Crystal and Molecular Structure of Glycyl-L-leucine

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The crystal structure of the title compound has been determined by direct methods from diffractometer data. Crystals are monoclinic, with $Z = 2$ in a unit cell of dimensions: $a = 6{\cdot}369(5)$, $b = 5{\cdot}565(5)$, $c = 15{\cdot}350(10)$ Å, $\beta = 102{\cdot}77(4)°$, space group $P2_1$. The structure was refined by least-squares to R 0·044 for 823 observed reflections. The four protons available for hydrogen-bond formation are a three-dimensional network which stabilizes the structure. There is significant non-planarity of the peptide linkage, the torsion angle about the peptide bond being $-11{\cdot}4°$. The nitrogen atom of the peptide group is significantly pyramidal. The molecular conformation is discussed.

THE investigation of the structure of glycyl-L-leucine (I) was undertaken as part of a project to determine the structures of simple peptides. The study of simple peptides throws light on the nature of the distortion of the peptide linkage, which was until recently assumed to be planar.

For example, significant non-planarity of the peptide linkage has been observed in crystal structures of glycyl-L-alanine hydrochloride,[1] α-glycylglycine,[2] and

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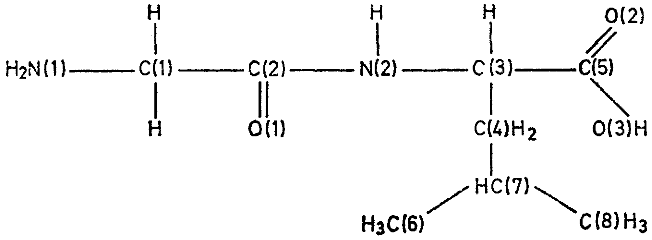
[1] P. S. Naganathan and K. Venkatesan, *Acta Cryst.*, 1972, **B28**, 552.

[2] A. B. Biswas, E. W. Hughes, B. D. Sharma, and J. N. Wilson, *Acta Cryst.*, 1968, **B24**, 40.

L-alanylglycine.[3] A preliminary account of this work has been given elsewhere.[4]



EXPERIMENTAL

Thin needle-shaped crystals elongated along *b*, were obtained by slow evaporation of an aqueous solution.

Crystal Data.—$C_8H_{16}N_2O_3$, $M = 188$. Monoclinic, $a = 6{\cdot}369(5)$, $b = 5{\cdot}565(5)$, $c = 15{\cdot}350(10)$ Å, $\beta = 102{\cdot}77(4)°$, $U = 530{\cdot}6$ Å^3, $D_m = 1{\cdot}18$ (by flotation) g cm^{-3}, $Z = 2$, $D_c = 1{\cdot}176$ g cm^{-3}. Space group $P2_1$ (C_2^2 No. 4) from systematic absences: $0k0$ when k is odd. These data were obtained on the diffractometer with Mo-K_α radiation, $\lambda = 0{\cdot}7107$ Å.

Initially intensity data ($h0$—$4l$) were obtained by use of Cu-K_α radiation and the multiple-film equi-inclination Weissenberg technique, with the crystal mounted about *b*. The intensities were estimated visually by use of a calibrated strip. Lorentz, polarization, and spot-shape[5] corrections were applied.

Although these data were used in the solution of the structure they later proved insufficient for the reliable location of hydrogen atoms. A second data set was therefore collected by use of a four-circle Picker diffractometer and graphite-monochromated Mo-K_α radiation. The θ—2θ scanwidth (2·0—2·3°) was varied according to dispersion, out to 2θ maximum 50°. The scan rate was 2° min^{-1} and background counts were measured each side of the peak for 30 s. The intensities of 3 reference reflections monitored every 25 measurements showed no significant variations during data collection.

Lorentz and polarization factors were applied to the 1069 net intensities and of these 823 were considered observed [$I_{\text{net}} > 1{\cdot}65\sigma(I)$]. The remaining unobserved reflections were set at the threshold value of $1{\cdot}65\sigma(I)$ for the purposes of refinement.

The structure was solved by a repeated iteration procedure[6] of the tangent formula[7] on 295 phases with $E \geqslant 1{\cdot}00$. Three reflections (3,0,9, 1,1,3, and 4,0,−3) were assigned phases of zero to specify the origin and the phase of another (3,3,−11) was permuted through values of $5\pi/4$, $3\pi/2$, and $7\pi/4$ to establish the enantiomorph. Two other reflections (3,0,7 and 1,0,2) were permuted through phases of 0 and π and included in the starting set of a series of separate tangent iteration calculations. The phasing process converged most rapidly for the permuted phase values of $5\pi/4$, π, and 0, and the resulting E map revealed twelve of the thirteen non-hydrogen atom positions. The position of the missing atom, a terminal carbon of the leucyl side-chain, was fixed from stereochemical considerations. Structure factors calculated with these atoms gave R 0·42. In this, and subsequent calculations, atomic scattering factors for carbon, nitrogen, and oxygen were taken from ref. 8, and for hydrogen from ref. 9. Refinement was performed with the visually estimated data but the lowest R obtained was only 0·095. Because of the importance in reliably locating hydrogen atoms, and to obtain more accurate information about the stereochemistry of the amide group, further refinement was carried out with the diffractometer data set. Full-matrix anisotropic least-squares, and all other crystallographic calculations, were performed by use of the '*X*-Ray' system of computer programs.[10]

TABLE 1

Positional and thermal parameters, with standard deviations in parentheses

(*a*) Positional parameters (× 10^4) of non-hydrogen atoms

Atom	x/a	y/b	z/c
C(1)	7388(8)	4801(9)	6229(4)
C(2)	6795(7)	2500(0)	6631(3)
C(3)	4301(6)	606(9)	7404(3)
C(4)	2898(8)	1441(9)	8053(3)
C(5)	2962(6)	−768(8)	6605(3)
C(6)	292(10)	704(6)	9007(4)
C(7)	1819(9)	−529(11)	8487(3)
C(8)	3396(11)	−2194(14)	9083(4)
O(1)	7640(5)	585(6)	6515(2)
O(2)	2128(5)	407(7)	5931(2)
N(1)	9261(5)	4396(7)	5825(2)
N(2)	5310(5)	2724(7)	7115(2)
O(3)	2760(5)	−3002(6)	6708(2)

(*b*) Anisotropic thermal parameters (× 10^4) of non-hydrogen atoms

	U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
O(3)	482	266	579	−63	76	−54
N(2)	396	254	501	26	164	39
C(1)	613	233	789	24	391	72
C(2)	358	247	520	−14	41	2
C(3)	325	290	389	−13	66	63
C(4)	553	347	398	−23	134	−26
C(5)	274	265	459	29	127	−44
C(6)	949	1040	739	−137	538	−13
C(7)	744	631	441	−243	248	−91
C(8)	1251	624	607	102	255	128
O(1)	603	308	822	29	337	93
O(2)	533	454	351	107	29	14
N(1)	371	272	377	−23	63	23

* In the form: $T = \exp[-2^2(h^2a^{*2}U_{11} + k^2b^{*2}U_{22} + l^2c^*U_{33} + 2hka^*h^*U_{12} + 2hla^*c^*U_{13} + 2klh^*c^*U_{23})]$.

(*c*) Positional and isotropic thermal parameters (× 10^3) of the hydrogen atoms

	X	Y	Z	U_{iso}
H(1)[C(1)]	786(6)	608(8)	672(2)	40
H(2)[C(1)]	615(8)	566(12)	579(3)	99
H(3)[N(2)]	453(6)	406(8)	710(3)	12
H(4)[C(3)]	554(5)	−48(7)	770(2)	10
H(5)[C(4)]	395(6)	254(10)	853(3)	59
H(6)[C(4)]	177(5)	255(8)	773(2)	35
H(7)[C(7)]	081(7)	−143(10)	801(3)	66
H(8)[C(6)]	−103(14)	192(22)	860(6)	237
H(9)[C(6)]	110(9)	179(13)	948(4)	128
H(10)[C(6)	−57(8)	−53(11)	913(3)	87
H(11)[C(8)]	243(11)	−367(16)	941(5)	186
H(12)[C(8)]	448(10)	−302(15)	888(4)	135
H(13)[C(8)]	428(9)	−118(13)	956(4)	126
H(14)[N(1)]	888(7)	447(10)	530(3)	64
H(15)[N(1)]	993(6)	279(10)	587(3)	47
H(16)[N(1)]	105·3(6)	532(9)	606(3)	43

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[3] M. H. J. Koch and G. Germain, *Acta Cryst.*, 1970, **B26**, 410.

[4] V. Pattabhi, K. Venkatesan, and S. R. Hall, *Cryst. Struct. Comm.*, 1973, **2**, 223.

[5] D. C. Phillips, *Acta Cryst.*, 1954, **7**, 746.

[6] S. R. Hall, 'Crystallographic Computing,' ed. F. R. Ahmed, Munksgaard, Denmark, 1970, p. 66.

[7] J. Karle and H. Hauptman, *Acta Cryst.*, 1956, **9**, 635.

[8] 'International Tables for *X*-Ray Crystallography,' vol. III, Kynoch Press, Birmingham, 1965, p. 202.

[9] R. F. Stewart, E. R. Davidson, and W. T. Simpson, *J. Chem. Phys.*, 1965, **42**, 3175.

[10] J. M. Stewart, G. J. Kruger, H. L. Ammon, C. Dickinson, and S. R. Hall, *X*-Ray system of Crystallographic Programs for any Computer, Technical Report TR 192 of the Computer Science Centre, Maryland, June 1972.

Unit weights were used throughout the least-squares refinement. The hydrogen atoms were located from a difference-Fourier map and included with isotropic thermal parameters in the refinement. Refinement was terminated when the calculated shifts were $<\sigma$. The final R for 823 observed reflections was 0·044.

Final atomic parameters are listed in Table 1. Figure 1 shows the thermal ellipsoids of the molecule. Observed and calculated structure factors are listed in Supplementary Publication No. SUP 21093 (2 pp.).*

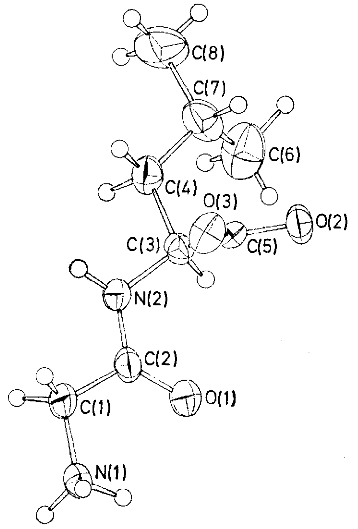

FIGURE 1 Anisotropic thermal ellipsoids

DISCUSSION

Bond lengths and angles corresponding to the final co-ordinates are listed in Table 2 (mean σ in bond lengths is 0·006 Å and in angles 0·4°); on the whole they do not deviate significantly from expected values. The value of 1·225(4) Å for the C(2)–O(1) (C′=O) bond is rather short compared to the weighted mean distance [1·240(4) Å].[11] The deviation is as large as 4σ. The short C(2)–O(1) distance could be due partly to the large thermal vibration of O(1) along the *c* axis. In cyclotetrasarcosyl [12] one of the C′–O distances is as short as 1·209(3) Å.

C(3)–N(2) would be expected to be shorter than C(1)–N(1), because N(2) is sp^2 whereas N(1) is sp^3 hybridized. Thus the weighted mean value for C(sp^3)–N(sp^2) is 1·487 and for C(sp^3)–N(sp^2) is 1·455 Å.[11] N(2)–C(3) and C(1)–N(1) are in good agreement with expected values. The angle at C^{β} [C(3)–C(4)–C(7) 116·5(5)°] is very much larger than the regular tetrahedral value, a feature common in other amino-acids and peptides.[12–15] The widening of this angle appears to be due to intramolecular overcrowding of atoms in this part of the molecule.

TABLE 2

Molecular geometry

(*a*) Bond lengths (Å)

C(2)–O(1)	1·225(4)	H(5)–C(4)	1·07(4)
C(2)–N(2)	1·331(4)	H(6)–C(4)	1·00(4)
C(2)–C(1)	1·505(6)	H(7)–C(7)	1·00(5)
N(1)–C(1)	1·478(6)	H(8)–C(6)	1·15(9)
N(2)–C(3)	1·458(5)	H(9)–C(6)	1·00(6)
C(3)–C(5)	1·534(6)	H(10)–C(6)	0·92(5)
C(3)–C(4)	1·549(6)	H(11)–C(8)	1·20(8)
C(4)–C(7)	1·523(7)	H(12)–C(8)	0·93(7)
O(2)–C(5)	1·240(5)	H(13)–C(8)	0·99(6)
O(3)–C(5)	1·263(5)	H(14)–N(1)	0·79(5)
C(6)–C(7)	1·548(8)	H(15)–N(1)	0·99(4)
C(7)–C(8)	1·516(9)	H(16)–N(1)	0·96(4)
H(1)–C(1)	1·03(4)	H(2)–C(1)	1·04(6)
H(3)–N(2)	0·89(4)	H(4)–C(3)	1·02(3)

(*b*) Bond angles (deg.)

O(1)–C(2)–N(2)	123·5(3)	C(1)–N(1)–H(14)	109·0(5)
O(1)–C(2)–C(1)	121·5(3)	C(1)–N(1)–H(15)	112·9(4)
N(2)–C(2)–C(1)	115·0(3)	C(1)–N(1)–H(16)	116·9(4)
N(1)–C(1)–C(2)	109·9(5)	C(2)–C(1)–H(1)	110·3(5)
C(2)–N(2)–C(3)	120·6(4)	C(2)–C(1)–H(2)	115·9(5)
N(2)–C(3)–C(4)	108·0(4)	C(5)–C(3)–H(4)	107·5(5)
N(2)–C(3)–C(5)	111·4(4)	C(4)–C(3)–H(4)	113·1(5)
C(4)–C(3)–C(5)	111·5(4)	C(3)–C(4)–H(5)	104·4(5)
C(7)–C(4)–C(3)	116·5(5)	C(3)–C(4)–H(6)	108·8(5)
O(2)–C(5)–O(3)	125·9(5)	C(7)–C(4)–H(5)	112·8(5)
O(2)–C(5)–C(3)	117·7(4)	C(7)–C(4)–H(6)	108·6(5)
O(3)–C(5)–C(3)	116·4(4)	C(7)–C(6)–H(8)	116·6(6)
C(4)–C(7)–C(6)	107·6(5)	C(7)–C(6)–H(9)	111·2(6)
C(4)–C(7)–C(8)	113·6(5)	C(7)–C(6)–H(10)	104·2(6)
C(6)–C(7)–C(8)	111·6(5)	C(4)–C(7)–H(7)	108·7(6)
N(1)–C(1)–H(1)	106·2(5)	C(6)–C(7)–H(7)	103·0(6)
N(1)–C(1)–H(2)	111·5(5)	C(8)–C(7)–H(7)	111·7(6)
C(2)–N(2)–H(3)	121·6(4)	C(7)–C(8)–H(11)	109·8(7)
C(3)–N(2)–H(3)	113·7(4)	C(7)–C(8)–H(12)	122·5(8)
N(2)–C(3)–H(4)	105·4(4)	C(7)–C(8)–H(13)	106·8(7)
H(8)–C(6)–H(9)	104(5)	H(11)–C(8)–H(12)	107(4)
H(14)–N(1)–H(16)	113(3)	H(14)–N(1)–H(15)	107(3)
H(15)–N(1)–H(16)	97(2)	H(11)–C(8)–H(13)	110(4)
H(8)–C(6)–H(10)	99(5)	H(1)–C(1)–H(2)	102(2)
H(5)–C(4)–H(6)	105(2)	H(9)–C(6)–H(10)	122(4)
H(12)–C(8)–H(13)	101(4)		

TABLE 3

Equations of least-squares planes and in square brackets deviations (Å) of relevant atoms from these planes. X,Y,Z are orthogonal (Å) co-ordinates defined by the a,b,c^* axes

Plane (1): Peptide group, C(1), C(2), N(2), C(3), O(1)

$$0\cdot5025X + 0\cdot1400Y + 0\cdot8531Z = 9\cdot6854$$

[C(1) −0·0568, C(2) 0·0188, O(1) 0·0117, C(3) −0·0720, N(2) 0·0963, H(3) −0·0666]

Plane (2): Amide group, C(1), C(2), N(2), O(1)

$$0\cdot5510X + 0\cdot1641Y + 0\cdot8182Z = 9\cdot4922$$

[C(1) 0·0003, C(2) −0·0010, O(1) 0·0004, N(2) 0·0003, C(3) −0·2474]

Plane (3): Carboxy-group, C(3), C(5), O(2), O(3)

$$-0\cdot9200X + 0\cdot1538Y + 0\cdot3604Z = 3\cdot8392$$

[C(3) 0·0031, C(5) −0·0109, O(2) 0·0039, O(3) 0·0039, N(2) −0·6531]

The carboxy-group exists in this structure in the ionized form CO_2^-. The two C–O bond lengths are essentially equal, mean 1·251(5) Å. Both oxygen atoms are involved in hydrogen bonding and the proton associated with this group has been accepted by the atom N(1). The least-squares plane through the

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* See Notice to Authors No. 7 in *J.C.S. Perkin II*, 1973, Index issue.

[11] R. E. Marsh and J. Donohue, *Adv. Protein Chem.*, 1967, **22**, 234.

[12] Y. C. Leung and R. E. Marsh, *Acta Cryst.*, 1958, **11**, 17.

[13] D. A. Wright and R. E. Marsh, *Acta Cryst.*, 1962, **15**, 54.

[14] P. S. Naganathan and K. Venkatesan, *Acta Cryst.*, 1971, **B27**, 1079.

[15] T. Ueki, T. Ashida, M. Kakudo, V. Sasada, and V. Katsube, *Acta Cryst.*, 1969, **B25**, 1840.

carboxy-group (Table 3) is planar. The deviation of the peptide nitrogen from this plane is large (0·653 Å).

The peptide group [C(1), C(2), O(1), N(2), C(3), and H(3)] is significantly non-planar. The best plane among its constituent atoms is that through C(1), O(1), C(2), and N(2) (Table 3). From this plane C^{α} atom [C(3)] at the *C*-terminal end deviates by 0·25 Å and the peptide hydrogen by 0·17 Å. Non-planarity of the peptide group has also been observed in several other structures, *e.g.* α-glycylglycine, L-alanylglycine, glycyl-L-alanine hydrochloride, glutathione,[16] and cyclotetrasarcosyl.[17] In most of these structures the best plane among the atoms of the peptide group was obtained by omitting the C^{α} atom at the *C*-terminal end. Winkler and Dunitz [18] have observed that the nitrogen atom of an amide group may be slightly pyramidal rather than planar, and our observations support this. By use of the CNDO/2 method, it has been shown [19] that in *N*-methylacetamide the peptide unit is non-planar with the NH and NC^{α}_2 bonds significantly out of the plane defined by atoms C^{α}_1, C′, O, and N. The non-planarity of the peptide linkage could be partly due to intermolecular influence, in particular of the hydrogen bond involving the hydrogen attached to the peptide nitrogen. The angle H(3)–N(2) · · · O(3) is 10·9°, but when this angle is calculated after fixing the hydrogen H(3) to be in the plane defined by C^{α}_1, C′, O, and N, this angle is increased to 20·1°, showing that the hydrogen bond becomes more non-linear. This would mean a decrease in the hydrogen-bond energy contribution. Thus it is clear that the out-of-plane displacement of H(3) from the peptide group observed in the present structure is dictated to some extent by the formation of good intermolecular hydrogen bonds.

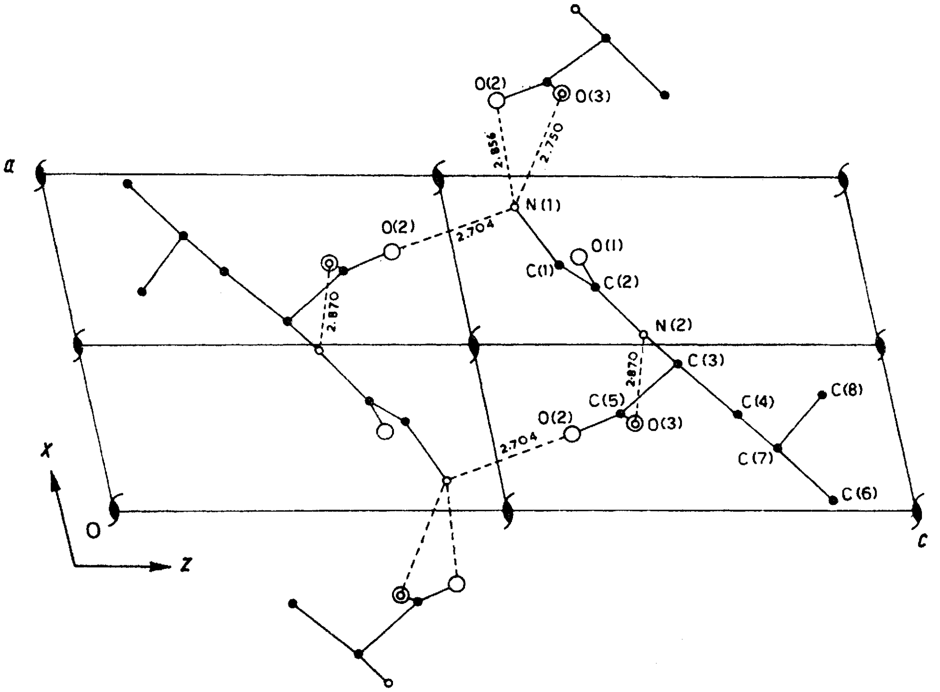

FIGURE 2 Intermolecular packing viewed down the *b* axis

TABLE 4

Hydrogen bond lengths (Å) and angles (deg.)

Hydrogen bond	D · · · A	H · · · A	C–D · · · A	D–H · · · A	H–D · · · A
N(1)–H(14) · · · $O(2^{II})$	2·704	1·93	105·7	167·2	9·1
N(1)–H(15) · · · $O(2^{I})$	2·856	1·94	131·3	152·1	18·5
N(1)–H(16) · · · $O(3^{III})$	2·750	1·80	110·7	169·2	7·1
N(2)–H(3) · · · $O(3^{IV})$	2·870	2·00	113·2	164·2	10·9

Roman numeral superscripts denote the following equivalent positions relative to the reference molecule at x, y, z:

I $1 + x, y, z$
II $-x, \frac{1}{2} + y, -z$
III $1 + x, 1 + y, z$
IV $x, 1 + y, z$
V $1 - x, \frac{1}{2} + y, 1 - z$

Crystal Packing and Hydrogen Bonding.—Figure 2 shows the packing of the molecules down the *b* axis. The orientation of the molecule is almost parallel to the short *a* axis. The molecule exists as zwitterion with NH_3^+ and CO_2^- groups. The peptide nitrogen N(2) is

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[16] F. E. Cole, 1971, personal communication.

[17] P. Groth, *Acta Chem. Scand.*, 1970, **24**, 780.

[18] P. K. Winkler and J. D. Dunitz, *J. Mol. Biol.*, 1971, **59**, 169.

[19] G. N. Ramachandran, A. V. Lakshminarayanan, and A. S. Kolaskar, *Biochim. et Biophys. Acta*, 1973, **303**, 8.

hydrogen bonded to the carboxylate O(3). The hydrogen bond distance N(2) $\cdots$ O(3) is longer than the other three hydrogen-bond distances between N(1) and oxygen atoms (Table 4). This situation is consistent with the observation [11] that in peptide structures the nitrogen of the peptide group forms a longer hydrogen bond than the amino-nitrogen. Three hydrogens attached to N(1), looking along the bond C(1)–N(1) are disposed in eclipsed positions (Figure 3). While atoms O(2) and O(3) of the CO_2^- group are each involved in two hydrogen bonds, the oxygen O(1) of the peptide group is not involved in any hydrogen bonding. Table 5 records all intermolecular contacts <4 Å. The loose packing of the molecules in the crystal is reflected in the low crystal density.

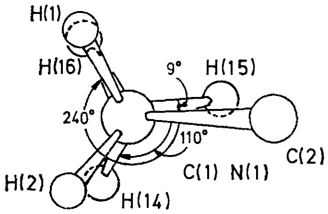

FIGURE 3 Surroundings of nitrogen N(1) viewed along the C(1)–N(1) bond

TABLE 5

Intermolecular contacts <4 Å

$C(2) \cdots O(2^{I})$	3·957	$C(1) \cdots C(5^{IV})$	3·883
$C(2) \cdots C(6^{I})$	3·958	$C(1) \cdots O(3^{IV})$	3·418
$N(1) \cdots O(2^{I})$	2·856	$N(2) \cdots C(5^{IV})$	3·930
$N(1) \cdots C(5^{I})$	3·742	$N(2) \cdots O(3^{IV})$	2·870
$C(1) \cdots O(2^{I})$	3·989	$C(3) \cdots O(3^{IV})$	3·781
$O(1) \cdots C(4^{I})$	3·677	$C(4) \cdots O(3^{IV})$	3·709
$O(1) \cdots O(2^{I})$	3·181	$C(4) \cdots C(8^{IV})$	3·863
$O(1) \cdots C(5^{I})$	3·445	$O(2) \cdots O(3^{IV})$	3·850
$O(1) \cdots O(3^{I})$	3·779	$N(1) \cdots O(2^{III})$	3·797
$O(1) \cdots C(6^{I})$	3·825	$N(1) \cdots C(5^{III})$	3·687
$O(1) \cdots C(7^{I})$	3·615	$N(1) \cdots O(3^{III})$	2·750
$N(2) \cdots C(6^{I})$	3·961	$C(1) \cdots O(3^{III})$	3·554
$C(2) \cdots O(3^{IV})$	3·608	$N(1) \cdots O(2^{V})$	2·704
$N(1) \cdots O(1^{IV})$	3·812	$N(1) \cdots C(5^{V})$	3·603
$C(1) \cdots O(1^{IV})$	3·248	$C(1) \cdots O(2^{V})$	3·414

Roman numeral superscripts are defined in footnote to preceding Table.

Molecular Conformation.—The notation followed in the description of the conformational parameters of this molecule is that of Edsall *et al.*[20] The rotations about the N–C$^\alpha$ and C$^\alpha$–C′ bonds are denoted by torsion angles ϕ and ψ respectively. In the present case there is one angle ψ for the *N*-terminal glycyl residue, one angle ϕ, and two angles ψ_1 and ψ_2 for the *C*-terminal leucyl residue. As in many peptides, the value (92·7°) of ϕ [C(2)–N(2)—C(3)–C(5)] is close to 90° (Figure 4). The observed values for the conformational angles fall clearly within the allowed regions of the (ϕ,ψ) map of Ramachandran [21] for peptide configuration. The nitrogen N(1) is almost in the plane through C(1), C(2), and O(1), the torsion angle N(1)–C(1)—C(2)–O(1) being —8·2°. Rotations about the various single bonds in the side-chain are described by a set of dihedral angles $\chi^1, \chi^2 \ldots \chi^i$ which are close to 60 (position I), 180 (position II), and 300° (position III), corresponding to the three staggered positions of the C$^\gamma$,C$^\delta$ . . . atoms.[22] In the present structure the C$^\gamma$ atom [C(7)] occupies position II with χ^1 184·2°, *i.e. trans* to N(2). The two C$^\delta$ atoms [C(8) and C(6)] occupy positions I (χ^{21} 62·9°) and II (χ^{22} 187·0°). The corresponding angles in other structures containing leucyl side-chains are given in Table 6. In spite of the differences in the mode of packing of the molecules in these crystals, it is sig-

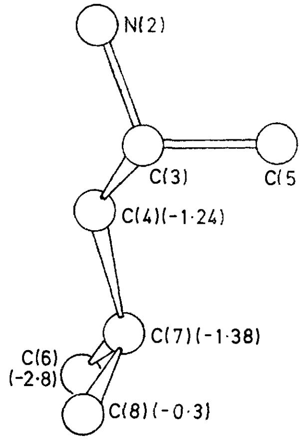

FIGURE 4 Backbone conformation showing the angles: (a) ϕ, (b) ψ for the *N*-terminal end, (c) ψ_1, and ψ_2 for the *C*-terminal leu, and (d) angle ω

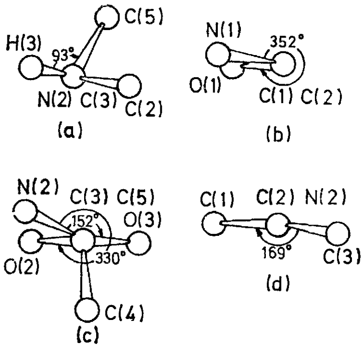

FIGURE 5 Projection of the side-group on the NC$^\alpha$C′ plane

TABLE 6

Dihedral angles (deg.) describing the conformation of the leucyl side-chain in different molecules. (These angles refer to the L-configuration of the chains)

Compound	χ^1	χ^{21}	χ^{22}
Gly-L-Leu	181	188	63
Gly-L-Pro-L-Leu-Gly	301	301	180
L-Leu-L-Pro-Gly	279	292	170
N-Me-DL,Leu-Gly,HBr	181	185	65
L-Leu,HBr	188	182	58
D-Leu-Gly,HBr	294	272	155
DL-Acetyl-leu *N*-methylamide	303	311	186
Di-L-leu,HCl	174	176	63
	171	174	59

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[20] J. T. Edsall, P. J. Flory, J. C. Kendrew, A. M. Liquori, G. Nemethy, G. N. Ramachandran, and H. A. Scheraga, *J. Mol. Biol.*, 1966, **15**, 399.

[21] G. N. Ramachandran, 'Collagen,' ed. N. Ramanathan, Academic Press, London, 1963, p. 25.

[22] A. V. Lakshminarayanan, V. Sasisekharan, and G. N. Ramachandran, 'Conformation of Biopolymers,' vol. 1, ed. G. N. Ramachandran, Academic Press, London, 1967, p. 61.

nificant that only two combinations are observed for χ^1, χ^{21}, and χ^{22}, *i.e.* (1) χ^1 300, χ^{21} 300, and χ^{22} 180°, and (2) χ^1 180, χ^{21} 180, and χ^{22} 60°. Although only seven structures with the leucyl side-chain are considered, it seems reasonable to conclude that the two combinations for the side-chain atoms are energetically more favourable than are others. Figure 5 illustrates the side-chain projected on the N,C$^\alpha$,C′ plane to show the orientation of the side-group with respect to the backbone.

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