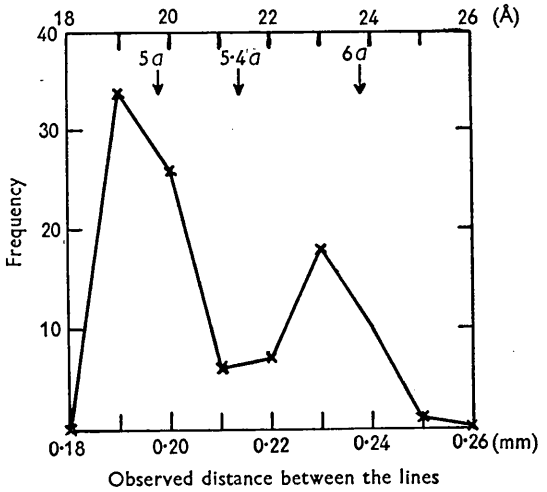

Fig. 5. Relation between the line distance and its frequency

It is very interesting to examine whether a mode of mixture of the two kinds of anti-phase domain is regular or irregular. As Fujiwara (1957) showed, a uniform irregular mixture and a uniform regular mixture yield a similar intensity distribution of diffraction. Thus the discrimination between them is very difficult to detect by a diffraction pattern. The mode of mixture, however, can be directly observed on electron micrographs. Examples of the observed mode of mixture are shown in terms of M, as follows:

...6555656655655655655...
...565565556565...,

where the measured domain size is classified into either of the two kinds, the experimental error being considered. The mixture in other parts was also almost similar to the above. That is to say, a uniform irregular mode of mixture seems to be substantially realized. Of course, a sufficiently large number of distances between the lines should be examined in various ordered alloy films with anti-phase domains, before a definite conclusion is drawn from such observations. So far as we have observed in a CuAu(II) film, however, the mode of mixture of anti-phase domains seems to be characterized by its uniformity but not by regularity, as concluded previously by Fujiwara (1957).

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The Crystal and Molecular Structure of Diformylhydrazine, OHC–HN–NH–CHO. II. On the Electronic Structure of the Molecule

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The electronic structure of the diformylhydrazine molecule has been investigated by the use of a simple *MO* method. Calculated values of the number of π-electrons, the charge and the total number of electrons associated with each atom (in which the σ-bond correction is made) are reasonable in comparison with those observed by the X-ray Fourier series method. In obtaining calculated heteropolar bond lengths, a correction term due to the charges has been introduced to the order-length relation of a bond, as the atoms in the molecule have large charges. The resonance structures and the fractional double bond characters of *VB* type have been discussed also. For the determination of the energy levels, non-orthogonality of the *AO*'s between adjacent atoms has been considered. The predominant factor contributing to the stability of the planar structure is the charge effect. The energy of conjugation between the two –HNCHO groups in the molecule does not exceed 4 kcal.mole^{-1}. Assignment of the near ultra-violet absorption spectra of the molecule in the crystal has been carried out group-theoretically using the results of the *MO* calculation and thus the existence of conjugation in this molecule has also been proved spectroscopically.

Introduction

In the crystal structure of diformylhydrazine (as determined by Tomiie, Koo & Nitta (1953), hereafter called (I)) the molecule has a planar S shape with

both –HNCHO groups in the *trans* form. This is unexpected for a derivative of hydrazine, because the latter is itself not planar (Penny & Sutherland, 1934).

In the present paper, the electronic structure of the molecule is treated theoretically by the simple *LCAO-MO* method. In our procedure the influence of the ionic character of the σ-bonds upon the π-electron system is considered. From our calculation, values of π-electron number (usually expressed as π-electron density), the charge of each atom, bond orders and bond lengths are obtained. These theoretical results are compared with the experimental ones obtained by the X-ray analysis (I). The calculated energy of the molecule is compared with that of a hypothetical skew molecule (Fig. 1) in which the two planar –HNCHO

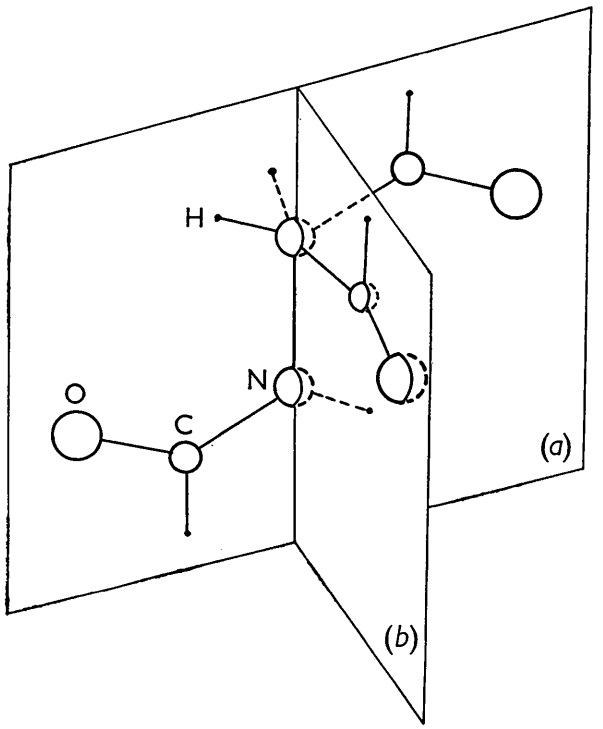

Fig. 1. Perspective drawing of the diformylhydrazine molecule. (*a*) The actual molecule. (*b*) The hypothetical skew molecule.

groups are perpendicular to each other. From the point of view of unsubstituted hydrazine, this configuration is a suitable one in which, however, π-electron conjugation between adjacent nitrogen atoms is not allowed. Along these lines the stability of the diformylhydrazine molecule will be discussed.

Method

Eight π-electrons and six $p\pi$-orbitals, i.e. the $2p\pi$-orbitals of nitrogen, carbon and oxygen, are considered in our treatment. In *LCAO* approximation the one-electron *MO*'s π_j are given as follows:

$$\pi_j = \sum_{r=1}^{6} c_{rj}\chi_r, \quad j = 1, 2, \ldots, 6, \tag{1}$$

where χ_r is the $2p\pi$–*AO* (atomic orbital) of the rth atom. Considering the molecular symmetry of C_{2h}, we can choose 'symmetry orbitals' τ_r (Parr & Mulliken, 1950) as follows:

$$\left.\begin{aligned} \tau_1 &= 1/N_1\cdot(\chi_N+\chi_{N'}),\\ \tau_2 &= 1/N_2\cdot(\chi_C+\chi_{C'}),\\ \tau_3 &= 1/N_3\cdot(\chi_O+\chi_{O'}), \end{aligned}\right\} \subset A_u$$
$$\left.\begin{aligned} \tau_4 &= 1/N_4\cdot(\chi_N-\chi_{N'}),\\ \tau_5 &= 1/N_5\cdot(\chi_C-\chi_{C'}),\\ \tau_6 &= 1/N_6\cdot(\chi_O-\chi_{O'}), \end{aligned}\right\} \subset B_g \tag{2}$$

where $1/N_r$ is the normalization coefficient and A_u and B_g are the irreducible representations to which the symmetry orbitals belong. Using these symmetry orbitals, the six one-electron *MO*'s (equation 1) are represented in simpler forms,

$$\begin{aligned} \pi_j &= \sum_{r=1}^{3} d_{rj}\tau_r, \quad j = 1, 2, 3, \subset A_u.\\ \pi_{j'} &= \sum_{r'=4}^{6} d_{r'j'}\tau_{r'}, \quad j' = 4, 5, 6, \subset B_g. \end{aligned} \tag{3}$$

The coefficients d_{rj} are determined so that the energy of the jth *MO*,

$$\varepsilon_j = \int \pi_j^* \mathrm{H}\pi_j\, dv,$$

is minimized, where H is the effective Hamiltonian operator. The minimized energies ε_j are the solutions of the following two secular equations,

$$\begin{aligned} |\mathrm{H}'_{qr} - \mathrm{S}'_{qr}\varepsilon| &= 0, \quad q, r = 1, 2, 3,\\ |\mathrm{H}'_{q'r'} - \mathrm{S}'_{q'r'}\varepsilon| &= 0, \quad q', r' = 4, 5, 6, \end{aligned} \tag{4}$$

where

$$\mathrm{H}'_{qr} = \int \tau_q^* \mathrm{H}\tau_r\, dv \quad \text{and} \quad \mathrm{S}' = \int \tau_q^*\tau_r\, dv.$$

After the roots ε_j of these equations have been obtained, the coefficients d_{rj} are determined from the linear equations

$$\sum_r d_{rj}(\mathrm{H}'_{qr} - \mathrm{S}'_{qr}\varepsilon_j) = 0.$$

Using the following quantities (Mulliken, 1949),

$$\alpha_r = \int \chi_r^* \mathrm{H}\chi_r\, dv \text{ (atomic integral)},$$

$$\mathrm{S}_{qr} = \int \chi_q^*\chi_r\, dv \text{ (overlap integral)}$$

and

$$\beta_{qr} = \int \chi_q^* \mathrm{H}\chi_r\, dv - \mathrm{S}_{qr}\bar{\alpha}_{qr} \text{ (bond integral)}$$

where $\bar{\alpha}_{qr} = \frac{1}{2}(\alpha_q+\alpha_r)$, and assuming the overlap integrals S_{qr} are negligibly small except for those of adjacent atom-pairs, the secular equations (equation 4) are rewritten as follows:

$$\begin{vmatrix} (\alpha_N+\beta_{NN'}+S_{NN'}\alpha_N)/N_1^2-\varepsilon & [\beta_{NC}+S_{NC}(\bar{\alpha}_{NC}-\varepsilon)]/N_1 & 0 \\ [\beta_{NC}+S_{NC}(\bar{\alpha}_{NC}-\varepsilon)]/N_1 & \alpha_C-\varepsilon & \beta_{CO}+S_{CO}(\bar{\alpha}_{CO}-\varepsilon) \\ 0 & \beta_{CO}+S_{CO}(\bar{\alpha}_{CO}-\varepsilon) & \alpha_O-\varepsilon \end{vmatrix} = 0$$

and

$$\begin{vmatrix} (\alpha_N-\beta_{NN'}-S_{NN'}\alpha_N)/N_4^2-\varepsilon & [\beta_{NC}+S_{NC}(\bar{\alpha}_{NC}-\varepsilon)]/N_4 & 0 \\ [\beta_{NC}+S_{NC}(\bar{\alpha}_{NC}-\varepsilon)]/N_4 & \alpha_C-\varepsilon & \beta_{CO}+S_{CO}(\bar{\alpha}_{CO}-\varepsilon) \\ 0 & \beta_{CO}+S_{CO}(\bar{\alpha}_{CO}-\varepsilon) & \alpha_O-\varepsilon\,, \end{vmatrix} = 0\,, \quad (5)$$

where $N_1^2 = 1+S_{NN'}$, and $N_4^2 = 1-S_{NN'}$.

To evaluate the ε_j, the following assumptions are adopted,

$$\begin{aligned} \alpha_r &= 2{\cdot}88x_r, \\ \beta_{qr} &= 10{\cdot}4S_{qr}, \end{aligned} \qquad \text{(in e.v.)} \quad (6)$$

where x_r represents the electronegativity of the rth atom in Pauling's scale. The value of the coefficient 2·88 has been determined from the electronegativity scale of carbon and the empirical α_C value (7·2 e.v.) in benzene. The latter has been derived from the ionization energy of benzene (9·24 e.v.) by taking α_C to be equal to $-\alpha_{izn.} = I+\beta_{spec.}/(1+S)$, where I is the ionization energy, $\beta_{spec.}$ is the spectroscopic β_{CC}, and S is the overlap integral (Mulliken, 1949). The value of the other coefficient, 10·4, has been obtained by Mulliken (1949) from the spectroscopic β_{CO} values for benzene, ethylene, acetylene and others. The values of overlap integrals S_{qr} were obtained from the Table of Mulliken, Rieke, Orloff & Orloff (1949) by using the observed bond lengths.

As for the hypothetical molecule mentioned above (Fig. 1(*b*)), we can obtain the *MO*'s and the secular equation by a similar procedure, and the secular equation may be divided into the two identical smaller ones, each corresponding to one half of this molecule. These secular equations are as follows:

$$\begin{vmatrix} \alpha_N-\varepsilon & \beta_{NC}+S_{NC}(\bar{\alpha}_{NC}-\varepsilon) & 0 \\ \beta_{NC}+S_{NC}(\bar{\alpha}_{NC}-\varepsilon) & \alpha_C-\varepsilon & \beta_{CO}+S_{CO}(\bar{\alpha}_{CO}-\varepsilon) \\ 0 & \beta_{CO}+S_{CO}(\bar{\alpha}_{CO}-\varepsilon) & \alpha_O-\varepsilon \end{vmatrix} = 0\,. \quad (7)$$

It is to be added that, to a first approximation, this secular equation (equation (7)) will also be applicable to the amide group, –HNCO–, in proteins and others.

π-Electron number, charge and bond order

For the calculation of the number of π-electrons on each atom and the mobile bond orders, the overlap integral can be neglected (Coulson & Longuet-Higgins, 1947). The secular equations are then:

$$\begin{vmatrix} \alpha_N\pm\beta_{NN'}-\varepsilon & \beta_{NC} & 0 \\ \beta_{NC} & \alpha_C-\varepsilon & \beta_{CO} \\ 0 & \beta_{CO} & \alpha_O-\varepsilon \end{vmatrix} = 0 \quad (5a)$$

for the actual molecule, and:

$$\begin{vmatrix} \alpha_N-\varepsilon & \beta_{NC} & 0 \\ \beta_{NC} & \alpha_C-\varepsilon & \beta_{CO} \\ 0 & \beta_{CO} & \alpha_O-\varepsilon \end{vmatrix} = 0\,. \quad (7a)$$

for half of the hypothetical molecule. The form of equation (7*a*) is the same as that adopted by Nagakura (1952) for the discussion of the amide group. The values of d_{rj} can be easily obtained in this way for each value of ε_j. The number of π-electrons* q_r associated with the rth atom and the mobile bond order p_{qr} between the two adjacent atoms are determined by the equations

$$q_r = 2\sum_j d_{rj}^2 \quad (8)$$

and

$$p_{qr} = 2\sum_j d_{qj}d_{rj}\,, \quad (9)$$

where the summations extend over all *MO*'s occupied in the ground state (Coulson & Longuet-Higgins, 1947).

The charge c_r (in electron units) of the rth atom will be given as

$$c_r = c(\pi)_r + c(\sigma)_r\,, \quad (10)$$

where $c(\pi)_r$ can be obtained from the value of the π-electron number q_r, while $c(\sigma)_r$ can be derived using the following empirical expression (11) for the percentage ionic character of a σ-bond (Hannay & Smyth, 1946):

$$16|x_r-x_q|+3{\cdot}5|x_r-x_q|^2, \quad (11)$$

where x_r is the electronegativity of the rth atom. If $c(\sigma)_r$ is neglected in our consideration of the formal charge, the migration of π-electrons will be overestimated.

The charges of the atoms having been determined, corrections to the electronegativity and the overlap integral need to be made. The correction for the x_r values is made by the method of Pauling (1940) and that for S_{qr} by the use of the Table of Mulliken *et al.* (1949) considering the change of the effective charges of the Slater *AO*'s. Thus it is possible to calculate new

* Usually defined as the 'π-electron density' at atom (Coulson & Longuet-Higgins, 1947). However, to avoid confusion between this quantity and the electron density in the crystal, we adopt the term 'π-electron number'.

values of c_r and then α_r and β_{qr} by equation (6). Using these new values, ε_j, q_r and c_r are recalculated. Such procedures are repeated until the final results of these quantities appear to be self-consistent (Kurita & Kubo, 1951).

Table 1(*a*). *The simple one-electron MO's of diformylhydrazine*

π_1, π_2, π_3, and π_4 are the occupied orbitals and π_5 and π_6 the unoccupied, suffices being now changed according to the order of energy. B_g and A_u are the irreducible representations to which *MO*'s belong

$$\begin{aligned}
\pi_1 &= 0{\cdot}4842\tau_1+0{\cdot}3972\tau_2+0{\cdot}3285\tau_3 \subset A_u\\
\pi_2 &= 0{\cdot}2461\tau_4+0{\cdot}4378\tau_5+0{\cdot}4979\tau_6 \subset B_g\\
\pi_3 &= 0{\cdot}4494\tau_1-0{\cdot}1046\tau_5-0{\cdot}5359\tau_3 \subset A_u\\
\pi_4 &= 0{\cdot}5208\tau_4+0{\cdot}2010\tau_5-0{\cdot}4342\tau_6 \subset B_g\\
\pi_5 &= 0{\cdot}2533\tau_1-0{\cdot}5776\tau_1+0{\cdot}3252\tau_3 \subset A_u\\
\pi_6 &= 0{\cdot}4115\tau_4-0{\cdot}5165\tau_5+0{\cdot}2530\tau_6 \subset B_g
\end{aligned}$$

Table 1(*b*). *The simple one-electron MO's of the hypothetical molecule and of an amide group*

π_1', π_2' are the occupied orbitals and π_3', the unoccupied

$$\begin{aligned}
\pi_1' &= 0{\cdot}4923\chi_N+0{\cdot}6128\chi_C+0{\cdot}6182\chi_O\\
\pi_2' &= 0{\cdot}7431\chi_N+0{\cdot}0740\chi_C-0{\cdot}6651\chi_O\\
\pi_3' &= 0{\cdot}4534\chi_N-0{\cdot}7867\chi_C+0{\cdot}4190\chi_O
\end{aligned}$$

In Table 1, the simple *MO*'s thus determined are shown for both diformylhydrazine and the hypothetical skew molecule. Here the suffixes are given anew in accordance with the order of energies of the *MO*'s.

In Fig. 2 are shown the number of π-electrons q_r

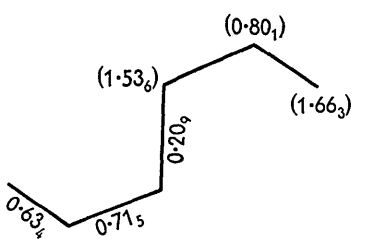

Fig. 2. The number of π-electrons associated with each atom and the mobile bond orders calculated by the *MO* treatment.

associated with each atom and the mobile bond orders p_{qr} calculated from the coefficients in the *MO*'s (Table 1) by using equations (8) and (9). Table 2 lists the formal charges c_r finally determined together with the components $c(\pi)_r$ and $c(\sigma)_r$.

Table 2. *The number of π-electrons q_r and the charge c_r together with the components $c(\pi)_r$ and $c(\sigma)_r$ associated with the r*th *atom (in electron unit)*

	N	C	O	H_N	H_O
		(Diformylhydrazine)			
q_r	1·536	0·801	1·663	—	—
$c(\pi)_r$	+0·464	+0·199	−0·663	—	—
$c(\sigma)_r$	−0·270	+0·109	−0·116	+0·188	+0·089
c_r	+0·194	+0·309	−0·783	+0·188	+0·089
		(Hypothetical molecule)			
q_r	1·589	0·762	1·649	—	—

Energy levels

For the calculation of the energy levels of the molecule, it is more accurate to use, instead of equations (5*a*) and (7*a*), equations (5) and (7) in which the overlap integrals are not neglected. The energies are easily determined if use is made of the final values of α_r, β_{qr}, and S_{qr} as determined above. In Table 3 are listed

Table 3. *The values of the energy levels calculated by equations* (5) *and* (7) (*in* e.v.)

Diformylhydrazine (Occupied)	Hypothetical molecule or amide group (Occupied)
$\varepsilon_1 = -11{\cdot}397$ ($\subset A_u$)	$\varepsilon_1' = -10{\cdot}910$
$\varepsilon_2 = -10{\cdot}766$ ($\subset B_g$)	$\varepsilon_2' = -9{\cdot}075$
$\varepsilon_3 = -9{\cdot}708$ ($\subset A_u$)	—
$\varepsilon_4 = -8{\cdot}181$ ($\subset B_g$)	—
(Unoccupied)	(Unoccupied)
$\varepsilon_5 = -3{\cdot}777$ ($\subset A_u$)	$\varepsilon_3' = -3{\cdot}388$
$\varepsilon_6 = -2{\cdot}382$ ($\subset B_g$)	—

the energy levels thus obtained in the order of the energy values. ε_1, ε_2, ε_3 and ε_4 are the energies of the occupied orbitals and the others are those of the unoccupied ones. For comparison, the energy values of the hypothetical molecule or the amide group are also listed in Table 3, where ε_1' and ε_2' are those of the occupied and ε_3' that of the unoccupied orbitals.

Discussion

(*a*) *Number of electrons in the atom or the group of atoms*

It is obvious from Table 2 that π-electrons of the nitrogen and carbon atoms migrate considerably onto the oxygen atom. On the other hand, as the ionic character of the σ-bonds is rather strong in this molecule, it is seen that we cannot ignore the σ-bond contribution to the charges of the atoms. As shown in Table 2, these two contributions are additive in the oxygen and carbon atoms whereas they roughly cancel each other in the nitrogen atom, so that the nitrogen and carbon atoms are positively charged while the oxygen has a large negative charge. From the calculated charges we can obtain calculated total number of electrons in each atom or atomic group; i.e. 8·78 for O, 6·60 for CH and 7·62 for NH (Table 4). These are to be compared with those read off from the (F_o-F_c)-map in (I): $8{\cdot}6_1$, $6{\cdot}6_0$ and $7{\cdot}7_2$ for O, CH, and NH, respectively. The agreement between observed and calculated values is satisfactory considering the accuracy of the calculation.

The strong NH · · · O hydrogen bond in the crystal (see I) may be due partly to the large charges on the nitrogen and oxygen atoms. The comparatively large

Table 4. *Calculated and observed number of electrons of each atom in diformylhydrazine molecule (in electron units)*

	Calculated	Observed
O	8·78	$8{\cdot}6_1$
CH	6·60	$6{\cdot}6_0$
NH	7·62	$7{\cdot}7_2$
Total	23·00	$22{\cdot}9_3$

density, 1·58 g.cm.$^{-3}$, of this crystal may also be accounted for along this line.

(*b*) *Order-length relation of the bonds*

Coulson (1939) has proposed a formula representing the relation between the length and the order of a bond, i.e.,

$$r = s-(s-d)/[1+K(1-p)/p]\,, \qquad (12)$$

where r is the bond length; s and d, the ideal single and double bond lengths (in Å unit) with no ionic character respectively; K, a constant chosen empirically as $\frac{2}{3}$; and p, the mobile bond order determined by the *MO* treatment. This formula applies to homopolar bonds but not to heteropolar bonds without suitable changes, especially for a molecule where the charges of the atoms are considerable. We assume that, if a correction is made for charge effect, equation (12) is still useful even for bonds with some ionic character. Such a correction term is

$$\Delta r = 1{\cdot}36c_qc_r/[(1+p)(x_qx_r)^{\frac{1}{2}}r^{\frac{1}{2}}]\,, \qquad (13)$$

where c_q and c_r (in electron unit) are charge values determined by the *MO* treatment and x_q and x_r represent the electronegativities in Pauling's scale. This relation is derived from a combination of a formula proposed by Coulson (1952) and Chalvet & Daudel (1952), with Gordy's 'Force constant-electronegativity relation' (1946), neglecting an unimportant term in it.* In our calculation, the standard single and double bond lengths of N–N are chosen as $s = 1{\cdot}465$ (average value in hydrazine, Collin & Lipscomb, 1951; Giguère & Schomaker, 1943) and $d = 1{\cdot}20$ Å (Pauling, 1940). Since, for heteropolar bonds, it is difficult to assign ideal double bond lengths with no ionic character, we adopt Cox & Jeffrey's values (1951) based on experimental data as a matter of convenience; 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 bond lengths thus calculated for diformylhydrazine are 1·397 for N–N, 1·326 for N–C and 1·219 Å for C–O (Table 5). The mean deviation between these and the observed bond lengths is 0·004 Å, the maximum being 0·005 Å. It is obvious from Table 5 that the bond length correction by equation (13) should be considered especially for the C–O bond in which the charges of the atoms are large.

A similar calculation has been carried out for the amide group of the hypothetical molecule (Fig. 1(*b*)), with results also listed in Table 5; it appears that conjugation between the two amide groups in diformylhydrazine has comparatively little effect on the bond lengths.

Table 5. *Bond orders and bond lengths derived from the MO and VB methods together with the observed X-ray values, where bond order* $= 1+p$; *p being the* π *bond order*

(*a*) *MO* method

Bond	Bond order	Bond length (Å) $r_{obs.}$	$r_{uncorr.}$	Δr	$r_{corr.}$
		(Diformylhydrazine)			
N–N	1·209	1·392	1·390	+0·007	1·397
N–C	1·715	1·325	1·317	+0·009	1·326
C–O	1·634	1·214	1·255	−0·036	1·219
		(Amide or hypothetical molecule)			
N–C	1·713	—	1·317	+0·009	1·326
C–O	1·659	—	1·250	−0·036	1·214

(*b*) *VB* method

		(Diformylhydrazine)			
N–N	1·10	—	1·399	—	1·406
N–C	1·49	—	1·326	—	1·335
C–O	1·41	—	1·267	—	1·231

(*c*) *Resonance structures and the bond lengths from the VB formula*

An empirical formula for the relation between the length and the fractional double bond character of a bond based on the *VB* method, has been given by Pauling (1940),

$$r = s-(s-d).3p'/(2p'+1)\,, \qquad (14)$$

where p' represents the fractional double bond character of *VB*-type. Comparing this with equation (12), (if such a comparison is of significance) we obtain a relation,

$$p' = p/(2-p)\,, \qquad (15)$$

where p is the mobile bond order of the *MO* method. Modifying the values of p' so that $\Sigma p' =$ the number of double bonds in a molecule, we obtain revised double bond characters of the bonds in the molecule, namely: 0·10 for N–N, 0·49 for N–C and 0·41 for C–O. From these values, the weights of the resonance structures (*A*), (*B*), (*C*) of the molecule in Fig. 3 can be directly derived as 0·41 for (*A*), 0·49 for (*B*) and 0·10 for (*C*).

The bond lengths calculated by equation (14) with the same correction term (13) are 1·406 for N–N, 1·335 for N–C and 1·231 Å for C–O (Table 5). The mean deviation between these and the observed bond

* $\Delta r = c_qc_re^2/kr^2$ (Coulson, 1952; Chalvet & Daudel, 1952), (*a*)

$k = 1{\cdot}67(1+p)(x_qx_r/r^2)^{\frac{1}{2}}+0{\cdot}30$ (Gordy, 1946), (*b*)

where k is the force constant.

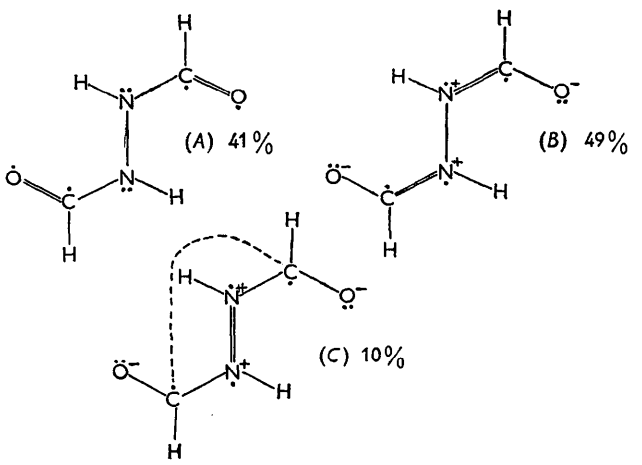

Fig. 3. The resonance structures of the diformylhydrazine molecule.

lengths is 0·014 Å (maximum 0·017 Å). It is again obvious that the correction term (13) is necessary for the C–O bond.

(d) The stability of the molecule

A measure for the stability of the planar structure of diformylhydrazine may be obtained by comparing the energy of the molecule with that of the hypothetical diamide molecule with a skew form having an angle of twist 90° (Fig. 1(*a*), (*b*)). In discussing this problem, two important factors must be considered. The first is the effect of conjugation, which will be given by the following equation

$$-E_{\text{res.}} = 2(\varepsilon_1+\varepsilon_2+\varepsilon_3+\varepsilon_4)-4(\varepsilon_1'+\varepsilon_2'), \quad (16)^*$$

where the values of ε_j are shown in Table 4. $E_{\text{res.}}$ means the 'resonance energy' due to the conjugation between the two halves of the molecule. The value obtained is 0·17 e.v. or 3·8 kcal.mole. We conclude from this that the *conjugation effect* exists in this molecule but is not very large.

The second factor which contributes to the planarity is the *charge effect*. Using the values of the charges (Table 2) and the molecular dimensions (Table 5), we can readily obtain the difference of the electrostatic energies of the two molecules (Fig. 1(*a*), (*b*)). The planar structure is found to be 27 kcal.mole^{-1} more stable than the skew form. If the observed charges (Table 4) are adopted and those of the hydrogen atoms are assumed suitable, (+0·09 for H_C and +0·14 for H_N), the difference of electrostatic energies for the two structures becomes 15 kcal.mole^{-1}.

Thus while the conjugation effect is not very large, the charge effect is strong enough to overcome the hybridization effect which is important in the hydrazine molecule itself.

The energy of each of the two hydrogen bonds of this molecule has been estimated to be 6·1 kcal.mole-bond (Suzuki, Onishi, Koide & Seki, 1956). Therefore, the total energy for the stability of the planar structure is somewhat larger than that of the hydrogen bonds. It is interesting to note that diacetylhydrazine, CH_3OC–HN–NH–$COCH_3$, which is iso-electronic in respect to the π-electron system, has a similar planar structure in the anhydrous crystal, while it has a kind of skew form in the monohydrate, the angle of twist being 135°, as found from X-ray investigation (Shintani, Tomiie & Nitta, to be published). This configuration is confirmed by infra-red analysis (Miyazawa & Yamaguchi, private communication). It is concluded from these observations that, since the π-conjugation between the two halves of these molecules is not very large, the influence of external forces upon the molecular structure is of great importance.

(e) Near ultra-violet absorption

Yamada & Tsuchida (1954) have investigated the dichroism in the near ultra-violet of diformylhydrazine crystals. They found two absorption bands, a very weak band at about 2800–3300 Å and a strong one at a wavelength somewhat shorter than 2600 Å. In the weak band the || absorption is very hyperchromic and slightly bathochromic to the ⊥ absorption, where || and ⊥ refer to the absorption spectra with the electric vector parallel and perpendicular to the $(20\bar{1})$ plane of the crystal, and hence approximately parallel and perpendicular to the molecular planes, these being inclined to the $(20\bar{1})$ plane at about 19°. In the following discussion we shall regard these || and ⊥ absorptions as being nearly equal to the parallel and perpendicular absorptions referred to the molecular plane. In the high intensity band, the || absorption is also bathochromic to the ⊥.

These experimental results can be explained group-theoretically by using the results of the *MO* treatment. Considering the molecular symmetry C_{2h}, we divide the 34 valence electrons into three classes; i.e. 18 σ-bonding electrons, 8 non-bonding σ-electrons and 8 π-electrons. σ-bonding electrons will make no contribution to the near ultra-violet absorption spectra under consideration. The *MO*'s (and irreducible representations to which they belong) of the non-bonding σ-electrons will be given as follows,

* In the case of aromatic hydrocarbons a different small value of β is usually adopted which is based on the observed 'resonance energy' of the molecule (e.g. β_{CC} in benzene is taken as 20 kcal.mole). In our energy consideration, however, we use the value of β (equation 6) which is based on spectroscopic data for benzene (Mulliken, 1949). Since the N–N bond shortening due to its double bond character is not very large and also since the changes of the other bond lengths are not very important as compared with those of the unconjugated diamide molecule (Table 3), the 'Compression Energy' (Mulliken & Parr, 1951), due to the change of bond lengths, will not be large. Therefore the value of β for the discussion of the energy of the present molecule will not differ considerably from the spectroscopic one, and thus the actual energy for stability will not differ markedly from that obtained above.

$$\left.\begin{aligned}\lambda_1 &= l_x+l_{x'}, \quad \subset A_g,\\ \lambda_2 &= l_y+l_{y'}, \quad \subset A_g,\\ \lambda_3 &= l_x-l_{x'}, \quad \subset B_u,\\ \lambda_4 &= l_y-l_{y'}, \quad \subset B_u,\end{aligned}\right\} \tag{17}$$

where l_x and l_y are both lone pair orbitals of one oxygen atom, which are orthogonal to each other and both in σ-state, and $l_{x'}$ and $l_{y'}$ are the corresponding orbitals of the other oxygen. The energy levels of these orbitals will be almost the same as those of lone pairs of isolated oxygen atoms since the overlapping between the two oxygens is negligibly small. The π-electron levels are already shown in Table 3. Then the approximate wave functions for the ground state and some of the lower excited states of the molecule are given as follows:

$$\begin{aligned}\Psi_g &= A.(\sigma_{1-9})^{18}(\pi_1)^2\ldots(\pi_4)^2(\lambda_1)^2\ldots(\lambda_4)^2.\mathrm{S} && \subset A_g\\ \Psi_{e1} &= A.(\sigma_{1-9})^{18}(\pi_1)^2\ldots(\pi_3)^2(\lambda_1)^2\ldots\\ &\qquad \times(\lambda_4)^2(\pi_4)(\pi_5).\mathrm{S} && \subset B_u\\ \Psi_{e2} &= A.(\sigma_{1-9})^{18}(\pi_1)^2\ldots(\pi_4)^2(\lambda_2)^2\ldots\\ &\qquad \times(\lambda_4)^2(\lambda_1)(\pi_5).\mathrm{S} && \subset A_u\\ \Psi_{e'2} &= A.(\sigma_{1-9})^{18}(\pi_1)^2\ldots\\ &\qquad \times(\pi_4)^2(\lambda_1)^2(\lambda_3)^2(\lambda_4)^2(\lambda_2)(\pi_5).\mathrm{S} && \subset A_u\end{aligned} \tag{18}$$

where Ψ_g, and Ψ_{e1} and Ψ_{e2} (or $\Psi_{e'2}$) are the wave functions for the ground and excited states respectively; σ_j and π_j the jth σ and πMO's, and λ_j that just given above; A is the antisymmetrizer and S is the properly given spin function. Three components of the molecular electric moment P_x, P_y, P_z have the irreducible representations $P_x, P_y \subset B_u$, $P_z \subset A_u$ respectively. Since an excited level will be active in combination with the ground state only if the direct product of its representation and that of P contains the identical representation A_g, the intensity of transition with absorption of light can be predicted as shown in Table 6. Two kinds of allowed transitions are possible, one is $\pi \to \pi$ and the other $n \to \pi$. In the former $\Psi_g \to \Psi_{e1}$ transition, the $\parallel$ absorption is allowed, whereas the $\perp$ absorption is forbidden. On the other hand, in the latter $\Psi_g \to \Psi_{e2}$ (or $\Psi_{e'2}$) transition the $\perp$ is allowed, while the $\parallel$ is forbidden.

Table 6. *Intensity of transition from the ground state to the lower excited levels of diformylhydrazine*

Ψ_g and Ψ_e are the wave functions of the ground and the excited state respectively

Transition	$\int \Psi_g P_{x,y} \Psi_e \, dv$	$\int \Psi_g P_z \Psi_e \, dv$
$\Psi_g \to \Psi_{e1}(\pi \to \pi)$	allowed	forbidden
$\Psi_g \to \Psi_{e2}(n \to \pi)$ (or $\to \Psi_{e'2}$)	forbidden	allowed

The energy difference which corresponds to the allowed $\pi \to \pi$ transition will be represented by

$$\Delta E_{\pi\to\pi} = (\varepsilon_5 - \varepsilon_4), \tag{19}$$

where ε_4 and ε_5 are π energy levels (Table 3 and Fig. 4). The calculated value of $\Delta E_{\pi\to\pi}$ is 4·40 e.v.

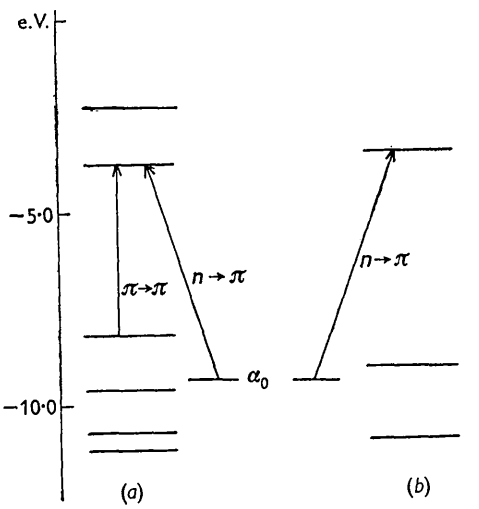

Fig. 4. The energy levels calculated by the *MO* treatment. The allowed transitions are also shown with arrows. (*a*) The actual molecule. (*b*) The hypothetical molecule.

which corresponds to 2800 Å. The corresponding energy difference $\Delta E_{n\to\pi}$ between the energy level of ε_5 and that of the non-bonding oxygen electrons may be given approximately as

$$\Delta E_{n\to\pi} = (\varepsilon_5 - \alpha_0), \tag{20}$$

where α_0 is the atomic integral of the oxygen atom. Since the final result of our *MO* treatment shows $\alpha_0 = 9{\cdot}35$ e.v., the value of $\Delta E_{n\to\pi}$ becomes 5·57 e.v. which corresponds to 2200 Å.

Experimentally, allowed transitions appear in the region more or less shorter than 2600 Å. The fact that the $\parallel$ absorption is bathochromic to the $\perp$ absorption is in accord with theoretical expectation; i.e. the $\parallel$ absorption is attributed to the $\Psi_g \to \Psi_{e1}(\pi \to \pi)$ transition which has a longer wave length than the $\Psi_g \to \Psi_{e2}(n \to \pi)$ transition. The discrepancy between the observed and calculated absorption positions might be improved if the energy differences of singlet and triplet levels were properly considered; also the shift of energy levels of the lone pairs due to the mutual interaction between electrons should be added, since the energy levels obtained by the *MO* treatment in the present paper correspond to the average values of singlet and triplet states owing to the assumptions made (Mulliken, 1949). However, more detailed discussion should not be based on such a treatment.

The single amide group does not show the $\pi \to \pi$ transition in the same region (Nagakura, 1952). So it seems likely that the conjugation in diformylhydrazine shifts the $\pi \to \pi$ absorption to comparatively longer wave length. These relations are shown schematically in Fig. 4 from which it is obvious that both $\pi \to \pi$ and $n \to \pi$ absorptions of diformylhydrazine will be at

longer wave lengths than the corresponding ones of the single amide group. Thus we conclude that the conjugation effect is recognizable spectroscopically. This phenomenon resembles somewhat the effect of substitution on absorption by benzene or the conjugated polyenes.

The very weak absorption at about 2800–3300 Å may be explained by forbidden bands due to the transitions from Ψ_g to the triplet states of Ψ_{e1} and Ψ_{e2}, with the $\parallel$ absorption mainly attributed to the $\pi \rightarrow \pi$ transition ($\Psi_g \rightarrow \Psi_{e1}$) and the $\perp$ absorption to the $n \rightarrow \pi$ transition ($\Psi_g \rightarrow \Psi_{e2}$). However, for these very weak absorption bands, further investigation is necessary before drawing definite conclusions.

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Crystal Structure of Chlorobenzene and Bromobenzene at −180 °C

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The Debye–Scherrer photographs of chlorobenzene and bromobenzene frozen and cooled to −180 °C. have been taken and from the analysis both the crystals have been found to belong to the orthorhombic system. The unit-cell dimensions for chlorobenzene are $a = 13{\cdot}72$, $b = 11{\cdot}32$, $c = 7{\cdot}75$ Å and those for bromobenzene are $a = 14{\cdot}3$, $b = 11{\cdot}48$ and $c = 7{\cdot}5$ Å. The densities of the crystals have been found to be 1·225 and 1·654 gm.cm.$^{-3}$ respectively. The restrictions of reflections show that both substances belong to the space group Q_h^{13} having 8 asymmetric molecules per unit cell, which shows that neither molecule possesses a two-fold axis or a plane of reflection in the solid state at −180 °C.

Introduction

In continuation of the work on the structure of crystals of toluene (Biswas & Sirkar, 1957) and pyridine (Biswas, 1958), the present investigation was undertaken to study the Debye–Scherrer patterns of chlorobenzene and bromobenzene at −180 °C. to find out their crystal structures. As will be evident from the following sections the frozen masses have been found to give patterns resembling those due to fibres and it has therefore been possible to assign the indices unequivocally and to determine the space groups to which these two crystals belong.

Experimental

Chlorobenzene and bromobenzene used in the investigation were of chemically pure quality. Debye–