Precision Neutron Diffraction Structure Determination of Protein and Nucleic Acid Components. III.* The Crystal and Molecular Structure of the Amino Acid α-Glycine†

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The crystal structure of α-glycine, $H_3N^+.CH_2.COO^-$, has been refined from three-dimensional neutron diffraction data. A correction for anisotropic extinction effects was included in the least-squares refinement. For the 757 observed reflexions, the final R value based on F^2 is 0·030. The positional parameters of the non-hydrogen atoms are in good agreement with those obtained by Marsh in a previous X-ray investigation. The intramolecular bond distances (not corrected for thermal motion) are: C–O, 1·250 (1) and 1·251 (1) Å; C–C, 1·526 (1) Å; C–N, 1·476 (1) Å; C–H, 1·089 (2) and 1·090 (2) Å. The average N–H bond length is 1·039 Å. The hydrogen bonds postulated from the X-ray studies are confirmed, except that the difference in strength between the two H···O contacts of the bifurcated hydrogen bond is larger than previously assumed.

Introduction

The crystal structures of nearly all the principal amino acids (or their salts) have been determined by X-ray diffraction methods. The results have been reviewed by Marsh & Donohue (1967) and in more detail by Gurskaya (1968). The hydrogen atoms were located for only a few of the structures, but in no case were they located very precisely. The only general way of obtaining accurate hydrogen positions is by neutron diffraction. A series of neutron diffraction studies of the principal amino acids and small peptides is now in progress at Brookhaven National Laboratory.

The present investigation involves a neutron diffraction study of the α form of the simplest amino acid, glycine. This structure was determined by Albrecht & Corey (1939) and was later reinvestigated by Marsh (1958) in a very careful X-ray study. A previous neutron diffraction study of α-glycine was reported briefly (Burns & Levy, 1958), but no final results have been published.

Experimental

The unit-cell dimensions were determined from a Guinier–Hägg powder photograph taken with monochromatic Cu $K\alpha_1$ radiation ($\lambda = 1.54051$ Å). Silicon ($a = 5.43054$ Å) was used as an internal standard. The cell parameters were fitted to the 52 measured θ values by the method of least squares. The results differ only slightly from the cell parameter values determined by Marsh (1958); the largest difference is 0·13% of the parameter value.

Crystal data

α-Glycine (aminoacetic acid), $H_3N^+.CH_2.COO^-$. F.W. 75·07. Monoclinic, $a = 5.1054$ (6),* $b = 11.9688$ (19), $c = 5.4645$ (9) Å, $\beta = 111.697$ (11)°, $V = 310.25$ Å³ at 25°C. $D_m = 1.606-1.607$ g.cm⁻³ (for references, see Marsh, 1958), $Z = 4$, $D_x = 1.607$ g.cm⁻³. Space group $P2_1/n$ (equivalent to $P2_1/c$, No. 14 in *International Tables for X-ray Crystallography*, 1952). General position coordinates: $\pm(x,y,z; \frac{1}{2}+x,\frac{1}{2}-y, \frac{1}{2}+z)$. Calculated neutron absorption coefficient: 2·23 cm⁻¹.

Data collection and reduction

Large single crystals were grown by slow evaporation of an aqueous solution. A crystal with a volume of 10·7 mm³ was mounted with the normal to the (110) planes along the φ axis on a four-circle diffractometer at the Brookhaven National Laboratory high flux beam reactor. The neutron wavelength was 1·035 Å. Intensity data were collected automatically under computer control (Beaucage, Kelley, Ophir, Rankowitz, Spinrad & van Norton, 1966). A region of reciprocal space extending out to $\sin \theta/\lambda = 0.685$ Å⁻¹ was examined using a $\theta-2\theta$ step-scan technique. Two standard reflexions were measured at regular intervals to provide a check on crystal and electronic stability. No significant changes were observed in these standards. 874 independent reflexions were measured of which 43 were space group absences. The space group symmetry $P2_1/n$ was confirmed.

The data were corrected for background and assigned standard deviations based on Poisson counting statistics. Values of F^2 and $\sigma_{count}(F^2)$ were

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* Numbers in parentheses here and throughout this paper are the estimated standard deviations in the least significant digits.

then calculated by applying the Lorentz factor and absorption corrections to the values of I and $\sigma(I)$. The crystal shape was defined by eight rational crystal boundary planes in the calculation of the absorption correction, which was done by a Gaussian integration with a 512 point grid. The resulting transmission factors fell in the range 0·52 to 0·71. The linear absorption coefficient of 2·23 cm^{-1} was calculated using a value of 34 barns for the incoherent scattering cross section for hydrogen.

The standard reflexions and some reflexions measured in duplicate were sorted together and the values of F^2 were averaged. The space-group absent reflexions were excluded from the data set, leaving 831 independent reflexions.

Location of the hydrogen atoms and refinement

A three-dimensional difference map, for which the calculated structure factors were based on the heavy-atom parameters given by Marsh (1958), revealed the positions of the hydrogen atoms. The structure was refined with the Brookhaven full-matrix least-squares program *LINUS*. The function minimized was $\sum w(|F_o^2| - |F_c^2|)^2$. Only the 757 reflexions with F^2 values larger than $2\sigma_{count}(F^2)$ were included. Each reflexion was assigned a weight w, inversely proportional to the estimated variance of the observation:

$$w^{-1} = \sigma^2(F^2) ,$$

where

$$\sigma^2(F^2) = \sigma_{count}^2(F^2) + (kF^2)^2,$$

k was 0·01, and σ_{count}^2 was based on counting statistics alone. The empirical correction term (kF^2) is included

to account for errors other than those from counting statistics. After a few cycles, where atomic positional and anisotropic thermal parameters for each atom were refined together with an overall scale factor, it became obvious that a number of the reflexions were affected by extinction. An isotropic extinction parameter was therefore included as a variable in the least-squares refinement. In the last cycle of refinement where these 92 parameters were varied, no parameter shifted by more than 0·1σ; the agreement factors at this stage were

$$R = \sum||F_o^2| - |F_c^2||/\sum|F_o^2| = 0·034$$

and

$$R_w = [\sum w(|F_o^2| - |F_c^2|)^2/\sum w|F_o^4|]^{1/2} = 0·045 .$$

Coppens & Hamilton (1970) have extended Zachariasen's (1967) theory of extinction to include the anisotropic case. Anisotropic extinction refinements were carried out for both Type I (mosaic-spread dominated) extinction and Type II (particle-size dominated) extinction. The reflexions were weighted exactly as described for the isotropic extinction refinement. After a few cycles, the parameter shifts were all less than 0·1σ; a summary of the agreement achieved is given in the following table:

	$R(F^2)$	$R_w(F^2)$	S	$m-n$
Isotropic extinction	0·034	0·0446	2·03	665
Type I extinction	0·030	0·0422	1·93	660
Type II extinction	0·030	0·0422	1·93	660

In this table, S is the standard deviation of an observation of unit weight, defined by $S = [\sum w(|F_o^2| - |F_c^2|)^2/(m-n)]^{1/2}$, where m is the total number of observations

Table 1. *Final positional and thermal parameters for α-glycine*

The positional parameters are given as fractional coordinates $\times 10^5$. The anisotropic thermal parameters ($\times 10^5$) are defined as
$$\exp[-(\beta_{11}h^2 + \beta_{22}k^2 + \beta_{33}l^2 + 2\beta_{12}hk + 2\beta_{13}hl + 2\beta_{23}kl)].$$
For each atom, the type II extinction result is given on the first line, and a comparison with the type I extinction result is given on the second line. The value given first on the second line is Δ, defined as the type I parameter value minus the type II parameter value, followed by $|\Delta|/\sigma$, where σ is the combined standard deviation.

	x	y	z	β_{11}	β_{22}	β_{33}	β_{12}	β_{13}	β_{23}
O(1)	30494 (17)	9439 (9)	23539 (16)	2050 (32)	521 (7)	1181 (28)	207 (12)	786 (24)	120 (11)
	4 0·2	0 0·0	−1 0·0	−13 0·3	1 0·1	3 0·1	0 0·0	−11 0·3	3 0·2
O(2)	−14722 (17)	14150 (10)	10708 (18)	1791 (32)	639 (8)	1873 (33)	35 (13)	1141 (27)	−117 (13)
	−1 0·0	−2 0·1	1 0·0	−11 0·2	0 0·0	3 0·1	1 0·1	−6 0·2	0 0·0
N	30116 (10)	8984 (5)	−25904 (10)	1945 (22)	448 (5)	1162 (19)	177 (7)	771 (16)	49 (7)
	−2 0·2	1 0·1	2 0·1	−15 0·5	1 0·2	5 0·2	0 0·0	−9 0·4	0 0·0
C(1)	7504 (13)	12486 (6)	6619 (13)	1552 (25)	274 (4)	1193 (24)	−34 (8)	735 (19)	−23 (8)
	1 0·0	0 0·1	−5 0·3	1 0·0	1 0·2	−3 0·1	0 0·0	−7 0·3	1 0·1
C(2)	6474 (13)	14485 (7)	−21308 (13)	1696 (26)	356 (5)	1227 (24)	120 (9)	682 (20)	111 (9)
	−2 0·1	0 0·0	−3 0·2	−8 0·2	2 0·3	5 0·2	1 0·0	−3 0·1	2 0·2
H(1)	28972 (34)	10036 (16)	−45414 (31)	3267 (63)	718 (15)	1768 (58)	185 (24)	1253 (49)	122 (22)
	16 0·3	−1 0·1	−2 0·0	−71 0·8	0 0·0	8 0·1	3 0·1	−36 0·5	3 0·1
H(2)	49450 (33)	11929 (18)	−13184 (34)	2450 (60)	863 (17)	2260 (62)	72 (24)	834 (52)	−72 (24)
	−7 0·2	−3 0·1	−20 0·4	−26 0·3	−1 0·0	5 0·1	0 0·0	1 0·0	12 0·4
H(3)	29935 (42)	561 (17)	−22613 (37)	5059 (90)	510 (13)	2713 (71)	555 (27)	1538 (64)	123 (23)
	−7 0·1	−4 0·2	−10 0·2	−39 0·3	2 0·1	−23 0·2	−4 0·1	−38 0·4	−1 0·0
H(4)	7688 (46)	23444 (16)	−24322 (41)	5633 (98)	444 (13)	3698 (79)	439 (28)	2677 (73)	416 (25)
	−1 0·0	3 0·1	−1 0·0	−30 0·2	2 0·1	−25 0·2	−4 0·1	−34 0·3	−1 0·0
H(5)	−13322 (33)	11439 (20)	−35718 (35)	2428 (59)	1055 (20)	2214 (64)	−65 (27)	538 (51)	−226 (26)
	−2 0·1	1 0·0	14 0·3	−26 0·3	1 0·0	14 0·2	−1 0·0	−1 0·0	10 0·3

and n is the number of parameters varied. Unit value is expected for S at convergence when the observational errors are randomly distributed and correctly estimated and the model is correct.

An R ratio test (Hamilton, 1965) shows that the improvement on going from isotropic to anisotropic extinction refinement is significant. There is no difference in agreement between the Type I and Type II refinements. Extinction is probably affected both by mosaic spread and particle size, and a proper description would lie between the models for Type I and Type II crystals. The results of the Type II refinement were somewhat arbitrarily selected as the final parameters and are presented in Table 1, which also gives a comparison with the corresponding Type I results. Both the positional and thermal parameters agree very closely between the two treatments, the average difference being only 0.12σ for the positional parameters and 0.17σ for the thermal parameters. A similar comparison between the final Type II parameters and the results of the isotropic extinction refinement revealed an average difference of 0.17σ for the positional parameters and 0.35σ for the thermal parameters. The largest differences were 0.6σ and 1.8σ respectively. The standard deviations were equal to within better than 3% between the corresponding Type I and Type II parameters, and they were about 5% lower than the standard deviations from the isotropic extinction refinement. The final extinction parameters for the different models are presented in Table 2, and the observed and calculated structure factors together with the extinction corrections to the intensities are listed in Table 3. The intensity of the most extinction-affected reflexion was reduced to 42% of its extinction-corrected value. The conventional R value based on F was 0.032 for the final Type II parameters. The neutron scattering lengths used were, in units of 10^{-12} cm:

0.577, 0.94, 0.665 and -0.372 for O, N, C, and H respectively.

Computing

The calculations were carried out on the CDC 6600 and 3600 computers at the Brookhaven National Laboratory and at the Uppsala Data Center respectively. The programs used have been briefly described by Jönsson & Liminga (1971).

Discussion

The glycine molecule

The glycine molecule is in the zwitterion form. The intramolecular bond distances and angles are illustrated in Fig. 1 and listed in Table 4. This Table also lists the corresponding results from the X-ray diffraction study by Marsh (1958). The heavy-atom distances and angles agree well between the two studies; no difference is larger than the limit of error in the X-ray results estimated by Marsh as 0.005 Å in the bond distances and $0.3°$ in the bond angles. The X-ray-obtained values for the N–H and C–H bonds are 0.13–0.19 Å shorter than the values obtained in the

Table 2. *Extinction parameters**

Extinction model	Parameter value	Corresponding mosaic spread (sec)	Corresponding particle size (μm)
Isotropic			
g'	0·277 (9)	21	0·29
Type I			
Z'_{11}	0·066 (5)	23	
Z'_{22}	0·080 (11)	21	
Z'_{33}	0·136 (16)	16	
Z'_{12}	−0·012 (6)		
Z'_{13}	−0·024 (6)		
Z'_{23}	−0·021 (9)		
Type II			
W'_{11}	8·9 (9)		0·35
W'_{22}	14·9 (13)		0·27
W'_{33}	7·3 (8)		0·38
W'_{12}	−3·9 (10)		
W'_{13}	−1·8 (6)		
W'_{23}	−1·3 (8)		

* See Coppens & Hamilton (1970) for an explanation of the notation.

(a)

(b)
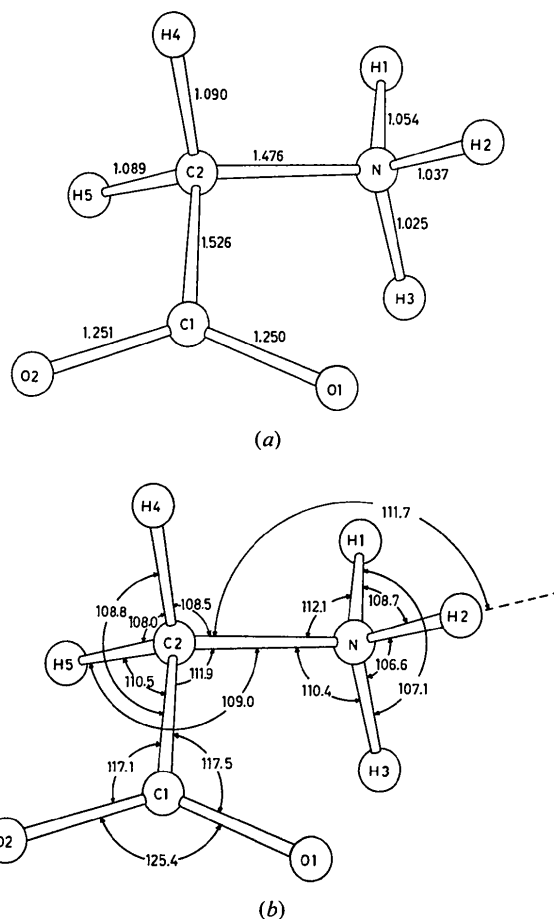
Fig. 1. (a) Bond distances and (b) angles.

present study. Such an apparent contraction in X-ray-obtained N–H and C–H bond lengths has commonly been observed.

The atoms C(1), C(2), O(1), and O(2) are nearly coplanar. The equation for the least-squares plane calculated according to Hamilton (1961) is given in Table 5. The weight for each atom was obtained from the inverse matrix of the final least-squares refinement cycle.

The torsion angles about the C(1)–C(2) and the C(2)–N bonds are illustrated in Figs. 2 and 3.

Hydrogen bonding and intermolecular contacts

The hydrogen bonding system of α-glycine has been described by Albrecht & Corey (1939) and by Marsh (1958). The present neutron study now provides more accurate information on the geometry of the hydrogen bonds and of the involvement of the hydrogen atoms in other intermolecular contacts. The dipolar glycine molecules are linked by two relatively short N–H···O hydrogen bonds to form layers parallel to the *ac* plane; the layers are connected, two by two, by weaker N–H···O bonds, forming antiparallel double layers. Fig. 4 shows a stereoscopic view perpendicular to the double layers. There are no N–H···O bonds between the different double layers. A view parallel to the layers is given in Fig. 5, where the shortest contacts between the double layers are indicated.

Table 3. *Observed and calculated neutron structure factors for α-glycine*

The five columns are, in order, the indices *k* and *l*, $100|F_o|$, $100|F_c|$, (in units of 10^{-12} cm) and $1000 \times E$, where *E* is the extinction correction to the intensity. The entry for *E* is blank when no extinction was indicated. The values of F_o have been divided by $E^{1/2}$. A negative value for F_o indicates a reflexion with $F^2 < 2\sigma_{count}(F^2)$ (not included in the least-squares refinement).

[Table 3: large multi-block table of observed and calculated neutron structure factors, organized by H index groups (H = -7, -6, -5, -4, -3, -2, -1, 0), each block listing columns k, l, $100|F_o|$, $100|F_c|$, and $1000 \times E$.]

The bonding situation around a glycine molecule is shown in Fig. 6, and the pertinent distances and angles are given in Table 6. The two shortest N–H···O bonds are nearly linear. For these bonds, the N–H and H···O distances are inversely correlated. This correlation is similar to the one found in nearly linear N–H···O bonds in hydrazinium compounds (Kvick, Jönsson & Liminga, 1972).

Albrecht & Corey (1939) proposed a hydrogen bond scheme for glycine, in which the hydrogen atom H(3) was shared between two acceptor oxygen atoms. This situation could be depicted schematically as
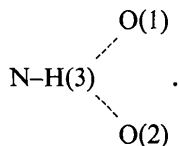
O(1)
/
N–H(3)
\
O(2)

Table 4. Covalent bond lengths and angles

Values in square brackets are corrected for rigid-body motion.

	Neutron	X-ray (Marsh, 1958)*
C(1)–O(1)	1·250 (1) [1·261] Å	1·253 Å
C(1)–O(2)	1·251 (1) [1·261]	1·256
C(2)–N	1·476 (1) [1·490]	1·475
C(1)–C(2)	1·526 (1) [1·539]	1·525
N——H(1)	1·054 (2) [1·062]	0·92
N——H(2)	1·037 (2) [1·042]	0·85
N——H(3)	1·025 (2) [1·033]	0·85
C(2)–H(4)	1·090 (2) [1·099]	0·91
C(2)–H(5)	1·089 (2) [1·095]	0·91
C(2)–C(1)–O(1)	117·46 (6) [117·47]°	117·4°
C(2)–C(1)–O(2)	117·09 (7) [117·08]	117·1
O(1)–C(1)–O(2)	125·45 (8) [125·44]	125·5
C(1)–C(2)–N	111·85 (5) [111·82]	111·8
C(2)–N——H(1)	112·09 (10) [112·07]	110
C(2)–N——H(2)	111·73 (12) [111·64]	110
C(2)–N——H(3)	110·37 (12) [110·65]	111
H(1)–N——H(2)	108·71 (15) [108·80]	106
H(1)–N——H(3)	107·13 (16) [107·07]	106
H(2)–N——H(3)	106·56 (17) [106·34]	113
C(1)–C(2)–H(4)	108·81 (12) [108·75]	106
C(1)–C(2)–H(5)	110·50 (11) [110·61]	108
N——C(2)–H(4)	108·51 (12) [108·79]	109
N——C(2)–H(5)	109·05 (12) [108·95]	110
H(4)–C(2)–H(5)	108·03 (18) [107·81]	112

* Recalculated with our cell dimensions.

Table 5. Least-squares plane

The equation of the plane is of the form: $Ax + By + Cz - D = 0$, where x, y, z are fractional coordinates of the unit cell axes a, b, and c, and D is the distance of the plane from the origin in Å. Atoms defining the plane are: O(1), O(2), C(1) and C(2). Equation:

$$0·97137x + 11·4311y + 0·76926z - 1·55395 = 0$$

Displacements from plane (Å)

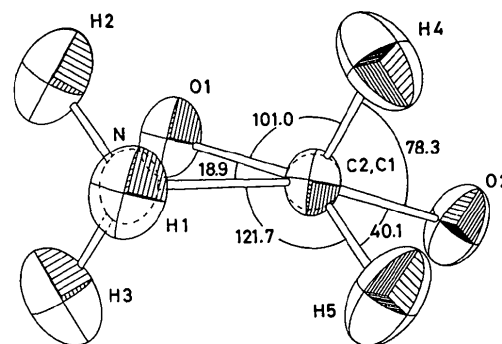|	
O(1)	0·0023 (10)
O(2)	0·0029 (12)
C(1)	−0·0029 (7)
C(2)	0·0008 (8)
N	−0·434

Fig. 2. The glycine molecule viewed down the C(2)–C(1) bond. The standard deviations in the torsion angles are all in the range 0·1–0·2°.
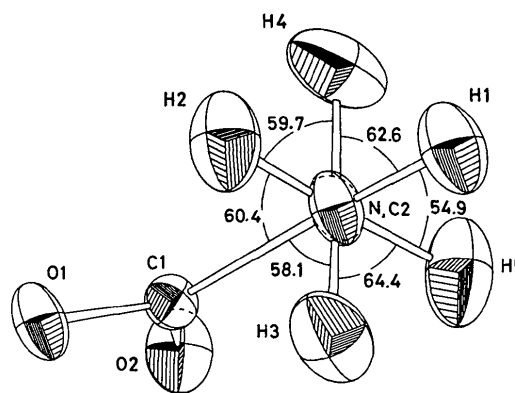

Fig. 3. The glycine molecule viewed down the N–C(2) bond. The standard deviations in the torsion angles are all in the range 0·1–0·2°

Such hydrogen bond situations were later termed 'bifurcated hydrogen bonds'; a survey has recently been given by Donohue (1968).

The conclusions of Albrecht & Corey (1939) are based mainly on the N···O separations, but this is unsatisfactory in discussing the strength of nonlinear hydrogen bonds. The N···O(1) distance of 2·955 Å is appreciably shorter than the N···O(2) distance of 3·075 Å. The H(3)···O(1) distance, however, is 2·365 Å, which is considerably longer than the H(3)···O(2) distance of 2·121 Å. The reason is, clearly, that the N–H(3)···O(1) bond is much more bent than the N–H(3)···O(2) bond. Hamilton (1968) gives an upper limit of 2·4 Å for the H···O distance in a hydrogen bond. The H(3)···O(1) distance of 2·365 Å is so close to this limit, and the angle N–H(3)···O(1) of 115·5° so unfavourable for hydrogen bond formation that this short contact is probably better classified as a short van der Waals contact rather than a very weak hydrogen bond.

In addition to the short H···O contacts associated with the N–H···O bonds, the atom H(4), attached to the α-carbon atom C(2), has two close oxygen neighbors

Table 6. *Hydrogen bonds* N–H···O *and short* H···O *van der Waals contacts*

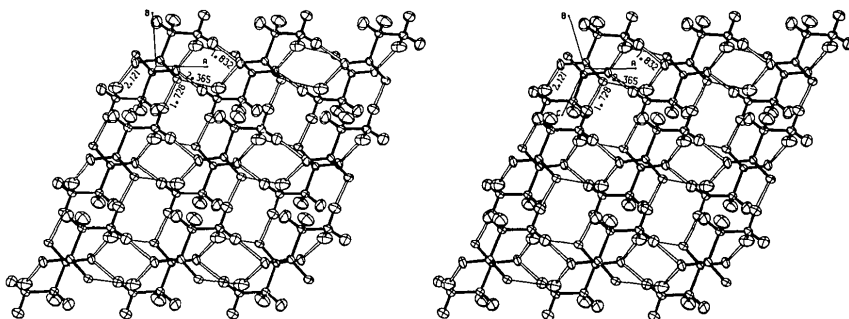| X	H	O	X···O	X–H	H···O	∠X–H···O	∠H···O–C(1)
N	H(1)	O(1)	2·770 (1) Å	1·054 (2) Å	1·728 (2) Å	169·3 (2)°	110·1 (1)°
N	H(2)	O(2)	2·855 (1)	1·037 (2)	1·832 (2)	168·5 (2)	125·6 (1)
N	H(3)	O(2)	3·075 (1)	1·025 (2)	2·121 (2)	154·0 (2)	112·4 (1)
N	H(3)	O(1)	2·955 (1)	1·025 (2)	2·365 (2)	115·5 (2)	135·0 (1)
C(2)	H(4)	O(2)	3·277 (1)	1·090 (2)	2·390 (2)	137·4 (2)	148·1 (1)
C(2)	H(4)	O(1)	3·362 (1)	1·090 (2)	2·453 (2)	140·0 (2)	98·7 (1)

Fig. 4. Stereoscopic illustration showing a hydrogen-bonded double layer of glycine. Covalent bonds are filled, H···O distances shorter than 2·2 Å are open, and other H···O distances shorter than 2·5 Å are drawn as single lines. Thermal ellipsoids are scaled to include 50% probability.
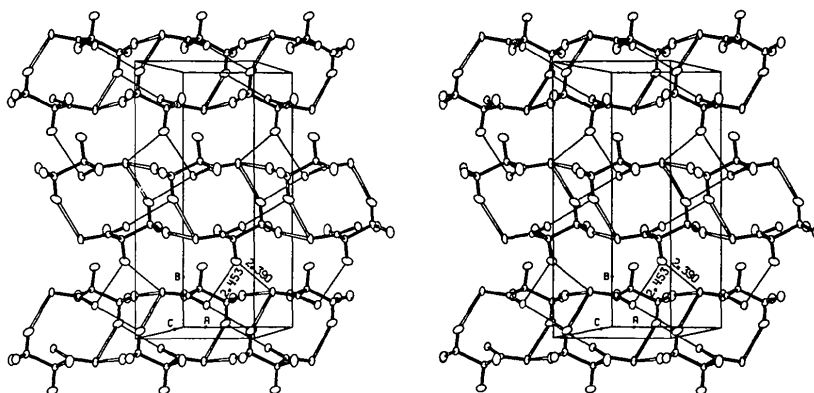
Fig. 5. Stereoview parallel to the hydrogen-bonded double layers of glycine with 20% probability ellipsoids.

Fig. 6. Stereoscopic illustration of the hydrogen bonding situation around a glycine molecule. All contacts where the H···O distances are less than 2·5 Å are included.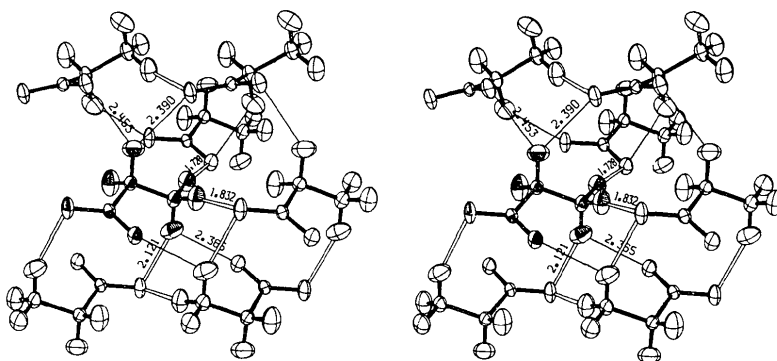 Thermal ellipsoids are scaled to include 50% probability. The atoms of the asymmetric unit are drawn with shaded ellipsoids; the numbering of these atoms can be inferred from Fig. 1, where the orientation of the molecule is approximately the same.

at 2·390 and 2·453 Å. Spectroscopic evidence for C–H···O hydrogen bonding in polyglycine II has been given by Krimm, Kuroiwa & Rebane (1967). The two C–H···O interactions in the present case must be very weak, since atom H(4), which is involved in both of these short H···O contacts, has a C–H distance equal, within the standard deviations, to the C(2)–H(5) distance; the latter should represent an undisturbed C–H bond. We would therefore hesitate to classify either of these interactions as a C–H···O hydrogen bond.

In addition to the short intermolecular contacts summarized in Table 6, only three contacts are shorter than the sum of the van der Waals radii (Pauling, 1960). These are C(1)···C(1)=3·104 Å, C(1)···H(1)= 2·456 Å, and H(2)···H(3)=2·376 Å.

Thermal motion

The root-mean-square (r.m.s.) vibrational amplitudes along the principal axes are given in Table 7. The directions of these axes can be seen in Figs. 4 and 6. The amplitudes of the hydrogen atoms are clearly larger than those for the nonhydrogen atoms. The anisotropic β_{ij} values were converted to thermal vibration tensor elements U_{ij}, referred to an orthogonal Cartesian axis system with axes parallel to a, b, and c^*. The tensor elements U_{ij} of the nonhydrogen atoms were fitted by a least-squares procedure to a general rigid-body motion model (Schomaker & Trueblood, 1968), in which the 20 independent rigid-body motion parameters are described in terms of translations, librations, and screw motions. The r.m.s. deviation of the experimental U_{ij} from those calculated from the values of T, L, and S is 0·0003 Å², which indicates that the amount of non-rigid-body motion present is small. The mean value of $\sigma(U_{ij})$ for O, N, and C from the structural refinement is 0·0003 Å². The r.m.s. amplitudes of

Table 7. *R.m.s. amplitudes of vibration*

The units are 10^{-3} Å.

	Axis 1	Axis 2	Axis 3
O(1)	115 (2)	146 (1)	200 (1)
O(2)	113 (2)	163 (1)	217 (1)
N	113 (1)	143 (1)	186 (1)
C(1)	109 (1)	135 (1)	143 (1)
C(2)	118 (1)	134 (1)	167 (1)
H(1)	139 (3)	189 (2)	232 (2)
H(2)	167 (2)	172 (2)	251 (3)
H(3)	168 (2)	184 (2)	258 (2)
H(4)	159 (3)	191 (2)	270 (2)
H(5)	158 (2)	184 (2)	279 (3)

translation along the principal axes are 0·13, 0·12, and 0·11 Å. The librations have r.m.s. amplitudes of 6·9, 4·8, and 2·5°, with the smallest libration about an axis approximately perpendicular to the molecular plane. The effective translations for the screw tensor are all less than 0·015 Å. Corrections to bond lengths and angles were derived from the rigid-body librations; the corrected values are included in Table 4.

References

ALBRECHT, G. & COREY, R. B. (1939). *J. Amer. Chem. Soc.* **61**, 1087.
BEAUCAGE, D. R., KELLEY, M. A., OPHIR, D., RANKOWITZ, S., SPINRAD, R. J. & VAN NORTON, R. (1966). *Nucl. Instrum. Methods*, **40**, 26.
BURNS, J. H. & LEVY, H. A. (1958). *Abstracts, American Crystallographic Association*, p. 38. Marquette Univ., Milwaukee, Wisconsin.
COPPENS, P. & HAMILTON, W. C. (1970). *Acta Cryst.* A**26**, 71.
DONOHUE, J. (1968). *Structural Chemistry and Molecular Biology*. Edited by A. RICH & N. DAVIDSON, p. 443. San Francisco and London: W. H. Freeman.
GURSKAYA, G. V. (1968). *The Molecular Structure of Amino Acids*. New York: Consultants Bureau.
HAMILTON, W. C. (1961). *Acta Cryst.* **14**, 185.
HAMILTON, W. C. (1965). *Acta Cryst.* **18**, 502.
HAMILTON, W. C. (1968). *Structural Chemistry and Molecular Biology*. Edited by A. RICH & N. DAVIDSON, p. 466. San Francisco and London: W. H. Freeman.
International Tables for X-ray Crystallography (1952). Vol. I, p. 99. Birmingham: Kynoch Press.
JÖNSSON, P.-G. & LIMINGA, R. (1971). *Acta Chem. Scand.* **25**, 1729.
KRIMM, S., KUROIWA, K. & REBANE, T. (1967). *Conformation of Biopolymers*. Edited by G. N. RAMACHANDRAN. Vol. 2, p. 439. New York: Academic Press.
KVICK, Å., JÖNSSON, P.-G. & LIMINGA, R. (1972). *Acta Chem. Scand.* **26**. In the press
MARSH, R. E. (1958). *Acta Cryst.* **11**, 654.
MARSH, R. E. & DONOHUE, J. (1967). *Advanc. Protein Chem.* **22**, 235.
PAULING, L. (1960). *The Nature of the Chemical Bond*. Ithaca: Cornell Univ. Press.
SCHOMAKER, V. & TRUEBLOOD, K. N. (1968). *Acta Cryst.* B**24**, 63.
ZACHARIASEN, W. H. (1967). *Acta Cryst.* **23**, 558.