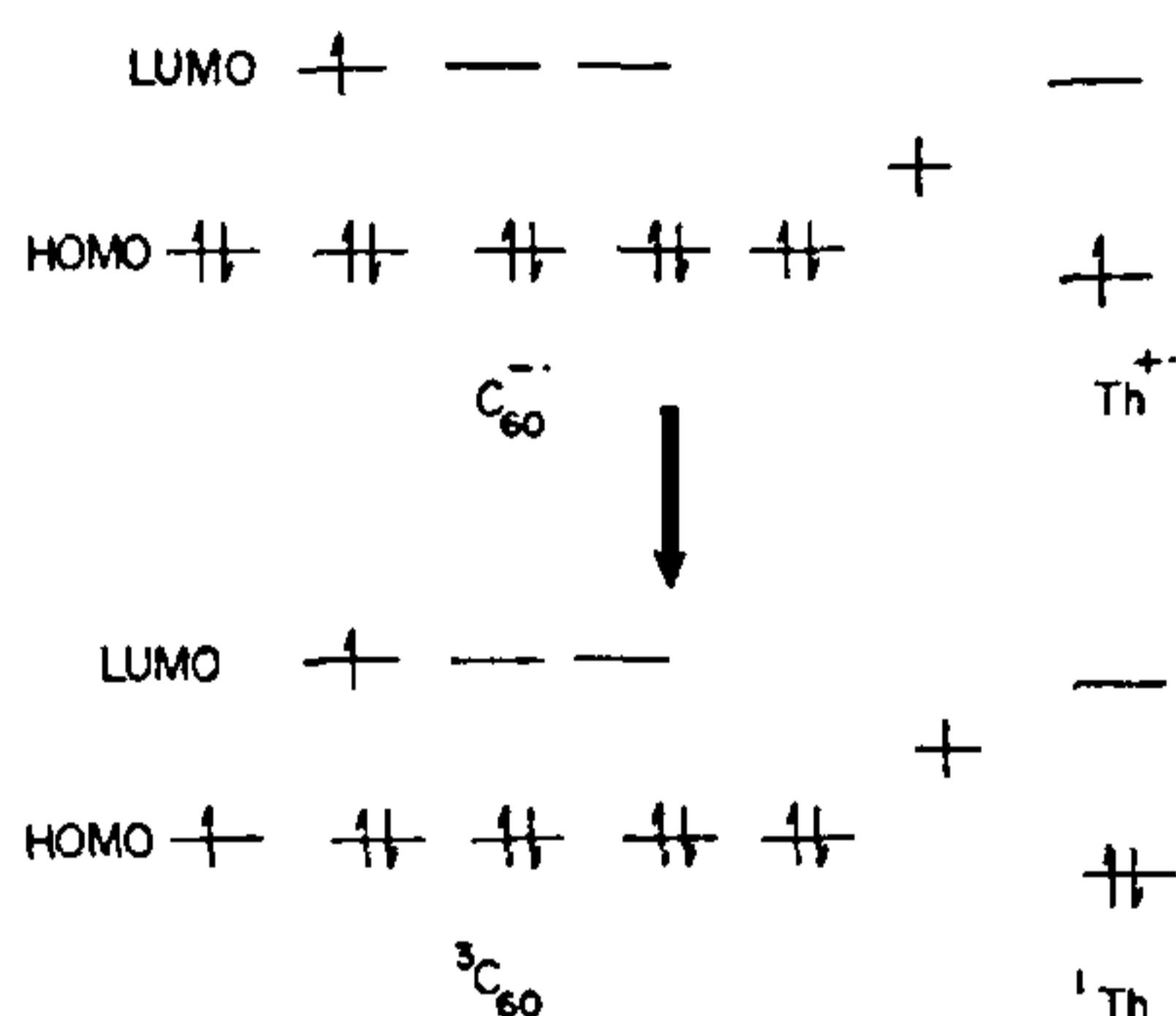


annihilation to produce  $C_{60}$  singlet state which subsequently can give a photon (chemiluminescence). There is a possibility of a heteroexcimer formation in these electron transfer reactions; however, we do not have yet any evidence for this process. Interestingly theoretical calculations have been performed on the distribution of the  $\pi$  electrons of  $C_{60}$  which show five highest occupied molecular orbitals ( $h_u$ ) as degenerate and three lowest vacant unoccupied molecular orbital with symmetry  $t_{1u}$  (ref. 21). The free radical anion has been shown to have an odd electron in one of the three vacant molecular orbitals; this arrangement then suggests the electron transfer reaction between fullerene anion and thianthrene cation as taking place via the following scheme.



This is an interesting case of a triplet formation through the degenerate molecular orbitals\*; in several other electron transfer reactions with aromatic hydrocarbons this degeneracy does not exist<sup>8,10</sup>.

\*After submitting this manuscript, we have carried out experiments on triplet state quenching by carrying out the electrolysis in the presence of  $O_2$ . The emission intensity is quenched by the presence of  $O_2$ . However, it should be noted here that  $O_2$  could also affect the stability of the radical anion of  $C_{60}$ .

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## Crystal structure of a tripeptide, glycyl-D, L-leucyl-L, D-alanine

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The crystal structure of a tripeptide, glycyl-D, L-leucyl-L, D-alanine has been determined by X-ray methods and refined to a final *R*-index of 0.079. There are two crystallographically independent molecules in a monoclinic unit cell with  $a=17.817(2)$ ,  $b=10.276(2)$ ,  $c=18.451(3)\text{\AA}$ ,  $\beta=116.95(3)$ ,  $Z=8$  and space group  $P2_1/n$ . Both the molecules exist as zwitterions and adopt essentially similar conformation, with the backbone folding characteristic of a type II reverse turn. Even the leucyl side chains assume essentially similar conformation in the two independent molecules. The packing of the molecules involves spatial segregation of the leucyl side chains.

STRUCTURAL and conformational studies on oligopeptides are useful in theoretical modelling studies of protein folding from amino-acid sequence data. Moreover, since the conformation of even small peptides appears to be the major determinant of their functional properties under physiological conditions, structural studies on peptides in general should provide valuable information in the analysis of structure-activity relationships in biologically important peptides. As part of a series of structural studies on peptides<sup>1</sup>, this paper describes the

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results of the X-ray crystallographic analysis on a tripeptide, glycyl-D, L-leucyl-L, D-alanine.

The tripeptide, glycyl-leucyl-alanine ( $C_{11}H_{16}N_3O_4$ , molecular weight, 263.3) was obtained from Sigma, USA and crystallized as thin plates from an aqueous solution at room temperature. Accurate unit cell parameters were obtained by least-squares analysis of the  $2\theta$  values for several high angle reflections measured on a diffractometer. The crystals are monoclinic, space group  $P2_1/n$  with  $a=17.817(2)$ ,  $b=10.276(2)$ ,  $c=18.451(3)\text{\AA}$ ,  $\beta=116.95(3)$ ,  $Z=8$  and density (calculated)= $1.144\text{ g cm}^{-3}$ . Three-dimensional intensity data were collected using  $CuK\alpha$  radiation ( $\lambda=1.5418\text{\AA}$ ) on an Enraf-Nonius CAD-4 diffractometer equipped with a graphite-crystal incident-beam monochromator. Three reflections were monitored periodically and they showed no systematic drift during data collection. Due to the small size and poor quality of the crystals, only 1014 reflections with  $I>2\sigma$  (out of a possible 3240 reflections within a shell of  $\sin\theta/\lambda\leq 0.6\text{\AA}^{-1}$ ) were available for structure analysis. The intensities were corrected for Lp factors and for absorption (to account for anisotropy of absorption arising from the use of a plate-like crystal).

The structure was solved by direct methods using the SHELX program<sup>2</sup> implemented on a microVax II computer. The trial structure was refined by full-matrix least-squares procedures using anisotropic temperature factors till convergence was reached at  $R=0.12$ . At this stage, efforts were made to locate hydrogen atoms by difference Fourier methods, but without success. Hence all the hydrogen atom positions (except those of water molecules) were calculated using standard geometry and known stereochemistry. The hydrogen atoms were then included with isotropic temperature factors in the structure factor calculations only, and the refinement of the non-hydrogen atoms continued. Convergence was reached at  $R$ -index of 0.079. In the final cycle of the refinement, the average parameter shifts were less than 1/5th of their estimated standard deviations. During the refinement, the function minimized was  $\sum w(|F_o| - |F_c|)^2$ , with the weights ( $w$ ) calculated using counting statistics.

The final parameters for the non-hydrogen atoms are listed in Table I. A stereo view of the molecule is shown in Figure 1. From the label identification of the starting material supplied by Sigma Chemicals, we expected that the racemic pairs of the molecules in the crystals would be gly-L-leu-L-ala and its enantiomer. However, the crystal structure determination shows the molecules to be gly-D-leu-L-ala and its enantiomer. (Such problems in commercially prepared samples have been encountered by others<sup>3,4</sup>.)

The molecules exist as zwitterions with terminal  $NH_3^+$  and  $COO^-$  groups. The peptide units are *trans* but show significant deviations from planarity. The peptide backbones for both the molecules assume a folded conformation characteristic of a type II reverse turn,

**Table 1.** Positional and equivalent thermal parameters for the non-hydrogen atoms (estimated standard deviations are in parentheses) Parameters are for the enantiomer glycyl-L-leucyl-D-alanine

Atom	Molecule A			Beq( $\text{\AA}^2$ )
	x	y	z	
N1	0.2944(6)	0.310(1)	0.3231(6)	4.2(6)
C1A	0.3348(7)	0.332(2)	0.2721(8)	3.2(7)
C1P	0.4280(9)	0.309(2)	0.321(1)	3.1(9)
O1	0.4571(6)	0.276(1)	0.3923(6)	4.0(6)
N2	0.4747(7)	0.330(1)	0.2824(6)	3.2(6)
C2A	0.5587(8)	0.286(2)	0.3149(8)	3.2(8)
C2P	0.6209(8)	0.378(2)	0.3761(8)	3.3(8)
O2	0.6218(6)	0.498(1)	0.3617(6)	4.0(6)
C2B	0.5794(9)	0.272(2)	0.2432(8)	4.1(8)
C2G	0.666(1)	0.224(2)	0.262(1)	6(1)
CD1	0.678(1)	0.083(3)	0.292(1)	11(2)
CD2	0.688(1)	0.222(3)	0.188(1)	13(2)
N3	0.6776(6)	0.323(1)	0.4447(5)	2.6(5)
C3A	0.7530(9)	0.396(2)	0.5019(8)	4.0(8)
C3P	0.7380(9)	0.489(2)	0.555(1)	4.2(10)
O31	0.6722(7)	0.480(1)	0.5659(6)	6.9(7)
O32	0.7944(7)	0.571(1)	0.5902(6)	5.4(7)
C3B	0.8176(9)	0.296(2)	0.5541(9)	4.6(8)
	Molecule B			
N1*	0.0652(6)	0.212(1)	0.0541(5)	3.4(6)
C1A*	0.0206(7)	0.154(1)	0.0945(7)	4.3(7)
C1P*	0.0626(8)	0.186(1)	0.1861(7)	2.9(7)
O1*	0.1331(5)	0.241(1)	0.2125(4)	4.2(5)
N2*	0.0204(6)	0.156(1)	0.2265(5)	3.1(6)
C2A*	0.0518(7)	0.193(1)	0.3109(7)	3.0(7)
C2P*	0.1251(9)	0.100(2)	0.3644(7)	3.7(8)
O2*	0.1154(6)	-0.018(1)	0.3596(7)	3.9(5)
C2B*	-0.0206(9)	0.180(2)	0.3298(8)	5.3(9)
C2G*	0.002(1)	0.213(3)	0.422(1)	9(2)
CD1*	0.015(2)	0.354(3)	0.438(1)	13(2)
CD2*	-0.069(2)	0.172(4)	0.437(1)	17(2)
N3*	0.1908(6)	0.155(1)	0.4230(5)	2.5(5)
C3A*	0.2570(7)	0.080(1)	0.4867(5)	2.7(6)
C3P*	0.3183(8)	0.016(2)	0.4603(9)	4.8(9)
O31*	0.3303(6)	0.073(1)	0.4065(5)	8.3(7)
O32*	0.3576(5)	-0.074(1)	0.5022(6)	5.0(5)
C3B*	0.3075(8)	0.174(1)	0.5568(7)	3.9(7)
	Water-molecules			
OW1	0.0281(5)	0.473(1)	0.0975(5)	4.0(5)
OW2	0.430(1)	0.030(1)	0.2395(7)	13(1)

with the torsion angles (corresponding to the enantiomer gly-L-leu-D-ala):

Residue	Angle	Molecule A	Molecule B
Gly	$\psi_2$	-178(1)	170(1)
	$\omega_1$	-166(1)	-175(1)
Leu	$\phi_2$	-84(2)	-77(2)
	$\psi_2$	133(1)	137(1)
	$\chi_1$	-179(2)	179(2)
	$\chi_{21}$	-175(2)	-169(2)
	$\chi_{22}$	67(2)	72(2)
	$\omega_2$	167(1)	169(1)
Ala	$\phi_3$	79(2)	78(2)
	$\psi_{31}$	-165(1)	-160(1)
	$\psi_{32}$	19(2)	30(2)

Figure 2 is a packing diagram of the structure,



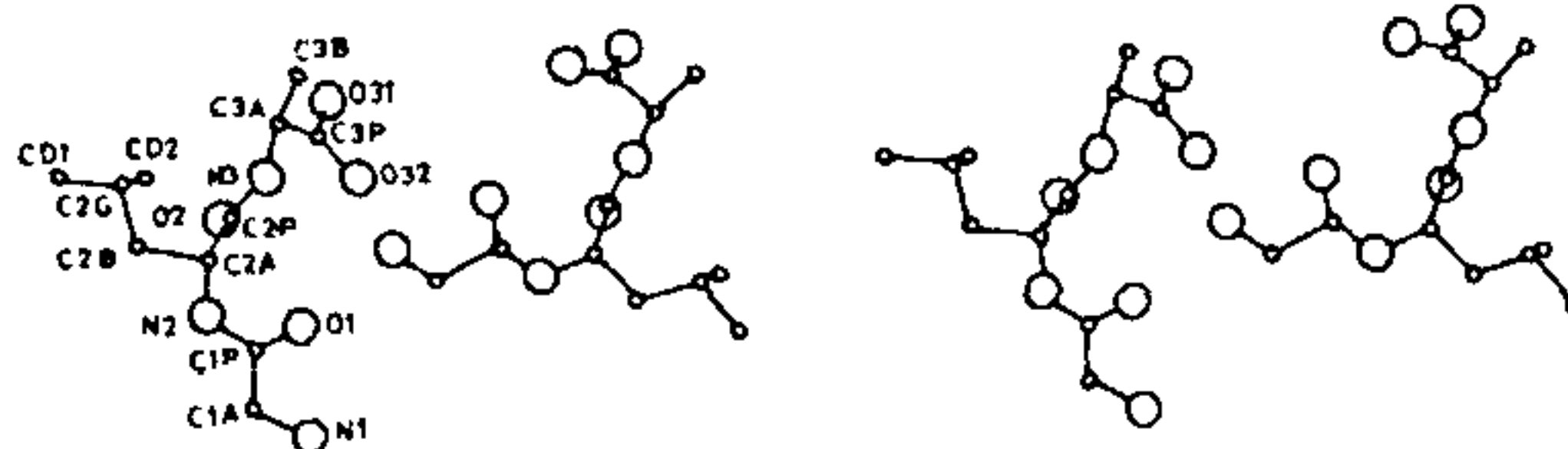


Figure 1. Stereo view of the molecules A and B: Glycyl-D, L-leucyl-L, D-alanine.

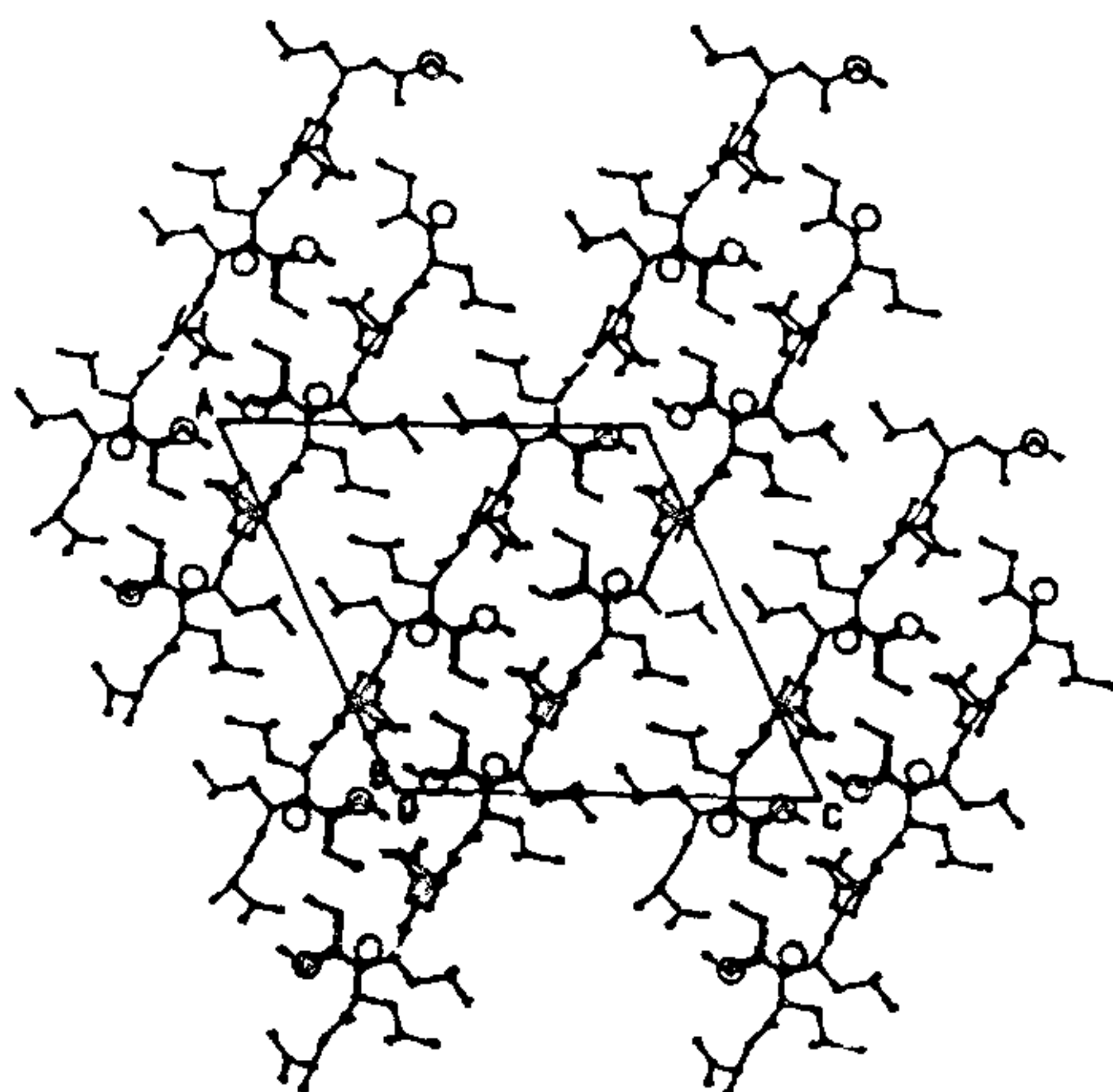


Figure 2. Packing diagram viewed down the b-axis, Open circles represent water molecules.

viewed down the crystallographic b-axis. Table 2 lists the distances of the proposed hydrogen bonds. All available protons are involved in the formation of the hydrogen bonds. The molecules pack with spatial segregation of non-polar and polar groups which form alternating layers constituting essentially the (2, 0, -2)

Table 2. Hydrogen bond distances

Hydrogen bond	Distance	Symmetry locations
N1...O31*	2.80Å	$x, y, z$
N1...O1*	2.76	$x, y, z$
N1...O32	2.98	$-x+1, -y+1, -z+1$
N2...O2*	2.84	$x+\frac{1}{2}, -y+\frac{1}{2}, z+\frac{1}{2}$
N3...O32*	2.91	$-x+1, -y, -z+1$
N1*...O1	2.74	$-x+\frac{1}{2}, y+\frac{1}{2}, -z+\frac{1}{2}$
N1*...O31	2.69	$-x+\frac{1}{2}, y+\frac{1}{2}, -z+\frac{1}{2}$
N1*...O32*	3.02	$x+\frac{1}{2}, -y+\frac{1}{2}, z+\frac{1}{2}$
N2*...O2	2.82	$x+\frac{1}{2}, -y+\frac{1}{2}, z+\frac{1}{2}$
N3*...O32	2.85	$-x+1, -y+1, -z+1$
OW1...OW2	2.81	$x+\frac{1}{2}, -y+\frac{1}{2}, z+\frac{1}{2}$
OW1...O1	2.94	$x+\frac{1}{2}, -y-\frac{1}{2}, z+\frac{1}{2}$
OW1...O31*	2.71	$x+\frac{1}{2}, -y+\frac{1}{2}, z+\frac{1}{2}$
OW2...O32	2.91	$-x+\frac{1}{2}, y+\frac{1}{2}, -z+\frac{1}{2}$

plane. The non-polar layer is made up exclusively of the side chain part of the leucyl residues. This kind of segregation of non-polar side chains appears to be a common feature observed in several amino acids and peptides possessing non-polar residues in the sequence<sup>5</sup>. In such cases, the network of hydrogen bonds is generally confined to the polar layer and does not penetrate the hydrophobic layer and hence does not have extended three-dimensional patterns. Moreover, the hydrophobic layer in the present case is about 7.6Å thick which is about twice the distance between atom C<sup>α</sup> and atom C<sup>σ</sup> (which is *trans* to C<sup>α</sup>). The implication of this observation is that the side chain parts of leucyl residues adopt a *trans* zig-zag orientation in a direction nearly normal to the layer and do not interdigitate in the packing scheme, as can be visualized from Figure 2. Such behaviour involving leu-leu interactions is quite common<sup>6,7</sup> and may be relevant to protein folding problem in view of the observations that i) hydrophobic interactions are considered to be profoundly important during protein folding, and ii) leu-leu interaction is the most frequently observed among pair-wise combinations of the 20 residues<sup>8,9</sup>.

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