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The Crystal Structure of Glycine¹

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Introduction

The present general interest in the constitution and structure of proteins and the accompanying activity of research in this field are among the many consequences of the application of chemical and physical techniques to biological problems. The conception that protein molecules consist of amino acids held together by peptide linkages has been accepted generally for many years. Recent refinements in analytical methods have suggested the possibility of definite periodicities in the arrangement of the amino acid residues in the peptide chain.² The stimulus thus given to an attack upon the constitution of proteins by purely chemical methods should be fruitful in producing more reliable information regarding their quantitative composition in terms of their amino acid constituents.

The fact that many proteins, such as silk fibroin, keratin and collagen, occur naturally in fibrous form and that others, hemoglobin, pepsin, insulin, etc., may be obtained in the crystalline state has encouraged a physical approach to the problem of protein structure by the use of X-ray diffraction methods. In the case of fibrous proteins³ these studies have led to interesting hypotheses concerning the possible arrangement of amino acid residues in peptide chains in accord with the physical properties and X-ray patterns of the substances investigated. For the crystalline proteins pepsin⁴ and insulin^{4c,5} X-ray analysis of single crystals has led to statements concerning the size of the molecules and their probable arrangement in the crystal lattice, but has yielded no information regarding the constitution of the molecules themselves. The great size and com-

plexity of protein molecules generally seem to preclude the probability of obtaining such information directly by these means. Especial emphasis is given to this view when it is realized that hitherto no correct determination had been made of the positions of the atoms in crystals of the simplest products of protein hydrolysis, the amino acids, and the only complete structure determination which has been carried out for any related substance is that of diketopiperazine,⁶ which was published within the last year. The reason for the lack of such fundamental information is inherent in the nature of the compounds themselves. The similarity in the scattering powers of atoms of carbon, oxygen and nitrogen, of which they are principally composed, does not facilitate the evaluation of the many parameters required by the low crystallographic and molecular symmetries which characterize these crystals. However, recent developments in Fourier series methods, and especially their extension by Patterson⁷ and Harker,⁸ now make it possible to attack this problem with considerable hope of success. The present determination of the atomic arrangement in crystals of glycine, the simplest of the amino acids, was therefore undertaken as a contribution to a program of research upon the constitution of proteins which is being carried on in these Laboratories. Although the analytical methods are not new, their use in the present instance seems to provide a straightforward procedure which should readily be applicable to other organic crystals involving the evaluation of many parameters. They are therefore described in some detail.

Thus far three papers dealing with the crystal structure of glycine have appeared. Bernal,⁹ in a preliminary paper, reported results of X-ray investigations of the units of structure and space group symmetries of fifteen amino acids and related compounds. The unit cell of α -glycine is there described as monoclinic, with $a_0 = 5.04 \text{ \AA}$, $b_0 = 12.1 \text{ \AA}$, $c_0 = 5.41 \text{ \AA}$, $\beta = 111^\circ 38'$, contain-

(1) The major portion of this work was presented at a meeting of the Pacific Division of the American Association for the Advancement of Science held in San Diego, California, June 23, 1938.

(2) M. Bergmann and C. Niemann, *J. Biol. Chem.*, **118**, 301 (1937).

(3) K. H. Meyer and H. Mark, *Ber.*, **16**, 1932 (1928); "Der Aufbau der hochpolymeren organischen Naturstoffe," Leipzig, 1930, p. 220 and ff.; O. Kratky, *Z. physik. Chem.*, **B5**, 297 (1929); O. Kratky and S. Kuriyama, *ibid.*, **B11**, 363 (1931); W. T. Astbury and co-workers, *Phil. Trans.*, **A230**, 75 (1930); **A232**, 333 (1933); *Proc. Roy. Soc. (London)*, **A150**, 533 (1935); and elsewhere.

(4) (a) J. D. Bernal and D. Crowfoot, *Nature*, **133**, 794 (1934); (b) W. T. Astbury and R. Lomax, *ibid.*, **133**, 795 (1934); (c) D. Crowfoot, *ibid.*, **136**, 591 (1935).

(5) D. Crowfoot, *Proc. Roy. Soc. (London)*, **A164**, 580 (1938).

(6) R. B. Corey, *THIS JOURNAL*, **60**, 1598 (1938).

(7) A. L. Patterson, *Z. Krist.*, **90**, 517 (1935).

(8) D. Harker, *J. Chem. Phys.*, **4**, 381 (1936).

(9) J. D. Bernal, *Z. Krist.*, **78**, 363 (1931).

ing four molecules of $\text{NH}_2\text{CH}_2\text{COOH}$. The space group is $C_{2h}^5 - P2_1/n$. The crystals are optically negative with α parallel to the b -axis. They cleave readily along (010). A possible arrangement of the molecules is discussed but no X-ray intensity data are given for any of the compounds studied and no attempt is made to assign atomic parameters. The arrangement suggested is not closely related to that found in this determination.

In the same year Hengstenberg and Lenel¹⁰ published a detailed study of the structure of glycine derived from spectrometric measurements of thirty-three reflections of $\text{Mo-K}\alpha$ radiation from planes of type ($h\bar{k}0$) and ($0kl$). That this structure, based upon inadequate data, is incapable of explaining the intensities of such simple reflections as ($20\bar{2}$), ($10\bar{3}$), ($30\bar{1}$), (202), ($20\bar{4}$) and (204) is shown in the second and third columns of Table I. Such lack of agreement between observed and calculated F 's, combined with serious structural abnormalities, is sufficient to show that this arrangement is not even approximately correct.

More recently Kitaygorodsky¹¹ has proposed a structure for glycine based upon the spectrometric data of Hengstenberg and Lenel supplemented with visually estimated intensities of a few additional reflections found on rotation and oscillation photographs. Although this arrangement gives better agreement for some reflections than that of Hengstenberg and Lenel, it still fails to explain the intensities of many planes having small indices (Table I). Interatomic distances and bond angles are in even less accord with established values than are those of the preceding paper, and this structure also must be rejected.

TABLE I

A COMPARISON OF THE SCATTERING POWERS FOUND FOR SOME PLANES WITH THOSE CALCULATED FROM THE STRUCTURES PROPOSED BY HENGSTENBERG AND LENEL (H. L.) AND BY KITAYGORODSKY (K.)

| Indices | Scattering power | | |
|-------------|------------------|-------|------|
| | Obsd. | H. L. | K. |
| $20\bar{2}$ | 0 | -41 | 14.4 |
| $10\bar{3}$ | 9 | -32.7 | -2.0 |
| $30\bar{1}$ | 18 | 12.4 | 2.4 |
| 202 | 23 | 5.3 | 18.2 |
| $20\bar{4}$ | 0 | 13.7 | 12.0 |
| 204 | 12 | -6.1 | 2.9 |

(10) J. Hengstenberg and F. V. Lenel, *Z. Krist.*, **77**, 424 (1931).

(11) A. Kitaygorodskv. *Acta physiochim. U. R. S. S.*, **5**, 749 (1936).

Preparation of Crystals

The crystals of glycine used in this investigation were prepared and studied crystallographically by one of the authors (G. A.) in the laboratory of Professor M. S. Dunn at the University of California at Los Angeles. They were made synthetically from chloroacetic acid by treatment with ammonium carbonate. Crystals were grown both by slow cooling of saturated aqueous solutions and by evaporation of saturated solutions at constant temperature. Specimens were obtained ranging in size from microscopic dimensions to about 1 cm. in diameter. They were generally somewhat elongated along the a -axis, but many were characterized by uniform development in all directions and were therefore especially adapted to X-ray photography. For this purpose crystals of about 0.1 to 0.3 mm. in greatest dimension were selected. Their axial ratio and pronounced basal cleavage were entirely in agreement with data given by Groth.¹²

The Unit Cell and Space Group Symmetry

Goniometric measurements of the crystals and oscillation and rotation photographs taken about the three crystallographic axes, using $\text{Cu-K}\alpha$ radiation, showed crystals of glycine to be built upon a monoclinic unit cell having $a_0 = 5.10 \text{ \AA.}$, $b_0 = 11.96 \text{ \AA.}$, $c_0 = 5.45 \text{ \AA.}$, $\beta = 111^\circ 38'$. The presence of all orders of (hkl) indicated a primitive lattice. Systematic absence of all ($h0l$) reflections having $h + l$ odd and of odd orders of ($0k0$) established the space group as $C_{2h}^5 - P2_1/n$. Unsymmetrical Laue photographs containing over a hundred first-order reflections confirmed these absences and also the size of the unit of structure. Taking the density of glycine to be 1.607,¹³ this cell will contain four molecules (calculated 4.02).

Determination of the Structure

The presence of four molecules of $\text{NH}_2\text{CH}_2\text{COOH}$ in the unit cell requires the placing of each atom in the four general positions xyz ; $\bar{x}\bar{y}\bar{z}$; $x + \frac{1}{2}, \frac{1}{2} - y, z + \frac{1}{2}$; $\frac{1}{2} - x, y + \frac{1}{2}, \frac{1}{2} - z$. If the hydrogen atoms are disregarded, since they contribute too little to X-ray scattering to permit determination of their positions, the establishment of the structure demands the assignment of values

(12) P. Groth, "Chemische Krystallographie," Vol. III, Leipzig, 1910, p. 98.

(13) The typographical error in the value 1.1607 given by T. Curtius, *J. prakt. Chem.*, [2] **26**, 158 (1882), has been pointed out by other authors (see ref. 10).

of x , y , and z to two oxygen and two carbon atoms and to one nitrogen atom, making 15 parameters in all to be evaluated. If one attempts to place the atoms by a trial and error method so as to obtain agreement between calculated spectra and observed X-ray data, it is soon apparent that too little is known regarding the shape of the molecules and their probable arrangement in the unit cell to make such an approach at all feasible. The presence of symmetry elements, two-fold screw axes and glide planes, suggests the possibility of obtaining at least approximate positions of all atoms directly from X-ray intensity data by the use of a three-dimensional Patterson analysis in the manner developed by Harker.⁸ X-Ray data for this purpose were obtained from rotation and oscillation photographs taken about the three axes of the crystal using Cu-K α radiation. For these photographs specimens less than 0.3 mm. in greatest dimensions were used, for which corrections for absorption were shown to be negligible. Complete series of photographs were made at different exposure times, and relative intensities were estimated by visual comparison of reflections found upon them. The data thus obtained are recorded in Tables II, III, IV, and V.

A Patterson three-dimensional "F²" series⁷

$$P(x,y,z) = \sum_h \sum_k \sum_l |F_{hkl}|^2 \cos 2\pi(hx + ky + lz)$$

gives maxima at points at vector distances from the origin equal to vector distances between atoms in the unit cell. Harker⁸ has developed modifications of this series which so utilize the symmetry elements of the crystal as to retain the essential information to be obtained from a three-dimensional analysis in one- and two-dimensional diagrams. Thus the presence of a diagonal glide plane of symmetry in glycine suggests the calculation of the one-dimensional series

$$P(\frac{1}{2}, y, \frac{1}{2}) = \sum_h \sum_k \sum_l |F_{hkl}|^2 \cos 2\pi(h/2 + ky + l/2) = \sum_k B_k \cos 2\pi ky$$

where

$$B_k = \sum_h \sum_l (-1)^{h+l} |F_{hkl}|^2$$

in which the positions of maxima represent the y -components of vectors connecting atoms in the crystal related by the operation of the glide plane. In Fig. 1 this function is plotted as ordinate against the Y -axis as abscissa. The two strong maxima surrounding $Y = 0.25$ indicate that the

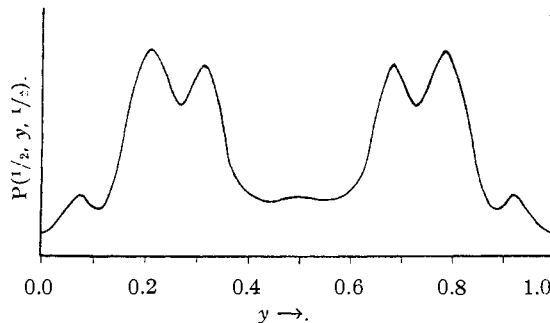


Fig. 1.—A plot of the function $P(\frac{1}{2}, y, \frac{1}{2})$. The strong maxima near $Y = \frac{1}{4}$ indicate that the atoms of glycine occur in layers about one-quarter of the unit distance apart along the Y -axis.

atoms of glycine fall in layers about one-fourth of the unit distance apart along the Y -axis. This calculation not only suggests that the molecules of glycine are nearly planar and lie approximately parallel to the XZ -plane, an arrangement which is also indicated by cleavage and optical properties, but from the individual maxima the y -parameters of the atoms may be established with some certainty. From the four general positions of the space group C_{2h}^5 it is seen that for atoms connected by the operation of the diagonal glide plane ($xyz; x + \frac{1}{2}, \frac{1}{2} - y, z + \frac{1}{2}$; etc.) the Y -component of the interatomic vector is $\frac{1}{2} - 2y$. Then from the more intense of the two maxima at $Y = \frac{1}{2} - 2y \cong 0.20$ we have $y \cong 0.15$ or 0.35 for the parameter of the atoms. In the same way the weaker maximum at $Y = \frac{1}{2} - 2y \cong 0.32$ corresponds to $y \cong 0.09$ or 0.41 . From the relative intensities of the two maxima it might therefore be expected that of the five heavier atoms of glycine, three would have y -parameters close to 0.35 and two would have values close to 0.41. How accurately these assumptions were confirmed is seen from the atomic positions finally resulting from the complete determination of the structure; namely, one oxygen atom and two carbon atoms at $y = 0.360, 0.380$, and 0.365 , respectively, and one oxygen atom and the nitrogen atom both at $y = 0.410$. The small maximum at $Y = 0.07$ is doubtless to be ascribed to the interaction of N and O_{II} within the same molecule. This peak, which would be expected at $Y = 0.05$, is displaced to the right by the strong maxima at about $Y = 0.2$.

Although glycine contains no mirror plane, the series

$$P(0, y, 0) = \sum_h \sum_k \sum_l |F_{hkl}|^2 \cos 2\pi ky = \sum_k B'_k \cos 2\pi ky$$

where

$$B_k = \sum_h \sum_l |F_{hkl}|^2$$

derived by Harker for crystals containing this symmetry element can be used to detect the distances between atoms lying in the same line parallel to the Y-axis. In the plot of this function, Fig. 2, no pronounced maxima are present (except at the origin, expressing the fact that every atom lies at zero distance from itself). It may therefore be assumed that the atomic arrangement in glycine is such that no two atoms have approximately the same x - and z -parameters. O_I and N lie close to the screw axes so that there is some "overlapping" of these atoms with their equivalent atoms related to them through the operation of the axes (see Figs. 6 and 7a). These atoms therefore give rise to the faint peak at $Y = 0.5$ in Fig. 2. Similarly the peak at $Y = 0.28$ (and 0.72) is doubtless to be ascribed to slight overlapping of atoms O_{II} and C_{II} which have y -parameters differing by 0.275.

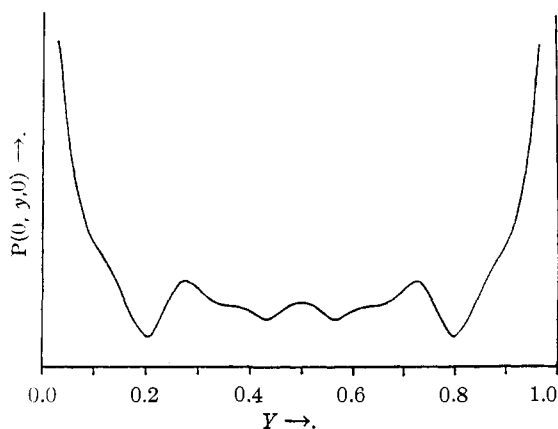


Fig. 2.—A plot of the function $P(0, y, 0)$. The absence of strong maxima, except at the origin, indicates that no two atoms of glycine have even approximately the same x - and z -parameters.

An approach to the determination of the x - and z -parameters can best be attained by the employment of a series corresponding to the section $Y = \frac{1}{2}$ of the three-dimensional Patterson diagram. The form of this series has been shown by Harker⁸ to be

$$\begin{aligned} P(x, \frac{1}{2}, z) &= \sum_h \sum_k \sum_l |F_{hkl}|^2 \cos 2\pi(hx + k/2 + lz) \\ &= \sum_h \sum_l C_{hl} \cos 2\pi(hx + lz) \end{aligned}$$

where

$$C_{hl} = \sum_k (-1)^k |F_{hkl}|^2$$

Harker has also pointed out that the projection upon the XZ -plane of the vector connecting two atoms related by the operation of the two-fold screw axis will be represented by a vector from the origin to a maximum in this section. Thus one-half of the vector from the origin to such a maximum gives directly the distance and direction of an atom from one of the screw axes of the crystal. If the unit cell is chosen so as to place a center of symmetry at the origin the two independent screw axes fall at $x = \frac{1}{4}$, $z = \frac{1}{4}$, and at $x = \frac{3}{4}$, $z = \frac{1}{4}$ (A and B of Fig. 3). If then

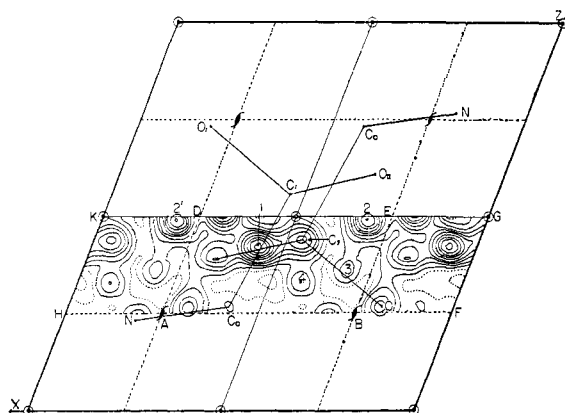


Fig. 3.—A plot of the function $P(x, \frac{1}{2}, z)$. Maxima indicate possible positions of atoms with respect to the two-fold screw axes of the crystal. Others (1,2,3,4) result from the interaction of atoms lying in nearly the same XZ -plane. Contour lines are in arbitrary units. Dotted lines indicate negative areas.

the scale of the plot of $P(x, \frac{1}{2}, z)$ is reduced by one-half and placed on the XZ -projection of the unit cell, with the origin of the plot coinciding with each of the independent screw axes, such maxima of the function $P(x, \frac{1}{2}, z)$ should represent projections on this plane of possible positions of the atoms. Such a plot having its origin coincident with the screw axis A is reproduced in section ADEB of Fig. 3. The corresponding plot with the screw axis B as origin is shown in sections HKDA and BEGF. It is thus evident, as pointed out in the discussion above, that the complete plot will not only contain peaks representing the positions of the atoms in the structure but also an equal number of additional peaks resulting from the inability of the function to distinguish between the two independent screw axes in the unit cell. Solution of the structure then requires a decision as to which of these peaks represent projections of atomic positions, and which are merely re-

productions of these peaks referred to the other screw axis.

If two or more atoms chance to lie in or near the same plane perpendicular to the two-fold axis, other maxima are to be expected. The reason for this readily may be seen by reference to Fig. 4. In this figure, A and B are two atoms lying in the same XZ -plane and A' and B' are atoms lying in corresponding positions resulting from the operation of the screw axis b . Vectors 1 and 2, which are components of distances between crystallographically identical atoms, A and A', B and B', connected by the operation of the screw axis, are of the sort discussed above, and will be the source of the kind of maxima already described. Vectors 3 and 4 are projections of the vectors connecting A with B' and B with A', and they will also give rise to maxima of a second sort which will lie exactly half-way between those of the first sort. Since these vectors are equal in magnitude and direction they will both contribute to the same "spurious" maximum which may therefore be expected to be of greater intensity than those corresponding to atomic positions in the crystal. Thus if the atoms A and B lie at nearly the same level and have approximately the same scattering powers, these "spurious" peaks will have twice the magnitude of the "real" ones. If the atoms are not at almost exactly the same level such a peak will be smaller and could easily be confused with one of the first sort.

The plot of $P(\frac{1}{2}, y, \frac{1}{2})$, Fig. 1, has already shown that different atoms of the glycine molecule lie in nearly the same XZ -plane and are probably divided into two groups, one of three atoms with $y = 0.35$ and one of two atoms with $y = 0.41$. Hence, in the case of glycine, the plot of $P(x, \frac{1}{2}, z)$, Fig. 3, will include "spurious" maxima of the sort described in the preceding paragraph. Let us now assume that the atoms O_I , O_{II} , C_I , C_{II} , and N are represented by the peaks shown in Fig. 3 (and by those obtained from these by the operation of the symmetry elements of the plot). The argument leading to this assignment will be given later. "Spurious" peaks are then shown at 1, 2, 3, and 4 in Fig. 3. The first (1) is the result of the superposition of two maxima, one lying half-way between C_I and C_{II} and the other between C_I and O_{II} . The second (2) is likewise derived from one between O_I and C_{II} and another between O_I and N, while peaks

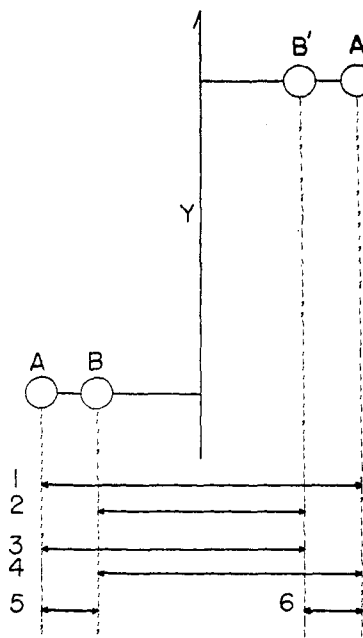


Fig. 4.—A diagrammatic sketch illustrating the origin of vectors giving rise to maxima in the projections of Figs. 3, 5 and 6.

3 and 4 are of simple origin. A peculiar case is presented by C_I which results from the approximate superposition of two maxima arising from different sources, one a "real" maximum resulting from the presence of an atom (carbon) and the other a "spurious" maximum falling midway between O_{II} and C_{II} . The peak at O_I is likewise complex, three different maxima contributing to it. Two of these are real maxima representing the positions of (a) the oxygen atom referred to one of the screw axes and (b) the nitrogen atom referred to the other screw axis. The third is the "spurious" maximum caused by the interaction of N and C_{II} .

When, as in Figs. 1 and 3, the plot of the function $P(x, \frac{1}{2}, z)$ suggests the presence of crystallographically different atoms lying in the same XZ -plane, confirmation of their positions may be obtained by plotting the expression

$$P(x, 0, z) = \sum_h \sum_k \sum_l |F_{hkl}|^2 \cos 2\pi(hx + lz)$$

which was originally derived by Harker for use with crystals possessing two-fold rotation axes, but which may also be used to detect the positions of atoms accidentally lying in the same XZ -plane. In such a plot the vector from the origin to a maximum will represent the direction of a line joining

such atoms and its magnitude will be very close to their actual interatomic distance. Vectors of this type are represented by 5 and 6 of Fig. 4. A plot of this function, $P(x,0,z)$, is shown in Fig. 5. The strong maximum halfway along the

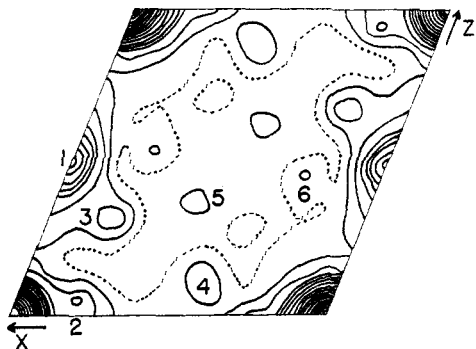


Fig. 5.—A plot of the function $P(x,0,z)$, in which the peaks represent vectorial distances between atoms lying in the same XZ -plane. Contour lines are in arbitrary units.

Z -axis (1) indicates the presence of two atoms in very nearly the same XZ -plane, and having very nearly the same x -parameter, separated at a distance of one-half the length of the Z -axis. Inspection of Fig. 3 shows a strong peak (2') lying one-quarter along the Z -axis from the maximum N, thus halfway between N and O_I , which is the same maximum referred to the other screw axis. These facts suggest the interpretation of the N maximum as representing the positions of two atoms with a "spurious" peak between them and it was the discovery of this possibility which eventually led to the correct assignment of atomic positions in the XZ -plane. Other peaks occurring in the plot $P(x,0,z)$, Fig. 5, are also readily explained in terms of the $P(x, \frac{1}{2}, z)$ diagram. Thus peak 2 represents the vectorial distances between N and C_{II} and between C_I and O_{II} ; peak 3 arises from the interactions of N with C_I and of C_{II} with O_{II} ; peak 4 represents the displacement between O_I and O_{II} ; and peaks 5 and 6 show the interactions of N with O_{II} and of O_I with C_{II} , respectively. The relative heights of the maxima are an approximate indication of the extent to which the atoms responsible for them approach the same XZ -plane in the crystal. As in the $P(0,y,0)$ diagram, Fig. 2, the strong peak at the origin merely expresses the coincidence of every atom with itself. It will be noticed that no such peak is found on the plot of $P(x, \frac{1}{2}, z)$, Fig. 3, because of

the translation along the Y -axis. If such a maximum were present it would indicate that two atoms were located on the same line parallel to this axis, an arrangement already shown not to exist by the plot of the function $P(0,y,0)$, Fig. 2.

The application of the information obtained from the plots of the various functions described above may now be indicated. The distribution of all the maxima of Fig. 3 over the projection of the unit cell is represented in Fig. 6. In this plot

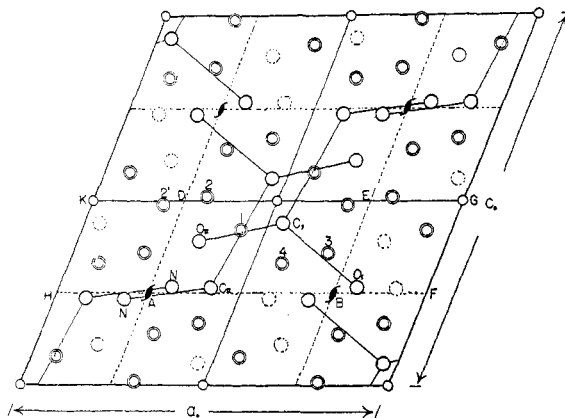


Fig. 6.—A projection on the XZ -plane showing the distribution of all maxima of Fig. 3 over the unit cell of glycine. Solid, single circles represent actual atomic positions; dotted circles, the positions of analogous peaks referred to a different screw axis. Double circles show the location of maxima produced solely by the interaction of atoms lying in the same XZ -plane. Atoms composing a molecule are joined by solid lines.

solid single circles show the positions of "real" peaks which represent actual atomic positions (as eventually determined), and dotted circles indicate the positions of analogous peaks referred to the other screw axis. Double circles represent "spurious" peaks produced by the interaction of atoms lying in or near the same XZ -plane. The interpretation of this plot, which provides directly the x - and z -parameters of the atoms of glycine, involves the identification of those peaks which represent atomic positions in the crystal. The resulting structure must also be capable of explaining all maxima found in this projection as well as those occurring on the various plots already described. A brief and more or less chronological outline of our procedure might be helpful to other investigators. In Fig. 6 there are eight peaks designated 1, 2, 3, 4, C_I , C_{II} , O_{II} , and N (which is identical with O_I). It was at first believed that these must correspond to the five atoms of glycine and three "spurious"

peaks, all of which might be identified in a purely analytical fashion, proceeding from the fact that there are only fifty-six possible arrangements for eight things taken five at a time. In addition, each peak is referred to two independent screw axes so that each may represent two crystallographically unrelated positions in the unit. Then for each group of five selected there are sixteen possible arrangements, thus making $16 \times 56 = 896$ "structures" in all to be tested. The crystallographically identical positions occupied by each peak may be represented by (1) xz ; $\bar{x}\bar{z}$; $x + \frac{1}{2}$, $z + \frac{1}{2}$; $\frac{1}{2} - x$, $\frac{1}{2} - z$; and the same positions referred to the other screw axis by (2) x , $z + \frac{1}{2}$; \bar{x} , $\frac{1}{2} - z$; $x + \frac{1}{2}$, z ; $\frac{1}{2} - x$, \bar{z} . The structure factors for even orders of ($h00$) and ($00l$) do not distinguish between these two sets of positions, so that the attempt was made to use the relative intensities of these reflections to select one group out of the possible fifty-six combinations, and then using ($h0l$) reflections to select the correct structure of the sixteen remaining. When these calculations were made it was found that no satisfactory agreement could be obtained with any of the possibilities, and this method of approach was therefore abandoned.

An attempt was next made to identify "spurious" peaks as lying half-way between others. As an aid in this selection a model of the molecule was prepared assuming accepted interatomic distances and bond angles established by previous structure investigations. The carbon-carbon and carbon-nitrogen separations were taken to be approximately the sums of the covalent radii,¹⁴ 1.54 and 1.47 Å., respectively, and the C-C-N bond angle was assumed to be close to the tetrahedral value ($109^{\circ}28'$). The atoms composing the carboxyl group and the adjacent alpha-carbon atom are known to be coplanar,¹⁵ with the angle between C-O bonds about 125° and the C-O distance 1.29 Å. The C-C bond makes equal angles with both C-O bonds. It is thus possible to construct a model of the glycine molecule in which the only feature not known within reasonable approximation is the orientation of the C-N bond with respect to the plane of the rest of the molecule. In fitting this model to the peaks in the projection all arrangements in which the plane of the molecule departs markedly from

the XZ-plane of the crystal are excluded by the plot of $P(\frac{1}{2}, y, \frac{1}{2})$, Fig. 1, already discussed. The model was used with a plot of the projection drawn to the same scale and in this way a selection of five out of the eight peaks was sought, but without success.

It was then recognized that peaks representing two atoms might be superimposed and this possibility was thoroughly investigated. The plot of the function $P(0, y, 0)$, Fig. 2, had already shown that no two atoms have the same x - and z -parameters, so that superposition could not result from this source. However, if the x - and z -parameters of two atoms were related in the manner of the crystallographically non-equivalent positions given above, namely, by a translation of one-half the unit distance parallel to the X- or Z-axis, these atoms would give rise to the same peak in the $P(x, \frac{1}{2}, z)$ plot. At this point the plot of $P(x, 0, z)$, Fig. 5, was prepared, the features of which have already been discussed. The strong maximum at $x = 0$, $z = \frac{1}{2}$ can be interpreted only as representing two atoms separated by one-half the length of the Z-axis and having almost exactly the same x - and y -parameters. Both thus give rise to the same peak on the $P(x, \frac{1}{2}, z)$ diagram, in which, therefore, four maxima represent the positions of five atoms, the four remaining peaks being of other origin. In the light of this discovery, another attempt was made to fit a model of the glycine molecule into the plot as described above. This time several arrangements were found which could explain the features of the various projections and at the same time involved no serious conflicts with the assumed spatial characteristics of the molecule itself. All but the correct one were eliminated readily by structure factor calculations and comparison with intensity data.

The positions of the maxima thus selected as representing atoms in the crystal of glycine correspond to the following atomic parameters

| | |
|-----------------|---------------------------|
| O _I | : $x = 0.81$, $z = 0.73$ |
| O _{II} | : $x = 0.33$, $z = 0.61$ |
| C _I | : $x = 0.54$, $z = 0.56$ |
| C _{II} | : $x = 0.58$, $z = 0.27$ |
| N | : $x = 0.81$, $z = 0.23$ |

Structure factors calculated for all ($h0l$) reflections using these parameters are listed in the sixth column of Table II. The atomic scattering powers used in these and all similar calculations are taken from the values given in the "International Tables for the Determination of Crystal

(14) L. Pauling and M. L. Huggins, *Z. Krist.*, **87**, 205 (1934).

(15) (a) L. Pauling and L. O. Brockway, *Proc. Natl. Acad. Sci.*, **20**, 336 (1935); (b) J. M. Robertson and I. Woodward, *J. Chem. Soc.*, 1817 (1936).

TABLE II
INTENSITIES AND STRUCTURE FACTORS FOR (*h*0*l*)
REFLECTIONS

| Indices | Obsd. intensities | | | <i>F</i> , obsd. | | <i>F</i> , calcd. from parameters | |
|--------------|-------------------|-------|----|------------------|----------|-----------------------------------|-------|
| | G. A. | R. B. | C. | G. A. | R. B. C. | Approx. ^a | Final |
| 10 $\bar{1}$ | 750 | 500 | | 11.9 | 10.6 | 10.1 | 17.1 |
| 101 | 1800 | 850 | | 25.9 | 18.6 | 34.4 | 33.5 |
| 002 | 2250 | 1500 | | 33.3 | 33.0 | -33.9 | -34.4 |
| 200 | 570 | 500 | | 15.2 | 15.1 | -18.6 | -15.1 |
| 20 $\bar{2}$ | 0 | 0 | | 0 | 0 | 2.9 | 5.1 |
| 10 $\bar{3}$ | 150 | 150 | | 9.1 | 9.3 | -10.8 | -11.1 |
| 30 $\bar{1}$ | 450 | 500 | | 17.0 | 19.1 | -11.3 | -15.2 |
| 202 | 750 | 500 | | 23.6 | 21.0 | 26.4 | 24.3 |
| 30 $\bar{3}$ | 150 | 150 | | 10.8 | 11.0 | 18.5 | 8.9 |
| 103 | 0 | 0 | | 0 | 0 | 4.7 | 1.0 |
| 301 | 0 | 0 | | 0 | 0 | 1.9 | 0.8 |
| 20 $\bar{4}$ | 0 | 0 | | 0 | 0 | 5.2 | -1.4 |
| 004 | 135 | 145 | | 11.0 | 11.7 | 10.6 | 11.6 |
| 40 $\bar{2}$ | 11 | 5 | | 3.1 | 2.1 | 16.5 | 1.1 |
| 400 | 30 | 15 | | 5.3 | 3.8 | -1.7 | -7.5 |
| 40 $\bar{4}$ | 210 | 200 | | 14.7 | 14.7 | 4.4 | 14.7 |
| 10 $\bar{5}$ | 0 | 0 | | 0 | 0 | -0.3 | 1.1 |
| 30 $\bar{5}$ | 120 | 135 | | 10.9 | 11.8 | 4.5 | 10.8 |
| 50 $\bar{1}$ | 26 | 7 | | 5.0 | 2.6 | 5.0 | -5.9 |
| 50 $\bar{3}$ | 180 | 153 | | 13.1 | 12.3 | 11.1 | 13.8 |
| 303 | 30 | 10 | | 5.3 | 3.0 | -3.7 | -3.3 |
| 204 | 210 | 135 | | 14.1 | 11.4 | -7.1 | -9.4 |
| 402 | 68 | 65 | | 7.7 | 7.6 | -6.0 | -7.2 |
| 105 | 14 | 10 | | 3.4 | 2.8 | -2.4 | -3.5 |
| 20 $\bar{6}$ | 38 | 27 | | 5.3 | 4.5 | 0.6 | 6.3 |
| 501 | 15 | 5 | | 3.1 | 1.8 | 1.4 | -2.9 |
| 50 $\bar{5}$ | 0 | 0 | | 0 | 0 | -4.2 | -1.8 |
| 40 $\bar{6}$ | 3 | 0 | | 1.2 | 0 | 2.8 | 1.7 |
| 006 | 555 | 300 | | 17.7 | 13.3 | -12.6 | -13.3 |
| 60 $\bar{2}$ | 0 | 0 | | 0 | 0 | -0.2 | -0.6 |
| 60 $\bar{4}$ | 60 | 40 | | 4.9 | 4.1 | 3.8 | 5.8 |
| 600 | 0 | 0 | | 0 | 0 | 5.3 | -0.1 |

^a Values calculated from preliminary parameters suggested by the Patterson-Harker projections.

Structures," Vol. II, pp. 571-574, with a Debye-Waller temperature factor having $B = 1.7 \times 10^{-16}$. Observed F 's of (*h*0*l*) planes were obtained from two independent visual estimations, by the two investigators, of the intensities of reflections occurring on series of rotation and oscillation photographs. Estimated intensities were corrected for secondary extinction by means of the approximation of Darwin,¹⁶ $\rho' = \rho / (1 + 2g\rho)$, in which ρ' is the observed integrated intensity and ρ is the integrated intensity for an ideally imperfect crystal. From the latter the values of F were computed. By applying a suitable factor to the observed intensities, the F -values were brought into the proper range to make possible a satisfactory agreement with those obtained from structure factor calculations.

(16) C. G. Darwin, *Phil. Mag.*, **43**, 800 (1922).

Estimated values of the intensities and the "observed F 's" calculated from them are given separately in the columns headed "G. A." and "R. B. C." Comparison of the observed values with those calculated from the atomic positions suggested by the Harker projections indicated need of considerable refinement of the atomic parameters.

In carrying out this refinement intensity data from (*0kl*) and (*hk0*) planes were also used. These data were obtained by visual comparison from series of Weissenberg photographs taken about the *a*- and *c*-axes, using Cu-K radiation. The scale of the intensities was adjusted and values of F were calculated in the manner described above. They are recorded in Tables III and IV.

TABLE III
INTENSITIES AND STRUCTURE FACTORS FOR (*0kl*) REFLECTIONS

| Indices | Intensities obsd. | <i>F</i> | |
|---------|-------------------|----------|--------|
| | | Obsd. | Calcd. |
| 020 | 1180 | 14.9 | 15.9 |
| 011 | 3340 | 28.7 | 28.5 |
| 021 | 65 | 4.4 | -11.0 |
| 031 | 2300 | 29.8 | -26.2 |
| 040 | 18380 | 86.4 | -73.1 |
| 041 | 0 | 0 | -0.1 |
| 002 | 4600 | 47.9 | -33.0 |
| 012 | 1110 | 23.9 | -19.1 |
| 022 | 360 | 14.0 | -13.2 |
| 051 | 200 | 10.3 | -9.2 |
| 032 | 790 | 13.1 | -14.4 |
| 060 | 395 | 16.4 | -17.8 |
| 042 | 430 | 17.5 | 16.7 |
| 061 | 41 | 5.6 | 4.3 |
| 052 | 144 | 10.9 | 12.9 |
| 013 | 57 | 7.1 | -5.8 |
| 023 | 755 | 26.2 | -21.6 |
| 071 | 430 | 19.9 | 14.6 |
| 062 | 430 | 20.4 | 19.0 |
| 033 | 32 | 5.6 | 6.6 |
| 080 | 505 | 22.7 | 17.4 |
| 043 | 40 | 6.5 | 6.1 |
| 081 | 0 | 0 | 1.5 |
| 072 | 41 | 6.8 | 5.7 |
| 053 | 0 | 0 | 2.1 |
| 063 | 115 | 12.1 | 16.7 |
| 082 | 0 | 0 | 3.8 |
| 091 | 1.4 | 1.3 | 4.8 |
| 004 | 115 | 12.2 | 11.6 |
| 014 | 54 | 8.3 | -7.9 |
| 024 | 29 | 6.1 | 7.7 |
| 034 | 1.4 | 1.3 | -5.1 |
| 073 | 6.5 | 3.0 | -4.9 |
| 0,10,0 | 0 | 0 | 3.8 |
| 092 | 6.5 | 3.0 | -6.6 |
| 044 | 6.5 | 3.0 | -6.2 |

TABLE III (Concluded)

| Indices | Intensities | | F | Calcd. | 260 | 250 | 13.4 | 16.0 |
|---------|-------------|-------|---|--------|--------|-----|------|-------|
| | obsd. | Obsd. | | | | | | |
| 0,10,1 | 0 | 0 | | 0.4 | 320 | 0 | 0 | 3.2 |
| 054 | 65 | 9.6 | | 9.8 | 080 | 400 | 17.4 | 17.5 |
| 083 | 29 | 6.4 | | -7.4 | 330 | 15 | 3.3 | 4.1 |
| 0,10,2 | 14 | 4.6 | | 3.8 | 180 | 400 | 18.1 | 23.6 |
| 064 | 65 | 9.6 | | -13.8 | 340 | 90 | 8.5 | 5.0 |
| 0,11,1 | 20 | 5.3 | | -7.5 | 270 | 34 | 5.2 | -3.7 |
| 093 | 0 | 0 | | -3.9 | 350 | 100 | 9.3 | -13.0 |
| 074 | 0 | 0 | | 3.7 | 190 | 0 | 0 | 3.5 |
| 015 | 0 | 0 | | -1.3 | 280 | 30 | 5.2 | 8.0 |
| 025 | 0 | 0 | | -0.1 | 360 | 30 | 5.3 | 4.9 |
| 0,11,2 | 0 | 0 | | -1.1 | 0,10,0 | 0 | 0 | 3.8 |
| 0,12,0 | 0 | 0 | | -0.5 | 400 | 30 | 5.4 | -6.6 |
| 035 | 0 | 0 | | 2.8 | 410 | 325 | 18.1 | -17.7 |
| 0,10,3 | 13.5 | 4.2 | | -9.9 | 1,10,0 | 0 | 0 | 5.3 |
| 0,12,1 | 0 | 0 | | -0.7 | 370 | 87 | 9.2 | 13.0 |
| 084 | 1.4 | 1.3 | | -2.5 | 420 | 10 | 3.1 | 2.8 |
| 045 | 0 | 0 | | 0.2 | 290 | 34 | 5.8 | -6.3 |
| 055 | 0 | 0 | | 3.1 | 430 | 325 | 18.3 | -18.8 |
| 0,12,2 | 29 | 5.8 | | -8.4 | 440 | 25 | 5.0 | 6.1 |
| 094 | 65 | 8.6 | | -7.5 | 380 | 35 | 5.9 | -5.5 |
| 0,11,3 | 0 | 0 | | 3.1 | 2,10,0 | 35 | 5.9 | -7.9 |
| 065 | 0 | 0 | | -1.5 | 1,11,0 | 150 | 12.3 | -14.4 |
| 0,13,1 | 0 | 0 | | -1.8 | 450 | 35 | 5.9 | 5.7 |
| 0,10,4 | 32 | 5.4 | | 8.1 | 390 | 10 | 3.1 | 4.8 |
| 0,13,2 | 0 | 0 | | -1.5 | 460 | 25 | 4.9 | -5.7 |
| 075 | 0 | 0 | | -2.3 | 0,12,0 | 0 | 0 | -0.5 |
| 0,12,3 | 25 | 4.6 | | 3.7 | 2,11,0 | 0 | 0 | -4.4 |
| 0,14,0 | 0 | 0 | | 4.7 | 1,12,0 | 33 | 5.5 | -8.3 |
| 006 | 430 | 18.6 | | -13.3 | 470 | 36 | 5.7 | 12.2 |
| 016 | 0 | 0 | | 1.8 | 3,10,0 | 35 | 5.5 | -8.8 |
| 085 | 0 | 0 | | 2.3 | 510 | 225 | 14.1 | -11.4 |
| 026 | 0 | 0 | | -2.7 | 520 | 100 | 9.3 | -10.5 |
| 0,14,1 | 0 | 0 | | -0.3 | 480 | 25 | 4.5 | -5.2 |
| 036 | 0 | 0 | | -0.8 | 530 | 30 | 4.9 | 5.7 |
| 0,11,4 | 0 | 0 | | -3.1 | 2,12,0 | 33 | 5.1 | -10.1 |
| 046 | 395 | 14.4 | | 9.8 | 1,13,0 | 0 | 0 | -3.3 |
| | | | | | 540 | 10 | 2.7 | 2.6 |
| | | | | | 3,11,0 | 30 | 4.5 | 9.3 |
| | | | | | 490 | 0 | 0 | 0.5 |
| | | | | | 550 | 100 | 8.2 | 10.1 |
| | | | | | 2,13,0 | 33 | 4.4 | 4.0 |
| | | | | | 0,14,0 | 0 | 0 | 4.8 |
| | | | | | 560 | 30 | 4.2 | 8.8 |
| | | | | | 1,14,0 | 0 | 0 | 5.8 |
| | | | | | 4,10,0 | 0 | 0 | 4.6 |
| | | | | | 3,12,0 | 0 | 0 | 0.9 |
| | | | | | 570 | 0 | 0 | 1.1 |
| | | | | | 2,14,0 | 0 | 0 | 0.6 |
| | | | | | 3,13,0 | 0 | 0 | -2.1 |
| | | | | | 600 | 0 | 0 | -0.7 |

TABLE IV

INTENSITIES AND STRUCTURE FACTORS FOR (*hk*0) REFLECTIONS

| Indices | Intensities | | F | Calcd. |
|---------|-------------|-------|---|--------|
| | Obsd. | Obsd. | | |
| 020 | 650 | 9.7 | | 15.9 |
| 110 | 1000 | 14.6 | | 19.1 |
| 120 | 2000 | 25.7 | | -32.1 |
| 130 | 1500 | 23.0 | | -29.2 |
| 040 | 5000 | 75.2 | | -73.1 |
| 140 | 1350 | 24.2 | | -31.5 |
| 200 | 500 | 14.3 | | -19.6 |
| 210 | 300 | 11.0 | | 12.4 |
| 220 | 300 | 11.4 | | -10.6 |
| 150 | 0 | 0 | | -4.8 |
| 230 | 500 | 15.8 | | 16.4 |
| 060 | 250 | 11.2 | | -17.7 |
| 240 | 36 | 4.3 | | 5.6 |
| 160 | 36 | 4.4 | | 3.4 |
| 250 | 0 | 0 | | 0.6 |
| 170 | 500 | 18.7 | | 23.1 |
| 310 | 125 | 9.3 | | 11.0 |

It is interesting to note that the values thus obtained are in good general agreement with the "absolute F's," based upon quantitative spectrometric measurements, published by Hengstenberg and Lenel.¹⁰ Their values (H. and L.) for the thirty-three reflections reported in their paper are compared with our "observed F's" (A. and C.) in the following columns.

| Indices | F | | Indices | F | |
|---------|-----------|-----------|---------|-------------------|-----------|
| | H. and L. | A. and C. | | H. and L. | A. and C. |
| 020 | 13.6 | 14.9 | 032 | 21.8 | 13.1 |
| 011 | 29.2 | 28.7 | 150 | 0 | 0 |
| 110 | 14.6 | 14.6 | 230 | 17.5 | 15.8 |
| 021 | w | 4.4 | 060 | 17.5 | 16.4 |
| 120 | 28.1 | 25.7 | 042 | 17.9 | 17.5 |
| 031 | 29.5 | 29.8 | 240 | w | 4.3 |
| 130 | 29.5 | 23.0 | 061 | 0 | 5.6 |
| 040 | 43.0 | 75.2 | 160 | w | 4.4 |
| 041 | w | 0 | 052 | 13.3 | 10.9 |
| 002 | 34.6 | 33.0 | 250 | w | 0 |
| 140 | 26.2 | 24.2 | 013 | w | 7.1 |
| 012 | 25.5 | 23.9 | 023 | 28.1 ^a | 26.2 |
| 200 | 13.2 | 14.3 | 071 | 15.6 | 19.9 |
| 022 | 14.2 | 14.0 | 170 | 19.5 | 18.7 |
| 210 | 13.0 | 11.0 | 062 | 19.3 | 20.4 |
| 220 | 12.2 | 11.4 | 260 | 15.8 | 13.4 |
| 051 | 10.2 | 10.3 | | | |

^a This value, believed by H. and L. to be an error, appears to be confirmed by our observation.

Data from Tables III and IV were used to assign tentative γ -parameters to the atoms. In the discussion of the plot of $P(\frac{1}{2}, \frac{1}{2})$, Fig. 1, it was pointed out that these parameters could not be far from 0.35 and 0.41. Values in this neighborhood were therefore investigated with the aid of intensity data from seven even orders of $(0k0)$ together with considerations regarding the size and shape of the molecule already discussed. The following tentative values of the γ -parameter were selected: O_I , 0.405; O_{II} , 0.355; C_I , 0.380; C_{II} , 0.355; N, 0.405.

In making the final adjustments of the atomic parameters from those suggested by the plots of the various sections through the Patterson diagram intensity data from $(h0l)$ reflections were first employed. Plots of the structure factor, $\cos 2\pi(hx + lz)$, were prepared for each $(h0l)$ plane and the atomic positions were indicated upon them. Comparison of calculated F 's with those observed for planes such as $(30\bar{5})$, (600) , $(40\bar{2})$, and $(40\bar{4})$ immediately indicated the directions in which the atoms must be shifted in order to improve the agreement. As the process of refinement proceeded it became more and more difficult to find a change in parameter which would improve existing discrepancies without introducing new ones, and in the final stages simultaneous displacements of several or all of the atoms by very small amounts were generally necessary. In such cases the molecular model already mentioned served as a useful guide in avoiding displacements, sometimes suggested by intensity data, which would have resulted in

serious distortion of the molecule. A point was finally reached at which there was no evident possibility of further improving the agreement among $(h0l)$ reflections. Structure factors for all $(0kl)$ and $(hk0)$ planes were then calculated and compared with observed scattering powers. The general agreement appeared quite satisfactory and plots of the $(0kl)$ structure factors made for many planes failed to suggest changes which would lead to improvement. Interatomic distances and bond angles were also in accord with accepted values within the limits of accuracy imposed by the data. It was found, however, that the carboxyl carbon was displaced from the plane containing the two oxygen atoms and the alpha-carbon atom by slightly more than 0.05 Å. Since it was thought very unlikely that a significant displacement of this nature existed in the glycine molecule, the structure was subjected to further investigation which resulted in slight changes in the parameters of all atoms except the carboxyl carbon and in significant improvement in the agreement among $(0kl)$ and $(hk0)$ intensity data. Positions of the atoms finally established as giving best agreement between observed and calculated scattering powers are defined by the following parameters

| | |
|----------|-------------------------------------|
| O_I | : $x = 0.805, y = 0.410, z = 0.740$ |
| O_{II} | : $x = 0.360, y = 0.360, z = 0.610$ |
| C_I | : $x = 0.575, y = 0.380, z = 0.560$ |
| C_{II} | : $x = 0.565, y = 0.365, z = 0.280$ |
| N | : $x = 0.800, y = 0.410, z = 0.245$ |

Comparison of the observed scattering powers with those calculated from these parameters for all prism planes is shown in Tables II, III, and IV. With few exceptions the agreement is very satisfactory. In making visual estimates of intensities by comparison of reflections found on photographs taken with different known exposures, little difficulty was experienced in obtaining concordant results except when the spots were at either extreme of the intensity scale, or when they differed markedly in their shape or appearance. An example is (040) , by far the most intense reflection observed. The F value calculated from the intensity estimated on $(0kl)$ photographs (Table III) is 15% higher than that obtained from $(hk0)$ negatives (Table IV). Although the relative scattering powers of strongly reflecting planes may be estimated so as to be entirely comparable among themselves, it seems difficult to be certain of their absolute values which are estab-

lished by the majority of the intensities observed. It is to be noted that the arbitrary "extinction coefficients" generally applied to improve the agreement among intense reflections may be more an expression of incorrect estimation of intensity than of extinction in the crystal. Similarly, although the estimated scattering powers of very weakly reflecting planes were generally reproducible among themselves, some difficulty was experienced in relating them to those of the stronger reflections. For example, in Table III, estimated intensities of 20 or below really mean that the spots were barely visible, and hence only slightly stronger than "absent" reflections. A most peculiar case was the reflection from the plane (006), which was conspicuous on all films on which it occurred, not only because of its great intensity but also because of its sharpness and of its form resulting from the complete resolution of the Cu-K α doublet. This splitting of the reflection introduced some uncertainty into the comparison of its intensity with those of unresolved spots, but repeated trials based upon many comparisons appeared to establish its absolute F-value as not far from 17. Although this is appreciably higher than that calculated from the atomic parameters, it seems possible that this abnormal intensity may be real and it may be attributed in part to the orientation of this plane in the crystal.⁶ Thus the fact that it stands very nearly perpendicular to the C-C bond and to the shortest (2.76 Å.) hydrogen bond might lead to the expectation of increased intensity and definition.

Table V lists the intensities of 124 (*hkl*) reflections used in the preparation of the Patterson-Harker projections. Although the accuracy of their estimation is certainly not as great as that of the prism reflections, the general agreement

| | | | |
|--------------|------|------|-------|
| 31 $\bar{2}$ | 924 | 23.9 | -21.4 |
| 31 $\bar{3}$ | 39 | 5.3 | - 7.6 |
| 113 | 350 | 16.3 | -15.2 |
| 11 $\bar{4}$ | 118 | 9.8 | - 5.8 |
| 41 $\bar{2}$ | 28 | 5.0 | 2.2 |
| 31 $\bar{4}$ | 468 | 20.7 | 23.5 |
| 41 $\bar{3}$ | 59 | 7.3 | 8.7 |
| 312 | 118 | 10.6 | - 9.9 |
| 41 $\bar{4}$ | 118 | 10.6 | -10.8 |
| 11 $\bar{5}$ | 39 | 6.0 | - 5.5 |
| 51 $\bar{2}$ | 350 | 12.1 | 12.8 |
| 51 $\bar{1}$ | 39 | 6.0 | - 6.4 |
| 214 | 39 | 5.9 | - 6.3 |
| 412 | 98 | 9.0 | 9.9 |
| 21 $\bar{6}$ | 39 | 5.4 | - 3.3 |
| 31 $\bar{6}$ | 59 | 6.4 | - 5.0 |
| 511 | 39 | 4.9 | - 4.3 |
| 41 $\bar{6}$ | 174 | 9.7 | 9.4 |
| 121 | 118 | 5.9 | - 5.9 |
| 12 $\bar{2}$ | 2800 | 30.3 | 47.1 |
| 22 $\bar{1}$ | 350 | 11.2 | 12.8 |
| 22 $\bar{2}$ | 700 | 17.4 | 13.9 |
| 122 | 468 | 15.1 | 14.6 |
| 221 | 308 | 12.6 | 11.3 |
| 12 $\bar{3}$ | 39 | 4.7 | 2.2 |
| 32 $\bar{1}$ | 28 | 4.1 | 5.2 |
| 32 $\bar{2}$ | 470 | 17.1 | -17.7 |
| 222 | 48 | 6.0 | 5.4 |
| 12 $\bar{4}$ | 118 | 9.8 | -10.9 |
| 22 $\bar{4}$ | 45 | 6.2 | - 3.3 |
| 42 $\bar{1}$ | 188 | 12.9 | -14.1 |
| 42 $\bar{2}$ | 0 | 0 | - 0.9 |
| 223 | 70 | 8.1 | - 9.6 |
| 124 | 700 | 25.9 | -27.9 |
| 32 $\bar{6}$ | 28 | 4.3 | 3.1 |
| 13 $\bar{1}$ | 59 | 3.3 | 1.0 |
| 13 $\bar{2}$ | 350 | 10.8 | 11.5 |
| 23 $\bar{1}$ | 700 | 15.9 | 11.6 |
| 23 $\bar{2}$ | 1120 | 22.0 | -18.1 |
| 132 | 175 | 9.3 | - 8.7 |
| 231 | 350 | 13.5 | -12.8 |
| 13 $\bar{3}$ | 235 | 11.3 | 11.6 |
| 33 $\bar{1}$ | 92 | 7.5 | - 4.7 |
| 33 $\bar{2}$ | 188 | 11.0 | 9.3 |
| 232 | 118 | 9.3 | - 9.6 |
| 33 $\bar{3}$ | 20 | 3.8 | - 6.4 |
| 133 | 70 | 7.3 | -11.3 |
| 23 $\bar{4}$ | 175 | 12.0 | 13.2 |
| 43 $\bar{2}$ | 78 | 8.4 | 10.0 |
| 33 $\bar{4}$ | 235 | 14.3 | -14.9 |
| 43 $\bar{3}$ | 154 | 11.8 | 11.4 |
| 43 $\bar{4}$ | 188 | 13.0 | -14.5 |
| 53 $\bar{2}$ | 28 | 4.9 | - 5.9 |
| 53 $\bar{1}$ | 28 | 4.7 | - 0.5 |
| 432 | 78 | 7.5 | 11.0 |
| 23 $\bar{6}$ | 62 | 6.2 | - 5.3 |
| 43 $\bar{6}$ | 280 | 10.6 | 11.1 |
| 63 $\bar{1}$ | 48 | 4.1 | 0.6 |
| 14 $\bar{1}$ | 700 | 11.1 | -10.8 |
| 141 | 1400 | 22.5 | -24.9 |
| 14 $\bar{2}$ | 468 | 12.4 | 15.9 |
| 142 | 350 | 13.2 | 17.5 |

TABLE V

INTENSITIES AND STRUCTURE FACTORS FOR (*hkl*) REFLECTIONS USED IN THE PREPARATION OF PATTERSON-HARKER PROJECTIONS

| Indices | Intensities | | F^a | |
|--------------|-------------|-------|--------|--|
| | Obsd. | Obsd. | Calcd. | |
| 11 $\bar{1}$ | 6.5 | 1.1 | 5.4 | |
| 111 | 235 | 8.4 | 14.9 | |
| 11 $\bar{2}$ | 154 | 7.3 | 5.1 | |
| 21 $\bar{1}$ | 235 | 9.2 | -10.7 | |
| 21 $\bar{2}$ | 350 | 11.8 | - 9.6 | |
| 112 | 350 | 12.9 | 10.3 | |
| 211 | 280 | 12.0 | 13.0 | |
| 11 $\bar{3}$ | 560 | 17.3 | 13.2 | |
| 31 $\bar{1}$ | 154 | 9.6 | - 8.7 | |

TABLE V (Concluded)

| Indices | Intensities | Obsd. | F^a | Calcd. |
|-----------------|-------------|-------|-------|--------|
| | Obsd. | | | |
| 241 | 59 | 5.5 | - | 4.2 |
| 14 $\bar{3}$ | 118 | 7.9 | - | 8.1 |
| 34 $\bar{1}$ | 175 | 10.2 | - | 13.2 |
| 34 $\bar{2}$ | 39 | 5.0 | - | 5.5 |
| 242 | 188 | 11.6 | - | 7.8 |
| 34 $\bar{3}$ | 118 | 9.2 | - | 9.1 |
| 14 $\bar{4}$ | 118 | 9.6 | - | 8.8 |
| 44 $\bar{2}$ | 14 | 3.4 | - | 0.8 |
| 34 $\bar{4}$ | 39 | 5.8 | - | 6.8 |
| 342 | 118 | 10.0 | - | 10.2 |
| 44 $\bar{4}$ | 188 | 12.4 | - | 13.1 |
| 24 $\bar{5}$ | 47 | 6.2 | - | 3.8 |
| 34 $\bar{5}$ | 118 | 9.7 | - | 8.4 |
| 54 $\bar{3}$ | 154 | 10.6 | - | 10.9 |
| 244 | 78 | 7.2 | - | 7.1 |
| 442 | 39 | 4.8 | - | 8.4 |
| 15 $\bar{1}$ | 87 | 5.8 | - | 8.1 |
| 151 | 78 | 5.9 | - | 4.1 |
| 161 | 154 | 9.2 | - | 10.6 |
| 26 $\bar{1}$ | 28 | 4.1 | - | 2.8 |
| 18 $\bar{1}$ | 28 | 4.5 | - | 5.6 |
| 35 $\bar{1}$ | 78 | 7.6 | - | 8.9 |
| 181 | 78 | 7.5 | - | 14.6 |
| 36 $\bar{1}$ | 28 | 4.7 | - | 7.3 |
| 28 $\bar{1}$ | 28 | 4.7 | - | 3.7 |
| 271 | 59 | 6.9 | - | 9.0 |
| 281 | 31 | 5.1 | - | 6.4 |
| 1,10,1 | 39 | 5.9 | - | 7.6 |
| 46 $\bar{1}$ | 78 | 8.4 | - | 10.5 |
| 1,11, $\bar{1}$ | 39 | 5.9 | - | 2.4 |
| 55 $\bar{1}$ | 28 | 4.5 | - | 5.3 |
| 15 $\bar{2}$ | 350 | 11.5 | - | 10.0 |
| 16 $\bar{2}$ | 235 | 10.6 | - | 15.6 |
| 152 | 53 | 5.4 | - | 7.5 |
| 26 $\bar{2}$ | 280 | 12.6 | - | 24.0 |
| 17 $\bar{2}$ | 235 | 11.9 | - | 15.5 |
| 35 $\bar{2}$ | 118 | 8.9 | - | 15.1 |
| 27 $\bar{2}$ | 59 | 6.2 | - | 9.1 |
| 18 $\bar{2}$ | 59 | 6.4 | - | 10.5 |
| 36 $\bar{2}$ | 39 | 5.3 | - | 7.3 |
| 182 | 59 | 6.8 | - | 13.7 |
| 262 | 70 | 7.4 | - | 8.6 |
| 29 $\bar{2}$ | 59 | 6.9 | - | 10.5 |
| 45 $\bar{2}$ | 59 | 6.9 | - | 9.4 |
| 272 | 59 | 6.9 | - | 7.6 |
| 2,10, $\bar{2}$ | 78 | 8.0 | - | 16.1 |
| 352 | 39 | 5.6 | - | 10.2 |
| 1,10,2 | 39 | 5.6 | - | 9.6 |
| 55 $\bar{2}$ | 39 | 5.2 | - | 10.1 |
| 49 $\bar{2}$ | 50 | 5.6 | - | 10.8 |
| 382 | 50 | 5.6 | - | 11.3 |
| 2,11,2 | 39 | 4.4 | - | 3.1 |
| 17 $\bar{1}$ | 84 | 7.1 | - | 2.7 |
| 15 $\bar{3}$ | 235 | 12.8 | - | 9.1 |

^a After making the Patterson-Harker plots a slight error was discovered in the calculation of some of the "Observed F's," but the corrections were too small to have an appreciable effect upon the positions of maxima in the diagrams. Corrected values are given in this table.

between the observed and calculated F's for these planes is interesting as additional confirmation of the structure.

Discussion of the Structure

The positions of the atoms of glycine in a unit cell are shown in Fig. 7a, which is a projection of these positions upon the XZ -plane, and in Fig. 7b, which is a similar projection made parallel to the a -axis of the crystal. The arrangement is found to consist of nearly flat glycine molecules bound together by hydrogen bonds to form discrete layers (A, B, C, D) parallel to the XZ -plane. Within the molecule interatomic distances are C_I-O_I , 1.27 Å.; C_I-O_{II} , 1.25 Å.; C_I-C_{II} , 1.52 Å.; and $C_{II}-N$, 1.39 Å. We would estimate that the probable error of these values (taking into account all of the sources of error which might enter) is ≈ 0.02 Å.; and we feel that it is very unlikely that any of the reported interatomic distances is in error by as much as 0.04 Å. The C-O distances, 1.25 and 1.27 Å., are in satisfactory agreement with those found in formic acid^{12a} (1.29 Å.) and in oxalic acid dihydrate^{12b} (1.24-1.30 Å.), structures which likewise involve the resonance associated with the carboxyl group. The difference, 0.02 Å., between the C-O distances is within the limit of accuracy of their determination, so that no significance is to be attached to it. The CH_2-N distance, 1.39 Å., is much shorter than that anticipated (1.47 Å.) and, in fact, agrees within the limit of the probable errors with that found (1.41 Å.) in diketopiperazine,⁶ "glycine anhydride." The C-C distance found in glycine, 1.52 ± 0.02 Å., is very close to the normal value (1.54 Å.), whereas in diketopiperazine this distance was found to be surprisingly short (1.47 Å.).

The general shape of the glycine molecule is shown in Fig. 8(A) which is a view perpendicular to a plane passed through the two oxygen atoms and the alpha-carbon. The departure of the carboxyl carbon from this plane, 0.013 Å., is well below the limit of accuracy attained, so that the coplanarity of the carboxyl group and its adjacent carbon atom may be considered to be strictly maintained. All bond angles are accurate within about 3°. The O-C-O angle, 122°, and the equal angles of 119° made by each C-O with the C-C bond are in accord with those predicted from the similar structures mentioned. The C-C-N angle, 112°, is reasonably close to tetrahedral

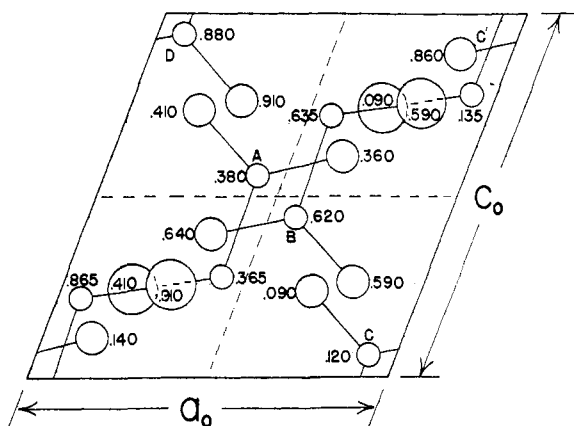


Fig. 7a.—A projection of the atomic positions in a glycine crystal upon the XZ -plane of the unit cell. Numerals show the y -parameters of the atoms. Letters identify molecules in subsequent drawings.

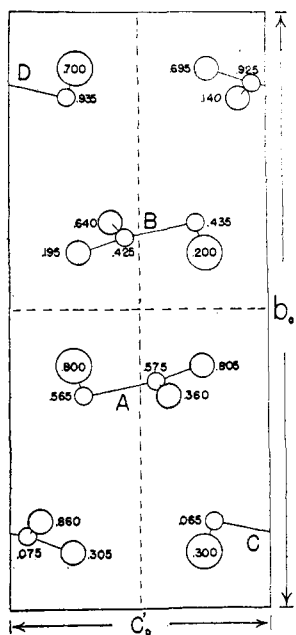


Fig. 7b.—A unit cell of glycine viewed parallel to the a -axis of the crystal. Numerals show the x -parameters of the atoms.

($109^{\circ}28'$). Fig. 8 (B) is a view parallel to the plane of A showing the extent (0.268 \AA .) to which the nitrogen atom departs from coplanarity with the rest of the molecule.

Interatomic distances between molecules of glycine may be summarized as follows:

| | | Same layer, \AA . | Between layers A and B, \AA . | Between layers A and C, \AA . |
|------------------------|-------------------|----------------------------|--|--|
| $\text{NH}_2\text{-O}$ | N-O_I | 2.76 | 2.93 | .. |
| | N-O_{II} | 2.88 | 3.05 | .. |

| | | | | |
|---------------------------|-------------------------------|------|------|------|
| $\text{CH}_2\text{-O}$ | $\text{C}_{II}\text{-O}_I$ | 3.65 | 3.27 | 3.52 |
| | $\text{C}_{II}\text{-O}_{II}$ | 3.41 | 3.34 | 3.35 |
| $\text{CH}_2\text{-NH}_2$ | $\text{C}_{II}\text{-N}$ | 3.87 | 3.87 | .. |
| $\text{CH}_2\text{-CH}_2$ | $\text{C}_{II}\text{-C}_{II}$ | .. | 4.22 | 4.05 |

It is of interest to compare these values with analogous distances found between molecules of diketopiperazine,⁶ namely

| | Same layer, \AA . | Between adjacent layers, \AA . |
|---------------------------|----------------------------|---|
| NH-O | 2.85 | .. |
| $\text{CH}_2\text{-O}$ | 3.32 | 3.33 |
| $\text{CH}_2\text{-NH}$ | 3.55 | .. |
| $\text{CH}_2\text{-CH}_2$ | 3.96 | 3.96 |

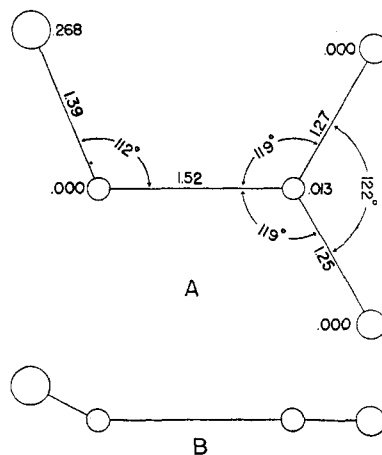


Fig. 8.—The glycine molecule viewed (A) perpendicular to a plane containing the two oxygen and the α -carbon atoms, and (B) parallel to this plane.

There is little doubt that each molecule of glycine is connected by hydrogen bonds (2.76 and 2.88 \AA .) to its four nearest neighbors in adjacent unit cells, thus forming a two-dimensional network throughout the crystal parallel to its XZ -plane. Such a single layer is represented in Fig. 9, which is a packing drawing showing one molecule (A) of glycine in four neighboring unit cells. In this and other packing drawings CH_2 is given a radius of 2.0 \AA ., NH_2 , 1.8 \AA ., and O , 1.35 \AA .. Hydrogen bonds, corresponding to the close approach of O and NH_2 , are indicated by double dashed lines. The "contacts" between O and CH_2 , 3.41 \AA ., and between CH_2 and NH_2 , 3.87 \AA ., are in good agreement with values suggested by other structures.

The closest approach of atoms in molecules composing different layers in the crystal is found between those layers which are connected by the centers of symmetry at $z = 0$ and $\frac{1}{2}$. Figure 10 is a view similar to Fig. 7b but extended to

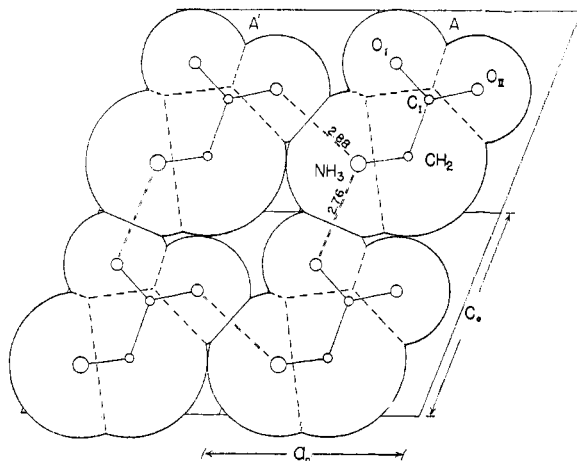


Fig. 9.—A packing drawing showing the linking of molecules into single layers parallel to the XZ -plane by means of hydrogen bonds, indicated by double dashed lines. One molecule, A, in each of four adjacent cells is shown.

show two unit cells and some of the molecules adjacent to them. It is seen that oxygen and nitrogen atoms in molecules of layer A (xyz) are turned toward and approach closely nitrogen and oxygen atoms of layer B ($\bar{x}\bar{y}\bar{z}$) above them. These N to O distances, 2.93 and 3.05 Å., are 0.1–0.2 Å. shorter than the sum of the “radii” of the groups concerned. One interpretation of these dimensions might therefore be that the shorter of the distances, 2.93 Å., represents the formation of a hydrogen bond between N and O_I and that the 3.05 Å. distance has no significance as far as bond formation is concerned. In such a structure there would be a distinct difference between the oxygen atoms, one (O_I) forming two hydrogen bonds to nitrogen and the other (O_{II}) only one. An arrangement of this sort would imply that the carboxyl hydrogen was attached to O_{II} which forms only one hydrogen bond. A hydrogen so attached would be expected to be coplanar with the atoms of the carboxyl group. The parameters, $x = 0.165$, $y = 0.335$, $z = 0.480$, may be assigned so as to place a hydrogen atom in the plane of the molecule, at an O–H distance of 1.03 Å. and with an angle H–O–C equal to 126° . It would then be 2.04 Å. from the nitrogen atom of the adjacent molecule. This structure appears to be the only plausible one if the glycine crystal is made up of non-polar molecules. However, the positions of the atoms, as established by the X-ray data, fail to show any differences in the oxygen atoms such as would be anticipated from this arrangement. The 3.05 Å. distance

between O_{II} and nitrogen also would remain unexplained.

An alternative and more satisfactory interpretation is suggested by the hydrogen bond angles and distances between the atoms. Thus the angle between the 2.76 and 2.88 Å. hydrogen bonds is $108\frac{1}{2}^\circ$, or nearly the tetrahedral angle, and both of these bonds form nearly equal angles (118 and 120°) with that joining nitrogen and carbon. These facts suggest the possibility of the presence of a hydrogen atom attached by a covalent bond to nitrogen in the fourth tetrahedral position and so placed as to be able to engage with about equal ease in the formation of a hydrogen bond to either O_I or O_{II} of the layer above. Parameters for hydrogen ($x = 0.795$, $y = 0.490$, $z = 0.245$) were therefore selected which placed it in the plane bisecting the angle between the hydrogen bonds (2.76 and 2.88 Å.) and at a distance 0.99 Å. from the nitrogen atom and almost directly above it such that the angle H–N– $C_{II} = 109^\circ$. Distances between this point and oxygen atoms O_I and O_{II} in the layer above are then 2.34 and 2.22 Å., respectively. These relationships suggest that in the glycine crystal the molecule has the “zwitter-ion” structure, $H_3N^+CH_2COO^-$, two of the three hydrogen atoms attached to nitrogen forming strong hydrogen bonds to oxygen atoms in the same layer and the third sharing its bond-forming capacity nearly equally between two nearest oxygen atoms in the adjacent layer. The glycine crystal would thus be made up of double layers of molecules held firmly intact by hydrogen bonds between nitrogen and oxygen atoms and also by the electrostatic forces effective between these same atoms which constitute the positive and negative extremes of the polar molecule. These double layers, AB and CD, are clearly seen in Fig. 10. Double solid lines, representing hydrogen bonds between molecules in the same layer, are tapered to indicate that they connect atoms in molecules in front of or behind those shown. Double dashed lines represent the “shared” hydrogen bonds responsible for the structure of the double layers.

The positions of the atoms in a portion of one such double layer extending through four adjacent unit cells are shown in Fig. 11a. As in each single layer, distances between CH_2 and O, 3.34 and 3.27 Å., and between CH_2 and NH_3 , 3.87 Å., are in accord with accepted values for atomic packing. These contacts between molecules composing a

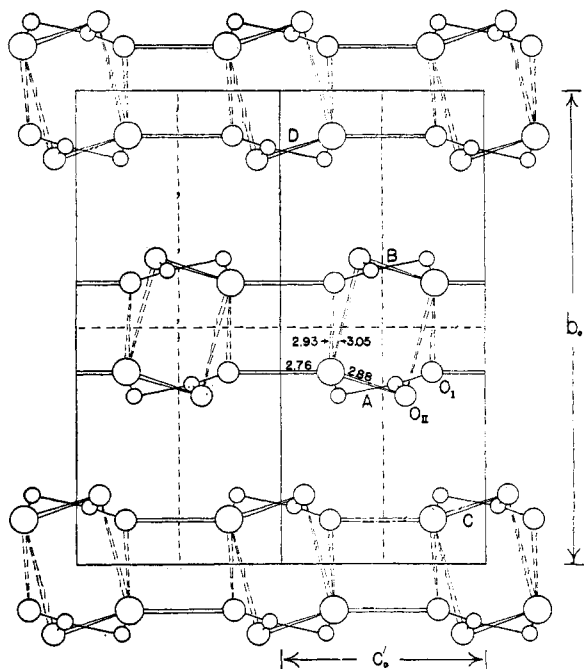


Fig. 10.—A view of the glycine structure parallel to the *a*-axis of the crystal, showing single and double layers of molecules held together by hydrogen bonds. The 3.05 Å. bonds connect atoms of the molecules A and B, whereas the 2.93 Å. bonds connect the N and O_I atoms of A with the O_{II} and N atoms of the molecule behind B. The 2.88 Å. bonds are likewise tapered to indicate that they connect with atoms in molecules in front of or behind those shown.

double layer are brought out in Fig. 11b, which shows four molecules of layer A and two molecules of layer B above them. Each oxygen atom is in contact with the CH₂ group of the molecule above or below, and each is bound to a nitrogen atom in a molecule of the opposite layer, O_{II} to one in the same unit cell (3.05 Å.) and O_I to one in an adjacent cell (2.93 Å.).

Between layers of molecules A and C, connected geometrically by the diagonal glide plane, only van der Waals forces are involved. The nitrogen atom is buried in the AB and CD double layers, so that contacts between A and C take place between oxygen atoms and the non-polar CH₂ group or between two CH₂ groups in different layers. Thus each CH₂ group in layer A rests between two CH₂ groups in layer C at a distance of 4.05 Å. Two oxygen neighbors, each in a different molecule, are distant 3.52 and 3.38 Å.

Some of the general relationships among the molecules of glycine may best be seen in Figs. 12a and 12b, which show views of the structure paral-

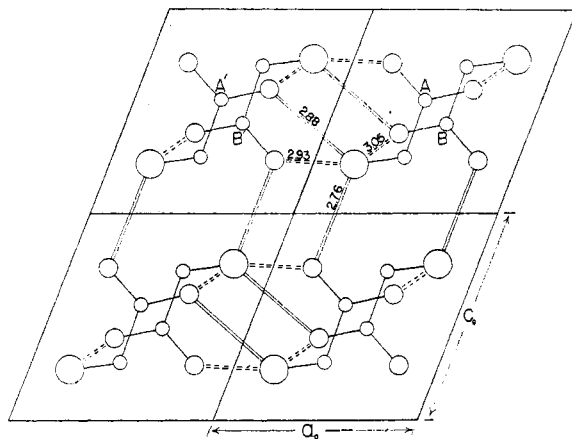


Fig. 11a.—A projection upon the XZ-plane showing one double layer of molecules in the crystal of glycine. Corresponding molecules in adjacent unit cells are linked together by hydrogen bonds (double lines) into continuous single sheets. These, in turn, are held together by bonds between O and NH₂ (double dashed lines) to form firmly knit double layers. The molecules of the layer shown are grouped about the centers of symmetry at $\frac{1}{2}, \frac{1}{2}, \frac{1}{2}$. A second such layer, not shown, is built about the centers at the origin.

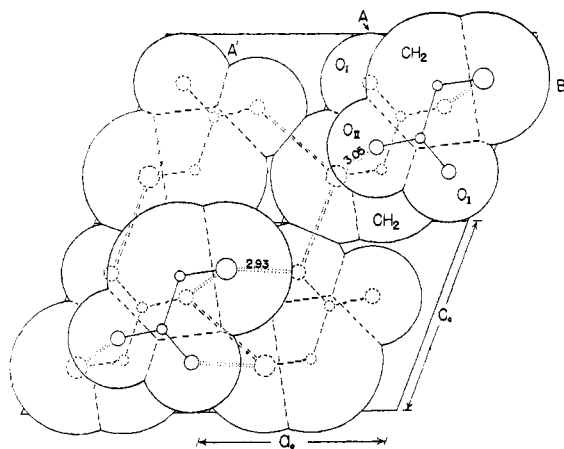


Fig. 11b.—A packing drawing of some of the molecules of Fig. 11a.

lel to the *c*-axis of the crystal. It is especially to be noted that the arrangement of the molecules is such that the nitrogen atom is closest to O_I of one molecule and to O_{II} of a neighboring one, a fact which fails to confirm the assumptions implied in a previous study of the structure of glycine⁹ in which nitrogen was placed so as to share its bonding capacity between the two oxygens of a molecule above or below it in a double layer. It seems that the directed forces resulting from the formation of hydrogen bonds having definite orientation with respect to the molecule are the

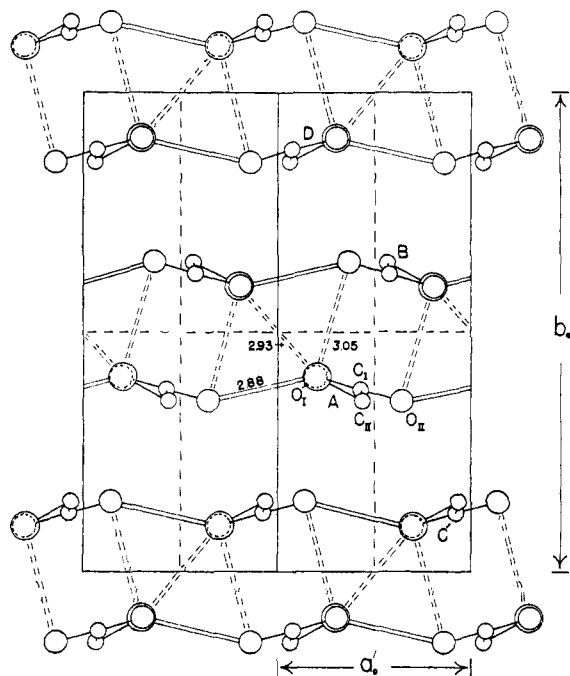


Fig. 12a.—A view of the glycine structure parallel to the c -axis of the crystal.

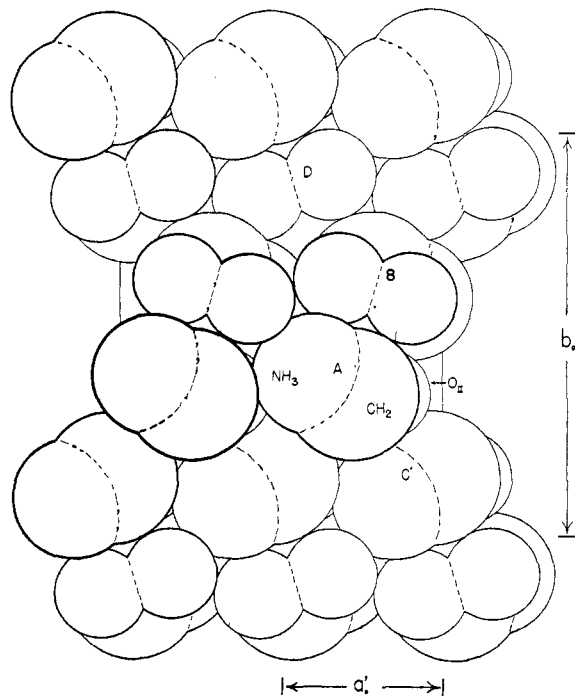


Fig. 12b.—A packing drawing of the molecules shown in Fig. 12a.

significant factors in determining the arrangement within the crystal rather than the distribution of the positive and negative electrostatic elements present in the molecular dipole there sug-

gested. Figure 12b shows the contacts between oxygen atoms and CH_2 groups forming the boundaries of the molecular double layers and responsible for the pronounced cleavage along (010).

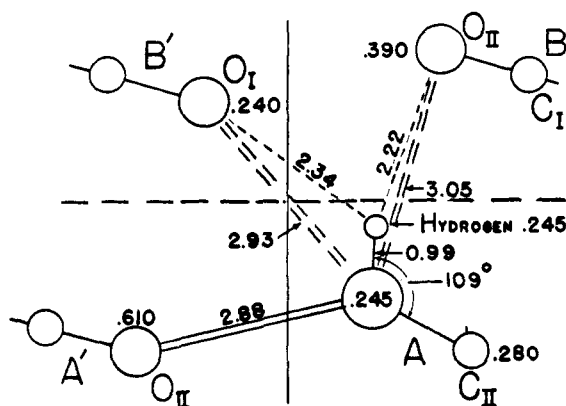


Fig. 13.—A portion of Fig. 12a showing a possible position for one of the hydrogen atoms suggested by the bond angles and interatomic distances. Numerals to the third decimal place are z -parameters of the atoms.

Figure 13 is a portion of Fig. 12a surrounding the nitrogen atom of molecule A and shows the position suggested by bond angles and interatomic distances for one of the hydrogen atoms of the NH_3 group. Numerals given to the third decimal place are z -parameters of the atoms. The hydrogen bond between nitrogen and O_I (2.76 Å.), which makes an angle of $108\frac{1}{2}^\circ$ with the 2.88 Å. hydrogen bond, is not shown since it is almost perpendicular to the plane of the paper and connects the nitrogen atom with an oxygen atom in the molecule directly in front of it. As pointed out earlier in the discussion, the arrangement of hydrogen in the three tetrahedral positions about the nitrogen atom, which appears to be the one most consistent with the structure, may be regarded as evidence in favor of the existence of glycine molecules in the form of zwitter ions in the crystal.

The determination of the structures of diketopiperazine and glycine enables us to make certain statements concerning the linkages present in the polypeptide chain in proteins, and to suggest the direction which future work should take in order to complete our knowledge of this fundamental unit of protein structure. In both glycine and diketopiperazine the distance between the nitrogen atom and the α -carbon atom is definitely established as being close to 1.40 Å., with a probable error of 0.02 Å. This is appreciably

shorter than the values near 1.47 Å. found for the structures of CH_3NO_2 ,¹⁷ CH_3N_3 ,¹⁸ CH_3NC ,¹⁹ and $\text{N}(\text{CH}_3)_3$.²⁰ There seems to be little doubt that this new distance, found in these hydrolytic products of proteins, exists also in the protein molecule itself. The carbon-carbon distance in diketopiperazine, 1.47 Å., is surprisingly short, whereas that in glycine, 1.52 ± 0.02 Å., is in entire accord with the normal value (1.54 Å.). Whether this abnormally short distance found in the cyclic dipeptide prevails also in the long peptide chains of protein molecules is a question which must await complete crystal structure studies of some simple straight-chain polypeptides and substituted diketopiperazines. Investigations of this nature are already in progress in these Laboratories. The distance between the nitrogen and oxygen atoms connected by the peptide link, $-\text{NH}-\text{CO}-$, was found in diketopiperazine to be 1.33 ± 0.03 Å., which is entirely in accord with the value anticipated for a resonating molecule of this type. Although it is quite probable that this separation is also maintained in the straight-chain linkages of the protein molecule, confirmation of the sort suggested above is needed before the assumption may be made with certainty.

Acknowledgment.—The authors are especially indebted to Professor Linus Pauling, who proposed the subject of this investigation, for his many helpful suggestions and criticisms and for continued interest and encouragement throughout

(17) L. O. Brockway, J. Y. Beach and L. Pauling, *THIS JOURNAL*, **57**, 2693 (1935).

(18) L. Pauling and L. O. Brockway, *ibid.*, **59**, 13 (1937).

(19) L. O. Brockway, *ibid.*, **58**, 2516 (1936).

(20) L. O. Brockway and H. O. Jenkins, *ibid.*, **58**, 2036 (1936).

the progress of the work. They also wish to express their thanks to Professor J. H. Sturdivant, who gave generously of his time and effort, especially during the earlier stages of the investigation.

Summary

X-Ray data show that crystals of glycine are built upon a simple monoclinic unit cell having $a_0 = 5.10$ Å., $b_0 = 11.96$ Å., $c_0 = 5.45$ Å. and $\beta = 111^\circ 38'$, containing four molecules. All atoms are in general positions of the space group $C_{2h}^5 - P2_1/n$. Analysis of photographic intensity data by means of Patterson-Harker projections served to establish the following atomic parameters: oxygen (I), $x = 0.805$, $y = 0.410$, $z = 0.740$; oxygen (II), $x = 0.360$, $y = 0.360$, $z = 0.610$; carbon, $x = 0.575$, $y = 0.380$, $z = 0.560$; methylene carbon, $x = 0.565$, $y = 0.365$, $z = 0.280$; nitrogen, $x = 0.800$, $y = 0.410$, $z = 0.245$. The structure consists of nearly flat glycine molecules held together by hydrogen bonds between adjacent nitrogen and oxygen atoms to form continuous layers throughout the crystal. Interatomic distances within the molecule are: carbon-oxygen, 1.25 Å. and 1.27 Å., carbon-carbon, 1.52 Å., carbon-nitrogen, 1.39 Å., each ± 0.02 Å. (probable error). Hydrogen bond distances between nitrogen and oxygen atoms in the same layer are 2.76 and 2.88 Å.; between neighboring layers, 2.93 and 3.05 Å. From a discussion of the probable positions of hydrogen atoms it is concluded that the atomic arrangement suggests a zwitter-ion structure for the glycine molecule in the crystal.

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