

at 20° of -51.82° ($c = 2.103$, $l = 2$). Sandqvist and Gorton¹² give the following values for stigmaterol isolated from soybean sterols: m. p. 169–170°; $[\alpha]_D -51.0^\circ$.

The stigmaterol content of the mixed sterols, as calculated on the basis of the crude stigmateryl acetate tetrabromide, is approximately 24% but some loss is experienced during purification so that this amount of stigmaterol is not recovered.

In respect to stigmaterol content, melting point, and specific rotation the glucosidic sterols bear a very close resemblance to the sterols occurring in the uncombined state in soybean oil.

Summary

1. Sterol glucosides occur to an appreciable extent in commercial expeller soybean oil.

(12) Sandqvist and Gorton, *Ber.*, **63**, 1935 (1930).

2. These glucosides were removed from the oil by adsorption methods and were obtained by acetone extraction of the adsorbed material.

3. The sugar was obtained from the glucosides in almost theoretical yield by first forming the ethyl glucoside and subsequently hydrolyzing the easily soluble ethyl glucoside. The sugar was identified as *d*-glucose.

4. The sterols obtained by hydrolysis of the glucosides are very similar to the uncombined sterols of the oil and consist of a mixture of sterols in which stigmaterol occurs to the extent of approximately 24%.

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The Crystal Structure of Rhombohedral Acetamide

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I. Introduction

The purpose of this research was to investigate the properties of the N–H–O bridge. Some such bridging must exist in crystalline acetamide, for, while it has the approximate molecular weight and is isoelectronic with acetone and 1,1-dimethylethylene, its melting point and boiling point are approximately 100° higher, thus indicating much stronger intermolecular forces.

We should expect two N–H–O bridges from each N in acetamide. One such bridge could be formed intramolecularly, but this is unlikely. Such a bridge should be weaker than a corresponding O–H–O bridge in formic acid; the structure of formic acid vapor^{1a} and molecular weight determinations indicate that formic acid is a dimer and that no intramolecular bridging occurs. Hence, we expect no intramolecular bridge in acetamide. If bridges are formed to other molecules there is no reason to suppose that the direction of the bridge is not the direction of the bond from one of the terminal atoms in the bridge to hydrogen. Consequently, locating the N–H–O bridges also partially locates the H atoms. The determination of the crystal structure of acetamide will thus furnish a great deal of information about the position of the bridging hydrogen atoms, although they have no appreciable effect on the diffraction of X-rays.

(1) American Can Company Fellow.

(1a) L. Pauling and I. O. Brockway, *Proc. Nat. Acad. Sci.*, **20**, 336 (1934).

The crystal structure of acetamide as determined by this investigation leads us to the conclusions (a) that the lengths of the N–H–O bridges are $2.86 \pm 0.05 \text{ \AA.}$; (b) the molecule of acetamide is planar; (c) the molecule exists in the keto form; and (d) the N–H bonds lie in the plane of the molecule.

II. Determination of the Unit Cell and Space Group.—Crystals of acetamide in the form of transparent, trigonal prisms were obtained by slowly cooling ethyl acetate saturated with c. p. acetamide at 50° . The prism faces on the crystals were well developed but rapidly disappeared upon exposure to air due to the extremely deliquescent nature of the compound. The crystal was mounted on a small glass rod by means of cellophane tape and this was placed in a thin-walled bulb blown from a 2-mm. Pyrex tube. The entire operation of mounting the crystal from the time it was removed from the mother liquid until it was mounted in its final position was done in a moisture-free atmosphere.

Three sets of oscillation photographs were taken: a 30° oscillation about the *c*-axis, a set of four 30° oscillations about the *a*-axis of the hexagonal cell, and a set of four 30° oscillation photographs about the $[10\cdot0]$ axis.

Measurements on these photographs gave values of $a_0 = 11.44 \pm 0.03 \text{ \AA.}$, and $c_0 = 13.49 \pm 0.03 \text{ \AA.}$ for the dimensions of the hexagonal unit

cell, in good agreement with the values of Hassel and Luzanski.² A Laue photograph taken perpendicular to the *c*-axis was indexed with the aid of a gnomonic projection and the wave length of the radiation producing each reflection calculated. It was found that no planes reflected in the first order unless the indices satisfied the condition imposed by the rhombohedral lattice, $2H + K + L = 0 \pmod{3}$, although many planes not satisfying the condition were in position to give first order reflections. The lattice is consequently rhombohedral and the unit cell has one-third the volume of the hexagonal cell for which the dimensions are given above. Using the value 1.157 for the density,³ the calculated number of formulas of C_2H_5ON in the rhombohedral unit cell is 6.02. There are thus 6 C_2H_5ON in the rhombohedral unit cell and 18 C_2H_5ON in the hexagonal unit cell.

In order to determine whether the crystal possesses a center of inversion, a pyroelectric experiment was performed. The crystal was attached to a fine silk thread and lowered into a small Dewar flask containing liquid air. Upon removing the crystal from the liquid air it was strongly attracted to the walls of the vessel, thus proving that the crystal is pyroelectric and cannot possess a center of inversion. Hence the crystal must belong to one of the rhombohedral point groups, C_3 , C_{3v} or D_3 .

No reflections of the type $(0K\cdot L)$, L odd, were observed in the first order on any photograph, although many planes of this type were in position to reflect on both the Laue and the oscillation photographs. These absences are compatible with the space group C_{3v}^6-R3c . Since a structure based on this space group and compatible with the data has been found, we may accept C_{3v}^6-R3c as the true space group of acetamide.

The general set of equivalent positions in $R3c$ is six-fold, so that locating one of the acetamide molecules in the rhombohedral unit cell will determine the structure completely.

III. Determination of the Structure.—There are 2 C, 1 O, 1 N, and 5 H to be located in the unit cell. Since the scattering power of H atoms is very low, their effect on the intensities of the diffracted X-rays is inappreciable and their approximate positions must be inferred from the po-

sitions of the other atoms. The positions of these other atoms are determined by twelve parameters: $X_O, Y_O, Z_O; X_{NH_2}, Y_{NH_2}, Z_{NH_2}; X_C, Y_C, Z_C;$ and $X_{CH_3}, Y_{CH_3}, Z_{CH_3}$. The Z parameter of any one of the atoms may arbitrarily be taken as zero, however, thus leaving eleven independent parameters to be determined.

To simplify this problem, some assumptions suggested by chemical evidence were made. Organic chemistry has shown that the atoms are bonded together as follows: $CH_3-C \begin{matrix} \diagup O \\ \diagdown NH_2 \end{matrix}$. On

the basis of this structure we may expect all the atoms in one molecule to lie in a plane. If the carbon-oxygen double bond consists of a pair of tetrahedral sp^3 bonds, as postulated by Pauling,⁴ we may expect the bond angles to be as follows: $CH_3-C=O = 125^\circ$, $O=C-NH_2 = 125^\circ$, and $CH_3-C-NH_2 = 110^\circ$. This probably is not the true structure of acetamide, however, for it is

likely that structures such as $CH_3-C \begin{matrix} O^- \\ \diagdown N^+ \\ \diagup H \\ \diagdown H \end{matrix}$ also

contribute to the state of the molecule. In the latter structure the hydrogens on the N lie in the plane of the other atoms. The same condition might be expected to hold in the true structure. Some reasonable assumptions concerning the bond lengths in this molecule were also made, on the basis of the following arguments. The C- CH_3 single bond length of 1.54 Å. is well established. The C-O and C-NH₂ distances may be assumed to be approximately equal to those found in urea⁵ where C-O = 1.25 Å., and C-NH₂ = 1.37 Å. (In diketopiperazine⁶ C-O = 1.25 Å., and C-NH = 1.33 Å.; in glycine⁷ C-O = 1.24 Å., and C-N = 1.42 Å.) These assumptions decrease the number of independent parameters to five. (For example, these may be taken to be $X_O, Y_O, X_{CH_3}, Z_{CH_3}$ and Z_{NH_2} . Various other combinations of coördinates would serve as well to locate the position of the molecule.)

In order to determine these parameters, the Patterson method was applied. This method requires a knowledge of the intensities of the reflections on the oscillation photographs. These intensities were estimated by comparison with a series of spots of known exposure time on a strip of film to which a number proportional to the ex-

(2) O. Hassel and N. Luzanski, *Z. physik. Chem.*, **3B**, 282-288 (1929).

(3) "Handbook of Chemistry and Physics," 23rd edition, Chemical Publishing Company, Cleveland, Ohio, 1939.

(4) L. Pauling, "The Nature of the Chemical Bond," Cornell University Press, Ithaca, N. Y., 1939, p. 85.

(5) R. W. G. Wyckoff and R. B. Corey, *Z. Krist.*, **89**, 462 (1934).

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

(7) G. Albrecht and R. B. Corey, *ibid.*, **61**, 1087 (1939).

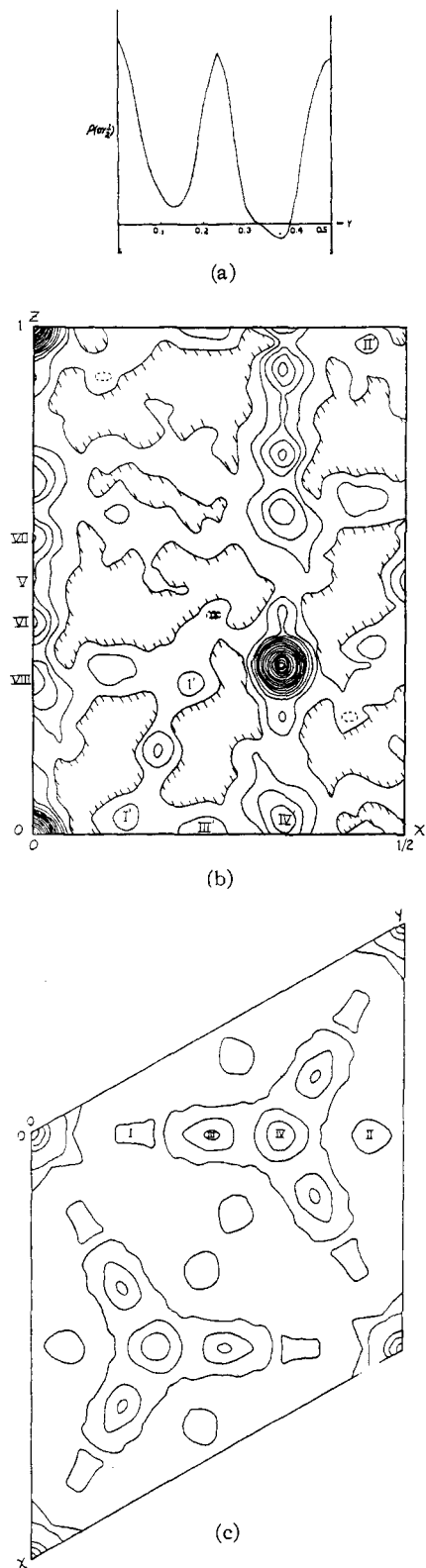


Fig. 1.—(a) Patterson line $P(0, Y, 1/2)$; (b) Patterson section $P(2X, X, Z)$; (c) Patterson section $P(X, Y, 0)$.

posure time had been assigned. The intensities of reflection on the three sets of oscillation photographs determined in this manner were not comparable, due to differences of exposure time and differences in the size of the crystals used in obtaining the photographs. Therefore, film factors were calculated by comparing intensities of reflections of planes which appeared on two or more photographs. One film was then chosen as a standard and the intensities of reflections on the other films were calculated on this basis. Values of $|F_{HK\cdot L}|^2$ were calculated from these by means of the formula

$$|F_{HK\cdot L}|^2 = \frac{I_{HK\cdot L} \sin 2\theta}{1 + \cos^2 2\theta}$$

where 2θ is the angle between the incident and reflected beam for the plane $(HK\cdot L)$.

The space group of the crystal being $R3c$, the Patterson function⁸ $P(0, Y, 1/2)$ was evaluated. If there is an atom whose coordinates in the hexagonal unit cell are X, Y, Z , this function will have three maxima, at $\pm(X - 2Y)$, $\pm(-2X + Y)$, and $\pm(X + Y)$, respectively. The curve of $P(0, Y, 1/2)$ plotted against Y appears in Fig. 1(a).

The four atoms should each produce three peaks $P(0, Y, 1/2)$ so that we expect twelve peaks altogether. However, considerable overlapping must have occurred, for there are only three peaks: at $Y = 0.000$, $Y = 0.233$ and $Y = 0.500$, respectively. To determine the X and Y coordinates of a given atom, the three peaks due to this atom must be selected. Since the peaks due to the four atoms are not resolved, there is no unique way of assigning peaks to individual atoms and we can only derive sets of atomic positions compatible with the observed positions of peaks. We may assign peaks at $Y = a$, $Y = b$, and $Y = c$, according to the following equations:

$$X - 2Y = a \quad (1)$$

$$Y - 2X = b \quad (2)$$

$$X + Y = c = -(a + b) \quad (3)$$

Only two peaks may be selected arbitrarily, the third must be equal to the sum of the other two with the opposite sign. We may select four independent sets of peaks:

$$(A) a = 0.000, b = 0.000, c = 0.000$$

$$(B) a = 0.000, b = 0.233, c = -0.233$$

$$(C) a = 0.000, b = 0.500, c = -0.500$$

$$(D) a = 0.233, b = 0.233, c = -0.467$$

Using the solution to equations (1), (2) and (3),

$$X = -\frac{a + 2b}{3} \quad Y = \frac{2a + b}{3}$$

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

we arrive at the following atomic positions and others derived from them by the symmetry elements of the crystal:

| | x | y |
|-----|-------|-------|
| (A) | 0.000 | 0.000 |
| (B) | 0.078 | 0.156 |
| (C) | 0.167 | 0.334 |
| (D) | 0.233 | 0.233 |

If the two positions $(0,0,Z)$ and $(0,0,Z + 1/2)$ derived from (A) are occupied, there must be atoms in the structure which possess three-fold axes. Since the chemical evidence indicates that none of the atoms in an acetamide molecule can possess a three-fold axis, these positions cannot be occupied and we can eliminate positions (A) from consideration.

The positions (B), (C) and (D) are not sufficient to locate the molecule. However, when a plot is made it is found that these positions determine interatomic vectors which are parallel to glide planes in the crystal. Therefore, it may be expected that the section $P(2X,X,Z)$ through Patterson space will determine Z coordinates of the atoms and accordingly it was evaluated. It is

$$P(2X,X,Z) = \sum_{H=-\infty}^{\infty} \sum_{K=-\infty}^{\infty} \sum_{L=-\infty}^{\infty} |F_{HK \cdot L}|^2 \cos 2\pi \{ (2H + K)X + LZ \}$$

$|F_{HK \cdot L}|^2$ values of all planes belonging to all forms which were observed to reflect on the photographs were used. A contour map of the function is shown in Fig. 1(b). The function was evaluated at 6° intervals over the map and no portion of the map was obtained from another by symmetry. From a consideration of the Patterson $P(0,Y,1/2)$ we can predict the positions of certain peaks in this map: peaks should occur at $(0.000, 0.000, 0.500)$ and $(0.467, 0.233, 0.000)$. The first peak corresponds to the peak at $Y = 0.000$ in $P(0,Y,1/2)$; in $P(2X,X,Z)$ a peak at this point (labeled V) is not resolved for there are large maxima at VI $(0.000, 0.000, 0.417)$ and VII $(0.000, 0.000, 0.583)$ which overlap at $(0.000, 0.000, 0.500)$. This overlap may represent the total contribution to this peak or it may be due to interatomic vectors. The peak at III' $(0.467, 0.233, 0.000)$ corresponds to vectors between atoms in positions derived from the set of peaks (D) related by the three-fold axis, thus giving definite evidence that the positions (D) are occupied.

If the plane of the acetamide molecule is vertical and parallel to the glide plane, there should be

peaks on the contour map $P(2X,X,Z)$ corresponding to each interatomic vector. These peaks are not observed, so that we may conclude that the plane of the molecule is at least somewhat inclined to the vertical.

To gain more information concerning the atomic positions, the Patterson function $P(X,Y,0)$ was evaluated. This function has maxima at positions determined by interatomic vectors between atoms related by the three-fold axis.⁸ For each atom, maxima are expected at $\pm(X+Y, 2Y-X, 0)$; $\pm(2X-Y, Y+X, 0)$; $\pm(X-2Y, 2X-Y, 0)$; and at points derived from these by the glide plane. Figure 1(c) is a contour map representing this function. There are sets of peaks on this map at I, II, III, IV and at positions derived from these. The first two peaks are relatively low and investigation of $P(2X,X,Z)$ discloses that they are due to peaks I' and II', respectively, which do not lie in the base plane of the Patterson space and this eliminates these peaks from consideration. The maximum in the function $P(X,Y,0)$ at III is confirmed by the maximum at III' in $P(2X,X,Z)$; it is the peak expected from atoms in positions (D) referred to above. The case for the peak at IV is not so clear-cut; it is of considerable magnitude, but $P(2X,X,Z)$ shows a peak at IV' of which IV may be a section, thus allowing the possibility that there are no atoms related by the three-fold axis which contribute to this peak. Accordingly we have two alternatives: (1) the peak IV in $P(X,Y,0)$ is accidental; and (2) it is not accidental.

Let us consider the first alternative. With this assumption only positions $(1/3, -1/12, Z)$, $(5/12, 1/12, Z)$, $(1/4, 0, Z)$ and positions derived from them by symmetry are occupied; that is, there are sets of three strings parallel to the c -axis arranged symmetrically about each three-fold screw axis on or near which the four kinds of atoms must be placed. This requires that more than one kind of atom be near each string. An inspection of the assumed planar molecule of acetamide reveals that there are several orientations of the molecule which can satisfy the above condition by placing three atoms of the molecule near one string and the other near another string. However, structures thus obtained require the plane of the molecule to be nearly vertical and parallel to the glide plane and, as stated before, there should be peaks on the contour map $P(2X,X,Z)$ corresponding to each interatomic vector. Since

these peaks are not observed, we can eliminate such structures from consideration.

Assumption 2—that the peak at (0.667, 0.333, 0.000) in $P(X, Y, 0)$ is not accidental and that there are atoms at (0.333, 0.000, Z) in the structure—must now be considered. The projections on (00·1) of the positions in which the atoms of one molecule of acetamide may now be placed lie near the vertices and the center of an equilateral triangle which is symmetrically placed about a three-fold screw axis. A structure satisfying these conditions places the atoms in the approximate positions: $X_C = 1/3$, $Y_C = 0$, $Z_C = ?$; $X_{NH_2} = 1/3$, $Y_{NH_2} = -1/12$, $Z_{NH_2} = ?$; $X_{CH_3} = 5/12$, $Y_{CH} = 1/12$, $Z_{CH_3} = ?$; $X_O = 1/4$, $Y_O = 0$, $Z_O = ?$. If chemical evidence is excluded, there is no reason, *a priori*, for not considering structures in which the CH_3 , NH_2 and O exchange positions. By requiring the structure to contain N-H-O bridges of 2.75–3.00 Å. in length, all structures are eliminated except the one given above and the structure resulting from it by exchanging the positions of the N and O.

The Z coordinates of the atoms in the first structure are approximately determined if the N-H-O bridges are considered to be of equal length and to lie in the plane of the molecule. By the methods of descriptive geometry the coordinates of the atoms satisfying these conditions were found to be $X_{CH_3} = 0.472$, $Y_{CH_3} = 0.117$, $Z_{CH_3} = 0.010$; $X_{NH_2} = 0.333$, $Y_{NH_2} = -0.091$, $Z_{NH_2} = 0.095$; $X_O = 0.225$, $Y_O = 0.000$, $Z_O = 0.000$; $X_C = 0.333$, $Y_C = 0.000$, $Z_C = 0.032$. This structure is substantiated by peaks at VI, VII, VIII, IX and I' in $P(2X, X, Z)$. Peaks VI and VIII are partially due to vectors between the NH_2 and O, and between NH_2 and CH_3 , respectively, of adjacent molecules related by the screw axis. In this structure other interatomic vectors between atoms of molecules not related by the three-fold screw axis also contribute to these peaks. Peak IX, which is indicated by a broken contour line (it is approximately one-half the height of the first contour line above the zero of the map), is due to the O-N vector between atoms of the same molecule, and peak I' is due to both O- CH_3 and N- CH_3 interactions of pairs of atoms, each pair contained in one molecule. Due to the overlapping, precise coordinates cannot be obtained from these peaks. $|F_{HK\cdot L}|^2$ values for all planes observed to reflect were calculated on the basis of these coordinates and qualitative agreement with the observed val-

TABLE I
COMPARISON OF OBSERVED AND CALCULATED^a $|F|^2$ VALUES
FOR (H0·L) AND (HK·0)

| HK·L | $ F_{HK\cdot L} ^2$ Fourier structure | $ F_{HK\cdot L} ^2$ obsd. | $ F_{HK\cdot L} ^2$ assumed structure |
|-----------------|---|------------------------------|---|
| 10· $\bar{2}$ | 3.9 | 1.1 | 3.2 |
| 20·2 | 2.7 | 3.3 | 2.4 |
| 30·0 | 7.8 | 8.1 | 7.5 |
| 10·4 | 12.1 | 8.2 | 7.8 |
| 20· $\bar{4}$ | 3.9 | 3.1 | 2.6 |
| 40· $\bar{2}$ | 19.6 | 16.7 | 14.9 |
| 00·6 | 3.7 | 5.5 | 4.1 |
| 40·4 | 14.6 | 8.7 | 10.5 |
| 50·2 | 3.0 | 1.1 | 3.5 |
| 30·6 | 0.4 | 1.6 | 0.2 |
| 30· $\bar{6}$ | 0.5 | 1.0 | 0.1 |
| 50· $\bar{4}$ | 6.3 | 4.0 | 3.7 |
| 10· $\bar{8}$ | 1.5 | <1 | 0.3 |
| 60·0 | 0.4 | 1.1 | 0.3 |
| 20·8 | 0.0 | abs | |
| 04·8 | 0.4 | abs | |
| 70· $\bar{2}$ | 0.5 | <1 | 0.3 |
| 10· $\bar{10}$ | 1.1 | 1.4 | 0.4 |
| 60· $\bar{6}$ | 1.2 | <1 | 1.8 |
| 60·6 | 1.8 | 2.8 | 0.9 |
| 20· $\bar{10}$ | 0.4 | <1 | 0.1 |
| 50·8 | 0.3 | <1 | 0.3 |
| 80·2 | 3.7 | 5.9 | 3.0 |
| 40·10 | 2.2 | 2.8 | 1.2 |
| 80· $\bar{4}$ | 1.0 | 1.9 | 0.9 |
| 50· $\bar{10}$ | 1.6 | 1.7 | 0.5 |
| 90·0 | 4.9 | 5.5 | 4.4 |
| 70· $\bar{8}$ | 0.0 | 1.8 | 0.2 |
| 30·12 | 0.2 | 1.3 | 0.1 |
| 30· $\bar{12}$ | 0.3 | 1.7 | 0.3 |
| 80·8 | 0.3 | <1 | 0.2 |
| 90· $\bar{6}$ | 0.5 | 1.3 | 0.6 |
| 10·0· $\bar{2}$ | 0.1 | <1 | 0.1 |
| 70·10 | 0.1 | <1 | 0.2 |
| 10·10 | 1.3 | <1 | 0.0 |
| 60·12 | 0.4 | <1 | 0.0 |
| 10·0· $\bar{8}$ | 0.0 | <1 | 0.0 |
| 11·0 | 17.4 | 11.2 | 14.8 |
| 30·0 | 7.8 | 8.1 | 6.3 |
| 22·0 | 21.1 | 20.5 | 17.9 |
| 41·0 | 9.1 | 8.0 | 7.9 |
| 33·0 | 2.4 | <1 | 2.2 |
| 60·0 | 0.4 | 1.1 | 0.4 |
| 52·0 | 4.2 | 5.2 | 3.7 |
| 44·0 | 4.6 | 4.4 | 3.8 |
| 17·0 | 0.2 | abs | |
| 71·0 | 0.2 | <1 | 0.3 |
| 36·0 | 0.2 | <1 | 0.2 |
| 55·0 | 0.2 | 1.8 | 0.2 |
| 90·0 | 4.2 | 5.5 | 4.1 |
| 82·0 | 0.1 | 1.3 | 0.4 |
| 47·0 | 0.2 | <1 | 0.3 |
| 10·1·0 | 0.4 | 1.0 | 0.3 |
| 39·0 | 0.1 | <1 | 0.2 |

^a Values for $|F_{HK\cdot L}|^2$ were calculated in case of the assumed structure for only those forms which were observed to reflect.

TABLE II
COMPARISON OF CALCULATED AND OBSERVED $|F|^2$ VALUES FOR GENERAL FORMS

| HK·L | $ F_{HK-L} ^2$ Fourier struc. | $ F_{HK-L} ^2$ obsd. | $ F_{HK-L} ^2$ assumed struc. | HK·L | $ F_{HK-L} ^2$ Fourier struc. | $ F_{HK-L} ^2$ obsd. | $ F_{HK-L} ^2$ assumed struc. | HK·L | $ F_{HK-L} ^2$ Fourier struc. | $ F_{HK-L} ^2$ obsd. | $ F_{HK-L} ^2$ assumed struc. |
|------|-------------------------------------|-------------------------|-------------------------------------|-------|-------------------------------------|-------------------------|-------------------------------------|--------|-------------------------------------|-------------------------|-------------------------------------|
| 21·1 | 0.6 | 1.5 | 0.9 | 44·3 | 0.1 | 1.0 | 0.2 | 37·2 | 0.6 | abs | |
| 11·3 | 36.5 | 16.8 | 37.7 | 23·8 | 0.0 | abs | | 81·4 | 0.4 | abs | |
| 12·2 | 4.2 | 3.4 | | 26·2 | 0.5 | <1 | 0.5 | 24·10 | 0.1 | abs | |
| 13·1 | 1.2 | 2.1 | 0.8 | 24·7 | 0.7 | <1 | 0.3 | 25·9 | 0.5 | 2.2 | 1.4 |
| 31·2 | 3.2 | 3.3 | 1.3 | 22·9 | 3.0 | 1.2 | 1.7 | 52·9 | 0.7 | 1.3 | 1.7 |
| 21·4 | 7.5 | 6.8 | 6.1 | 61·5 | 3.0 | 2.0 | 3.3 | 63·6 | 0.3 | <1 | 0.5 |
| 22·3 | 2.0 | <1 | 2.0 | 35·4 | 0.1 | abs | | 34·8 | 0.2 | <1 | 0.0 |
| 32·1 | 0.3 | <1 | 0.1 | 51·7 | 1.2 | 1.4 | 1.0 | 23·11 | 0.3 | abs | |
| 12·5 | 6.7 | 4.4 | 11.5 | 52·6 | 0.3 | abs | | 51·10 | 0.1 | abs | |
| 23·2 | 1.3 | 1.4 | 1.2 | 25·6 | 0.0 | abs | | 54·4 | 1.0 | abs | |
| 13·4 | 0.8 | <1 | 1.1 | 62·4 | 0.6 | <1 | 0.5 | 28·3 | 0.4 | 1.0 | 0.9 |
| 11·6 | 0.2 | <1 | 0.3 | 21·10 | 0.8 | 1.6 | 0.5 | 82·3 | 0.3 | 1.0 | 1.0 |
| 41·3 | 0.7 | 1.6 | 0.4 | 17·3 | 1.9 | 2.5 | 1.6 | 64·5 | 0.1 | abs | |
| 14·3 | 0.6 | 1.5 | 1.0 | 71·3 | 2.3 | 2.6 | 1.4 | 22·12 | 0.2 | 2.4 | 0.4 |
| 31·5 | 0.2 | 1.0 | 0.1 | 54·1 | 0.1 | <1 | 0.2 | 43·10 | 0.2 | abs | |
| 32·4 | 1.0 | 1.0 | 0.9 | 53·5 | 0.1 | abs | | 65·1 | 0.1 | <1 | 0.1 |
| 24·1 | 0.0 | 1.2 | 0.0 | 42·8 | 0.1 | 1.3 | 0.1 | 19·1 | 0.0 | <1 | 0.0 |
| 42·2 | 1.7 | 2.0 | 1.5 | 45·2 | 2.0 | 1.2 | 2.1 | 37·5 | 1.6 | 1.4 | 0.9 |
| 51·1 | 0.2 | <1 | 0.4 | 43·7 | 0.9 | 1.4 | 0.5 | 91·2 | 0.0 | <1 | 0.0 |
| 22·6 | 0.7 | 1.1 | 0.9 | 41·9 | 0.3 | 1.4 | 0.2 | 55·6 | 0.3 | abs | |
| 33·3 | 8.9 | 10.3 | 9.0 | 14·9 | 0.4 | <1 | 0.6 | 16·10 | 0.2 | 1.0 | 0.2 |
| 23·5 | 4.8 | 3.5 | 4.7 | 26·5 | 0.6 | abs | | 38·1 | 0.2 | <1 | 0.2 |
| 15·2 | 0.8 | 2.2 | 0.5 | 15·8 | 0.1 | <1 | 0.2 | 81·7 | 0.0 | <1 | 0.0 |
| 21·7 | 13.0 | 8.7 | 11.3 | 13·10 | 0.2 | 1.1 | 0.1 | 83·2 | 0.1 | abs | |
| 24·4 | 0.8 | 1.0 | 0.8 | 27·1 | 0.6 | 1.3 | 0.4 | 19·4 | 0.1 | abs | |
| 43·1 | 0.5 | <1 | 0.5 | 44·6 | 0.7 | 1.3 | 3.8 | 71·9 | 0.4 | abs | |
| 34·2 | 0.1 | 1.1 | 0.1 | 36·3 | 0.1 | <1 | 0.6 | 72·8 | 0.0 | abs | |
| 51·4 | 0.2 | abs | | 63·3 | 0.1 | <1 | 0.0 | 82·6 | 0.4 | abs | |
| 13·7 | 0.8 | 1.0 | 0.1 | 72·2 | 0.2 | <1 | 0.3 | 92·1 | 0.4 | <1 | 0.6 |
| 14·6 | 0.4 | abs | | 16·7 | 3.5 | 3.2 | 2.7 | 91·5 | 0.3 | abs | |
| 41·6 | 0.4 | 1.0 | 0.7 | 33·9 | 0.5 | 1.0 | 3.6 | 54·7 | 0.0 | abs | |
| 42·5 | 0.1 | abs | | 53·8 | 0.1 | 1.1 | 0.0 | 73·7 | 0.0 | abs | |
| 12·8 | 0.0 | abs | | 12·11 | 2.1 | 1.6 | 0.4 | 29·2 | 0.3 | <1 | 0.2 |
| 16·1 | 0.2 | <1 | 0.2 | 32·10 | 0.2 | <1 | 0.1 | 62·10 | 0.5 | abs | |
| 52·3 | 0.6 | abs | | 81·1 | 0.1 | <1 | 0.2 | 63·9 | 0.4 | <1 | 0.3 |
| 25·3 | 0.1 | abs | | 27·4 | 0.3 | abs | | 64·8 | 0.0 | abs | |
| 15·5 | 1.5 | 1.6 | 1.0 | 35·7 | 0.1 | abs | | 83·5 | 0.1 | abs | |
| 61·2 | 1.7 | 2.0 | 1.3 | 18·2 | 0.8 | 1.1 | 0.7 | 92·4 | 0.0 | abs | |
| 32·7 | 3.1 | abs | | 46·1 | 0.2 | abs | | 53·11 | 0.0 | abs | |
| 33·6 | 0.7 | 1.3 | 0.9 | 71·6 | 0.3 | abs | | 48·2 | 0.9 | 1.1 | 0.6 |
| 11·9 | 0.4 | 1.1 | 3.0 | 17·6 | 0.6 | <1 | 0.5 | 54·10 | 0.7 | abs | |
| 31·8 | 0.1 | <1 | 0.1 | 61·8 | 0.0 | abs | | 19·7 | 0.1 | <1 | 0.2 |
| 35·1 | 0.1 | <1 | 0.0 | 64·2 | 0.2 | <1 | 0.2 | 10·2·2 | 0.2 | <1 | 0.2 |
| 34·5 | 0.0 | abs | | 62·7 | 1.3 | abs | | 72·11 | 0.3 | abs | |
| 53·2 | 0.4 | 1.5 | 0.8 | 31·11 | 0.0 | abs | | 82·9 | 0.1 | abs | |
| 16·4 | 0.6 | abs | | 73·1 | 2.3 | <1 | 0.8 | 92·7 | 0.0 | abs | |
| 62·1 | 0.6 | abs | | 55·3 | 0.1 | <1 | 0.1 | 94·2 | 0.8 | <1 | 0.7 |
| | | | | 72·5 | 0.6 | 1.6 | 0.3 | 1·10·3 | 0.6 | <1 | 0.5 |

ues was found. These values are given in Tables I and II. The atomic scattering factors for O, NH₂ and C used in these calculations were those determined experimentally for urea,⁵ while the scattering factor for CH₃ was taken to be the same as that found for CH₂ in hexamethylenetetramine.⁹

(9) R. W. G. Wyckoff and R. B. Corey, *Z. Krist.*, **89**, 462 (1934).

The structure which results from an interchange in position of the O and N atoms must also be considered. This structure cannot be ruled out by a comparison of observed and calculated $|F|^2$ values because N and O have very nearly the same scattering factor, but our knowledge of the chemical properties of nitrogen and oxygen provides a good

basis for eliminating this structure. It seems unlikely that both hydrogens are attached to the oxygen, for the removal of two protons from $-\text{NH}_2$ leaves the strongly basic $(=\text{N}^-)$ and chemically we expect this group to be a much stronger base than the $(-\text{O}^-\text{H})$, and therefore we would expect an additional proton to attach itself to the former rather than to the latter. There remains the possibility that one H atom is bonded to the N atom, while the other is bonded to the O atom. In this case there is no reason for the molecule to lie in either of the planes determined by either the two O's adjacent to an N, or the two N's adjacent to an O. It seems reasonable to expect a molecule belonging to such a structure to be in some intermediate position. The type of structure possessed by acetamide allows such an intermediate position to be taken up by the acetamide molecules without the occurrence of any unreasonably short interatomic distances between molecules and, therefore, since this is not the observed structure, the H atoms do

not lie one on an N, and one on an O. It must be admitted that the argument just cited is not overwhelming, but it is certainly reasonable and serves to eliminate this structure on a level of rigor at least not lower than arguments advanced in its favor on the basis of organic chemical data.

To confirm the structure and to refine the parameters, the Fourier projections of the structure on $(00\cdot1)$ and $(1\bar{2}\cdot0)$ were made. The contour map of the projection on $(00\cdot1)$ given in Fig. 2(a) shows peaks in excellent agreement with those expected, but the maxima due to the CH_3 , NH_2 and O near the string $(\frac{5}{12}, \frac{1}{12}, Z)$ are not resolved, neither are the peaks due to the three C atoms near $(\frac{1}{3}, 0, Z)$, and it is therefore impossible to obtain precise coordinates from this projection.

The projection on $(1\bar{2}\cdot0)$ given in Fig. 2(b) is also in good agreement with the assumed structure. Well resolved peaks can be found for all atoms except the central carbon. The coordinates (referred to an arbitrary origin) derived from these peaks are $X_{\text{O}} = 0.225$, $Y_{\text{O}} = 0.000$, $Z_{\text{O}} = 0.000$; $X_{\text{NH}_2} = 0.343$, $Y_{\text{NH}_2} = -0.083$, $Z_{\text{NH}_2} = 0.097$; $X_{\text{CH}_3} = 0.489$, $Y_{\text{CH}_3} = 0.122$, $Z_{\text{CH}_3} = 0.000$, with the position of the central carbon atom not precisely determined. Only the position of the methyl group has undergone appreciable change from that in the assumed structure.

To obtain better values for the parameters than are afforded by the Fourier projections on $(1\bar{2}\cdot0)$ and $(00\cdot1)$ in which overlapping of peaks is encountered, the Fourier sections $(X, 0, Z)$ and $(X, Y, 0)$ were evaluated.

All atoms in the structure having Z coordinates very close to zero should be represented by peaks in the section $(X, Y, 0)$. Since $Z_{\text{O}} = 0.000$, $Z_{\text{CH}_3} = 0.010$, $Z_{\text{C}} = 0.032$, $Z_{\text{NH}_2} = 0.095$, we expect well-defined peaks for O, CH_3 and C, with a much lower peak and consequently less accurate parameter determination for the N atom. Section $(X, Y, 0)$ is given in Fig. 3(b). The center of each peak was considered to lie at the center of the triangle determined by the intersection of three ridge lines of the peak. Points on the ridge lines were obtained by plotting sections perpendicular to the ridge lines of the peaks taken at six-degree intervals. Figure 3(d) shows a peak on which the ridge lines have been drawn. This section gives good values for the X and Y coordinates of the CH_3 , C and O atoms, but not for the N atom since it is too far removed from the section—as evidenced by its low peak.

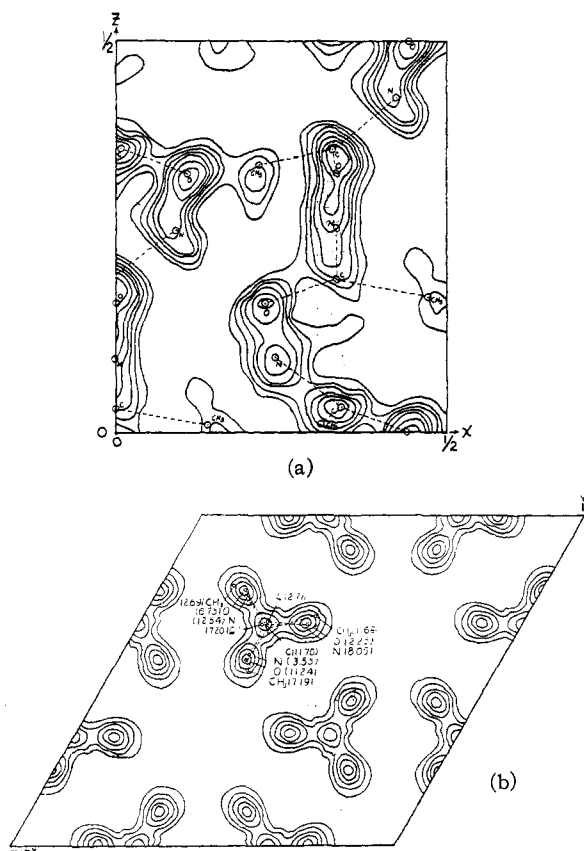


Fig. 2.—(a) Fourier projection on $(1\bar{2}\cdot0)$; (b) Fourier projection on $(00\cdot1)$.

All atoms in the structure having Y coordinates very close to zero should produce maxima in the section $(X,0,Z)$. There is one position about each three-fold screw axis for the CH_3 , N and O which lies close to this section, while there are three such positions for the central carbon atom (since it lies very close to the screw axis). A contour map of the section $(X,0,Z)$ is given in Fig. 3(a). The centers of the peaks were again determined by the intersection of the ridge lines. From this section X and Z parameters were obtained for all of the atoms. In the case of the central carbon atom, three determinations were given, in so far as the mechanics of the method are concerned. Thus we have four values for the X coordinate of the central C atom and these we may use to give a fair indication of the error involved in determining centers of peaks on the contour maps. The probable deviation from their mean of the X 's so determined is estimated to be $\pm 0.03 \text{ \AA}$.

Neither section $(X,Y,0)$ nor $(X,0,Z)$ determines the Y coordinate of the N atom. Hence the line (X_N, Y, Z_N) was investigated by evaluating the corresponding Fourier series. This function is plotted in Fig. 3(c); it shows $Y_N = 0.000$.

The values of the X , Y and Z coordinates as determined from the preceding sections and line are $X_O = 0.225$, $Y_O = -0.004$, $Z_O = 0.000$; $X_{\text{CH}_3} = 0.477$, $Y_{\text{CH}_3} = 0.123$, $Z_{\text{CH}_3} = 0.033$; $X_N = 0.333$, $Y_N = -0.090$, $Z_N = 0.096$; $X_C = 0.333$, $Y_C = 0.005$, $Z_C = 0.034$.

The observed values of $|F_{(\text{HK}\cdot\text{L})}|^2$ appear in Tables I and II, where they are compared with the corresponding numbers calculated from the assumed structure and from the final structure determined by the use of the Fourier method. Table I presents the values of $|F_{(\text{HK}\cdot 0)}|^2$ and $|F_{(\text{H}0\cdot\text{L})}|^2$ and Table II presents the values of $|F_{(\text{HK}\cdot\text{L})}|^2$.

Inspection of Table I reveals moderately good agreement of the observed values of $|F_{(\text{HK}\cdot 0)}|^2$ and of $|F_{(\text{H}0\cdot\text{L})}|^2$ with those calculated on the basis of either the assumed or the final structure. There seems to be no reasonable way of determining which of the two structures is nearer the true one on the basis of these data alone, but it would be justified to say that either one is a good approximation. The agreement between the observed and calculated values of $|F_{(\text{HK}\cdot\text{L})}|^2$ for the general forms, shown in Table II, is poor for both structures and again it is impossible to say which

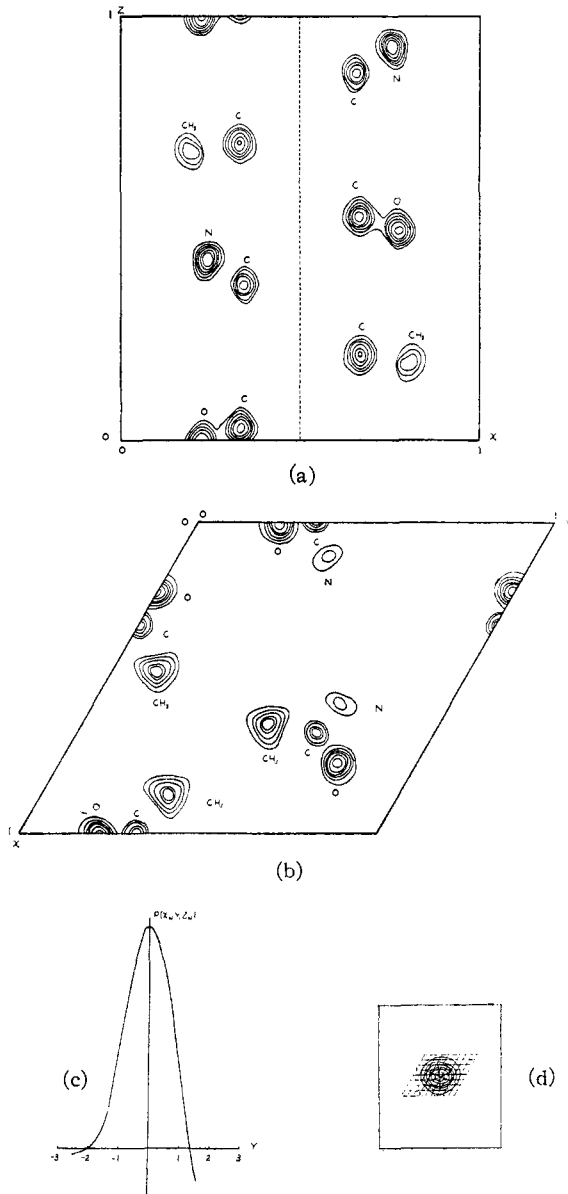


Fig. 3.—(a) Fourier section $(X,0,Z)$; (b) Fourier section $(X,Y,0)$; (c) Fourier line (X_N, Y, Z_N) ; (d) a peak from Fourier section showing ridge lines for location of center.

set of calculated values is in better (or worse) accord with observation.

It has now become customary in X-ray crystallography to consider an assumed structure which is not in reasonable accord with all the data as being incorrect, and it is clear that this argument could be applied forcibly to the structure of acetamide as determined in this work. On the other hand, it has recently been considered satisfactory to obtain a structure by means of the

Fourier series in essentially the way used by the authors. However, most two-dimensional Fourier series used in previous structure determinations possessed centers of inversion and, therefore, the phases of the F_{HKL} 's could have only the values 0° and 180° . Thus, when a set of atomic positions had been obtained from a Fourier series which gave calculated F_{HKL} 's with phases which were *the same* as those used in evaluating the series, no further improvement in atomic positions by the use of the Fourier series method was possible.

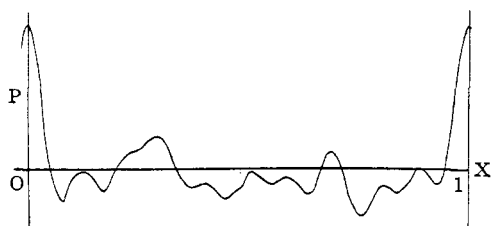


Fig. 4.—Fourier series representation of a one-dimensional structure.

On account of this difference between the series used in this investigation and the previous ones, an artificial example was constructed in order to discover whether the use of phases determined from an approximate structure without a center of inversion would lead to a Fourier series representing closely the true structure. This example was that of a one-dimensional crystal with an identity distance of 10.00 Å., with a sulfur atom at $X = 0.000$ and an oxygen atom at $X = 0.300$. (The coordinate X varied from 0.000 to 1.000 as the distance along the identity direction varied from a point to its next neighboring identical point; *i. e.*, 10.00 Å.) The $|F|^2$'s, $|F|$'s and δ 's of the first ten orders of "reflection" from the planes perpendicular to the identity direction were calculated in the usual way and are listed in Table III. The $|F|^2$'s were assumed to be those "observed" from the structure. It was then supposed

TABLE III

$|F|^2$, $|F|$ AND δ VALUES FOR THE "TRUE STRUCTURE"

| Order of reflection | $ F ^2$ | $ F $ | $\delta(^\circ)$ |
|---------------------|---------|-------|------------------|
| 1 | 218.9 | 14.77 | 329.9 |
| 2 | 79.3 | 8.91 | 28.0 |
| 3 | 309.8 | 17.60 | 12.0 |
| 4 | 177.8 | 13.32 | 337.9 |
| 5 | 26.0 | 5.10 | 0.0 |
| 6 | 117.5 | 10.83 | 20.2 |
| 7 | 126.1 | 11.23 | 349.8 |
| 8 | 33.3 | 5.77 | 342.8 |
| 9 | 49.0 | 7.00 | 19.9 |
| 10 | 82.0 | 9.06 | 0.0 |

that some line of reasoning had led an investigator of this one-dimensional crystal to predict its structure as follows: a sulfur atom at $X = 0.000$ and an oxygen atom at $X = 0.250$. $|F|^2$'s, $|F|$'s and δ 's were calculated from this "assumed structure" and appear in Table IV.

TABLE IV

$|F|^2$, $|F|$ AND δ VALUES FOR THE "ASSUMED STRUCTURE"

| Order of reflection | $ F ^2$ | $ F $ | $\delta(^\circ)$ |
|---------------------|---------|-------|------------------|
| 1 | 291.9 | 17.09 | 332.9 |
| 2 | 42.3 | 6.50 | 0.0 |
| 3 | 187.2 | 13.68 | 26.9 |
| 4 | 256.0 | 16.00 | 0.0 |
| 5 | 118.2 | 10.88 | 334.4 |
| 6 | 25.5 | 5.05 | 0.0 |
| 7 | 81.0 | 9.00 | 21.9 |
| 8 | 115.6 | 10.75 | 0.0 |
| 9 | 60.4 | 7.78 | 341.0 |
| 10 | 21.6 | 4.65 | 0.0 |

The δ 's from the "assumed structure" and the "observed" $|F|$'s were then used to evaluate the one-dimensional Fourier series representing the projection of the structure on its X -axis. This series is plotted in Fig. 4. It is clear that the series is an almost perfect representation of the "true structure," the coordinates of the highest peaks in the series being $X = -0.002$ and $X = 0.293$. This example shows that the Fourier method of structure determination is successful for at least one crystal not possessing a center of inversion. No rigorous proof of the convergence of the Fourier method being available to the authors, it was considered reasonable to suppose that the Fourier treatment used in this investigation should lead to about as rapid convergence in the case of a real crystal as in the case of the artificial example discussed above. Since in the artificial example the sulfur to oxygen distance changed from the "assumed structure" 80% of the way toward the corresponding distance in the "true structure" by the use of the Fourier method, we could *assume* that this is the rapidity of the convergence of the method.

The changes in the parameters of the acetamide structure due to the application of the Fourier method are listed below

| | x | y | z |
|-----------------|-------|-------|-------|
| O | 0.000 | 0.004 | 0.000 |
| CH ₃ | 0.005 | 0.005 | 0.023 |
| N | 0.000 | 0.001 | 0.001 |
| C | 0.000 | 0.003 | 0.002 |

The assumption at the end of the last paragraph leads to the conclusion that all the final param-

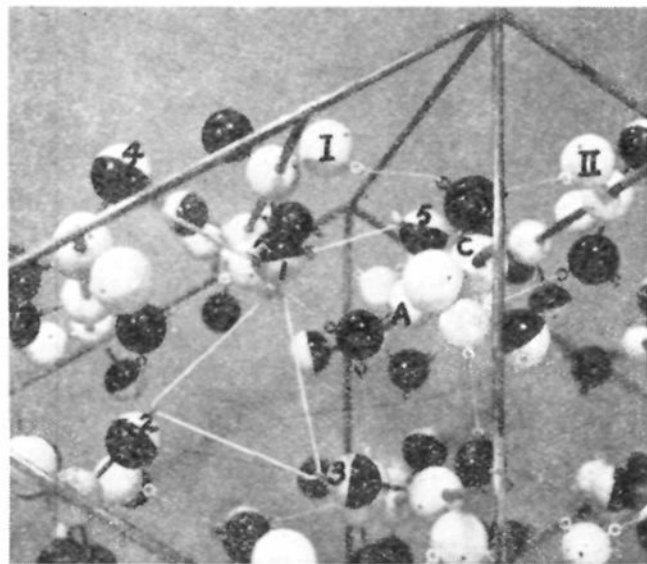


Fig. 5.

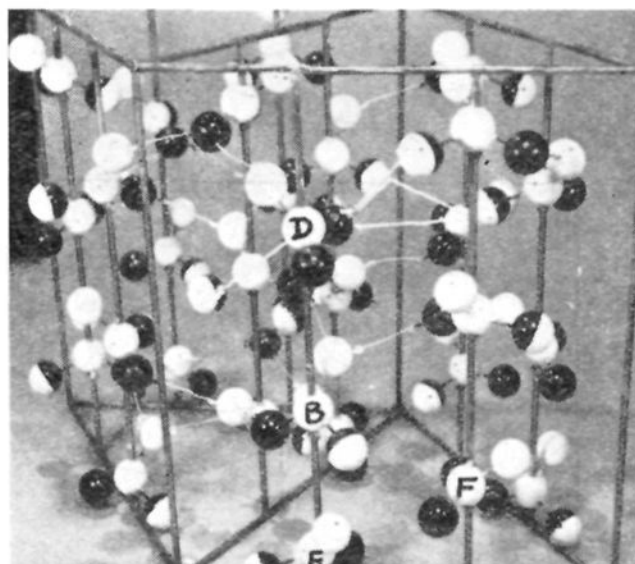


Fig. 6.

Figs. 5 and 6.—Photographs of a model of the structure of acetamide. Black spheres represent O atoms, black and white spheres represent methyl C atoms, white spheres on screw axes represent C atoms, the remaining white spheres represent N atoms. Narrow white lines represent N-H-O bridges, broad white lines indicate CH₃-CH₃ contacts.

ters except Z_{CH_3} are correct to 0.002 or better, but that Z_{CH_3} may be incorrect by as much as 0.005.

Professor Linus Pauling¹⁰ states that, in his experience, the convergence of the Fourier method for structures not possessing a center of inversion is such as to reduce the error in parameters by about 50% for each approximation. This result requires the probable errors in parameters to be assigned as follows

X_{CH_3} and Y_{CH_3} : probable error, ± 0.005

Z_{CH_3} : probable error, ± 0.023

All other parameters: probable error, ± 0.004 or less

It is possible that variations in atomic parameters within the limits of error about their determined values would remove the discrepancies between the calculated and observed intensities, but the labor involved in calculating the intensities of about 200 $|F_{\text{HK.L}}|^2$'s for variations in eleven parameters is so great that it was thought better to publish the results as they stand rather than embark upon a course so lengthy and the final result of which would lead to so small an increase in knowledge compared to other problems of equal difficulty.

It is hoped to study the structure of the orthorhombic modification of acetamide in this Laboratory in the near future. This substance has been subjected to a preliminary investigation by one of us (F. S.) and has been found to have the axial lengths: $a_0 = 7.78 \pm 0.05 \text{ \AA}$, $b_0 = 19.01 \pm 0.05 \text{ \AA}$, $c_0 = 9.37 \pm 0.05 \text{ \AA}$ and to belong to the space group D_{2h}^{14} —Pbcn. This unit cell contains six-

(10) Linus Pauling, private communication.

teen molecules of the formula CH₃CONH₂, if the density is approximately the same as that of the rhombohedral modification. Inasmuch as this orthorhombic modification of acetamide possesses a center of inversion, it may well prove possible to determine its crystal structure with greater convenience than in the case of the rhombohedral modification.

Discussion of the Structure

The arrangement of the molecules in the structure of acetamide is shown in Figs. 5, 6 and 7. In Fig. 2(a) appears the projection of the structure on (00·1). The Z -coordinates (in Ångström units) of the atoms in molecules related by one screw axis are indicated by the numbers in parentheses.

The molecule of acetamide is found to be planar, as is predicted from either of the resonance structures $\text{CH}_3-\text{C} \begin{matrix} \text{O} \\ // \\ \text{NH}_2 \end{matrix}$ or $\text{CH}_3-\text{C} \begin{matrix} \text{O}^- \\ // \\ \text{NH}_2^+ \end{matrix}$, the deviation of any atom from the median plane through the molecule being less than 0.01 Å.—which is well within the limits of accuracy of this investigation.

The interatomic distances in the molecule are C-O = 1.28 Å., C-CH₃ = 1.51 Å., and C-N = 1.38 Å., all accurate to about ± 0.05 . The C-O distance, 1.28 Å., is in agreement with that found in formic acid¹¹ (1.29 Å.), oxalic acid dihydrate¹² (1.25–1.30 Å.), urea⁵ (1.24 Å.), diketopiperazine⁶

(11) L. Pauling and L. O. Brockway, *Proc. Nat. Acad. Sci.*, **20**, 336 (1934).

(12) J. M. Robertson, *J. Chem. Soc.*, 1817 (1936); W. H. Zachariasen, *Z. Krist.*, **89**, 442 (1934).

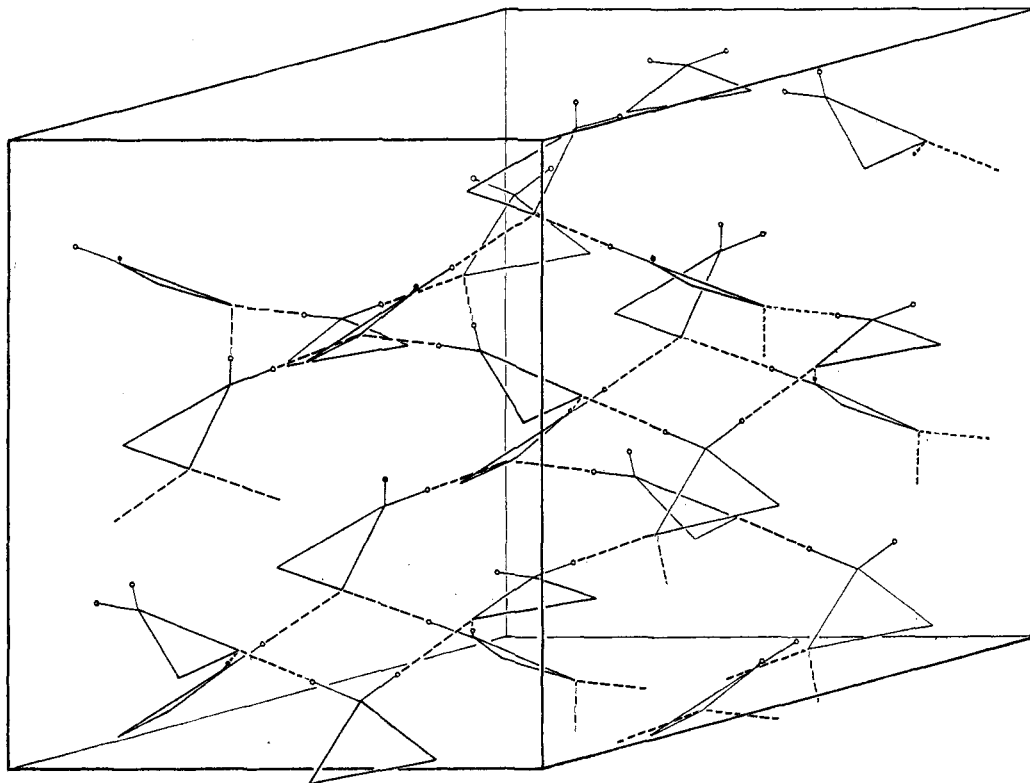


Fig. 7.—Cabinet projection of the structure of acetamide. The planar molecule of acetamide is represented by a triangle. The O, N, and methyl C atoms lie at the vertices of this triangle. H atoms are represented by small circles and are connected to the N atoms by heavy lines and to the O atoms by light lines.

(1.24 Å.), and glycine⁷ (1.25 Å. and 1.27 Å.)—structures which involve a similar type of resonance. The C—C distance of 1.51 Å. does not differ from the normal value (1.54 Å.) by more than the limits of accuracy, and no significance can be attached to the apparent shortening. The C—N distance of 1.38 Å. is in agreement with the value 1.37 Å. found in urea⁵ and 1.35 Å. found in thiourea,¹³ but is somewhat greater than the value 1.33 Å. found in diketopiperazine.⁶

The angles found in the molecule are $\text{CH}_3\text{—C—O} = 129^\circ$, $\text{CH}_3\text{—C—NH}_2 = 109^\circ$, and $\text{NH}_2\text{—C—O} = 122^\circ$. These values are probably accurate to about $\pm 5^\circ$.

As shown in Figs. 5 and 6, the structure consists of planar molecules of acetamide arranged in rings of six, adjacent molecules in the ring being held together by N—H—O bridges. In these figures the O atoms are represented by black spheres, the methyl C atoms by black and white spheres, and the N and central C atoms by white spheres. The N atoms and central C atoms are distinguished by the fact that the latter are pierced by screw

axes which are indicated by rods in the figure. The directions of the N—H—O bridges are represented by the narrow white lines in the figures, while the methyl—methyl contacts are indicated by the heavy white lines.

In Fig. 5 the O—N_I and O—N_{II} distances are 2.89 and 2.83 Å., respectively, which do not deviate from their mean, 2.86 Å., by more than the estimated probable error. The rings of six molecules are also interconnected by N—H—O bridges, as is shown in Fig. 5, by the molecule whose central carbon atom is designated by the letter A.

The plane of the molecule is approximately the plane determined by the N atom and the two O atoms to which it is bridged. This is shown by molecule B in Fig. 6. The methyl C atom and central C atom lie somewhat above this plane; the maximum deviations from the median plane are about 0.1 Å. It can be seen from the position of molecule C in Fig. 5, that the plane of the molecule is far from the plane determined by the O atoms and the two N atoms to which it is bridged. This indicates that the H atoms are covalently bound to the N atom.

(13) R. W. G. Wyckoff and R. B. Corey, *Z. Krist.*, **81**, 386 (1932).

The methyl-methyl contacts are indicated by the heavy white lines in Fig. 5. In this figure the C atoms, designated 1, 2 and 3, lie in a plane parallel to the base of the unit cell, while atoms 4 and 5 are above and below this plane, respectively. The distances C_1-C_2 and C_1-C_3 are both 3.98 Å.; C_1-C_4 and C_1-C_5 are both 4.15 Å. These distances are about the same as the methyl-methyl distances in many other organic crystals.

The distances between CH_3 and the O and N atoms of adjacent molecules are shown in Fig. 6. In this figure the distance between the methyl C atom of molecule B to the O atom of molecule D is 4.07 Å.; the distance to the N atom of molecule E is 3.74 Å.; and the distance to the O atom of molecule F is 3.54 Å.; the last distance probably represents a CH_3-O contact—the other distances are probably too large.¹⁴

Acknowledgment.—One of the authors, Fred-eric Senti, wishes to express his gratitude to the American Can Company for their financial assistance without which this work would not have been possible. The authors are also indebted to Alice Senti for the painstaking assistance she has given in performing the lengthy calculations, to Dr. Edward R. Blanchard of this department for the use of his calculating machine, to Mr. John

(14) The distances taken by L. Pauling, ("The Nature of the Chemical Bond," Cornell University Press, Ithaca, N. Y., 1939, p. 177) to represent intermolecular contacts are $CH_2-CH_2 = 3.96$, $CH_2-O = 3.32$, 3.33 , $CH_2-N = 3.55$, 3.69 in diketopiperazine, and $CH_2-CH_2 = 4.05$, $CH_2-O = 3.38$, 3.52 in glycine.

Graham for preparing the photographs for Figs. 5 and 6, and to Dr. S. B. Hendricks for the use of his set of Beevers and Lipson sine and cosine strips.

Summary

The crystal structure of acetamide has been determined. Its space group is C_{3v}^6-R3c ; $a_0 = 11.44 \pm 0.03$ Å., $c_0 = 13.49 \pm 0.03$ Å. referred to the smallest hexagonal unit cell which contains eighteen molecules of CH_3CONH_2 . The structure is completely determined by stating the coordinates of the atoms in one molecule.

| | |
|------------------------------|-------------------------------|
| $X_O = 0.225 \pm 0.004$ | $Y_O = -0.004 \pm 0.004$ |
| $X_{CH_3} = 0.477 \pm 0.005$ | $Y_{CH_3} = 0.123 \pm 0.005$ |
| $X_{NH_2} = 0.333 \pm 0.004$ | $Y_{NH_2} = -0.090 \pm 0.004$ |
| $X_C = 0.333 \pm 0.004$ | $Y_C = 0.005 \pm 0.004$ |
| | $(Z_O = 0.000)$ |
| | $Z_{CH_3} = 0.033 \pm 0.023$ |
| | $Z_{NH_2} = 0.096 \pm 0.004$ |
| | $Z_C = 0.034 \pm 0.004$ |

This structure leads to the conclusions (a) that the length of the N-H-O bridge is 2.86 ± 0.05 Å., (b) the molecule of acetamide is planar, (c) the molecule exists in the keto form, and (d) the N-H bonds lie in the plane of the molecule. The intramolecular distances are $C-CH_3 = 1.51 \pm 0.05$ Å., $C-NH_2 = 1.38 \pm 0.05$ Å., $C-O = 1.28 \pm 0.05$ Å., and the bond angles are $CH_3-C-NH_2 = 109 \pm 5^\circ$, $CH_3-C-O = 129 \pm 5^\circ$, and $NH_2-C-O = 122 \pm 5^\circ$.

BALTIMORE, MD.

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[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF THE UNIVERSITY OF CALIFORNIA]

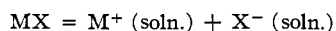
Ionic Entropies and Free Energies and Entropies of Solvation in Water-Methanol Solutions

BY WENDELL M. LATIMER AND CYRIL M. SLANSKY¹

Sufficient thermodynamic data are now available for the calculation of the partial molal entropies of a number of ions in water-methanol solutions whose compositions range from pure water to pure alcohol. This paper will present these calculations and discuss the entropy and free energy of solvation with reference to the general picture of the solvation process.

Ionic Entropies.—The calculation of partial molal ionic entropies in any solvent will follow the method used in aqueous solutions by Latimer

and co-workers.² In short it involves the calculation of the entropy of solution of a substance MX from the heat and free energy of solution by the equation $\Delta F^\circ = \Delta H^\circ - T\Delta S^\circ$. All of the calculations in this paper are at 298.1°K. The process of solution is written



From the ΔS° of solution and the entropy of MX, one obtains the sum of the positive and negative ionic entropies.

$$\bar{S}^\circ_{M^+} + \bar{S}^\circ_{X^-} = \Delta S^\circ + S^\circ_{MX}$$

(1) Shell Research Fellow in chemistry, academic year 1939-1940. Present address, The Dow Chemical Co., Midland, Michigan.

(2) W. M. Latimer and R. M. Buffington, *THIS JOURNAL*, **48**, 2297 (1926).