

## The Crystal and Molecular Structure of Diformylhydrazine, OHC–HN–NH–CHO. I. The X-ray Analysis

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Crystals of diformylhydrazine have been investigated carefully by X-ray methods. There are two formula units in the unit cell of dimensions,  $a = 8.939 \pm 0.004$ ,  $b = 6.253 \pm 0.002$ ,  $c = 3.565 \pm 0.002$  Å,  $\beta = 112.5 \pm 0.1^\circ$ . The space group is  $C_{2h}^2-P2_1/a$ . Most signs of  $F(hk0)$  and  $F(h0l)$  were determined by the inequality method using Sakurai's chart. Atomic coordinates including those of hydrogen have been determined by  $(F_o - F_c)$ -syntheses along the [001] and [010] axes. To distinguish the contribution of the anisotropic thermal vibration from that of the non-spherical distribution of the electron density around the atoms 'partial'  $(F_o - F_c)$ -syntheses were applied. The bond distances and their standard deviations (in parentheses) are N–N = 1.392 (0.007), N–C = 1.325 (0.004), C–O = 1.214 (0.005), N–H = 0.82, C–H = 0.94, N–H...O = 2.799 (0.006) Å. The bond angles are N–N–C = 121.3° (0.3°) and N–C–O = 124.9° (0.4°). The number of electrons at the atoms or the atomic groups read off from the  $(F_o - F_c)$ -synthesis on (001) are 8.6, 6.6 and 7.7 for O, CH and NH groups respectively. The fact that the molecule has a planar structure is explained by conjugation and charge effects. The deformation of the valence-shell electron distribution has also been discussed. The molecules are linked by N–H...O hydrogen bonds forming two-dimensional network in the (201) planes, which correspond to the cleavage plane.

### Introduction

The geometrical configuration of the hydrazine molecule has been explained by Penny & Sutherland (1934) in a typical example of the application of the VB (valence bond) treatment. According to their calculation, the most important factor determining the azimuth of one-half of the molecule with respect to the other is the  $p$ -state contribution to the two lone pair orbitals on the adjacent nitrogen atoms, since the interaction of such lone pairs depends strongly on the azimuthal angle. In other words, the molecular form depends largely on the *hybridization effect* on the lone pair orbitals at the nitrogen atoms. They concluded from their calculation that the hydrazine molecule does not have a *trans* form with the molecular symmetry  $C_{2h}$ , the azimuthal angle being  $180^\circ$ , but a *gauche* form with lower symmetry,  $C_2$ , the azimuthal angle being  $110^\circ$ . An X-ray analysis of the crystal structure of hydrazine (Collin & Lipscomb, 1951) has shown that the molecule has a kind of *eclipsed* form with the symmetry  $C_2$  and azimuthal angle  $120^\circ$ , which quite resembles that proposed by Penny & Sutherland (1934). Electron diffraction studies of gaseous hydrazine (Giguère & Schomaker, 1943), and of N,N- and N,N'-dimethylhydrazine (Beamer, 1948) have also been made, the results being comparable with the theoretical expectations of Penny & Sutherland (1934).

The configuration of a hydrazine derivative will be markedly affected if the substituted radicals have a strong influence upon the electronic structure, changing the  $p$ -state contribution to the lone pairs. We have therefore investigated the crystal structure of difor-

mylhydrazine to obtain some information on such substituent effects, hoping that the formyl radical may attract strongly the lone pair electrons from the nitrogen atom and lead to a *conjugation effect*. The substance is also of interest from the point of view of the formation of NH...O type hydrogen bond and of the relation to the structure of the amide group –CONH– in peptides and other substances.

In connexion with these problems, the energy of the hydrogen bond (Suzuki, Onishi, Koide & Seki, 1956), the infra-red absorption spectra (Miyazawa, 1955) and the near ultra-violet absorption spectra (Yamada & Tsuchida, 1954) of this crystal have also been investigated on the basis of the crystal and molecular structure determined by the present authors. In a following report (Tomiie, hereafter (II)), some theoretical considerations of the electronic structure of this molecule will be given by applying the simple *MO* (molecular orbital) method and the result will be compared with experiment.

The material used for our present study was kindly given us by Dr J. B. Class of Prof. J. G. Aston's Laboratory, the Pennsylvania State University.

### Experimental

Small crystals were obtained from a saturated aqueous solution by slow evaporation in a desiccator at room temperature. The crystals were well-formed prisms or needles elongated along the monoclinic  $c$  axis and showed an excellent cleavage parallel to the (201) plane. The samples used for the structure determination were rods the diameters of which were in the range

from 0.15 to 0.30 mm. There are two formula units in the unit cell of the dimensions,

$$a = 8.939 \pm 0.004, \quad b = 6.253 \pm 0.002, \quad c = 3.565 \pm 0.002 \text{ \AA}, \\ \beta = 112.5 \pm 0.1^\circ,$$

and the space group is  $C_{2h}^5-P2_1/a$ . The calculated density is  $1.58 \text{ g.cm.}^{-3}$ .

Useful X-ray data were obtained from oscillation and Weissenberg photographs around  $a$ ,  $b$ ,  $c$  and  $[102]$  axes taken with filtered  $\text{Cu } K\alpha$  radiation using the multiple-film technique. Accurate intensities of the  $(hk0)$  and  $(h0l)$  reflexions were obtained from the photographs using an integrating Weissenberg camera (Wiebenga & Smits, 1950). They were measured with a microphotometer by comparing with standard intensity scales. The intensity ratios among the multi-films were determined by means of a Geiger-Müller counter. Intensities of  $(0kl)$  and other reflexions were measured visually. From the features of the Laue photographs and the opacity of the samples the extinction effect seemed not to be very appreciable. Comparison of independent measurements gave the standard deviation for 66  $F(hk0)$ 's as  $\sigma(F_o) = 0.15$ , and that for 37  $F(h0l)$ 's as 0.22 ( $F(000) = 92$ ).

#### Determination of the structure

Relative values of the observed structure factors of the  $(hk0)$  and  $(h0l)$  reflexions were converted to absolute scale by Wilson's method (Wilson, 1942). There was no need to calculate a Patterson function, since the inequality method could be easily applied for the determination of signs of the structure factors. The signs of 37 out of 66  $F(hk0)$ 's and of 30 out of 37  $F(h0l)$ 's were directly determined by the Harker-Kasper inequality method (Harker & Kasper, 1948) using Sakurai's chart (Sakurai, 1952). (None of  $F(hk0)$ 's and 8 of  $F(h0l)$ 's differed from the final signs.) Thus the approximate electron-density distributions projected along the  $[001]$  and  $[010]$  axes were

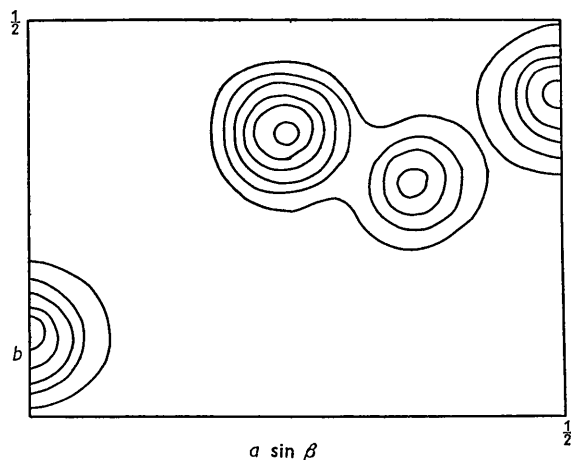


Fig. 1. Electron-density distribution projected on the plane perpendicular to the  $c$  axis. Contours are at every  $2 \text{ e.}\text{\AA}^{-2}$ .

calculated. Though the latter contained eight terms with wrong signs, the calculation fortunately gave a sufficiently clear map as the first step. The final syntheses along  $[001]$  and  $[010]$  with all observed  $F$ 's were both made after three successive calculations. After obtaining the atomic coordinates from these maps, the electron-density projection along  $[100]$  was also calculated. The results are shown in Figs. 1, 2 and 3.

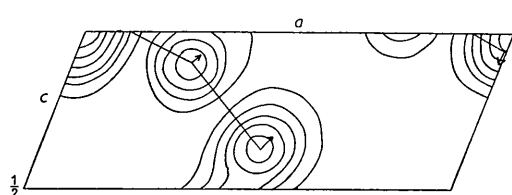


Fig. 2. Electron-density distribution projected on  $(010)$ . Contours are at every  $2 \text{ e.}\text{\AA}^{-2}$ . The directions of maximum thermal vibration are shown by arrows.

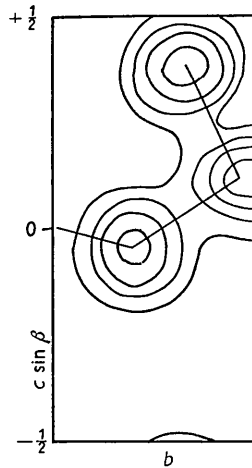


Fig. 3. Electron-density distribution projected on the plane perpendicular to the  $a$  axis. Contours are at every  $2 \text{ e.}\text{\AA}^{-2}$ , the contour at  $2 \text{ e.}\text{\AA}^{-2}$  level being omitted.

#### Refinement of the structure

The refinement of the structure was carried out by the use of  $(F_o - F_c)$ -syntheses (Cochran, 1951) along the  $[001]$  and  $[010]$  axes. Besides the refinement of the atomic coordinates, an attempt was made to separate the thermal vibration effect from the non-spherical distribution of the valence electrons around the atoms. The electrons in a second row atom are divided into the inner core ( $K$ -shell) and the valence-shell ( $L$ -shell) electrons. The distribution of the valence-shell electrons will be affected by the bonding states, whereas the inner core will practically not be affected. McWeeny (1951) expressed the atomic scattering factor of a second period atom by adding up the component scattering factors  $f(1s)$ ,  $f(2s)$  and  $f(2p)$  which were derived from the squares of the variational

1s, 2s and 2p orbitals of Duncanson & Coulson (1944). The distribution of the 1s electron is given by

$$\varphi^2(1s) = c^3/\pi \cdot \exp(-2cr),$$

where, if the atomic unit is chosen as the unit of length,  $c$  is the effective nuclear charge for the  $K$ -shell electrons which is given by Duncanson & Coulson (1944) or by Slater (1932). Then the value of  $f(1s)$  is

$$f(1s) = 1/(1+x^2)^2, \text{ where } x = 2\pi \sin \theta/c\lambda. \\ (\lambda \text{ in atomic unit.})$$

Subtracting twice the  $f(1s)$  value from the atomic scattering factor given by McWeeny (1951), we obtain the scattering factor of the valence-shell electrons. In Fig. 4 are shown the scattering factors of the  $K$ -shell

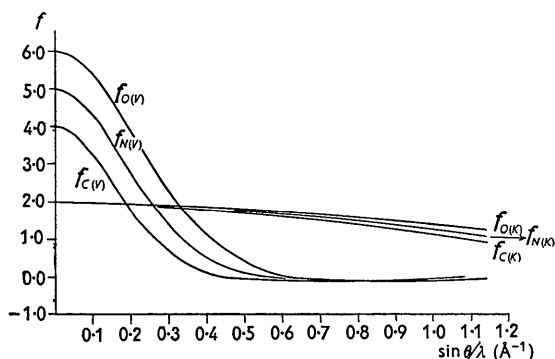


Fig. 4. The scattering factors of the  $K$ -shell electrons and of the valence-shell electrons for carbon, nitrogen and oxygen atoms calculated by using McWeeny's procedure.

electrons and those of the  $L$ -shell electrons in the average distributions for carbon, nitrogen and oxygen atoms. From Fig. 4, we find that the scattering of the valence-shell electrons decreases rapidly and has practically little contribution to the atomic scattering factor in the range of  $(\sin \theta/\lambda)$  larger than 0.35 for carbon, 0.45 for nitrogen and 0.50 for oxygen. On the other hand, the scattering of the inner core electrons does not decrease so rapidly. Therefore these atomic scattering factors will be given approximately as equal to the  $2f(1s)$  at higher diffraction angles. Since the 1s electron distribution is spherical, the 'partial  $(F_o - F_c)$ -synthesis', in which exclusive use is made of structure factors of high indices, will be valid for the determination of the anisotropic temperature factors of the atoms. If we observe in the map of this synthesis anisotropic electron distribution around an atom, it will be attributed to the anisotropic thermal vibration of the atom. In practical application to crystals which contain only carbon, nitrogen and oxygen atoms, we may use data in the range of  $(\sin \theta/\lambda)$  larger than 0.4. On the other hand, Cruickshank (1949) has given the formula for the standard deviation of the atomic coordinate  $x_n$  of the  $n$ th atom as follows,

$$\sigma(x_n) = 2\pi\{\sum h^2(\Delta F)^2\}^{1/2}/aVC_n,$$

where  $C_n$  is the curvature of its peak electron-density. Since it is obvious from this formula that the data for higher indices have an important influence on the accuracy of the atomic coordinates, the partial  $(F_o - F_c)$ -synthesis mentioned above will also be useful in the course of the refinement of the atomic parameters. Once the atomic coordinates and temperature factors are thus determined, information about the valence-electron distribution of the atoms will be obtained from the ordinary  $(F_o - F_c)$ -synthesis on the basis of these values.

In the present case, the  $x$  and  $y$  parameters and the temperature factors of the atoms were obtained after six successive partial  $(F_o - F_c)$ -syntheses along [001] using 41 structure factors with  $(\sin \theta/\lambda)$  values larger than 0.39. These are shown in Tables 1 and 2. In our

Table 1. Final atomic coordinates

	$x$	$y$	$z$
N	0.0030	0.1046	-0.0633
C	0.1389	0.2148	0.1088
O	0.2606	0.1477	0.3758
H <sub>C</sub>	0.130	0.355	0.010
H <sub>N</sub>	-0.075	0.160	-0.240

Table 2. Temperature factors (in  $\text{\AA}^2$  unit) of the atoms for the electron-density projections along [001] and [010]

	$(x, y \text{ plane})$		$(x, z \text{ plane})$	
	$\alpha = \beta$	$\beta$	$\gamma$	$\psi$
N	1.90	1.85	0.35	9°
C	1.90	1.65	1.00	15
O	1.95	1.30	2.50	20

The temperature factor has the form  $\alpha_i = \beta_i + \gamma_i \times \cos^2(\varphi - \psi_i)$  where  $\psi_i$  is the angle which the direction of maximum thermal vibration makes with the  $c$  axis, and  $(\varphi - \psi_i)$  is the angle which the direction of maximum thermal vibration makes with the normal of the reflexion plane.

calculation we adopted the atomic scattering factors of McWeeny (1951), of which  $f_o = (f'' + 2f')/3$  was

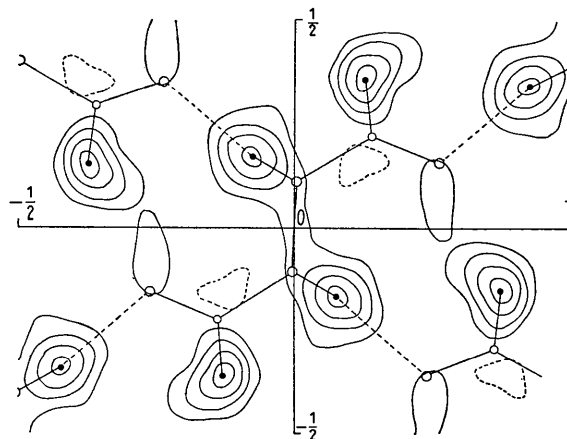


Fig. 5. The  $(F_o - F_c)$ -map on the plane perpendicular to the  $c$  axis. The  $F_c$ 's do not include the hydrogen contribution. Contours are at every 0.2 e. $\text{\AA}^{-2}$ , the zero contour being omitted.

used. The value of the  $R$  factor for all  $(hkl)$ 's became 0.068. The ordinary  $(F_o - F_c)$ -synthesis along  $[001]$  was then calculated by using all  $F(hk0)$ 's based on the final partial synthesis. Fig. 5 shows the  $(F_o - F_c)$ -map thus obtained in which the calculated structure factors do not include the hydrogen contribution. The positions of the hydrogen atoms have been determined from this map and are also listed in Table 1. The deviation of the electron distribution from that of free atoms can be read off from this map and also the actual total number of electrons associated with each atom is readily obtained. Table 3 shows the number of

Table 3. Number of electrons and the charge (in parentheses) associated with each atom from the final  $(F_o - F_c)$ -synthesis along  $[001]$

Oxygen	CH group	NH group
8.6 <sub>1</sub>	6.6 <sub>0</sub>	7.7 <sub>2</sub>
(-0.6 <sub>1</sub> )	(+0.4 <sub>0</sub> )	(+0.2 <sub>8</sub> )

electrons thus determined at the atoms, and Fig. 6 shows the area of each atom in which the number of electrons has been calculated.

After six successive partial  $(F_o - F_c)$ -syntheses on  $(010)$  with 21 structure factors with  $(\sin \theta/\lambda)$  values larger than 0.39,  $z$  parameters and temperature factors were obtained assuming that the  $x$  parameters determined from the projection along  $[001]$  were correct.

The parameters of the hydrogen atoms were obtained by the same procedure as in the case along  $[001]$ .

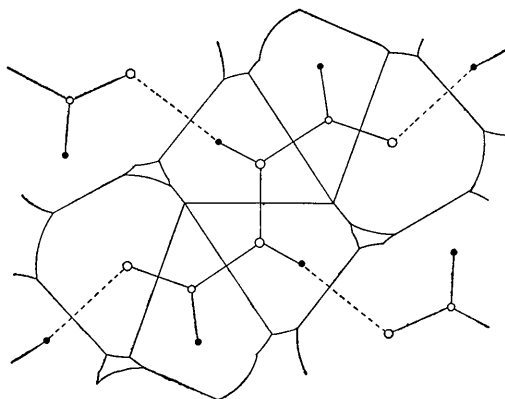


Fig. 6. Area associated with each atom or atomic group in which electron counts were made.

The results are shown in Tables 1 and 2. The value of the  $R$  factor for all  $F(h0l)$ 's is 0.107. If the anisotropic thermal vibrations of the atoms are not considered, the  $R$  factor becomes 0.16. The observed and calculated  $F(hk0)$ 's and  $F(h0l)$ 's are listed in Table 4. The bond lengths and bond angles derived from the atomic coordinates are listed in Table 5.

Table 4. Observed and calculated structure factors

$hkl$	$F_o$	$F_c$	$hkl$	$F_o$	$F_c$	$hkl$	$F_o$	$F_c$
200	6.62	- 5.91	830	0	+ 0.47	001	15.08	+16.52
400	20.69	+19.65	930	0.76	+ 0.67	201	20.71	+19.56
600	1.40	+ 1.51	040	15.52	-15.55	20 $\bar{1}$	38	+45.08
800	14.31	+13.18	140	9.86	+10.72	401	7.48	- 7.21
10,0,0	2.34	- 1.84	240	1.00	+ 0.75	40 $\bar{1}$	6.79	- 6.07
110	20.18	+21.31	340	3.69	- 3.48	601	19.96	+18.20
210	13.60	-14.47	440	16.18	-16.02	60 $\bar{1}$	10.93	+11.10
310	15.66	+14.80	540	0	- 0.40	801	0	- 0.12
410	1.12	+ 0.30	640	1.48	+ 1.48	80 $\bar{1}$	8.17	+ 8.14
510	5.12	+ 5.12	740	2.66	- 2.97	10,0, $\bar{1}$	3.08	+ 2.72
610	8.48	+ 8.19	840	4.07	- 4.20	002	10.01	+ 8.86
710	7.82	+ 7.63	940	3.05	+ 3.35	202	3.80	- 2.59
810	5.49	- 5.50	150	3.42	- 3.35	20 $\bar{2}$	15.77	+17.81
910	1.29	+ 1.56	250	3.64	- 3.39	402	8.45	+ 7.21
10,1,0	0	- 0.69	350	10.51	- 9.99	40 $\bar{2}$	0	- 0.37
020	16.92	-17.37	450	2.28	+ 2.12	602	5.44	+ 4.69
120	26	-25.70	550	5.81	- 5.89	60 $\bar{2}$	3.16	+ 3.64
220	11.88	+12.08	650	0	- 0.37	80 $\bar{2}$	3.82	+ 4.10
320	16.09	+15.49	750	0.82	- 0.69	10,0, $\bar{2}$	5.07	+ 5.15
420	7.37	+ 6.58	850	0.82	+ 0.94	003	3.72	+ 4.26
520	9.02	- 8.50	060	0	+ 0.13	203	3.38	- 4.25
620	1.89	+ 1.61	160	0	+ 0.42	20 $\bar{3}$	2.23	+ 1.38
720	4.98	+ 5.13	260	6.96	- 7.27	403	5.88	+ 5.72
820	2.95	- 2.76	360	4.99	- 5.13	40 $\bar{3}$	6.21	+ 6.87
920	4.98	- 5.18	460	1.42	+ 1.06	603	6.78	- 6.50
10,2,0	3.47	+ 3.39	560	5.87	+ 5.84	803	4.19	+ 4.72
130	8.78	- 9.14	660	5.45	- 5.14	10,0, $\bar{3}$	1.10	+ 1.08
230	7.58	+ 7.31	170	2.85	- 2.85	004	5.05	- 5.16
330	3.48	- 3.02	270	0	+ 0.43	204	3.83	+ 4.51
430	3.29	- 3.45	370	3.42	+ 3.15	404	0	- 0.94
530	0.94	+ 1.32	470	0	+ 0.07	604	0	- 0.54
630	3.21	- 2.90	570	0	- 0.40	804	2.45	- 2.84
730	6.38	- 6.84	080	2.22	+ 2.14			

Table 5. Bond lengths (in Å unit) and bond angles (°) with their standard deviations

N-N	1.392 (0.007)	N-N-C	121.3 (0.3)
N-C	1.325 (0.004)	N-C-O	124.9 (0.4)
C-O	1.214 (0.005)	O-C-H	120.5
C-H	0.94	N-N-H	117
N-H	0.82	N-N...O	129.5
NH...O	2.799 (0.006)	H-N...O	12.5

*Accuracy of the numerical results*

From a comparison of independent measurements, a lower limit of the standard deviation  $\sigma(F_o)$  can be obtained, while from a comparison of values of  $F_o$  with those of  $F_c$ , an upper limit of  $\sigma(F_o)$  is obtained. The lower limits are 0.15 for  $F(hk0)$  and 0.22 for  $F(h0l)$ , as already shown, and the upper limits are 0.47 and 0.80 respectively. We shall adopt  $\sigma(F_o) = 0.4$  for  $F(hk0)$  and 0.6 for  $F(h0l)$  as safe overestimates.

The standard deviation of the electron density is estimated by using the formula given by Cochran (1951). We find  $\sigma(\rho_o) = 0.1 \text{ e.}\text{Å}^{-2}$  for  $\rho(x, y)$  and  $0.2 \text{ e.}\text{Å}^{-2}$  for  $\rho(x, z)$ .

The standard deviation of the  $x$ -coordinate of the  $r$ th atom may be estimated from Booth's formula (1947) in which one puts  $p = 6.6$ . From the observed  $\rho(x, y)$  we have  $\sigma(x_N) = 0.002_8$ ,  $\sigma(x_C) = 0.003$ ,  $\sigma(x_O) = 0.002_4$  Å and from the observed  $\rho(x, z)$ ,  $\sigma(z_N) = 0.005_6$ ,  $\sigma(z_C) = 0.006_2$ ,  $\sigma(z_O) = 0.005_7$  Å respectively.

The standard deviation  $\sigma(d)$  of an interatomic distance between the atoms  $q$  and  $r$  is estimated from (Ahmed & Cruickshank, 1953),

$$d^2 \sigma^2(d) = d_x^2 \sigma^2(d_x) + d_y^2 \sigma^2(d_y) + d_z^2 \sigma^2(d_z),$$

where

$$\sigma^2(d_x) = \sigma^2(x_q) + \sigma^2(x_r), \text{ etc.},$$

or when there is a centre of symmetry in the bond,

$$\sigma(d_x) = 2\sigma(x_r), \text{ etc.},$$

where  $d_x, d_y$  and  $d_z$  are the three components of  $d$ . Taking  $\sigma(y_r)$  equal to  $\sigma(x_r)$  on the  $\sigma(x, y)$  distribution, we calculate from the above formula  $\sigma(\text{N-N}) = 0.007$ ,  $\sigma(\text{N-C}) = 0.004$  and  $\sigma(\text{C-O}) = 0.005$  Å.

The standard deviation of a bond angle is derived by applying the formula given by Cruickshank & Robertson (1953). The standard deviations of N-C-O and N-N-C are 21' and 18' respectively.

The standard deviation  $\sigma(n_o)$  of the number  $n_o$  of electrons of each atom can be estimated by the procedure given by Cochran (1951). Since the average area of each atom, over which electron counts were made, is about  $4.0 \text{ Å}^2$  in  $\sigma(x, y)$  (Fig. 6), we have  $\sigma(n_o) = 0.1 \text{ e.}\text{Å}^{-2}$ .

**Discussion***Planarity of the molecule*

Putting aside the positions of hydrogen atoms for the moment, the molecule has a planar S shape with a

centre of symmetry in it. The deviation of the position of an oxygen atom from the plane formed by the two nitrogen and the two carbon atoms is only 0.01 Å. For a derivative of hydrazine, this planar form is rather remarkable in view of the previously mentioned work (Penny & Sutherland, 1934); the repulsion between the two lone-pairs on the adjacent nitrogen atoms should generally be very strong due to their  $p\pi$  nature. To explain the stability of the planar structure, there should be other characteristic features in the electronic structure of the molecule. Since the formyl radicals have a tendency to attract electrons, one expects a considerable charge effect together with conjugation, both of which will enhance the stability of the planar form. Actually, in the present case, large values of the charges of the atoms (Table 3) and N-N and N-C bond shortenings are observed. Thus, it is concluded that electrons of the lone-pairs migrate onto the formyl oxygen and the remaining  $p\pi$ -electrons on the adjacent nitrogen atom are operative in forming  $p\pi$ -bonds alternatively between nitrogen and carbon, which contribute to the stability of the planar molecule. It appears that one should take into account two factors, the effects of charges and conjugation besides the hybridization effect as discussed by Penny & Sutherland. In the present case the former two effects overcome the latter, which tends to break the planarity of the molecule. This problem has also been treated quantitatively by the use of a simple MO method (II).

*The molecular dimensions*

Table 5 shows the bond lengths and bond angles together with their standard deviations. The N-N bond length is 1.392 Å, a value smaller than that found in hydrazine, 1.46-1.47 Å (Collin & Lipscomb, 1951; Giguère & Schomaker, 1943) and also smaller than those of  $\text{N}^+-\text{N}^+$ , 1.42-1.40 Å found in  $\text{N}_2\text{H}_6\text{F}_2$  (Kronberg & Harker, 1942),  $\text{N}_2\text{H}_6\text{Cl}_2$  (Donohue & Lipscomb, 1947) and  $\text{N}_2\text{H}_6\text{SO}_4$  (Nitta, Sakurai & Tomiie, 1951), and  $\text{N}^+-\text{N}$ , 1.45 Å found in  $\text{N}_2\text{H}_5\text{Cl}$  and  $\text{N}_2\text{H}_5\text{Br}$  (Sakurai & Tomiie, 1952). The shortening of the distance suggests more or less double bond character, in accordance with the consideration given in the previous paragraph.

The configuration of -HNCO- group is of the so-called *trans* type and the N-C and C-O bond lengths are 1.325 and 1.214 Å respectively. For the sake of comparison Table 6 shows the bond lengths of the amide group in polypeptides and related molecules. The dimensions of the -HNCO- group in the diformylhydrazine are not unusual for an amide group and are even sensibly the same as those postulated for the -HNCO- group in proteins by Pauling (1953).

Using these results, Miyazawa (1955) investigated the infra-red spectra of this crystal and obtained valuable information about the assignment of the absorption bands of peptides and related molecules.

Table 6. Bond lengths in amide groups

	C-O (Å)	C-N (Å)	∠N-C-O (°)	Ref.†
(-CONH <sub>2</sub> )				
Formamide	1.25 <sub>5</sub>	1.30 <sub>0</sub>	121.5	(1)
Acetamide	1.28	1.38	122	(2)
Oxamide*	1.24 <sub>3</sub>	1.31 <sub>5</sub>	125.7	(3)
Succinamide*	1.23 <sub>8</sub>	1.33 <sub>3</sub>	122	(4)
Chloroacetamide	1.23	1.33	130.1	(5)
Nicotinamide	1.22	1.34	125	(6)
Glutamine	1.27	1.28	123	(7)
Glycylasparagine*	1.22	1.36	120	(8)
Urea*	1.26 <sub>2</sub>	1.33 <sub>5</sub>	121	(9)
(-CONH-)				
Diformylhydrazine	1.21 <sub>4</sub>	1.32 <sub>5</sub>	124.9	(10)
Diketopiperazine	1.25	1.33	—	(11)
Acetanilide*	1.22 <sub>6</sub>	1.33 <sub>0</sub>	121.7	(12)
N,N'-Diacetyl- hexamethylenediamine	1.22	1.35	124	(13)
N-Acetylglycine*	1.24	1.32	121	(14)
Glycyltyrosine.HCl.H <sub>2</sub> O	1.16	1.45	132	(15)
β-Glycylglycine	1.23	1.29	125	(16)
α-Glycylglycine	1.24	1.32	124.4	(17)
Cysteylglycine. ½NaI*	1.21	1.32	107	(18)
N,N'-Diglycyl- cystine. 2 H <sub>2</sub> O*	1.21	1.35	125.3	(19)
Glycylasparagine*	1.23	1.32	124	(20)
Polypeptide chain	1.24	1.32	125	(21)
Cyanuric acid*	1.21	1.35	122	(22)
Parabanic acid	1.21 <sub>2</sub>	1.36 <sub>0</sub>	126.1	(23)
	—	1.38 <sub>1</sub>	129.3	—
Uracil	1.23 <sub>0</sub>	1.34 <sub>4</sub>	119.9	(24)
	1.24 <sub>1</sub>	1.38 <sub>4</sub>	124.5	—
	—	1.37 <sub>4</sub>	118.5	—

\* Determined by three-dimensional investigation.

† (1) Ladell & Post, 1954. (2) Senti & Harker, 1940. (3) Ayerst & Duke, 1954. (4) Davies & Pasternak, 1956. (5) Dejace, 1955. (6) Wright & King, 1954. (7) Cochran & Penfold, 1952. (8) Pasternak, Katz & Corey, 1954; (4). (9) Vaughan & Donohue, 1952. (10) This work. (11) Corey, 1938. (12) Brown & Corbridge, 1954. (13) Bailey, 1955. (14) Carpenter & Donohue, 1950. (15) Smits & Wiebenga, 1953. (16) Hughes & Moore, 1949. (17) Hughes, Wilson & Biswas. (18) Dyer, 1951. (19) Yakel & Hughes, 1954. (20) Pasternak, Katz & Corey, 1954. (21) Pauling, 1953. (22) Wiebenga, 1952. (23) Davies & Blum, 1955. (24) Parry, 1954.

#### Location of the hydrogen atoms

From the ( $F_o - F_c$ )-syntheses along [001] and [010] axes, the positions of the hydrogen atoms have been determined. The C-H and N-H bond lengths are estimated to be 0.94 and 0.82 Å respectively. These are considerably shorter than the accepted values (1.07 and 1.02 Å respectively) obtained spectroscopically. The X-ray analysis tells us not the position of the nucleus but the electron-density distribution, of which a maximum will ordinarily be attributed to the position of the nucleus. Atoms other than hydrogen have non-bonded *K*-shell electrons whose density is sufficiently high at the centre of the atom so that the nuclear coordinates of an ordinary atom will be given by the maximum of the electron-density distribution. But for the hydrogen atom, the *K*-shell itself is the valence shell and we must not expect the maximum density at the position of the proton in a bonding

state. We have discussed this problem of the location of the bonded hydrogen atom using a simple *VB* method, the details of which will be published elsewhere. We concluded that the position of the maximum electron density for the bonded hydrogen with thermal vibration does not coincide with that of the proton. For example, the apparent C-H bond length calculated is 0.91 Å for the two-dimensional case assuming 7% bond ionic character and the temperature factor,  $B = 2.232 \text{ \AA}^2$ . The apparent shortening of the C-H bond (and also that of the N-H) has thus been explained theoretically. However, we must be careful whether the difference between the values obtained by the X-ray method and by spectroscopy is significant.

The hydrogen atom attached to the nitrogen lies approximately in the plane determined by the nitrogen and carbon atoms and the deviation of the hydrogen attached to the carbon from this plane does not exceed 0.03 Å; all the atoms including hydrogen lie on one plane within the experimental error.

#### Number of electrons in certain atoms or groups of atoms

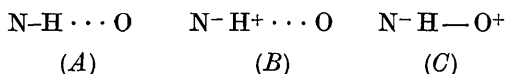
The number of electrons and the charges associated with each atom have been read off from the final ( $F_o - F_c$ )-synthesis along [001] axis (Fig. 5) and are shown in Table 3. As already stated, the number of the electrons are found to be 8.6<sub>1</sub>, 6.6<sub>0</sub> and 7.7<sub>2</sub> for O atoms, CH and NH groups respectively, while the standard values are 8, 7 and 8 respectively. From these values we may conclude that the migration of the  $\pi$ -electrons in the molecule is rather pronounced since the ionic character of the  $\sigma$ -bonds is not sufficient to explain such large charges on the atoms. The tendency of the  $\pi$ -electrons to migrate has been explained theoretically by the *MO* treatment (II).

That the molecule has not a zig-zag chain but an S shape, is explained by the electrostatic attraction between the positively charged nitrogen and the negatively charged oxygen atoms. Besides the conjugation effect mentioned already, this intramolecular electrostatic interaction may also contribute more or less to the planarity of the molecule. Considering a hypothetical skew molecule, in which the two planes formed by the two -HNCHO groups are perpendicular to each other, and comparing the electrostatic energy of the hypothetical molecule with that of the planar one, we can obtain a measure for the energy of stabilization due to the charges. Assuming suitable values suggested by (II) for the charges; i.e. -0.61 at O, +0.14 at N, +0.14 at H<sub>N</sub>, +0.31 at C and +0.09 at H<sub>C</sub>, the energy of the stabilization is estimated to be 15 kcal.mol.<sup>-1</sup>.

#### Distribution of the valence-electrons

From the final ( $F_o - F_c$ )-synthesis along the [001] (Fig. 5) we obtain some information about the non-

spherical distribution of the valence-electrons in the molecule. The oxygen atom has two  $\sigma$ -lone-pairs, one of which is free while the other is the proton acceptor for the  $\text{NH} \cdots \text{O}$  hydrogen bond in the crystal. From Fig. 5 it is observed that the electron-density at the region of the free  $\sigma$ -lone-pair is higher than that of the hydrogen-bonded one, on the average. Since  $\sigma(\rho_0)$  is estimated to be  $0.1 \text{ e.}\text{\AA}^{-2}$ , the difference between the densities of these regions is apparently significant, for the actual value of the difference amounts to  $0.4 \text{ e.}\text{\AA}^{-2}$ . This suggests that the electron distribution of the oxygen atom is considerably deformed by the hydrogen bond. This may be interpreted as due to a considerable contribution of the following resonance component (C) of the  $\text{NH} \cdots \text{O}$  hydrogen bond.



A similar theoretical discussion has been given by Coulson & Danielsson (1954) about  $\text{OH} \cdots \text{O}$  hydrogen bonds.

The negative region in Fig. 5 near the C atom and opposite to the C-H bond may be similar in origin to that of the negative region observed in the central part of the benzene ring of salicylic acid (Cochran, 1953) or of the heteroaromatic rings of adenine hydrochloride (Cochran, 1951).

#### Hydrogen bond

The length of the  $\text{NH} \cdots \text{O}$  hydrogen bond is  $2.799 \text{ \AA}$ , the standard deviation being  $0.006 \text{ \AA}$ . In Table 7 for compounds containing amide groups, we find that the  $\text{NH} \cdots \text{O}$  distance in diformylhydrazine is more or less shorter than those in ordinary amide crystals. In Table 8 for polypeptides one finds strong hydrogen bonds when the proton donor is  $-\text{NH}_3^+$  group, but not such strong ones when the donor is amino or

Table 7. *The lengths of  $\text{NH} \cdots \text{O}$  hydrogen bonds formed by molecules with amide groups*

	Distance ( $\text{\AA}$ )	Ref.†
Formamide	$2.95_3, 2.88_0$	(1)
Acetamide	$2.83, 2.99$	(2)
Oxamide	$2.94_1, 2.94_9$	(3)
Succinamide*	$2.93_9, 2.94_2$	(4)
Chloroacetamide	$2.82, 3.01$	(5)
Nicotinamide	$2.99$	(6)
Urea*	$2.99, 3.04$	(9)
Diformylhydrazine	$2.79_9$	(10)
Diketopiperazine	$2.85$	(11)
Acetanilide*	$2.96_9$	(12)
N:N-Diacetyl-hexamethylenediamine	$2.88$	(13)
Cyanuric acid*	$2.83, 2.88$	(22)
Parabanic acid	$2.84, 2.87$	(23)
Uracil	$2.81, 2.86$	(24)
Polypeptide chain	$2.79 \pm 0.12$	(21)

\* Determined by three-dimensional investigation.

† Reference number is the same as that in Table 6.

Table 8. *The length of  $\text{NH} \cdots \text{O}$  hydrogen bond in polypeptide crystals*

	Distance ( $\text{\AA}$ )			Ref.†
	(A)*	(B)*	(C)*	
Glutamine	$\left\{ \begin{array}{l} 2.94 \\ 2.91 \end{array} \right.$	$\left\{ \begin{array}{l} 2.85 \\ 2.79 \end{array} \right.$	$2.91$	(7)
$\beta$ -Glycylglycine	$3.07$	$\left\{ \begin{array}{l} 2.68 \\ 2.80 \end{array} \right.$	$2.81$	(16)
N-Acetylglycine	$3.03\ddagger$	—	—	(14)
N,N'-Diglycylcystine. 2 $\text{H}_2\text{O}$	—	$\left\{ \begin{array}{l} 2.75 \\ 2.75 \\ 2.89 \end{array} \right.$	—	(19)
Glycylasparagine	$\left\{ \begin{array}{l} 2.88 \\ 2.88 \\ 2.93 \end{array} \right.$	$2.75$	$\left\{ \begin{array}{l} 2.86 \\ 3.03 \end{array} \right.$	(20)

\* The values show those of (A) ( $-\text{NH}_2$  or  $-\text{NH}$ )  $\cdots$  ( $-\text{CO}_2^-$ ), (B) ( $-\text{NH}_3^+$ )  $\cdots$  ( $-\text{CO}_2^-$ ), (C) ( $-\text{NH}_3^+$ )  $\cdots$  ( $>\text{C}=\text{O}$ ).

† Reference number is the same as that in Table 6.

‡ The acceptor is  $-\text{COOH}$  group.

imino nitrogen. The hydrogen bond distance in diformylhydrazine rather resembles those formed by  $-\text{NH}_3^+$  in polypeptides or aminoacids. This short hydrogen bond may be partly due to the very large positive and negative charges at the nitrogen and the oxygen atoms respectively. The angle which the  $\text{N} \cdots \text{O}$  direction of the hydrogen bond makes with the plane formed by the molecule is about  $3^\circ$ ; i.e. the deviation of the neighbouring oxygen from the molecular plane is  $0.15 \text{ \AA}$ . The deviation of the N-H bond out of the  $\text{N} \cdots \text{O}$  direction is  $12.5^\circ$ . The angle of  $\text{N}-\text{N} \cdots \text{O}$  is  $129.5^\circ$ . The angle which the  $\text{O} \cdots \text{H}$  direction makes with the molecular plane in which the oxygen lies is about  $20^\circ$ . The angle  $\text{C}-\text{O} \cdots \text{H}$  of the hydrogen bond is  $122.5^\circ$ , which is approximately the same as the ( $sp^2$ ) hybridized valence angle.

In the infra-red absorption spectra of this crystal, Miyazawa (1955) has chosen the strongest absorption at  $3100 \text{ cm.}^{-1}$  as  $\nu(\text{N}-\text{H})$ , which is much lower than values for ordinary amide crystals such as N-methylacetamide ( $3250 \text{ cm.}^{-1}$ ) or N-methylformamide ( $3250 \text{ cm.}^{-1}$ ). This also suggests the existence of a strong hydrogen bond in this crystal.

The energy of this hydrogen bond has been estimated by Suzuki, Onishi, Koide & Seki (1956) to be  $6.1 \text{ kcal.mol.}^{-1}$  bond from the determination of the heat of sublimation of this crystal. This is a rather large value as compared with the  $\text{NH} \cdots \text{O}$  hydrogen bond energies found so far. Thus it has been confirmed, by the X-ray, infra-red and thermal investigations, that strong hydrogen bonds occur in this crystal.

The molecules are linked together by hydrogen bonds, forming a two-dimensional network parallel to  $(20\bar{1})$ , thus explaining the remarkable cleavage parallel to  $(20\bar{1})$ .

#### Thermal vibration of the atoms

As seen from Table 2, the anisotropy of the temperature factors of the atoms is considerable in  $(010)$

but is not so notable in the plane perpendicular to [001]. Fig. 2 shows the direction of maximum thermal vibration of the atoms in the projection on (010). As the oscillation of the atoms perpendicular to the molecular plane is far greater than those in other directions and the magnitude of the displacement from the mean position of each atom becomes greater in the order of nitrogen, carbon, oxygen, we may conclude that the molecular vibration in the crystal mainly takes place about an axis approximately coincident with the N-N bond.

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