2.97	3.40
1	0	-13	5.80	6.24
1	0	-12	9.74	10.72
1	0	-11	1.82	3.31
1	0	-10	4.35	4.42
1	0	-8	14.22	13.32
1	0	-7	14.93	10.98
1	0	-6	9.95	6.63
1	0	-5	14.14	10.41
1	0	-4	8.01	6.72
1	0	-3	3.20	1.48
1	0	-2	7.21	5.37
1	0	1	4.78	3.37
1	0	2	10.92	8.86
1	0	3	12.99	9.82
1	0	4	2.88	3.53
1	0	5	2.67	3.76
1	0	6	15.71	12.27
1	0	7	4.84	3.85
1	0	8	5.60	2.63
1	0	9	7.87	8.17
1	0	10	4.35	2.68
1	0	12	6.20	5.63
1	0	13	10.45	11.76
1	0	17	3.36	3.93
1	1	-17	2.96	3.47
1	1	-15	4.00	3.70
1	1	-14	4.41	3.61
1	1	-13	3.16	2.99
1	1	-12	10.53	11.47
1	1	-11	10.17	9.90
1	1	-10	4.92	4.39
1	1	-9	10.61	8.92
1	1	-8	11.92	12.61
1	1	-7	6.61	5.45
1	1	-6	11.38	11.53
1	1	-5	13.65	14.54
1	1	-4	19.55	18.07
1	1	-3	14.81	14.40
1	1	-2	16.62	16.33
1	1	-1	16.90	23.85
1	1	0	44.87	65.86
1	1	1	28.64	37.35
1	1	2	36.64	38.11
1	1	3	37.05	37.57
1	1	4	34.57	33.34
1	1	5	26.83	27.92
1	1	6	29.42	30.99
1	1	7	17.19	15.85
1	1	8	22.61	25.10
1	1	9	13.12	13.01
1	1	10	10.82	14.28
1	1	11	8.14	6.02
1	1	12	7.84	6.70
1	1	13	5.66	6.14
1	1	14	5.95	5.80
1	1	15	6.57	6.36
1	1	16	3.81	3.76
1	1	17	1.31	2.37
1	2	-17	4.64	4.95
1	2	-16	2.68	2.90
1	2	-15	5.65	6.16
1	2	-14	4.63	4.55
1	2	-13	3.25	2.41
1	2	-12	6.09	5.94
1	2	-11	8.13	7.38
1	2	-10	14.73	14.96
1	2	-9	8.78	8.74
1	2	-8	7.93	6.52
1	2	-7	8.04	7.33
1	2	-6	9.21	7.50
1	2	-5	8.35	7.09
1	2	-4	13.40	11.74
1	2	-3	16.55	10.35
1	2	-2	5.51	6.58
1	2	-1	8.52	9.46
1	2	0	20.67	22.27
1	2	1	9.82	9.58
1	2	2	10.82	8.78
1	2	3	13.31	10.17
1	2	4	13.58	10.07
1	2	5	18.32	13.97
1	2	6	6.48	6.22
1	2	7	10.51	10.24
1	2	8	11.45	11.32
1	2	9	7.83	7.14
1	2	10	13.78	13.18
1	2	11	7.97	8.32
1	2	12	5.38	5.38
1	2	13	3.50	3.78
1	2	14	2.78	2.86
1	2	15	3.96	3.79
1	2	16	3.02	3.47
1	3	-16	2.50	1.77
1	3	-15	6.08	5.92
1	3	-14	6.89	5.55
1	3	-13	6.67	5.92
1	3	-12	5.82	5.72
1	3	-11	7.90	7.16
1	3	-10	11.26	12.29
1	3	-9	12.10	13.54
1	3	-8	4.01	3.47
1	3	-7	6.74	6.97
1	3	-6	9.78	9.41
1	3	-5	4.96	5.72
1	3	-4	14.13	14.62
1	3	-3	18.65	18.99
1	3	-2	7.37	6.82
1	3	-1	25.55	26.30
1	3	0	11.54	10.76
1	3	1	12.40	10.80
1	3	2	14.21	13.60
1	3	3	26.74	25.92
1	3	4	19.18	17.99
1	3	5	4.11	3.33
1	3	7	5.44	4.93
1	3	8	9.22	9.09
1	3	9	5.86	6.28
1	3	10	6.56	6.51
1	3	11	2.89	2.07
1	3	12	4.03	3.33
1	3	15	3.29	3.16
1	4	-14	5.19	5.07
1	4	-13	3.80	4.24
1	4	-12	3.37	3.59
1	4	-11	9.02	8.50
1	4	-10	6.51	6.90
1	4	-9	6.24	5.94
1	4	-8	3.94	3.71
1	4	-7	7.05	7.17
1	4	-6	9.46	8.93
1	4	-5	9.67	10.11
1	4	-4	6.19	5.65
1	4	-3	5.19	5.49
1	4	-2	9.31	9.16
1	4	-1	5.84	5.27
1	4	0	11.34	12.62
1	4	1	7.63	6.95
1	4	2	6.00	6.03
1	4	3	7.42	7.32
1	4	4	5.01	4.59
1	4	5	9.54	9.72
1	4	6	11.38	8.55
1	4	7	5.17	5.61
1	4	8	6.07	6.66
1	4	9	4.85	5.38
1	4	10	6.82	6.72
1	4	11	2.72	2.98
1	4	13	4.23	5.13
1	4	14	5.95	6.93
1	5	-8	5.43	4.99
1	5	-7	2.82	2.50
1	5	-6	7.51	7.37
1	5	-5	7.33	7.25
1	5	-3	2.37	1.59
1	5	-2	2.75	2.68
1	5	-1	3.38	3.22
1	5	0	9.25	9.67
1	5	1	6.61	5.14
1	5	2	3.76	3.10
1	5	3	4.43	3.95
1	5	4	4.28	3.06
1	5	5	6.91	7.34
1	5	6	4.20	6.00
1	5	8	4.99	6.23
1	5	9	2.77	3.35
1	5	10	4.28	5.03
1	6	-8	4.72	5.04
1	6	-7	4.71	4.87
1	6	-5	2.61	3.04
1	6	-4	4.42	4.00
1	6	-3	1.87	2.96
1	6	-2	3.67	3.84
1	6	-1	1.94	2.55
1	6	1	6.80	5.99
1	6	2	7.42	7.74
1	6	3	4.35	4.49
1	6	5	7.31	7.67
1	6	7	4.96	4.06
1	6	8	2.73	5.29
2	0	-16	3.71	3.63
2	0	-13	8.23	8.19
2	0	-9	9.27	10.10
2	0	-8	4.81	4.27
2	0	-7	13.71	12.42
2	0	-6	4.02	2.28
2	0	-5	39.23	42.85
2	0	-4	9.49	10.80
2	0	-2	12.56	15.97
2	0	-1	5.87	3.21
2	0	0	39.75	56.66
2	0	1	50.07	63.57
2	0	2	42.77	48.83
2	0	3	29.46	41.51
2	0	4	28.66	30.81
2	0	5	17.75	19.64
2	0	6	7.62	7.43
2	0	7	17.93	18.55
2	0	8	26.95	28.38
2	0	9	9.43	9.15
2	0	10	3.25	4.05
2	0	11	7.62	8.52
2	0	12	8.96	10.17
2	0	13	2.44	3.34
2	0	17	2.72	2.94
2	1	-17	3.89	2.85
2	1	-14	6.02	5.03
2	1	-13	6.60	5.42
2	1	-12	2.70	2.48
2	1	-11	4.05	4.20
2	1	-10	11.42	11.99
2	1	-9	8.82	9.98
2	1	-8	5.01	2.80
2	1	-7	10.73	7.50
2	1	-6	11.22	9.27
2	1	-5	7.01	6.08
2	1	-4	21.77	22.49
2	1	-3	14.29	15.14
2	1	-2	14.66	11.69
2	1	-1	40.81	40.94
2	1	0	23.83	23.02
2	1	1	9.87	8.70
2	1	2	21.93	19.71
2	1	3	20.33	16.82
2	1	4	12.23	10.07
2	1	5	15.33	12.39
2	1	6	18.06	13.97
2	1	7	9.98	8.55
2	1	8	14.27	13.18
2	1	9	7.80	7.51
2	1	10	15.31	15.90
2	1	11	12.36	11.85
2	1	12	4.95	4.89
2	1	13	4.60	3.60
2	1	15	5.77	5.57
2	1	16	6.81	5.38
2	2	-17	2.14	2.60
2	2	-15	6.86	6.78
2	2	-14	7.55	6.22
2	2	-13	4.10	3.18
2	2	-12	7.31	6.97
2	2	-11	7.06	7.06
2	2	-10	11.38	11.47
2	2	-9	23.74	26.88
2	2	-8	13.43	13.94
2	2	-7	11.41	12.12
2	2	-6	7.92	6.56
2	2	-5	16.48	17.27
2	2	-4	28.39	26.15
2	2	-3	25.29	28.91
2	2	-2	5.59	5.39
2	2	-1	9.75	6.15
2	2	0	7.82	6.63
2	2	1	6.16	5.36
2	2	2	15.47	12.84
2	2	3	34.10	34.89
2	2	4	20.99	20.82
2	2	5	12.56	10.91
2	2	6	7.56	6.72
2	2	7	12.73	12.34
2	2	8	18.53	19.16
2	2	9	17.40	17.88
2	2	10	8.18	8.70
2	2	12	2.34	4.53
2	2	13	8.13	8.11
2	2	14	5.77	5.87
2	2	15	5.82	4.91
2	2	16	3.91	3.59
2	3	-16	2.35	3.01
2	3	-15	5.04	5.15
2	3	-14	3.78	4.23
2	3	-12	3.34	4.21
2	3	-11	5.66	5.57
2	3	-10	9.12	9.63
2	3	-9	12.44	13.19
2	3	-8	5.95	5.15
2	3	-7	10.16	10.55
2	3	-6	8.72	8.72
2	3	-5	15.61	16.55
2	3	-4	8.89	8.29
2	3	-3	4.37	7.19
2	3	-2	11.56	11.25
2	3	-1	13.23	11.86
2	3	0	7.45	6.60
2	3	1	12.82	12.11
2	3	2	17.41	15.00
2	3	3	17.34	11.24
2	3	4	10.65	10.27
2	3	5	15.76	14.75
2	3	6	8.40	8.64
2	3	7	8.20	7.57
2	3	8	4.41	4.30
2	3	9	3.85	5.05
2	3	10	5.98	4.99
2	3	11	3.06	2.79
2	3	12	3.87	3.34
2	3	13	2.67	1.93
2	3	14	3.10	3.02
2	3	15	2.21	3.76
2	4	-14	3.64	3.31
2	4	-13	4.77	5.06
2	4	-12	5.99	6.35
2	4	-10	4.73	3.63
2	4	-9	8.24	8.47
2	4	-8	6.94	7.14
2	4	-6	5.27	5.09
2	4	-5	8.12	7.26
2	4	-4	8.16	7.63
2	4	-3	9.48	9.55
2	4	-2	7.79	7.89
2	4	-1	9.75	10.34
2	4	0	4.04	2.85
2	4	1	1.66	3.20
2	4	2	1.54	3.65
2	4	3	8.40	8.23
2	4	4	3.80	4.12
2	4	5	1.11	1.59
2	4	6	3.77	4.12
2	4	7	2.41	4.98
2	4	8	1.83	4.23
2	4	9	10.03	8.99
2	4	13	5.33	5.24
2	5	-12	4.14	5.02
2	5	-11	5.24	6.08
2	5	-8	6.29	5.47
2	5	-7	9.64	8.13
2	5	-6	7.86	7.66
2	5	-4	9.02	9.21
2	5	-3	6.19	7.89
2	5	-2	4.16	6.08
2	5	0	4.91	7.85
2	5	1	10.20	10.89
2	5	2	7.01	7.71
2	5	4	5.84	5.14
2	5	5	5.72	7.27
2	5	9	3.57	4.70
2	6	-7	4.33	4.69
2	6	-6	2.86	3.33
2	6	-5	3.28	2.75
3	0	-16	3.36	3.37
3	0	-11	2.82	1.24
3	0	-10	8.08	8.17
3	0	-9	2.97	3.60
3	0	-8	3.53	2.20
3	0	-6	12.92	14.47
3	0	-5	16.62	15.81
3	0	-4	3.57	3.14
3	0	-3	8.19	6.87
3	0	-2	3.78	3.17
3	0	-1	2.03	1.27
3	0	0	4.21	3.29
3	0	1	17.84	18.63
3	0	2	7.26	6.10
3	0	3	1.75	1.11
3	0	4	8.87	7.65
3	0	7	18.28	18.52
3	0	9	12.76	12.93
3	0	10	4.90	5.43
3	0	11	5.45	5.40
3	0	14	2.64	1.69
3	0	16	5.13	7.95
3	1	-16	3.22	4.10
3	1	-15	4.55	4.07
3	1	-14	8.22	7.67
3	1	-13	3.12	3.38
3	1	-12	5.51	5.37
3	1	-11	4.31	4.37
3	1	-10	13.30	13.05
3	1	-9	23.07	28.01
3	1	-8	13.10	13.20
3	1	-7	16.62	18.81
3	1	-6	21.53	24.81
3	1	-5	26.87	28.49
3	1	-4	34.08	40.03
3	1	-3	24.44	25.29
3	1	-2	34.64	38.53
3	1	-1	44.63	52.82
3	1	0	34.96	41.10
3	1	1	5.92	1.52
3	1	2	15.86	15.26
3	1	3	38.66	37.87
3	1	4	24.71	25.46
3	1	5	13.12	12.02
3	1	6	7.32	6.06
3	1	7	14.80	13.56
3	1	8	15.98	14.00
3	1	9	15.93	15.80
3	1	10	5.24	3.01
3	1	11	8.75	7.28
3	1	12	8.86	7.89
3	1	13	7.87	7.22
3	1	15	3.52	1.73
3	2	-16	3.53	3.51
3	2	-12	4.39	5.40
3	2	-11	3.25	5.90
3	2	-10	2.64	2.18
3	2	-9	10.24	7.41
3	2	-8	10.15	10.70
3	2	-7	9.45	9.60
3	2	-6	4.75	4.06
3	2	-5	2.89	5.33
3	2	-4	8.99	7.76
3	2	-3	5.12	5.95
3	2	-2	18.29	17.53
3	2	-1	9.69	8.56
3	2	0	6.27	6.52
3	2	1	17.76	14.61
3	2	2	10.42	10.22
3	2	3	11.21	9.49
3	2	4	13.89	12.88
3	2	5	15.01	12.28
3	2	6	9.05	8.51
3	2	7	4.79	4.75
3	2	8	12.00	11.81
3	2	9	10.38	10.44
3	2	10	5.45	4.73
3	2	11	10.03	9.49
3	2	12	4.70	4.08
3	2	14	2.50	3.00
3	3	-15	5.70	5.97
3	3	-14	5.66	6.09
3	3	-13	1.38	3.04
3	3	-11	4.21	3.95
3	3	-10	5.80	6.62
3	3	-9	12.80	13.90
3	3	-8	6.46	6.98
3	3	-7	6.40	6.45
3	3	-6	5.18	5.96
3	3	-5	8.01	7.28
3	3	-4	7.13	6.29
3	3	-3	14.07	15.16
3	3	-2	4.54	5.17
3	3	-1	12.31	13.55
3	3	0	5.96	5.74
3	3	1	3.45	4.74
3	3	2	9.41	9.76
3	3	3	10.84	9.60
3	3	4	4.67	3.63
3	3	5	7.37	7.39
3	3	6	5.12	3.94
3	3	7	11.20	10.63
3	3	8	10.17	9.71
3	3	9	1.57	2.03
3	3	10	5.38	5.14
3	3	11	4.63	4.45
3	3	12	5.66	5.45
3	3	13	2.79	2.11
3	3	14	3.12	2.54
3	3	15	2.13	2.90
3	4	-14	2.26	1.96
3	4	-13	3.09	2.84
3	4	-12	3.75	3.66
3	4	-11	9.88	9.24
3	4	-10	3.33	4.20
3	4	-9	5.95	6.65
3	4	-8	7.40	7.73
3	4	-7	15.00	16.27
3	4	-6	16.15	13.17
3	4	-5	4.56	5.29
3	4	-4	17.41	18.15
3	4	-3	16.30	17.47
3	4	-2	13.23	13.38
3	4	-1	10.84	10.34
3	4	0	13.58	14.83
3	4	1	23.60	25.49
3	4	2	5.66	5.51
3	4	3	4.47	3.91
3	4	5	5.05	5.29
3	4	6	8.51	8.78
3	4	8	4.30	4.21
3	5	-10	3.33	4.31
3	5	-9	3.06	4.45
3	5	-8	4.88	5.59
3	5	-7	4.31	4.50
3	5	-6	4.10	5.42
3	5	-5	8.16	7.71
3	5	-4	6.67	6.93
3	5	3	4.98	5.51
3	5	5	6.11	6.12
3	5	6	3.82	4.09
3	5	8	3.34	2.53
3	5	9	3.39	3.41
3	6	-6	2.26	3.05
3	6	-5	2.80	3.43
3	6	-2	3.61	5.08
3	6	1	2.42	3.40
3	6	3	5.00	3.75
3	6	4	4.84	4.67
3	6	5	5.31	6.17
3	6	6	5.79	6.00
4	0	-17	2.18	2.87
4	0	-14	4.40	4.68
4	0	-13	9.37	9.97
4	0	-12	13.31	14.56
4	0	-11	6.86	7.03
4	0	-10	6.80	6.99
4	0	-9	4.05	3.57
4	0	-8	5.19	4.16
4	0	-7	3.10	2.29
4	0	-6	6.99	7.51
4	0	-5	1.72	2.86
4	0	-4	21.79	23.61
4	0	-3	27.83	32.93
4	0	-2	10.85	6.24
4	0	0	32.29	40.30
4	0	1	43.48	46.21
4	0	2	18.63	16.70
4	0	3	10.80	11.60
4	0	4	3.65	4.43
4	0	5	22.42	25.13
4	0	6	33.97	39.57
4	0	7	18.98	18.83
4	0	8	4.28	3.66
4	0	10	13.37	14.31
4	0	11	15.21	19.76
4	0	12	8.40	9.66
4	0	13	3.25	3.72
4	0	15	4.90	7.48
4	0	16	3.80	6.52
4	1	-17	3.81	4.09
4	1	-16	4.71	3.66
4	1	-14	4.78	4.01
4	1	-13	5.50	5.29
4	1	-12	4.61	4.32
4	1	-11	6.24	4.63
4	1	-10	8.66	8.70
4	1	-9	6.53	6.80
4	1	-8	7.91	7.85
4	1	-7	6.63	6.59
4	1	-6	10.64	12.28
4	1	-5	8.39	8.26
4	1	-4	5.08	5.19
4	1	-3	12.13	12.62
4	1	-2	16.23	17.92
4	1	-1	10.85	10.54
4	1	0	16.64	19.09
4	1	1	10.79	11.09
4	1	2	12.60	10.07
4	1	3	10.92	9.17
4	1	4	13.15	10.64
4	1	5	9.47	7.87
4	1	6	12.67	12.52
4	1	7	6.74	6.04
4	1	8	4.46	3.79
4	1	9	10.63	11.56
4	1	10	5.60	5.86
4	1	11	14.13	13.25
4	1	12	4.24	3.11
4	1	13	4.64	3.74
4	1	14	2.63	1.88
4	1	16	4.98	5.63
4	2	-16	3.35	2.37
4	2	-14	2.95	6.78
4	2	-12	4.59	4.02
4	2	-10	5.04	3.24
4	2	-9	11.77	12.12
4	2	-8	11.05	11.16
4	2	-7	10.58	11.38
4	2	-6	6.48	6.05
4	2	-5	9.49	9.12
4	2	-4	8.88	8.82
4	2	-3	10.53	9.00
4	2	-2	4.36	4.06
4	2	-1	21.71	26.01
4	2	0	13.30	12.95
4	2	1	12.58	12.24
4	2	2	14.70	11.87
4	2	3	3.07	2.72
4	2	4	7.26	7.21
4	2	5	10.49	10.03
4	2	6	13.74	13.85
4	2	7	3.23	2.97
4	2	8	8.13	8.96
4	2	9	8.10	7.61
4	2	10	1.11	2.09
4	2	11	3.78	3.49
4	2	12	0.87	2.70
4	2	13	5.49	5.53
4	3	-14	2.43	3.29
4	3	-13	3.54	3.19
4	3	-10	2.35	2.28
4	3	-8	2.65	2.60
4	3	-7	4.02	3.29
4	3	-6	4.93	6.13
4	3	-5	1.31	1.59
4	3	-4	0.76	1.89
4	3	-3	5.63	4.25
4	3	-2	3.25	3.35
4	3	-1	11.13	13.43
4	3	0	7.42	6.42
4	3	1	9.96	9.14
4	3	2	4.31	4.53
4	3	3	6.56	6.05
4	3	4	6.23	4.66
4	3	5	6.52	6.70
4	3	6	5.38	5.20
4	3	7	7.87	8.20
4	3	9	3.06	2.60
4	3	10	2.95	3.72
4	3	11	2.86	2.32
4	3	13	2.86	2.79
4	3	14	2.28	1.64
4	4	-13	1.90	2.21
4	4	-12	2.41	1.88
4	4	-11	4.34	4.74
4	4	-10	6.24	6.82
4	4	-9	3.94	3.91
4	4	-7	7.33	7.87
4	4	-6	14.86	16.27
4	4	-5	11.90	12.09
4	4	-4	8.86	9.61
4	4	-3	3.46	3.62
4	4	-2	10.96	11.73
4	4	-1	19.69	20.47
4	4	0	13.62	13.36
4	4	1	4.01	4.40
4	4	2	8.23	7.30
4	4	3	9.43	9.25
4	4	4	11.44	11.96
4	4	5	5.09	4.16
4	4	6	1.51	2.28
4	4	7	4.98	3.89
4	4	8	1.97	0.83
4	4	9	3.71	3.29
4	4	10	1.70	2.45
4	5	-11	3.64	4.55
4	5	-10	1.51	2.15
4	5	-9	3.09	3.48
4	5	-8	3.46	3.78
4	5	-7	3.88	4.47
4	5	-6	5.32	5.46
4	5	-4	9.16	9.56
4	5	-3	7.64	8.13
4	5	-2	7.72	9.00
4	5	-1	7.68	8.90
4	5	0	5.81	5.43
4	5	1	11.86	11.72
4	5	2	8.33	8.29
4	5	3	8.61	8.56
4	5	4	10.45	10.25
4	5	5	8.19	7.21
4	5	7	6.35	6.34
4	5	8	7.57	7.52
4	5	9	7.23	8.12
4	5	10	3.50	4.25
4	6	-6	2.01	1.66
4	6	-5	1.40	2.01
4	6	-4	3.02	3.56
4	6	-3	1.54	2.31
4	6	1	3.11	3.07
4	6	3	1.97	1.87
4	6	4	2.82	3.80
4	6	5	2.93	3.32
5	0	-16	3.00	1.45
5	0	-12	6.50	6.01
5	0	-9	7.23	7.85
5	0	-8	3.00	3.88
5	0	-7	5.63	4.62
5	0	-6	3.62	3.20
5	0	-5	2.73	2.50
5	0	-4	17.88	19.92
5	0	-2	6.65	9.45
5	0	-1	5.75	5.06
5	0	0	6.22	6.70
5	0	1	8.29	8.17
5	0	2	18.53	21.91
5	0	4	4.14	2.80
5	0	5	2.62	1.17
5	0	6	4.35	3.72
5	0	7	7.49	8.23
5	0	8	7.65	9.42
5	0	9	11.19	13.88
5	0	10	9.50	10.67
5	0	11	5.44	5.97
5	0	12	3.11	2.43
5	0	14	5.25	4.67
5	0	15	2.97	3.18
5	1	-16	3.86	2.89
5	1	-15	2.51	1.83
5	1	-14	7.88	6.92
5	1	-13	6.44	6.12
5	1	-12	9.72	9.07
5	1	-11	7.34	6.55
5	1	-10	11.71	11.09
5	1	-9	12.26	12.40
5	1	-8	6.11	5.84
5	1	-7	15.29	15.95
5	1	-6	18.89	21.60
5	1	-5	13.14	11.98
5	1	-4	10.86	9.48
5	1	-3	7.05	4.81
5	1	-2	23.63	24.17
5	1	-1	22.60	25.34
5	1	0	18.20	19.46
5	1	1	10.71	9.86
5	1	2	13.65	14.04
5	1	3	17.50	19.41
5	1	4	10.96	10.39
5	1	5	10.39	8.54
5	1	6	5.16	4.78

Table 2 (*cont.*)

5	1	7	3.86	2.39
5	1	8	5.28	4.65
5	1	9	6.45	5.27
5	1	10	4.95	3.86
5	1	11	7.81	6.69
5	1	12	3.93	3.34
5	1	13	3.42	3.01
5	1	15	5.29	6.57
5	2	-15	3.55	3.76
5	2	-14	7.35	7.47
5	2	-13	8.53	7.31
5	2	-12	3.43	3.77
5	2	-11	5.61	5.39
5	2	-10	9.24	9.04
5	2	-9	7.31	8.29
5	2	-8	5.75	5.43
5	2	-7	3.68	3.38
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5	2	1	12.08	13.11
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5	2	3	5.14	4.15
5	2	4	10.25	11.71
5	2	5	9.11	7.42
5	2	6	7.31	6.11
5	2	7	7.10	7.22
5	2	9	6.20	6.12
5	2	10	6.79	6.84
5	2	12	3.22	2.67
5	2	14	2.55	2.41
5	3	-14	2.65	2.69
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5	3	4	16.71	17.78
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10	3	5	4.60	4.40
10	4	-4	4.15	6.85
10	4	-3	4.76	4.84
10	4	-2	4.12	4.22
10	4	-1	3.44	3.85
10	4	0	4.78	4.94
11	0	-9	4.80	5.05
11	0	-8	3.32	2.24
11	0	-7	7.70	7.70
11	0	-6	6.37	5.74
11	0	-4	3.96	4.87
11	0	-1	7.09	7.07
11	0	0	8.94	7.96
11	0	1	3.63	3.83
11	0	3	4.31	3.75
11	0	4	4.44	4.14
11	0	5	3.46	4.13
11	1	-9	3.57	6.83
11	1	-8	2.74	4.87
11	1	-7	7.58	5.85
11	1	-6	6.54	5.68
11	1	-5	7.90	6.66
11	1	-4	5.34	4.63
11	1	-3	4.02	4.00
11	1	-2	5.56	4.67
11	1	0	3.80	3.07
11	1	1	5.34	5.26
11	1	2	4.92	5.03
11	1	3	6.06	5.95
11	1	4	4.46	3.91
11	1	5	5.16	5.61
11	1	6	7.68	9.66
11	2	-6	3.06	2.66
11	2	-5	2.01	1.75
11	2	-4	3.64	3.23
11	2	-3	2.16	2.50
11	2	-2	4.22	3.79
11	2	1	2.40	3.47
11	2	2	5.10	4.95
11	2	3	2.37	2.77
11	2	4	2.01	1.82
11	3	-5	2.94	2.38
11	3	-3	3.04	3.06
11	3	-2	1.59	1.57
11	3	-1	2.88	1.75
11	3	0	2.79	1.32
12	0	-6	8.74	10.13
12	0	-5	9.50	11.32
12	0	-4	7.08	6.64
12	0	-2	8.46	6.93
12	0	-1	10.48	10.49
12	0	0	8.67	10.82
12	0	1	4.88	5.72
12	1	-5	1.54	2.34
12	1	-4	2.97	2.23
12	1	-3	2.56	2.60
12	1	-2	1.56	1.47
12	1	0	4.31	4.05
12	1	1	4.32	3.71

Table 1. A comparison of observed and calculated structure factors is given in Table 2.

Discussion of the structure

Molecular structure

Fig. 1 shows the molecular structure of L-isoleucine. Bond lengths and angles along with their standard deviations are listed in Table 3. The crystal contains two independent molecules, *A* and *B*. Differences of the corresponding bond lengths in these molecules are (Table 3) only significant with a probability of 20%, except those of C(2)–C(3) for which the differences are rather significant.

Table 3 also shows the comparison of the values found for isoleucine molecules in various compounds: D-isoleucine HBr.H_2O and D-isoleucine HCl.H_2O (Trommel & Bijvoet, 1954); bis(L-isoleucinato)copper-(II) monohydrate (Weeks, Cooper & Norton, 1969). The values are close to each other except those involved in the carboxyl group. Isoleucine molecules in the present crystal take the form of a zwitterion.

The conformation of the molecule is characterized by the two planes: one formed by the carboxyl group and the other involving the side chains. Equations of the least-squares planes and deviations of the atoms are shown in Table 4. Each carboxyl group of *A* and *B* molecules is planar with the C^{α} atom, but the nitrogen

Table 3. *Bond lengths and angles of isoleucine molecules found in crystals**

	L-Isoleucine		D-Isoleucine	D-Isoleucine	Copper complex of L-isoleucine	
	(*A*)	(*B*)	HBr.H_2O	HCl.H_2O	'unprimed molecule'	'primed molecule'
O(1)–C(1)	1·254 (9) Å	1·253 (11) Å	1·33 (5) Å	1·27 (5) Å	1·293(4–10)Å	1·284(4–10)Å
O(2)–C(1)	1·243 (13)	1·269 (13)	1·22	1·27	1·224	1·225
C(1)–C(2)	1·527 (13)	1·540 (11)	1·51	1·51	1·537	1·522
C(2)–C(3)	1·570 (11)	1·537 (11)	1·54	1·55	1·531	1·550
C(3)–C(4)	1·548 (16)	1·568 (13)	1·56	1·53	1·541	1·528
C(3)–C(6)	1·549 (12)	1·530 (18)	1·53	1·54	1·532	1·527
C(4)–C(5)	1·554 (15)	1·534 (15)	1·54	1·52	1·509	1·512
C(2)–N(1)	1·499 (13)	1·508 (12)	1·45	1·43	1·469	1·490
O(1)–C(1)–O(2)	124·5 (7)°	124·9 (7)°	125 (10)°	124 (10)°	122·3(2–6)°	121·7(2–6)°
O(1)–C(1)–C(2)	118·0 (7)	117·2 (7)	114	117	116·9	118·3
O(2)–C(1)–C(2)	117·4 (7)	117·8 (7)	121	119	120·7	120·1
C(1)–C(2)–N(1)	109·6 (6)	108·0 (7)	108	115	110·1	109·6
C(1)–C(2)–C(3)	112·1 (7)	110·1 (7)	113	104	114·9	108·7
N(1)–C(2)–C(3)	110·0 (6)	110·4 (7)	118	119	111·8	114·5
C(2)–C(3)–C(4)	109·4 (7)	111·3 (7)	112	109	114·8	113·4
C(2)–C(3)–C(6)	112·6 (7)	110·0 (8)	103	111	112·2	110·5
C(4)–C(3)–C(6)	111·9 (8)	110·9 (9)	115	109	111·1	113·5
C(3)–C(4)–C(5)	114·3 (9)	113·7 (10)	113	119	113·4	112·8
State of rotation about C(2)–C(3)	*Gauche* I	*Trans*	*gauche* I	*gauche* II	*gauche* I	*gauche* II
State of rotation about C(3)–C(4): C(5) is *trans* to	C(2)	C(2)	C(6)	C(2)	C(6)	C(2)
Reference	(1)	(1)	(2)	(2)	(3)	(3)

* Standard deviations are shown in parentheses denoting the least significant digits of the corresponding values.

(1) Present paper.

(2) Trommel & Bijvoet (1954)

(3) Weeks, Cooper & Norton (1969)

atom deviates from the plane by 0·418 Å in *A* and 0·908 Å in *B*. Deviations are very close to the corresponding values found in L-valine. C^{β}, C^{γ} and C^{δ} side-chain atoms [C(3), C(4) and C(5) in molecule *A* and C(13), C(14) and C(15) in *B*] are extended in *trans* planar form from the α carbon atom. In molecule *B*, this planar zigzag chain is further extended to involve the carboxyl carbon atom C(11).

Table 4. *Perpendicular distances of the atoms from the least-squares plane*

Planes are of the form $AX+BY+CZ=D$, where X, Y, Z and D are in Å units relative to the axes a, b and c^*.

Molecule *A*

(I)		(II)	
O(1)	−0·006 Å	C(2)	0·033 Å
O(2)	−0·006	C(3)	−0·029
C(1)	0·018	C(4)	−0·037
C(2)	−0·005	C(5)	0·034
N(1)*	0·418		

(I): $0{\cdot}3417X+0{\cdot}2297Y+0{\cdot}9113Z=5{\cdot}5813$

(II): $0{\cdot}9608X-0{\cdot}2296Y+0{\cdot}1555Z=3{\cdot}9410$

Molecule *B*

(III)		(IV)	
O(11)	−0·009 Å	C(11)	0·004 Å
O(12)	−0·009	C(12)	0·013
C(11)	0·024	C(13)	−0·021
C(12)	−0·007	C(14)	−0·014
N(11)*	0·908	C(15)	0·018

(III): $0{\cdot}5081X-0{\cdot}0055Y+0{\cdot}8613Z=7{\cdot}5141$

(IV): $0{\cdot}2805X+0{\cdot}9088Y-0{\cdot}3088Z=3{\cdot}8573$

* Omitted from least-squares plane calculation.

Conformations of the isoleucine molecules, *A* and *B*, are very similar to those of the corresponding molecules in L-valine, if the δ carbon atom in isoleucine is disregarded. The arrangements of the γ and γ′ atoms about the C^{α}–C^{β} bond are also found to be *gauche* I in *A* and *trans* in *B*. Table 5 shows the various internal rotation angles defining the conformation of the molecules. Values are compared with those found in L-valine and isoleucine in various compounds. As in the case of valine, all three possible rotational isomers about the C^{α}–C^{β} bond, *trans*, *gauche* I and *gauche* II, are also found in isoleucine. The δ carbon atom is situated at the *trans* position with respect to either the α or γ′ carbon atom.

Hydrogen bonds

Table 6 shows the values of short intermolecular N···O distances and C–N···O angles. Fig. 2 shows the arrangement of oxygen atoms around the amino nitrogen atom in stereographic projection, in which the suggested N–H directions are also indicated. Figs.

Table 5. *Internal rotation angles of isoleucine and valine molecules found in crystal*

	ψ_2	χ_{11}	χ_{12}	χ_{21}	State of rotation about C^{α}–C^{β}	C^{δ} is *trans* to:	Reference*
L-Isoleucine							
Molecule *A*	−19·5°	204·5°	79·4°	174·7°	*gauche* I	C^{α}	(1)
Molecule *B*	−42·4	299·9	176·7	182·7	*trans*	C^{α}	
Copper complex							
'Unprimed molecule'	6·6	196·5	68·3	52·1	*gauche* I	$C^{\gamma'}$	(2)
'Primed molecule'	−10·4	66·7	298·0	160·5	*gauche* II	C^{α}	
L-Isoleucine .HBr.H_2O	−14·3	191·7	66·5	68·1	*gauche* I	$C^{\gamma'}$	(3) (2)
L-Isoleucine .HCl.H_2O	6·4	48·4	287·5	172·1	*gauche* II	C^{α}	(3) (2)
L-Valine							
Molecule *A*	−19·5	206·4	81·8	–	*gauche* I	–	(4)
Molecule *B*	−43·7	300·7	179·2	–	*trans*	–	

In the case of crystalline L-isoleucine the conformation angles, ψ_2, χ_{11}, χ_{12} and χ_{21} defined by Lakshiminarayanan, Sasisekharan & Ramachandran (1967), are equivalent to the following internal rotation angles:

$$\psi_2=\tau[O(1)\text{–}C(1)\text{–}C(2)\text{–}N(1)]$$
$$\chi_{11}=\tau[N(1)\text{–}C(2)\text{–}C(3)\text{–}C(4)]$$
$$\chi_{12}=\tau[N(1)\text{–}C(2)\text{–}C(3)\text{–}C(6)]$$
$$\chi_{21}=\tau[C(2)\text{–}C(3)\text{–}C(4)\text{–}C(5)]$$

where $\tau[A\text{–}B\text{–}C\text{–}D]$ is defined as the angle formed by the projection of the *A–B* bond with that of *C–D* when the projection is taken along the *B–C* bond. The positive direction of the angle is taken, coinciding with that of the right-handed screw advancing along the *B–C* bond.

* (1) present paper, (2) Weeks, Cooper & Norton (1969), (3) Trommel & Bijvoet (1954) and (4) Torii & Iitaka (1970).

2 & 3 suggest that the amino nitrogen atom of molecule *A* forms three hydrogen bonds nearly in tetrahedral directions, while in molecule *B* one hydrogen atom is shared in two hydrogen bonds {N(11)···O(1)[I(100)] and N(11)···O(2)[I(100)]}, forming a bifurcated hydrogen bond. The situation is somewhat different from that of the L-valine crystal despite the hydrogen-bond systems in these two amino-acid crystals being quite similar. In L-valine, O(12) [II(010)] is situated closer (3·194 Å) to N(1), and the bifurcated hydrogen bond was suggested between O(12) [II(010)] and O(11) [II(000)].

Table 6. *Intermolecular short N···O distances and C–N···O angles*

	N···O	C–N···O
Molecule *A*		
N(1)–O(11) [II($0\bar{1}0$)]	2·844 ± 0·009 Å	87·8 ± 0·5°
N(1)–O(2) [I($0\bar{1}0$)]	2·867 ± 0·011	119·5 ± 0·5
N(1)–O(11) [I($0\bar{1}0$)]	2·812 ± 0·008	113·9 ± 0·5
N(1)–O(12) [II($0\bar{2}0$)]	3·439 ± 0·010	145·4 ± 0·5
Molecule *B*		
N(11)–O(1) [II(000)]	2·794 ± 0·008	107·3 ± 0·5
N(11)–O(12) [I($0\bar{1}0$)]	2·845 ± 0·011	115·7 ± 0·5
N(11)–O(1) [I(100)]	2·993 ± 0·008	139·5 ± 0·5
N(11)–O(2) [I(100)]	3·028 ± 0·008	100·1 ± 0·5

Numbers I and II denote the operations,
I: x, y, z
II: $1-x$, $\frac{1}{2}+y$, $1-z$
where the values of x, y and z are given in Table 1.

Crystal structure

Fig. 3 shows the projection of the crystal structure of L-isoleucine along the *b* axis. Note that the structure is made up of hydrogen-bonded double layers of molecules extending parallel to (001). This crystal structure is quite similar to that found in L-valine. Close approaches of the side-chain carbon atoms shorter than 4·2 Å are listed in Table 7 and shown in Fig. 3. No abnormal distances exist and they are nearly of the same order of magnitude as those found in usual hydrocarbon-chain packings.

Table 7. *Intermolecular short contacts less than 4·2 Å between side-chain carbon atoms*

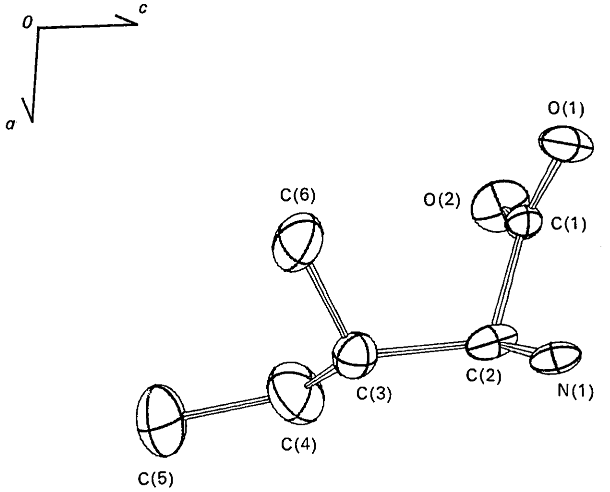
Within single layer:	
C(4) [I(000)]—C(3) [I(010)]	4·07 ± 0·02 Å
C(4) [I(000)]—C(6) [I(010)]	3·80 ± 0·02
C(16) [I(000)]–C(3) [I(010)]	4·19 ± 0·02
C(16) [I(000)]–C(5) [I(010)]	3·93 ± 0·02
C(16) [I(000)]–C(14) [I(010)]	3·90 ± 0·02
C(16) [I(000)]–C(15) [I(010)]	3·74 ± 0·02
C(14) [I(000)]–C(6) [I(100)]	4·07 ± 0·02
C(14) [I(000)]–C(6) [I(110)]	3·89 ± 0·02
Between double layers:	
C(15) [I(000)]–C(6) [II($00\bar{1}$)]	4·10 ± 0·01 Å
C(6) [I(000)]—C(5) [II($00\bar{1}$)]	4·20 ± 0·02

For symmetry-operation notation see Table 6.

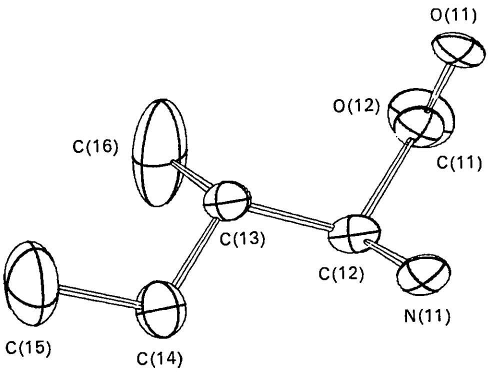
The arrangement of the molecules within the layer is illustrated in Fig. 4, which shows a stereoscopic view of the packing of the side-chains along a direction from the hydrophobic region between the double layers down to the hydrophilic region. Fig. 1 illustrates another view of the molecules along the *b* axis. These Figures are drawn by the plotter program *ORTEP* (Johnson, 1965). The area covered by the ellipsoids corresponds to a 50% probability of finding the centre of the atom in it. The orientation of each thermal ellipsoid and the root-mean-square displacements of each atom along the principal axes are listed in Table 8. The maximum vibration of the atoms is seen in C(16) along the third principal axis lying nearly parallel to the *a* axis. This vibration is clearly revealed in Fig. 4 and is interpreted as being caused by oscillatory motion of the side-chain atoms about the C^{α}–C^{β} bond.

The crystal structures of the related L-α-amino acids

Comparing Fig. 4 of this paper with Fig. 7 of the paper on L-valine (Torii & Iitaka, 1970), a close re-



Molecule *A*



Molecule *B*

Fig. 1. Conformation of L-isoleucine molecules viewed along the *b* axis.

Table 8. *R.m.s. displacements and directions of principal axes of thermal vibration*

	Principal axis (*j*)	*U*(*j*)	cos α_{1j}	cos α_{2j}	cos α_{3j}
Molecule *A*					
O(1)	1	13 Å	−0·996	0·029	0·082
	2	18	−0·019	0·848	−0·530
	3	21	−0·085	−0·530	−0·844
O(2)	1	13	−0·367	0·917	−0·156
	2	19	0·811	0·397	0·430
	3	22	−0·456	−0·031	0·889
N(1)	1	10	−0·845	0·486	−0·222
	2	16	−0·434	−0·867	−0·246
	3	19	0·311	0·111	−0·944
C(1)	1	11	0·874	−0·414	0·254
	2	14	−0·159	0·250	0·955
	3	17	0·459	0·875	−0·153
C(2)	1	12	0·926	0·026	0·376
	2	15	0·105	0·941	−0·323
	3	20	−0·362	0·339	0·869
C(3)	1	15	0·398	−0·650	0·647
	2	17	−0·211	0·621	0·754
	3	17	0·893	0·437	−0·110
C(4)	1	17	0·646	0·460	−0·609
	2	23	−0·429	−0·441	−0·788
	3	27	−0·632	0·770	−0·087
C(5)	1	16	−0·245	−0·317	0·916
	2	26	0·939	0·159	0·305
	3	33	−0·242	0·935	0·259
C(6)	1	16	0·304	0·372	0·877
	2	22	0·663	−0·744	0·086
	3	23	−0·684	−0·555	0·473
Molecule *B*					
O(11)	1	9	0·843	−0·537	0·037
	2	16	−0·430	−0·631	0·646
	3	22	0·323	0·560	0·763
O(12)	1	15	−0·241	0·970	0·044
	2	21	0·922	0·243	−0·303
	3	25	0·304	0·032	0·952
N(11)	1	10	0·735	−0·678	−0·028
	2	17	0·478	0·487	0·731
	3	21	−0·482	−0·551	0·682
C(11)	1	10	−0·635	0·753	−0·176
	2	17	0·720	0·492	−0·490
	3	19	−0·282	−0·437	−0·854
C(12)	1	14	0·972	0·033	0·231
	2	16	−0·094	0·961	0·260
	3	20	−0·213	−0·275	0·938
C(13)	1	14	−0·971	−0·046	−0·236
	2	17	0·192	0·446	−0·874
	3	19	0·146	−0·894	−0·424
C(14)	1	14	−0·256	0·361	0·897
	2	21	0·960	−0·013	0·279
	3	35	−0·112	−0·933	0·343
C(15)	1	19	−0·195	0·269	0·943
	2	30	0·548	−0·768	0·333
	3	32	0·813	0·582	0·003
C(16)	1	18	−0·170	0·477	−0·862
	2	25	0·402	−0·765	−0·503
	3	42	−0·900	−0·432	−0·062

The r.m.s. displacement *U*(*j*) is directed along the *j*th axes of the ellipsoid, where α_{1j}, α_{2j} and α_{3j} are the angles between *j*th axis and the *a*, *b* and *c** axes respectively.

semblance exists between the two structures, where the molecules are held together through two kinds of N–H···O hydrogen bonds to form a single layer. Their structures, especially those corresponding to the network of hydrogen bonding, are very similar to the structure found in α-glycine (Marsh, 1958) and β-glycine (Iitaka, 1960). The third hydrogen bond from the amino nitrogen atom, for which a bifurcated type is assumed in molecule *A* of L-valine and in molecule *B* of L-isoleucine, link the single layers to form a double layer. The linkage of the two single layers also resembles that found in α-glycine with respect to the hydrogen bonding. The double layers are stacked in such a way that their terminal groups of the side chain face each other and form alternate layers of hydrophilic and hydrophobic regions. The main feature of these structures resembles that found in long-chain compounds having a polar group at the end. We have pointed out that the packing of the side chains in the L-valine crystal resembles the O⊥ packing of the long-chain hydrocarbons, and that the difference in the two kinds of side-chain conformations within the same crystal results from the fact that while the side chains are forced to fit into the above mentioned packing scheme, the polar groups assume a different structure resembling that found in glycine.

It is clear from Fig. 3 that this kind of crystal structure is still capable of embracing longer carbon chains between the double layers. Table 9 shows the crystal data of several common L-α-amino acids having hydrophobic side chains. Except L-alanine and L-norleucine, the crystals have similar lattice constants and the same space group. Furthermore, the length of the *c* axis (which reflects the separation of the double layers) becomes larger as the length of the side chain increases. In L-alanine (Simpson & Marsh, 1966), the crystal structure is characterized by a three-dimensional network of hydrogen bonds and belongs to another type of structure; but in L-norleucine whose structure is now being determined, the molecules are supposed to be arranged essentially in the same way as in L-valine, although the side chains adopt a parallel packing.

Powder data of L-isoleucine

Recently, Khawas (1970) reported lattice constants and a space group for L-isoleucine that are different from our results on the basis of a powder-diffraction pattern and rotation photograph about one axis. His observed intensities and spacings of the powder lines, however, agree well with those obtained with the present crystal, and no doubt Khawas dealt with the same crystalline form. Consequently we calculated the spacings of the powder lines from our lattice constants and compared them with those reported by Khawas (Table 10).

The authors express their sincere gratitude to Professor M. Tsuboi. They also thank Mr K. Tanada for collecting the diffraction data of the L-isoleucine crystal and the staff of the C. Itoh Electronic Computing Service Co Ltd for making the CDC 3600 computer available to us. This work was supported by a research grant from the Ministry of Education.

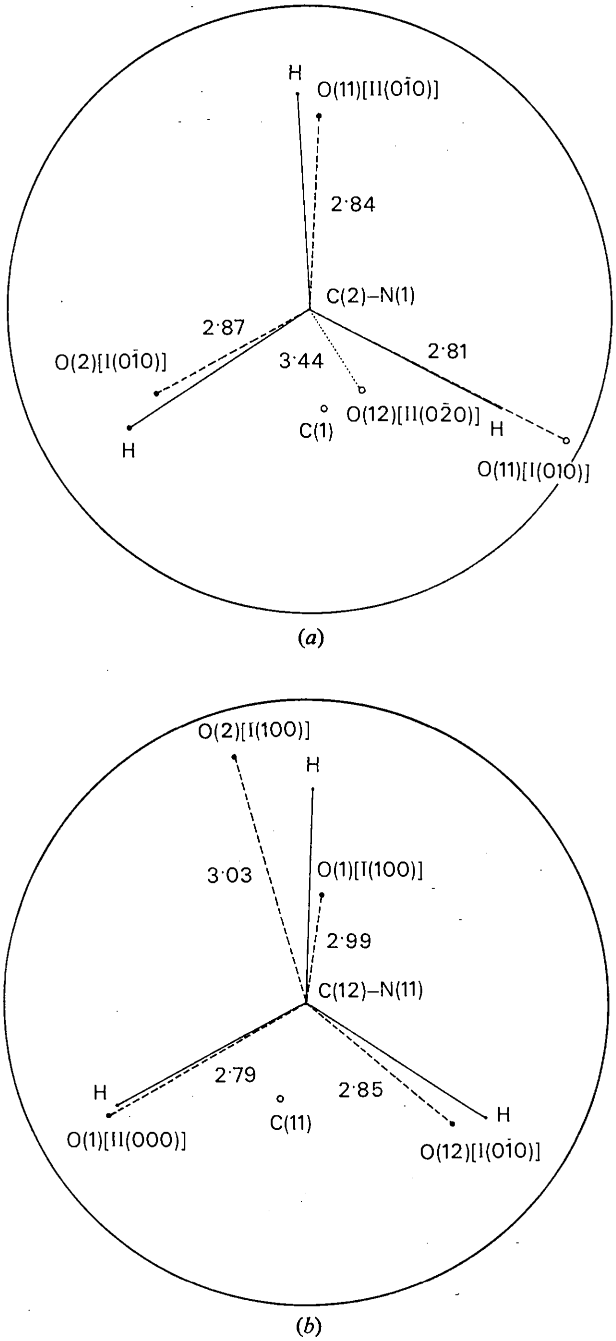


Fig. 2. Stereographic projections showing the arrangement of oxygen atoms around the nitrogen atom. Notation of the symmetry operations is shown in Table 6. Direction of the C–N bond is taken as the polar axis and suggested N–H directions are indicated. (*a*) Molecule*A*, (*b*) molecule *B*.

Table 9. *Crystal data for the related* L-α-*amino acids*

	a (Å)	b (Å)	c(Å)	β(°)	D_m	D_x	Z	Space group	Reference*
(I) Straight chain:									
L-Alanine	6·032	12·343	5·784	–	–	–	4	$P2_12_12_1$	(1)
L-Norleucine	9·58	5·26	15·43	95·6	–	1·126	4	$C2$	(2)
L-Cysteine	11·51	5·24	9·52	109°8′	1·483	1·483	4	$P2_1$	(3)
L-Methionine	9·52	5·19	15·32	97·9	1·316	1·321	4	$P2_1$	(4)
(II) Branched chain:									
L-Valine	9·71	5·27	12·06	90·8	1·263	1·261	4	$P2_1$	(5)
L-Isoleucine	9·75	5·32	14·12	95·8	1·202	1·196	4	$P2_1$	(6)
L-Leucine	9·63	5·33	14·62	93·9	1·156	1·165	4	$P2_1$	(7)

* (1) Simpson & Marsh (1966), (3) Harding & Long (1968), (5) Torii & Iitaka (1970), (6) present paper, (2) (4) (7) Torii & Iitaka (to be published).

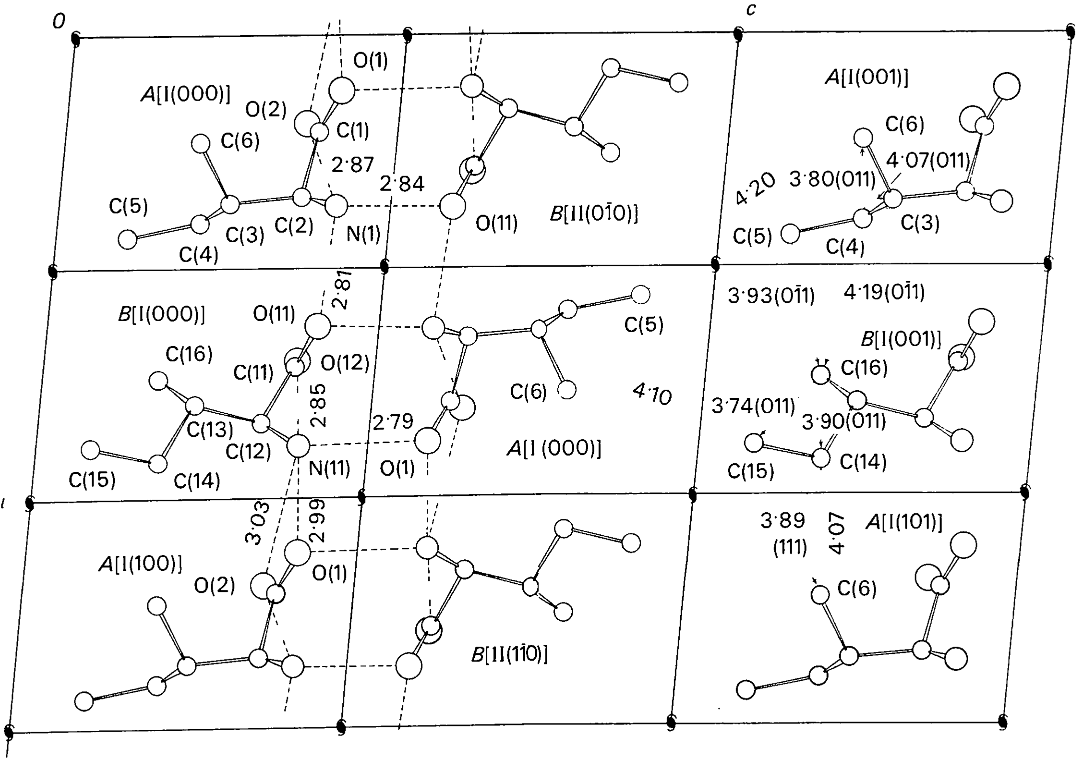


Fig. 3. Projection of the crystal structure along the *b* axis. Hydrogen bonds are shown by broken lines and the closest approaches of the side-chain atoms are shown by dotted lines.

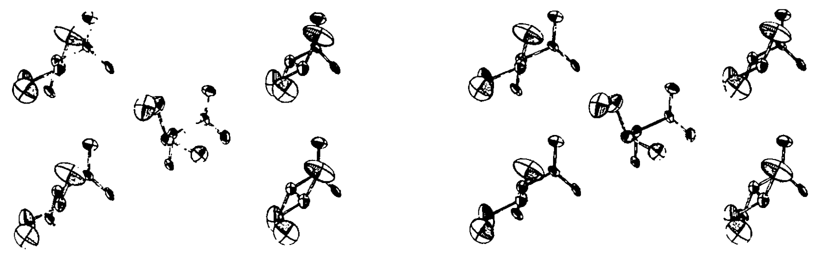


Fig. 4. Stereoscopic drawing of the crystal structure viewed along the *c* axis. The ellipsoid encloses the area of finding the centre of the atom in it by 50% probability.

Table 10. *Powder diffraction data for L-isoleucine*

Present study						Khawas (1970)				
h	*k*	*l*	Intensity	d_{calc}	d_{obs}	d_{obs}	*h*	*k*	*l*	Intensity
0	0	1	*vvs*	13·95	14·59	13·81	1	0	0	*vs*
0	0	2	*vs*	6·974	6·982	6·972	2	0	0	*s*
1	0	2	*w*	5·427	5·422					
2	0	0	*s*	4·844	4·844	4·849	1	1	1	*m*
							2	3	0	
1	1	0	*vs*	4·694	4·697	4·695	0	2	1	*vs*
2	0	1	*s*	4·450	4·454	4·475	3	1	0	*m*
							1	2	1	
0	1	2	*m*	4·253	4·260	4·261	2	0	1	*vw*
1	0	3	*w*	4·048	4·037	4·040	0	5	0	*vw*
							1	3	1	
−1	1	2	*w*	3·978	3·977					
1	1	2	*s*	3·816	3·806	3·885	2	2	1	*s*
							1	5	0	
						3·652	0	4	1	*vw*
						3·548	1	4	1	*m*
0	0	4	*vs*	3·487	3·497	3·485	2	5	0	*s*
2	1	1	*w*	3·425	3·409	3·421	4	1	0	*vw*
3	0	0	*s*	3·229	3·223	3·251	2	4	1	*m*
2	1	2	*w*	3·110	3·110	3·138	1	5	1	*w*
0	1	4	*m*	2·924	2·919	2·922	2	5	1	*vvw*
0	0	5	*vs*	2·790	2·792	2·854	4	4	0	*s*
−3	1	1	*s*	2·756	2·755		0	6	1	
						2·812	1	7	0	*w*
							4	2	1	
−3	1	2	*m*	2·645	2·647	2·687	0	0	2	*w*
1	2	1	*m*	2·531	2·531	2·573	5	3	0	*w*
0	1	5	*w*	2·475	2·475	2·522	4	4	1	*vw*
							0	8	0	
2	1	4	*w*	2·422	2·420	2·468	5	0	1	*vw*
2	2	0	*s*	2·347	2·342	2·375	2	8	0	*s*
−1	2	3	*m*	2·284	2·290	2·259	3	2	2	*vw*
							6	2	0	
3	0	4	*m*	2·267	2·267	2·185	6	3	0	*vw*
0	2	4	*w*	2·126	2·129	2·139	5	6	0	*m*
−4	0	4	*w*	2·081	2·080					
−3	1	5	*m*	2·047	2·049	2·047	4	7	1	*m*
							3	8	1	
							1	9	1	
0	0	7	*w*	1·993	1·993	1·910	3	6	2	*vvw*
1	2	5	*vw*	1·873	1·879	1·877	4	5	2	*vw*
0	1	7	*vw*	1·868	1·867	1·847	3	10	0	*vw*
							7	4	0	
−4	2	1	*w*	1·799	1·800	1·780	7	5	0	*vw*
−1	2	6	*vw*	1·750	1·750	1·718	0	9	2	*vvw*
−6	0	2	*vw*	1·606	1·606	1·630	8	2	1	*vvw*
2	0	8	*vw*	1·594	1·594	1·579	3	12	0	*vvw*
							0	6	3	
						1·525	9	2	0	*vvw*

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