The Crystal Structure of γ-Glycine

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Glycine has three polymorphs, among them the γ-form crystallizes in the hexagonal space group $P3_1$ or $P3_2$ with unit-cell dimensions $a = 7.037$, $c = 5.483$ Å. Its crystal structure has been determined by two-dimensional Fourier and three-dimensional least-squares methods. The dimensions of the molecule are close to those found in the other forms. The structure consists of hydrogen bonded molecular chains which are held together by lateral hydrogen bonds forming a three-dimensional network.

Introduction

Three polymorphic forms of glycine have so far been reported as follows.

(1) An ordinary form α. The crystal structure (Albrecht & Corey, 1939) was redetermined by Marsh (1958) very precisely, in which the hydrogen bonded double layers of molecules are packed by van der Waals forces.

(2) An unstable form β. First described by Fischer (1905). Recent structure analysis (Iitaka, 1959) showed that single molecular layers, whose internal arrangement is the same as in the α form, are held together by hydrogen bonds throughout the crystal.

(3) The third form γ. It is strongly piezoelectric and crystallizes with trigonal hemihedral symmetry (Iitaka, 1954), and crystal structure has been reported briefly (Iitaka, 1958).

We shall describe the results of a more extensive analysis of this third form, special attention being paid to the hydrogen bond system and structural relationship among these three forms.

Experimental

Single crystals of γ-glycine were grown by slow cooling of aqueous solutions of glycine made acidic with acetic acid or basic with ammoniumhydroxide. They were often obtained in a massive aggregate, but well formed crystals were trigonal pyramidal (hemihedral). Fig. 1 represents an actual crystal, about 6 mm. long,
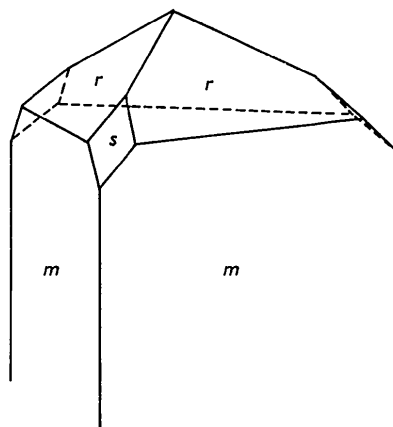
Now temporarily at the Mineralogical Institute, University of Bern, Sahlistrasse 6, Bern, Switzerland.

Fig. 1. γ-Glycine crystal, $m\{10\bar{1}0\}$, $r\{10\bar{1}1\}$, $s\{01\bar{1}1\}$.

which was measured on the goniometer. The prism zone is sometimes poorly developed.

The crystal shows a marked piezoelectric property along the c-axis. A comparison of piezoelectric response observed on the three forms of glycine is shown in Fig. 2, which was measured by pressing a small fragment of crystals under the vibrating electrode (Iitaka, 1953). Since the crystals of α-glycine have a centre of symmetry, they did not show any response.

γ-Glycine crystallizes in hexagonal with space group $P3_1$ or $P3_2$ and shows weak cleavage parallel to the c-axis. In this paper we take the space group as $P3_2$ later. The cell dimensions obtained using a Geiger counter diffractometer (powder) were

$$a = 7.037, \quad c = 5.483 \text{ Å}$$

Table 1. *Comparison of the cell dimensions and space groups of α-, β- and γ-glycine*

Form	Cell size (Å)			β	Volume (Å³)	Space group	No. of molecules per cell	Molecular volume (Å³)
	a	b	c					
α*	5.102_0	11.970_9	5.457_5	$111° 42'_3$	309.6_9	$P2_1/n$	4	77.4_2
β†	5.077_4	6.267_6	5.379_9	$113° 12'$	157.3_6	$P2_1$	2	78.6_8
γ	7.037		5.483		235.1_4	$P3_1$ or $P3_2$	3	78.3_8

* Marsh, 1958. † Iitaka, 1960.

(a)

(b)

(c)

Fig. 2. Comparison of the piezoelectric response for crystals of glycine displayed on the oscilloscope.

(a) γ-form (with reduced gain ½), (b) β-form, (c) α-form.

(the wave length of Cu $K\alpha_1$ radiation taken as 1·5405 Å).

In Table 1, a comparison of the cell dimensions and the space groups of α-, β- and γ-glycine is given.

Complete three-dimensional intensity data for Cu $K\alpha$ radiation were obtained from equi-inclination integrating Weissenberg photographs taken about the c- (up to the 4th layer) and a-axis (up to the 6th layer) using multiple-film technique. The X-ray specimens for the c-axis were about 0·1 mm. × 0·2 mm. in cross section and 2 mm. in length, and for the a-axis were about 0·1 mm. × 0·5 mm. × 0·7 mm. Intensities were measured by visual estimation with the aid of a photometer. They were corrected for Lorentz and polarisation factors but no absorption correction was applied. The corrected intensities were put on a single scale by correlating the various layers.

The atomic scattering factors of McWeeny (1951) were used in the early stages of refinement but for the

three-dimensional refinement the atomic scattering factors given by Berghuis et al. (1955) were used for carbon, nitrogen and oxygen atoms.

Determination of the trial structure

A marked piezoelectric property along the c-axis suggested the dipolar molecules are arranged along the c-axis. This view was further confirmed by the fact that the length of the c-axis in γ-glycine is nearly equal to the c-axis of α-glycine, the latter corresponds to the head-to-tail packing period of the glycine molecules.
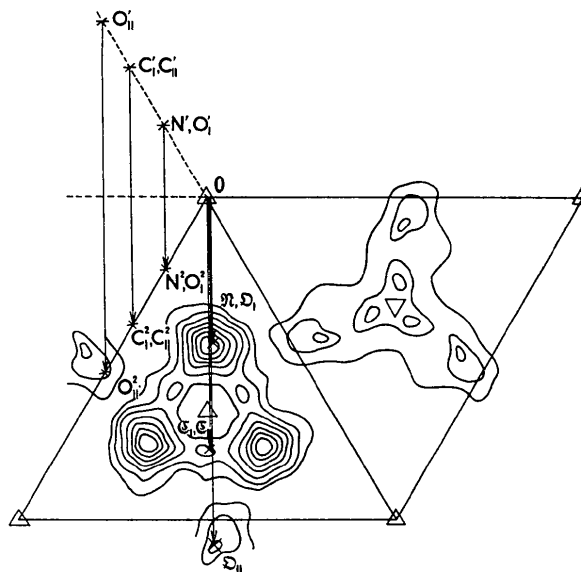
Fig. 3. Harker section at $w = \frac{1}{3}$.

To obtain the exact values of x and y parameters a Harker section was computed. Since the space group of the γ-form is $P3_1$ (or $P3_2$), it was anticipated that the disposition of the molecules might be found by calculating a Harker section at $w=\frac{1}{3}$ (Harker, 1936; Buerger, 1946). Fig. 3 shows the Harker section calculated from the intensity data up to $l=3$. The vectors O–$\mathfrak{N}$, $\mathfrak{D}_I$; O–$\mathfrak{C}_I$, $\mathfrak{C}_{II}$ and O–$\mathfrak{D}_{II}$ in the vector space may be interpreted as indicating the symmetry-operated intermolecular vectors N′, O'_I–N^2, O^2_I; C'_I, C'_{II}–C^2_I, C^2_{II} and O'_{II}–O^2_{II} in the crystal space, thus the approximate x and y coordinates can be determined without ambiguities. It may be clearly seen that the projected figures of the molecule are buried in the map magnified by a factor of $\sqrt{3}$ and rotated 30° around the c-axis. The z parameters were obtained by adopting the known molecular dimensions. The correctness of the trial structure was supported by a Patterson projection along the a-axis.

At this stage, we assumed that the molecules are completely planar. The approximate x, y and z coordinates obtained on this model gave the R factors 29% and 25% for $(hk\cdot0)$ and $(0k\cdot l)$ structure factors

(a)

(b)
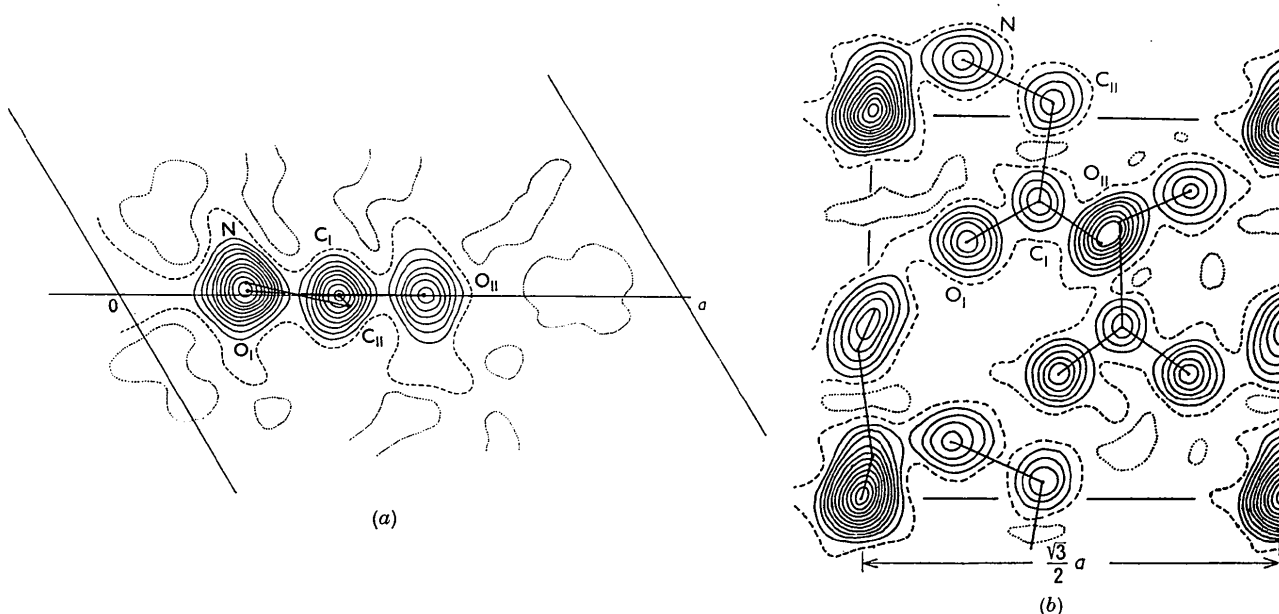
Fig. 4. Fourier projections along (a) c-axis, (b) a-axis. Contours at intervals of 2 e.Å⁻²
Broken lines indicate 2 e.Å⁻², and dotted lines 0 e.Å⁻²

respectively. Successive Fourier syntheses of the electron-density projections along the c- and a-axis showed that the N–C bond should be somewhat twisted around the C–C bond. Recalculation of the structure factors based on this non-planar molecule improved the R factors to 24% and 21% for $(hk\cdot0)$ and $(0k\cdot l)$ planes.

Refinement of parameters

Two-dimensional refinements

The atomic positional parameters were at first refined by means of electron-density projections and then difference Fourier projections for both along the c- and a-axis. Several repeated cycles including structure factor calculations showed a fair measure of agreement with the observed amplitudes, with the R factor 13·9% $(hk\cdot0)$ and 15·4% $(0k\cdot l)$, for which individual isotropic temperature factors were taken into account.

At this stage, it became apparent that some of the strong low order reflexions were seriously affected by extinction. An attempt was made to reduce extinction by using small crystals for the measurement of these strong intensities. For the four strongest reflexions in $(hk\cdot0)$ and five in $(0k\cdot l)$ reflexions, namely $(11\cdot0)$, $(21\cdot0)$, $(02\cdot0)$, $(12\cdot0)$ and $(01\cdot1)$, $(03\cdot2)$, $(01\cdot\bar{2})$, $(02\cdot\bar{2})$, $(00\cdot3)$, the intensities from a specimen having 0·05 mm. × 0·05 mm. cross section showed a good agreement with the calculated values. The R factors were reduced to 11·8% and 14·2% for $(hk\cdot0)$ and $(0k\cdot l)$ planes respectively, when the new F_o values were used for these planes.

Although the $(0k\cdot l)$ projection was adequate to refine the parameters—all x, y and z could have been

obtained from this projection only, provided atoms be well resolved—a subsequent difference synthesis showed further refinement of the parameters to be very difficult, mainly because of the serious overlapping of the atoms and the non-centrosymmetric nature of the structure. The refinement of atomic parameters along this line was now given up. The final F_o syntheses for both projections are shown in Fig. 4(a), (b). The three-dimensional structure factors were then calculated which gave the R factor 14·9% for all planes within a limit of sphere $\sin\theta = 0\cdot85$. The interatomic distances and bond angles were calculated. Although some of them seemed to be unsatisfactory, these values have been reported in a short note in this journal (Iitaka, 1958). At this stage further refinement was delayed until a new electronic computer could be set up in our department.

Three-dimensional refinements

In late 1958, the parametron digital computer PC-1 (Takahashi *et al.*, 1959; Gotō, 1959) had become available for us and we programmed several calculations which arose during the determination and refinement of crystal structures (Iitaka & Sakurai, 1960). The three-dimensional least-squares calculation accommodated to the space group $P3_2$ was then programmed together with the calculation of structure factors.

For non-centrosymmetric space groups the minimization function may be taken as

$$E = \sum_{hkl} w(|F_o| - |F_c|)^2,$$

which leads to the following normal equations, neg-

lecting cross terms involving interaction of any of the parameters of different atoms.

$$\sum_{hkl} w \left\{ \left(\frac{\partial |F_c|}{\partial x_j} \right)^2 \Delta x_j + \left(\frac{\partial |F_c|}{\partial x_j} \right) \left(\frac{\partial |F_c|}{\partial y_j} \right) \Delta y_j \right\}$$
$$= \sum_{hkl} w(|F_o| - |F_c|) \frac{\partial |F_c|}{\partial x_j} ,$$

$$\sum_{hkl} w \left\{ \left(\frac{\partial |F_c|}{\partial y_j} \right) \left(\frac{\partial |F_c|}{\partial x_j} \right) \Delta x_j + \left(\frac{\partial |F_c|}{\partial y_j} \right)^2 \Delta y_j \right\}$$
$$= \sum_{hkl} w(|F_o| - |F_c|) \frac{\partial |F_c|}{\partial y_j} ,$$

$$\sum_{hkl} w \left(\frac{\partial |F_c|}{\partial z_j} \right)^2 \Delta z_j = \sum_{hkl} w(|F_o| - |F_c|) \frac{\partial |F_c|}{\partial z_j} ,$$

$$\sum_{hkl} w \left(\frac{\partial |F_c|}{\partial B_j} \right)^2 \Delta B_j = \sum_{hkl} w(|F_o| - |F_c|) \frac{\partial |F_c|}{\partial B_j} ,$$

where F_c is expressed as (*International Tables*, No. 145, $P3_2$)

$$F_c = A + iB = \sum_j f_j \exp \left\{ - B_j (\sin \theta / \lambda)^2 \right\}$$
$$\times \{ \exp 2\pi i (hx_j + ky_j + lz_j)$$
$$+ \exp 2\pi i (kx_j - (h+k)y_j + lz_j - l/3)$$
$$+ \exp 2\pi i (-(h+k)x_j + hy_j + lz_j + l/3) \} ,$$

and the derivatives have the following form

$$\frac{\partial |F_c|}{\partial x_j} = \frac{\partial A}{\partial x_j} \cos \alpha + \frac{\partial B}{\partial x_j} \sin \alpha ,$$
$$\text{etc. ,}$$

where α denotes the phase angle of the structure factor.

With the capacity of the present computer* it was almost impossible to introduce anisotropic temperature factors, and only an individual isotropic temperature factor for each atom was considered. The weighting function, w, used in the calculation was chosen as unity except for those planes which have observed F smaller than a certain value. For the planes $F_o \leq 2\cdot0$, w was taken as $1/16$. The atomic scattering factors were computed in the machine by the two-term Gaussian expansion. The coefficients of the formula were taken from the paper by Vand *et al.* (1957), who evaluated the coefficients from the tabulated values of atomic scattering factors by Berghuis *et al.* (1955) with the exception of hydrogen for which McWeeny's (1951) values were used.

Further refinement of the parameters for the nitrogen, carbon and oxygen atoms was then carried out by the successive use of three-dimensional least-squares methods in which all terms up to $\sin \theta = 0\cdot960$ were included. Starting with the parameters which

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*This computer has 512 short storage locations each capable of retaining 18 binary digits, of which about 130 locations were used for read-in or print-out routines.

had given the R factor $15\cdot2\%$ including contributions from the hydrogen atoms, no appreciable change in coordinate could be observed at the sixth cycle of refinement and this factor reduced to $10\cdot8\%$. At each stage the scale factor was adjusted so as to make each totals of F_o and F_c being equal. Hydrogen atoms were placed at the assumed positions which gave a C–H length of $1\cdot05$ Å and a N–H length of $1\cdot00$ Å with a tetrahedral arrangement with respect to the N–C bond.

Table 2. *Final atomic parameters and temperature factors.*

Final atomic parameters and their standard deviations

	x	y	z	B (Å^{-2})
N	0·2414	0·0263	0·5035	2·03
O_I	0·2325	0·0083	0·0139	2·49
O_{II}	0·5425	0·0011	−0·0150	3·08
C_I	0·3929	0·0012	0·1033	2·00
C_{II}	0·4010	−0·0222	0·3794	1·98
H_I (NH$_3^+$)*	0·248	0·013	0·686	1·50
H_{II} (NH$_3^+$)	0·274	0·183	0·458	1·50
H_{III} (NH$_3^+$)	0·084	−0·079	0·441	1·50
H_{IV} (CH$_2$)	0·567	0·089	0·446	1·50
H_V (CH$_2$)	0·369	−0·186	0·427	1·50

Standard deviations of the positional parameters

	$\sigma(x)$	$\sigma(y)$	$\sigma(z)$
N	0·0074 Å	0·0071 Å	0·0091 Å
O_I	0·0066	0·0063	0·0073
O_{II}	0·0075	0·0071	0·0069
C_I	0·0086	0·0088	0·0081
C_{II}	0·0084	0·0084	0·0076

$\sigma(B) \simeq 0\cdot1$ Å^{-2} (for heavy atoms).

* Hydrogen atoms are placed at the assumed positions.

The average parameter changes during the refinements were about $0\cdot04$ Å in each of the three axial directions, a few atoms, however, moved as much as $0\cdot08$ Å, and some significant increase in temperature factors was observed. The final atomic parameters and temperature factors for the atoms are listed in Table 2. A comparison of the final calculated and observed structure factors is given in Table 3.

Accuracy

The final value of the R factor was $10\cdot8\%$ for all planes which are listed in Table 3. Thermal motions of the atoms were assumed isotropic even though anisotropic corrections would give more interesting results.

The standard deviations for the atomic parameters were calculated from the coefficients of the normal equations in the last least-squares cycle by the formula (Shoemaker *et al.*, 1950)

$$\sigma(\Delta \xi_j) = \{ \Sigma w \Delta F^2 D_{jj}^{-1} / (m - s) \}^{\frac{1}{2}},$$

where, m is the number of observational equations, s is the number of parameters and D_{jj}^{-1} is the jth

Table 3. *Comparison of calculated and observed structure factors*

(hk·0)

h	k	$|F_o|$	$|F_c|$	A_c	B_c
0	1	5·2	6·2	6·2	−0·4
1	1	39·1	40·3	−24·7	31·8
2	1	20·2	20·8	−17·1	12·0
3	1	6·4	5·3	−1·0	5·2
4	1	5·7	5·3	4·7	2·4
5	1	2·5	2·5	−2·1	−1·3
6	1	9·8	9·1	−5·3	7·4
7	1	4·4	2·8	−1·0	−2·6
0	2	19·5	20·2	19·5	5·2
1	2	21·5	24·0	−15·5	18·4
2	2	2·1	1·9	0·6	1·8
3	2	6·4	6·7	5·3	−4·1
4	2	6·3	4·8	−2·1	−4·3
5	2	4·9	5·6	1·8	5·3
6	2	3·3	3·4	−1·7	2·9
0	3	6·8	7·6	6·8	3·3
1	3	9·2	10·8	−8·2	7·0
2	3	6·3	6·3	−1·2	−6·2
3	3	11·1	11·5	−7·6	−8·6
4	3	5·2	5·0	−3·3	3·8
5	3	1·4	0·3	−0·2	0·1
0	4	16·2	16·6	16·6	−1·3
1	4	1·6	1·9	1·8	0·3
2	4	11·6	12·3	−5·2	−11·2
3	4	1·5	0·6	0·6	0·1
4	4	2·6	2·9	1·7	−2·4
0	5	16·9	16·0	16·0	0·6
1	5	3·3	4·1	−4·1	0·3
2	5	4·2	3·1	1·2	2·9
3	5	5·0	4·8	4·6	−1·3
0	6	2·5	2·0	−1·9	0·7
1	6	11·4	12·1	−5·7	10·7
2	6	1·2	1·4	−1·4	−0·1
0	7	3·2	3·0	2·0	2·2
1	7	1·2	1·4	−1·4	−0·3

(hk·1)

h	k	$|F_o|$	$|F_c|$	A_c	B_c
0	1	16·3	18·5	9·5	15·9
1	1	6·0	5·5	−5·2	1·7
2	1	8·1	9·5	4·0	8·6
3	1	4·9	4·9	0·5	4·9
4	1	1·2	0·8	−0·8	−0·1
5	1	5·8	5·6	4·1	3·8
6	1	1·8	1·0	−1·0	−0·3
0	2	8·2	9·7	9·0	−3·7
1	2	13·1	14·5	−11·4	−8·9
2	2	8·6	10·2	10·2	−0·3
3	2	9·3	10·0	−8·7	−5·0
4	2	4·1	4·1	4·1	−0·4
5	2	2·7	2·5	−0·9	−2·3
6	2	2·1	2·0	−1·0	1·8
0	3	4·9	5·3	1·8	5·0
1	3	4·8	4·5	−0·5	4·4
2	3	2·6	2·5	−0·9	2·4
3	3	4·1	4·4	−1·5	4·1
4	3	3·0	2·2	−0·8	−2·1
5	3	2·2	2·3	−0·3	2·3
0	4	6·9	7·2	7·2	0·2
1	4	9·0	9·4	−7·1	−6·1
2	4	5·8	5·8	5·6	1·5
3	4	4·4	5·1	−3·3	−3·9
4	4	2·1	1·6	0·8	−1·4
0	5	1·5	0·8	−0·1	0·8
1	5	3·0	2·6	−0·3	2·6
2	5	1·9	2·0	2·0	−0·2
3	5	2·6	2·8	−2·3	1·7
0	6	6·3	6·2	5·1	3·5
1	6	2·6	2·7	−1·2	−2·4
2	6	2·5	2·4	2·0	1·3
1	7	2·1	2·7	−2·6	0·5

(hk·$\bar{1}$)

h	k	$|F_o|$	$|F_c|$	A_c	B_c
0	1	14·7	15·6	14·4	−6·1
1	1	11·1	13·1	−9·7	−8·8
2	1	3·7	3·6	3·6	0·3
3	1	9·6	10·1	−4·8	−8·9
4	1	2·0	0·7	−0·7	0·1
5	1	3·9	4·6	−1·6	−4·3
6	1	1·5	0·7	0·4	−0·5
0	2	10·6	12·2	1·0	−12·2
1	2	7·0	7·0	5·6	4·3
2	2	2·2	1·9	−1·6	−1·1
3	2	3·0	3·6	1·3	−3·3
4	2	2·7	2·8	1·0	2·6
5	2	4·5	4·3	2·5	−3·6
6	2	2·7	2·8	1·7	2·2
0	3	12·2	13·5	12·2	5·6
1	3	2·2	2·1	0·0	2·1
2	3	3·9	5·0	1·9	4·6
3	3	2·3	1·3	−0·4	1·2
4	3	2·4	2·4	0·6	2·3
5	3	1·4	0·7	−0·3	0·6
0	4	7·8	7·4	−0·6	−7·4
1	4	4·0	2·9	−2·4	−1·6
2	4	3·0	2·8	−2·8	0·2
3	4	4·5	4·8	−1·7	−4·5
4	4	1·8	1·5	−1·4	0·5
0	5	4·1	5·1	5·0	0·6
1	5	4·2	3·8	2·5	2·9
2	5	2·6	2·6	1·8	1·9
3	5	2·2	1·1	0·4	1·1
0	6	2·5	2·2	−1·5	−1·6
1	6	2·0	2·8	−1·9	−2·0
1	7	3·1	2·7	2·1	1·6

(hk·2)

h	k	$|F_o|$	$|F_c|$	A_c	B_c
0	1	4·0	5·8	5·4	−1·9
1	1	16·5	15·9	−14·6	6·4
2	1	6·5	5·8	3·4	−4·8
3	1	15·9	15·9	−6·5	−14·5
4	1	3·6	3·8	0·8	−3·7
5	1	4·5	4·1	−3·9	1·2
6	1	2·2	2·2	−1·6	1·6
0	2	10·3	11·5	9·7	6·2
1	2	5·6	6·4	4·8	4·3
2	2	7·5	7·8	−4·7	−6·3
3	2	7·8	7·8	−2·6	−7·3
4	2	2·6	3·0	0·0	3·0
5	2	2·8	2·5	1·0	2·3
0	3	21·9	22·3	22·3	1·0
1	3	3·3	2·3	−1·3	−1·9
2	3	3·0	3·2	0·1	−3·2
3	3	1·8	2·4	−0·5	−2·3
4	3	6·3	6·1	6·1	0·2
5	3	2·2	2·6	2·1	−1·5
0	4	3·7	4·2	2·9	2·9
1	4	4·7	6·3	−4·4	4·6
2	4	5·3	5·6	−2·0	5·2
3	4	3·4	3·4	3·4	−0·1
4	4	5·0	4·8	4·6	1·3
0	5	2·7	3·1	−0·7	3·1
1	5	9·0	9·1	−5·6	7·1
2	5	1·4	2·0	−0·6	1·9
3	5	1·7	1·2	−0·4	−1·1
0	6	1·7	1·1	−0·7	0·9
1	6	2·8	2·5	−1·2	−2·2
0	7	3·1	5·5	5·3	1·4

(hk·$\bar{2}$)

h	k	$|F_o|$	$|F_c|$	A_c	B_c
0	1	31·5	35·1	35·1	−0·5
1	1	3·7	2·4	1·8	1·5
2	1	6·5	8·0	−3·6	−7·1
3	1	6·7	6·6	−4·2	−5·2
4	1	4·0	3·6	3·4	1·3
5	1	6·4	5·9	5·7	−1·2
6	1	5·3	4·5	−3·9	−2·2
0	2	21·7	22·7	22·6	−2·4
1	2	2·6	2·6	−1·1	−2·4
2	2	4·3	4·3	−1·1	4·2
3	2	3·8	3·6	2·9	−2·3
4	2	10·7	10·5	10·5	−0·8
5	2	2·7	2·8	1·7	−2·3
6	2	2·2	1·4	0·4	1·3
0	3	4·7	4·3	1·0	4·2
1	3	16·7	17·2	−8·5	15·0
2	3	8·1	9·3	−3·9	8·4
3	3	3·5	2·7	2·7	0·6
4	3	1·9	1·8	−1·6	0·9
5	3	3·4	3·9	−0·3	3·9
0	4	3·5	3·9	2·7	2·8
1	4	4·2	5·4	−4·4	3·1
2	4	3·2	3·0	1·4	−2·7
3	4	8·5	7·0	−3·7	−6·0
4	4	2·4	0·7	0·2	0·6
0	5	4·3	5·0	4·8	1·2
1	5	1·7	0·7	0·4	0·6
3	5	1·3	1·4	−1·2	−0·7
0	6	9·0	9·6	9·5	−1·5
1	6	3·3	3·0	−2·4	−1·9
0	7	1·1	1·5	1·5	0·5

(hk·3)

h	k	$|F_o|$	$|F_c|$	A_c	B_c
0	0	19·6	19·3	13·3	14·0
0	1	3·0	2·1	−1·9	−1·0
1	1	13·2	13·6	−13·0	−4·1
2	1	1·9	1·4	0·6	1·3
3	1	9·6	9·7	−9·0	−3·7
4	1	1·6	1·2	−1·1	−0·6
5	1	3·8	3·2	−2·3	−2·3
6	1	3·0	2·8	−2·8	−0·2
0	2	7·7	7·8	7·6	1·6
1	2	3·0	2·9	1·1	2·7
2	2	5·7	6·5	6·4	−1·3
3	2	3·9	3·8	0·8	3·7
4	2	4·8	4·6	3·6	−3·0
5	2	3·6	2·8	1·8	2·1
0	3	3·0	2·7	−0·2	2·7
1	3	9·3	9·1	−8·3	−3·9
2	3	3·4	3·0	0·6	2·9
3	3	5·8	5·6	−4·8	−2·9
4	3	1·4	1·6	−1·4	−0·9

Table 3 (cont.)

h	k	$|F_o|$	$|F_c|$	A_c	B_c	h	k	$|F_o|$	$|F_c|$	A_c	B_c	h	k	$|F_o|$	$|F_c|$	A_c	B_c
0	4	5·3	5·5	5·0	−2·1	3	2	3·7	4·5	1·0	−4·4	0	3	3·4	2·3	2·3	−0·2
1	4	3·4	2·9	1·6	2·5	4	2	9·4	8·4	8·1	2·5	1	3	0·0	0·6	0·5	0·3
2	4	6·2	6·1	5·7	−2·4							2	3	0·0	0·4	0·3	0·2
3	4	0·9	1·0	0·0	1·0	0	3	5·8	6·2	−5·7	2·4	3	3	0·0	0·9	0·6	−0·7
						1	3	11·1	10·6	−4·7	9·5						
0	5	5·8	5·7	1·9	5·4	2	3	5·1	5·9	−2·7	5·3	0	4	1·0	1·8	−1·1	−1·4
1	5	2·6	2·4	−2·2	−1·2	3	3	1·1	1·7	−1·3	1·1	1	4	0·8	1·1	−0·8	0·7
2	5	3·6	2·7	−0·3	2·7	4	3	3·9	3·8	3·4	1·7						
												0	5	2·3	2·4	0·5	−2·3
0	6	3·8	3·4	1·5	−3·1	0	4	3·0	2·6	−1·5	2·1						
1	6	3·3	3·0	−3·0	−0·5	1	4	4·0	4·1	−2·5	−3·2	(hk·5̄)					
						2	4	0·0	0·8	−0·6	−0·5	0	1	2·1	1·8	1·0	1·5
(hk·3̄)						3	4	4·5	5·8	−1·2	−5·7	1	1	3·3	2·6	−2·5	0·7
0	1	3·5	3·1	−3·1	−0·7							2	1	3·3	3·2	−0·5	3·2
1	1	5·9	5·7	5·0	2·7	0	5	2·6	2·9	2·2	1·8	3	1	3·9	3·3	−2·3	2·4
2	1	7·6	8·7	−7·5	4·3	1	5	0·0	0·4	0·3	0·3	4	1	0·0	0·6	−0·6	0·2
3	1	3·4	2·5	2·5	−0·4												
4	1	2·7	3·3	−2·8	1·7	0	6	2·6	2·5	2·1	1·3	0	2	3·4	2·5	1·4	−2·1
5	1	2·4	1·8	−1·6	−0·8							1	2	5·2	4·1	0·0	−4·1
6	1	4·2	3·5	1·5	3·2	(hk·4̄)						2	2	2·5	2·7	2·5	1·0
						0	1	4·7	3·5	−1·2	3·3	3	2	2·7	3·0	−0·6	−3·0
0	2	8·9	9·4	8·2	−4·5	1	1	7·7	7·1	−3·2	6·4						
1	2	5·4	5·4	−4·7	2·6	2	1	6·0	6·5	0·6	6·5	0	3	1·4	1·6	0·5	1·5
2	2	3·3	2·9	1·0	2·8	3	1	10·6	10·6	−7·1	−7·8	1	3	2·6	2·0	0·3	2·0
3	2	3·4	3·7	−1·0	−3·6	4	1	4·6	4·6	0·9	4·6	2	3	2·5	2·2	0·4	2·2
4	2	3·7	3·4	−2·6	2·3	5	1	4·8	4·6	−3·4	3·1	3	3	2·6	1·9	−1·2	1·5
5	2	2·9	2·9	1·9	−2·2												
						0	2	2·9	3·6	−2·4	−2·7	0	4	1·4	1·1	1·1	−0·3
0	3	5·3	5·9	−0·5	−5·9	1	2	6·2	6·8	4·6	−5·0	1	4	2·8	2·7	−0·6	−2·7
1	3	4·4	4·5	4·5	0·6	2	2	10·3	10·5	−8·9	−5·6						
2	3	2·6	2·3	−1·4	−1·8	3	2	8·6	8·5	−4·4	−7·2	0	5	1·6	1·3	0·7	−1·1
3	3	3·0	2·3	−0·4	−2·3	4	2	0·0	1·4	0·3	−1·3						
4	3	2·5	1·8	1·4	1·1							(hk·6)					
						0	3	15·0	15·1	15·1	0·9	0	0	8·0	5·4	5·3	1·2
0	4	3·6	3·5	3·5	0·6	1	3	4·4	4·3	2·6	−3·4	0	1	3·3	2·6	2·3	1·2
1	4	2·4	2·0	0·5	1·9	2	3	5·2	5·1	1·7	4·8	1	1	3·8	2·9	−2·9	0·4
2	4	4·9	4·6	−3·2	3·4	3	3	3·7	3·7	1·9	−3·2	2	1	5·8	4·3	−2·0	3·8
3	4	2·3	1·9	1·9	0·2	4	3	7·0	6·7	6·4	2·0	3	1	1·9	1·0	0·6	−0·8
0	5	6·0	6·0	1·8	−5·7	0	4	4·6	4·6	−4·4	−1·4	0	2	1·8	1·1	−1·1	−0·3
1	5	1·4	0·6	0·6	−0·1	1	4	5·0	4·5	−2·1	4·0	1	2	7·6	6·3	−3·6	5·1
2	5	1·4	0·8	0·5	0·6	2	4	5·1	4·9	−3·3	3·6	2	2	1·7	1·7	−0·7	1·6
						3	4	1·5	1·9	−0·5	−1·8						
0	6	1·3	0·8	−0·6	−0·5							0	3	1·4	1·3	−1·0	0·9
1	6	3·3	3·4	2·4	2·4	0	5	4·8	4·2	1·0	4·1	1	3	2·6	2·0	−1·5	−1·4
						1	5	2·6	1·6	0·5	1·5						
(hk·4̄)												(hk·6̄)					
0	1	7·5	5·7	5·2	2·4	(hk·5̄)						0	1	2·6	2·0	1·9	−0·7
1	1	8·1	7·9	7·9	−0·2	0	1	5·1	4·0	2·6	−3·1	1	1	1·3	1·1	0·8	0·8
2	1	7·3	7·0	−4·8	−5·1	1	1	4·5	3·6	−3·3	−1·4	2	1	6·0	5·8	−2·1	5·4
3	1	4·3	4·1	−2·1	−3·6	2	1	2·7	2·1	2·0	−0·6	3	1	4·7	3·6	3·0	−2·1
4	1	5·1	4·8	4·7	−0·8	3	1	3·5	3·0	−0·4	−3·0						
5	1	2·1	1·9	−0·0	1·9	4	1	0·8	0·7	0·7	−0·1	0	2	2·4	2·0	−1·1	1·7
												1	2	6·2	5·7	−1·8	5·5
0	2	12·9	12·7	12·6	1·7	0	2	1·9	2·3	−2·1	−1·0	2	2	3·9	3·3	0·6	3·2
1	2	6·4	5·4	−2·5	−4·8	1	2	3·8	3·2	1·3	2·9						
2	2	6·0	6·2	1·7	6·0	2	2	0·8	0·5	−0·1	0·5	0	3	1·7	1·6	−1·4	0·6
						3	2	0·0	0·3	−0·0	0·3	1	3	3·0	2·4	2·0	−1·4

diagonal element of the matrix inverse to the matrix D_{ij} which is formed from the coefficients of the normal equations. In Table 2, the standard deviations for each parameter as calculated with the formula are presented. The average value 0·0077 Å may be taken as representative of the determination as a whole.

Description and discussion of the structure

Molecular configuration

Intramolecular atomic distances and angles in γ-glycine calculated from the final coordinates are given in Table 4. For the sake of comparison, the values for α and β-glycine are also given. The standard deviations of the values in γ-glycine are about 0·011 Å and 0·7°, without including any allowance for the error introduced by the anisotropic thermal vibrations of atoms. The dimensions of the glycine molecule in the γ-form are very close to the other forms, with the exception of the rather short C_I–O_{II} bond length of 1·237 Å. This may be interpreted partly due to the shortening caused by the angular oscillations of the oxygen atom around a center near the C_I atom. Since no allowance has been made for the anisotropic

Table 4. *Intramolecular atomic distances and angles*

	γ-Form	β-Form	α-Form		γ-Form	β-Form	α-Form
N–C$_{II}$	1·491 Å	1·484 Å	1·474 Å	C$_I$–C$_{II}$–N	110·8°	110·8°	111·8°
C$_{II}$–C$_I$	1·527	1·521	1·524	O$_I$–C$_I$–O$_{II}$	125·4	126·2	125·5
C$_I$–O$_I$	1·254	1·233*	1·252 (1·261*)	C$_{II}$–C$_I$–O$_I$	118·3	117·8	117·4
C$_I$–O$_{II}$	1·237	1·257*	1·255 (1·265*)	C$_{II}$–C$_I$–O$_{II}$	116·2	115·9	117·1
N–O$_I$	2·687	2·701	2·690				
	±0·011	±0·015	±0·005†		±0·7	±0·9	±0·3†

* Corrected for rotational oscillations of the molecule.   † Limits of error.

γ-Form: present investigation.   β-Form: Iitaka, 1960.   α-Form: Marsh, 1958.

thermal motion in the present investigation, accurate correction for the shortening is not at the moment practicable. However, if the anisotropic thermal motions of the O$_{II}$ atom are of the same order as in the other forms (this may be reasonable since the O$_{II}$ atom has the largest vibration comparable with the oxygen atoms (O$_{II}$) in both α- and β-glycine for which the shortening of the C$_I$–O$_{II}$ bond was calculated as 0·010 Å), the true bond length would be estimated as 1·247 Å, appreciably longer than the observed value.

Table 5. *Perpendicular distances of the atoms from the best plane through* C$_I$, C$_{II}$, O$_I$ *and* O$_{II}$ *atoms*

O$_I$	−0·006 Å
O$_{II}$	−0·006
C$_I$	0·017
C$_{II}$	−0·005
N	0·309

The dimensions of the carboxyl group and the arrangement of oxygen atoms around the nitrogen atom suggest the molecule, likewise in the α- and β-forms, exists as a zwitter ion.

The carboxyl group are almost coplanar, the deviation of the atoms from the best plane through the C$_I$, C$_{II}$, O$_I$, O$_{II}$ atoms obtained by least squares (Schomaker *et al.*, 1959) are given in Table 5. The nitrogen atom is 0·309 Å out of this plane, which is significantly smaller than in the other forms, namely 0·436 Å in the α and 0·583 Å in the β-form. This corresponds to an angular displacement of the C–N bond from the least-squares plane (a twist around the C$_I$–C$_{II}$ bond) by 12·8° as compared with 18·6° in α- and 24·8° in β-glycine. A reason for the difference may be considered to be a steric effect. As indicated in Table 7, rather close approach of the nitrogen and oxygen atoms to the methylene group of the neighbouring molecules (N $\cdots$ C$_{II}^{T'}$, O$_{II}$ $\cdots$ C$_{II}^{T_{\bar c}^2}$) would prevent the displacement. It may be interesting to investigate to

what extent the molecular dimensions are influenced by the environment.

Hydrogen bonds

In Table 6 are listed intermolecular short N $\cdots$ O distances together with C–N $\cdots$ O angles. It may be seen that the nitrogen atom is surrounded by five oxygen atoms at short distances, which suggest the presence of hydrogen bond, and the situation is more complicated than in the other forms. A convenient and straightforward method for depicting the situation may be a stereographic projection. In Fig. 5 such projections for γ-, α- and β-glycine are prepared, in which the direction of the C–N bond is taken as the polar axis and the suggested N–H directions are also indicated. It is clear that the three oxygen atoms O$_I^{Mc}$, O$_{II}^{T'}$ and O$_I^{T'_{\overline{ab}}}$ in the γ-form are arranged approximately in the tetrahedral directions with the maximum deviation about 20° from the tetrahedral angle. Moreover, if the tetrahedron be inclined about 15° from the normal position in such a way that the O$_I^{T_{\bar a}^2}$ atom just lies on a line passing through the nitrogen atom and the center of the tetrahedron, the three oxygen atoms would be arranged almost exactly (within a few degrees) in the tetrahedral directions. We conclude that these three oxygen atoms are taking part in hydrogen bonds. Other oxygen atoms O$_I^{T_{\bar a}^2}$ and O$_{II}^{T_{\overline{ab}}^2}$ are linked by the electrostatic attraction to the NH$_3^+$ group. The situation is very similar to that found in orthorhombic hydrazonium sulphate around the N$_I$ atom (Nitta, Sakurai & Tomiie, 1951).

In α- and β-glycine, two oxygen atoms (O$_I^{Mc}$ and O$_{II}^{Ma}$) are situated nearly in the tetrahedral directions and are participating in the strong hydrogen bonds which hold the molecule in a sheet. The third hydrogen atom is situated on the line nearly bisecting the angle O$_I^{Ma}$–N–O$_{II}^{M}$ or O$_I^{Wab}$–N–O$_{II}^{Wb}$, and forms a bifurcated

Table 6. *Intermolecular short* N $\cdots$ O *distances and* C–N $\cdots$ O *angles*

	N $\cdots$ O$_I^{Mc}$	N $\cdots$ O$_{II}^{T'}$	N $\cdots$ O$_I^{T'_{\overline{ab}}}$	N $\cdots$ O$_I^{T_{\bar a}^2}$	N $\cdots$ O$_{II}^{T_{\overline{ab}}^2}$
N $\cdots$ O (Å)	2·801*	2·817*	2·970*	2·901	3·065
C–N $\cdots$ O (°)	116·6	91·0	117·0	165·6	86·0

* Hydrogen bond suggested.

(a)

(b)

(c)
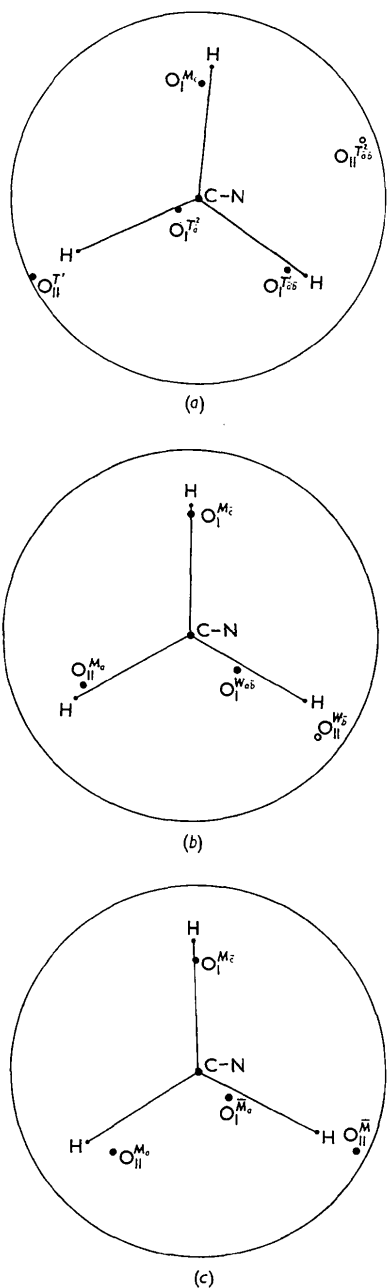
Fig. 5. Stereographic projections of the hydrogen
bond directions.
(a) γ-form, (b) β-form, (c) α-form.

by lattice translations are designated with subscript denoting the translation vectors. It may be seen that the dominating feature of the intermolecular packing is the hydrogen bonding between amino nitrogen and
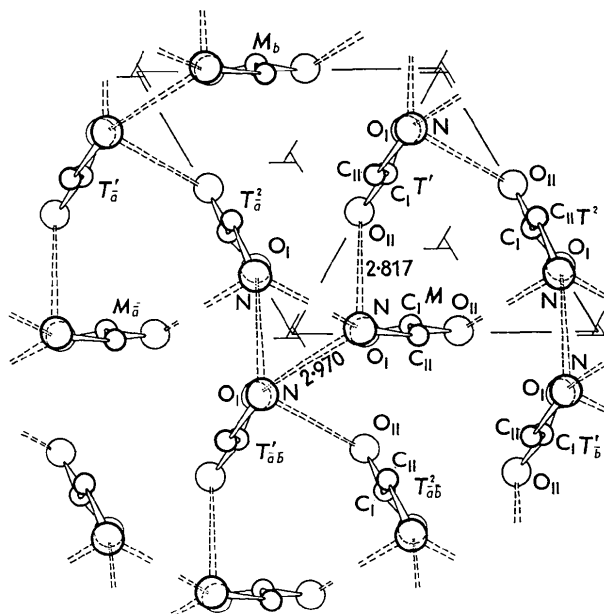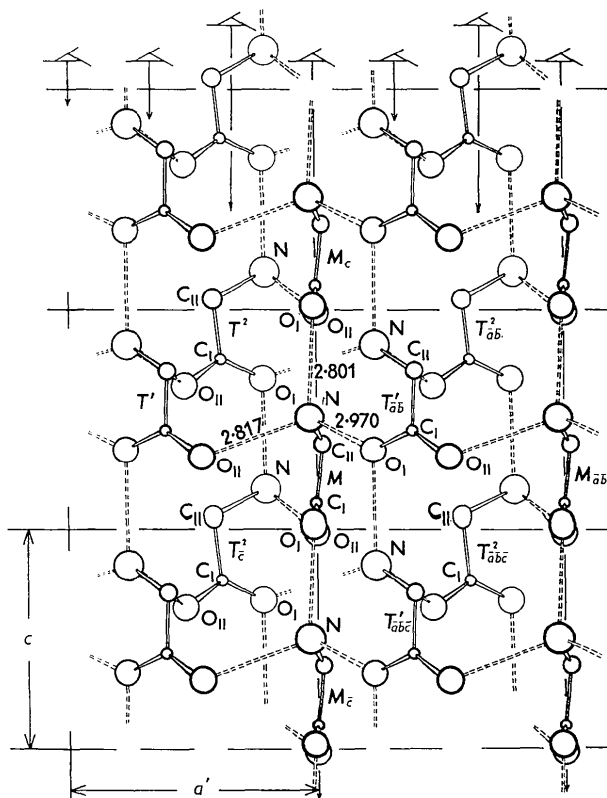

Fig. 6. Projection of the structure along the c-axis.

hydrogen bond which accounts for the cohesion of the sheets.

Framework features and packing

Figs. 6 and 7 show the structural arrangement of the γ-glycine crystal projected along the c- and a-axis. In these figures two types of molecules related to M by a threefold screw axis are designated by T' and T², and other molecules which are related to these three

Fig. 7. Projection of the structure along the a-axis.

carboxyl oxygen atoms ($N\overset{M}{\cdots}O_I^{Mc}$, $O_{II}^{T'}$) which links the molecule into helical chains about the threefold screw axes parallel to the c-axis. These chains are packed together by the lateral hydrogen bonds ($N\overset{M}{\cdots}O^{T'_{\bar{ab}}}_I$), forming a three-dimensional network of the hydrogen bonds. The effect of such bonding will be enhanced by the electrostatic forces between oppositely charged groups. Furthermore, the directional property of the hydrogen bond seems to be more fully satisfied in this case than in the corresponding hydrogen bonds in the other forms. It may be worth while to note, in this connexion, a study of infrared absorption spectra with these three polymorphs of glycine suggests that this lateral hydrogen bond would be
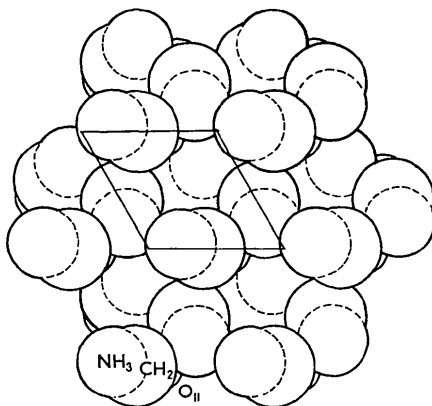
Fig. 8. Packing drawing of glycine molecules viewed along the c-axis.
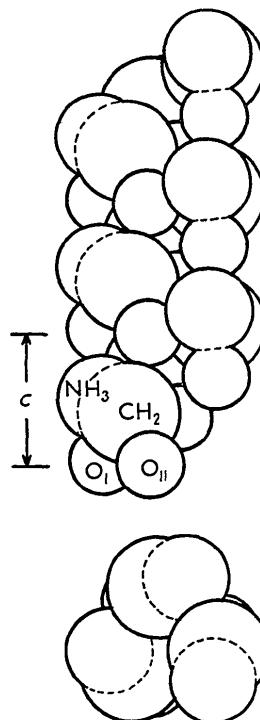
Fig. 9. The chain of glycine molecules found in the γ-form

Table 7. *Interatomic distances between molecules of glycine*

	Same chain		Between chains			
	From M to	Distance (Å)	From M to	Distance (Å)	From M to	Distance (Å)
NH_3–O_I	M_c	2·801	$T'_{\bar{ab}}$	2·970	$T^2_{\bar{a}}$	2·901
NH_3–O_{II}	T'	2·817	$T^2_{\bar{ab}}$	3·065		
	M_c	3·445				
NH_3–CH_2	T'	3·690	$T'_{a\bar{b}}$	4·262	$T^2_{\bar{ac}}$	4·558
			$T^2_{\bar{abc}}$	4·487		
NH_3–NH_3			$T'_{\bar{ab}}$	3·340	$T^2_{\bar{ac}}$	3·340
			$T'_{\bar{abc}}$	4·602	T^2_a	4·602
CH_2–CH_2	T'	4·310	$T^2_{\bar{abc}}$	3·908	$T'_{\bar{b}}$	3·908
	T^2_c	4·310				
O_I–CH_2	$M_{\bar{c}}$	3·716	$T'_{\bar{abc}}$	4·362	$T^2_{\bar{ac}}$	3·881
	$T'_{\bar{c}}$	3·975	$T^2_{\bar{abc}}$	3·617		
O_{II}–CH_2	T^2_c	3·210	$T^2_{\bar{abc}}$	3·894	$T'_{\bar{bc}}$	3·313
	$M_{\bar{c}}$	3·447				
	$T'_{\bar{c}}$	4·356				
O_I–O_{II}	T'	3·206	$T^2_{\bar{abc}}$	3·470		
O_I–O_I			$T'_{\bar{ab}}$	3·331	$T^2_{\bar{ab}}$	3·331
			$T'_{\bar{abc}}$	4·595	T^2_a	4·595
O_{II}–O_{II}	T'	3·988	$T^2_{\bar{abc}}$	4·008	$T'_{\bar{b}}$	4·008
	T^2_c	3·988				

stronger than either of the interlayer hydrogen bond existing in α- or β-glycine (Iitaka, 1960).

Fig. 8 shows a packing drawing of the structure viewed along the c-axis, in which CH_2, NH_3 and O are drawn with van der Waals radii of 2·0, 1·8 and 1·35 Å, respectively. A single chain having a symmetry 3_2 is shown in Fig. 9. The enantiomorphic chain (symmetry 3_1) which forms different crystals, is expected for the enantiomorphous molecules. The interatomic distances between molecules of glycine are summarized in Table 7, which may be compared with Table 7 of the previous paper (Iitaka, 1960). The packing distances are reasonable. However, the methylene–methylene or methylene–oxygen distances are somewhat longer than that observed between the double layers of α-glycine, and the packing of the molecules within the crystal is less compact as compared with the α-form. Probably, the decrease in van der Waals energies is overcome by the hydrogen bond and electrostatic energies and hence renders the structure stable.

Relationships among the three forms

It is now possible to give an overall picture on polymorphism of glycine from the structural point of view. Although, little is known on the thermodynamical relationship at the moment, it seems worth while to describe some observations which indicate the stability relations among these forms.

γ-Glycine may be a stable form at least at room temperature. It changes into the α-form upon heating at about 165 °C. (Iitaka, 1954), and the heat of transition was measured to be about 600 cal./mol. (unpublished work. The measurement is difficult since the transition speed is rather slow and the temperature at which the transition takes place lies near the decomposition temperature). The reverse change, however, could not be observed under usual conditions.

The β-form changes into the α-form upon heating (not higher than 100 °C.) or grinding or any other mechanical shocks. It has a great tendency to transform into the α- and γ-form at room temperature, and the transformation is very much accelerated by the presence of water vapor, although the formation of the γ-form is not observed in such a rapid change.

It seems very likely that the mechanism of crystallization of glycine from aqueous solutions is complicated. It grows in many forms, even unstable ones. It is very interesting that from heavy water solutions the γ-form crystallizes more easily without adding any substance except the seeding crystals. Furthermore, for deuterated α-glycine (powder) the transformation from the α- to the γ-form has actually been observed at room temperature. A similar effect has been observed in β to α transformation of resorcinol (Robertson & Ubbelohde, 1938).

As was mentioned in the previous paper on the β-form (Iitaka, 1960), the change that takes place in the arrangement of the molecules during these transformations seems very surprising. Since these three kinds of crystals are formed by such arrangements of the strongly dipolar molecules as consisting of parallel chain, $(+)(+)(+)^*\ldots$ in the γ-form, antiparallel double layer, $(+)(-)(-)(+)(+)(-)\ldots$ in the α-form, alternating antiparallel layer, $(+)(-)(+)(-)\ldots$ in the β-form, the transformations involve a rearrangement of dipoles such as observed in ferroelectric and anti-ferroelectric transitions. However, here the transformation would only be achieved by a drastic rearrangement of the molecules within the crystal.

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* The chains or layers in which the nitrogen atoms facing in the $+c$ direction are designated by the sign $(+)$, and the reverse with $(-)$.