On the Electronic Structure of the Carbonyl and the Amide Groups

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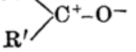
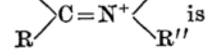
Introduction

To the state of the molecule with the carbonyl or the amide group, the partially ionic structure,  $\begin{matrix}R\\R'\end{matrix}\!\!>C^{+}-O^{-}$ or  $\begin{matrix}O^{-}\\R\end{matrix}\!\!>C=N^{+}\!\!<\begin{matrix}R'\\R''\end{matrix}$ is expected to make large contributions.⁽¹⁾ By the use of these resonance structures, very satisfactory results have been obtained in the qualitative interpretation of many interesting physico-chemical properties of these groups, such as the large dipole moment⁽²⁾ and the relatively low basicity of amide.⁽³⁾

In the present paper, the contributions of the partially ionic structures are theoretically treated by the molecular orbital method. The values of energy levels, resonance energies and π-electron densities are calculated for these two groups. Then these theoretical predictions are checked by the experimental values of resonance energies, dipole moments and near ultraviolet absorption spectra. Especially, as to absorption spectra, measurements were made in this laboratory with acetone, acetylchloride, acetic acid, ethyl acetate and N-methylacetamide. From these theoretical and experimental investigations, it is suggested that the weak near ultraviolet absorption spectrum characteristic of the unconjugated carbonyl group is due to the $n\rightarrow\pi^*$ transition, as was shown by Mulliken,⁽⁴⁾ McMurry,⁽⁵⁾ Baba⁽⁶⁾ and Kasha.⁽⁷⁾

Theoretical

As is usual, only the π-electrons, of which there are two in the carbonyl group and four in the amide group, are considered. The molecular π-orbitals ψ_j $(j=1,2,3)$ in amide may be taken as linear combinations of the $2p$ atomic orbitals of oxygen, carbon and nitrogen atoms which are denoted by φ_O, φ_c and φ_N respectively. Using this approximation (LCAO), the following equation is obtained

$$\psi_j=a_{Oj}\varphi_O+a_{Cj}\varphi_C+a_{Nj}\varphi_N \qquad (1)$$

Neglecting the overlap integral S_{AB} between two atomic orbitals φ_A and φ_B, ies energthe E of these molecular orbitals are given approximately as the solutions of the following secular equation,

$$\begin{vmatrix}\alpha_O-E & \beta_{CO} & 0\\ \beta_{CO} & \alpha_C-E & \beta_{CN}\\ 0 & \beta_{CN} & \alpha_N-E\end{vmatrix}=0 \qquad (2)$$

where α_A is the coulomb integral of A-atom and β_{AB} is the exchange integral between adjacent atomic orbitals φ_A and φ_B.

To evaluate the values of E, the following assumptions were made

$$\alpha_A=\chi_A\alpha/\chi_C,^{(8)}\ \beta_{AB}=S_{AB}\beta/S,^{(9)}\ \alpha=k\beta^{(8)} \qquad (3)$$

where χ_A represents the electronegativity of A-atom, S is the overlap integral between atomic orbitals belonging to adjacent carbon atoms

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(1) L. Pauling, The Nature of the Chemical Bond, Cornell University Press 1940, p. 75, 133.

(2) W. D. Kumler and C. W. Porter, *J. Am. Chem. Soc.*, **56**, 2549 (1934).

(3) M. J. S. Dewar, The Electronic Theory of Organic Chemistry, Oxford University Press (1949), p. 94.

(4) R. S. Mulliken, *J. Chem. Phys.*, **3**, 564 (1935).

(5) H. L. McMurry, *J. Chem. Phys.*, **9**, 231 (1941).

(6) H. Baba, *J. Chem. Soc. Japan*, **72**, 214 (1951).

(7) M. Kasha, Discuss. Farad. Soc., Spectroscopy and Molecular Structure, 14. (1950).

(8) C. Sandorfy, *Bull. soc. chim. France*, (1949), 615.

(9) G. W. Wheland, *J. Am. Chem. Soc.*, **64**, 900 (1942).

Table 1

The Final Results of the Molecular Orbital Calculation with Amide

	I*	II*	III*	IV*	V*	VI*
α_C	4.297β	4.078β	4.378β	4.301β	4.085β	4.383β
α_O	5.355β	5.098β	5.546β	5.362β	5.106β	5.551β
α_N	5.109β	4.864β	5.331β	5.096β	4.849β	5.323β
β_{CO}	0.889β	0.891β	0.884β	0.919β	0.919β	0.919β
β_{CN}	0.822β	0.822β	0.818β	0.761β	0.761β	0.761β
E_1	6.081β	5.841β	6.240β	6.075β	5.833β	6.240β
E_2	5.213β	4.963β	5.422β	5.196β	4.945β	5.408β
E_3	3.466β	3.236β	3.593β	3.489β	3.262β	3.610β
Q_C	+0.360	+0.346	+0.404	+0.366	+0.356	+0.408
Q_O	−0.700	−0.680	−0.712	−0.700	−0.676	−0.702
Q_N	+0.338	+0.336	+0.308	+0.338	+0.324	+0.294

* Values of various parameters used in each calculation are as follows: $\chi_C=2.5$ in all calculations; $\chi_O=3.5$ and $\chi_N=3.0$ in I, II, IV and V; $\chi_O=3.6$ and $\chi_N=3.15$ in III and VI; $k=4.1$ in I, III, IV and VI; $k=3.9$ in II and V; $r_{CO}=1.23$ A. and $r_{CN}=1.32$ A. in I, II and III; $r_{CO}=1.21$ A. and $r_{CN}=1.37$ A. in IV, V and VI.

in benzene, α and β are the coulomb and the exchange integrals in the same molecule respectively, and k is the constant representing the ratio between α and β. Sandorfy has assigned 4.1 for the value of k. In the present calculation, two values of k, 4.1 and 3.9 were adopted. The latter value was determined as the ratio of the ionization potential of the carbon atom to the value of β estimated by Platt.(10) The overlap integrals necessary for the determination of the exchange integrals were obtained from the Table of Mulliken *et al.*(11) using the following two sets of bond distances:

C=O, 1.23 A., C−N, 1.32 A.;(12)
C=O, 1.21 A., C−N, 1.37 A..(13)

Under these conditions, three values of E can be evaluated in units of β. Then the values of a_{aj} in Eq. (1) can be calculated for each value of E. And it is possible to determine the π-electron density q_a of a-atom by the following equation,(14)

$$q_a=2\sum_j a^2_{aj} \qquad (4)$$

where the summation extends over the molecular orbitals which are occupied in the ground state.

From the value of q_a obtained by Eq. (4), the formal charge Q_a (in electron units) of a-atom can be known. Each atom having the positive or negative formal charge, correction terms for the electronegativity χ_a and the overlap integral S_{ab} should be considered. Corrections for these two quantities were made by the method of Pauling(15) and by the use of the table of Mulliken *et al.*(11) respectively. Thus it is possible to calculate new values of α_a and β_{ab} by Eq. (3). Using these new values, E, q_a and Q_a are calculated again by Eqs. (2) and (4). These procedures are repeated seven or eight times until the final results of these quantities are self-consistent.(16) They are given in Table 1, together with values of several parameters used in the last calculation.

Next, the similar calculation was made with

Table 2

The Final Results of the Molecular Orbital Calculation with the Carbonyl Group

	I′	II′	III′
χ_C	2.5	2.5	2.5
χ_O	3.5	3.5	3.6
k	4.1	3.9	4.1
α'_C	4.35β	4.16β	4.40β
α'_O	5.44β	5.20β	5.62β
β'_{CO}	0.838β	0.838β	0.838β
E'_1	5.895β	5.666β	6.045β
E'_2	3.895β	3.694β	3.975β
Q'_O	−0.544	−0.528	−0.590
Q'_C	+0.544	+0.528	+0.590

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(10) The value of β estimated by Platt is −23,000cm.$^{-1}$ =−2.84 ev. J. R. Platt, *J. Chem. Phys.*, **18**, 1168 (1950).

(11) R. S. Mulliken, C. A. Rieke, D. Orloff and H. Orloff, *J. Chem. Phys.*, **17**, 1248 (1949).

(12) R. B. Corey and J. Donohue, *J. Am. Chem. Soc.*, **72**, 2899 (1950).

(13) The private communication from Mr. M. Kimura in Department of Chemistry, University of Nagoya.

(14) G. W. Wheland and L. Pauling, *J. Am. Chem. Soc.*, **57**, 2086 (1935).

(15) L. Pauling, The Nature of the Chemical Bond, Cornell University Press, 1940, p. 65.

(16) G. W. Wheland and D. E. Mann, *J. Chem. Phys.*, **17**, 264 (1949); Y. Kurita and M. Kubo, This Bulletin **24**, 13 (1951).

the carbonyl group because it was necessary for the evaluations of the resonance energy of the amide group and of the shift in the wave length due to the substitution of the methyl group of acetone by the amino group. In this case, the distance between carbon and oxygen atoms was set equal to 1.24 A.(17)

Experimental

N-methylacetamide is the same sample as used in the previous investigation.(18) Acetylchloride was prepared from glacial acetic acid and phosphorous trichloride. It was purified by the distillation in the atmosphere excluding moisture (b. p. 51.3°C.). Acetic acid, ethyl acetate and acetone were purified by the method of "Organic Solvent." Petroleum benzine used as the solvent was shaken with concentrated sulphuric acid for several days. Then it was treated with potassium permanganate and distilled after drying with sodium metal.

The absorption spectrum was measured with a Beckman spectrophotometer model DE. The results of the measurements are shown in Figs. 1 and 2. In these figures, molar extinction coefficients ε_M are plotted against wave lengths in mμ.

It was observed that the absorption intensities of ethyl acetate and acetylchloride decrease during the absorption measurements. This fact seems to mean that the decomposition of these molecules is induced by the near ultraviolet light. So the measured values of absorption intensities of these two molecules may not be said to be very accurate. But the wave length of the absorption maximum can be determined reliably as 220 mμ and 207 mμ for acetylchloride and ethyl acetate respectively in their solutions of petroleum benzine. The absorption maximum of acetic acid cannot be observed in this experiment, but it may be inferred from its absorption curve that its maximum probably appears near 200 mμ.(19) The absorption maximum of N-methylacetamide seems to appear in the side of shorter wave lengths rather than those of the above three substances as shown in Fig. 2.(20) This maximum cannot be measured with a Beckman spectrophotometer model DU.

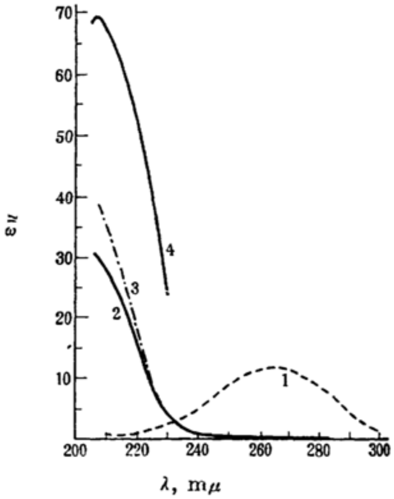

Fig. 1.—Absorption spectra of acetone, acetic acid and ethyl acetate: 1, acetone in water; 2, acetic acid in petroleum benzine; 3, ethyl acetate in water; 4, ethyl acetate in petroleum benzine.

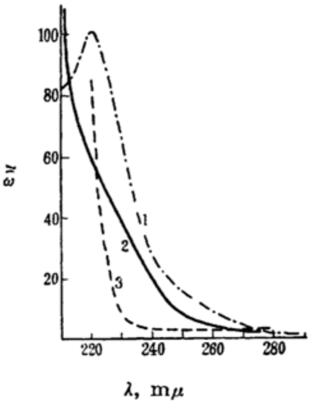

Fig. 2.—Absorption spectra of acetylchloride and N-methylacetamide: 1, acetylchloride in petroleum benzine; 2, N-methylacetamide in petroleum benzine; 3, N-methylacetamide in water.

At all events, it is evident from the above-mentioned experiments that the weak absorption band of acetone is intensified and shifted to the side of shorter wave lengths when one of the methyl groups is substituted by Cl atom, OR or NR_2 group.

Discussion

Calculated values of the resonance energies, π-electron distributions, and ground or exited energy levels of carbonyl and amide groups will be discussed comparing them with the observed or the estimated values of these quantities.

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(17) M. Kimura and Y. Kurita, *J. Chem. Soc. Japan*, **72**, 396 (1951).

(18) S. Mizushima, T. Shimanouchi, S. Nagakura, K. Kuratani, M. Tsuboi, H. Baba and O. Fujioka, *J. Am. Chem. Soc.*, **72**, 3490 (1950).

(19) Ley and Arends observed the absorption maximum of acetylchloride, methyl acetate and acetic acid in pure liquids at 234.5 mμ, 208.5 mμ and 204 mμ respectively. The value of acetylchloride, which differs from that of the present experiment, seems to be incorrect because their measurements are not made in the wave lengths near the maximum. H. Ley and B. Arends, *Z. physik. Chem.*, (B) **17**, 177 (1932).

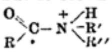
(20) Anslow pointed out with amide that very weak absorption maximum appeared about 280 mμ. In the present experiment, the similar phenomenon is observed in the concentrated aqueous solution of N-methylacetamide. Anslow regarded this absorption as due to associated amide molecules, but it seems more probable to consider that it is due to  or some impurities. G. A. Anslow, Discuss. Farad. Soc., Spectroscopy and Molecular Structure, 299 (1950).

Table 3

Calculated Values of ΔE_{res}, μ_π, and $\Delta\nu$ of Amide

	I	II	III	IV	V	VI
ΔE_{res} a) (kcal./mole.)	19.2	18.3	18.0	18.2	17.3	17.5
μ_π (D)	5.54	5.38	5.42	5.51	5.32	5.32
$\Delta\nu$ (cm.$^{-1}$) b)	7910	8200	7090	7550	7780	6810

a) The value of β is assigned-20 kcal./mole.
b) The value of β is assigned-23000 cm^{-1}.

(A) Resonance Energy of the Amide Group.—According to Pauling,(21) the resonance energy of amide is 21 kcal./mole. From the standpoint of the molecular orbital theory, this quantity can be represented approximately by the following equation, $\Delta E_{res}=2(E'_1+\alpha'_N)-2(E_1+E_2)$, where α'_N is the value of the coulomb integral for the neutral nitrogen atom. Calculated values of ΔE_{res} are given in Table 3. It is to be noticed that the values of ΔE_{res} evaluated by different methods I-VI may be regarded as almost the same,—that is to say, they are little affected by the values of various parameters used in each method. And it may be seen that the agreement between the calculated and the observed values are fairly good.

(B) π-Electron Densities and Dipole Moments of Carbonyl and Amide Groups.—The values of π-electron density, q_a calculated by the Eq. (4) indicate that in the carbonyl group about half of a π-electron moves from carbon to oxygen (see Table 2). This fact is in good accord with the conclusion derived by Pauling(1) from the study on the contribution of the polar resonance structure to the dipole moment of acetone or similar substances.

As to the amide group, it is shown that the non-bonding electrons in nitrogen partially migrate into the C=O bond. As the result of this electron migration, the nitrogen atom comes to have a partially positive charge. Thus it will be seen that the dipole moment of amide group becomes large, and the basic property of it decreases. From the values of Q_a, the dipole moment due to π-electron distributions, μ_π, can be calculated as shown in Table 3. The observed value of the dipole moment is 3.79D for dimethylacetamide in dioxan. So the calculated values are somewhat larger than the observed one.(22)

(C) Excited Electronic Levels and Near Ultraviolet Absorption Spectra of Carbonyl and Amide Groups.—Low intensity absorption band characteristic of unconjugated carbonyl bond appears at 279 mμ and 265 mμ in petroleum benzine and in water respectively. This absorption has been studied in detail by McMurry(5); and from the theoretical investigation of the absorption intensity, it considered that this absorption might be due to the transition of non-bonding oxygen electron to the excited π-electron level of carbonyl group. This transition is shown schematically in Fig. 3. And it has been called the $n\rightarrow\pi^*$ or the $1\rightarrow\pi$ transition by Kasha(7) or Baba(6) respectively.

The results of our molecular orbital calculation on the electronic levels of carbonyl group are consistent with this view. The energy difference $\Delta E'$ between energy levels of the upper π-molecular orbital and of non-bonding oxygen electrons may be approximately represented by the following equation, $\Delta E'=E'_2-\alpha'_0$. The values of this quantity calculated by the methods I', II' and III' become -1.54, -1.51 and -1.64β respectively. The observed value can be determined as -1.56β, if the said absorption spectrum of acetone is due to the $n\rightarrow\pi^*$ transition. Therefore both values are in good agreement. But if it is assumed that this absorption band is due to the $\pi\rightarrow\pi^*$ transition, energy differences between upper and lower π-electron levels become -2.00, -1.97 and -2.07β. These values are larger than the observed value. Furthermore, the solvent effect of this absorption spectrum can be also explained from the same point of view. As shown in Table 4 the value of $\Delta E'$ calculated by the above equation becomes larger with the increase of $|\alpha'_0|$. This means that the above-mentioned absorption band shifts to the side of shorter wave lengths the contribution of the partially ionic resonance structure increases. The experimental result, namely that its wave length becomes smaller with he increment of the polarity of solvents,(23) conforms to the above theoretical expectation.

Table 4

The Relation between $\Delta E'$ and α'_0

α'_0	4.92β	5.41β	5.74β	6.07β	6.56β
Q'_0	-0.570	-0.640	-0.678	-0.710	-0.748
$\Delta E'$	-1.34β	-1.72β	-1.99β	-2.28β	-2.72β

Values of k, α'_c and β'_{co} used in these calculations are 4.1, 4.1β and 0.838β respectively.

Next the effect of substitution on the absorption spectrum of acetone will be discussed. When the methyl group of acetone is replaced by the group with non-bonding π-electrons such as amino or hydroxyl group, the absorption band shifts to the side of shorter wave lengths as shown in Figs. 1 and 2. On the other hand, in benzene the absorption spectrum due to the $A_{1g}\rightarrow B_{2u}$ transition shifts to the side of the longer wave lengths by

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(21) L. Pauling, The Nature of the Chemical Bond, Cornell University Press (1940), p. 138.

(22) The dipole moment due to σ-electron distribution is expected to be very small for dimethylacetamide as well as C=O bond(1) So their dipole moments will be principally determined by π-electron distribution alone.

(23) According to Burawoy, this experimental result was regarded as one of the facts which could not be explained from the stand-point of $n\rightarrow\pi^*$ transition. But this difficulty for the $n\rightarrow\pi^*$ transition is surely removed by the present theoretical consideration. A. Burawoy, Discuss. Farad. Soc., Spectroscopy and Molecular Structure, 70 (1950).

the same substitutions.(24)(25) It is interesting that the effect of the substitution on the absorption spectrum is quite different in acetone and benzene. This difference was discussed by Baba.(6) He applied the theory of the electron migration developed by Sklar(25) and Herzfeld(25) to explain qualitatively this fact. The same phenomenon can be treated by the LCAO molecular orbital method as follows. As shown in Fig. 3 and Tables 1 and 2, the calculated value of the empty π-electron level of amide group is higher than that of acetone. So it may be regarded as reasonable that the absorption maximum of acetone appears in a longer wave length than that of amide. This fact can be readily understood by a glance at Fig. 3. And it is possible to calculate the wave number difference $\Delta\nu$ between these two absorption spectra by the equation, $\Delta\nu=(\Delta E-\Delta E')/ch=(E_3-\alpha_0-E'_2+\alpha'_0)/ch$. The calculated values of $\Delta\nu$ are given in Table 3. The absorption maximum of N-methylacetamide appears probably below 205 mμ in petroleum benzine solution. So the observed value of $\Delta\nu$ may be estimated to be larger than 12900 cm.$^{-1}$ The calculated value for this quantity is smaller than the observed one. But it will be difficult to obtain more accurate values by the simple approximation of LCAO.

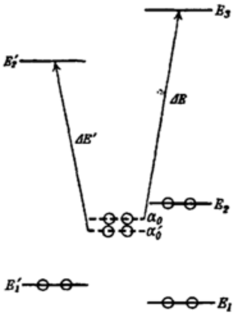

Fig. 3.—Energy levels of acetone and amide

The shift of absorption spectra of acetylchloride, acetic acid and ethyl acetate can also be understood on the basis of the $n\rightarrow\pi^*$ transition. In these molecules as well as amide, the substituents have the non-bonding π-electrons which are able to migrate into carbonyl group, and the rate of electron migration probably increases in the order of Cl atom, OR and NR_2 groups as observed in the case of monosubstituted benzene.(25)(27) It can be shown on the hand, that the value of E_3 becomes larger with the increment of the electron migration.(26) So it is expected from the standpoint of the $n\rightarrow\pi^*$ transition that these absorption spectra shift to the side of the shorter wave lengths in the order of acetylchloride, acetic acid or ethyl acetate, and N-metylacetamide. This expectation is qualitatively fulfilled by the present experiment.

Summary

1) Electronic structures of carbonyl and amide groups were investigated by the use of the molecular orbital method; calculated values of resonance energy and π-electron densities may be regarded as reasonable compared with these which were observed.

2) Near ultraviolet absorption spectra were measured with acetone, acetylchloride, acetic acid, ethyl acetate and N-methylacetamide. As the result of these measurements, it becomes evident that the low intensity absorption band of acetone shifts to the side of shorter wave lengths when the methyl group of acetone is replaced Cl atom or OR and NR_2 groups. These results can be explained by the present theoretical consideration if this absorption band is due to the $n\rightarrow\pi^*$ transition.

I wish to express cordial thanks to Prof. S. Mizushima and Prof. K. Higasi for stimulating and directing this research and to Mr. H. Baba for his helpful discussion. My thanks are also due to Mr. A. Kuboyama and Miss C. Tsurumi for their kind co-operation in performing this research. I am indebted to the budget of the Ministry of Education for this investigation.

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(24) S. Nagakura and H. Baba, *J. Chem. Soc. Japan*, **71**, 527 (1950).

(25) K. F. Herzfeld, *Chem. Rev.*, **41**. 233 (1947).

(26) A. L. Sklar, *J. Chem, Phys.*, **7**, 984 (1939).

(27) F. A. Matsen, *J. Am. Chem. Soc.*, **72**, 5243 (1950).

(28) This is apparent from the fact that $\partial E_3/\partial\alpha_N$ is positive.