Acta Cryst. (1972). B**28**, 1265

The Structure of Di-L-Leucine Hydrochloride: An X-ray Diffraction Study*

BY LJUBO GOLIČ†

Faculty of Science and Technology, University of Ljubljana, Ljubljana, Yugoslavia

AND WALTER C. HAMILTON

Chemistry Department, Brookhaven National Laboratory, Upton, New York 11973, *U.S.A.*

(*Received* 1 *July* 1971)

Di-L-leucine hydrochloride $[(CH_3)_2CHCH_2CHNH_2COOH]_2HCl$, M.W. 298·81, crystallizes in space group $P2_1$, $a=11\cdot152$ (1), $b=5\cdot116$ (1), $c=15\cdot405$ (2) Å, and $\beta=108\cdot94$ (2)°, $V=831\cdot3$ Å^3, $Z=2$, $D_m=1\cdot187$ g.cm^{-3}, $D_x=1\cdot194$ g.cm^{-3}. The structure has been refined to $R=5\cdot5$ % for 1360 visually estimated intensities from Cu $K\alpha$ Weissenberg films. In agreement with the infrared spectrum, we find that the structure has a very strong hydrogen bond with an O···O distance of 2·429 (7) Å between two leucine units. Refinement of the hydrogen position in the short hydrogen bond leads to O–H bond lengths of 1·06 (9) and 1·37 (9) Å, so that whether the bond is symmetric could not be definitively established. A symmetric bond seems likely from the equality of the C–O bond lengths: 1·280 (6) and 1·288 (6) Å. The resulting bimolecular units and chlorine atoms are linked into a two-dimensional array parallel to the (001) plane by weaker hydrogen bonds, producing a perfect layer structure with only van der Waals contacts between layers.

Introduction

Although L-leucine is one of the most common naturally occurring α-amino acids, the structure of the free acid is not known. [Cell constants and space groups have been reported by Dawson & Mathieson (1951), and by Möller (1949).] The structure of L-leucine hydrobromide has been reported by Subramanian (1967) and the isomorphous hydriodide by Chaney, Seeley & Steinrauf (1971). The structure of the leucyl residue has been determined in peptide structures such as *N*-methyl-DL-leucylglycine hydrobromide (Chandrasekaran & Subramanian, 1969) and leucylprolylglycine (Leung & Marsh, 1958). Our particular interest in the structure of di-L-leucine hydrochloride was aroused by the indication of a very strong symmetric hydrogen bond by the broad intense absorption bond lying between 400 cm^{-1} and 1300 cm^{-1} in the infared spectrum (Hadži & Marciszewski, 1967).

Experimental

Crystals of di-L-leucine hydrochloride were obtained by slow evaporation of a solution of L-leucine in dilute hydrochloric acid by the method of Rolski, Zdunska & Popko (1963). The crystals are prismatic, elongated in the **b** direction. They are stable on exposure to air, but show a pronounced cleavage parallel to (001) which causes them to be very sensitive mechanically.

Crystal data were obtained from zero-layer Weissenberg photographs ($h0l$) and ($0kl$), taken with Cu $K\alpha$ radiation. Values for the cell dimensions and their standard deviations were derived from a least-squares treatment of a number of high-order reflections, whose values for sinθ were determined by comparison with superimposed powder lines of aluminum ($a=4.04907$ Å). Crystal data are: $a=11\cdot152$ (1), $b=5\cdot116$ (1), $c=15\cdot405$ (2) Å, $\beta=108\cdot94$ (2)°, $V=831\cdot3$ Å^3, D_m(flotation) $=1\cdot187$ g.cm^3, $D_x=1\cdot194$ g.cm^{-3}, $Z=2$, μ(Cu $K\alpha$)$=2\cdot14$ mm^{-1}. The only absent reflections are $0k0$ for $k=2n+1$, indicating $P2_1$ as the probable space group.

A crystal of size 0·18 × 0·10 × 0·20 mm and 0·2 mm in the b-axis direction, was used for data collection. Equi-inclination Weissenberg photographs, $h0l$, $h1l$, $h2l$, $h3l$ were obtained using the multiple-film technique with Cu $K\alpha$ radiation. In addition, multi-exposure precession photographs of the $0kl$, $1kl$, $2kl$, $hl0$ and $hk1$ layers were taken with Mo $K\alpha$ radiation. Intensities were estimated visually. The precession data were used mainly for scaling the Weissenberg data along the b axis. 1491 independent nonzero reflections were collected; this includes 131 high-angle precession data which did not appear on the Cu $K\alpha$ films. An absorption correction was not applied. This neglect could lead to maximum errors of 10% (but generally much less) in the measured intensities.

The structure was determined by a three-dimensional Patterson synthesis and by electron density syntheses. This was followed by a series of least-squares refinement cycles, using Cruickshank's (1961) weighting scheme, $w=(1\cdot96+|F_o|+0\cdot0206|F_o|^2)^{-1}$. In the initial cycles, both the precession and Weissenberg data sets were used. Refinement of nine scale factors and all heavy atoms with isotropic thermal parameters resulted in a value of $R=0\cdot147$. Hydrogen atoms H(1)–H(4)

---

* Research performed in part under the auspices of the U.S. Atomic Energy Commission.

† Participant in the exchange program between the Yugoslav Council of the Academies and the National Academy of Sciences, U.S.A.

and H(14)–H(17), bonded to C(2)–C(4) and C(8)–C(10), were introduced at chemically reasonable positions; further refinement of scale factors, a chlorine atom with anisotropic thermal parameters, and all other atoms (except hydrogen atoms, which were fixed) with isotropic thermal parameters resulted in $R=0·112$. Difference Fourier sections through predicted hydrogen positions of four methyl and two amino groups resulted in the location of the positions of all remaining hydrogen atoms except H(27), the one in the short hydrogen bond. These hydrogen atoms were then included in the structure-factor calculation but were not refined. The resulting value of R was 0·097. The nine scale factors were then reduced to one, and anisotropic temperature factors were refined for all nonhydrogen atoms. Throughout all these refinements, atomic scattering factors for neutral atoms were taken from Cromer & Waber (1965), with an anomalous dispersion correction for chlorine for Cu $K\alpha$ radiation (Cromer, 1965), although some data (9%) were included which were taken with Mo $K\alpha$ radiation. Positions of hydrogen atoms were readjusted to chemically sensible positions from cycle to cycle using the *HYGEN* program (Ross, 1971).* A difference electron density map calculated for the region between O(2) and O(3) revealed an approximate position for H(27). In the final cycles using the Cu $K\alpha$ data only, the positional parameters of this hydrogen atom were included, as was an isotropic extinction correction (Zachariasen, 1967). All other hydrogen atoms were, however, kept fixed. The final values of the agreement factors are:

$$R_1=\sum||F_o|-|F_c||/\sum|F_o|=0·055$$

and

$$R_2=[\sum w(F_o-F_c)^2/\sum wF_o^2]^{1/2}=0·074.$$

An analysis of the weighted residuals $(|F_o|-|F_c|)/\sigma(F_o)$ showed no systematic trends with intensity or scattering angle, indicating that the relative weights were satisfactory. The estimated standard deviation of an observation of unit weight was 0.20, indicating that the σ's used (and tabulated) were too large on an absolute scale by a factor of 5. Individual residuals (R_1 and R_2) calculated for layers of constant h, k, and l were also in good agreement.

The final refined parameters for the heavy atoms appear in Table 1, and unrefined hydrogen atom positions for H(1) to H(26) and the refined position of H(27) are presented in Table 2. The final calculated

Table 2. *Positions of hydrogen atoms*

	Bonded to	Calculated x	y	z	B
H(1)	C(2)	0·54707	1·14704	0·15081	4·12
H(2)	C(3)	0·40355	1·11310	0·23365	4·12
H(3)	C(3)	0·41591	0·80490	0·23155	4·12
H(4)	C(4)	0·62692	0·83846	0·32670	4·12
H(5)	C(5)	0·46353	0·76719	0·39325	6·93
H(6)	C(5)	0·57822	0·94308	0·46301	6·93
H(7)	C(5)	0·44704	1·07849	0·40231	6·93
H(8)	C(6)	0·67206	1·26901	0·28729	6·93
H(9)	C(6)	0·70528	1·24322	0·39911	6·93
H(10)	C(6)	0·57810	1·39064	0·33746	6·93
H(11)	N(1)	0·32571	1·15984	0·07512	4·38
H(12)	N(1)	0·39776	1·02533	0·00851	4·38
H(13)	N(1)	0·32318	0·84740	0·06071	4·38
H(14)	C(8)	−0·09309	−0·06130	0·17594	4·12
H(15)	C(9)	0·12343	0·25452	0·25164	4·12
H(16)	C(9)	0·12699	−0·05343	0·26287	4·12
H(17)	C(10)	−0·00417	0·28406	0·34062	4·12
H(18)	C(11)	0·21675	0·32797	0·41140	6·93
H(19)	C(11)	0·15188	0·20126	0·48358	6·93
H(20)	C(11)	0·22932	0·02039	0·43468	6·93
H(21)	C(12)	0·02274	−0·26504	0·37558	6·93
H(22)	C(12)	−0·04230	−0·06221	0·42687	6·93
H(23)	C(12)	−0·10673	−0·12152	0·31649	6·93
H(24)	N(2)	0·06627	−0·15019	0·10808	4·38
H(25)	N(2)	−0·05549	−0·00392	0·03364	4·38
H(26)	N(2)	0·07286	0·15595	0·08468	4·38
		Refined			
H(27)	O(1), O(2)	0·750 (6)	0·602 (20)	0·185 (4)	5·2

Table 1. *Positional and thermal parameters for di-*L*-leucine hydrochloride*

The Debye–Waller factor is defined as $\exp(-\sum 2\pi^2 a_i{}^* a_j{}^* h_i h_j U_{ij})$. The numbers in parentheses are the e.s.d.'s in the last significant figure of the tabulated quantities. Atoms O(1) through C(6) belong to one leucine molecule, atoms O(3) through C(12) belong to the other.

ATOM	X	Y	Z	U11	U22	U33	U12	U13	U23
CL	.20779(9)	.50000	.10078(7)	353(5)	355(13)	509(6)	5(6)	125(4)	-3(7)
O1	.52263(31)	.59568(97)	.07449(22)	491(16)	293(45)	467(16)	50(17)	206(13)	-54(17)
O2	.69083(32)	.76772(127)	.17983(29)	342(16)	528(49)	827(25)	98(21)	144(16)	-148(26)
N1	.37814(31)	1.01095(150)	.06695(22)	369(16)	354(41)	376(16)	102(27)	128(13)	84(28)
C1	.57341(40)	.76457(138)	.13126(30)	334(19)	224(57)	409(22)	13(22)	175(16)	6(23)
C2	.49718(36)	.99118(164)	.14676(26)	355(17)	145(44)	365(17)	33(26)	141(14)	1(26)
C3	.46027(43)	.96980(187)	.23408(30)	419(21)	555(63)	392(20)	34(31)	191(17)	-45(31)
C4	.56727(47)	.97672(202)	.32527(31)	496(24)	520(66)	390(21)	76(36)	130(18)	11(33)
C5	.51107(70)	.93491(260)	.40235(37)	861(42)	1377(124)	403(26)	113(58)	275(27)	57(43)
C6	.63761(92)	1.23668(281)	.33840(54)	1121(63)	967(114)	655(41)	-323(69)	187(40)	-205(51)
O3	-.18239(40)	.37443(126)	.19320(31)	643(23)	598(51)	847(26)	297(28)	443(21)	158(28)
O4	-.10798(35)	.46556(121)	.07910(24)	602(19)	324(43)	597(19)	167(24)	260(15)	118(24)
N2	.01442(32)	.01190(142)	.09320(23)	402(16)	210(39)	407(16)	55(26)	147(13)	-44(25)
C7	-.11372(39)	.32834(165)	.14189(30)	292(19)	342(51)	429(22)	40(24)	130(16)	41(29)
C8	-.03777(41)	.07915(145)	.16882(30)	371(19)	173(58)	439(22)	-11(22)	164(17)	35(22)
C9	.07527(46)	.10157(162)	.25785(35)	417(23)	543(77)	497(26)	29(28)	121(20)	30(30)
C10	.04791(56)	.12846(185)	.34626(37)	562(29)	670(79)	472(26)	99(36)	132(23)	-65(33)
C11	.17014(77)	.17861(320)	.42458(49)	809(46)	1657(135)	563(36)	119(69)	11(32)	-60(58)
C12	-.02662(95)	-.09334(273)	.36736(50)	1186(65)	1369(148)	650(41)	-227(76)	410(43)	171(58)

---

* Other computer programs used have been describedby Schlemper, Hamilton & La Placa (1971).

and observed structure factors (with standard deviations used in the refinement) are presented in Table 3. Bond distances and angles are presented in Table 4, where they are compared with the corresponding values for the hydrobromide, the hydriodide, and for the leucyl residue in peptides studied by Chandrasekaran & Subramanian (1969) and by Leung & Marsh (1958). Torsion angles are given in Table 5, and parameters for the hydrogen bonds are presented in Table 6.

Discussion

The most striking feature of the structure is the existence of a hydrogen-bonded, dimeric cation consisting of two leucine molecules sharing a proton in a very short (2·43 Å) hydrogen bond between the two carboxyl groups. This configuration is illustrated in Fig. 1. These dimers are more weakly hydrogen-bonded through the chloride ions to form double layers parallel to the (001) plane (see Fig. 2). There is also a single N–H...O hydrogen bond. These layers are terminated on both sides in the **c** direction with nonpolar methyl groups. The shortest C–C contact between layers is 3·91(2) Å [C(5)–C(11) $(1-x,\frac{1}{2}+y,-1z)$]. The only H---H contacts (based on the calculated positions) smaller than 2·6 Å are 2·373, 2·539, 2·366, 2·440, and 2·482 Å. These are all normal van der Waals contacts.

The structure contains two crystallographically dis-

Table 3. *Structure amplitudes* (×10) *in electrons-cell*$^{-1}$ *for di-*L*-leucine hydrochloride*

FO = Observed structure amplitude (including a small extinction correction),
FC = Calculated structure amplitude for the parameters of Tables 1 and 2,
SIG = Standard deviation of FO used in structure refinement. The tabulated values should be divided by 5 to obtain estimated standard deviations on an absolute scale.

H	L	FO	SIG	FC
*** K= 0 ***				
0	2	157	53	93
0	3	212	57	263
0	4	851	159	845
0	5	251	63	248
0	6	261	65	270
0	7	255	64	266
0	8	115	40	109
0	9	69	29	69
0	10	44	26	36
0	11	91	35	91
0	12	206	55	195
0	13	27	22	26
0	14	67	25	37
1	-18	67	26	41
1	-17	59	31	55
1	-16	96	36	86
1	-15	95	36	87
1	-14	16	19	14
1	-13	35	24	35
1	-12	86	35	81
1	-11	261	65	249
1	-10	106	38	99
1	-9	17	19	15
1	-8	66	30	60
1	-7	405	88	438
1	-6	180	51	203
1	-5	301	72	316
1	-4	175	51	175
1	-3	266	66	274
1	-1	158	48	159
1	0	57	29	59
1	1	206	56	185
1	2	21	20	19
1	3	365	82	381
1	4	310	73	342
1	5	376	83	405
1	6	101	37	115
1	7	309	72	309
1	8	189	53	178
1	9	58	29	51
1	11	160	48	154
1	12	51	27	53
1	13	133	43	119
1	14	69	31	60
1	15	86	34	78
1	16	26	21	22
2	-18	61	29	53
2	-17	41	25	40
2	-16	17	19	19
2	-15	42	25	38
2	-14	39	25	33
2	-13	238	61	226
2	-12	209	56	196
2	-11	68	31	76
2	-10	73	32	77
2	-9	65	30	71
2	-8	35	24	30
2	-7	128	42	149
2	-6	281	68	280
2	-5	204	55	204
2	-4	91	36	99
2	-3	306	72	294
2	-2	489	102	466
2	-1	170	50	168
2	0	647	127	581
2	1	262	65	240
2	2	262	65	228
2	3	174	51	187
2	4	181	52	201
2	5	93	36	105
2	6	185	52	194
2	7	21	21	21
2	8	137	44	129
2	9	83	34	86
2	10	262	65	237
2	11	106	38	100
2	12	54	28	50
2	14	87	35	81
2	15	80	33	65
3	-18	56	29	52
3	-17	54	28	41
3	-15	32	23	33
3	-14	37	24	39
3	-13	71	31	67
3	-12	15	18	17
3	-11	59	29	55
3	-10	166	49	170
3	-8	37	24	42
3	-7	63	34	83
3	-6	585	116	589
3	-5	348	79	329
3	-4	118	40	131
3	-3	224	59	215
3	-2	320	75	326
3	-1	278	68	294
3	0	303	72	289
3	2	124	42	111
3	3	631	123	640
3	4	215	57	228
3	5	124	42	119
3	6	41	25	48
3	7	106	38	105
3	8	99	37	98
3	9	115	40	118
3	10	40	25	36
3	11	96	36	90
3	16	24	22	25
4	-18	35	23	30
4	-17	60	29	48
4	-16	38	24	33
4	-15	90	35	92
4	-14	181	52	177
4	-13	60	29	55
4	-12	34	23	38
4	-11	42	25	40
4	-10	141	45	142
4	-9	80	33	83
4	-8	105	38	97
4	-7	108	39	106
4	-6	71	31	65
4	-4	83	34	88
4	-3	281	68	297
4	-2	165	49	141
4	-1	59	29	66
4	0	168	46	142
4	1	127	42	113
4	2	197	54	185
4	3	62	30	66
4	4	287	69	275
4	5	25	21	26
4	6	80	33	81
4	7	87	35	92
4	8	44	26	34
4	9	40	25	37
4	10	59	29	58
4	11	84	34	77
4	12	68	31	66
4	13	51	27	45
4	14	31	23	22
4	15	49	27	44
5	-18	31	23	27
5	-17	34	23	30
5	-16	35	24	31
5	-15	79	33	75
5	-14	68	31	71
5	-13	54	28	62
5	-12	42	25	42
5	-11	133	43	143
5	-10	194	54	207
5	-9	273	67	282
5	-8	120	41	116
5	-7	226	59	212
5	-6	31	23	28
5	-5	178	51	171
5	-4	155	47	158
5	-3	120	41	114
5	-2	98	37	98
5	-1	129	42	126
5	0	99	37	103
5	1	47	26	51
5	2	77	31	72
5	3	162	48	155
5	4	96	36	114
5	5	109	39	117
5	6	64	31	64
5	8	88	35	87
5	9	108	39	101
5	10	81	33	81
5	11	35	24	38
5	12	40	25	40
5	13	67	31	66
5	14	52	28	49
6	-18	23	21	25
6	-16	17	19	10
6	-15	12	18	12
6	-14	18	19	12
6	-13	51	27	60
6	-12	59	29	56
6	-11	44	26	42
6	-10	27	22	24
6	-9	210	56	241
6	-8	269	66	274
6	-7	213	57	223
6	-6	156	47	153
6	-5	178	51	172
6	-4	204	55	201
6	-3	322	75	335
6	-2	350	79	369
6	-1	218	58	219
6	0	135	44	114
6	1	171	50	175
6	2	247	62	241
6	3	371	82	387
6	4	232	60	254
6	5	59	29	62
6	6	67	31	69
6	7	71	31	76
6	8	49	27	47
6	9	61	29	55
6	10	68	31	57
6	11	20	20	18
6	12	22	20	15
6	13	26	21	20
7	-18	32	23	34
7	-17	31	23	28
7	-16	38	24	40
7	-15	58	29	63
7	-14	55	28	63
7	-12	60	29	71
7	-11	59	29	74
7	-10	78	31	81
7	-9	68	31	68
7	-8	98	37	111
7	-7	96	36	101
7	-5	127	42	129
7	-4	196	54	203
7	-3	87	35	86
7	-2	83	34	89
7	-1	140	44	142
7	0	158	48	148
7	1	91	35	91
7	2	34	23	34
7	3	64	31	67
7	5	82	33	84
7	6	158	48	170
7	7	112	39	118
7	8	33	23	25
7	9	35	24	35
7	10	82	34	80
7	11	50	27	46
7	12	28	22	30
8	-17	15	19	17
8	-16	40	25	48
8	-15	101	38	104
8	-14	68	31	68
8	-13	60	29	59
8	-12	57	29	59
8	-11	131	43	131
8	-10	106	38	107
8	-9	138	44	137
8	-7	62	30	57
8	-6	32	23	26
8	-5	16	19	14
8	-4	43	25	41
8	-3	110	39	117
8	-2	51	27	46
8	-1	57	28	59
8	0	81	34	83
8	1	93	36	89
8	2	153	47	167
8	3	25	21	21
8	4	34	23	35
8	5	38	24	41
8	6	56	28	60
8	7	53	28	50
8	8	35	24	30
8	9	43	26	37
8	10	26	21	17
9	-15	62	30	65
9	-14	76	33	74
9	-13	35	24	31
9	-12	33	23	33
9	-11	27	22	25
9	-10	110	39	103
9	-9	122	41	117
9	-8	88	35	86
9	-7	86	34	89
9	-6	34	23	26
9	-5	190	53	184
9	-4	161	48	163
9	-3	124	41	116
9	-1	99	37	95
9	0	67	31	64
9	1	86	34	77
9	2	27	22	27
9	3	31	23	31
9	4	13	18	6
9	5	63	30	65
9	6	65	30	65
9	7	72	32	63
9	8	26	21	15
9	9	43	25	39
10	-16	33	23	38
10	-13	43	25	52
10	-12	92	36	89
10	-11	138	44	136
10	-10	67	31	70
10	-9	97	36	91
10	-8	99	37	90
10	-7	56	28	56
10	-6	68	31	63
10	-5	59	29	56
10	-4	69	31	70
10	-3	50	27	43
10	-2	60	29	53
10	-1	84	34	85
10	0	125	42	126
10	1	164	49	159
10	2	32	23	29
10	3	102	37	102
10	4	113	40	112
10	5	75	32	75
10	6	51	27	47
10	7	34	23	29
11	-14	19	20	18
11	-13	41	25	43
11	-12	44	26	41
11	-11	64	30	67
11	-10	76	32	80
11	-8	120	41	115
11	-7	131	43	128
11	-6	135	43	128
11	-4	147	46	136
11	-3	106	38	101
11	-2	57	28	58
11	0	28	22	23
11	1	35	24	31
11	2	43	25	42
11	3	26	21	26
12	-14	32	23	47
12	-12	18	19	17
12	-11	34	23	36
12	-10	56	28	61
12	-9	67	31	74
12	-7	47	26	48
12	-6	51	27	62
12	-5	74	32	82
12	-4	43	25	46
12	-3	31	23	29
12	-2	23	21	15
12	-1	88	35	87
12	0	70	31	71
12	1	37	24	34
12	2	22	20	18
13	-10	29	22	33
13	-9	27	22	29
13	-8	33	23	28
13	-6	49	27	46
13	-4	45	26	42
13	-3	26	21	23
13	-2	62	30	60
13	-1	55	28	56
*** K= 1 ***				
0	2	549	111	525
0	3	173	50	175
0	4	166	49	165
0	5	70	31	64
0	6	106	38	106
0	7	122	41	127
0	8	185	52	189
0	9	175	50	177
0	10	61	29	61
0	11	154	47	147
0	12	104	38	107
0	14	31	23	29
0	15	28	22	28
0	16	21	20	26
1	-18	26	21	27
1	-16	75	32	70
1	-15	76	33	75
1	-14	80	33	83
1	-13	44	26	40
1	-12	130	43	125
1	-11	71	32	72
1	-9	147	46	150
1	-8	116	40	116
1	-7	97	36	95
1	-6	54	28	50
1	-5	191	53	207
1	-4	189	53	193
1	-3	178	51	185
1	-2	271	67	248
1	-1	403	89	425
1	0	106	38	111
1	1	310	73	312
1	2	306	72	333
1	3	43	26	42
1	4	231	60	269
1	5	166	49	177
1	6	65	30	61
1	7	63	30	58
1	8	120	41	116
1	9	111	39	107
1	10	198	54	196
1	11	81	34	72
1	12	98	37	101
1	13	48	27	43
1	14	91	35	90
1	15	62	30	61
1	16	37	24	36
1	17	29	22	28
2	-19	27	22	25
2	-18	20	20	24
2	-17	40	25	42
2	-16	41	25	39
2	-15	54	28	53
2	-14	37	24	39
2	-13	165	49	160
2	-12	62	30	53
2	-11	73	32	78
2	-10	66	31	72
2	-9	44	26	33
2	-8	79	33	83
2	-7	267	65	273
2	-6	171	50	178
2	-5	215	57	222
2	-4	154	47	147
2	-3	546	110	567
2	-2	364	82	373
2	-1	920	170	871
2	0	122	41	106
2	1	547	111	553
2	2	119	41	124
2	3	226	59	224
2	4	81	33	87
2	5	135	44	138
2	6	78	33	78
2	7	97	37	109
2	8	111	39	114
2	9	65	30	63
2	10	57	29	53
2	11	22	20	21
2	12	100	37	94
2	13	73	32	76
2	14	54	28	48
2	15	44	26	40
2	16	22	22	32
2	17	58	29	70
3	-18	29	22	26
3	-17	32	23	25
3	-15	30	22	29
3	-14	32	23	26
3	-13	55	28	53
3	-12	77	33	65
3	-11	93	36	95
3	-10	224	59	222
3	-9	237	61	247
3	-8	336	77	361
3	-7	126	42	125
3	-6	449	95	454
3	-5	376	83	367
3	-4	537	108	513
3	-3	424	91	431
3	-2	390	86	374
3	-1	135	44	131
3	0	427	91	407
3	1	616	121	620
3	2	550	110	516
3	3	314	73	319
3	4	290	69	293
3	5	187	53	193
3	6	269	63	271
3	7	188	53	196
3	8	144	45	136
3	9	82	34	86
3	10	73	32	80
3	11	72	32	69
3	12	124	42	124
3	13	42	25	47
3	14	28	22	36
3	15	21	20	22
3	16	24	21	30
4	-19	58	29	60
4	-17	34	23	34
4	-16	69	31	61
4	-15	46	26	49
4	-14	116	40	112
4	-13	66	30	67
4	-12	92	36	90
4	-11	83	34	85
4	-10	84	34	80
4	-9	88	35	85
4	-8	64	30	64
4	-7	148	46	157
4	-6	216	57	209
4	-5	263	65	273
4	-4	131	43	132
4	-3	130	43	121
4	-2	223	59	217
4	-1	155	47	159
4	0	144	45	146
4	1	218	58	221
4	2	193	54	188
4	3	138	44	136
4	4	281	68	290
4	5	347	78	377
4	6	95	36	104
4	7	42	25	47
4	8	112	39	112
4	9	137	44	141
4	10	75	32	80
4	11	82	34	82
4	12	23	20	25
4	13	37	24	32
4	14	37	24	33
4	15	24	21	26
5	-19	65	30	68
5	-18	60	29	57
5	-17	57	29	54
5	-16	65	30	61
5	-15	80	33	70
5	-14	36	24	39
5	-13	115	40	106
5	-12	110	39	110
5	-11	112	39	119
5	-10	51	27	53
5	-9	195	54	195
5	-8	127	42	121
5	-7	219	61	242
5	-6	232	60	225
5	-5	157	47	157
5	-4	94	36	79
5	-3	110	39	102
5	-2	33	23	40
5	-1	71	31	62
5	0	153	47	153
5	1	148	46	147
5	2	89	35	93
5	3	103	38	96
5	4	218	58	214
5	5	86	34	78
5	6	97	37	97
5	7	82	34	78
5	8	61	29	58
5	9	48	27	52
5	10	87	35	87
5	11	66	31	64
5	12	51	28	51
5	13	40	25	39
5	15	23	21	26
6	-18	16	19	14
6	-17	25	21	30
6	-16	46	26	46
6	-15	46	26	50
6	-14	59	29	61
6	-13	50	27	54
6	-12	32	23	33
6	-11	103	38	109
6	-10	140	44	141
6	-9	87	35	81
6	-8	165	49	165
6	-7	112	39	119
6	-6	191	53	203
6	-5	170	50	192
6	-4	153	47	157
6	-3	87	35	88
6	-2	108	39	101
6	-1	184	52	172
6	0	187	53	198
6	1	175	50	176
6	2	22	20	22
6	3	202	55	209
6	4	65	30	71
6	5	71	31	68
6	6	83	34	87
6	7	18	19	24
6	8	37	24	41
6	9	35	24	46
6	10	43	25	52
6	11	36	24	38
6	12	24	21	20
6	14	33	23	40
7	-19	26	21	23
7	-18	23	21	28
7	-17	40	25	40
7	-16	38	24	37
7	-15	17	19	16
7	-14	62	30	56
7	-13	106	38	109
7	-12	119	41	131
7	-11	98	37	102
7	-9	183	52	188
7	-8	192	53	192
7	-7	76	33	74
7	-6	89	35	91
7	-5	107	38	102
7	-4	116	40	113
7	-3	157	47	150
7	-2	189	53	190
7	-1	154	47	148
7	0	97	37	93
7	1	57	29	54
7	2	64	30	62
7	3	124	42	126
7	4	144	45	146
7	5	41	25	48
7	6	59	29	54
7	7	80	33	79
7	8	98	37	99
7	9	40	25	47
7	10	20	20	19
7	11	31	23	31
7	12	34	23	41
8	-18	27	22	34
8	-17	23	21	15
8	-16	42	25	38
8	-15	48	26	39
8	-14	60	29	63
8	-13	86	34	87
8	-12	56	28	52
8	-11	33	23	27
8	-10	161	48	155
8	-9	164	49	165
8	-8	77	33	64
8	-7	46	30	63
8	-6	98	37	85
8	-5	104	38	87
8	-4	110	39	94
8	-3	122	41	111
8	-2	105	38	99
8	-1	41	25	39
8	0	50	27	45
8	1	59	29	50
8	2	167	49	155
8	3	81	33	79
8	4	78	33	75
8	5	88	35	77
8	6	58	29	59
8	7	53	28	55
8	9	45	26	40
8	10	47	26	43
8	11	48	27	51
9	-17	24	21	23
9	-16	35	24	35
9	-13	36	24	42
9	-12	61	29	52
9	-11	24	21	26
9	-10	39	25	40
9	-9	80	33	82
9	-8	41	25	45
9	-7	152	46	143
9	-6	176	51	159
9	-5	189	53	162
9	-4	30	22	33
9	-3	147	46	135
9	-2	178	51	162
9	-1	184	52	167
9	0	121	41	116
9	1	57	29	46
9	2	69	31	65
9	3	114	40	107
9	4	89	35	83
9	5	72	33	74
9	6	32	23	39
9	7	28	22	29
9	9	45	26	45
9	10	39	25	41
10	-17	27	22	28
10	-16	66	30	59
10	-14	42	25	42
10	-13	42	25	45
10	-12	33	23	29
10	-9	53	28	46
10	-8	73	33	71
10	-7	25	21	20
10	-6	68	31	64
10	-5	47	26	37
10	-4	82	34	71
10	-3	94	36	76
10	-2	101	37	85
10	-1	31	23	26
10	0	125	42	104
10	1	135	44	107
10	2	42	25	40
10	3	42	25	41
10	4	30	22	30
10	5	29	22	31
10	6	36	24	48
10	7	48	27	50
10	8	42	26	55
11	-16	44	26	45
11	-15	68	31	68
11	-14	56	28	52
11	-13	51	27	51
11	-12	19	19	13
11	-11	59	29	58
11	-10	81	33	80
11	-9	35	24	29
11	-8	56	28	53
11	-7	67	31	60
11	-6	30	22	29
11	-5	65	30	62
11	-4	62	31	61
11	-3	45	26	40
11	-1	36	24	36
11	0	37	24	35
11	2	20	20	26
11	3	33	23	35
11	4	37	24	47
11	5	42	25	49
11	6	16	19	19
12	-15	16	19	17
12	-13	54	28	49
12	-12	62	30	61
12	-11	34	23	39
12	-10	20	20	16
12	-9	55	28	51
12	-8	62	30	61
12	-7	81	33	86
12	-6	77	33	77
12	-5	58	29	61
12	-4	49	27	52
12	-3	105	38	100
12	-2	62	30	57
12	-1	25	21	23
12	0	36	24	38
12	1	39	25	42
12	2	53	28	57
12	3	38	24	38
12	4	18	19	18
13	-13	17	19	21
13	-12	27	22	23
13	-11	44	26	42
13	-10	67	31	69
13	-9	62	30	68
13	-8	34	23	36
13	-7	30	22	32
13	-6	50	27	50
13	-5	116	40	114
13	-4	76	32	83
13	-3	30	22	37
13	-2	25	21	31
13	-1	42	25	46
13	0	64	30	66
13	1	57	28	62
14	-8	25	21	28
14	-7	40	25	47
14	-6	42	25	47
14	-5	21	20	25
*** K= 2 ***				
0	2	214	57	218
0	3	86	34	86
0	4	166	49	163
0	5	326	75	334
0	6	381	84	347
0	7	197	54	191
0	8	31	23	27
0	9	72	32	65
0	10	112	39	112
0	11	112	39	106
0	12	124	42	120
0	13	74	32	76
0	14	40	25	37
0	15	50	27	56
0	16	46	26	48
0	17	26	21	25
1	-18	17	19	16
1	-17	37	24	39
1	-16	38	24	37
1	-15	54	28	56
1	-14	75	32	73
1	-13	43	26	34
1	-12	85	34	85
1	-11	175	50	172
1	-10	85	34	84
1	-8	88	35	81
1	-7	171	50	173
1	-6	139	44	147
1	-5	184	52	183
1	-4	62	30	60
1	-3	79	33	88
1	-2	373	83	336
1	-1	424	91	401
1	0	74	32	75
1	1	351	80	366
1	2	312	71	323
1	3	220	58	223
1	4	183	52	187
1	5	81	33	69
1	6	54	28	59
1	7	78	33	76
1	8	117	40	116
1	9	81	33	78
1	10	79	33	82
1	11	72	32	72
1	12	67	31	64
1	13	91	35	89
1	14	55	28	57
1	15	29	22	33
1	16	30	21	27
2	-18	53	28	57
2	-17	50	27	46
2	-15	36	24	35
2	-14	52	28	49
2	-13	130	41	122
2	-12	141	45	135
2	-11	57	29	53
2	-10	41	26	42
2	-9	111	39	112
2	-8	181	52	185
2	-7	143	45	141
2	-6	90	35	86
2	-5	115	40	119
2	-4	58	29	67
2	-3	101	37	82
2	-2	187	52	165
2	-1	410	88	377
2	0	275	67	261
2	1	107	38	91
2	2	128	42	112
2	3	99	37	96
2	4	28	22	28
2	5	177	51	181
2	6	163	48	171
2	7	81	33	81
2	8	66	30	71
2	9	107	39	111
2	10	103	38	105
2	11	118	40	121
2	15	32	23	27
3	-18	29	22	30
3	-17	47	26	49
3	-16	52	27	54
3	-15	41	25	35
3	-14	49	27	51
3	-13	108	39	104
3	-12	124	42	122
3	-11	69	31	65
3	-10	36	24	35
3	-9	100	37	99
3	-8	97	37	100
3	-7	61	29	58
3	-6	63	30	66
3	-5	103	38	99
3	-4	97	37	96
3	-3	100	37	104
3	-2	242	62	248
3	-1	202	55	211
3	0	286	69	272
3	1	73	32	71
3	2	164	49	161
3	3	199	54	194
3	4	169	49	165
3	5	96	34	84
3	6	96	36	92
3	7	34	24	30
3	8	87	35	94
3	9	153	47	160
3	10	72	32	76
3	12	40	25	40
3	13	73	31	71
3	14	57	28	57
3	16	32	23	32
4	-15	68	31	62
4	-14	86	34	85
4	-11	75	32	76
4	-10	41	25	45
4	-9	88	35	88
4	-8	232	60	236
4	-7	300	71	296
4	-6	90	35	85
4	-5	99	37	109
4	-4	283	68	284
4	-3	293	70	290
4	-2	260	68	276
4	-1	178	51	166
4	0	251	63	227
4	1	169	49	161
4	2	166	49	160
4	3	68	31	65
4	4	165	49	155
4	5	109	39	103
4	6	73	32	76
4	7	86	34	84
4	8	30	22	21
4	9	86	34	89
4	10	38	24	31
4	11	63	30	55
4	12	42	25	43
4	13	26	21	25
5	-18	30	22	27
5	-16	56	28	53
5	-15	68	31	65
5	-14	72	32	67
5	-13	50	27	53
5	-12	64	30	70
5	-11	170	50	167
5	-10	174	50	177
5	-9	108	39	123
5	-8	65	30	68
5	-7	210	56	212
5	-6	124	42	120
5	-5	75	32	76
5	-4	133	43	137
5	-3	95	36	89
5	-2	177	51	171
5	-1	137	44	136
5	0	154	47	151
5	1	158	48	147
5	2	162	48	166
5	3	49	27	44
5	4	115	40	117
5	5	136	44	164
5	7	67	31	71
5	8	38	24	31
5	9	50	27	56
5	10	61	29	58
5	11	44	26	45
5	14	56	28	60
6	-18	49	27	48
6	-17	48	27	42
6	-14	53	28	50
6	-13	102	37	100
6	-12	60	29	59
6	-11	32	23	31
6	-10	60	29	56
6	-9	147	46	147
6	-8	150	46	160
6	-7	80	33	76
6	-6	96	36	101
6	-5	54	28	56
6	-4	175	50	186
6	-3	161	48	166
6	-2	133	43	148
6	-1	144	45	143
6	0	32	23	22
6	2	124	42	126
6	3	248	63	254
6	4	263	65	266
6	5	119	41	114
6	6	48	26	44
6	7	108	39	116
6	8	165	49	165
6	9	69	31	83
6	10	27	22	14
6	11	21	20	28
6	12	49	27	53
6	13	26	21	25
7	-17	16	19	20
7	-16	26	21	28
7	-15	25	21	24
7	-14	57	29	56
7	-13	55	28	52
7	-12	69	31	71
7	-11	40	25	38
7	-10	69	31	77
7	-9	54	28	46
7	-8	153	47	156
7	-7	107	38	105
7	-6	99	37	97
7	-5	106	38	108
7	-4	140	44	148
7	-3	132	43	130
7	-2	85	34	77
7	-1	115	40	114
7	0	186	52	187
7	1	179	51	183
7	2	139	44	146
7	3	111	39	107
7	4	98	37	101
7	5	61	29	72
7	6	58	29	65
7	11	40	25	43
7	12	36	24	40
8	-17	47	26	49
8	-16	63	30	69
8	-15	63	30	67
8	-14	33	23	33
8	-13	38	24	33
8	-12	41	25	44
8	-11	36	24	39
8	-10	81	33	74
8	-9	104	38	106
8	-8	110	39	114
8	-7	59	29	54
8	-6	70	31	67
8	-5	76	32	77
8	-4	70	31	65
8	-3	70	31	63
8	-2	27	22	23
8	-1	39	25	31
8	0	59	29	54
8	1	106	38	114
8	2	59	29	61
8	3	52	27	50
8	6	27	22	30
8	7	37	24	36
8	8	56	28	56
8	9	50	27	48
9	-16	15	19	19
9	-15	45	26	44
9	-14	55	28	62
9	-13	54	28	60
9	-12	41	25	37
9	-11	41	25	42
9	-10	142	45	150
9	-9	128	42	127
9	-7	42	25	43
9	-6	54	28	62
9	-5	50	27	46
9	-4	46	26	41
9	-2	87	35	88
9	-1	78	33	81
9	0	67	31	58
9	1	76	32	73
9	2	104	38	112
9	3	61	29	66
9	4	38	24	37
9	5	78	33	84
9	6	77	33	83
9	7	57	29	60
9	9	36	24	39
10	-16	47	26	46
10	-12	85	34	86
10	-11	95	36	101
10	-10	69	31	72
10	-9	49	27	46
10	-7	85	34	83
10	-6	152	47	164
10	-5	156	47	168
10	-4	128	42	136
10	-3	105	38	100
10	-2	140	44	141
10	-1	101	38	101
10	0	78	33	75
10	1	45	26	46
10	3	48	27	57
10	4	47	26	53
10	5	48	27	53
10	6	27	22	26
10	7	24	21	27
11	-15	21	20	15
11	-14	31	23	27
11	-13	47	26	55
11	-12	45	26	42
11	-9	47	26	47
11	-8	79	33	92
11	-7	67	31	70
11	-6	58	29	60
11	-5	43	26	44
11	-4	62	30	66
11	-3	69	31	63
11	-2	72	32	68
11	-1	70	31	73
11	1	53	28	46
11	2	60	29	66
11	3	48	27	48
12	-10	30	22	28
12	-9	36	24	32
12	-8	30	22	26
12	-6	43	25	50
12	-5	46	26	53
12	-4	46	26	50
12	-3	40	25	39
12	-2	29	22	26
12	-1	52	28	56
12	0	49	27	53
12	1	35	24	38
12	2	31	23	36
13	-11	40	25	46
13	-9	37	24	37
13	-8	55	28	60
13	-7	41	25	40
13	-6	18	19	16
13	-5	23	21	19
13	-4	24	21	22
13	-3	42	25	41
13	-2	44	26	42
13	-1	28	22	27
*** K= 3 ***				
0	2	141	45	165
0	3	118	40	125
0	4	137	46	154
0	5	54	28	56
0	6	71	31	67
0	7	135	43	133
0	8	119	41	117
0	9	43	25	45
0	10	41	25	40
0	11	56	28	58
0	12	143	45	128
0	13	48	26	54
0	16	40	25	42
1	-17	16	19	18
1	-16	30	22	35
1	-15	50	27	44
1	-14	51	27	46
1	-13	67	31	64
1	-12	42	25	46
1	-11	106	38	111
1	-10	79	33	84
1	-9	131	43	133
1	-8	117	40	116
1	-7	29	22	21
1	-6	84	34	89
1	-5	157	47	174
1	-4	202	55	219
1	-3	150	46	166
1	-2	14	18	16
1	-1	206	55	208
1	0	178	51	177
1	1	165	49	171
1	2	65	30	70
1	3	144	45	156
1	4	86	34	87
1	5	40	25	46
1	6	40	25	38
1	9	79	33	77
1	10	110	39	108
1	11	85	34	82
1	13	55	28	56
1	14	43	26	46
1	15	30	22	32
1	16	17	19	18
2	-17	27	22	28
2	-16	29	22	30
2	-14	66	30	63
2	-13	59	29	55
2	-12	68	31	64
2	-11	24	21	23
2	-10	57	28	52
2	-9	64	30	59
2	-8	77	33	73
2	-7	121	41	134
2	-6	149	46	149
2	-5	66	31	72
2	-4	18	19	15
2	-3	80	33	92
2	-2	189	53	195
2	-1	258	64	244
2	0	184	52	182
2	1	74	32	73
2	2	199	55	200
2	3	273	67	261
2	4	155	47	151
2	6	88	35	86
2	7	116	40	120
2	8	133	43	131
2	9	66	30	68
2	10	34	23	28
2	11	20	20	16
2	12	21	20	17
2	13	64	30	65
2	14	30	22	35
2	15	21	20	17
3	-17	29	22	32
3	-15	31	23	32
3	-14	56	28	55
3	-13	81	34	75
3	-12	75	32	74
3	-11	87	35	83
3	-10	123	41	130
3	-9	156	47	154
3	-8	124	42	121
3	-7	73	32	68
3	-6	106	38	99
3	-5	194	54	213
3	-4	210	56	218
3	-3	253	63	238
3	-2	131	43	111
3	-1	249	61	233
3	0	134	43	126
3	1	158	48	142
3	2	192	53	177
3	3	161	48	152
3	4	80	33	78
3	6	187	51	184
3	7	174	50	178
3	8	91	35	90
3	9	55	28	57
3	10	50	27	53
3	11	92	36	89
3	12	66	30	65
3	13	40	25	45
4	-17	32	23	30
4	-16	48	26	44
4	-15	62	30	63
4	-14	82	34	79
4	-13	61	29	61
4	-12	96	36	100
4	-11	105	38	113
4	-10	123	41	140
4	-9	71	31	72
4	-8	96	36	98
4	-7	73	32	69
4	-6	83	34	79
4	-5	145	45	144
4	-4	112	39	108
4	-3	101	37	111
4	-2	69	31	59
4	-1	97	36	87
4	0	158	47	163
4	1	141	44	133
4	2	94	36	96
4	3	79	33	77
4	4	123	41	131
4	5	106	38	111
4	6	68	31	67
4	7	60	29	64
4	8	90	35	89
4	9	83	34	82
4	10	77	33	78
4	11	34	23	35
4	13	16	19	15
4	14	14	18	20
5	-17	32	23	35
5	-16	21	20	25
5	-14	29	22	33
5	-12	55	28	54
5	-11	51	27	48
5	-10	69	31	78
5	-9	63	30	75
5	-8	56	28	65
5	-7	89	35	86
5	-6	133	43	128
5	-2	59	29	56
5	-1	28	22	24
5	0	79	33	73
5	1	50	27	44
5	2	109	39	100
5	3	145	45	142
5	4	41	25	48
5	5	99	37	99
5	6	92	36	94
5	7	118	40	124
5	8	30	22	31
5	9	33	23	38
5	10	38	24	66
5	11	41	25	46
5	12	29	22	29
5	13	10	17	17
6	-17	24	21	22
6	-16	35	23	36
6	-15	47	26	48
6	-14	44	26	44
6	-13	42	25	42
6	-12	52	28	51
6	-11	74	32	77
6	-10	60	29	57
6	-9	95	36	98
6	-8	47	26	48
6	-7	139	44	132
6	-6	77	33	77
6	-5	66	30	51
6	-4	107	38	96
6	-3	92	36	87
6	-2	84	34	71
6	-1	126	42	113
6	0	126	42	113
6	1	32	23	33
6	2	105	38	102
6	3	77	33	82
6	4	66	30	65
6	5	49	27	51
6	6	36	24	40
6	7	23	21	26
6	8	28	22	37
6	9	57	29	55
6	10	66	30	67
6	11	40	25	43
7	-17	37	24	43
7	-14	60	29	55
7	-13	82	34	79
7	-12	103	38	102
7	-11	100	37	90
7	-10	65	30	60
7	-9	73	32	81
7	-8	209	56	207
7	-7	187	52	178
7	-6	142	45	140
7	-5	68	31	67
7	-4	107	38	98
7	-3	127	42	127
7	-2	110	39	97
7	-1	100	37	95
7	0	65	30	57
7	1	35	24	29
7	2	122	41	119
7	3	129	42	130
7	4	110	39	103
7	5	69	31	72
7	6	40	25	45
7	7	32	23	37
7	8	43	26	47
7	9	28	22	31
8	-16	20	20	20
8	-15	56	28	58
8	-14	54	28	50
8	-13	19	20	21
8	-11	67	31	71
8	-10	80	33	75
8	-9	46	26	53
8	-8	65	30	66
8	-7	68	31	63
8	-5	90	35	84
8	-4	135	43	126
8	-3	167	49	157
8	-2	99	37	95
8	-1	48	27	50
8	0	92	35	80
8	1	156	47	158
8	2	128	42	123
8	3	52	27	61
8	4	45	26	51
8	5	72	32	76
8	6	76	32	77
8	7	43	25	42
8	9	21	20	21
9	-15	24	21	28
9	-14	31	23	34
9	-12	26	21	32
9	-11	39	25	48
9	-10	30	22	32
9	-9	33	23	28
9	-8	36	24	36
9	-7	82	34	81
9	-6	75	32	75
9	-5	48	27	47
9	-4	73	32	67
9	-3	77	33	75
9	-2	84	34	74
9	-1	90	35	83
9	0	101	37	94
9	1	30	23	32
9	2	67	31	66
9	3	65	30	65
9	4	54	28	61
9	5	52	27	54
9	6	34	23	29
9	7	18	19	17
10	-14	33	23	31
10	-13	30	22	32
10	-12	37	24	38
10	-11	48	26	48
10	-10	25	21	17
10	-9	66	30	72
10	-8	75	32	74
10	-7	61	29	58
10	-5	71	31	71
10	-4	70	31	72
10	-3	53	28	52
10	-2	39	24	33
10	-1	46	26	42
10	0	63	30	61
10	1	52	28	50
10	2	31	23	32
10	3	24	21	23
10	4	19	20	20
10	5	20	20	24
11	-13	15	18	18
11	-12	23	21	23
11	-11	40	25	40
11	-10	35	24	32
11	-5	37	24	38
11	-4	47	26	46
11	-3	29	22	30
11	-2	38	24	41
11	-1	61	29	58
11	0	25	21	25
11	1	22	20	19
11	2	14	18	10
11	3	34	23	37
12	-11	14	18	17
12	-10	15	19	18
12	-9	28	22	32
12	-8	45	26	44
12	-7	33	23	34
12	-6	36	24	37
12	-4	23	21	22
12	-3	29	22	28
12	-2	26	21	26
12	-1	28	22	30
12	0	15	19	16

Table 4. *Bond distances and angles in di-*L*-leucine hydrochloride and comparison with the values for the hydrobromide* (*Subramanian*, 1967), *the hydriodide* (*Chaney, Seeley & Steinrauf*,1971), *for the dipeptide studied by Chandrasekaran & Subramanian* (1969), *and for the tripeptide studied by Leung & Marsh* (1958).

The terminology is that of IUPAC-IUB (1970). In this structure, we make the following identifications: [O′: O(1), O(4)], [O″: O(2), O(3)], [C′: C(1), C(7)], [C^{α}: C(2), C(8)], [C^{β}: C(3), C(9)], [C^{γ}: C(4), C(10)], [$C^{\delta 1}$: C(5), C(11)], [$C^{\delta 2}$: C(6), C(12)].

Molecule 1		Molecule 2		Mean (this structure)		Hydro-bromide*	Hydro-iodide†	C & S peptide‡	L & M peptide
C(1)-O(1)	1·229 (7) Å	C(7)—O(4)	1·214 (7) Å	C′=O′	1·221 (5) Å	1·20 Å	1·19 Å	1·226 Å	1·27 (2) Å
C(1)-O(2)	1·280 (6)	C(7)—O(3)	1·288 (6)	C′–O″	1·284 (4)	1·30	1·30	—	—
C(1)-C(2)	1·502 (9)	C(7)—C(8)	1·512 (10)	$C'–C^{\alpha}$	1·507 (7)	1·55	1·53	1·545	1·50 (2)
C(2)-N(1)	1·492 (5)	C(8)—N(2)	1·501 (6)	$C^{\alpha}–N$	1·497 (4)	1·51	1·53	1·506	1·49 (2)
C(2)-C(3)	1·533 (5)	C(8)—C(9)	1·537 (6)	$C^{\alpha}–C^{\beta}$	1·535 (4)	1·51	1·52	1·545	1·54 (2)
C(3)-C(4)	1·520 (6)	C(9)—C(10)	1·496 (7)	$C^{\beta}–C^{\gamma}$	1·508 (5)	1·51	1·51	1·531	1·52 (2)
C(4)-C(6)	1·524 (15)	C(10)-C(12)	1·503 (14)	$C^{\gamma}–C^{\delta 2}$	1·513 (10)	1·49	1·56	1·523	1·51 (4)
C(4)-C(5)	1·527 (7)	C(10)-C(11)	1·521 (9)	$C^{\gamma}–C^{\delta 1}$	1·524	1·53	1·57	1·560	1·51 (4)
O(1)-C(1)-O(2)	124·9 (6)°	O(4)—C(7)—O(3)	125·4 (7)°	O′=C′–O″	125·2 (5)°	124°	122°	—	—
C(2)-C(1)-O(1)	120·1 (4)	C(8)—C(7)—O(4)	122·4 (4)	$C^{\alpha}—C'=O'$	121 3 (3)	126	126	120·5°	119 (1)°
C(2)-C(1)-O(2)	114·9 (5)	C(8)—C(7)—O(3)	112·2 (5)	$C^{\alpha}—C'–O''$	113·5 (4)	110	111	—	—
C(1)-C(2)-N(1)	108·6 (5)	C(7)—C(8)—N(2)	107·7 (4)	$C'—C^{\alpha}–N$	108·2 (3)	105	105	107·1	108 (1)
C(3)-C(2)-N(1)	107·9 (3)	C(9)—C(8)—N(2)	107·3 (4)	$C^{\beta}–C^{\alpha}–N$	107·6 (3)	108	106	110·0	112 (1)
C(1)-C(2)-C(3)	114·3 (5)	C(7)—C(8)—C(9)	114·0 (5)	$C'—C^{\alpha}–C^{\beta}$	114·2 (4)	113	113	111·2	112 (1)
C(2)-C(3)-C(4)	111·0 (7)	C(8)—C(9)—C(10)	118·0 (4)	$C^{\alpha}—C^{\beta}–C^{\gamma}$	114·0	119	114	114·0	118 (1)
C(3)-C(4)-C(5)	108·5 (5)	C(9)—C(10)-C(11)	110·0 (5)	$C^{\beta}–C^{\gamma}–C^{\delta 1}$	109·3 (4)	111	108	109·9	109 (3)
C(3)-C(4)-C(6)	111·0 (7)	C(9)—C(10)-C(12)	114·7 (7)	$C^{\beta}–C^{\gamma}–C^{\delta 2}$	112·9 (5)	114	109	108·9	111 (3)
C(5)-C(4)-C(6)	110·0 (7)	C(11)-C(10)-C(12)	111·8 (8)	$C^{\delta 2}–C^{\gamma}–C^{\delta 1}$	110·9 (6)	112	108	111·2	110 (3)

* E.s.d.'s are 0·03→0·04 Å in distances and 4° in angles

† E.s.d.'s are 0·02→0·03 Å in distances and 1–2° in angles.

‡ E.s.d.'s are 0·013 Å in distances and 1° in angles.

tinct L-leucine molecules (Fig. 1). The agreement between the geometry of these and that of the other determinations of the leucyl residue geometry is satisfactory; this study has provided the smallest standard deviations available. The bond lengths for the two molecules in the asymmetric unit agree well, but there are marked differences in the angles about the carbon atoms in the side chain, particularly at the β carbon atom. It is interesting to note that these are the very angles for which there is the most variation between the geometries of the hydrobromide and hydriodide salts and the peptidyl leucine residue. The unusually large value of 118° for molecule 2 is identical to that found by Leung & Marsh in L-leucyl-L-prolylglycine. Apparently, this angle can easily adapt in response to steric constraints in the intermolecular environment.

Even without the location of H(27), the difference between the C–O bond lengths clearly indicates, for each molecule, the presence of a double-bonded oxygen atom and an approximately single-bonded oxygen atom (*e.g.*, see the tabulation by Nardelli, Fava & Giraldi, 1962), although the value 1·284 (4)Å for the latter is somewhat shorter than the mean value of 1·303Å for the single C–O bonds tabulated by Nardelli *et al.* and the value of 1·305 (4)Å found in the neutron diffraction study of trichloroacetic acid (Jönsson & Hamilton, 1972); this shortening is consistent with the fact that a hydrogen atom is shared nearly equally between the two carboxyl groups.

The L-leucine molecule may be characterized by two planes: one through the carboxyl group and the other through the side chain. Both carboxyl groups are nearly coplanar with the α carbon atom. Atoms O(1), O(2), C(1), C(2), and O(3), O(4), C(7), C(8) lie in the planes:

$$0{\cdot}4707\,X+0{\cdot}5206\,Y-0{\cdot}7123\,Z=3{\cdot}3798\ \text{Å}$$

and

$$0{\cdot}5785\,X+0{\cdot}5158\,Y+0{\cdot}6319\,Z=1{\cdot}0306\ \text{Å}\,,$$

where the coordinates are in Å parallel to the *a*, *b*, and c^* axes. The deviations of the individual atoms from the planes are: O(1), 0·0018; O(2), 0·0016; C(1), −0·0047, and C(2), 0·013 Å from the first plane and O(3), 0·0006; O(4), 0·007; C(7), −0·0019 and (C8), 0·0005 Å from the second plane. The least-squares plane for the side chain of molecule 1 through atoms C(2) to C(5) is defined by

$$-0{\cdot}1282\,X+0{\cdot}9910\,Y+0{\cdot}0383\,Z=4{\cdot}5133\ \text{Å}\,.$$

Table 5. *Torsion angles in di-*L*-leucine hydrochloride, in leucine hydrobromide* (*Subramanian*, 1967), *and in leucine hydriodide* (*Chaney, Seely, & Steinrauf*, 1971).

The notation is that of Table 4, and the conventions are those of IUPAC-IUB (1970). The principal torsion angles ψ, $\chi^{\alpha\beta}$, and $\chi^{\beta\gamma}$ are illustrated in Fig. 3.

		Molecule 1	Molecule 2	Mean	HBr	HI
ψ:	$O'=C'-C^{\alpha}-N$	−17·7 (6)	−13·1 (7)	−15·4	−15·2	−13·3
	$O''-C'-C^{\alpha}-N$	161·3 (5)	167·3 (5)	164·3	172·8	179·6
$\chi^{\alpha\beta}$:	$N-C^{\alpha}-C^{\beta}-C^{\gamma}$	−173·6 (7)	−171·2 (7)	−172·4	−172·2	−172·4
	$O''-C'-C^{\alpha}-C^{\beta}$	−78·1 (6)	−73·8 (6)	−76·0	−69·4	75·2
	$O'-C'-C^{\alpha}-C^{\beta}$	102·8 (5)	105·8 (6)	104·3	102·7	101·8
	$C'-C^{\alpha}-C^{\beta}-C^{\gamma}$	65·4 (9)	69·7 (8)	67·5	71·9	73·4
$\chi^{\beta\gamma}$:	$C^{\alpha}-C^{\beta}-C^{\gamma}-C^{\delta 1}$	−176·3 (8)	−173·6 (9)	−174·9	−175·5	−178·6
	$C^{\alpha}-C^{\beta}-C^{\gamma}-C^{\delta 2}$	62·6 (9)	59·2 (9)	60·9	56·6	65·0

Table 6. *Hydrogen bond distances and angles in di-*L*-leucine hydrochloride**

C–Y–H···X				$R(Y$–H)	R(H···X)	$R(Y\cdots X)$	∠YHX	∠CYH
C(2^{ii})	N(1^{ii})	H(11^{i})	Cl	0·99 Å	2·29 Å	3·284 (6) Å	177°	109·1 (4)°
C(2)	N(1)	H(12)	O(1^{iv})	1·00	1·81	2·779 (5)	162	100·5 (2)
C(2)	N(1)	H(13)	Cl	1·02	2·39	3·370 (7)	160	102·4 (4)
C(8^{i})	N(2^{i})	H(24^{i})	Cl	0·99	2·41	3·370 (6)	161	123·8 (4)
C(8^{iii})	N(2^{iii})	H(25^{iii})	Cl	1·00	2·21	3·204 (4)	175	110·5 (2)
C(8)	N(2)	H(26)	Cl	1·02	2·28	3·277 (6)	166	102·4 (4)
C(1)	O(2)	H(27)	O(3^{v})	1·06 (9)	1·37 (9)	2·429 (7)	175 (7)	119·7 (5)
C(7^{v})	O(3^{v})	H(27)	O(2)	1·37 (9)	1·06 (9)	2·429 (7)	175 (7)	123·0 (5)

Donor angles around Cl

N(2)–Cl–N(2^{i})	100·6 (1)°	N(2^{iii}) Cl–N(2)	71·4 (1)°
N(2)–Cl–N(1^{ii})	79·7 (2)	N(2^{iii})–Cl–N(1)	98·4 (1)
N(1)–Cl–N(1^{ii})	100·5 (1)	N(2^{iii})–Cl–N(1^{ii})	100·3 (1)
N(1)–Cl–N(2^{i})	77·2 (1)	N(2^{iii})–Cl–N(2^{i})	70·2 (1)

* The coordinates of the hydrogen atoms, except H(27), were not refined but merely placed in geometrically reasonable positions; hence, no errors on quantities involving hydrogen are quoted .A final adjustment of hydrogen positions was not made following the last series of least-squares cycles; this accounts for the nonconstant N–H bond lengths. Symmetry equivalent positions are i $(x,1+y,z)$, ii $(x,y-1,z)$, iii $(-x,\frac{1}{2}+y,-z)$, iv $(1-x,\frac{1}{2}+y,-z)$, v $(x+1,y,z)$.

The deviations from the plane are; C(2), −0·023; C(3), 0·026; C(4), 0·018, and C(5), −0·021 Å. N(1) lies 0·152 Å from the plane and C(1) lies −1·299 Å from the plane. The same arrangement is found for the second molecule. The side chain with carbon atoms C(8) to C(11) has a least-squares plane with equation:

$$-0{\cdot}0475\,X+0{\cdot}9913\,Y-0{\cdot}1226\,Z=0{\cdot}1208\ \text{Å}\,.$$

Deviations for individual atoms from the plane are C(8), 0·039; C(9), −0·045; C(10), −0·031, and C(11), 0·037 Å. N(2) lies 0·212 Å from the plane and C(7) lies 1·385 Å from the plane. These results compare well with the results of Subramanian (1967): the nitrogen atom is 0·186 Å out of the plane through the side chain, while the carboxylic carbon atom is 1·419 Å from the plane.

The mean value for the C–C bond lengths is 1·521 Å for the first molecule and 1·514 Å for the second, in good agreement with the value of 1·52 Å in L-leucine hydrobromide (Subramanian, 1967) and slightly less than the pure aliphatic C–C single-bond length of 1·533(3) Å (Bartell, 1959). This shortening appears as well in other amino acid structures (Parthasarathy, 1966; Wright & Marsh, 1962). The mean values for the C–C–C bond angles are 111·0 and 113·5°, in good agreement with 113·8° in L-leucine hydrobromide and with the value of 112·4° for straight-chain aliphatic hydrocarbons (Bonham & Bartell, 1959).

The network of hydrogen bonds is shown in Fig. 2. The distances and the angles involved are summarized in Table 6. All seven hydrogen atoms in the asymmetric unit which can take part in hydrogen bonds do so. The chloride ion is hydrogen-bonded to five nitrogen atoms at distances ranging from 3·204 Å to $N(2^{iii})$, to 3·370 Å to $N(2^{i})$ and N(1). N(1), $N(1^{ii})$, N(2) and

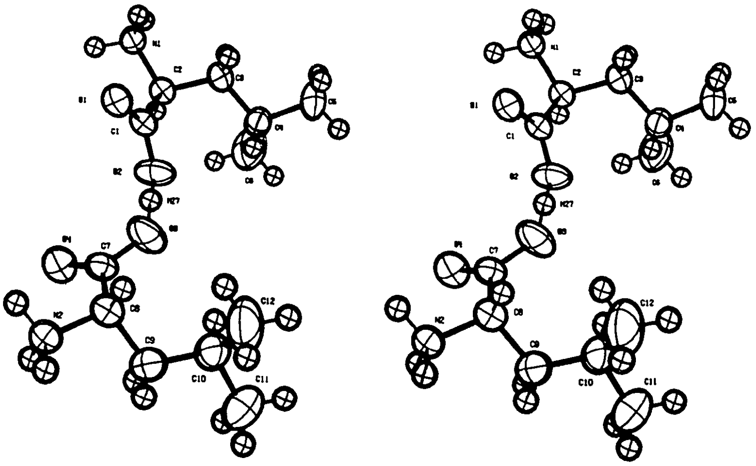

Fig. 1. The two crystallographically independent leucine molecules joined by a short hydrogen bond to form a dimeric cation. The view is approximately along the *b* axis. Thermal ellipsoids for the heavy atoms are drawn at the 50% probability level. Spheres of arbitrary size are shown for hydrogen atoms.

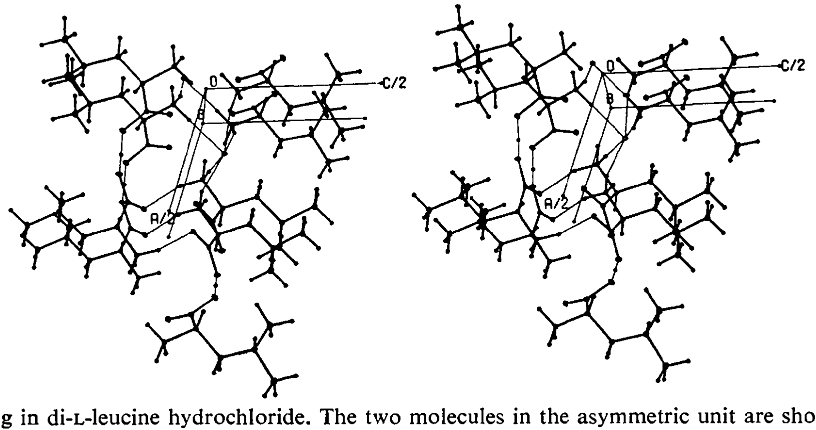

Fig. 2. Hydrogen bonding in di-L-leucine hydrochloride. The two molecules in the asymmetric unit are shown together with all molecules hydrogen-bonded to the basic molecules or to the Cl^{-1} ion, which is seen involved in five hydrogen bonds. Note that all the hydrogen bonds lie near the $z=0$ plane, while nonpolar contacts lie along $z=\frac{1}{2}$.

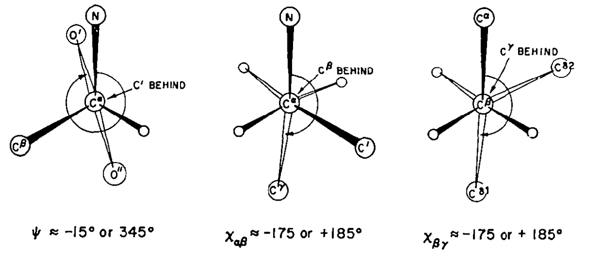

Fig. 3. Definition of the principal torsion angles in peptide residues and amino acids. The values indicated are the approximate mean configurations in di-L-leucine hydrochloride and L-leucine hydrobromide.

N(2$^{\mathrm{i}}$) form a rectangle with edges 5·116(1) and 4·205(5) Å and angles 89·9(1)° at N(1) and 90·1(1) at N(2) with the chlorine atom nearly in the center. The fifth nitrogen atom N(2$^{\mathrm{iii}}$) is at the vertex of the distorted rectangular pyramid. The shortest hydrogen atom contacts from the other side to chlorine are H(3) and H(15) at distances of 2·97 and 3·05 Å, which are too long to be accepted as hydrogen bonds. N(2) is hydrogen-bonded to three chlorine atoms related by a screw diad and by a translation along the *b* axis. Nitrogen atom N(1) is hydrogen-bonded to two chlorine atoms, related by a translation in the direction of the *b* axis and to oxygen atom O(1$^{\mathrm{iv}}$) at a distance of 2·779 (5) Å. The shortest hydrogen bond in the structure is between oxygen atoms O(2) and O(3$^{\mathrm{v}}$): 2·429(7) Å, which connects two L-leucine groups. The only nonhydrogen bonded polar atom is O(4), which is the nearest oxygen atom to the chlorine ion [3·432(4) Å] and is 3·160 (5) Å away from N(2$^{\mathrm{iii}}$). Both distances are longer than usual hydrogen bonds.

The short O...O hydrogen bond is confirmed; the length of this bond is typical of those in dianions which appear in the acid salts of carboxylic acids (Speakman, 1967). In such salts, the hydrogen bond is almost always symmetric – with a single minimum potential function; here the refined O–H bond lengths are 1·06(9) and 1·37(9) Å, not significantly different, so that the results are consistent with a symmetric bond but give no unqualified support for it. A stronger case for a symmetric bond may be made on the basis of the C–O bond lengths, 1·280(6) and 1·288(6) Å. If the bond were very asymmetric, we would expect a marked difference in these bond lengths. Furthermore, neither is quite long enough to be considered a normal C–O single bond (ideal value 1·30).

A neutron diffraction study for the resolution of the symmetry of the hydrogen bond would be worthwhile, although the infrared data of Hadži & Marciszewski (1967) and the heavy atom distances here strongly suggest a symmetric bond.

References

BARTELL, L. S. (1959). *J. Amer. Chem. Soc.* **81**, 3597.
BONHAM, R. A. & BARTELL, L. S. (1959). *J. Amer. Chem. Soc.* **81**, 3491.
CHANDRASEKARAN, R. & SUBRAMANIAN, E. (1969). *Acta Cryst.* **B25**, 2599.
CHANEY, M. O., SEELY, O. & STEINRAUF, L. K. (1971). *Acta Cryst.* **B27**, 544.
CROMER, D. T. (1965). *Acta Cryst.* **18**, 17.
CROMER, D. T. & WABER, J. T. (1965). *Acta Cryst.* **18**, 104.
CRUICKSHANK, D. W. J. (1961). In *Computing Methods and the Phase Problem in X-ray Crystal Analysis.* New York: Pergamon Press.
DAWSON, B. & MATHIESON, A. MCL. (1951). *Acta Cryst.* **4**, 475.
HADŽI, D. & MARCISZEWSKI, H. (1967). *Chem. Commun.* 2.
IUPAC-IUB Commission on Biochemical Nomenclature (1970). *J. Mol. Biol.* **52**, 1.
JÖNSSON, P. G. & HAMILTON, W. C. (1972). *Acta Cryst.* Submitted for publication.
LEUNG, Y. & MARSH, R. E. (1958). *Acta Cryst.* **11**, 17.
MÖLLER, C. K. (1949). *Acta Chem. Scand.* **3**, 1326.
NARDELLI, M., FAVA, G. & GIRALDI, G. (1962). *Acta Cryst.* **15**, 737.
PARTHASARATHY, R. (1966). *Acta Cryst.* **21**, 422.
ROLSKI, S., ZDUNSKA, A. & POPKO, A. (1963). *Acta Polon. Pharm.* **20**, 141.
ROSS, F. (1971). Private communication.
SCHLEMPER, E. O., HAMILTON, W. C. & LA PLACA, S. J. (1971). *J. Chem. Phys.* **54**, 3990.
SPEAKMAN, J. S. (1967). *Chem. Commun.* 32.
SUBRAMANIAN, E. (1967). *Acta Cryst.* **22**, 910.
WRIGHT, D. A. & MARSH, R. E. (1962). *Acta Cryst.* **15**, 54.
ZACHARIASEN, W. H. (1967). *Acta Cryst.* **23**, 558.