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Electronic Structure of Porphyrins. I. SCF-MO-CI Calculation Based on π-Electron Approximation

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The electronic structure and electronic spectra of metal free and metal porphyrins have been investigated by the MO method. In order to elucidate the effect of electron correlation on the electronic transitions, a new approximation for electron repulsion integral has been examined. For metal free porphyrin, the effect of hydrogen bondings on the electronic transitions has also been investigated. In metal porphyrin, the present calculation showed that almost two units of charges are transferred from the ligand porphyrin to the central metal ion through σ-type co-ordination bond. A satisfactory agreement between the calculated results and the experimental data was obtained when a new expression for electron repulsion integral, in which the effect of electron correlation is considered, was used. It was found that the Soret band of metal free porphyrin consists of almost degenerated B_x and B_y species.

Metal porphyrins are very important molecules in the field of biochemistry and biology. From this reason, a number of studies of the physico-chemical properties of these molecules have been carried out.[1] It is well known that hemoglobin, myoglobin, and cytochrome contain iron porphyrins. Vitamin B_{12} and chlorophyll also contain porphyrins. The porphyrin parts play most important roles in the chemical behavior of these molecules. Howver, their electronic spectra have not been clarified. Kobayashi,[2] Weiss *et al.*[3] and others[4—6] have calculated two strong allowed transitions for metal free porphyrin in the region of 400 nm. However, the observed spectra show only one strong absorption band in this region, so-called the Soret band. The excited energy levels of the molecule should be important, for understanding its photo-chemical behavior. One of the main purposes of this paper is to elucidate the nature of the Soret band, so that we have carried out SCF-MO-CI calculations. The effect of electron correlation on the electronic transitions is an interesting theoretical subject. So that, we used two kinds of approximations for electron repulsion integrals, one of them is older one[7] and another[8] is newly derived from a quantum field theory.

Calculation

SCF-MO-CI calculation based on π-electron approximation was carried out. Parameters were evaluated as following manner.

(*A*) *The Framework and Core Charges.* Webb and Fleischer[9] studied the crystal structure of metal free porphyrin by X-ray analysis. They treated the two hydrogen atoms attached to the nitrogens as four half-atoms. The two hydrogen can be considered to be statistically disordered or involved in the rapid interconversion of N–H tautomers. From the infrared spectroscopy,[10] it has been confirmed that inner hydrogens form hydrogen bonds with neighboring non-bonded nitrogens (Fig. 1). In order to elucidate the effect of hydrogen bond on the electronic structure of the porphyrin, we carried out MO calculations in which the core charges of nitrogens are assumed to change with the hydrogen bond formation. For the sake of simplicity, we assumed the D_{4h} symmetry for the porphyrin molecular frame-work. The bond distances and the bond angles were taken to be the same as those for the metal porphyrins. However, this causes no serious effect on the calculated results of electronic structure, since we used the variable β approximation.[11] Fleischer,[12] and Fleischer *et al.*[13] measured molecular dimensions of various metal porphyrins by X-ray analysis. The average interatomic distances associated with C–N, β–β, α–β, α–meso, and metal–N bonds are 1.38 Å, 1.35 Å, 1.44 Å, 1.40 Å, and 2.00 Å, respectively. In this paper we assumed the following interatomic distances: C–C 1.40 Å, C–N 1.38 Å, N:N (opposite to each other) 4.00 Å. When the value of CNC angle is assumed to be 108°, the other bond angles can be evaluated as shown in Fig. 2, because of the D_{4h} symmetry.

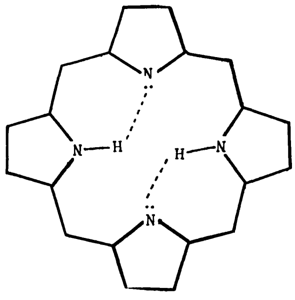

Fig. 1. Hydrogen bonds in metal free porphin.

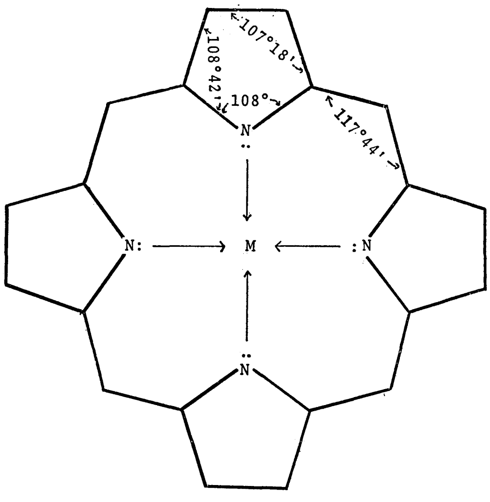

Fig. 2. Assumed porphin frame-work.

The number of π electrons is assumed to be 26 which is the same as that of free porphyrin. In the metal porphyrin, the lone pair electrons of a nitrogen should be largely transferred to the central metal ion by the formation of σ-type co-ordination bond. The net charge of central divalent metal ion is, therefore, expected to be considerably decreased. We have assumed the following various core charges for a nitrogen, +1.0, +1.3 and +1.5, which correspond to the net charges of the central metal ion, +2.0, +0.8, and 0.0, respectively.

(*B*) *One-center Core Integral.* When we neglect the penetration integrals, the core integral $\alpha_{\mu\mu}$ can be written as

$$\alpha_{\mu\mu} = \int\phi_\mu(1)H_{\mathrm{core}}(1)\phi_\mu(1)\mathrm{d}\tau = -I_\mu - \sum_{\nu\neq\mu}Q_\nu\gamma_{\mu\nu} \qquad (1)$$

where ϕ_μ: 2pπ AO of atom μ

I_μ: valence state ionization potential of atom μ

Q_ν: core charge of atom ν

$\gamma_{\mu\nu}$: two-center electron repulsion integral.

I_μ can be represented by the following quadratic equation of core charge Q:[14]

$$I_\mu(Q) = (1/2)\{I(2)-2I(1)+EA\}Q^2 - (1/2)\{I(2)-4I(1)+3EA\}Q + EA \qquad (2)$$

where $I(2)$: second ionization potential

$I(1)$: first ionization potential

EA: electron affinity.

(C) Two-center Core Integral. The two-center core integral $\beta_{\mu\nu}$ associated with μ–ν bond,

$$\beta_{\mu\nu} = \int\phi_\mu(1)H_{\mathrm{core}}(1)\phi_\nu(1)\mathrm{d}\tau$$

has been evaluated by the variable β approximation.[11] They are expressed as,

$$\beta_{\mu\nu}(\text{C–C}) = -0.51P_{\mu\nu} + \beta^0(\text{C–C}) \text{ eV}$$
$$\beta_{\mu\nu}(\text{C–N}) = -0.53P_{\mu\nu} + \beta^0(\text{C–N}) \text{ eV} \qquad (3)$$

where $P_{\mu\nu}$ is the bond order associated with μ–ν bond. For non-neighbors, the $\beta_{\mu\nu}$'s are neglected. The values of β^0's are estimated to reproduce the lowest transition energy of the molecule.

(D) One-center Electron Repulsion Integral. This integral can be evaluated by the Pariser-Parr approximation:

$$\gamma_{\mu\mu} = \int\phi_\mu^2(1)(e^2/r_{12})\phi_\mu^2(2)\mathrm{d}\tau = I_\mu - EA_\mu \qquad (4)$$

where EA_μ represents the electron affinity associated with ϕ_μ. When we consider a core charge dependence on the valence state energy, $\gamma_{\mu\mu}$ will be given by the following linear equation of core change Q.[14]

$$\gamma_{\mu\mu}(Q) = \{\gamma_{\mu\mu}(2)-\gamma_{\mu\mu}(1)\}Q + 2\gamma_{\mu\mu}(1) - \gamma_{\mu\mu}(2) \qquad (5)$$

where

$$\gamma_{\mu\mu}(2) = I_\mu(2) - I_\mu(1)$$
$$\gamma_{\mu\mu}(1) = I_\mu(1) - EA_\mu$$

The values of parameters are summarized in Table 1.

(E) Two-center Electron Repulsion Integral. Two-center repulsion integral,

$$\gamma_{\mu\nu} = \int\phi_\mu^2(1)(e^2/r_{12})\phi_\nu^2(2)\,\mathrm{d}\tau$$

are calculated by two kinds of approximation, NM[7] and KHN[8]. In NM approximation, $\gamma_{\mu\nu}$ is given by

$$\gamma_{\mu\nu} = e^2/(R+a)$$

where R is the interatomic distance between μ and ν atoms. Recently, we[8] have derived the following expression for $\gamma_{\mu\nu}$ from Brueckner equation,[15] by assuming ZDO and point charge interaction.

$$\gamma_{\mu\nu} = e^2/(R+(\Delta E_{\mathrm{B}}/\Delta E)A_{\mathrm{B}}) = \mathrm{e}^2/(R+kA_{\mathrm{B}}) \qquad (6)$$

where A_{B}: parameter for benzene

ΔE_{B}: average transition energy of benzene

ΔE: average transition energy of the molecule

k: correlation parameter ($\Delta E_{\mathrm{B}}/\Delta E$).

NM expression can be obtained, when we put $k=1$. For the porphyrin molecule, $\Delta E_{\mathrm{B}}/\Delta E$ is estimated to be 2.0 from the Soret band. In order to examine the effect of k on the electronic transition energies, the value is varied from 1 to 2.5.

TABLE 1. THE VALUES OF PARAMETERS

Atom	Q	I(eV)	EA (eV)	$\gamma_{\mu\mu}$ (eV)
C	+1.0	11.16	0.03	11.13
N	+1.0	14.12	1.78	12.34
N	+1.1	15.37	2.52	12.85
N	+1.2	16.62	3.26	13.36
N	+1.5	20.38	5.49	14.89
N	+1.8	24.17	7.75	16.42
N	+1.9	25.43	8.50	16.93
N	+2.0	26.70	9.26	17.44

Results and Discussion

Electronic Spectra. In order to elucidate the effect of σ-donation from the ligand porphyrin to the central metal ion, SCF-MO-CI calculations based on various models for the σ-framework have been carried out. First of all, we used NM approximation for two-center repulsion integrals and various β^0's. Models and the values of β^0 are shown in Table 2. In the calculation of metal porphyrin, we neglected the dπ-pπ interaction. The calculated results are summarized in Tables 3 and 4, together with the experimental data. It was found that better results are obtained by Model

TABLE 2. VARIOUS MODELS FOR FREE AND METAL PORPHINS

(A) Free porphin

Model	Core charge of pyrrole type nitrogen	Core charge of pyridine type nitrogen	β^0 (C–C) (eV)	β^0 (C–N) (eV)
I	2.0	1.0	−1.80	−1.86
II	2.0	1.0	−2.04	−2.24
III	1.9	1.1	−2.04	−2.24
IV	1.8	1.2	−2.04	−2.24

(B) Metal porphin

Model	Core charge of nitrogen	β^0 (C–C)	β^0 (C–N)
V	1.3	−1.80	−1.86
VI	1.5	−1.80	−1.86
VII	1.0	−2.04	−2.24
VIII	1.3	−2.04	−2.24
IX	1.5	−2.04	−2.24

Table 3. Calculated transition energies (in eV) and oscillator strengths for free porphin (NM approximation)

Model		Q_x	Q_y	B_x	B_y
I	ΔE	1.69	2.01	3.00	3.40
	f	(0.008)	(0.028)	(0.461)	(2.30)
II	ΔE	1.91	2.21	3.27	3.61
	f	(0.018)	(0.057)	(0.666)	(2.60)
Expt[a]	ΔE	2.01	2.39	3.13	
	$\varepsilon\times10^3$	(0.86)	(2.64)	(2.60)	

a) Ref. 17.

Table 4. Calculated transition energies (in eV) and oscillator strengths for metal porphin (NM approximation)

Model		Q	B	N
V	ΔE	1.80	3.20	3.86
	f	(0.014)	(2.34)	(2.41)
VI	ΔE	1.87	3.41	3.98
	f	(0.018)	(5.30)	(1.19)
VII	ΔE	1.78	3.23	4.05
	f	(0.092)	(3.45)	(1.84)
VIII	ΔE	2.02	3.48	4.32
	f	(0.048)	(5.01)	(1.09)
IX	ΔE	2.09	3.62	4.29
	f	(0.045)	(5.81)	(1.03)
Expt[a]	ΔE	2.23	3.13	
(Cu-porphin)	f	(0—0.1)	(1.1—1.6)	

a) Ref. 18.

Table 5. Calculated transition energies (in eV) and oscillator strengths of metal free porphin (KHN approximation)

Model			Q_x	Q_y	B_x	B_y
II	k=1.5	ΔE	1.87	2.28	3.07	3.26
	22 CI[a]	f	(0.049)	(0.040)	(0.879)	(2.45)
II	k=2.0	ΔE	1.84	2.32	2.93	3.03
	22 CI	f	(0.087)	(0.025)	(1.05)	(2.34)
II	k=2.0	ΔE	1.89	2.33	3.05	3.10
	4 CI	f	(0.098)	(0.024)	(2.68)	(2.83)
II	k=2.5	ΔE	1.81	2.35	2.83	2.87
	22 CI	f	(0.126)	(0.012)	(1.18)	(2.27)
III	k=2.0	ΔE	1.90	2.30	2.99	3.06
	22 CI	f	(0.073)	(0.022)	(1.53)	(2.54)
IV	k=2.0	ΔE	1.97	2.26	3.03	3.07
	22 CI	f	(0.061)	(0.022)	(1.99)	(2.70)

a) Number of singly excited configurations included in the CI calculation

Table 6. Calculated transition energies (in eV) and oscillator strengths for metal porphin (KHN approximation)

Model			Q	B	N
IX	k=1.5	ΔE	2.12	3.30	4.06
	20 CI	f	(0.056)	(5.69)	(0.585)
IX	k=2.0	ΔE	2.13	3.08	3.88
	25 CI	f	(0.069)	(5.29)	(0.596)
IX	k=2.0	ΔE	2.15	3.10	
	4 CI	f	(0.064)	(5.84)	
IX	k=2.5	ΔE	2.12	2.92	3.79
	25 CI	f	(0.093)	(5.12)	(0.506)

II for free porphyrin and Model IX for metal porphyrin. These results suggest that the appropriate values of β^0's are β^0 (C–C) = −2.04 eV and β^0 (C–N) = −2.24 eV, respectively. The values fit benzene and its derivatives. According to our previous work,[11] the best value of β^0 is usually reduced with an increase in the size of the cata-condensed hydrocarbon system. Since porphyrin is a much larger conjugated system than benzene, the present estimation seems to be unusual. However, there are some exceptions. For an example, in polyenes, it is not necessary to decrease the value of β^0 with increase in the length of conjugated system.[16] An improvement was obtained in the present study as compared with the previous investigation.[3] However, the calculated interval between Q and B bands is still too large.

In order to examine the effect of electron correlation on the electronic transitions, we have carried out SCF-MO-CI calculation based on KHN approximation. In the calculation, correlation parameter k in Eq. 6 is used as an adjusting parameter. We have varied the value of k from 1.0 to 2.5. The calculated results are given in Tables 5 and 6. The interval between Q and B bands decreases considerably with the increase in the value of k. A satisfactory agreement between the experimental and calculated results is obtained for k=2.0. In KHN approximation, the value of k is given by the ratio of the transition energy associated with p-band of benzene to that of a given molecule. In porphyrin, the value is to be 2.0, which agrees with the above mentioned best value. It is of interest to note that the results are not affected by the number of excited configurations taken into the calculation of configuration interaction. Namely, a satisfactory result is also obtained by a so-called four orbital model. This fact suggests us that KHN approximation takes fairly well the effect of electron correlation into account. In the case of free porphyrin, Rimington *et al.*[17] pointed out that the B_y band should lie very close to the strongest B_x band. Their suggestion seems to be of significance in porphyrin chemistry. This has been justified by the present study. Recently, Hatano[19] showed from MCD experiment that the Soret band consists of very closed B_x and B_y species. The calculated oscillator strengths of free porphyrin based on KHN approximation are considerably influenced by σ-framework. The second band (Q_y) seems to be too weak theoretically. However, there is a possibility of acquiring an intensity from the neighboring very intense Soret band, similar to the case of benzene's p-band.

It has been suggested by infrared spectroscopy[10] that there are hydrogen bonds between inner hydrogens and pyridine type nitrogens in free porphyrin. The wave function of a hydrogen bonded system can be, to a first approximation, expressed by the linear combinations of a non-dative and a proton transferred dative structure. Thus, in a simple treatment, the effect of hydrogen bond formation on the electronic structure of porphyrin can be considered by the variation of

TABLE 7. CALCULATED ORBITAL ENERGIES (IN eV) OF HIGHEST OCCUPIED (HOMO) AND LOWEST UNOCCUPIED (LUMO) ORBITALS (NM APPROXIMATION)

Model	I	II	V	VI	VII	VIII	IX
HOMO	−8.06	−8.10	−5.38	−7.99	−1.36	−5.40	−8.03
LUMO	−3.72	−3.65	−1.05	−3.57	2.75	−0.96	−3.49

core charges of nitrogens. Models III and IV were used for this purpose (Table 2). The calculated results are given in Table 5. It is expected that when the degree of proton transfer from N–H bond to pyridine type nitrogen increases, the interval between Q_x and Q_y and also that of B_x and B_y decrease.

Orbital Energy. According to Koopmans' theory,²⁰⁾ the ionization potential and the electron affinity of a molecule can be calculated by the orbital energies associated with the highest occupied and the lowest unoccupied molecular orbitals. The calculated results are given in Table 7. As seen from this Table, Model IX for metal porphyrin gives almost the same ionization potential and electron affinity with those of free porphyrin. The experimental values of the half-wave potentials of metal porphyrins for oxidation21) and reduction22) are very close to those of free porphyrin.21) This experimental result can be explained fairly well by means of Model IX. This provides another evidence that the Model IX in which the core charge of nitrogen is assumed to be 1.5 should be most appropriate for metal porphyrin. The model suggests that the net charge of the central metal ion varies from +2.0 to 0 by the formation of σ-type co-ordination bond.

The calculated MO energies of free porphyrin and the metal porphyrin are summarized in Tables 8 and 9, respectively. When k increases, the orbital spacings become narrow. The reason for this is as follows. Larger k corresponds to an increase in the effect of electron correlation. As a result, the two-center electron repulsion integral is reduced, so that the magnitude of off-diagonal Hartree-Fock element becomes small.

TABLE 8. ORBITAL ENERGIES (IN eV) OF FREE PORPHIN CALCULATED BY MODEL II

Symmetry	$k=1.0$	$k=1.5$	$k=2.0$
$5A_{1u}$	1.807	1.231	0.850
$4A_{1u}$	0.720	0.234	−0.092
$5B_{2g}$	0.544	0.073	−0.238
$5B_{3g}$	0.332	−0.155	−0.493
$6B_{1u}$	−0.116	−0.554	−0.861
$3A_{1u}$	−1.986	−2.380	−2.645
$4B_{2g}$	−3.550($4B_{3g}$)	−3.808	−3.927
$4B_{3g}$	−3.651($4B_{2g}$)	−3.848	−4.047
$5B_{1u}$	−8.101	−7.904	−7.752
$2A_{1u}$	−8.734	−8.515	−8.347
$3B_{2g}$	−9.991	−9.514	−9.193
$4B_{1u}$	−10.037	−9.566	−9.251
$3B_{3g}$	−10.783	−10.388	−10.097
$2B_{2g}$	−11.155($3B_{1u}$)	−10.757	−10.409
$3B_{1u}$	−11.230($2B_{2g}$)	−10.777	−10.494
$2B_{3g}$	−11.271	−10.906	−10.660
$1A_{1u}$	−12.375	−11.828	−11.457
$2B_{1u}$	−13.902	−13.365	−12.999
$1B_{2g}$	−14.188	−13.604	−13.210
$1B_{3g}$	−15.536	−15.030	−14.702
$1B_{1u}$	−15.598	−15.078	−14.742

TABLE 9. ORBITAL ENERGIES (IN eV) OF METAL PORPHIN CALCULATED BY MODEL IX

Symmetry	$k=1.0$	$k=1.5$	$k=2.0$
$4A_{2u}$	2.024	1.451	1.061
$6E_g$	1.936	1.379	1.001
$3B_{1u}$	1.864	1.321	0.954
$2A_{1u}$	0.924	0.423	0.084
$5E_g$	0.662	0.166	−0.176
$3B_{2u}$	0.141	−0.326	−0.657
$2B_{1u}$	−1.891	−2.257	−2.513
$4E_g$	−3.492	−3.707	−3.865
$3A_{2u}$	−8.033	−7.839	−7.698
$1A_{1u}$	−8.585	−8.357	−8.194
$3E_g$	−10.485($2B_{2u}$)	−10.044	−9.737
$2B_{2u}$	−10.488($3E_g$)	−10.046	−9.742
$2A_{2u}$	−10.516	−10.074	−9.768
$2E_g$	−10.914	−10.488	−10.195
$1B_{1u}$	−12.164	−11.630	−11.272
$1B_{2u}$	−14.161	−13.627	−13.268
$1E_g$	−14.700	−14.120	−13.734
$1A_{2u}$	−15.049	−14.446	−14.046

Electron Density and Bond Order. The effect of correlation parameter k on the electron distribution in the ground state of free porphyrin is shown in Fig. 3. When k increases, the electron density of α-carbon decreases slightly and that of nitrogen increases, for the pyrrole type ring. Reverse changes are found in another ring which has no N–H bond. Referring to the bond orders associated with aromatic hydrocarbons, we might say that mobile π-electrons move along bonds,

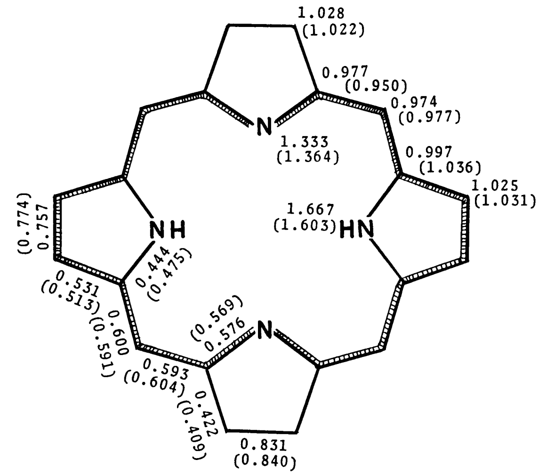

Fig. 3. Charge densities and bond orders of free porphin in the ground state, calculated by $k=2.0$. The results calculated by $k=1.0$ are shown in the parentheses.

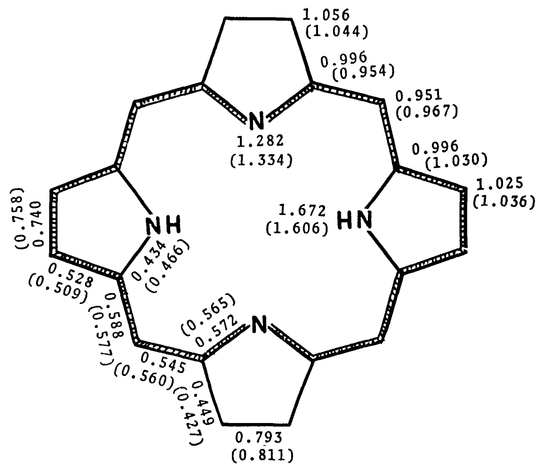

Fig. 4. Charge densities and bond orders of free porphin in the lowest excited singlet state, calculated by $k=2.0$. The results calculated by $k=1.0$ are shown in the parentheses.

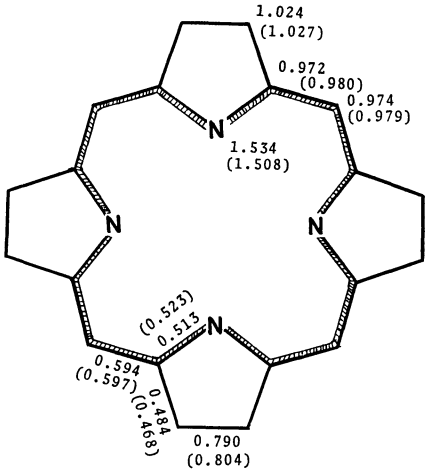

Fig. 5. Charge densities and bond orders of metal porphin in the ground state, calculated by $k=2.0$. The results calculated by $k=1.0$ are shown in the parentheses.

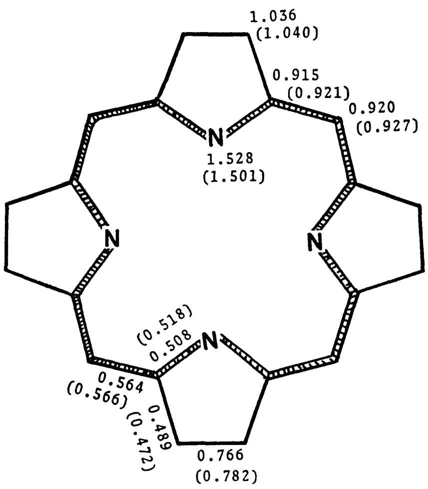

Fig. 6. Charge densities and bond orders of metal porphin in the lowest excited singlet state, calculated by $k=2.0$. The results calculated by $k=1.0$ are shown in the parentheses.

where bond orders are in the range 0.5—0.75. Thus, the path of mobile electrons in metal free porphyrin can be described by a shaded line in Fig. 3. The electron correlation might cause a slight increase in the mobility of π-electrons. The molecular diagram of free porphyrin in the lowest excited singlet state calculated by Model II is shown in Fig. 4. The effect of excitation causes a very small decrease in the electron densities of meso carbon and pyridine type nitrogen. The effect of k value on the electron distribution in metal porphyrin calculated by Model IX is shown in Fig. 5. It is seen from this figure that the mobility of π-electron along the outer ring increases slightly with increase in the value of k. The shaded framework includes 17.75 π-electrons; namely Huckel's $4n+2$ rule is approximately satisfied.

The 0–0 transitions of the Soret bands of both free and metal porphyrins are extremely intense. This fact suggests that the change of molecular framework by an excitation is very small. The molecular diagram of metal porphyrin in the lowest excited singlet state is shown in Fig. 6. The present calculation predicts that the changes of bond orders by an electronic transition are very small.

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