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The Crystal and Molecular Structure of Anhydrous Diacetylhydrazine $(-NHCOCH_3)_2$

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The crystal of anhydrous diacetylhydrazine is of the symmetry D_{2h}^{18}–*Ccma* having four molecules in a unit cell with the dimensions $a = 18{\cdot}30$, $b = 6{\cdot}51$ and $c = 4{\cdot}79$ Å. The crystal and molecular structure have been determined to a high degree of accuracy by the three-dimensional Fourier and least-squares methods. The positions of hydrogen atoms have also been determined. The molecule with a centre of symmetry is planar and lies in the (010) plane except two of the three hydrogen atoms in the methyl group. The N–N bond distance (1·396 Å) is slightly shorter than the average single bond distance and close to that of diformylhydrazine. The C–C bond (1·504 Å) is slightly but significantly shorter than the normal C–C single bond, showing influence of the hyperconjugation. According to a nuclear magnetic resonance experiment, it is found that the methyl groups are rotating about the C–C axis at room temperature. The difference map shows, however, clearly the peaks of hydrogen atoms of the methyl group as well as of the amide group. The N–C and C–O bond lengths are 1·341 and 1·221 Å, respectively. The molecules are linked by the N–H $\cdots$ O hydrogen bonds (2·877 Å) extended in the *c*-axis direction, forming molecular belts parallel to the (010) plane. As for the hydrogen bond, the angle N $\cdots$ O–C is 168·5°. The thermal motion of the molecule may be described by the superposition of the libration about the centre of symmetry and the translational vibration, the ellipsoid of which has its principal axes in the directions of the crystallographic axes. The thermal expansion coefficients have also been measured between −150 and 30 °C. by the X-ray method, the average linear expansion coefficients being

$$\beta_a = 4{\cdot}9 \times 10^{-5},\quad \beta_b = 2{\cdot}0 \times 10^{-4},\quad \beta_c = 3{\cdot}5 \times 10^{-5}\ \text{deg.}^{-1}.$$

Introduction

As part of crystal and molecular structure determination of hydrazine derivatives, diacetylhydrazine has been investigated. It has been found by the present X-ray investigation that there are at least two forms; i.e., anhydrous and monohydrated. 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 with the azimuthal angle 120°. Electron diffraction studies of gaseous hydrazine (Giguère & Schomaker, 1943) and N,N′-dimethylhydrazine (Beamer, 1948) have shown that both molecules are not planar. Recently, diformylhydrazine, which has an iso-electronic structure in the π-system with diacetylhydrazine, has been determined to a high degree of precision by the X-ray methods (Tomiie, Koo & Nitta, 1958), and its lattice energy has also been measured (Suzuki, Onishi, Koide & Seki, 1956). In that crystal the molecule has a planar '*S*' shape skeleton with the symmetry C_{2h} and hydrogen atoms are lying in this plane. The N–N bond length is more or less short (1·392 Å) for a single bond, and a strong N–H $\cdots$ O hydrogen bond is observed (2·788 Å). The number of electrons associated with each atom is obtained which coincides with the theoretical value by the use of molecular orbital treatment (Tomiie, 1958*b*). It is of interest to compare the molecular and crystal structure and other physical properties of diacetylhydrazine with those of diformylhydrazine. This paper describes the accurate determination of the crystal structure of anhydrous diacetylhydrazine and the comparison of its structure with that of diformylhydrazine. As for the monohydrate of diacetylhydrazine, the structure determination has also been carried out and the results will be published shortly. The sublimation pressures of anhydrous diacetylhydrazine between 69 and 80 °C. have been measured to obtain the experimental lattice energy which compared with the calculated energy (Takagi, Shintani, Chihara & Seki, 1959), and a nuclear magnetic resonance experiment has been also carried out (Shintani, Chihara, Itoh & Nitta, 1958). Moreover, Yamaguchi (1958) carried out a study on the anhydrous and monohydrate forms of diacetylhydrazine and those of deuterated by infra-red spectroscopy.

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Experimental

As has been mentioned, the diacetylhydrazine has two forms; i.e., anhydrous and monohydrated. This was confirmed by the X-ray diffractometry, density measurement and differential thermal analysis. The sample was recrystallized from aqueous solution and dehydrated in high vacuum. The anhydrous crystals are so hygroscopic that they change into monohydrate easily by absorbing water vapour under ordinary condition. Small single crystals with plate-like shape were obtained from a saturated *n*-butylalcohol solution by slow evaporation in a desiccator at room temperature. The crystals thus obtained were kept under a low pressure (several mm. Hg.) to prevent moisture. The samples used for the structure determination were cut into rods having almost square cross-section by a razor blade and sealed in thin glass capillaries. The specimens were about 0·25 in edge and 1·5 mm. in length. The orthorhombic unit-cell dimensions are

$$a=18{\cdot}30\pm0{\cdot}05,\quad b=6{\cdot}51\pm0{\cdot}02,\quad c=4{\cdot}79\pm0{\cdot}02\ \text{Å}\,,$$

and the formula units in a cell are four, calculated density being 1·35 g.cm.$^{-3}$.

Useful X-ray data were obtained from oscillation and Weissenberg photographs around the *b*- and *c*-axes taken with filtered Cu $K\alpha$ radiation. The observed systematic absences of spectra are hkl when $h+k$ is odd and $0kl$ when k or l odd; they are characteristic of the space group C^{17}_{2v}–Cca (8 general positions) or D^{18}_{2h}–$Ccma$ (centro-symmetric, 16 general positions), the latter being proved to be more adequate. Relative intensity values from the zeroth to the fifth layer in respect to k were obtained from a *b*-axis rod crystal by the integrating Weissenberg procedure and were read off several times visually in comparison with a calibrated intensity scale. The multiple-film technique was used to correlate weak and strong reflections. The ratio between maximum and minimum intensities is approximately 12000 to 1. Relative values of the observed $(h0l)$ structure factors were converted into the absolute scale by Wilson's method. No absorbtion correction was taken, since $\mu r(=0{\cdot}12)$ was very small. The thermal expansion coefficients between −150 and 30 °C. were measured by taking oscillation photographs at eight points of temperature using the same film. The average linear expansion coefficients thus determined were

$$\beta_a=4{\cdot}9\times10^{-5},\quad \beta_b=2{\cdot}0\times10^{-4},\quad \beta_c=3{\cdot}5\times10^{-5}\ \text{deg.}^{-1}.$$

Determination of the structure

For the *b*-axis reflections, the observed intensity distributions are much the same in the layer lines with k even and with k odd, respectively. This shows an almost perfect layer structure parallel to the (010) plane, the layers of molecules lying at $y=0$ and $\frac{1}{2}$ coincident with the mirror planes of the space group $Ccma$. The arrangement of molecules was in consistence with the space group $Ccma$ with four centro-symmetric molecules in the unit cell and the possibility of the space group Cca has been exclusively eliminated. The configuration of the molecule and the arrangement of the molecules within a layer were easily derived. The signs of 32 out of the observed $57F(h0l)$'s were directly determined by the Harker–Kasper inequality method using Sakurai's chart (1952), possible reflections being 62. Three of the signs were found to differ from the final results. In the structure factor calculation McWeeny's scattering factors (1951) were adopted throughout, of which $f_0=(f^{\parallel}+2f^{\perp})/3$. An approximate electron-density distribution projected on the (010) plane was calculated by using determined signs. Although this calculation contained three terms with wrong signs which have considerably large unitary structure factors, a sufficiently reasonable map could be obtained for the first step. Von Eller's equipment (1951*a*, *b*) was applied repeatedly to obtain Fourier maps and the Patterson function. The carbon atom is superposed almost perfectly upon the oxygen atom in the Fourier projection. This is shown in Fig. 1. In order to separate both atoms, the bounded projection

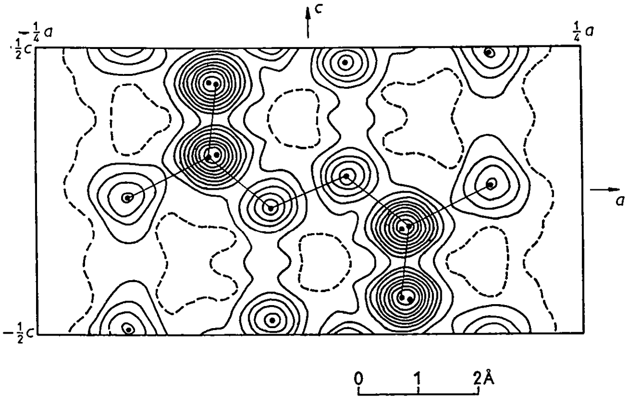

Fig. 1. Electron-density distribution projected on (010) plane. Contours are at every 2 e.Å^{-2} and dotted line shows 1 e.Å^{-2}.

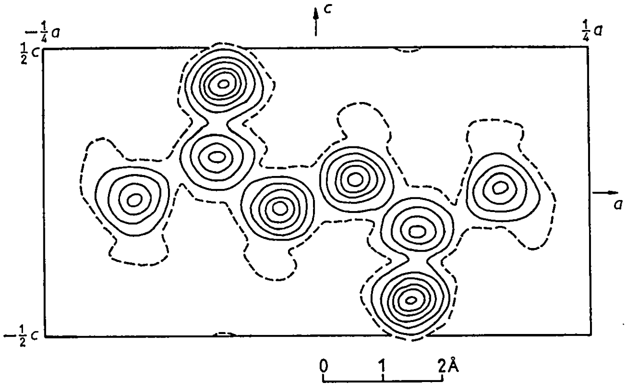

Fig. 2. The bounded projection ($y=-\frac{1}{4}$ to $+\frac{1}{4}$) on (010) plane. Contours are at every 2 e.Å^{-2} and dotted line shows 1 e.Å^{-2}.

technique ($y=-\frac{1}{4}$ to $+\frac{1}{4}$) was used (Booth, 1945). For the present crystal, the bounded half cell projection is given by the following equation,

$$\begin{aligned} B_{-\frac{1}{4}b}^{+\frac{1}{4}b}(X, Z) &= \int_{-\frac{1}{4}b}^{+\frac{1}{4}b} \varrho(X, Y, Z)dY \\ &= (b/V)[\tfrac{1}{2}\Sigma\Sigma F(h0l) \cos 2\pi(hX+lZ) \\ &\quad +(2/\pi)\ \Sigma\Sigma F(h1l) \cos 2\pi(hX+lZ) \\ &\quad -(2/3\pi)\Sigma\Sigma F(h3l) \cos 2\pi(hX+lZ) \\ &\quad +(2/5\pi)\Sigma\Sigma F(h5l) \cos 2\pi(hX+lZ) \\ &\quad -\ldots]\,. \qquad (1) \end{aligned}$$

Since, in the present case, corresponding reflections with the same set of h and l for

$$F(h1l),\ F(h3l),\ F(h5l),\ \ldots$$

are nearly equal, equation (1) can be approximated as follows:

$$\begin{aligned} B_{-\frac{1}{4}b}^{+\frac{1}{4}b}(X, Z) \approx \frac{b}{2V}[\Sigma\Sigma F(h0l) \cos 2\pi(hX+lZ) \\ +\Sigma\Sigma F(h1l) \cos 2\pi(hX+lZ)]\,. \qquad (2) \end{aligned}$$

Therefore, as a preliminary stage, only $F(h0l)$ and $F(h1l)$ structure factors were used to carry out a bounded projection. The final map is shown in Fig. 2.

Refinement of the structure

The refinement of the structure has been carried out by the use of the (F_o-F_c) synthesis (Cochran, 1951) on the (010) plane, for both the ordinary and bounded ($y=-\frac{1}{4}$ to $+\frac{1}{4}$) projections, followed by the least-squares method. For the observed structure factors of the nine strong reflections, the extinction correction was made by the use of equation (3). Since the extinction effect was considerable, nine strong reflections for which $(I_{\text{corr.}}-I_o)/I_{\text{corr.}}$ were larger than 5%, were correlated by the formula

$$I_o=I_{\text{corr.}} \exp(-gI_{\text{corr.}})\,, \qquad (3)$$

where g was suitably determined as $3{\cdot}25 \times 10^{-5}$, except the (200) reflection. The observed intensity value of the (200) reflection, which was the strongest, was extraordinarily smaller than the calculated value ($I_o=12100$, $I_{\text{corr.}}=30900$ and the ratio $I_{\text{corr.}}/I_o=2{\cdot}55$). The multiple reflection of (200) plane did not occur and was checked by taking photograph with filtered Co $K\alpha$ radiation. In place of the observed Fourier coefficient F_o for the (200) reflection was used the calculated value including contribution on hydrogen atoms, because as already mentioned, the observed (200) intensity was too small. The bounded (F_o-F_c) projection shows the peaks of hydrogen atoms of the methyl group as well as the amide group even at early stage of trial. Besides, this map shows the anisotropic vibration of the atoms in the xz plane, especially that of the oxygen atom, the direction of the largest vibration lying nearly in the a-axis direction. Moreover, it also shows that the farther the atom lies from the mass centre of molecule, the larger is the thermal motion. From the intensity ratios of reflections with the same h and l belonging to different layer lines are used to obtain the coefficient of the thermal factor along the b-axis. The coefficients of the thermal factor of the atoms along b-axis are remarkable. The general expression for the thermal factor has been given by Cruickshank (1956); i.e.,

$$\begin{aligned} S=\exp[-\tfrac{1}{4}(\alpha a^{*2}h^2+\beta b^{*2}k^2+\gamma c^{*2}l^2 \\ +2\delta a^*b^*hk+2\zeta b^*c^*kl+2\eta a^*c^*hl)]\,. \qquad (4a) \end{aligned}$$

From the symmetry reasons for the present crystal, this is slightly simplified as follows,

$$S=\exp[-\tfrac{1}{4}(\alpha a^{*2}h^2+\beta b^{*2}k^2+\gamma c^{*2}l^2+2\eta a^*c^*hl)]. \qquad (4b)$$

Here, α, β and γ are the average anisotropic temperature-factor coefficients along the reciprocal axes, and η is a coefficient related to the orientation of the ellipsoid of anisotropy with respect to a^* and c^*. These coefficients are given in the same units as the isotropic temperature factor B. The final bounded (F_o-F_c) map, in which F_c values contain no contribution of hydrogen atoms but have anisotropic temperature factors is shown in Fig. 3. The general background in this map is rather low, less than $\pm 0{\cdot}2$ e Å^{-2} almost everywhere. The x- and z-co-ordinates of hydrogen atoms are determined by this map. In order to obtain the y-co-ordinates of the two hydrogen atoms of the methyl group, two line (F_o-F_c) syntheses are calculated along the lines ($x=22/120$, $z=-1/30$) and (23/120, $-1/30$), which are shown in Fig. 4. In this calculation, the ($0k0$) reflections are omitted, since any reasonably adequate intensity data for these were not available because of the different extinction effects from crystals of other orientations.

The final co-ordinates and temperature-factor coefficients of the atoms thus determined are listed in

Table 1. *Final atomic co-ordinates and temperature factors*

Atomic co-ordinates

Atom	x	y	z
N	0·0352	0	0·0560
C	0·0921	0	−0·1203
O	0·0843	0	−0·3734
C (methyl)	0·1656	0	0·0204
H (amide)	0·038	0	0·247
H_1 (methyl)	0·156	0	0·227
H_2 (methyl)	0·188	0·108	−0·038

Temperature factors (in Å^2 unit)

Atom	α	β	γ	η
N	2·1	5·6	1·3	
C	2·5	5·9	1·6	
O	3·2	5·6	1·3	0·2
C (methyl)	3·1	6·5	2·2	
H (amide)	2·5	5·9	1·6	
H (methyl)	3·4	6·8	2·5	

The temperature factor has the form equation (4*b*).

Table 2. *Observed and calculated structure factors*

h k l	F_o	F_c
h 0 0		
0	—	248
2	43·4†	+68·2
4	44·1*	−46·1
6	25·8	−25·8
8	46·2*	−43·7
10	7·3	+ 7·1
12	26·8	+28·9
14	16·9	−16·0
16	31·6	−30·8
18	12·1	−12·6
20	3·6	− 2·9
22	4·5	+ 6·3
h 0 1		
2	38·7*	−41·7
4	37·6*	−37·0
6	20·5	+20·2
8	55·8*	+53·4
10	26·9	+26·8
12	4·6	− 4·8
14	14·3	−14·8
16	11·4	−10·3
18	0·6	+ 1·8
20	5·2	+ 5·5
22	—	− 0·4
h 0 2		
0	48·2*	+49·7
2	8·5	+ 6·2
4	2·5	+ 3·4
6	23·6	+23·0
8	12·2	−12·0
10	13·5	−13·0
12	—	+ 0·5
14	12·8	−12·8
16	9·7	− 9·8
18	1·7	+ 1·0
20	3·1	− 2·9
22	1·4	− 0·8
h 0 3		
2	20·2	−18·2
4	13·5	−13·1
6	17·1	+17·2
8	35·3	+36·4
10	18·8	+19·6
12	—	− 0·8
14	8·5	− 9·2
16	9·6	− 9·6
18	—	− 0·4
20	2·6	+ 2·7
h 0 4		
0	16·0	−16·1
2	15·2	−15·2
4	14·4	+13·0
6	35·0	+33·8
8	1·9	+ 2·7
10	18·9	−18·1
12	10·7	−11·1
14	5·0	−5·3
16	5·3	+ 5·7
h 0 5		
2	19·7	+20·1
4	15·1	+15·1
6	7·3	+ 6·9
8	—	+ 1·4
10	2·7	+ 3·1
12	5·2	+ 5·5
h 0 6		
0	1·1	− 1·1
2	5·1	− 5·6
4	2·7	− 3·9
h 1 1		
1	48·6*	+51·8
3	11·8	−11·9
5	40·1*	+40·2
7	21·6	+22·3
9	22·8	−21·6
11	10·3	− 9·4
13	15·1	−15·2
15	22·9	−23·0
17	3·0	− 3·9
19	3·3	+ 3·6
21	2·6	− 1·4
h 1 2		
1	14·4	+15·5
3	27·1	+28·1
5	22·2	+21·9
7	17·0	+15·4
9	3·4	− 3·3
11	5·3	− 5·3
13	3·5	+ 2·5
15	4·2	+ 4·2
17	—	+ 1·2
19	—	− 0·7
21	6·2	− 6·3
h 1 3		
1	25·4	+24·8
3	4·5	− 4·8
5	4·5	+ 4·1
7	1·7	− 2·0
9	15·4	−14·4
11	1·6	+ 2·2
13	3·6	+ 3·1
15	7·5	+ 6·7
17	—	− 1·8
19	1·4	− 2·4
h 1 4		
1	4·2	+ 5·1
3	5·9	+ 6·6
5	7·8	+ 7·4
7	16·1	+15·6
9	11·2	+11·4
11	3·0	+ 3·3
13	3·4	+ 3·3
15	1·2	− 1·6
17	5·3	− 5·3
h 1 5		
1	3·1	+ 2·2
3	6·2	− 6·2
5	1·5	+ 1·4
7	—	+ 0·8
9	7·1	− 6·1
11	2·3	+ 2·4
13	5·7	+ 5·5
h 1 6		
1	3·3	+ 3·4
3	1·6	+ 1·7
h 2 0		
2	56·8*	+56·9
4	29·8	−30·5
6	23·4	−23·9
8	28·2	−28·1
10	4·0	+ 4·3
12	21·7	+24·5
14	12·8	−12·3
16	24·9	−26·0
18	9·4	−10·3
20	2·1	− 2·5
22	4·6	− 5·4
h 2 1		
2	31·3	−29·2
4	29·3	−27·4
6	16·2	+15·0
8	40·2	+38·7
10	20·2	+20·1
12	3·1	− 4·3
14	12·5	−12·1
16	8·5	− 8·0
18	1·2	+ 1·6
20	4·6	+ 4·7
22	—	− 0·5
h 2 2		
0	34·2	+33·4
2	9·0	+ 7·4
4	1·8	+ 2·9
6	14·6	+15·7
8	6·9	− 6·6
10	10·8	−10·1
12	—	+ 0·3
14	10·4	−10·4
16	8·3	− 8·8
18	—	+ 1·0
20	2·0	− 2·5
h 2 3		
2	15·2	−13·0
4	11·4	−11·2
6	14·4	+14·3
8	29·3	+29·6
10	15·6	+15·7
12	—	− 0·3
14	8·0	− 7·9
16	7·6	− 8·0
18	—	− 0·3
h 2 4		
0	13·3	−13·5
2	11·8	−12·1
4	11·4	+10·4
6	26·9	+27·2
8	1·3	+ 2·4
10	15·3	−15·4
12	9·3	− 9·2
14	3·9	− 4·2
16	5·0	+ 4·9
h 2 5		
2	15·5	+16·7
4	12·6	+12·4
6	6·2	+ 6·0
8	1·0	+ 1·1
10	1·3	− 2·6
12	4·9	+ 4·8
h 3 1		
1	24·4	+21·2
3	1·1	+ 0·5
5	17·2	+17·7
7	13·1	+13·7
9	11·9	−11·5
11	6·7	− 7·0
13	8·5	− 8·8
15	16·7	−15·9
17	2·7	− 3·0
19	2·1	+ 2·5
21	1·1	+ 1·1
h 3 2		
1	7·9	+ 9·0
3	14·1	+15·6
5	12·7	+12·2
7	12·2	+10·1
9	2·9	+ 0·9
11	2·1	− 3·0
13	—	+ 1·4
15	1·2	+ 2·3
17	—	+ 1·1
19	—	− 0·5
h 3 3		
1	14·7	+14·6
3	1·3	− 1·9
5	2·6	+ 2·3
7	—	− 0·7
9	10·1	− 9·6
11	—	+ 0·6
13	2·1	+ 2·3
15	4·8	+ 4·8
17	—	− 1·4
h 3 4		
1	3·2	+ 4·1
3	4·2	+ 4·3
5	5·3	+ 4·8
7	11·6	+11·1
9	8·1	+ 7·6
11	2·5	+ 2·4
13	2·0	+ 2·5
h 3 5		
1	1·1	+ 1·3
3	3·8	− 4·1
5	1·3	+ 1·2
7	—	+ 0·6
9	5·1	− 4·4
h 4 0		
2	20·2	+23·1
4	11·6	−12·2
6	12·6	−12·4
8	10·3	−11·1
10	2·1	+ 1·9
12	11·0	+11·6
14	7·8	− 6·7
16	14·6	−15·1
18	4·9	− 5·9
20	1·1	− 1·5
h 4 1		
2	14·1	−12·6
4	12·1	−12·2
6	8·0	+ 6·6
8	18·2	+17·9

Table 2 (*cont.*)

h k l	F_o	F_c
10	10·1	+ 9·8
12	1·3	− 1·7
14	6·7	− 6·8
16	3·6	− 4·5
18	—	+ 1·1
20	2·1	+ 2·8
h 4 2		
0	15·9	+14·2
2	5·2	+ 4·2
4	0·9	+ 1·2
6	7·5	+ 7·2
8	2·6	− 3·2
10	6·3	− 6·0
12	—	+ 0·3
14	5·8	− 5·7
16	5·2	− 5·5
18	—	+ 0·6
h 4 3		
2	7·5	− 6·0
4	6·1	− 6·1
6	8·9	+ 8·3
8	17·2	+16·5
10	9·2	+ 8·6
12	—	− 0·1
14	4·6	− 4·8
16	4·2	− 4·9
h 4 4		
0	6·8	− 7·9
2	6·2	− 6·7
4	6·5	+ 6·0
6	17·2	+17·7
8	—	+ 1·5
10	9·9	− 9·0
12	5·9	− 5·5
h 4 5		
2	10·4	+10·2
4	8·2	+ 7·4
6	4·0	+ 3·8
h 5 1		
1	10·4	+ 7·4
3	—	+ 0·3
5	5·5	+ 6·3
7	4·1	+ 5·0
9	4·4	− 4·8
11	1·9	− 2·9
13	4·1	− 3·9
15	8·4	− 8·0
17	1·7	− 1·7
h 5 2		
1	2·5	+ 3·5
3	3·6	+ 7·6
5	5·4	+ 4·9
7	6·9	+ 5·0
9	2·7	+ 1·0
11	1·0	− 1·3
13	—	+ 0·4
15	—	+ 0·8
17	—	+ 0·6
h 5 3		
1	6·2	+ 6·2
3	—	− 0·8
5	2·5	+ 1·4
7	—	0
9	4·6	− 4·6
11	—	+ 0·1
13	—	+ 1·0
15	2·1	− 2·4
h 5 4		
1	1·2	+ 2·0
3	1·8	+ 2·1
5	3·1	+ 2·4
7	6·1	+ 5·6
9	4·1	+ 3·9
11	1·0	+ 1·3

* The correction was made for the extinction effect by the formula $I_o=I_{\text{corr.}}\exp(-gI_{\text{corr.}})$, where $g=3{\cdot}25\times10^{-5}$.

† No correction was made, for the observed intensity was extra-ordinarily smaller than the calculated intensity.

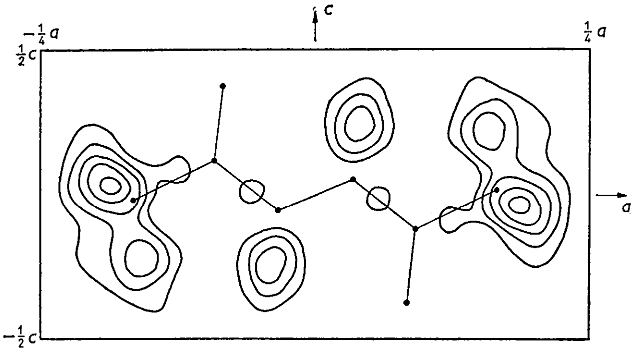

Fig. 3. The bounded (F_o-F_c)-map ($y=-\frac{1}{4}$ to $+\frac{1}{4}$) on (010) plane. The F_c's do not include the hydrogen contribution. Contours are at every 0·25 e.Å^{-2}, the zero contour being omitted.

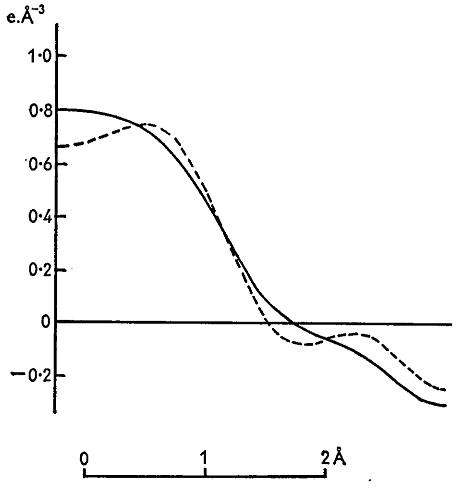

Fig. 4. The line (F_o-F_c)-syntheses along ($x=22/120$, $z=-1/30$, full line) and ($x=23/120$, $-1/30$, dotted line).

Table 1. The observed and calculated structure factors are listed in Table 2. The discrepancy index ($R=(\Sigma|F_o|-|F_c|)/\Sigma|F_o|$) up to about $\sin\theta/\lambda=0{\cdot}64$ is 0·073 over all reflections, assuming the values of the unobserved structure factors to be zero.

Accuracy of the numerical results

The standard deviations of the electron density $\sigma(\varrho)$, the atomic co-ordinates $\sigma(x)$, $\sigma(z)$, the bond lengths $\sigma(l)$, and the bond angles $\sigma(\varphi)$ were estimated by using the formulae given by Cruickshank (1949) and by Cruickshank & Robertson (1953),

$$\sigma(\varrho)=\frac{b}{V}\{\Sigma\Sigma w^2(F_o-F_c)^2\}^{\frac{1}{2}}, \tag{5a}$$

$$\sigma(X_n)=\frac{b}{V}\frac{2\pi\{\Sigma\Sigma w^2h^2(F_o-F_c)^2\}^{\frac{1}{2}}}{aC_n}, \tag{5b}$$

where C_n is the central curvature of the nth atom and obtained from Fig. 2. In this calculation the data of the zeroth and odd-order layers with respect to k were used, since the bounded half cell projection technique was adopted. As already mentioned, the weight w of $F(hkl)$ should vary with the value of k in the Fourier summation and the standard deviations were estimated by using those weights; i.e., $\frac{1}{2}$ for $F(h0l)$, $2/\pi$ for $F(h1l)$, $2/3\pi$ for $F(h3l)$, $2/5\pi$ for $F(h5l)$. The standard

Table 3. *The standard deviations of the atomic co-ordinates*

Atom	$\sigma(X_n)$	$\sigma(Z_n)$
N	0·005 Å	0·004 Å
C	0·007	0·005
O	0·005	0·003
C (methyl)	0·007	0·006

deviation of the electron density thus determined is 0·1 e.Å^{-2}. The standard deviations of the atomic co-ordinates are shown in Table 3, and those of the bond lengths and angles are listed in Table 4.

Discussion

Molecular configuration

The structure of diacetylhydrazine is shown in Fig. 5. The molecule has a planar structure with a centre of symmetry lying in the crystallographic *b*-plane except two of the three hydrogen atoms of the methyl group.

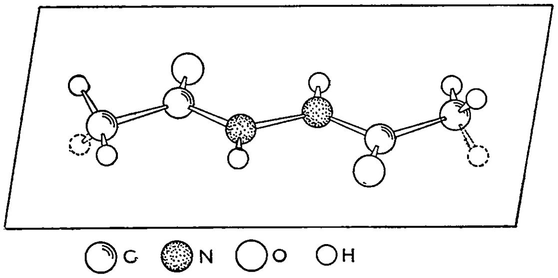

Fig. 5. Perspective drawing of the diacetylhydrazine molecule.

The skeleton of the molecule excluding the methyl group has '*S*' shape with a strong resemblance to diformylhydrazine. The two hydrogen atoms of the methyl group lie symmetrically on both sides of the molecular plane, which coincides with a symmetry plane, and the third lies in the plane. The hydrogen atom of the amide group is also lying in this plane. The bond lengths and angles in diacetylhydrazine derived from the atomic co-ordinates given in Table 1 are listed in Table 4 with those of diformylhydrazine for comparison.

Table 4. *The bond lengths (in Å unit) and bond angles (°) with their standard deviations of diacetylhydrazine and those of diformylhydrazine*

Bond	$(-NHCOCH_3)_2$	$(-NHCHO)_2$
Bond lengths		
N–N	1·396 (0·009)	1·392
N–C	1·341 (0·008)	1·325
C–O	1·221 (0·006)	1·214
C–C	1·504 (0·009)	
N–H	0·92	0·82
C–H		0·94
C–H (methyl)	1·01, 0·86	
N–H · · · O	2·877 (0·006)	2·788*
Bond angles		
N–N–C	118·4 (0·5)	121·3
N–C–O	122·3 (0·5)	124·9
C–C–O	123·3 (0·6)	
C–C–H (methyl)	109·5	
H–C–H (methyl)	109·5, 113·5	
O–C–H		120·5
N–N–H	116	117
N–N · · · O	130·8	129·5
H–N · · · O	15	12·5

* Calculated based on the co-ordinates of diformylhydrazine (Tomiie, Koo & Nitta, 1958).

The corresponding values for the two substances are close to each other. According to the discussion of diformylhydrazine, the energy of stability of the planar structure due to the conjugation effect is not very large and is estimated to be less than 4 kcal.mole.$^{-1}$. In diacetylhydrazine this energy may be of the same order. This is in accord with the following experimental fact; i. e., the X-ray investigation shows that the molecular structure of diacetylhydrazine is planar in the anhydrous crystal whereas not so in the monohydrate. Two halves of the molecule are twisted about the N–N bond, the azimuthal angle being approximately 135°. This fact seems to be due to the effect of hydrogen bondings between the molecules of diacetylhydrazine and water. The similar conclusion of the molecular structure has been reached by the infrared spectroscopy of the crystalline state (Yamaguchi, 1958).

Diacetyl- and diformylhydrazine molecules are isoelectronic in respect to the π-orbitals. Although the former possesses two methyl groups in place of two hydrogen atoms, an analogous discussion to that given for the latter (Tomiie, 1958*b*) will be also applicable. In diacetylhydrazine, the C–C bond (1·504 Å) is slightly but significantly shorter than the normal single C–C bond. This bond shortening will be explained by the effect of the hyperconjugation. The fractional double bond character is estimated to be 6% from Pauling's *VB* method (1945), and the mobile bond order is estimated to be 12% from Coulson's *MO* method (1939).

Arrangement of the molecules

The molecules of diacetylhydrazine are linked by the N–H · · · O hydrogen bonds forming a kind of belts extended in the *c*-axis direction parallel to the (010) plane. Fig. 6 shows a part of such belts of the molecules thus formed. The packing of the molecular belts is in such a way that, in the (010) projection, a C–O group overlaps almost precisely another of the neighbouring belt in the antiparallel direction (Fig. 1). The shortest methyl–methyl distance between belts, which lie in the same plane, is 3·91 Å. Since the densities of diacetyl- and diformylhydrazine are 1·35 and 1·58 g.cm.$^{-3}$, respectively, the former crystal is more loosely packed than the latter. From such structural feature it will be concluded that the cohesive energy of the crystal lattice is thus predominantly contributed by the hydrogen bonds, which link molecules into belts, and by the C–O dipole–dipole attraction between belts which are piled up in the *b*-axis direction. For the *a*-axis direction, it may be said that there only exerts the van der Waals attraction. In diformylhydrazine, the molecules are linked by the N–H · · · O hydrogen bonds into layers nearly parallel to the $(20\bar{1})$ plane. An oxygen atom is superposed almost precisely on the C–H bond of the neighbouring molecule if viewed

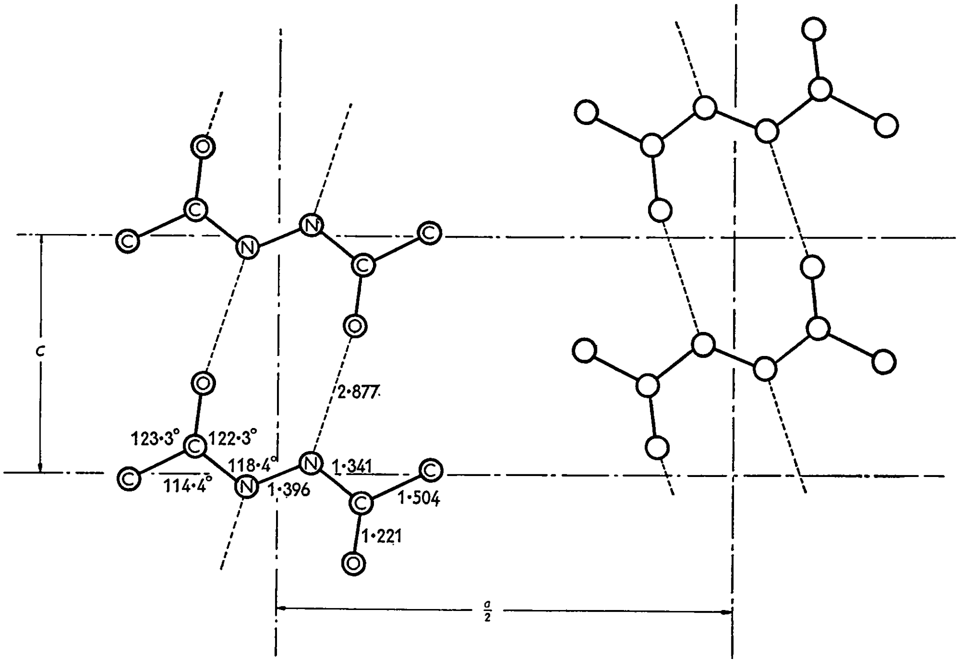

Fig. 6. Molecular arrangement showing a part of molecular belts.

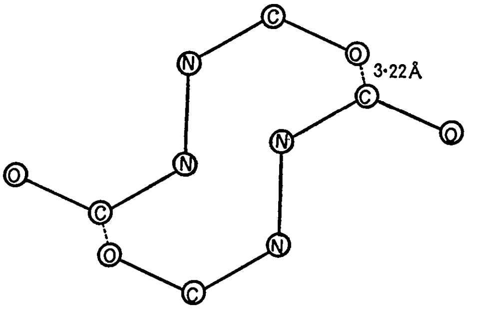

Fig. 7. Packing of the diformylhydrazine molecules viewed in the direction of normal to molecular plane.

in the direction normal to the common molecular plane (Fig. 7).

The distances between the molecular planes are $3{\cdot}25_5$ Å in diacetylhydrazine and 3·19 Å in diformylhydrazine, and the values of the C · · · O distances are 3·26 Å in the former and 3·22 Å in the latter, both of which nearly correspond to the sum of the van der Waals radii of the aromatic carbon and oxygen atoms, though those values of diformylhydrazine are slightly shorter. It seems that there is also the charge attraction between molecular layers, which is formed by the electro-positive CH group and electro-negative oxygen atoms.

Location of the hydrogen atoms

From the bounded and line ($F_o - F_c$) syntheses, the positions of the hydrogen atoms have been determined, from which the C–H and N–H bond lengths could be estimated. The C–H distances in the methyl group (Fig. 8(*a*)) are 1·01 Å for the one in the molecular plane and 0·86 Å for the other pair, respectively. On the other hand, the distance between the electron-density maxima of the C–H bond has been calculated by Tomiie (1958*a*) to be 0·91 Å for both two and three dimensional cases using *MO* method. The angles C–C–H are roughly equal to the tetrahedral angle.

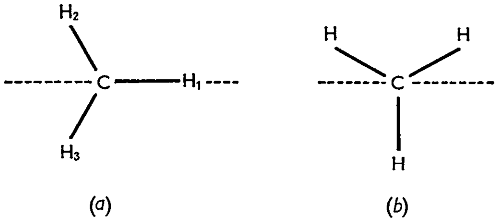

Fig. 8. The possible configurations of the hydrogen atoms of methyl group.

From the general point of view of the hyperconjugation, it may be said that the two configurations in Fig. 8(*a*) and (*b*) have approximately the same energy. However, for the present crystal the configuration of Fig. 8(*a*) has actually been found, which is not in contradiction to the qualitative argument of the potential minimum of the methyl group from symmetry consideration.

There is still a third possibility of the arrangement of the methyl group in the molecule such as shown in Fig. 9(*b*), which will be obtained by 180° rotation of the methyl group about the C–C bond. Fig. 9(*a*) shows the configuration found in the actual crystal as given in Fig. 8(*a*) and, moreover, the relationship to the neighbouring molecules in *b*-axis direction.

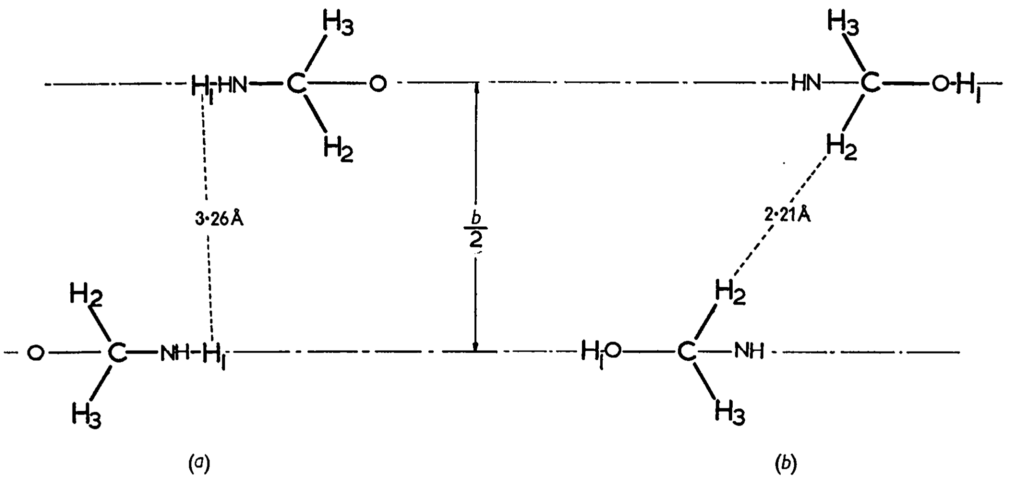

Fig. 9. The possible packings of the diacetylhydrazine molecules in *b*-axis direction.

As shown in Fig. 9(*b*), two hydrogen atoms of the methyl group are lying on the same side as that of the amide group. Although, for the compounds having similar radicals, for example acetamide crystal (Senti & Harker, 1940), and gaseous acetamide and N-methylacetamide (Kimura & Aoki, 1953), the positions of the hydrogen atoms of the methyl group were not yet clearly determined, the location of the hydrogen atoms of CH_2 group was found in succinamide crystal (Davies & Pasternak, 1956). In succinamide, too, two hydrogen atoms of CH_2 group are lying on the same side as that of the amide group. It seems that the energy difference between the two types of orientations (Fig. 9(*a*) and (*b*)) of the methyl group is not large. As for the intermolecular force, the shortest distances between hydrogen atoms of the methyl groups of neighbouring molecules are 3·26 Å ($H_1 \cdots H_1$) in the case *a* and 2·21 Å ($H_2 \cdots H_2$) in *b*. The H_2 and H_3 hydrogen atoms may be slightly charged electropositively owing to the hyperconjugation, but the H_1 has practically no influence of the hyperconjugation. Therefore, there may be slight Coulomb repulsion between the hydrogen atoms H_2 and H_3 and hence the packing of Fig. 9(*a*) seems to be more likely than that of 9(*b*).

On the other hand, if the methyl group is at rest, the peak density of the electron distribution at the H_2 position must be twice that at the H_1 position in the projection along the *b*-axis, since at the H_2 position the hydrogen atom is superposed precisely upon the other. In fact, however, the bounded ($F_o - F_c$) synthesis shows that the peak densities at the H_1 and H_2 positions are 0·9 and 1·4 e.$Å^{-2}$, respectively. This will be explained by a large angular oscillation of the methyl group about the C–C axis. On the other hand, the result of a nuclear magnetic resonance experiment is to show that the methyl group rotates about the C–C bond at higher temperature than the liquid nitrogen point (Shintani, Chihara, Itoh & Nitta, 1958). As for such apparent contradiction of the results of these two experiments, it is suggested that the methyl groups are in a state of hindered rotation in which the probability of the configuration as given in Fig. 8(*a*) is much greater than all others. Thus it is dangerous in many cases to conclude that atoms or molecule be at rest only from the evidence of clear peaks of electron-density distribution on Fourier or difference maps.

The N–H bond length is 0·92 Å and the peak density of the electron distribution at the hydrogen atom is 0·9 e.$Å^{-2}$. Though care should be paid as for the accuracy of the present value, these C–H and N–H bond lengths seem to be slightly shorter than the accepted values (1·07 and 1·02 Å, respectively) obtained by the spectroscopic means. In view of the present investigation the agreement between the observed and theoretical values is rather good. The angle N–N–H is 116°.

Hydrogen bond

The length of the N–H $\cdots$ O hydrogen bond is 2·877 Å. This is a normal value found in compounds containing amide groups. The deviation of the N–H bond out of the N $\cdots$ O direction is 15°. The angle of N–N $\cdots$ O of the hydrogen bond is 130·8°. The angle C–O $\cdots$ N is 168·5°, which corresponds more or less to the *sp* hybridized valence angle. As for other examples, the angle C–O $\cdots$ N of the N–H $\cdots$ O hydrogen bond which is nearly 180° is also found in N-acetylglycine (Carpenter & Donohue, 1950) and cyanuric acid (Wiebenga, 1952). There are two kinds of hydrogen bonds in cyanuric acid and the angle C–O $\cdots$ N of the remaining hydrogen bond is nearly 120°.

The energy of the hydrogen bond of the present crystal has been estimated (Takagi, Shintani, Chihara & Seki, 1959) to be 3·0 kcal.mole.$^{-1}$ bond^{-1} from the determination of the heat of sublimation. This is an ordinary value as compared with the N–H $\cdots$ O hydrogen bond energies found so far. Moreover, in the infra-red absorption spectra of this crystal, the strong absorption at 3235 cm.$^{-1}$ has been chosen as ν(N–H) (Yamaguchi, 1958). This is also an ordinary value for an amide crystal such as N-methylacetamide (3280 cm.$^{-1}$) or N-methylformamide (3280 cm.$^{-1}$) (Miyazawa, 1956). The distance of the non-straight N–H · · · O hydrogen bond in diacetylhydrazine is slightly shorter than that of straight hydrogen bond 2·93 Å given by the diagram of wave number against bond distance (Nakamoto, Margoshes & Rundle, 1955). However, the sum of N–H and H · · · O distances in this crystal is 2·93 Å which is equal to the value given above. In diformylhydrazine, the distance of the N–H · · · O hydrogen bond is 2·788 Å, its energy is roughly 5·0 ~ 6·1 kcal.mole.$^{-1}$ bond^{-1} (Suzuki, Onishi, Koide & Seki, 1956) and the strongest absorption in infra-red spectra occurs at 3100 cm.$^{-1}$ as ν(N–H) (Miyazawa, 1955).

Thus it has been confirmed by the X-ray, thermal and infra-red investigations that the hydrogen bond in this crystal shows characteristics as an ordinary amide crystal and is weaker than that of diformylhydrazine.

Thermal motion of the atoms and expansion coefficients

As listed in Table 1, the farther the atom lies from the centre of molecule, the larger becomes the thermal motion. It seems that the molecule has an angular oscillation about the centre of molecule. The anisotropy of the temperature factor of the oxygen atom is found in the (010) projection, the angle between the a^*-axis and the direction of maximum vibration being 6°. In the b-axis direction, that is perpendicular to the molecular plane, the vibration of the molecule is remarkable, but less in the a-axis and the least in the c-axis direction. The molecules are connected by the hydrogen bonds in the c-axis direction, and this conforms to the anisotropy of thermal motions. From this feature, the thermal motion of the molecule may be approximately described as a superposition of the translational vibration in the a- and b-axes directions and the libration about the centre of symmetry.

The thermal expansion coefficients are measured along the three crystal axes in the range between −150 and 30 °C. The magnitude of the coefficients is in the order of the b-, a-, and c-axis directions, the coefficient for the b-axis being much larger than the other two. This characteristic is in parallel with that of the anisotropic thermal motion of the molecule.

Resonance structure

An empirical formula, representing the relation between the bond length and the fractional double bond character of a bond has been given by Pauling (1945),

$$r=s-(s-d).3p/(2p+1)\,, \qquad (6)$$

where p represents the fractional double bond character, and s and d are the single and double bond length, respectively. In using equation (6), the standard single and double bond lengths are chosen as $s=1{\cdot}465$ (average value in hydrazine molecule, Collin & Lipscomb, 1951; Giguère & Schomaker, 1943) and $d=1{\cdot}20$ Å (Pauling, 1945) for N–N, and $s=1{\cdot}54$ and $d=1{\cdot}33$ Å for C–C. Since, for the bonds between different atoms, it is difficult to assign the ideal double bond lengths with no ionic character, Cox & Jeffrey's values (1951) are adopted; i.e., $s=1{\cdot}475$ and $d=1{\cdot}28$ Å for C–N, and $s=1{\cdot}437$ and $d=1{\cdot}185$ Å for C–O. The double bond characters by the use of the above formula are 0·10 for N–N, 0·42 for N–C, 0·65 for C–O, and 0·06 for C–C. From these values, the weights of the possible valence bond structures in resonance, (A), (B), (C), and (D), of the molecule in Fig. 10 can be easily obtained as 0·53 for (A), 0·34 for (B), 0·08 for (C), and 0·05 for (D).

While the C–C bond length is rather short, the weight

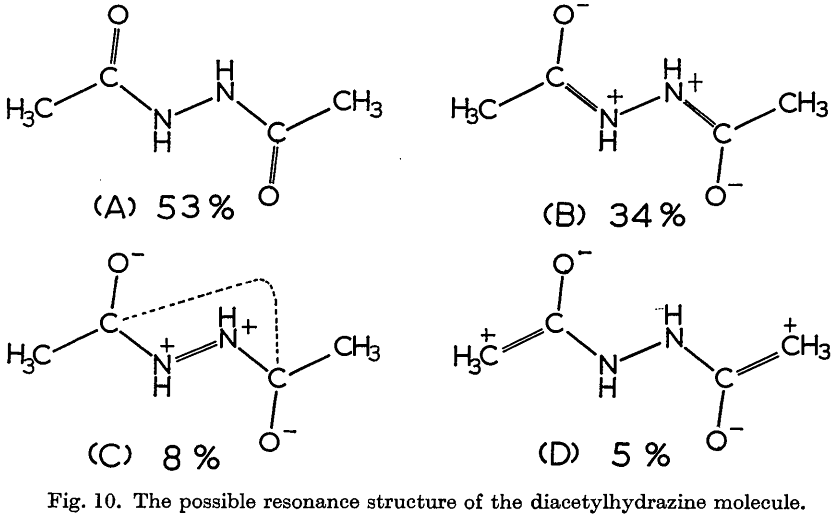

Fig. 10. The possible resonance structure of the diacetylhydrazine molecule.

of (*D*) is small, and the general feature of the weights of resonance structures resemble those of diformylhydrazine. The oxygen atom is definitely charged electro-negatively, since the sum of the contribution of (*B*), (*C*), and (*D*), is large. Like diformylhydrazine the skeleton of the molecule excluding the methyl group has '*S*' shape. This is explained by the electrostatic attraction between the electro-positive nitrogen and the electro-negative oxygen atoms. In addition to the conjugation effect, this intramolecular electrostatic interaction will also contribute to the stability of the planar molecule. As already mentioned, Tomiie (1958*b*) discussed more fully about the conjugation effect in diformylhydrazine which can be applied analogously to diacetylhydrazine.

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X-ray Incoherent Scattering Functions for Non-Spherical Charge Distributions. II. Ti^+, V^{+2}, Mn^{+2}, Mn and Fe

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Compton incoherent scattering functions have been calculated for the transition elements, Ti^+, V^{+2}, Mn^{+2}, Mn^+, Mn and Fe using available Hartree–Fock free atom wave functions. The methods reported earlier for including the effects of non-spherical charge distributions on the scattering function have been employed in these calculations as well. In agreement with previous results, large differences are found from the values of James & Brindley, due mainly to the inclusion of all the exchange terms in the Waller–Hartree theory.

1

For many years, the most widely used values of the Compton scattering intensities were those calculated by James & Brindley (1931). These were based, for the most part, on wave functions calculated by the self-consistent field (SCF) method without exchange.