

the surface of the paper. It is seen that the maximum vibrations of the spermidine and water molecules occur mostly in a direction perpendicular to the sheet [parallel to (001)] whereas in the phosphate groups the oscillatory motions seem to be predominant.

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Crystal Structure of Glycylglycine Hydrochloride

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Crystals of glycylglycine hydrochloride ($C_4N_2O_3H_9 \cdot Cl \cdot H_2O$) are monoclinic, space group $P2_1/c$ with four molecules in the unit cell. The cell parameters at $22^\circ \pm 3^\circ C$ are: $a = 8.813 \pm 0.003$, $b = 9.755 \pm 0.005$, $c = 9.788 \pm 0.003$ Å, $\beta = 104.10^\circ \pm 0.02^\circ$ ($Cu K\alpha_1 = 1.54051$ Å). Using a G.E. XRD-3 diffractometer, equipped with goniostat, three-dimensional intensity data were collected by the stationary-crystal stationary-counter method, to the limit $2\theta = 140^\circ$. The structure has been refined by Fourier and least-squares method to a final R value of 0.065. The crystal structure is stabilized by a network of hydrogen bonds. An interesting structural feature is the occurrence of apparently bifurcated hydrogen bonds, involving each of the three hydrogen atoms on the terminal nitrogen atom. It is found that in all these bifurcated hydrogen bonds, the hydrogen atom lies close to the plane through the donor and the two acceptor atoms. The planarity of the peptide and the conformation of the molecule are discussed in detail.

Introduction

Accurate crystal structure determinations of amino acids and simple peptides are of fundamental importance in arriving at the configurations of polypeptides and proteins. Such studies have greatly aided the establishment of stereochemical criteria for polypeptide and protein chain conformations (for a review, see Schellman & Schellman, 1964). The present article describes an accurate three-dimensional structure analysis of a dipeptide, glycylglycine hydrochloride. A thorough analysis of the hydrogen bonding and conformation angles is presented.

Glycylglycine hydrochloride was selected for analysis for several reasons. Excellent crystals of glycylglycine can be grown from aqueous solutions by slow evaporation. In this laboratory, many glycine peptides are being studied by paramagnetic resonance techniques (Box, Freund & Lilga, 1961) and detailed X-ray studies on these peptides are in progress.

Experimental

Single crystals of glycylglycine hydrochloride were grown by slow evaporation from aqueous solutions. Excellent crystals in the form of fine needles elongated

along the c axis were observed. The dimensions of the unit cell were obtained using a G.E. XRD-3 diffractometer equipped with goniostat. They were found to be:

$$\begin{aligned} a &= 8.813 \pm 0.003 \text{ \AA}, \\ b &= 9.775 \pm 0.005 \\ c &= 9.788 \pm 0.003 \\ \beta &= 104.10^\circ \pm 0.02^\circ \\ (\text{Cu } K\alpha_1 &= 1.5405 \text{ \AA}). \\ \mu &= 40 \text{ cm}^{-1}. \end{aligned}$$

The observed density of the crystals, measured by flotation, is 1.51 g.cm^{-3} . The density calculated on the basis of four molecules of dipeptide hydrochloride and four molecules of water in one unit cell is 1.513 g.cm^{-3} . The systematic absences observed in the X-ray data are: $0k0$ with k odd; $h0l$, l odd; no absences in hkl ; these absences are consistent with the space group $P2_1/c$. Complete three-dimensional intensity data were obtained employing Cu $K\alpha$ radiation. The stationary-crystal stationary-counter technique (Furnas & Harter, 1955) was used for obtaining the intensities. A total of 1600 non-equivalent reflections were measured, of which 1450 were considered to have non-zero intensity. The crystal used for the data collection had the dimensions $0.12 \times 0.12 \times 0.36 \text{ mm}$ and was almost circular in cross section. The crystal was mounted with $[001]$ along the φ axis of the goniostat. The difference in absorption as a function of angle φ was measured for the 002 and 004 reflections; it was found that there was no observable anisotropy of absorption. The intensities were corrected for Lorentz and polarization factors, but no correction for absorption was applied.

The data were placed approximately on an absolute scale by Wilson's (1942) method.

Derivation and refinement of the structure

The structure determination for glycylglycine hydrochloride was carried out by the heavy atom method. The chlorine positions were determined from a three-dimensional Patterson map, and the structure was readily recovered from the first Cl-phased Fourier synthesis. The structure was refined by a series of least-squares refinements, using individual isotropic temperature factors, carried out on an IBM 7040 computer. This reduced the R value from 0.35 for the trial structure, to 0.14. Another three cycles of refinement using individual anisotropic temperature factors reduced the R index to 0.080. During the refinement, the block-diagonal matrix approximation was used. Reflections too weak to be observed were given zero weight during the refinement and for the R index calculations. A $1/f$ weighting with f for the nitrogen atom was adopted in the final stages of the refinement. The atomic scattering factors and the dispersion corrections for Cl were those reported in *International Tables for X-ray Crystallography* (1962).

An analysis of the weighting scheme was carried out to check its efficacy by plotting $\sum w(\Delta|F|)^2$ as a function of $(\sin \theta/\lambda)$ and $|F_{\text{obs}}|$. These plots indicated that $\sum w(\Delta|F|)^2$ is reasonably independent of $|F_{\text{obs}}|$ and $(\sin \theta/\lambda)$.

An electron density difference map at this stage ($R=0.08$) clearly indicated the positions of all eleven hydrogen atoms, the peak heights of which varied

Table 1. *Final positional and thermal parameters*

Standard deviations as obtained from the block diagonal matrix are indicated in parentheses. The B values for hydrogen atoms were assumed to be equal to 2.0 \AA^2 . The anisotropic temperature factor is given by:

$$TF = \exp[-(\beta_{11}h^2 + \beta_{22}k^2 + \beta_{33}l^2 + \beta_{12}hk + \beta_{13}hl + \beta_{23}kl)].$$

	x	y	z	β_{11}	β_{22}	β_{33}	β_{12}	β_{13}	β_{23}	
Cl	0.4422 (1)	0.3133 (1)	0.4143 (1)	0.0089 (1)	0.0053 (1)	0.0078 (1)	-0.0004 (2)	0.0041 (2)	-0.0005 (2)	
O(1)	0.8489 (4)	0.3684 (3)	0.3604 (3)	0.0082 (4)	0.0075 (3)	0.0079 (3)	0.0032 (6)	0.0014 (5)	-0.0014 (5)	
O(2)	0.7171 (4)	0.0423 (4)	0.3657 (4)	0.0095 (4)	0.0083 (3)	0.0100 (3)	0.0019 (6)	0.0084 (5)	0.0006 (6)	
O(3)	0.9269 (4)	-0.0745 (4)	0.3413 (4)	0.0123 (4)	0.0077 (3)	0.0140 (4)	0.0087 (6)	0.0126 (6)	0.0070 (6)	
O(4)	0.8632 (4)	0.7135 (4)	0.4869 (4)	0.0084 (4)	0.0090 (3)	0.0170 (4)	0.0030 (6)	0.0040 (6)	0.0033 (6)	
N(1)	0.6149 (4)	0.5503 (4)	0.2850 (4)	0.0100 (4)	0.0051 (3)	0.0076 (3)	0.0041 (6)	0.0047 (6)	0.0014 (6)	
N(2)	0.7609 (3)	0.2358 (4)	0.1669 (4)	0.0110 (5)	0.0052 (3)	0.0075 (3)	-0.0021 (7)	0.0009 (7)	0.0003 (6)	
C(1)	0.6418 (6)	0.4554 (5)	0.1763 (5)	0.0113 (6)	0.0062 (4)	0.0069 (4)	0.0039 (8)	0.0025 (8)	-0.0003 (7)	
C(2)	0.7607 (5)	0.3472 (4)	0.2442 (4)	0.0084 (4)	0.0051 (3)	0.0059 (3)	0.0014 (7)	0.0036 (6)	0.0008 (6)	
C(3)	0.8704 (5)	0.1247 (4)	0.2093 (5)	0.0103 (5)	0.0050 (3)	0.0088 (4)	0.0023 (8)	0.0061 (7)	-0.0004 (7)	
C(4)	0.8273 (5)	0.0288 (4)	0.3140 (4)	0.0085 (5)	0.0058 (4)	0.0072 (4)	0.0012 (7)	0.0039 (7)	-0.0014 (7)	
			x	y	z	$B (\text{\AA}^2)$				
			H(1)	0.558 (7)	0.513 (7)	0.349 (7)	2.0			
			H(2)	0.559 (8)	0.620 (7)	0.239 (7)	2.0			
			H(3)	0.706 (8)	0.585 (7)	0.341 (7)	2.0			
			H(4)	0.547 (7)	0.410 (7)	0.132 (6)	2.0			
			H(5)	0.695 (9)	0.512 (7)	0.103 (6)	2.0			
			H(6)	0.689 (7)	0.230 (7)	0.100 (6)	2.0			
			H(7)	0.875 (6)	0.065 (5)	0.121 (5)	2.0			
			H(8)	0.979 (7)	0.164 (6)	0.257 (6)	2.0			
			H(9)	0.891 (8)	-0.148 (8)	0.410 (7)	2.0			
			H(10)	0.947 (8)	0.699 (8)	0.534 (8)	2.0			
			H(11)	0.790 (8)	0.729 (8)	0.521 (7)	2.0			

Table 3. Bond lengths and angles in a peptide

Present work		Pauling (1960)	
C(1)-C(2)	1.522 (0.06) Å	C(α)-C	1.53 Å
C(2)-O(1)	1.229 (0.05)	C=O	1.24
C(2)-N(2)	1.325 (0.05)	C-N	1.32
N(2)-C(3)	1.443 (0.06)	N-C(α)	1.47
∠C(1)-C(2)-O(1)	120.0 (0.4)°	∠C(α)-C=O	121°
C(1)-C(2)-N(2)	114.6 (0.4)	C(α)-C-N	114
O(1)-C(2)-N(2)	125.4 (0.4)	O=C-C-N	125
C(2)-N(2)-C(3)	123.0 (0.4)	C-N-C(α)	123
N(2)-C(3)-C(4)	113.7 (0.4)	N-C(α)-C	110

ages taken from a number of earlier peptide studies (Pauling, 1960) (Table 3). The C-H and N-H distances average to 1.03 Å and 0.89 Å respectively. The average standard deviation for these distances is 0.06 Å.

The most important characteristics common to all these peptides are: (1) the planarity of the peptide groups; (2) the constancy of their linear and angular dimensions.

The atoms O(1), N(2), C(1), C(2) and C(3) define the peptide group and are at distances of 0.000 Å,

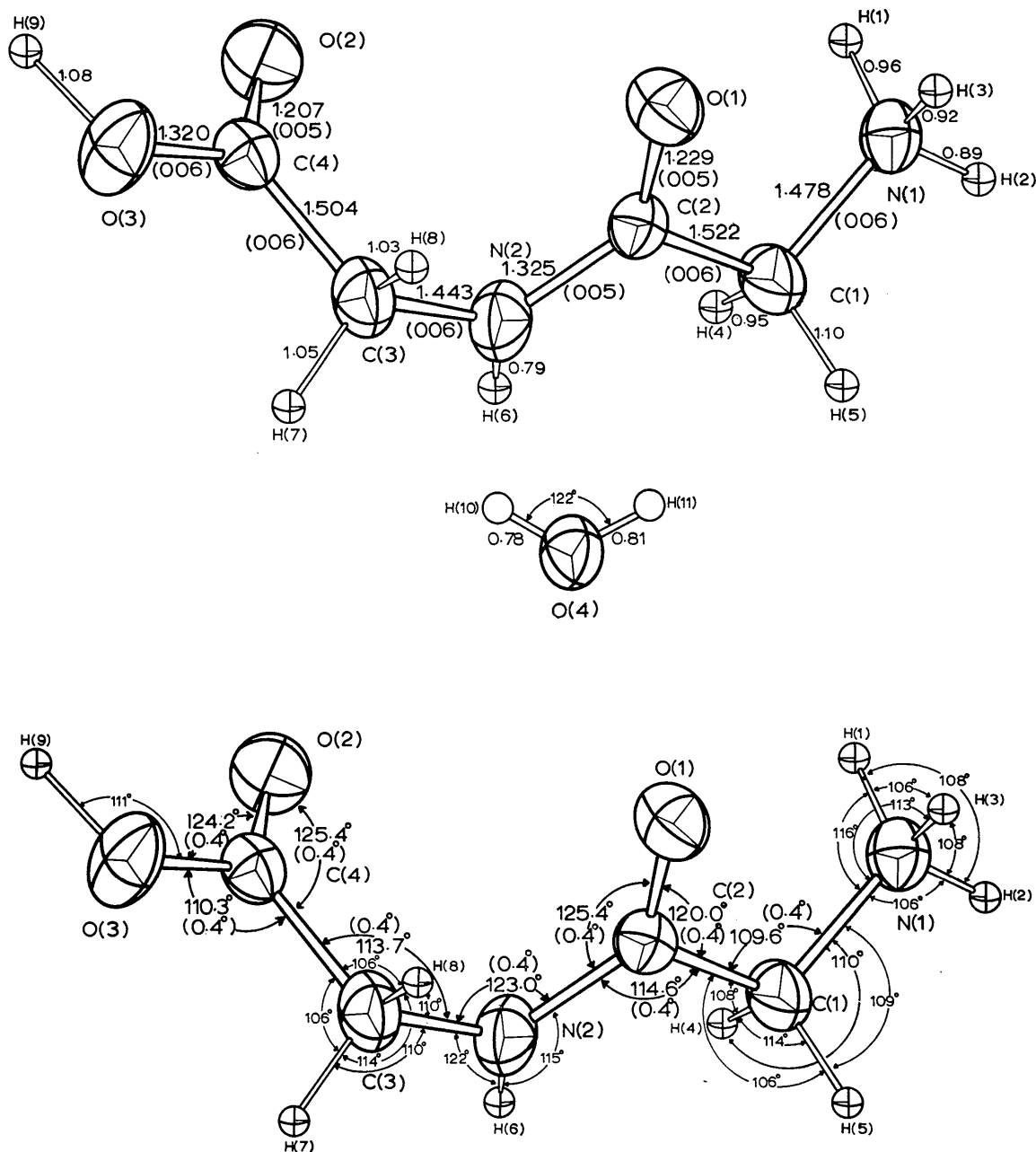


Fig. 1. Bond distances and angles as observed in glycyglycine hydrochloride. The quantities in parentheses denote the e.s.d.'s of the bond distances and angles.

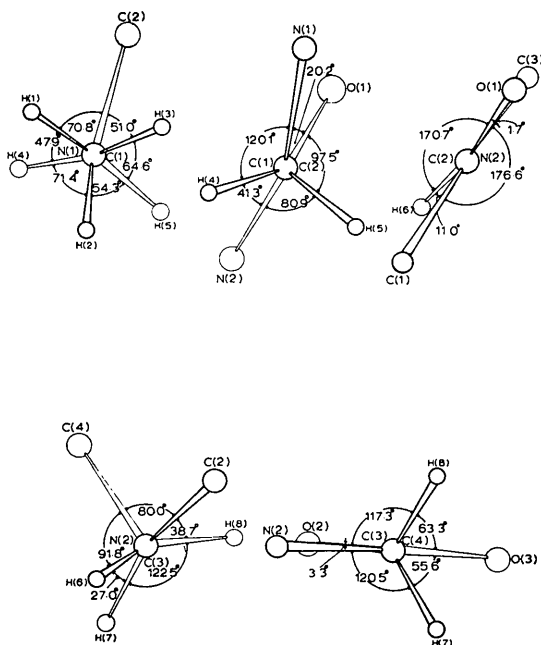


Fig. 2. Projected valency angles.

-0.023 \AA , 0.017 \AA , -0.014 \AA and 0.020 \AA from the least-square plane $0.7928X + 0.433Y - 0.4287Z = 5.341$. The coefficients of X , Y and Z are the direction cosines of the normal to the plane relative to a , b and c^* ; X , Y , Z are cartesian coordinates in Angstrom units. H(6) is at a distance of -0.15 \AA from this plane.

A comparison of the dimensions of the peptide unit obtained in the present work with those used by other workers in this field is shown in Table 3. It is seen that the $N-C(\alpha)-[N(2)-C(3)]$ distance and the $N-C(\alpha)-C[N(2)-C(3)-C(4)]$ angle are significantly different in the present structure from the corresponding quantities being used by other workers.

The atoms C(3), C(4), O(2) and O(3) are at distances -0.001 \AA , 0.003 \AA , -0.001 \AA and -0.001 \AA respectively from the plane $0.4035X + 0.5223Y + 0.7512Z = 5.023$. The peptide plane and the plane containing the carboxyl group are inclined at 77.9° . It has been observed that in all the earlier structure determinations of peptides, the carboxyl group is either nearly parallel or nearly perpendicular to the adjacent peptide plane (Marsh & Glusker, 1961; Freeman, Robinson & Schoone, 1964).

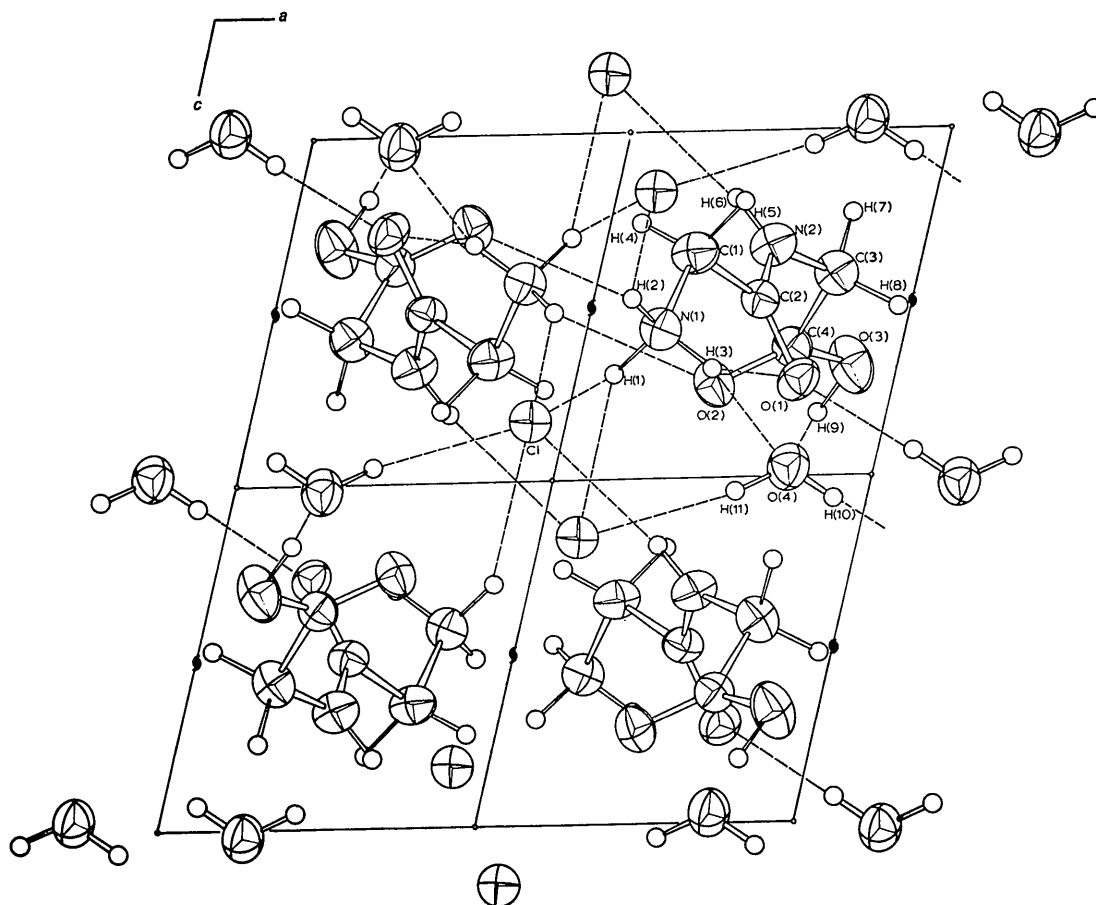


Fig. 3. Thermal ellipsoids, hydrogen bonding scheme and packing diagrams.

It is usually observed that the terminal H_3N-C bond in the zwitterionic form of a peptide is usually longer than other $N-C(\alpha)$ bonds (Hahn, 1957). Typical values of terminal and non-terminal $N-C$ bonds in other peptides are: 1.51 Å, 1.48 Å, in β -glycylglycine (Hughes & Moore, 1949); 1.497 Å, 1.462 Å, in α -glycylglycine (Biswas, Hughes, Sharma & Wilson, quoted in Freeman, Robinson & Schoone, 1964); 1.49 Å, 1.45 Å, in L-leucyl-L-prolyllylglycine (Leung & Marsh, 1958); 1.46 Å and 1.46 Å in glycyl-L-phenylalanyllylglycine (Marsh & Glusker, 1961). The last example occurred in a structure which could not be highly refined. The values of terminal and non-terminal $N-C$ bonds in glycylglycine hydrochloride are 1.473 Å and 1.443 Å, both slightly shorter than usual. A much shorter terminal $N-C$ bond of 1.44 Å has been observed (Freeman, Robinson & Schoone, 1964) in glycylglycinocopper(II) chloride sesquihydrate.

The carbon-oxygen bond lengths in the carboxyl group are 1.320 and 1.207 Å for $C(4)-O(3)$ and $C(4)-O(2)$ respectively. This result suggests that $C(4)-O(2)$ and $C(4)-O(3)$ do not possess purely double and purely single bond character respectively, and the angular dimensions of the carboxylic group are in agreement with such a description. $H(9)$ is at a distance of -0.083 Å from the least-square plane through the carboxyl group.

Conformational angles

The conformation of the molecule and the projected valency angles are shown in Fig. 2. In order to com-

pare the values of the conformational angles with other structures, the standard notation for φ and ψ (Edsall, Flory, Kendrow, Liquori, Nemethy, Ramachandran & Scheraga, 1966) are used. In terms of these angles, for the N-terminal residues there are three values for φ corresponding to the three hydrogen atoms of the N-terminal and one value for ψ . For the C-terminal residue, there is one value for φ and two values for ψ ,

corresponding to the two oxygen atoms of the $C \begin{array}{l} \text{OH} \\ \diagup \\ \text{C} \\ \diagdown \\ \text{O} \end{array}$ group.

Considering the N-terminal residue, the observed values of φ are 70.8° , 190.1° and 309.0° for $H(1)$, $H(2)$ and $H(3)$ respectively. The value of ψ for the N-terminal residue is 20.2° . For the C-terminal residue $\varphi = 280.0^\circ$, $\psi_1 = 183.9^\circ$ for $O(3)$ and $\psi_2 = 3.3^\circ$ for $O(2)$. The allowed ranges of φ and ψ for glycyl residues (Ramakrishnan & Ramachandran, 1965) are consistent with the values of φ and ψ observed in glycylglycine hydrochloride.

Hydrogen bond network

The network of hydrogen bonds is shown in Figs. 3 and 4. The hydrogen-bond distances and the angles involved in these bonds are summarized in Table 4. To facilitate discussion, equivalent atoms are identified as follows:

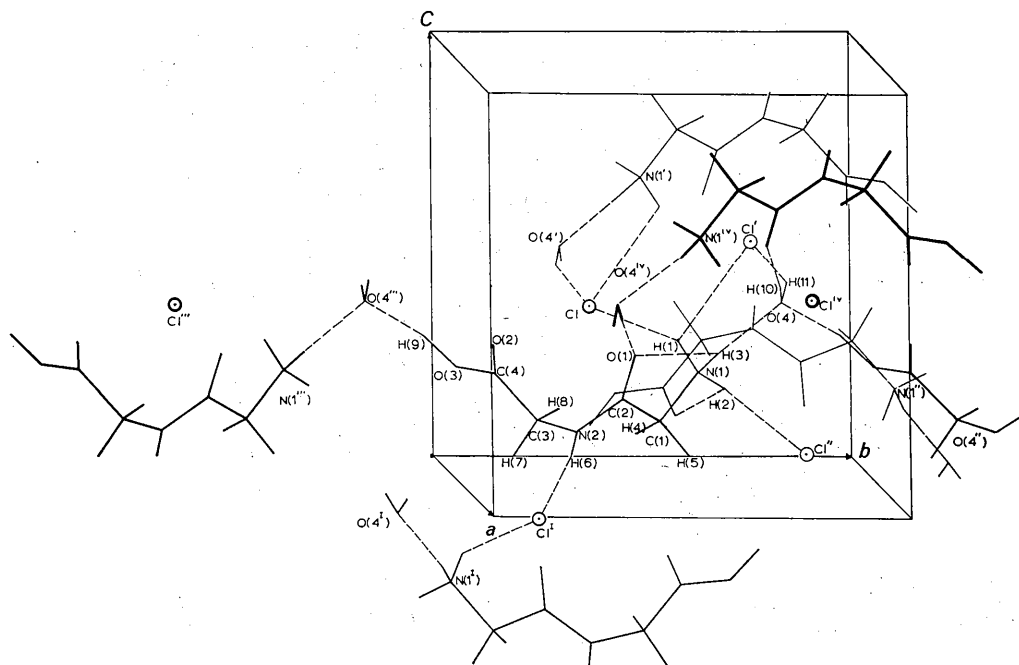


Fig. 4. A clinographic projection of the structure and hydrogen bonding.

Superscript	Coordinate		
	x	y	z
None	x	y	z
'	$1-x$	$1-y$	$1-z$
''	$1-x$	$\frac{1}{2}+y$	$\frac{1}{2}-z$
'''	x	$y-1$	z
I	x	$\frac{1}{2}-y$	$\frac{1}{2}+z-1$
II	x	$\frac{1}{2}-y$	$\frac{1}{2}+z$
III	$1-x$	$-\frac{1}{2}+y$	$\frac{1}{2}-z$
IV	$2-x$	$1-y$	$1-z$
V	$2-x$	$-\frac{1}{2}+y$	$\frac{1}{2}-z$

The terminal nitrogen atom N(1) has six short contacts which are of the right order of distance for hydrogen bond formation. They are: N(1)-Cl, 3.195 Å; N(1)-Cl', 3.378 Å; N(1)-Cl'', 3.189 Å; N(1)-O(2''), 2.940 Å; N(1)-O(4), 3.031 Å; N(1)-O(1), 2.685 Å. The first five contacts are intermolecular, whereas the last

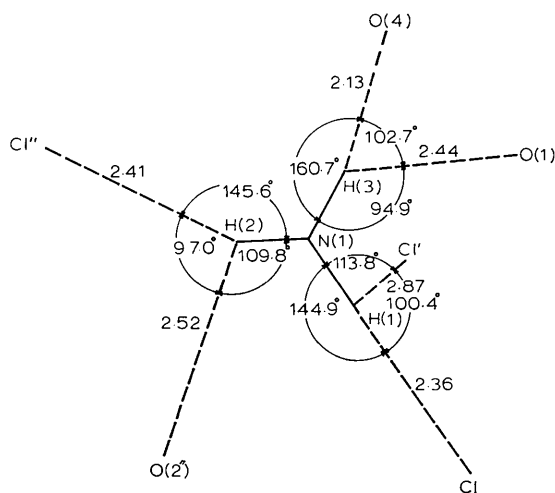


Fig. 5. Environment of the terminal nitrogen atom viewed along the C(1)-N(1) bond.

one is intramolecular. The environment of the terminal nitrogen atom N(1) as viewed along the C(1)-N(1) bond is shown in Fig. 5. It is seen that each of the hydrogen atoms on N(1) mediates two short contacts between N(1) and two other acceptor atoms. In general, such an arrangement, in which the hydrogen atom has a coordination number of three, may be called a 'bifurcated hydrogen bond' if the acceptor atoms interact significantly, and nearly equally, with the hydrogen atom.

It is seen from Table 5 that many interactions listed in this Table do not correspond to this ideal situation. One of the interactions with the acceptor atom is markedly weaker than the other. For example, the H(1)-Cl', H(2)-O(2'') and H(3)-O(1) interactions are clearly weaker than, respectively, the interactions H(1)-Cl, H(2)-Cl'' and H(3)-O(4). For these weaker interactions, the deviations from linearity of the N-H-Y systems, where Y is the acceptor atom, are greatest. For all the interactions listed in Table 5, it is found that the hydrogen atom lies close to the plane through the donor and the two other interacting atoms.

In addition to these, the structure is stabilized by four more hydrogen bonds. The oxygen atom O(3) of the carboxyl group donates the hydrogen atom H(9) to the oxygen atom of the water molecule. This hydrogen bond is quite strong (2.648 Å) and is approximately linear. The peptide nitrogen N(2) donates its hydrogen H(6) to the chlorine Cl^I; this bond is nearly linear. The chloride ion is at hydrogen bonding distances from five atoms: Cl-N(1), 3.195 Å; Cl-N(1'), 3.378 Å, Cl-N(1''), 3.184 Å; Cl-O(4'), 3.085 Å; Cl-N(2^{II}), 3.294 Å. In the first three contacts, the Cl atom shares the hydrogen atom with another acceptor; in the other two cases the chloride ion is the only acceptor.

The oxygen atom of the water molecule O(4''') accepts two hydrogen atoms H(9) and H(3''') from O(3) and N(1''') respectively. In addition, O(4) donates H(11) to Cl^I and H(10) to O(1'). Figs. 3 and 4 illustrate

Table 4. Hydrogen bond distances and angles

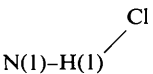

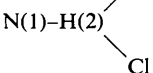
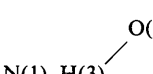
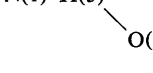
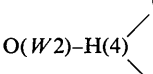
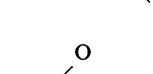
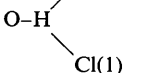
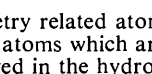
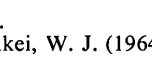
E.s.d. are given in parentheses.

I	N(1)-H(1)-Cl	3.195 (004) Å	N(1)-H(1)-Cl	145 (5)
	H(1)-Cl	2.36 (07)		
II	N(1)-H(2)-Cl''	3.189 (004)	N(1)-H(2)-Cl''	146 (6)
	H(2)-Cl''	2.41 (07)		
III	N(1)-H(3)-O(4)	3.021 (005)	N(1)-H(3)-O(4)	161 (6)
	H(3)-O(4)	2.13 (07)	C(1)-N(1)-O(4)	125.9 (0.3)
IV	O(3)-H(9)-O(4''')	2.648 (005)	O(3)-H(9)-O(4''')	164 (7)
	H(9)-O(4''')	1.60 (07)	C(4)-O(3)-O(4''')	119.2 (0.3)
V	O(4)-H(11)-Cl ^I	3.085 (004)	O(4)-H(11)-Cl ^I	158 (7)
	H(11)-Cl ^I	2.32 (07)	H(9''')-O(4)-H(3)	109 (3)
			H(11''')-O(4''')-H(9)	106 (6)
			H(10''')-O(4''')-H(9)	102 (6)
			H(11)-O(4)-H(3)	86 (6)
			H(10)-O(4)-H(3)	131 (5)
			O(4)-H(10)-O(1 ^{IV})	170 (8)
VI	O(4)-H(10)-O(1 ^{IV})	2.731 (005)		
	H(10)-O(1 ^{IV})	1.95 (07)		
VII	N(2)-H(6)-Cl ^I	3.294 (004)	N(2)-H(6)-Cl ^I	170 (6)
	H(6)-Cl ^I	2.51 (06)	C(2)-N(2)-Cl ^I	115.4 (0.3)
			C(3)-N(2)-Cl ^I	119.7 (0.3)

Table 5. *Hydrogen bond interactions involving two acceptors**

Compounds		H-A(1)	D-A(1)	$\angle D-H-A(1)$	$\angle A(1)-H-A(2)$	Dist. of H from plane	Ref. No.
		H-A(2)	D-A(2)	$\angle D-H-A(2)$			
		(Å)	(Å)	(°)	(°)		
α -glycine		2.44	2.950	119.7	84.10	-0.07	1
Violic acid monohydrate		2.11	2.967	150.10	78.50	0.00†	2
MgSO ₄ · 4H ₂ O		2.59	3.286	131.90	94.30	-0.217	3
Lincomycin hydrochlorine monohydrate		2.21	2.692	110.3	84.0	-0.03	4
		1.97	2.897	165.3			
Triaminotrinitro- benzene		2.52	2.799	119.4	86.4	-0.26	4
		2.41	2.837	142.2			
		1.81	2.504	135.0	97.6	-0.060	5
		2.34	2.995	126.6			
		1.84	2.485	132.4	99.0	0.100	5
		2.40	2.958	124.5			
		1.94	2.511	130.70	93.10	-0.04	5
		2.40	2.988	136.0			
		1.68	2.461	127.3	110.7	0.01	5
		2.24	2.936	121.9			
-		1.81	2.494	134.2	97.1	-0.01	5
		2.38	2.992	128.5			
-		1.74	2.481	131.3	103.4	-0.17	5
		2.36	2.927	117.7			

Table 5 (cont.)

		(Å)	(Å)	(°)	(°)		
Glycylglycine hydrochloride monohydrate		2.36	3.195	144.7	100.6	-0.08	
		2.87	3.378	113.9			
		2.52	2.940	109.6	97.2	0.21	
-		2.41	3.188	145.8			
-		2.44	2.685	95.0	102.6	-0.08	
BaCl ₂ ·2H ₂ O		2.14	3.021	160.8			
		2.61	3.259	125.5	94.4	0.19	6
		2.50	3.243	135.2			
Tetrachloro- hydroquinone		2.03	2.918	151.80	93.60	0.10	7
		2.45	2.959	112.60			

* In this table, symmetry related atoms have not been distinguished. The original papers should be consulted to determine the symmetry equivalent atoms which are involved in the interactions.

† All the atoms involved in the hydrogen bond interactions are located on a crystallographic mirror plane.

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the packing of the molecules. A list of packing distances shorter than 3.6 Å between heavy atoms and shorter than 3 Å between a heavy atom and a hydrogen atom are given in Table 6.

Table 6. Packing distances shorter than 3.6 Å between heavy atoms and shorter than 3 Å between a heavy atom and a hydrogen atom

O(1)-C(3 ^{II})	3.376 Å	O(1)-H(7 ^{II})	2.59 Å
O(1)-N(2 ^{II})	3.431	O(2)-H(1 ^{III})	2.81
O(2)-C(1 ^{III})	3.204	O(2)-H(4 ^{III})	2.67
O(2)-C(1 ^{II})	3.267	O(3)-H(10 ^{IV})	2.88
O(3)-O(1 ^V)	3.164	O(3)-H(8 ^V)	3.92
O(3)-N(2 ^V)	3.334	O(4)-H(8 ^{IV})	2.82
O(3)-C(2 ^V)	3.161	C(2)-H(10 ^{IV})	2.97

Analysis of thermal anisotropy

The magnitudes and direction cosines of the principal axes of thermal motion as derived from parameters of Table 1 are listed in Table 7. The corresponding thermal ellipsoids are shown in Fig. 3. The maximum root mean square amplitudes of thermal motions of various atoms range from 0.280 Å for O(3) to 0.180 Å for C(2);

the minimum amplitudes range from 0.141 Å for N(1) to 0.168 Å for O(2) and O(4). It seems appropriate to remark that the atoms N(2), C(1) and C(2) have very similar thermal anisotropy, while the anisotropy of O(2) is not quite similar to the other atoms in the peptide. Most of the atoms have their direction of minimum amplitudes along the *b* axis. The two oxygens of the carboxyl group have their direction of maximum amplitude perpendicular to the carboxyl group plane. The overall magnitudes of thermal vibration for all the atoms seem to be quite small, and this may be the result of the close packing of the structure held tight by a number of hydrogen bonds.

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Table 7. Description of thermal ellipsoids

$B_i = 8\pi^2 U_i^2$ where U_i is the root-mean square displacement corresponding to the i axis of the ellipsoid. Cia , Cib , Cic^* are the direction cosines of the i axis with respect to the crystal axes a , b , c^* .

	Axis i	U_i	Cia	Cib	Cic^*
Cl	1	0.16	-0.0858	-0.9904	-0.1083
	2	0.18	-0.9934	0.0933	-0.0613
	3	0.19	-0.0758	0.1019	-0.9919
O(1)	1	0.16	0.8037	-0.5082	0.3092
	2	0.18	0.0793	0.6066	0.7910
	3	0.22	-0.5897	-0.6112	0.5279
O(2)	1	0.17	-0.9194	0.2430	0.3092
	2	0.20	-0.1191	-0.9214	0.3698
	3	0.22	0.3748	-0.3031	-0.8761
O(3)	1	0.15	-0.6067	0.7803	-0.1515
	2	0.20	-0.6936	-0.4267	0.5803
	3	0.28	0.3881	0.4571	0.8001
O(4)	1	0.17	0.8573	-0.4104	0.3106
	2	0.20	0.5144	0.7037	-0.4900
	3	0.22	-0.0175	0.5799	0.8144
N(1)	1	0.14	0.4209	-0.8919	0.1652
	2	0.19	0.3947	0.0161	-0.9187
	3	0.20	-0.8167	-0.4579	-0.3587
N(2)	1	0.15	-0.2525	-0.9639	-0.0845
	2	0.18	-0.3841	0.1800	-0.9055
	3	0.22	-0.8881	0.1961	0.4156
C(1)	1	0.17	-0.4430	0.8907	-0.1013
	2	0.18	0.0952	0.1592	0.9826
	3	0.22	-0.8915	-0.4256	0.1553
C(2)	1	0.15	0.2407	-0.8899	0.3873
	2	0.17	0.3938	-0.2752	-0.8770
	3	0.18	-0.8871	-0.3636	-0.2843
C(3)	1	0.15	0.3531	-0.9304	-0.0979
	2	0.19	0.7534	0.3449	-0.5599
	3	0.20	-0.5548	-0.1289	-0.8227
C(4)	1	0.16	0.4398	-0.8283	-0.3469
	2	0.18	-0.7586	-0.1360	-0.6371
	3	0.19	0.4806	0.5434	-0.6883

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