BULLETIN OF THE CHEMICAL SOCIETY OF JAPAN, VOL. 45, 742—749(1972)

Electronic Spectra and Structures of Organic π-Systems. VI. Electronic States of Diazomethane, Ketene, Diazocyclopentadiene and Benzenediazonium Ion[1]

Zen-ichi YOSHIDA and Tsunetoshi KOBAYASHI*
Department of Synthetic Chemistry, Faculty of Engineering, Kyoto University, Yoshida, Kyoto

(Received February 8, 1971)

The electronic states of diazomethane, ketene, diazocyclopentadiene and benzenediazonium ion were studied by the semi-empirical ASMO LCAO SCF CI method. Both π- and $\bar{\pi}$-systems were taken into consideration. Two types of approximations, Mulliken's formula and a new semitheoretical formula, were used in the evaluation of the core resonance integrals. The latter gives satisfactory results though it contains no arbitrary adjustable parameters. The longest wavelength singlet-singlet transition of diazomethane, ketene or diazocyclopentadiene is $^1\pi^* - {^1\bar{\pi}}$, and that of benzenediazonium ion $^1\pi^* - {^1\pi}$.

Cumulated systems such as diazomethane, ketene, diazocyclopentadiene and benzenediazonium ion are interesting from both physicochemical and organochemical view points. Orville-Thomas and Jones[2] treated diazomethane and ketene by the Hückel method. Hoffmann[3] treated diazomethane by his extended Hückel method. Evleth and Cox[4] treated benzenediazonium ion by the Hückel method and the free electron theory. Sukigara and Kikuchi[5] treated benzenediazonium ion by Pariser-Parr's ASMO LCAO CI method. Dixon and Kirby[6] treated ketene by the open shell SCFMO method. However, so far we have not come across the Pariser-Parr-Pople type SCFMO treatments of diazocyclopentadiene and benzenediazonium ion.

We wish to report on the study on the electronic states of diazomethane, ketene, diazocyclopentadiene, and benzenediazonium ion by the semiempirical ASMO LCAO SCF CI method. The $\bar{\pi}$-systems (inplane π-systems) of these compounds are explicitly taken into consideration. In the evaluation of the core resonance integrals two types of approximations, Mulliken's formula and a new semi-theoretical formula containing no arbitrary adjusting parameters,[7] are used.

Method of Calculation

The self-consistent field molecular orbital theory[8] has been used to calculate the π-electronic charge distributions and the spectra of diazomethane, ketene, diazocyclopentadiene and benzenediazonium ion. Both

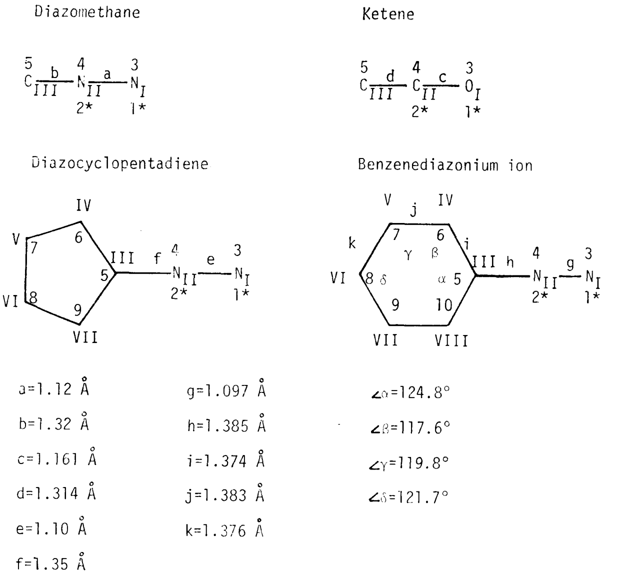


Fig. 1. Assumed structures and numberings of atoms (in Roman numerals) and numberings of atomic orbitals (in Arabic numerals) of diazomethane, ketene, diazocyclopentadiene and benzenediazonium ion. ('*' denotes an inplane $2p_{\bar{\pi}}$-atomic orbital.)

---

[1] Partly presented at the 20th Annual Meeting of the Chemical Society of Japan, Tokyo, March, 1967 and at the Symposium on Molecular Structure, Sapporo, October, 1967.

* Present Address: The Institute for Solid State Physics, The University of Tokyo, Roppongi, Minato-ku, Tokyo.

[2] W. J. Orville-Thomas and W. J. Jones, *Zeit. Elektrochem.*, **64**, 714 (1960).

[3] R. Hoffmann, *Tetrahedron*, **22**, 539 (1966).

[4] E. M. Evleth and R. J. Cox, *J. Phys. Chem.*, **71**, 4082 (1967).

[5] M. Sukigara and S. Kikuchi, This Bulletin, **40**, 461 (1967).

[6] R. N. Dixon and G. H. Kirby, *Trans. Faraday Soc.*, **62**, 1406 (1966).

[7] Z. Yoshida and T. Kobayashi, *J. Chem. Phys.*, **54**, 4538 (1971).

[8] C. C. J. Roothaan, *Rev. Mod. Phys.*, **23**, 69 (1951).

the π- and the $\bar{\pi}$-systems are considered explicitly.

The molecular structural data of diazomethane and ketene obtained by Cox, Thomas, and Sheridan[9,10] on the basis of the microwave spectral study were used. The molecular structure of benzenediazonium ion is assumed as that in benzenediazonium chloride determined by X-ray crystal analysis.[11] The molecular dimension of diazocyclopentadiene is assumed to be as shown in Fig. 1 using the structural data of benzenediazonium chloride and diazomethane. The five-membered ring of diazocyclopentadiene is assumed to be a regular pentagon. The carbon-carbon bond lengths of diazocyclopentadiene are assumed to be 1.40 Å.

The numberings of the atomic orbitals (in Arabic numerals) and the atoms (in Roman numerals) in the molecules are also given in Fig. 1.

The molecular orbitals (MO's), ϕ_i's, are taken as linear combinations of $2p_\pi$- and $2p_{\bar{\pi}}$-atomic orbitals (AO's), χ_r's.

$$\phi_i = \sum_r C_{ir}\chi_r \tag{1}$$

The total Hamiltonian, H, is given by

$$H = \sum_\mu H_\mu^{\text{core}} + \sum_{\mu<\nu}\frac{e^2}{r_{\mu\nu}} \tag{2}$$

$$H_\mu^{\text{core}} = -\frac{1}{2}\Delta(\mu) - \sum_{\text{A}}\frac{e^2Z_{\text{A}}}{r_{\mu\text{A}}} \tag{3}$$

where the Greek subscripts denote electrons, and Z_{A} the core charge of atom A left by removal of π-(and $\bar{\pi}$-) electrons.

For the closed-shell molecular species, the Roothaan SCF equation[8] is written as follows.

$$\sum_r C_{ir}(F_{rs}-S_{rs}\varepsilon) = 0 \quad (s = 1, 2, \cdots) \tag{4}$$

where

$$F_{rs} = H_{rs} + \sum_{t,u}P_{tu}\left[\langle rs\,|\,tu\rangle - \frac{1}{2}\langle rt\,|\,su\rangle\right]$$

$$S_{rs} = \int\chi_r\chi_s\mathrm{d}\tau$$

$$H_{rs} = \int\chi_r(\mu)H_\mu^{\text{core}}\chi_s(\mu)\mathrm{d}\tau_\mu$$

$$\langle rs\,|\,tu\rangle = \int\chi_r(\mu)\chi_s(\mu)\frac{e^2}{r_{\mu\nu}}\chi_t(\nu)\chi_u(\nu)\mathrm{d}\tau_\mu\mathrm{d}\tau_\nu$$

$$P_{tu} = 2\sum_i^{\text{occ}}C_{it}C_{iu}$$

For the sake of simplicity we used the Goeppert-Mayer and Sklar potential[12] and the so-called zero-differential overlap approximation.[13] We neglected non-neighbour core resonance integrals and penetration integrals of neutral atoms but not one-centre exchange integrals.

One-centre Coulomb repulsion integrals, $\langle rr|rr\rangle$'s, are evaluated using appropriate electron-transfer reactions as proposed by Pariser.[14]

$$\langle rr\,|\,rr\rangle = I_r - A_r$$

where I_r and A_r denote the valence state ionization potential and the valence state electron affinity of the atomic orbital r, respectively. All the necessary values of I_r's and A_r's are taken from Hinze and Jaffé's tables.[15]

One-centre Coulomb repulsion integrals of the type $\langle rr|\bar{r}\bar{r}\rangle$'s are evaluated according to the formula

$$\langle rr\,|\,\bar{r}\bar{r}\rangle = \langle rr\,|\,rr\rangle - 6F_2^{\text{pp}}$$

where $\bar{r}$ and r are the $2p_\pi$-atomic orbitals of the same atom and orthogonal to each other. F_2^{pp} is the Slater-Condon parameter and the values of F_2^{pp}'s are taken from Pilcher and Skinner's table.[16]

One-centre exchange integrals are also evaluated using the Slater-Condon parameters as follows.

$$\langle r\bar{r}\,|\,r\bar{r}\rangle = 3F_2^{\text{pp}}$$

Two-centre Coulomb repulsion integrals $\langle tt|uu\rangle$'s and $\langle tt|\bar{u}\bar{u}\rangle$'s are evaluated using the parabolic formula when the distance R is shorter than 4 Å.

$$\langle tt\,|\,uu\rangle = \frac{\langle tt\,|\,tt\rangle + \langle uu\,|\,uu\rangle}{2} + aR + bR^2$$

$$\langle tt\,|\,\bar{u}\bar{u}\rangle = \frac{\langle tt\,|\,\bar{t}\bar{t}\rangle + \langle uu\,|\,\bar{u}\bar{u}\rangle}{2} + a'R + b'R^2$$

where the coefficients a, b, a', and b', are evaluated using the $\langle tt|uu\rangle$ values or the $\langle tt|\bar{u}\bar{u}\rangle$ values calculated at distances R=4 Å and 5 Å by the point charge approximation. When R is greater than 4 Å, $\langle tt|uu\rangle$'s and $\langle tt|\bar{u}\bar{u}\rangle$'s are evaluated by the point charge approximation.

The overlap integrals, S_{rs}'s, are evaluated according to Mulliken and coworkers' table.[17]

The H_{rr} term in Eq. (4) is given by

$$\begin{aligned}H_{rr} &= \int\chi_r(\mu)\left(-\frac{1}{2}\Delta(\mu) - \frac{e^2Z_{\text{A}}}{r_{\mu\text{A}}}\right)\chi_r(\mu)\mathrm{d}\tau_\mu \\ &\quad - \sum_{\text{B}\neq\text{A}}\chi_r(\mu)\frac{e^2Z_{\text{B}}}{r_{\mu\text{B}}}\chi_r(\mu)\mathrm{d}\tau_\mu \\ &= \alpha_r + \sum_{\text{B}\neq\text{A}}\langle\text{B}\,|\,rr\rangle\end{aligned}$$

where

$$\alpha_r = \int\chi_r(\mu)\left(-\frac{1}{2}\Delta(\mu) - \frac{e^2Z_{\text{A}}}{r_{\mu\text{A}}}\right)\chi_r(\mu)\mathrm{d}\tau_\mu$$

$$\langle\text{B}\,|\,rr\rangle = -\int\chi_r(\mu)\frac{e^2Z_{\text{B}}}{r_{\mu\text{B}}}\chi_r(\mu)\mathrm{d}\tau_\mu$$

The core attraction integrals of the $\langle\text{B}|rr\rangle$ type are given as follows.

$$\langle\text{B}\,|\,rr\rangle_{\text{B=I}} = -\frac{Z_{\text{I}}}{2}\{\langle 11\,|\,rr\rangle + \langle 33\,|\,rr\rangle\}$$

$$\langle\text{B}\,|\,rr\rangle_{\text{B=II}} = -\frac{Z_{\text{II}}}{2}\{\langle 22\,|\,rr\rangle + \langle 44\,|\,rr\rangle\}$$

$$\langle\text{B}\,|\,rr\rangle_{\text{B}\neq\text{I,II}} = -\langle rr\,|\,2P_{\pi_{\text{B}}}, 2P_{\pi_{\text{B}}}\rangle$$

---

[9] A. P. Cox, L. F. Thomas, and J. Sheridan, *Nature*, **181**, 1000 (1958).

[10] A. P. Cox, L. F. Thomas, and J. Sheridan, *Spectrochim. Acta*, **15**, 542 (1959).

[11] Chr. Römming, *Acta Chem. Scand.*, **17**, 1444 (1963).

[12] M. Goeppert-Mayer and A. L. Sklar, *J. Chem. Phys.*, **6**, 645 (1963).

[13] R. Pariser and R. G. Parr, *ibid.*, **21**, 466, 767 (1953).

[14] R. Pariser, *ibid.*, **21**, 568 (1953).

[15] J. Hinze and H. H. Jaffé, *J. Amer. Chem. Soc.*, **84**, 540 (1962); J. Hinze and H. H. Jaffé, *J. Phys. Chem.*, **67**, 1501 (1963).

[16] G. Pilcher and H. A. Skinner, *J. Inorg. Nucl. Chem.*, **1962**, 952.

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

TABLE 1. ATOMIC PARAMETERS

	$C_{trtrtr\pi}$	$C_{didi\pi\pi}$	$C^+{}_{didi\pi}$	$N_{didi\pi^2\pi}$	$N^+{}_{didi\pi\pi}$	$N_{di^2di\pi\pi}$	$O_{di^2di\pi^2\pi}$
ζ[a]	1.625	1.625	1.8	1.95	2.125	1.95	2.275
W'(eV)[b]	−11.16	−11.19	−23.86	−14.11	−28.70	−14.18	−17.91
α(eV)[c]	−11.16	−20.922	−23.86	−34.181	−43.266	−24.766	−43.418
$<rr\|rr>$(eV)	11.13	11.09	14.03	11.97	16.64	12.52	15.20
$<rr\|\bar{r}\bar{r}>$(eV)	10.044	10.004	12.747	10.423	14.981	10.973	13.243
$<r\bar{r}\|r\bar{r}>$(eV)	0.543	0.543	0.642	0.774	0.830	0.774	0.978
Z[d]	1.0	2.0	2.0	3.0	3.0	2.0	3.0
Z'[e]	4.0	4.0	4.0	5.0	5.0	5.0	6.0
n_{2s}[e]	1.0	1.0	1.0	1.0	1.0	2.0	2.0
n_{2p_σ}[e]	1.0	1.0	1.0	1.0	1.0	1.0	1.0
N[f]	1.0	1.0	1.0	1.0	1.0	1.0	1.0
$\bar{N}$[f]	1.0	1.0	0.0	2.0	1.0	1.0	2.0

a) Slater's orbital exponent.
b) See formulas (5), (6), and (7) in the text.
c) See formula (5) in the text.
d) See formula (3) in the text.
e) See formula (9) in the text.
f) See formulas (5) and (7) in the text.

α_r's are approximated as follows.

$$\alpha_{r_A}(r=1\sim4) = W'_{r_A} - (N_A-1)\langle rr|rr\rangle - (\bar{N}_A)\left\{\langle rr|\bar{r}\bar{r}\rangle - \frac{1}{2}\langle r\bar{r}|r\bar{r}\rangle\right\} \tag{5}$$

$$\alpha_r(r=5\sim10) = -\ 11.16\,\text{eV}$$

where N_A and $\bar{N}_A$ in Eq. (5) are the numbers of electrons in the $2p_\pi$-atomic orbitals r and $\bar{r}$ of the atom A, respectively. Here the atomic orbital $\bar{r}$ is orthogonal to the atomic orbital r. $-W'_{t_A}$ is approximately equal to the first or second valence state ionization potential of the atomic orbital r. The values of α_r, W_r', N, $\bar{N}$, $<rr|rr>$, $<rr|\bar{r}\bar{r}>$ and $<r\bar{r}|r\bar{r}>$ are given in Table 1.

Two methods of approximations were employed in the evaluation of core resonance integrals, β_{tu}'s.

a) Mulliken's formula

$$\beta_{tu} = \frac{0.86767}{2} S_{tu}(W_t' + W_u') \tag{6}$$

The coefficient 0.86767 was evaluated using the empirical β_{CC}-value of benzene. This might be referred to as Eβ-approximation.

b) Theoretical formula

$$\beta_{t_Au_B} = \frac{S_{tu}}{2}\{W'_{t_A} + W'_{u_B} - \langle u|U_A|u\rangle - \langle t|U_B|t\rangle - \langle tt|uu\rangle(N_A+N_B-2) - \langle uu|\bar{t}\bar{t}\rangle(\bar{N}_A+\bar{N}_B)\} - \frac{1}{2}\{\langle t|T|u\rangle + \langle u|T|t\rangle\} \tag{7}$$

This might be referred to as Tβ-approximation. Formula (7) is derived as follows. We can easily obtain the following formula for the β_{tu} in the $\pi+\bar{\pi}$-systems as in the VI/2 method,[7] if the electron density change is taken into consideration.

$$\beta_{t_Au_B} = \frac{S_{tu}}{2}\{W'_{t_A} + W'_{u_B} - \langle u|U_A|u\rangle - \langle t|U_B|t\rangle - \langle tt|uu\rangle(P_{tt}+P_{uu}-2) - \langle uu|\bar{t}\bar{t}\rangle(P_{\bar{t}\bar{t}}+P_{\bar{u}\bar{u}})\} - \frac{1}{2}\{\langle t|T|u\rangle + \langle u|T|t\rangle\} \tag{8}$$

where W'_{t_A} is the orbital energy of the atomic orbital t_A and depends on the electron density of the atom in the molecule.

$$\langle u_B|U_A|u_B\rangle \fallingdotseq -\langle u_B|e^2Z_A'/r|u_B\rangle + n_{2s_A}\langle 2s_A2s_A|u_Bu_B\rangle + n_{2p_{\sigma_A}}\langle 2p_{\sigma_A}2p_{\sigma_A}|u_Bu_B\rangle \tag{9}$$

$\langle u|e^2Z'_A/r|u\rangle$, $\langle 2s_A2s_A|u_Bu_B\rangle$, $\langle 2p_{\sigma A}2p_{\sigma A}|u_Bu_B\rangle$ and $\langle t|T|u\rangle$ are evaluated theoretically using the Slater atomic orbitals according to Roothaan.[18] Z_A' is the core-charge left by removal of electrons of principal quantum number 2 of the atom A. n_{2s_A} and $n_{2\sigma p_A}$ are the numbers of electrons in the atomic orbitals $2s_A$ and $2p\sigma_A$, respectively. If we put $P_{tt}=N_A$, $P_{uu}=N_B$, $P_{\bar{t}\bar{t}}=\bar{N}_A$ and $P_{\bar{u}\bar{u}}=\bar{N}_B$ in (8) we get (7).

For the sake of simplicity we used the fixed β_{tu}-values evaluated by (7) at certain limiting cases, where $P_{tt}=N_A$, $P_{uu}=N_B$, $P_{\bar{t}\bar{t}}=\bar{N}_A$ and $P_{\bar{u}\bar{u}}=\bar{N}_B$.

Two kinds of approximations were used in the evaluation of the atomic parameters of atom II: a) atom II is regarded as neutral (abbreviated as N-approximation) and b) atom II is regarded as positive (abbreviated as P-approximation). Thus all together four possible sets of approximations, NEβ, NTβ, PEβ, and PTβ, are used for each molecule.

The atomic parameters necessary in the calculation are given in Table 1.

The β_{tu}-values calculated by formulas (6) and (7) are given in Table 2.

The starting set of coefficients of MO's is obtained by the Hückel method. The eigenvalues and the eigenvectors are made self-consistent, and the electronic transition energies are then calculated by the configuration interaction (CI) method, all the singly excited configurations being taken into account.

The calculation has been carried out on a HITAC 5020 computer at the computation centre, the University of Tokyo, and on a FACOM 230-60 computer at the computation centre of Kyoto University.

---

18) C. C. J. Roothaan, *ibid.*, **19**, 1445 (1951).

TABLE 2. CORE-RESONANCE INTEGRAL, β_{ij}, IN eV

Bond	NEβ	NTβ	PEβ	PTβ
Diazomethane				
1—2	−3.292	−3.404	−4.512	−4.128
4—5	−2.437	−2.225	−3.384	−2.811
Ketene				
1—2	−3.043	−3.309	−3.988	−3.559
4—5	−2.731	−2.863	−3.797	−3.270
Diazocyclopentadiene				
1—2	−3.424	−3.588	−4.706	−4.361
4—5	−2.304	−2.059	−3.189	−2.602
5—6	−2.364	−2.359	−2.364	−2.359
6—7	−2.367	−2.363	−2.367	−2.363
7—8	−2.366	−2.361	−2.366	−2.361
Benzenediazonium ion				
1—2	−3.444	−3.616	−4.736	−4.397
4—5	−2.156	−1.877	−2.973	−2.373
5—6	−2.471	−2.506	−2.471	−2.506
6—7	−2.434	−2.455	−2.434	−2.455
7—8	−2.463	−2.495	−2.463	−2.495

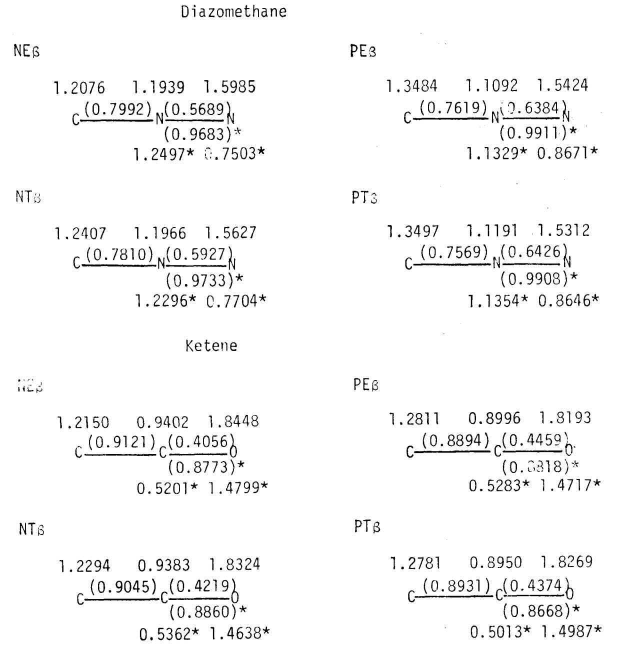
Results

The molecular diagrams of these compounds are given in Fig. 2.

The calculated and the observed transition energies are summarized in Table 3. CI coefficients are also given.

Discussion

As is shown in Table 2, with diazomethane β_{12}- and β_{45}-values calculated by formula (6) are slightly larger than those given by formula (7) in P-approximation. The same tendency is also observed with ketene, diazocyclopentadiene and benzenediazonium ion. In the cases of diazocyclopentadiene and benzenediazonium



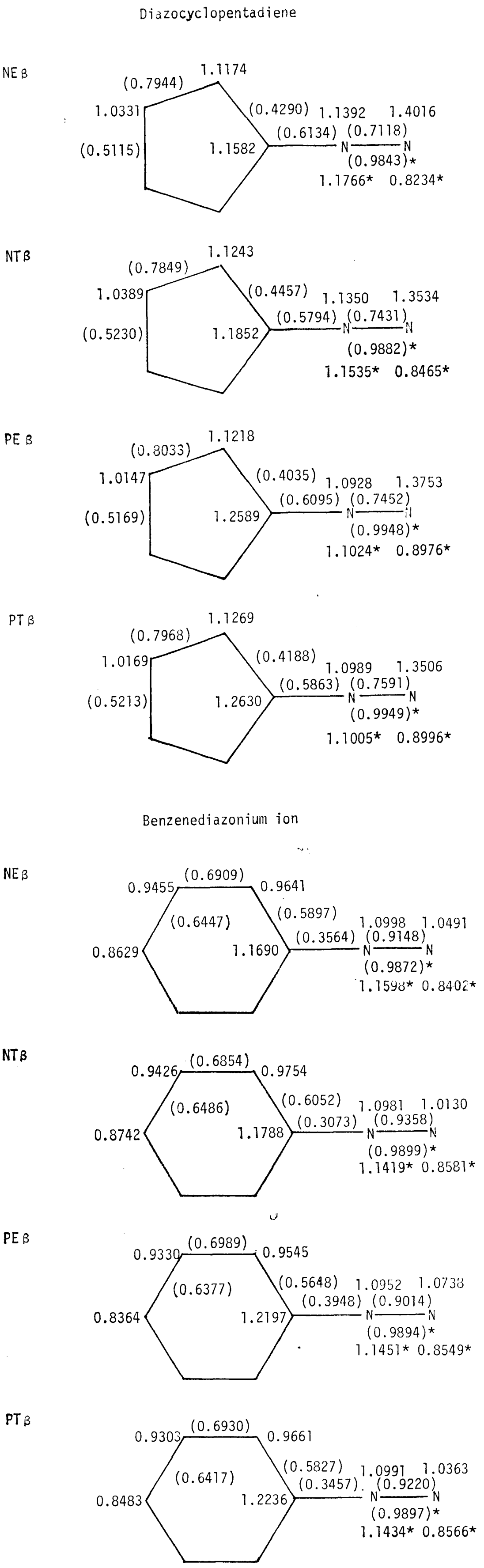


Fig. 2. Electron densities and bond orders (in parentheses).
('*' denotes a P_{ij} of an in-plane $\bar{\pi}$-system.)

TABLE 3. CALCULATED TRANSITION ENERGIES IN eV

Sym.	E	f	CI Composition[a]		Sym.	E	f	CI Composition[a]		Obsd	
										E	log ε
Diazomethane											
	NEβ approximation					NTβ approximation					
$^1A_2$	1.642	0.0	3—4	0.993	$^1A_2$	1.621	0.0	3—4	0.994	3.14[21]	
$^1A_1$	4.666	0.379	3—5	0.936	$^1A_1$	4.512	0.407	3—5	0.949	5.77[22]	
			2—4	−0.342							
$^1A_2$	7.567	0.0	1—4	0.973	$^1A_2$	7.593	0.0	1—4	0.973		
$^3A_2$	1.097		3—4	0.986	$^3A_2$	1.125		3—4	0.987		
$^3A_1$	1.550		3—5	0.998	$^3A_1$	1.295		3—5	0.999		
$^3A_1$	5.197		2—4	0.994	$^3A_1$	5.373		2—4	0.992		
	PEβ approximation					PTβ approximation					
$^1A_2$	2.849	0.0	3—4	0.998	$^1A_2$	2.417	0.0	3—4	0.998	3.14[21]	
$^1A_1$	6.335	0.619	3—5	0.967	$^1A_1$	5.635	0.566	3—5	0.969	5.77[22]	
$^1A_2$	9.675	0.0	1—4	0.978	$^1A_2$	8.641	0.0	1—4	0.977		
$^3A_2$	2.424		3—4	0.995	$^3A_2$	2.009		3—4	0.995		
$^3A_1$	3.099		3—5	0.998	$^3A_1$	2.321		3—5	0.998		
$^3A_1$	6.924		2—4	0.995	$^3A_1$	6.146		2—4	0.993		
Ketene											
	NEβ approximation					NTβ approximation					
$^1A_2$	2.668	0.0	3—4	0.994	$^1A_2$	2.834	0.0	3—4	0.995	3.87	1.1[6,19]
$^1A_1$	6.133	0.302	3—5	0.923	$^1A_1$	6.378	0.352	3—5	0.937	6.36∼	
			2—4	0.372				2—4	0.338	7.29[23]	
$^1A_2$	7.345	0.0	1—4	0.992	$^1A_2$	7.893	0.0	1—4	0.993		
$^3A_2$	2.373		3—4	0.993	$^3A_2$	2.541		3—4	0.994	2.61∼	
$^3A_1$	3.285		3—5	0.998	$^3A_1$	3.500		3—5	0.998	3.22[6]	
$^3A_1$	5.439		2—4	0.999	$^3A_1$	5.943		2—4	0.999		
	PEβ approximation					PTβ approximation					
$^1A_2$	3.949	0.0	3—4	0.999	$^1A_2$	3.454	0.0	3—4	0.999	3.87	1.1[6,19]
$^1A_1$	8.178	0.512	3—5	0.951	$^1A_1$	7.382	0.481	3—5	0.956	6.36∼	
$^1A_2$	9.549	0.0	1—4	0.996	$^1A_2$	8.569	0.0	1—4	0.996	7.29[23]	
$^3A_2$	3.655		3—4	0.998	$^3A_2$	3.165		3—4	0.999	2.61∼	
										3.22[6]	
$^3A_1$	5.020		3—5	0.996	$^3A_1$	4.149		3—5	0.995		
$^3A_1$	7.271		2—4	0.999	$^3A_1$	6.497		2—4	0.998		
Diazocyclopentadiene											
	NEβ approximation					NTβ approximation					
$^1A_2$	1.857	0.0	4—7	0.950	$^1A_2$	1.828	0.0	4—7	0.954	2.70^{sh}[24]	
$^1B_2$	2.483	0.024	5—6	0.999	$^1B_2$	2.376	0.019	5—6	0.999	3.35^{sh}	∼2.7
$^1B_1$	3.533	0.0	5—7	1.0	$^1B_1$	3.315	0.0	5—7	1.0		
$^1A_1$	3.737	0.746	4—6	0.951	$^1A_1$	3.576	0.709	4—6	0.957	4.13	4.1
$^1A_1$	6.008	0.0	3—6	0.708	$^1A_1$	6.011	0.003	3—6	0.685		
			5—9	0.471				5—9	0.500		
			4—8	−0.373				4—8	−0.440		
			2—7	−0.317							
$^1B_2$	6.365	0.095	5—8	0.874	$^1B_2$	6.246	0.100	5—8	0.878	6.05	3.5
			4—9	0.472				4—9	0.467		
$^1A_1$	6.595	0.124	4—8	−0.667	$^1A_1$	6.459	0.049	4—8	0.661		
			3—6	−0.556				3—6	0.614		
			5—9	0.434				5—9	−0.360		
$^1A_2$	6.709	0.0	3—7	0.782	$^1A_2$	6.727	0.0	3—7	0.839		
			1—7	−0.530				1—7	−0.446		
$^1A_1$	7.392	1.107	5—9	0.661	$^1A_1$	7.413	1.113	5—9	0.739		
			4—8	0.478				4—8	0.535		
			2—7	0.448				2—7	0.330		
$^3A_1$	0.995		4—6	0.968	$^3A_1$	0.914		4—6	0.967		

Table 3. Calculated transition energies in eV (continued)

Sym.	E	f	CI Composition[a)]		Sym.	E	f	CI Composition[a)]		Obsd	
										E	log ε
Diazocyclopentadiene											
PEβ approximation					PTβ approximation						
${}^1A_2$	2.991	0.0	4—7	0.933	${}^1A_2$	2.530	0.0	4—7	0.938	2.70^{sh} [24)]	
			3—7	0.357				3—7	0.344		
${}^1B_2$	3.413	0.066	5—6	0.997	${}^1B_2$	3.017	0.041	5—6	0.998	3.35^{sh}	~2.7
${}^1B_1$	4.402	0.0	5—7	1.0	${}^1B_1$	3.894	0.0	5—7	1.0		
${}^1A_1$	4.697	0.873	4—6	0.948	${}^1A_1$	4.346	0.875	4—6	0.956	4.13	4.1
${}^1A_1$	6.692	0.434	5—9	0.656	${}^1A_1$	6.388	0.135	4—8	0.607	6.05	3.5
			3—6	0.512				5—9	−0.568		
			4—8	−0.504				3—6	−0.521		
${}^1B_2$	6.702	0.069	5—8	0.872	${}^1B_2$	6.404	0.111	5—8	0.900		
			4—9	0.476				4—9	0.425		
${}^1A_1$	7.347	0.367	3—6	0.780	${}^1A_1$	7.035	0.102	3—6	0.791		
			5—9	−0.528				4—8	0.425		
${}^3B_2$	2.125		5—6	0.933	${}^3A_1$	1.675		4—6	0.956		
Benzenediazonium ion											
NEβ approximation					NTβ approximation						
${}^1A_2$	3.492	0.0	4—7	0.912	${}^1B_2$	3.582	0.035	5—6	0.979	4.13	3.25[25)]
			3—7	0.387							
${}^1B_2$	3.513	0.043	5—6	0.977	${}^1A_2$	3.639	0.0	3—7	0.373		
${}^1A_1$	3.869	0.398	4—6	0.919	${}^1A_1$	3.891	0.329	4—6	0.925	4.77	4.05
${}^1B_1$	4.179	0.0	5—7	1.0	${}^1B_1$	4.092	0.0	5—7	1.0		
${}^1B_2$	5.512	0.001	5—8	0.752	${}^1B_2$	5.446	0.004	5—8	0.764		
			4—9	−0.627				4—9	−0.616		
${}^1A_1$	5.615	0.066	5—9	0.662	${}^1A_1$	5.628	0.054	5—9	0.680		
			4—8	0.626				4—8	0.660		
${}^1A_1$	6.507	0.199	2—7	0.432	${}^1A_1$	6.678	0.114	1—6	−0.343		
			3—6	0.651				3—6	0.696		
			4—6	−0.367				4—6	−0.346		
			1—6	−0.328				2—7	0.439		
			5—9	−0.317							
${}^3A_1$	2.426		4—6	0.901	${}^3A_1$	2.695		4—6	0.894		
			3—6	0.348				3—6	0.343		
PEβ approximation					PTβ approximation						
${}^1B_2$	4.043	0.091	5—6	0.942	${}^1B_2$	3.927	0.068	5—6	0.958	4.13	3.25[25)]
${}^1A_1$	4.550	0.450	4—6	0.894	${}^1A_2$	4.245	0.0	4—7	0.901		
			5—8	0.343				3—7	−0.422		
${}^1A_2$	4.628	0.0	4—7	0.894	${}^1A_1$	4.395	0.441	4—6	0.906	4.77	4.05
			3—7	0.435							
${}^1B_1$	5.364	0.0	5—7	1.0	${}^1B_1$	4.764	0.0	5—7	1.0		
${}^1B_2$	6.150	0.040	4—8	0.675	${}^1B_2$	5.784	0.0	5—9	0.751		
			5—9	−0.663				4—8	0.603		
			5—6	0.321							
					${}^1A_1$	5.906	0.280	5—8	0.679		
								4—9	−0.605		
${}^3B_2$	3.007		5—6	0.933	${}^3A_1$	3.006		4—6	0.899		

a) The transition, indicated by *i—j*, refers to a one-electron excitation from orbital *i* to virtual orbital *j*. The second column gives the CI coefficient of the configuration *i—j*.

ion the β_{CC}-values calculated by formulas (6) and (7) are similar to each other.

In the case of diazomethane the four sets of approximations, NEβ, NTβ, PEβ, and PTβ, give similar eigenvector to one another. However, E_i-values obtained by P-approximation slightly differ from those given by N-approximation. Similar tendencies are also observed with ketene and diazocyclopentadiene. Estimated ionization potentials of diazomethane and ketene from SCF eigenvalues are 10.974—9.923 eV and 10.881—11.582 eV, respectively. The values are slightly larger than the observed ones, 8.99 eV (diazomethane[22)]) and 9.607 eV (ketene[22)]), respectively. Hoffmann[3)] treated

---

19) K. Knox, R. G. W. Norrish, and G. Porter, *J. Chem. Soc.*, **1952**, 1477.

20) Z. Yoshida and T. Kobayashi, *J. Chem. Phys.*, in press.

21) F.W. Kirkbride and R.G. W. Norrish, *J. Chem. Soc.*, **1933**, 119.

22) G. Herzberg, "Molecular Spectra and Molecular Structure III. Electronic Spectra and Electronic Structure of Polyatomic Molecules," D. van Nostrand Co., Toronto, Inc. (1967).

23) W. C. Price, J. P. Teegan, and A. D. Walsh, *J. Chem. Soc.*, **1951**, 920.

24) W. von E. Doering and C. H. De Puy, *J. Amer. Chem. Soc.*, **75**, 5955 (1953).

25) C. H. Harberts, P. M. Heertjes, L. J. N. van der Hulst, and H. I. Waterman, *Bull. Soc. Chim. Fr.*, **3**, 643 (1936).

diazomethane by his extended Hückel method. He obtained the value of -11.964 eV as the orbital energy of the highest occupied π-orbital. This is by about 1—2 eV smaller than ours. Dixon and Kirby[6)] treated ketene by the PPP method. They made the π- and the $\bar{\pi}$-systems self-consistent independently. The eigenvectors they obtained are qualitatively similar to ours, but their eigenvalues differ from ours. Their orbital energy might lead to a large value of the ionization potential.

In the case of benzenediazonium ion the E_i- and the C_{ij}-values calculated by N-approximation differ slightly from those calculated by P-approximation.

The molecular diagrams of these compounds are shown in Fig. 2. In the case of diazomethane all the four sets of parameters give similar molecular diagrams. Every set of parameters suggests that nitrogen atom II bears a large positive charge and that the terminal carbon atom III and nitrogen atom I bear negative charges. The π-bond order of the nitrogen-nitrogen bond is 1.5—1.6. The molecular diagrams suggest that the carbon-nitrogen bond has a large double bond character.

In the case of ketene all the four sets of parameters give similar molecular diagrams and suggest that the central carbon atom II bears a charge of about $+0.6$ and the terminal oxygen atom a charge of about -0.3. The bond order of the carbon-oxygen bond is about 1.3. The bond order of the carbon-carbon bond is 0.9, suggesting that this bond has a large double bond character. Orville-Thomas and Jones[2)] treated diazomethane and ketene by the simple Hückel method with and without π-hyperconjugation. The bond orders they obtained without hyperconjugation are similar to those shown in Fig. 2. The molecular diagram obtained from Dixon and Kirby's[6)] SCF eigenvectors shows that the terminal oxygen atom is slightly positive and that carbon atom II is slightly negative in the ground state.

In the case of diazocyclopentadiene also the four sets of parameters give similar molecular diagrams. Nitrogen atom II bears a charge of about $+0.7$—0.8. This is larger than that of diazomethane. The terminal nitrogen atom I bears a charge of about -0.20—-0.27. This is slightly smaller than that in diazomethane. The bond order of the nitrogen-nitrogen bond is about 1.7 and is larger than that in diazomethane. This suggests that the triple bond character of the nitrogen-nitrogen bond in diazocyclopentadiene is larger than that in diazomethane. The bond order of the carbon-nitrogen bond in diazocyclopentadiene is smaller than that of the corresponding bond in diazomethane. This suggests that the double bond character of the carbon-nitrogen bond in diazomethane is larger than that of the corresponding bond in diazocyclopentadiene. In the ground state a charge of about -0.5 is distributed over the five-membered ring. Thus it is anticipated that the contribution of the canonical formula R^{-}–N_2^{+} to the ground state is not small. From the bond orders it can be anticipated that in the ground state the five-membered ring is not a regular pentagon but a slightly bond alternated pentagon in which the carbon(IV)-carbon(V) and the carbon(VI)-carbon(VII) bonds are slightly shorter than the carbon(III)-carbon(IV), the carbon(V)-carbon(VI), and the carbon(III)-carbon(VII) bonds.

In the case of benzenediazonium ion nitrogen atom II and terminal nitrogen atom bear charges of about $+0.75$ and $+0.1$ respectively. The carbon-nitrogen bond order is about 0.3—0.4 and smaller than that of diazomethane and diazocyclopentadiene. Thus the double bond character of the carbon-nitrogen bond in benzenediazonium ion might be smaller than that of diazomethane or diazocyclopentadiene. The nitrogen-nitrogen bond order is about 1.9 and is greater than that of diazomethane or diazocyclopentadiene, suggesting that the nitrogen-nitrogen bond has a greater triple bond character than that of diazomethane or diazocyclopentadiene. The greater part of the $+1$ charge of the cation exists on nitrogen atom II in the case of benzenediazonium ion.

From the above discussions the extent of contribution of the canonical formula R^{-}–N_2^{+} or R–N_2^{+} to the ground state might be in the order: diazomethane $<$ diazocyclopentadiene $<$ benzenediazonium ion. The triple bond character of the nitrogen-nitrogen bond might be in the order: diazomethane $<$ diazocyclopentadiene $<$ benzenediazonium ion. The double bond character of the carbon-nitrogen bond might be in the order: benzenediazonium ion $<$ diazocyclopentadine $<$ diazomethane. This is consistent with the observed nitrogen-nitrogen bond lengths and carbon-nitrogen bond lengths of diazomethane and benzenediazonium ion.

Evleth and Cox[4)] treated benzenediazonium ion by the simple Hückel method. The π-electron densities ($P_{N_I}=0.706$, $P_{N_{II}}=1.340$) of nitrogen atoms I and II they gave differ from ours.

The calculated transition energies and the observed ones are summarized in Table 3. In the case of diazomethane, agreement between the calculated and the observed transition energies is best with PTβ-approximation. This is consistent with the molecular diagram. The observed 5.77 eV band can be assigned to $\pi-{}^1\pi^*$ transition. The observed 3.14 eV band is tentatively assigned to $\pi-{}^1\bar{\pi}^*$ transition. The calculated 2.417 eV $\pi-{}^1\bar{\pi}^*$ transition has the character of charge-transfer transition caused by electron migration from carbon III to the diazo-group. Hoffmann[3)] assigned the longest wavelength transition to $\pi-\bar{\pi}^*$ by his extended Hückel method. This is consistent with our result.

In the case of ketene the observed bands can be assigned as in Table 3. Also in this case the long wavelength weak bands are $\pi\text{-}{}^{1,3}\bar{\pi}^*$ transitions. From the MO coefficients it is anticipated that these two transitions have a large character of the intramolecular charge-transfer bands caused by the electron migration from carbon III to the CO-group. The strong band observed between 6.36—7.29 eV can be assigned to $\pi-{}^1\pi^*$. The transition energies calculated by Dixon and Kirby[6)] are similar to ours. Knox, Norrish, and Porter[19)] observed a weak band between 5.77—6.36 eV (max: 5.77 eV; log ε: 1.8). This band has been tentatively assigned to $\pi-{}^1\sigma^*$ by us[20)] using the

ASMO-LCAO-SCF-CI method for the valence electron systems.

In the case of diazocyclopentadiene PTβ-approximation gives the best result as anticipated from the molecular diagrams. PEβ-approximation also gives a result similar to that given by PTβ-approximation. The 2.530 eV, 3.017 eV, 3.894 eV, and 4.346 eV transitions calculated by PTβ-approximation have the character of intramolecular charge-transfer bands caused by electron transfer from the five-membered ring to the diazo-group. The longest wavelength weak shoulder observed at about 2.70 eV is $\pi-{}^1\bar{\pi}^*$ transition.

In the case of benzenediazonium ion PEβ-approximation gives the best result. PTβ-approximation also gives a result similar to that given by PEβ-approximation. NEβ- and NTβ-approximations give unsatisfactory results. This is also anticipated from the molecular diagrams in Fig. 2. The 3.927, 4.245, and 4.395 eV transitions by PTβ-approximation have the character of intramolecular charge-transfer bands caused by electron migration from the benzene-ring to the diazo-group. In the case of benzenediazonium ion the longest wavelength singlet-singlet transition is $\pi-\pi^*$. On the other hand, as we have seen, the longest wavelength singlet-singlet transition is $\pi-\bar{\pi}^*$ in the case of diazomethane, ketene, and diazocyclopentadiene within $\pi+\bar{\pi}$-approximation. Sukigara and Kikuchi[5] have treated benzenediazonium ion by the PP type ASMO LCAO CI method taking the π-system only into consideration. They adjusted two parameters β_{NN} and ω (ω is the $\bar{\pi}$-electron density on nitrogen atom II) so as to reproduce the observed transition energies. They obtained -3.10 eV as β_{NN} and 1.05 as ω. The ω-value is close to the $\bar{\pi}$-electron density we obtained. This β_{NN}-value is slightly smaller than ours. They used $\beta_{CN}=-2.42$ eV and $\beta_{CC}=-2.39$ eV, which are similar to our values. The transitions they calculated by adjusting parameters β_{NN} and ω are similar to our results.

Conclusion

The molecular diagrams suggest that the triple bond character of the nitrogen-nitrogen bonds of these compounds is in the order, diazomethane < diazocyclopentadiene < benzenediazonium ion; and the double bond character of the carbon-nitrogen bonds in the order, benzenediazonium ion < diazocyclopentadiene < diazomethane. This is consistent with the observed carbon-nitrogen and nitrogen-nitrogen bond lengths of diazomethane and benzenediazonium ion. The extent of the contribution of the canonical formula $R^{-}-N_2^{+}$ or $R-N_2^{+}$ to the ground state may be in the order, diazomethane<diazocyclopentadiene<benzenediazonium ion.

The longest wavelength singlet-singlet transition is $\pi-\bar{\pi}^*$ in diazomethane, ketene, and diazocyclopentadiene and $\pi-\pi^*$ in benzenediazonium ion.

The semitheoretical formula (7) for the core resonance integral proposed in this paper gives satisfactory results though it contains no arbitrary adjustable parameters.