The Effect of Σ-Π Interaction on the Electronic Structure of Molecules in the Excited States. II. Oscillator Strength

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The effect of Σ-Π interaction on the oscillator strength of π-π* transition has been investigated in terms of the configuration interaction method considering all singly excited configurations. It has been found that the transition moment associated with π-π* excitation is modified by σ-electrons. The correction term of the transition moment resulting from the Σ-Π interaction can be expressed by the bond index matrix. The present theory has been applied to the calculation of the oscillator strength of benzene and naphthalene derivatives. Agreement between the calculated values and experimental data is satisfactory. The effect of Σ-Π interaction on the transition moment has been demonstrated pictorially.

In the previous paper,[1] the effective π-electron Hamiltonian for the excited state which includes the Σ-Π interaction was derived using the partitioning technique.[2] The effective electron repulsion integrals were represented in terms of the bond index matrix.

The oscillator strength calculated by the traditional π-electron theory is generally larger than that obtained by experiments.[3] This discrepancy might be caused by neglecting the Σ-Π interaction[4] and the π-electron correlation.[5] In the present paper, we consider the effect of Σ-Π interaction on the oscillator strength of π-π* transition.

The theoretical procedure is as follows. We consider the wave function including the σ-σ* configurations in the excited state, and represent the transition moment in terms of the bond index matrix. Applying this theory to benzene, naphthalene, pyridine, pyrazine, phenol, aniline, quinoline, and isoquinoline, we show the role of the σ-electrons on the transition moments associated with the π-π* transitions. We then analyze the effect of induced σ-electron polarization on the π-π* transition moment, and show that the induced σ-electron polarization can be assigned to the individual localized σ-bonds.

Theoretical

The effective total π-electron Hamiltonian for the excited state is expressed as follows:[1]

$$\tilde{\boldsymbol{H}}(\pi) = \boldsymbol{H}(\pi) - \boldsymbol{VP}\frac{1}{\boldsymbol{H}-\boldsymbol{EI}}\boldsymbol{PV}, \tag{1}$$

where $\boldsymbol{V}$ denotes the electron repulsion interaction between σ and π electrons and $\boldsymbol{P}$ is the projection operator defined by

$$\boldsymbol{P} = \sum_{k\gamma}\left|\begin{matrix}\gamma\\ k\end{matrix}\right\rangle\left\langle\begin{matrix}\gamma\\ k\end{matrix}\right|, \tag{2}$$

where $\left|\begin{matrix}\gamma\\ k\end{matrix}\right\rangle$ is the singly excited configuration associated with the excitation of an electron from the k-th occupied σ-MO to the γ-th unoccupied σ*-MO. In this paper the following notations are used: i,j for the occupied π-MO, α,β for the unoccupied π*-MO, k,l for the occupied σ-MO, γ,δ for the unoccupied σ*-MO, μ,ν for the π-AO and r,s for the σ-AO. In accordance with the prescribed P-P-P method,[6] the zero differential overlap (ZDO) approximation is also used.

With use of the effective total π-electron Hamiltonian[1] the corresponding excited wave function, $|\Phi\rangle$, expressed by the linear combination of the π-π* singly excited configurations, can be obtained from the following equation:

$$\tilde{\boldsymbol{H}}(\pi)|\Phi\rangle = \boldsymbol{E}|\Phi\rangle, \tag{3}$$

where

$$|\Phi\rangle = \sum_{i\alpha}C_{i\alpha}\left|\begin{matrix}\alpha\\ i\end{matrix}\right\rangle, \tag{4}$$

$|\Phi\rangle$ is normalized in the subspace associated with π-π* configurations, and $C_{i\alpha}$ is the variation parameter.

On the other hand, the actual wave function, $|\Psi\rangle$, for the lower excited state is given by the linear combinations of the π-π* and σ-σ* singly excited configurations as follows:

$$|\Psi\rangle = \frac{1}{\sqrt{N}}\Big[\sum_{i\alpha}C_{i\alpha}\left|\begin{matrix}\alpha\\ i\end{matrix}\right\rangle + \sum_{k\gamma}C_{k\gamma}\left|\begin{matrix}\gamma\\ k\end{matrix}\right\rangle\Big], \tag{5}$$

where $\sqrt{N}$ is the normalization factor. According to the partitioning technique,[2] $C_{k\gamma}$ in Eq. 5 is written as follows:

$$C_{k\gamma} = -\sum_{i\alpha}[(\boldsymbol{H}-\boldsymbol{EI})_{k\gamma,k\gamma}]^{-1}\left\langle\begin{matrix}\gamma\\ k\end{matrix}\right|\boldsymbol{V}\left|\begin{matrix}\alpha\\ i\end{matrix}\right\rangle C_{i\alpha}. \tag{6}$$

Substituting Eq. 6 into Eq. 5, we obtain

$$|\Psi\rangle = \frac{1}{\sqrt{N}}\left(|\Phi\rangle - \boldsymbol{P}\frac{1}{\boldsymbol{H}-\boldsymbol{EI}}\boldsymbol{PV}|\Phi\rangle\right). \tag{7}$$

The normalization factor is given by

$$N = 1 + \sum_{i\alpha}\sum_{j\beta}C_{i\alpha}C_{j\beta}\sum_{k\gamma}\frac{4V_{ik\alpha\gamma}V_{jk\beta\gamma}}{[(\boldsymbol{H}-\boldsymbol{EI})_{k\gamma,k\gamma}]^2}, \tag{8}$$

where $V_{ik\alpha\gamma}$ means the exchange type MO integral which is defined as follows:

$$V_{ik\alpha\gamma} = \iint i^*(1)k^*(2)v_{12}\alpha(1)\gamma(2)\,\mathrm{d}\tau_1\mathrm{d}\tau_2.$$

As we did in the previous paper,[1] the averaged energy parameter is used instead of the denominator in Eq. 8. Then, the normalization factor can be written as

$$N = 1 - \frac{1}{\boldsymbol{e}^2}\sum_{i\alpha}\sum_{j\beta}C_{i\alpha}C_{j\beta}\sum_{\mu\nu}\sum_{AB}d_{i\mu}d_{j\nu}d_{\alpha\mu}d_{\beta\nu}\gamma_{\mu A}\mathbf{B}_{AB}\gamma_{B\nu}, \tag{9}$$

in terms of the bond index matrix $\mathbf{B}$. $d_{i\mu}$ is the coefficient of the μ-th AO of the i-th MO. $\boldsymbol{e}$ is an averaged energy parameter. The bond index matrix element $\mathbf{B}_{AB}$ is defined as follows:[1]

$$\mathbf{B}_{AB} = -\sum_{r}^{A}\sum_{s}^{B}\sum_{k}^{\sigma}\sum_{\gamma}^{\sigma^*}4d_{kr}d_{ks}d_{\gamma r}d_{\gamma s}.$$

The value of $\sqrt{N}$ calculated by means of Eq. 9 is almost 1.0. Thus $\sqrt{N}$ is put to be 1.0 in the calculation.

The transition moment $\mathbf{m}$ associated with the excitation of an electron from the ground state to an excited singlet state, Ψ, is given by

$$\mathbf{m} = \langle 0|\sum_i \mathbf{r}_i|\Psi\rangle, \tag{10}$$

Substituting Eq. 7 into Eq. 10, we obtain the transition moment including the effect of Σ-Π interaction as follows:

$$\mathbf{m} = \langle 0|\sum_i \mathbf{r}_i|\Phi\rangle - \langle 0|\sum_i \mathbf{r}_i \boldsymbol{P}\frac{1}{\boldsymbol{H}-\boldsymbol{E}\boldsymbol{I}}\boldsymbol{P}\boldsymbol{V}|\Phi\rangle, \tag{11}$$

where $\mathbf{r}_i$ is the position vector of the i-th electron. The first term of Eq. 11 corresponds to the transition moment of the traditional P-P-P scheme, the second term being the correction due to the Σ-Π interaction. According to the usual P-P-P method, the transition moment from the ground state to the excited configuration, $\left|\begin{smallmatrix}\beta\\ j\end{smallmatrix}\right\rangle$, can be expanded by means of LCAO coefficients as

$$\langle 0|\sum_i \mathbf{r}_i\left|\begin{matrix}\beta\\ j\end{matrix}\right\rangle = \sqrt{2}\sum_\mu d_{j\mu}d_{\beta\mu}\mathbf{r}_\mu, \tag{12}$$

where $\mathbf{r}_\mu$ represents the coordinate of the μ-th atom. Therefore, Eq. 11 becomes

$$\mathbf{m} = \sqrt{2}\sum_{i\alpha} C_{i\alpha}\sum_\mu d_{i\mu}d_{\alpha\mu}\left(\mathbf{r}_\mu + \frac{1}{2e}\sum_{AB}\mathbf{r}_A\mathbf{B}_{AB}\gamma_{B\mu}\right). \tag{13}$$

By means of this equation, the oscillator strength, f, including the Σ-Π interaction is written as follows:

$$f = 0.0875 \times \mathbf{m}^2 \times \Delta E \times G, \tag{14}$$

where ΔE (in eV) is the excitation energy and G is the degree of the degeneracy of the excited state.

Let us further consider the transition moment $\mathbf{m}$. Equation 13 can be rewritten as

$$\mathbf{m} = \mathbf{m}_0 + \Delta\mathbf{m},$$

where $\mathbf{m}_0$ and $\Delta\mathbf{m}$ are given by

$$\mathbf{m}_0 = \sqrt{2}\sum_{i\alpha}\sum_\mu C_{i\alpha}d_{i\mu}d_{\alpha\mu}\mathbf{r}_\mu,$$

$$\Delta\mathbf{m} = \frac{1}{\sqrt{2}\,e}\sum_{i\alpha}\sum_\mu C_{i\alpha}d_{i\mu}d_{\alpha\mu}\sum_{AB}\mathbf{r}_A\mathbf{B}_{AB}\gamma_{B\mu}. \tag{15}$$

$\Delta\mathbf{m}$ is rewritten as

$$\Delta\mathbf{m} = \sum_{AB}\mathbf{r}_A\mathbf{B}_{AB}\mathbf{X}_B, \tag{16}$$

where $\mathbf{X}_B$ is given by

$$\mathbf{X}_B = \frac{1}{\sqrt{2}\,e}\sum_{i\alpha}\sum_\mu C_{i\alpha}d_{i\mu}d_{\alpha\mu}\gamma_{B\mu}.$$

Since $\Sigma\mathbf{B}_{AB}=0$, $\Delta\mathbf{m}$ becomes as follows:

$$\begin{aligned}
\Delta\mathbf{m} &= \frac{1}{2}\sum_A\sum_B(\Delta\mathbf{m}_{AB}+\Delta\mathbf{m}_{BA})\\
&= \frac{1}{2}\Big[\sum_A\sum_B\mathbf{r}_A\mathbf{B}_{AB}\mathbf{X}_B + \sum_A\sum_B\mathbf{r}_B\mathbf{B}_{BA}\mathbf{X}_A\Big]\\
&= \frac{1}{2}\Big[\Big(\sum_A\sum_B\mathbf{r}_A\mathbf{B}_{AB}\mathbf{X}_B - \sum_B\mathbf{r}_B\mathbf{X}_B\sum_A\mathbf{B}_{AB}\Big)\\
&\quad + \Big(\sum_B\sum_A\mathbf{r}_B\mathbf{B}_{BA}\mathbf{X}_A - \sum_A\mathbf{r}_A\mathbf{X}_A\sum_B\mathbf{B}_{BA}\Big)\Big]\\
&= \frac{1}{2}\Big[\sum_A\sum_B(\mathbf{r}_A-\mathbf{r}_B)\mathbf{B}_{AB}\mathbf{X}_B + \sum_B\sum_A(\mathbf{r}_B-\mathbf{r}_A)\mathbf{B}_{BA}\mathbf{X}_A\Big]\\
&= \sum_{A>B}(\mathbf{r}_A-\mathbf{r}_B)\mathbf{B}_{AB}(\mathbf{X}_B-\mathbf{X}_A)\\
&= \sum_{A>B}\Delta\mathbf{M}_{AB},
\end{aligned} \tag{17}$$

where

$$\Delta\mathbf{M}_{AB} = (\mathbf{r}_A-\mathbf{r}_B)\mathbf{B}_{AB}(\mathbf{X}_B-\mathbf{X}_A).$$

Thus, $\Delta\mathbf{m}$ can be decomposed into the contributions of individual σ-bonds. $\Delta\mathbf{M}_{AB}$ is the induced σ-polarization associated with the σ-bond, A–B, caused by the π-π* transition. The present theory has been applied to the calculation of the oscillator strength of π-π* transition of some aromatic compounds.

Results and Discussion

The calculated transition moments and oscillator strengths of benzene and naphthalene are summarized in Table 1. The calculated and experimental excitation energies and oscillator strengths of benzene and naphthalene are compared in Fig. 1, where PPP-NM denotes the conventional P-P-P calculation using Nishimoto-Mataga formula[6] for the two center electron repulsion integrals. We see that the calculated results based on the present theory agree with the experimental ones satisfactorily for both the singlet and triplet states. It should be noted that the present theory brings about an appreciated improvement in the oscillator strength. The conventional P-P-P method gives too large values of oscillator strengths. The Σ-Π interaction gives rise,

TABLE 1. CALCULATED TRANSITION MOMENTS AND OSCILLATOR STRENGTHS OF BENZENE AND NAPHTHALENE

		Transition moments[b)]						Oscillator strengths[c)]		
	States[a)]	$\mathbf{m}_0$		$\Delta\mathbf{m}$		$\mathbf{m}$		f_0	f	f/f_0
		x	y	x	y	x	y			
Benzene	$^1B_{2u}$	0.	0.	0.	0.	0.	0.	0.	0.	—
	$^1B_{1u}$	0.	0.	0.	0.	0.	0.	0.	0.	—
	$^1E_{1u}$	0.	1.400	0.	−0.424	0.	0.976	1.201	0.584	0.487
	$^1E_{1u}$	1.400	0.	−0.424	0.	0.976	0.	1.201	0.584	0.487
Naphthalene	$^1B_{3u}$	0.	0.	0.	0.	0.	0.	0.	0.	—
	$^1B_{2u}$	0.	0.755	0.	−0.264	0.	0.491	0.233	0.099	0.421
	^1A_g	0.	0.	0.	0.	0.	0.	0.	0.	—
	$^1B_{3u}$	1.984	0.	−0.423	0.	1.561	0.	1.999	1.237	0.619

a) Singlet state is placed in the order of increasing energy. b) x and y denote the component of the transition moment. c) f_0 and f are calculated by using $\mathbf{m}_0$ and $\mathbf{m}$, respectively.

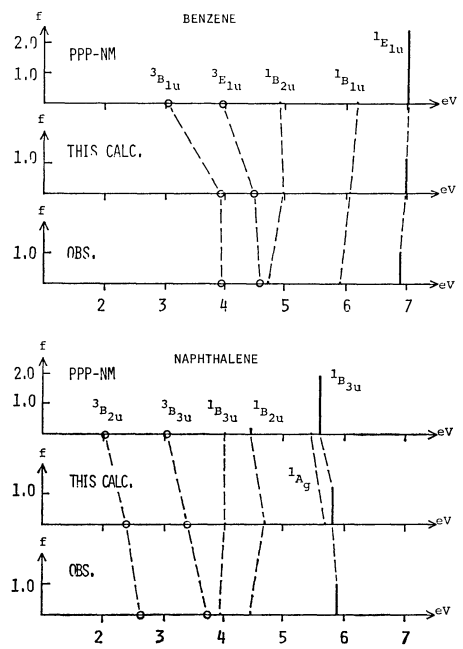

Fig. 1. The calculated experimental (OBS) excitation energies and oscillator strengths of benzene and naphthalene. (The experimental values are taken from Ref. 8.)

therefore, to a substantial reduction in the conventionally calculated oscillator strength. For an example, the calculated *f*-value (oscillator strength) associated with the $^1A_{1g}\rightarrow{}^1E_{1u}$ transition of benzene varies from 2.40 to 1.17, when the Σ-Π interaction is considered (experimental value, 1.0[8]). The *f*-value of naphthalene corresponding to the transition with a medium intensity ($^1A_g\rightarrow{}^1B_{2u}$) and that with the strongest intensity ($^1A_g\rightarrow{}^1B_{3u}$) also vary from 0.23 and 2.00 to 0.10 and 1.24, respectively. The corresponding experimental values are 0.10 and 1.0,[8] respectively. The reason for this improvement in the oscillator strength is that the π-π^* transition induces the polarization of σ-electrons in the direction opposite to the π-π^* transition moment.

It is convenient to demonstrate the effect of Σ-Π interaction on the transition moment pictorially. Figure 2 shows the transition moments of benzene and naphthalene, where $\mathbf{m}_0$ (Eq. 15) is shown by a shaded arrow and induced moment $\Delta\mathbf{m}$ is shown by a hollow arrow. The total transition moment is the sum of these two moments. In the case of the lower $^1B_{2u}$ state of naphthalene, the value of $\mathbf{m}_0$ is 0.76 eÅ (in unit of electron angstrom) and $\Delta\mathbf{m}$ is -0.26 eÅ, so that the sum is to be 0.50 eÅ. Consequently, the oscillator strength is to be reduced to about one-half of its initial value. The value of $\mathbf{m}_0$ of the strongly allowed transition ($^1A_g\rightarrow{}^1B_{3u}$) is 1.98 eÅ and that of induced moment is -0.42 eÅ. Generally speaking, the larger π-π^* transition moment causes the larger induced moment

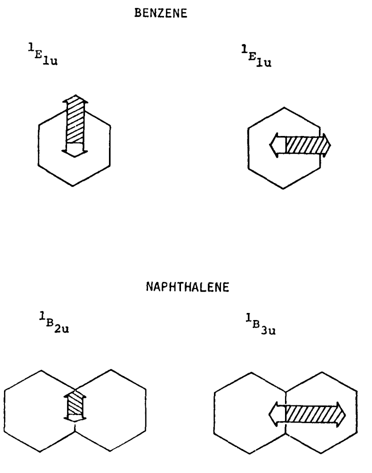

Fig. 2. The transition moments of benzene and naphthalene. $\mathbf{m}_0$ and $\Delta\mathbf{m}$ are represented by a shaded and a hollow arrows, respectively.

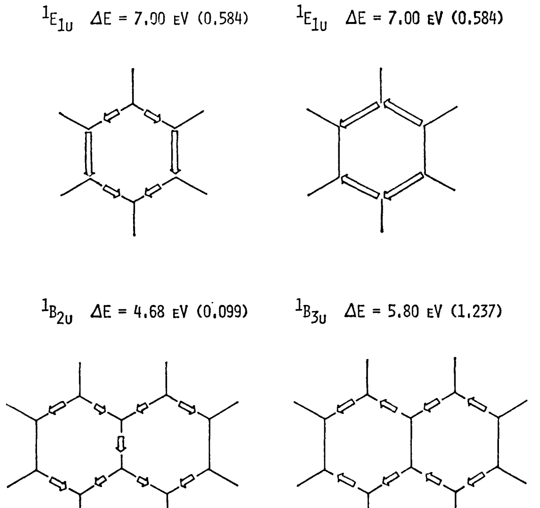

Fig. 3. The divided induced transition moments, $\Delta\mathbf{M}_{AB}$'s, of benzene and naphthalene.

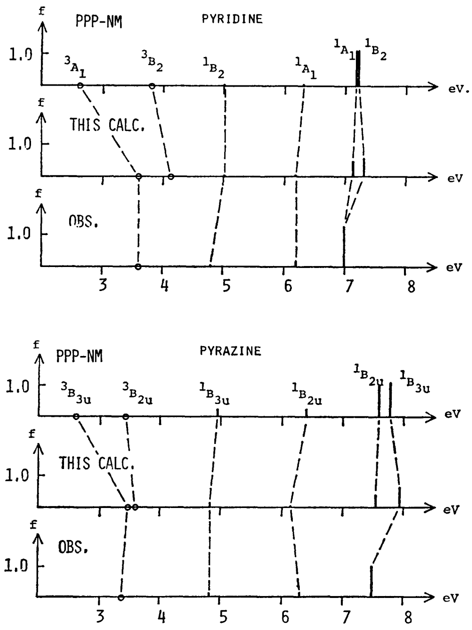

Fig. 4. The calculated and experimental (OBS) excitation energies and oscillator strengths of pyridine and pyrazine. (The experimental values are taken from Refs. 10, 11, and 12.)

Table 2. Calculated transition moments and oscillator strengths of pyridine, pyrazine, aniline, phenol, quinoline, and isoquinoline

	State[a)]	Transition moments[b)] $\mathbf{m}_0$ x	$\mathbf{m}_0$ y	$\Delta\mathbf{m}$ x	$\Delta\mathbf{m}$ y	$\mathbf{m}$ x	$\mathbf{m}$ y	Oscillator strengths[c)] f_0	f	f/f_0
Pyridine	$^1B_2$	0.453	0.	−0.137	0.	0.316	0.	0.090	0.044	0.489
	$^1A_1$	0.	0.284	0.	−0.078	0.	0.206	0.044	0.023	0.523
	$^1A_1$	0.	1.334	0.	−0.440	0.	0.894	1.112	0.499	0.449
	$^1B_2$	1.305	0.	−0.395	0.	0.910	0.	1.088	0.529	0.486
Pyrazine	$^1B_{3u}$	0.784	0.	−0.237	0.	0.547	0.	0.260	0.126	0.485
	$^1B_{2u}$	0.	0.582	0.	−0.175	0.	0.407	0.182	0.089	0.489
	$^1B_{2u}$	0.	1.222	0.	−0.454	0.	0.768	0.988	0.390	0.395
	$^1B_{3u}$	1.214	0.	−0.368	0.	0.847	0.	1.026	0.499	0.486
Aniline	$^1B_2$	0.490	0.	−0.160	0.	0.330	0.	0.089	0.041	0.461
	$^1A_1$	0.	1.050	0.	−0.217	0.	0.832	0.499	0.314	0.629
	$^1A_1$	0.937	0.	−0.303	0.	0.635	0.	0.500	0.229	0.458
	$^1B_2$	0.	1.244	0.	−0.317	0.	0.927	0.908	0.504	0.551
Phenol	$^1B_2$	0.354	0.	−0.107	0.	0.247	0.	0.051	0.025	0.490
	$^1A_1$	0.	0.691	0.	−0.181	0.	0.510	0.236	0.128	0.542
	$^1B_2$	0.	1.384	0.	−0.387	0.	0.996	1.135	0.588	0.518
	$^1A_1$	1.245	0.	−0.377	0.	0.868	0.	0.920	0.447	0.486
Quinoline	S_1	0.430	0.103	−0.091	−0.034	0.339	0.069	0.069	0.042	0.609
	S_2	−0.096	0.699	0.023	−0.256	−0.073	0.444	0.204	0.083	0.407
	S_3	1.177	−0.078	−0.251	0.036	0.925	−0.042	0.678	0.418	0.617
	S_4	1.374	0.111	−0.291	−0.032	1.084	0.079	1.011	0.628	0.622
	S_5	0.342	0.896	−0.076	−0.295	0.266	0.601	0.501	0.236	0.471
Isoquinoline	S_1	0.162	0.427	−0.037	−0.145	0.126	0.281	0.073	0.033	0.452
	S_2	−0.177	0.669	0.037	−0.233	−0.140	0.436	0.199	0.087	0.437
	S_3	0.488	0.294	−0.111	−0.096	0.377	0.198	0.160	0.089	0.556
	S_4	1.779	−0.046	−0.403	0.031	1.375	−0.015	1.610	0.962	0.598
	S_5	0.280	−0.214	−0.063	0.076	0.216	−0.138	0.067	0.036	0.537

a), b), c) See the footnotes of Table 1.

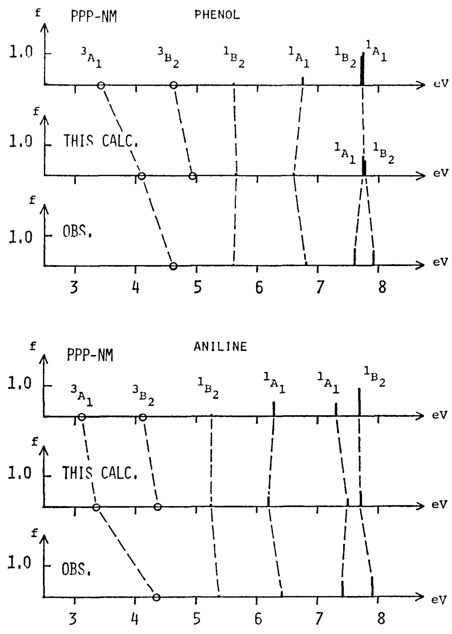

Fig. 5. The calculated and experimental (OBS) excitation energies and oscillator strengths of phenol and aniline. (The experimental values are taken from Refs. 9 and 10.)

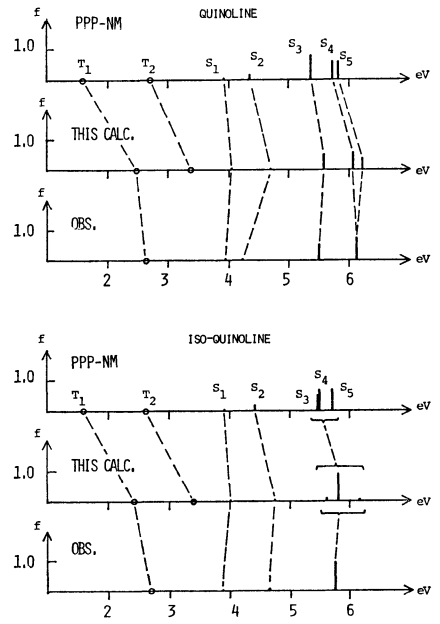

Fig. 6. The calculated and experimental (OBS) excitation energies and oscillator strengths of quinoline and isoquinoline. (The experimental values are taken from Refs. 7 and 8.)

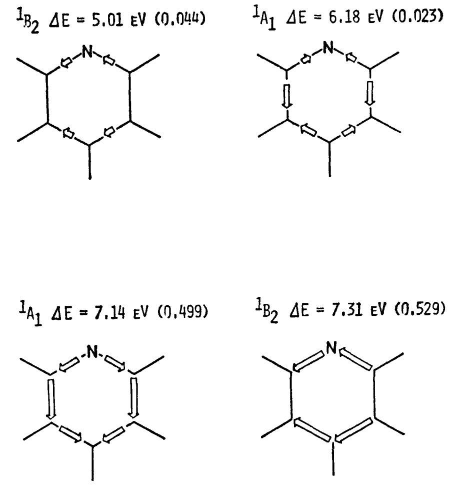

Fig. 7. The divided induced transition moments, $\Delta\mathbf{M}_{AB}$'s, of pyridine.

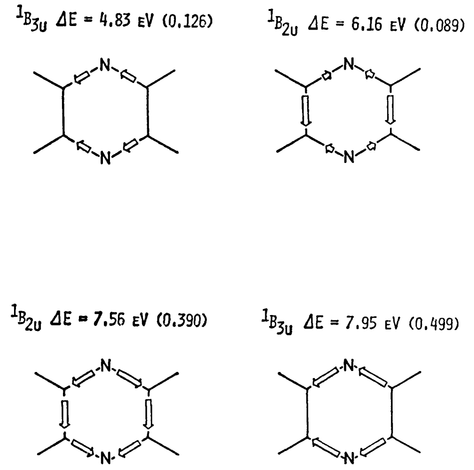

Fig. 8. The divided induced transition moments, $\Delta\mathbf{M}_{AB}$'s, of pyrazine.

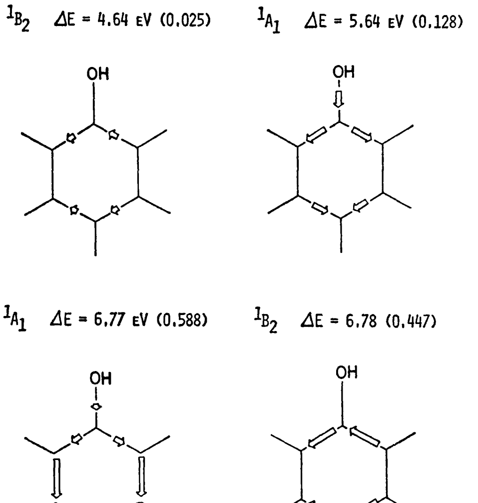

Fig. 9. The divided induced transition moments, $\Delta\mathbf{M}_{AB}$'s, of phenol.

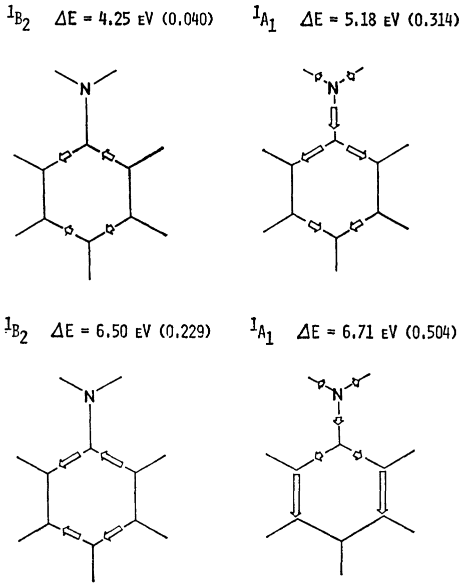

Fig. 10. The divided induced transition moments, $\Delta\mathbf{M}_{AB}$'s, of aniline.

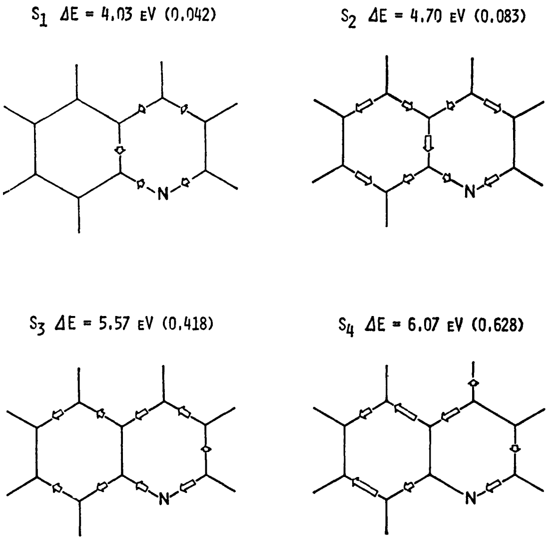

Fig. 11. The divided induced transition moments, $\Delta\mathbf{M}_{AB}$'s, of quinoline.

in the opposite direction. However, there is no quantitative relation between these two moments.

According to Eq. 17, the induced moment, $\Delta\mathbf{m}$, for a given transition can be divided into $\Delta\mathbf{M}_{AB}$ associated with the σ-bond A–B. Figure 3 shows such $\Delta\mathbf{M}_{AB}$ for benzene and naphthalene. The values of ΔE and f in this figure are the calculated transition energy and oscillator strength, respectively.

The calculated transition moment and oscillator strength of pyridine, pyrazine, aniline, phenol, quinoline, and isoquinoline are summarized in Table 2. The calculated and experimental excitation energies and oscillator strengths (f) of these molecules are compared in Figs. 4—6. The divided induced moment, $\Delta\mathbf{M}_{AB}$, associated with each transition of molecules is shown in Figs. 7—12.

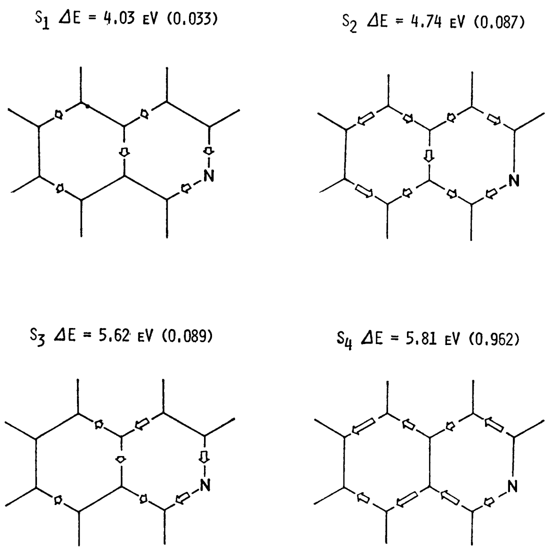

Fig. 12. The divided induced transition moments, $\Delta \mathbf{M}_{AB}$'s, of isoquinoline.

For the molecules considered in the present study, the absolute value of $\Delta \mathbf{m}$ is *ca.* 1/5—1/3 of the corresponding $\mathbf{m}_0$ (Tables 1 and 2). Thus the ratio of f (oscillator strength calculated by $\mathbf{m}$) to f_0 (oscillator strength calculated by $\mathbf{m}_0$) is found to be *ca.* 0.4—0.6. The oscillator strength of π-π^* transition calculated by the conventional P-P-P method is larger by about twice that obtained by experiment.[5,7] For azanaphthalenes, Baba and Yamazaki[7] showed that when the value of the oscillator strength calculated by P-P-P method is multiplied by 0.596, it is in a good agreement with the experimental ones. From Tables 1 and 2, it is found that their prescription is appreciated as a good approximation. In the cases of quinoline and isoquinoline which have no molecular symmetry, the two moments, $\mathbf{m}_0$ and $\Delta \mathbf{m}$, do not lie on a straight line. Thus the π-π^* transition moment is not only reduced but also altered it's direction by means of the Σ-Π interaction. For *N*-heterocycles, the diagonal matrix element of the bond index matrix associated with *N* atom is set to be -2.0, namely the lone pair orbital is treated as completely localized. In spite of this approximation, the results for these molecules are good for both the excitation energies and oscillator strength, (Figs. 4-6). This suggests that the present method is also applicable to *N*-heterocycles.

In the present theory, the electron correlation between π-electrons which reduces the oscillator strength has not been considered. Although Σ-Π interaction is a kind of electron correlation, the effect might be overestimated in the present method. It is obvious that the Σ-Π interaction has a very large effect on the π-π^* excitation energies and oscillator strengths.

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