The Electronic Structures and Electronic Spectra of Benzylidene Methyl Amine N-Oxide[*2] *and Its Related Compounds*[*1]

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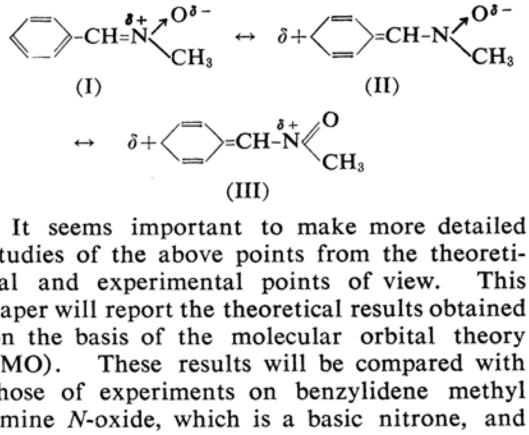
In a previous paper,¹⁾ the electronic spectra of many nitrones and their related compounds were recorded, and the configurations of some nitrones were determined by measuring their dipole moments. As a result, we found that the behavior of the electronic spectra of nitrones, especially with regard to solvent effects, is very similar to that of heterocyclic *N*-oxides. That is, in hydrogen-bonding solvents, a remarkable blue shift of the electronic spectra is always observed with an increase in solvent polarity. In addition, it was established that the electronic spectra of nitrones without a large steric hindrance exhibit a behavior which can be expressed as resonance hybridization, such as I, II and III.



(I) (II)

(III)

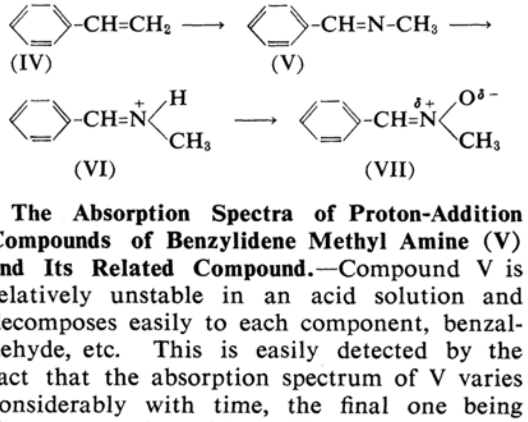
It seems important to make more detailed studies of the above points from the theoretical and experimental points of view. This paper will report the theoretical results obtained on the basis of the molecular orbital theory (MO). These results will be compared with those of experiments on benzylidene methyl amine *N*-oxide, which is a basic nitrone, and its related compounds.

Experimental

The ultraviolet absorption spectra were measured with a Hitachi recording spectrophotometer, Model EPS-2. Measurements were usually carried out at room temperature and at a slow scanning speed, using a 1 cm. light path quartz cell. The organic solvents used were purified according to the methods recommended by Weissberger and Proskauer;²⁾ special care was taken to remove any contaminating water. The anhydrous ethanol containing hydrogen chloride was prepared by introducing hydrogen chloride gas, which has been carefully dried with concentrated sulfuric acid, into anhydrous ethanol. The concentration of hydrochloric acid was decided by titration with a sodium hydroxide solution. The samples used were benzylidene methyl amine, its *N*-oxide, and benzaldoxime *O*-methyl ether.³⁾ The synthetic and purification methods and the physical properties of these compounds were reported in a previous paper.¹⁾

Experimental Results

The electronic structure and the spectrum of benzylidene methyl amine *N*-oxide were analyzed according to the following system, where styrene was selected as the basic compound, because the electronic structure and the electronic spectra of styrene have been investigated in detail by several authors, as will be mentioned later. Figure 1 shows the spectra of styrene⁴⁾ and benzylidene methyl amine and its *N*-oxide, these spectra being measured by a method previouly reported.



(IV) (V)

(VI) (VII)

The Absorption Spectra of Proton-Addition Compounds of Benzylidene Methyl Amine (V) and Its Related Compound.—Compound V is relatively unstable in an acid solution and decomposes easily to each component, benzaldehyde, etc. This is easily detected by the fact that the absorption spectrum of V varies considerably with time, the final one being the same as that of benzaldehyde.

However, the spectrum corresponding to VI

[*1] Presented at the International Symposium on Molecular Structure and Spectroscopy, Tokyo, September, 1962.

[*2] The tertiary amine N-oxides of this type are frequently called "nitrone."

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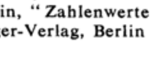
1) T. Kubota, M. Yamakawa and Y. Mori, This Bulletin, 36, 1549 (1963).

2) A. Weissberger and E. Proskauer, "Organic Solvents," 2nd Ed. Interscience Pub., Inc., New York (1955).

3) This is a syn-type compound; that is,



4) The spectrum of styrene has been cited in these papers: a) E. M. Layton, Jr., *J. Mol. Spectroscopy*, 5, 181 (1960); b) E. Merkel, *Z. Elektrochem.*, 63, 373 (1959); c) Landolt-Börnstein, "Zahlenwerte und Funktionen," I. Band 3 Teil, Springer-Verlag, Berlin (1951), p. 266.

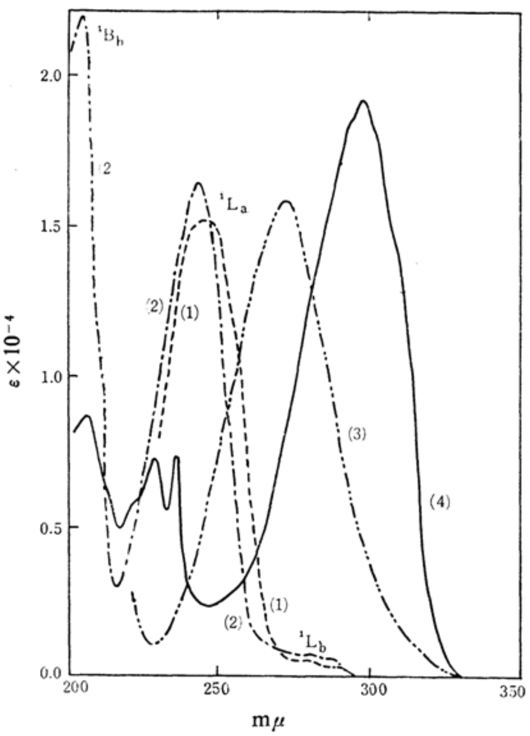


Fig. 1. The absorption spectra of the compounds.

(1) ---- Styrene in cyclohexane

(2) —·—· Ph-CH=N-CH$_3$ in *n*-heptane

(3) ---- Ph-CH=$\overset{+}{N}$H-CH$_3$ in 3.57 N H$_2$SO$_4$

(4) —— Ph-CH=$\underset{\displaystyle CH_3}{\underset{|}{N}}\rightarrow$O in *n*-heptane

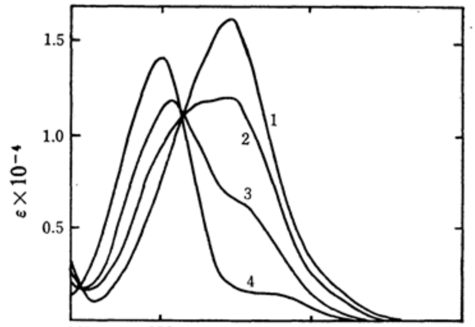


Fig. 2. Time dependence of the absorption spectra of Ph-CH=N-CH$_3$ in 3.57 N H$_2$SO$_4$.

1. After about 10 min. 2. After about 1 hr.
3. After about 4 hr. 4. Benzaldehyde

can be obtained by recording the spectra as soon as possible after dissolving V in sulfuric acid solutions of various concentrations. The recorded spectra are shown in Figs. 1 and 2. The absorption spectra of V dissolved in anhydrous ethanol containing hydrochloric acid also show a time dependence, but the mechanism of decomposition may be considered to be different from that in the acidic aqueous solution mentioned above,[5] because the spectrum obtained after 2 hr. is completely different from that of benzaldehyde. As has been stated above, however, the spectrum of VI was also obtained by recording it quickly after the sample had been dissolved. The spectra in various acid concentrations are shown in Fig. 3.

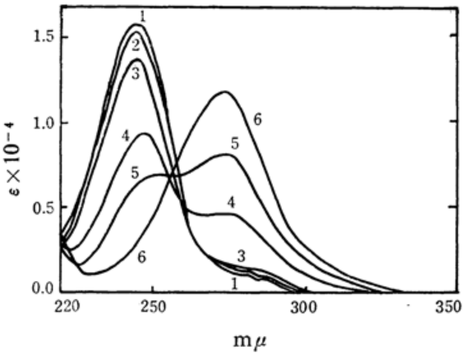


Fig. 3. The spectra of Ph-CH=N-CH$_3$ in anhydrous ethanol containing hydrogen chloride of various concentrations.

Concentrations of HCl
1. 0.000 mol./l.
2. 1.996×10^{-5}
3. 3.992×10^{-5}
4. 9.98×10^{-5}
5. 1.996×10^{-4}
6. 9.98×10^{-4}

The spectra were recorded as soon as possible after dissolving the sample in solvents.

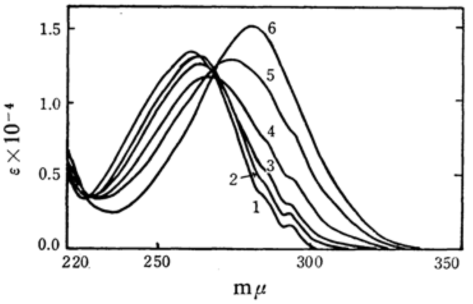


Fig. 4. The spectra of Ph-CH=N-OCH$_3$ in anhydrous ethanol containing hydrogen chloride of various concentrations.

Concentrations of HCl
1. in abs-EtOH
2. 4.83 mol./l.
3. 5.80
4. 6.76
5. 7.73
6. 8.69

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[5] Considering that weter may play an important role in the decomposition of V to benzaldehyde, etc., in an acidic aqueous medium, we carried the experiment out under the anhydrous condition.

On the other hand, benzaldoxime *O*-methyl ether is stable in an acidic medium, and the spectra of the proton-addition compound could be recorded easily, as may be seen in Fig. 4. In this case it may reasonably be thought that the proton addition will occur at the nitrogen atom in the molecule.

A comparison of the spectrum of benzaldoxime *O*-methyl ether with that of V shows that the former absorbs light at a longer wavelength than the latter. The resonance effect of the OCH_3 group may be the main reason for this.

Theoretical

In order to analyze the electronic structure and the spectrum of benzylidene methyl amine *N*-oxide (VII), MO methods were applied to the IV, V, VI and VII compounds. As VII is quite a complex molecule, in practice it is difficult to treat it under higher order conditions. In this paper, the theoretical calculations were based on the π-electron approximation, partly taking electron repulsion terms into account and including the zero differential overlap approximation, proposed by Goodman and Shull[6] and by Baba and Suzuki,[7] to interpret the spectra of benzene derivatives.

Electronic State and Spectroscopic Exchange Integrals, β_s's, of Styrene.—The electronic spectrum and the electronic structure of styrene have been reported by many workers, and the spectrum has reasonably been assigned.[4a,8-11] As is shown in Fig. 1, the absorption bands of styrene have been assigned to ^1L_b, ^1L_a and ^1B_b (Platt's notation) in the order of decreasing wavelength. It may reasonably be considered that these bands are related to the four orbitals ϕ_3, ϕ_4, ϕ_5 and ϕ_6 in the Hückel MO's of styrene shown in Fig. 5.[12,13] Here, the configuration $^1\chi_{4\to5}$ arising from the one electron transition from ϕ_4 to ϕ_5 has the symmetry of $^1A_1$ and the lowest transition energy. The other transitions belonging to the $^1A_1$ symmetry have far larger transition energies than that of $^1\chi_{4\to5}$ (cf. Fig. 5). The interaction between $^1\chi_{4\to5}$ and other $^1A_1$ configurations seems to be relatively small. Assuming that the transition energy, $1.3243\,\beta$, of the $^1\chi_{4\to5}$ configuration, obtained from the simple molecular orbital (SMO) calculations, is equal to the observed value, 5.009 eV., for the ^1L_a band, we can obtain 3.78 eV. for the spectroscopic exchange integral β_s belonging to $^1A_1$. This value was applied to the calculations for V, VI and VII. The configurations, $^1\chi_{4\to6}$ and $^1\chi_{3\to5}$, belonging to $^1B_1$ have the same energy, since styrene is an alternant hydrocarbon. Therefore, the two excited states corresponding to Eqs. 1 and 2 may be written:

$$\Psi_1=\frac{1}{\sqrt{7}}({}^1\chi_{3\to5}-{}^1\chi_{4\to6}) : {}^1B_1^- \tag{1}$$

$$\Psi_2=\frac{1}{\sqrt{2}}({}^1\chi_{3\to5}+{}^1\chi_{4\to6}) : {}^1B_1^+ \tag{2}$$

These correspond to the ^1L_b and the ^1B_b bands respectively. The interaction between $^1\chi_{3\to5}$ and $^1\chi_{4\to6}$ was calculated by means of Eq. 3:

$$({}^1\chi_{4\to6}|H|{}^1\chi_{3\to5})=2(36|G|54)^{\mathrm{MO}}-(36|G|45)^{\mathrm{MO}} \tag{3}$$

The values of (pp/pp) and (pp/qq), which are one-center and two-center π-coulomb repulsion integrals respectively, were calculated on the basis of Pariser-Parr's Ball approximation.[14] The quantity (pp/pp) is obtained from the relation: $(pp/pp)=I_p-E_A$.

In the case of the $2p\pi$-electron in the carbon atom, as was seen in a previous paper,[15] the ionization potential (I_p) and the electron affinity (E_A) on the valence state of sp^3 (V_4) were taken from the data of Pritchard and Skinner.[16] These data lead to $(pp/pp)_c=11.42-0.58=10.84$ eV.

When the distance (γ) between nuclei $\geqq 2.80$ Å, the quantity (pp/qq) is given by Eq. 4 on the basis of the Ball approximation:[14]

$$(pp/qq)_{\mathrm{eV}}=\frac{7.1975}{\gamma}\left[\left\{1+\left(\frac{1}{2\gamma}\right)^2(R_p-R_q)^2\right\}^{-1/2}+\left\{1+\left(\frac{1}{2\gamma}\right)^2(R_p+R_q)^2\right\}^{-1/2}\right] \tag{4}$$

Since Slater's effective nuclear charge of the $2p\pi$-electron in the carbon-atom is 3.25, $R_p=R_q=1.4145$ Å is obtained by the aid of the Pariser-Parr method. However, for the case of $\gamma<2.80$ Å, the quantity (pp/qq) is obtained by

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[6] L. Goodman and H. Shull, *J. Chem. Phys.*, **27**, 1388 (1957).

[7] H. Baba and S. Suzuki, ibid., **32**, 1706 (1960).

[8] J. F. Music and F. A. Matsen *J. Am. Chem. Soc.*, **72**, 5256 (1950).

[9] H. C. Longuet-Higgins and J. N. Murrell, *Proc. Phys. Soc.*, **68**, 7-A, 601 (1955).

[10] W. W. Robertson, J. F. Music and F. A. Matsen. *J. Am. Chem. Soc.*, **72**, 5260 (1950).

[11] J. R. Platt, *J. Chem. Phys.*, **18**, 1168 (1950).

[12] We have assumed here that IV, V, VI and VII have the symmetry of C_{2v} from the view-point of π-electron systems, and that all exchange integrals are equal to β.

[13] C. A. Coulson and R. Daudel, "Dictionary of Values of Molecular Constants," Vol. III, Centre National de la Récherche Scientifique, I. C. I. Ltd., Paris, p. 50.

[14] R. Pariser and R. G. Parr, *J. Chem. Phys.*, **21**, 466, 767 (1953).

[15] T. Kubota, This Bulletin, **35**, 946 (1962); *J. Chem. Soc. Japan, Pure Chem. Sec.* (*Nippon Kagaku Zasshi*), **80**, 578 (1959).

[16] H. O. Pritchard and H. O. Skinner, *Chem. Revs.*, **55**, 745 (1955).

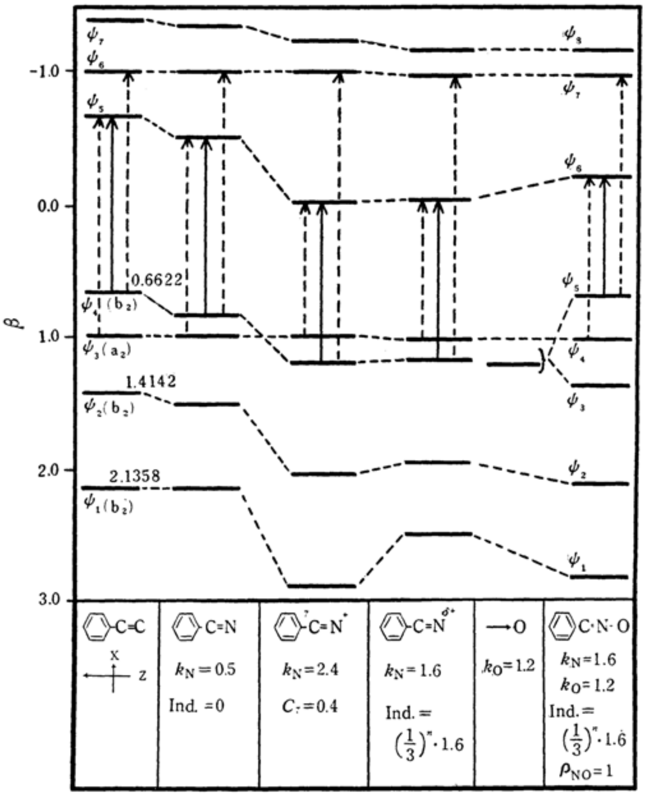


Fig. 5. The orbital energies of styrene, benzylidene methyl amine and its related compounds, and benzylidene methyl amine *N*-oxide.

extrapolating the values evaluated at longer distances to $\gamma=0$, using Eq. 5 as determined by the method of quadratic equation:

$$(pp/qq)=0.2463\gamma^2-2.8237\gamma+10.84 \qquad (5)$$

The values of $(pp/qq)_c$ and of Eq. 3 thus obtained are shown in Table I.

On the basis of the SMO approximation, $E(^1\chi_{4\to6})$ and $E(^1\chi_{3\to5})$ are equal to 1.66215 β, as can be understood from Fig. 5. The interaction between them leads to the two states shown in Fig. 6, in which the observed values of ^1L_b and ^1B_b are also given.[4a]

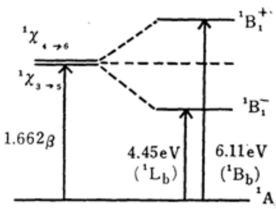
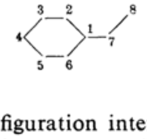


Fig. 6. The configuration interaction between $^1\chi_{4\to6}$ and $^1\chi_{3\to5}$ states in styrene.

TABLE I. THE VALUES OF VARIOUS INTEGRALS
(Unit is in eV.)



(11/11) = 10.84
(11/22) = 7.370
(11/33) = 5.441
(11/44) = 4.865

Configuration interaction matrix elements between two $^1B_1$ states.

$(^1\chi_{4\to6}\|H\|^1\chi_{3\to5})$	Compounds
0.6032	Ph−C=C
0.6281	Ph−C=N
0.5814	Ph−C=$N^{\delta+}$
$(^1\chi_{4\to6}\|H\|^1\chi_{5\to7})$	
0.3677	Ph−C=N→O

Now, the spectroscopic exchange integral, β_s, is evaluated to satisfy the observed values in Fig. 6.[17] $\beta_s=3.04$ eV. is obtained to reproduce the observed value of ^1L_b, whereas $\beta_s=3.31$ eV. is obtained from that of the ^1B_b band. The difference between these two β_s values apparently results from the fact that

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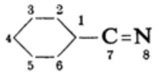
17) The dimensions of styrene were estimated on the basis of the bond order-bond length relation derived by Coulson.[18,24]. We assumed that the benzene ring is a regular hexagon, the bond distance of which is 1.40 Å. It should be noted that the terms (pp/qq) necessary to calculate Eq. 3 are reduced to those consisting of the carbon atoms appearing in the benzene ring in the molecule because of the assumed C_{2v} symmetry.

18) C. A. Coulson, *Proc. Roy. Soc.*, **A207**, 91 (1951).

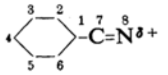
TABLE II. SIMPLE MOLECULAR ORBITALS

("Eigenvalue" shows the δ in the equation: $E=\alpha+\delta\beta$)



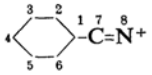
	Eigenvalue	Symmetry	C_{i4}	C_{i3}	C_{i2}	C_{i1}	C_{i7}	C_{i8}
ψ_1	2.15033	b_2	+0.29424	+0.31636	+0.38603	+0.51374	+0.33265	+0.20157
ψ_2	1.50352	b_2	+0.45320	+0.34070	+0.05905	−0.25192	−0.49686	−0.49512
ψ_3	1.00000	a_2	0	+0.50000	+0.50000	0	0	0
ψ_4	0.84491	b_2	+0.43872	+0.18534	−0.28212	−0.42371	+0.20625	+0.59797
ψ_5	−0.50310	b_2	+0.37706	−0.09485	−0.32934	+0.26054	+0.52761	−0.52598
ψ_6	−1.00000	a_2	0	+0.50000	−0.50000	0	0	0

$C_{i2}=\pm C_{i6}$: $C_{i3}=\pm C_{i5}$ (+ and − represent b_2 and a_2 orbitals respectively). $\varepsilon_7=-1.36792$: $\varepsilon_8=-2.12775$



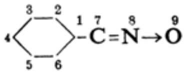
	Eigenvalue	Symmetry	C_{i4}	C_{i3}	C_{i2}	C_{i1}	C_{i7}	C_{i8}
ψ_1	2.48625	b_2	+0.11593	+0.14411	+0.23953	+0.43721	+0.53024	+0.59830
ψ_2	1.95552	b_2	+0.36826	+0.36007	+0.32875	+0.26333	−0.18937	−0.53265
ψ_3	1.03970	a_2	0	+0.49504	+0.50491	0	0	0
ψ_4	1.17915	b_2	+0.53955	+0.31811	−0.17074	−0.50932	−0.16854	+0.40047
ψ_5	−0.02882	b_2	+0.34519	−0.00497	−0.34495	+0.03535	+0.68260	−0.41908
ψ_6	−0.96069	a_2	0	+0.50491	−0.49504	0	0	0

$C_{i2}=\pm C_{i6}$: $C_{i3}=\pm C_{i5}$ (+ and − represent b_2 and a_2 orbitals respectively). $\varepsilon_7=-1.17856$: $\varepsilon_8=-2.02342$



	Eigenvalue	Symmetry	C_{i4}	C_{i3}	C_{i2}	C_{i1}	C_{i7}	C_{i8}
ψ_1	2.89629	b_2	+0.02657	+0.03848	+0.08487	+0.20734	+0.43076	+0.86797
ψ_2	2.04204	b_2	+0.36504	+0.37271	+0.39605	+0.43604	+0.09830	−0.27462
ψ_3	1.00000	a_2	0	+0.50000	+0.50000	0	0	0
ψ_4	1.20279	b_2	+0.55039	+0.33100	−0.15226	−0.51414	−0.31387	+0.26217
ψ_5	−0.00867	b_2	+0.36064	−0.00156	−0.36063	+0.00469	+0.72121	−0.29942
ψ_6	−1.00000	a_2	0	+0.50000	−0.50000	0	0	0

$C_{i2}=\pm C_{i6}$: $C_{i3}=\pm C_{i5}$ (+ and − represent b_2 and a_2 orbitals respectively). $\varepsilon_7=-1.24063$: $\varepsilon_8=-2.09181$



	Eigenvalue	Symmetry	C_{i1}	C_{i2}	C_{i3}	C_{i4}	C_{i7}	C_{i8}	C_{i9}
ψ_1	2.80865	b_2	+0.24348	+0.10736	+0.05169	+0.03681	+0.42584	+0.72544	+0.45096
ψ_2	2.12615	b_2	+0.47043	+0.38909	+0.33378	+0.31397	+0.13840	−0.25000	−0.26993
ψ_3	1.36987	b_2	−0.40396	−0.03880	+0.35310	+0.51553	−0.40395	+0.06604	+0.38876
ψ_4	1.03970	a_2	0	+0.50491	+0.49504	0	0	0	0
ψ_5	0.69624	b_2	−0.27258	−0.24954	+0.11363	+0.32640	+0.35775	+0.33086	−0.65677
ψ_6	−0.19804	b_2	+0.10732	−0.29936	−0.03030	+0.30595	+0.55838	−0.51570	+0.36888
ψ_7	−0.96069	a_2	0	−0.49504	+0.50491	0	0	0	0

$C_{i2}=\pm C_{i6}$: $C_{i3}=\pm C_{i5}$ (+ and − represent b_2 and a_2 orbitals respectively). $\varepsilon_8=-1.18828$: $\varepsilon_9=-2.02446$

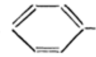
the calculated values of Eq. 3 are not suitable. If one calculates the value of Eq. 3 so as to reproduce the observed ^1L_b and ^1L_a bands, one obtains 0.8307 eV., which is a little greater than that listed in Table I. The main reasons for this discrepancy are as follows: (a) The MO's used here are not the SCF-MO, which are believed to be most desirable. (b) We assumed that the symmetry of styrene is C_{2V}. (c) In these calculations, only the configuration interaction (C. I.) between $^1\chi_{3\to5}$ and $^1\chi_{4\to6}$ was evaluated. If we are rigorous we must consider the C. I. among the other configurations. Therefore, 3.17 eV., that is, the mean value between 3.04 eV. and 3.31 eV., was adopted here as the approximate value for the β_s corresponding to the $^1B_1$ bands. This value was applied to the calculations of V, VI and VII.

The SMO Calculations for Benzylidene Methyl Amine (V) and Its Proton-Addition Compound (VI).—The SMO's on V and VI were calculated by a method analogous to that used for styrene. In this case, the selection of the Coulomb integral is important for the N-hetero atom in Eq. 6:

$$\alpha_{\text{hetero}}=\alpha+k_{\text{hetero}}\beta \tag{6}$$

So far, much information about the Coulomb integral for the heterocyclic nitrogen atoms has been obtained by many authors. It has been reported that the value 0.4∼0.5 is the best for the parameter, k_N, of the sp^2 type, just as for the nitrogen atom in pyridine.[19] Assuming that the parameter of the nitrogen atom in V is nearly equal to that in pyridine, we used $k_N=0.5$.[19a] For the $k_N{}^+$ of the $\gt\overset{+}{N}-H$ type, we made use of 2.4 (0.4 β is adopted on the carbon atom adjacent to the N$^+$-atom), which was decided by the SCF-MO calculations for the pyridine cation.[20] The results are listed in Table II.

The SMO Calculation of Benzyliden Methyl Amine *N*-Oxide (VII).—This compound is the simplest and most typical nitrone. Previously, we studied the electronic structure of such heterocyclic *N*-oxides as pyridine *N*-oxide and determined reasonable parameters to describe the hetero atoms of these molecules. Here, in order to compare the results of nitrones with those of heterocyclic *N*-oxides, the parameters,[21] except for that of the oxygen atom of VII, were taken to be equal to those of the heterocyclic *N*-oxides derived previously by us: $k_N=1.6$, and inductive effects$=(1/3)^n\cdot k_N$.

Furthermore, under the conditions mentioned above, we also calculated the SMO of the hypothetical molecule $-C=N^{\delta+}$, which is obtained by dividing the VII into the composite systems consisting of the oxygen atom and its residual part.[22] The MO's thus obtained are listed in Table II. Next, the parameter of the oxygen atom in VII was determined so as to reproduce the observed dipole moment (3.49 D. U.) of VII.[1] As was described in a previous paper,[1] although VII is probably distorted somewhat from a planar structure, for the sake of simplicity the planar structure was assumed for the calculation of the dipole moment. The molecular dimensions of VII were obtained by a method analogous to that used in the calculation of styrene. The bond-order bond-length relation was used, where the order-length relationships of the N–O and C–N bonds are the same as those of our previous papers,[15] and as those used in Kobayashi's and in Cox and Jeffrey's papers respectively.[23] Moreover, we assumed that each of the C–C–N and C–N–O angles is 120°, the configuration of the molecule being the same as that discussed in a previous paper,[1,24] and that the benzene ring is a regular hexagon.

The values of the σ-moments were determined with reference to those obtained by the analysis of the dipole moments of, for instance, pyridine *N*-oxide, and diazine mono *N*-oxide[15,26] and by the analysis of the NMR

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[19] a) N. Mataga and K. Nishimoto, *Z. Phys. Chem. N. F.*, **13**, 140 (1957); b) See also T. Kubota, *Progress Reports on Electronic Processes in Chemistry*, **2**, 39 (1960), published by the Japanese Reseach Group on Electronic States.

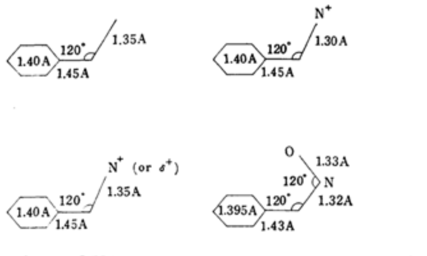
[20] S. Mataga and N. Mataga, *Z. physik. Chem. N. F.*, **19**, 231 (1959).

[21] The effect based on the methyl group was neglected.

[22] It seems to be very useful to compare the energy level of the oxygen atom with those of the residual part stated above.

[23] a) E. G. Cox and G. A. Jeffrey, *Proc. Roy. Soc.*, **A207** 110 (1951); b) H. Kobayashi, *J. Chem. Soc. Japan, Pure Chem. Sec.* (*Nippon Kagaku Zasshi*), **82**, 272 (1961).

[24] The dimensions and configurations for V, VI and VII are as follows:



The dimensions of VII were estimated by averaging the molecular diagrams obtained by using the following two sets of parameters: $k_N=1.6$, inductive effects$=(1/3)^n k_N$, $\rho_{NO}=1$ and $k_O=0.8$; $k_N=1.6$, $k_O=0.8$, $\rho_{NO}=0.7$, and inductive effects$=0$.[15,25] These averaged values are almost the same as those in the molecular diagram shown in Fig. 10.

[25] The latter set of parameters is nearly equal to that adopted by W. Maier, A. Saupe and A. Englert, *Z. physik. Chem. N. F.*, **10**, 273 (1957).

[26] T. Kubota and H. Watanabe, This Bulletin, **36**, 1093 (1963), where the symbol "N–O" in Table II must be read as H–C because of misprint.

spectra of pyrimidine:[27] $\overset{(+)}{\mathrm{N}}\rightarrow\overset{(-)}{\mathrm{O}}$ (dative bond) $=4.55$ D., $\overset{(+)}{\mathrm{H}}-\overset{(-)}{\mathrm{C}}=0.40$ D., $\mathrm{C(sp^2)-N(sp^2)}=0.0$ D., and the lone pair moment of the $\mathrm{N(sp^2)}$ atom is 1.0 D. Under these conditions, the MO's were calculated by using the various parameters of the oxygen atom. It was found that $k_{\mathrm{O}}=1.2$ is a suitable value. The results thus obtained are shown in Table II. It is important to point out that 1.2 is larger than the value decided previously for pyridine *N*-oxide (0.8β). This fact shows that the electron migration from the oxygen atom to the conjugated system in VII is smaller than that in heterocyclic *N*-oxides, as will be mentioned in a later section.

The Calculation of the Transition Energy and the Oscillator Strength of Benzylidene Methyl Amine (V), Its Proton-Addition Compound VI, and Benzylidene Methyl Amine *N*-Oxide (VII). —These values are calculated by using the MO's and the eigen values shown in Table II and the spectroscopic exchange integrals, β_s, mentioned in the preceding section. The one electron transition from the highest occupied orbital to the lowest vacant orbital belongs to the $^1\mathrm{A}_1$ symmetry (shown with a solid arrow line in Fig. 5); this state may be expressed by a single configuration as in the case of styrene. Both transitions shown with a dotted arrow line in Fig. 5 belong to the $^1\mathrm{B}_1$ symmetry, and these will interact with each other, as may be seen in Table I. The observed and calculated values of electronic spectra are shown in Fig. 7, in which the observed values are indicated by a circle. The transition moment corresponding to each excited state was also computed. The numbers shown in Fig. 7 indicate the square value of $\vec{Q}$:

$$\vec{Q}=\int \Psi_{\mathrm{g}}(^1\Gamma)\,\vec{\gamma}\,\Psi_{\mathrm{exc.}}\ (^1\Gamma)\mathrm{d}\tau \qquad (7)$$

where $\Psi_{\mathrm{exc.}}$ $(^1\mathrm{B}_1^{\pm})$ is as shown in Table III. Under our approximation, $\vec{Q}$ is reduced to each term expressed as $q_{i-j}=\sqrt{2}\sum_{\nu}C_{i\nu}\cdot C_{j\nu}\cdot\vec{\gamma}_{\nu}$.[28] Assuming that side chain group in the molecules has the bent structure (120°), the calculation of the transition moments for the $^1\mathrm{A}_1$ species was carried out.[24] The $^1\mathrm{A}_1$ level has a transition moment along the long axis of molecules, while the $^1\mathrm{B}_1$ levels have their transition moments parallel with the X-axis, as Fig. 5 shows. The character of the $^1\mathrm{B}_1$ bands may be considered to be localized in the benzene ring.

Discussion and Results

On the Electronic Spectra of Benzylidene Methyl Amine *N*-Oxide (VII) and Its Related Compounds.—As is shown in Fig. 7, the calculated values of V agreed well with the observed values. It should be noted that the level arising from $^1\mathrm{B}_1^-$ increases to an intensity slightly more than that of styrene[29] because the MO is disordered when the nitrogen atom is introduced.

The calculated transition energy and intensity of the $^1\mathrm{A}_1$ level of VI are also in good agreement with the experimental results, as may be seen in Fig. 7. Furthermore, on the basis of this calculation, it is thought that a band having the $^1\mathrm{B}_1$ symmetry will exist in the longest wavelength region. An inspection of the experimental curve of VI in Figs. 1, 2 and 3 will show that the curve in the above wavelength region has a considerably prolonged tail, where an absorption band may be hidden. In the light of the calculated results, this hidden band may conceivably be ascribed to the $^1\mathrm{B}_1^-$ band, although the calculated value does not thoroughly agree with the observed value. The main reason for this disagreement on the $^1\mathrm{B}_1^-$ level may be attributed to the selection of Coulomb parameters (i.e., the $k_{\mathrm{N}^+}=2.4$ used here for N^+ is relatively large). Therefore, the MO values, ψ_4 and ψ_5, of styrene shown in Fig. 5 are largely stabilized in spite of the small change of the ψ_3 and ψ_6 MO's. As a result, the $^1\mathrm{B}_1^-$ level undergoes a large red shift. When a large net charge such as N^+ is introduced into the molecule, it is believed that the same treatment of the VI as of the pyridine cation is not totally valid. The calculated results of VII shown in Fig. 7 differ from those of other compounds in the following points: a band having the $^1\mathrm{B}_1$ symmetry and a lower intensity than that of the strong $^1\mathrm{A}_1$ band existing at about 4 eV. must appear in the region of 5.35 eV. In fact, we can find a new band having vibrational structures at about 5.35 eV., as may be seen in Figs. 1, 7 and Table III.[30] On the basis of the above findings, we may reasonably conclude

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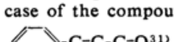
[27] W. Seiffert, H. Zimmermann and G. Sheibe, *Angew. Chem.*, **74**, 249 (1962).

[28] R. S. Mulliken and C. A. Rieke, *Report Progress Physics*, **8**, 231 (1941); R. Daudel, R. Lefebrre and C. Moser, "Quantum Chemistry," Interscience Publishers, New York (1959).

[29] On this approximation, if the vibronic interaction is not considered, the $^1\mathrm{B}^-{}_1$ of styrene is forbidden by accident.

[30] We could not obviously conclude from this calculation whether or not the absorption band arising mainly from the $^1\chi_{3\rightarrow6}$ configuration $(^1\mathrm{A}_1)$ is overlapped in this band. A problem analogous to this was discussed by Inuzuka in the case of the compound:



[31]

[31] K. Inuzuka, This Bulletin, **34**, 1557 (1961).

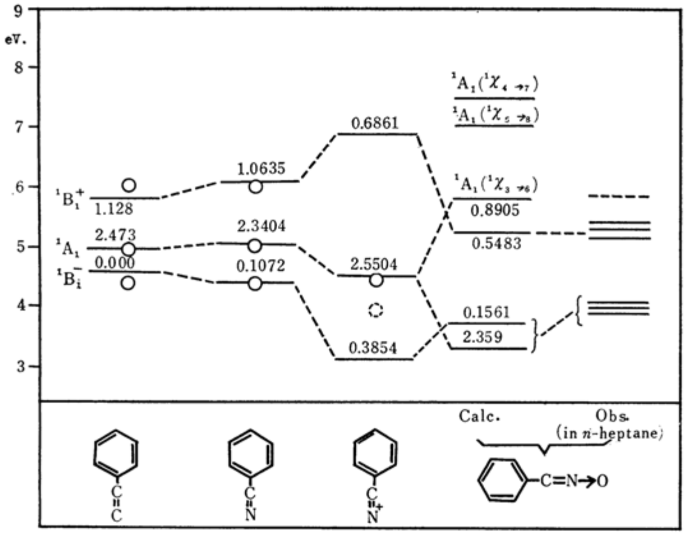


Fig. 7. The calculated energy levels, the observed values, and Q^2 values (refer to equation 7 in text.)
○: Observed value (Number is the value of Q^2)

TABLE III. THE CALCULATED AND OBSERVED VALUES OF $^1A_1$ AND $^1B_1$ BAND

Compound	$^1A_1$		$^1B_1^-$ and $^1B_1^+$		Wave functions of $^1B_1^-$ and $^1B_1^+$ states	
	Obs.	Calcd.	Obs.	Calcd.		
Ph-C=C	5.009	5.009	4.451	4.666	$1/\sqrt{2}\ (^1\chi_{3\to5}-{}^1\chi_{4\to6})$	$^1B_1^-$
			6.112	5.872	$1/\sqrt{2}\ (^1\chi_{3\to5}+{}^1\chi_{4\to6})$	$^1B_1^+$
Ph-C=N	5.081	5.095	4.475	4.477	$0.9092\ (^1\chi_{3\to5})-0.4164\ (^1\chi_{4\to6})$	$^1B_1^-$
			6.033	6.136	$0.4164\ (^1\chi_{3\to5})+0.9092\ (^1\chi_{4\to6})$	$^1B_1^+$
Ph-C=N+	4.531	4.579	~4.0[a]	3.197	Only single configuration : $^1\chi_{3\to5}$	$^1B_1^-$
Ph-C=N→O	b)	3.382	b)	3.829	$0.9682\ (^1\chi_{4\to6})-0.2501\ (^1\chi_{5\to7})$	$^1B_1^-$
	5.976[c]	5.930[c]	5.259 5.410[c] 5.551	5.347	$0.2501\ (^1\chi_{4\to6})+0.9682\ (^1\chi_{5\to7})$	$^1B_1^+$

a) Estimated value from the recorded curve.
b) $^1B_1^-$ band will be hidden below the strong $^1A_1$ band appearing at 3.974 eV., 4.066 eV., 4.157 eV. (maximum), and 4.226 eV. in *n*-heptane solution.
c) See footnote 30 in the text.

that the characteristic strong π-π* band of VII can be assigned to a $^1A_1$ band superposed on a weak $^1B_1$ band, although the calculated energy levels do not perfectly agree with the observed levels because of various approximations and assumptions made in carrying out the calculations. From the standpoint of what has been mentioned above, it should be emphasized that the change in the electronic state in becoming the *N*-oxide compound is very large. It can be stated that the excited wave function of the strong π-π* band ($^1A_1$) consists mainly of the $^1\chi_{5\to6}$ configuration. The comparison between the ψ_5 and ψ_6 MO's of the VII compound shown in Table II suggests that the charge transfer from the oxygen atom to the conjugated system can be expected when the π-π* transition from ψ_5 to ψ_6 takes place; this finding is similar to that of heterocyclic *N*-oxides.[15,32] The observed blue shift phenomenon of the π-π* band always caused by the solvent effect on nitrone compounds[1] may be considered to be due to the decrease in the π-electron density at the oxygen atom of the N→O bond in the excited state, because the hydrogen bonding power at the excited state may decrease in this case.

The Molecular Diagrams of V, VI and VII.—Figures 8a, b, c, show the molecular diagrams calculated on the basis of the results described in the "Theoretical" section. A comparison of the molecular diagram in Fig. 8c with those of heterocyclic *N*-oxide compounds[15] is of much interest from the following standpoints:

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[32] T. Kubota and M. Yamakawa, ibid., 35, 555 (1962).

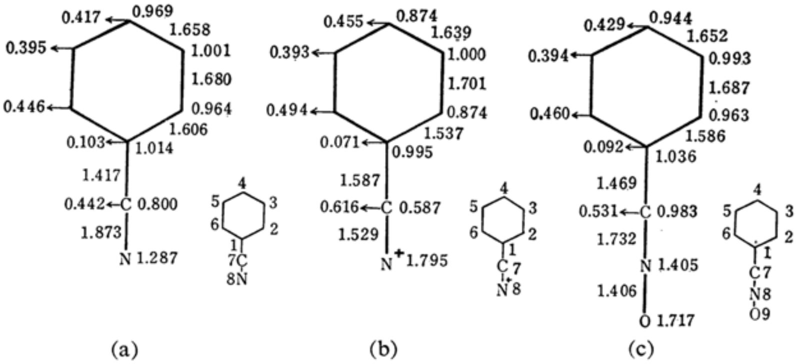

Fig. 8. The molecular diagrams of the compounds shown in Fig. 7.

(i) The double bond character of the N→O bond is decreased;

(ii) The net-charge at the carbon atom 7, which is adjacent to the N→O bond, becomes positive, and

(iii) The electron migration to a benzene ring from the N→O group is comparatively small.

The investigation of the infrared spectra of many nitrones published recently by Shindo[33] shows that the N→O stretching frequency of VII, which was assigned to the very strong band appearing at 1171 cm^{-1}, exists at a longer wavelength than the frequency (1265 cm^{-1}) of pyridine *N*-oxide.[15] This fact is believed to be in agreement with the conclusion obtained from the molecular diagram. The application of Fukui's frontier orbital method,[34] giving a good predictition for the reactivities of heterocyclic *N*-oxides,[15] to the prediction of the reactivities of nitrones is also of interest.

As may easily be understood from the MO's in Table II, the frontier electron density at C_7 (except for the nitrogen and oxygen atoms) is largest in both frontier orbitals, ϕ_5 and ϕ_6. This fact suggests that the carbon atom, C_7, is very active in both electrophilic and nucleophilic reactions, and that this position may be easily attacked by reagents. In the course of our experiments, as has been stated in the "Experimental" section, we have also established that VII, etc., (i. e., nitrones) are relatively unstable in an acidic medium and show behavior indicating that the carbon atom, C_7, is the reaction center. Thus the spectrum of VII changes into that of benzaldehyde in an acidic aqueous medium and into a composite spectrum of compounds considered to be HCl-addition substances to the C=N bond in the molecule in mixed solvents consisting of absolute alcohol and absolute hydrogen chloride. In the later case, the altered spectra are analogous to those of simple benzene derivatives. These facts support our theoretical predictions.

Summary

The ultraviolet absorption spectra of benzylidene methyl amine, its proton-addition compound and benzylidene methyl amine *N*-oxide have been examined under various conditions. SMO calculations on those compounds have been carried out, and various physicochemical properties have been discussed.

On the basis of these calculations, the spectra of the above compounds have reasonably been assigned by using the spectroscopic exchange integrals $\beta_s(^1A_1)$ and $\beta_s(^1B_1)$, which were evaluated from the spectra and the MO, including C. I., of styrene.

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[33] H. Shindo and B. Umezawa, *Chem. Pharm. Bull.*, **10**, 492 (1962).

[34] K. Fukui, T. Yonezawa and H. Shingu, *J. Chem. Phys.*, **20**, 722 (1952); K. Fukui, T. Yonezawa, C. Nagata and H. Shingu, ibid., **22**, 1433 (1954).