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Semi-Empirical Molecular Orbital Calculations The Electronic Structure and the Spin-Orbit Coupling in Azabenzenes

TEIJIRO YONEZAWA, HAJIME KATÔ,* and HIROSHI KATO
Department of Hydrocarbon Chemistry, Kyoto University, Kyoto, Japan

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Electronic structures of pyridine, pyrazine, pyrimidine and pyridazine are studied by a semi-empirical SCF method for valence electron systems previously proposed by the present authors. The charge distributions, transition energies and oscillator strengths of these compounds are calculated. The calculated results show fairly good agreement with the observed ones. Using these results, we have further calculated the oscillator strengths of singlet-triplet transitions ($f_{T_1 \to S_0}$) and the life times of the triplet states (τ). In this treatment, we have considered the mixing of various singlets with T_1 and triplets with S_0, and the effect of σ-electrons is studied.

Es werden nach einer von den Autoren dieser Arbeit vorgeschlagenen Methode die Elektronenstrukturen von Pyridin, Pyrazin, Pyrimidin und Pyridazin studiert. Die halbempirische SCF-Methode für Valenzelektronensysteme gestattet die Berechnung der Ladungsverteilungen, Übergangsenergien und Oszillatorstärken, die in recht guter Übereinstimmung mit der Beobachtung stehen. Ferner werden die Oszillatorstärken von Singulett-Triplett-Übergängen ($f_{T_1 \to S_0}$) und die Lebensdauer von Triplett-Zuständen (τ) berechnet.

Les structures électroniques de la pyridine, de la pyrazine, de la pyrimidine et de la pyridazine sont étudiées par une méthode SCF semiempirique pour les électrons de valence proposée précédemment par les auteurs. Les distributions de charge, les énergies de transition et les forces oscillatrices de ces composés sont calculées, donnant des résultats en bon accord avec l'expérience. De plus nous avons calculé les forces oscillatrices des transitions singulet-triplet ($f_{T_1 \to S_0}$) et les durées de vie des états triplets (τ). Dans ce calcul nous avons inclus l'interaction de configuration et l'étude de l'effet des électrons σ.

Introduction

Semi-empirical treatments to estimate $n \to \pi^*$ transition energies of azine compounds have been proposed by Sidman [20], Goodman [8], and Anno and Sado [1]. In their treatment a localized model of the lone pair at the nitrogen or oxygen atoms is adopted. Lindner *et al.* [17] performed semi-empirical calculations involving π- and σ-electrons on some nitrogen containing heterocycles. Clementi [5] got the SCF wave functions including all electrons for the ground state of pyridine and pyrazine. In the present paper, using a semi-empirical SCF method for valence electron systems [23, 15], transition energies, oscillator strengths, atomic populations, and bond orders are calculated and compared with experiments.

The spin-orbit interaction in the singlet-triplet transition of azines has been treated previously by several authors [6, 9, 21, 25]. In their procedures the lone pair (n) orbital was always treated as a localized hybrid orbital at the nitrogen atom. Goodman and Krishna [9] considered the mixing of various singlet states

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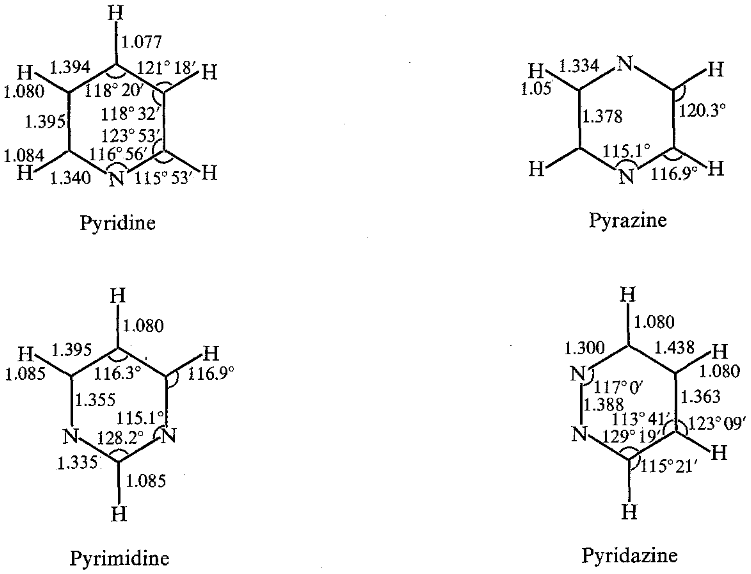
[*] Present address: Department of Chemistry, Faculty of Science, Kobe University, Kobe, Japan.

with the lowest excited triplet T_1 and triplet states mixed with the ground singlet state S_0 but neglected the effect of σ-molecular orbitals. With the explicit consideration of σ-MO's, the oscillator strength of a singlet-triplet transition and the life times of the triplet states are studied in the present paper by considering the mixing of singlet and triplet states.

Theoretical

In the present paper, calculations are made by a semi-empirical SCF method for valence electron systems previously proposed by some of the present authors. Namely, the one-center integrals are estimated by means of empirical values, while the two-center Coulomb integrals are calculated by the Ohno approximation [19], the other electron repulsion integrals are calculated by the Mulliken approximation [18]. All overlap integrals in the secular equation are taken into account explicitly.

The molecular geometries adopted in this treatment are taken from the values given in Ref. [12, 22] and are shown in Fig. 1.



Pyridine

Pyrazine

Pyrimidine

Pyridazine

Fig. 1. Molecular geometry (bond length; Å)

Electronic Structures of Azabenzenes

a) Lone Pair Orbital

The calculated orbital energies of the higher five occupied and the lower three unoccupied molecular orbitals (MO's) are given in Table 1. The calculated ionization potentials due to lone pair electrons (n) of pyridine, pyrazine, pyrimidine and pyridazine are 10.73, 10.12, 10.62 and 10.24 eV respectively and the observed

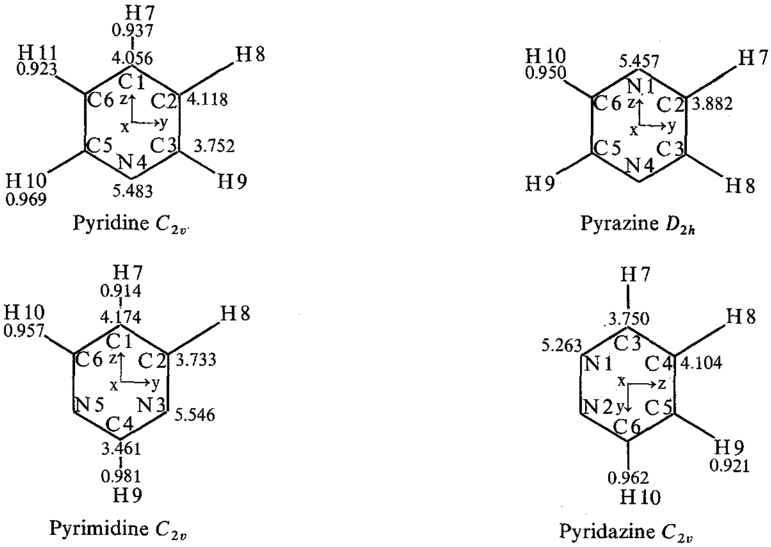
Table 1. *Calculated orbital energies and orbital character*

No. of MO[a]	Orbital energy (the character)			
	Pyridine	Pyrazine	Pyrimidine	Pyridazine
11	-12.69 (π)	-12.59 (σ)	-13.02 (π)	-13.10 (σ)
12	-11.96 (σ)	-12.48 (n)	-11.20 (n)	-11.36 (π)
13	-10.73 (n)	-11.12 (π)	-11.03 (π)	-11.27 (π)
14	-10.57 (π)	-10.88 (π)	-10.76 (π)	-11.04 (π)
15[b]	-10.55 (π)	-10.12 (n)	-10.62 (n)	-10.24 (n)
16[c]	0.88 (π^*)	0.39 (π^*)	0.18 (π^*)	0.36 (π^*)
17	1.22 (π^*)	1.12 (π^*)	0.85 (π^*)	0.92 (π^*)
18	6.74 (π^*)	6.31 (π^*)	5.65 (π^*)	5.76 (π^*)

[a] We number the MO's from lower orbital energies to higher ones by 1, 2, 3, ...
[b] The highest occupied orbital.
[c] The lowest vacant orbital.

ionization potentials are 9.76, 9.86, 9.91 and 10.01 eV. The partial atomic orbital populations of these n MO's at the nitrogen atoms are as follows: 1.271 for the $2p$ atomic orbital (AO) and 0.027 for the $2s$ AO in pyridine, 0.691, 0.929 for the $2p$ AO and 0.012, 0.036 for the $2s$ AO in pyrazine. In the same way, they are 0.642, 0.835 for $2p$ AO and 0.013, 0.018 for $2s$ AO in pyrimidine, and 0.609, 0.809 for $2p$ AO and 0.046, 0.001 for $2s$ AO in pyridazine. These two values in pyrazine, pyrimidine and pyridazine represent partial AO populations at the nitrogen atom for the higher and the lower n orbitals respectively. Thus, in the diazine molecules, the lone pair electrons occupying the higher n-MO's show fairly larger delocalization, on the other hand, the electrons occuping the lower one do not delocalize so much.

The directions of the symmetry axes and the atomic populations of the four molecules are shown in Fig. 2.



Pyridine C_{2v}

Pyrazine D_{2h}

Pyrimidine C_{2v}

Pyridazine C_{2v}

Fig. 2. Atomic population

Table 2. *Formal charges of the valence π- and σ-electrons*

Molecule	Atom	Formal charges		
		σ-electrons	π-electrons	total
Pyridine	N_1	−0.471	−0.012	−0.483
	C_2 C_6	0.234	0.014	0.248
	C_3 C_5	−0.101	−0.017	−0.118
	C_4	−0.074	0.018	−0.056
	H_2 H_6	0.031		0.031
	H_3 H_5	0.077		0.077
	H_4	0.063		0.063
Pyrazine	N_1 N_4	−0.478	0.022	−0.456
	C_2 C_6 C_3 C_5	0.189	−0.011	0.178
	H_2 H_6 H_3 H_5	0.051		0.051
Pyrimidine	N_1 N_3	−0.511	−0.035	−0.546
	C_2	0.493	0.046	0.539
	C_4 C_6	0.220	0.047	0.267
	C_5	−0.124	−0.050	−0.174
	H_2	0.019		0.019
	H_4 H_6	0.044		0.044
	H_5	0.086		0.086
Pyridazine	N_1 N_2	−0.248	−0.015	−0.263
	C_3 C_6	0.244	0.006	0.250
	C_4 C_5	−0.122	0.008	−0.104
	H_3 H_6	0.038		0.038
	H_4 H_5	0.079		0.079

b) Dipole Moment

The calculated formal charges[1] of the valence σ- and π-electrons are collected in Table 2. The total electronic dipole moments are divided into two parts,

$$D = D_P + D_A ,$$

where the term D_P represents the contribution due to the formal charges and the term D_A is the one from atomic dipoles.

These calculated values are listed in Table 3. As we can see in Table 2, the formal charges of the σ-electrons are larger than those of the π-electrons. Thus, our results show that σ-electrons contribute to D_P much more than π-electrons.

Table 3. *Calculated and observed electron dipole moments (Debyes)*

Molecule	Calculated D_P	Calculated D_A	Calculated total moment	Observed D^a
Pyridine	0.68	0.96	1.64	2.2
Pyrazine	0	0	0	0
Pyrimidine	2.15	1.14	3.29	2.4
Pyridazine	3.28	1.88	5.16	3.9

[a] Landolt-Börnstein: Zahlenwerte und Funktionen, Bd. 1.3. Berlin-Göttingen-Heidelberg: Springer 1951.

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[1] The atomic charges are obtained by the Mulliken populations.

c) Excitation Energy

Table 4 presents the calculated results for some lower excitation energies ΔE and oscillator strengths f. In the calculation, the limited number of configurations corresponding to singly excited states are considered. Except for pyridine, both of the present calculations, with and without CI calculation, have lowest triplet states of (n, π^*) character. The calculated lower $n \rightarrow \pi^*$ and $\pi \rightarrow \pi^*$ transition energies are in satisfactory agreement with the observed values except for the

Table 4a. *Excitation energies (ΔE) and oscillator strengths (f)*

Pyridine			
State	Calculated		Observed
	no CI	CI	
	ΔE (eV) f	ΔE (eV) f	ΔE (eV) f
$^3A_1(\pi, \pi^*)$	4.02	3.44	3.68[a]
$^3B_1(n, \pi^*)$	3.90	3.57	
$^3A_2(n, \pi^*)$	5.24		
$^1B_1(n, \pi^*)$	4.49 ($0.29 \cdot 10^{-3}$)	4.29 ($0.28 \cdot 10^{-3}$)	4.31 (0.003)[b]
$^1A_2(n, \pi^*)$	5.34		
$^1B_2(\pi, \pi^*)$	6.14 (0.40)	5.10 (0.08)	4.75 ($0.4 \cdot 10^{-1}$)[b]
$^1A_1(\pi, \pi^*)$	6.54 (0.60)	5.05 (0.02)	6.17 (0.2)[c,d]
$^1B_2(\pi, \pi^*)$	6.49 (0.54)	7.51 (1.00)	6.82 (1.3)[c,d]
$^1A_1(\pi, \pi^*)$	6.78 (0.61)	7.88 (1.19)	

[a] Evans, D. F.: J. chem. Soc. (London) 3885 (1957).

[b] Sponer, H., and J. Rush: J. chem. Physics **20**, 1847 (1952).

[c] Picket, L. W., M. E. Corning, G. M. Wieder, D. A. Semenow, and J. M. Buckley: J. Amer. chem. Soc. **75**, 1618 (1953).

[d] Kleven, H., and J. R. Platt: University of Chicago Technical Report (1953–1954).

Table 4b. *Excitation energies (ΔE) and oscillator strengths (f)*

Pyrazine			
State	Calculated		Observed
	no CI	CI	
	ΔE (eV) f	ΔE (eV) f	ΔE (eV) f
$^3B_{2u}(n, \pi^*)$	2.83	2.65	3.32[a]
$^1B_{2u}(n, \pi^*)$	3.44 ($0.2 \cdot 10^{-2}$)	3.17	3.83 (0.01)[b,c]
$^1B_{3g}(n, \pi^*)$	5.49	4.99	
$^3B_{1u}(\pi, \pi^*)$	3.55	3.11	
$^3B_{3u}(\pi, \pi^*)$	4.67	4.58	
$^1B_{3u}(\pi, \pi^*)$	5.96 (0.42)	5.08 (0.02)	4.69 4.81 (0.1)[c]
$^1B_{1u}(\pi, \pi^*)$	6.49 (0.63)	5.22 (0.02)	6.31 (0.15)[c]
$^1B_{3u}(\pi, \pi^*)$	6.56 (0.51)	7.42 (0.95)	7.52 (1.0)[a]
$^1B_{1u}(\pi, \pi^*)$	7.16 (0.70)	8.25 (1.35)	

[a] Parkin, J. E., and K. K. Innes: J. molecular Spectroscopy **15**, 407 (1965).

[b] Mason, S. F.: J. chem. Soc. (London) 1240 (1959).

[c] See Ref. d, Table 4a.

Table 4c. *Excitation energies (ΔE) and oscillator strengths (f)*

Pyrimidine State	Calculated no CI ΔE(eV) f	 CI ΔE(eV) f	Observed ΔE(eV) f
$^3B_1(n, \pi^*)$	3.39	3.33	3.63[a]
$^1B_1(n, \pi^*)$	3.79 $(0.11 \cdot 10^{-2})$	3.78 $(0.11 \cdot 10^{-2})$	3.85 (0.0069)[b,c]
$^1A_2(n, \pi^*)$	6.08 (0.54)	4.80	
$^3B_2(\pi, \pi^*)$	4.70	4.08	
$^1B_2(\pi, \pi^*)$	6.08 (0.54)	4.80 (0.01)	5.00 (0.052)[c]
$^1B_1(n, \pi^*)$	5.26 $(0.13 \cdot 10^{-3})$	5.25 $(0.17 \cdot 10^{-3})$	6.34? (0.005)[d]
$^1A_1(\pi, \pi^*)$	5.84 (0.49)	5.08 (0.04)	6.49? (0.16)[c]
$^1A_1(\pi, \pi^*)$	6.53 (0.48)	7.20 (0.89)	7.25 (1)[d]
$^1B_2(\pi, \pi^*)$	6.48 (0.59)	7.23 (1.16)	

[a] Goodman, L.: (unpublished) Ref. [5].
[b] See Ref. b, Table 4b.
[c] See Ref. c, Table 4b.
[d] See Ref. a, Table 4b.

Table 4d. *Excitation energies (ΔE) and oscillator strengths (f)*

Pyridazine State	Calculated no CI ΔE(eV) f	 CI ΔE(eV) f	Observed ΔE (eV) f
$^3B_1(n, \pi^*)$	3.31	2.73	3.01[a]
$^1B_1(n, \pi^*)$	3.83 $(0.13 \cdot 10^{-2})$	3.57	3.30 (0.0058)[b,c]
$^1A_2(n, \pi^*)$	4.12	3.86	
$^3A_1(\pi, \pi^*)$	4.76	3.94	
$^1A_1(\pi, \pi^*)$	6.54 (0.30)	5.37 (0.05)	4.90[c]
$^1B_2(\pi, \pi^*)$	6.12 (0.43)	5.36 (0.01)	6.20[c]
$^1B_2(\pi, \pi^*)$	6.54 (0.45)	7.13 (0.90)	7.10[d]
$^1A_1(\pi, \pi^*)$	6.82 (0.58)	7.74 (0.87)	

[a] Hochstrasser, R. M., and C. Marzzacco: J. chem. Physics **46**, 4155 (1967).
[b] See Ref. b, Table 4b.
[c] See Ref. c, Table 4b.
[d] See Ref. a, Table 4b.

lowest $n \rightarrow \pi^*$ transition in pyrazine. Also the calculated singlet-triplet separations in the lowest $n \rightarrow \pi^*$ transitions are reasonable to be compared with experiments.

For some higher excited states, the calculated excitation energies are in poor agreement with experimental values, especially with the CI calculation the second $\pi \rightarrow \pi^*$ excitation energy comes out too small in these compounds, but these discrepancies may be not so serious in the semi-quantitative discussions on the singlet-triplet transition.

S—T Transition by Spin-Orbit Coupling

The oscillator strength of an electronic transition from the ground singlet state (S_0) to the triplet state (T_1) is defined as;

$$f_{S_0 \to T_1} = \frac{mhc}{\pi e^2} \sigma \boldsymbol{B}_{S_0 \to T_1}, \tag{1}$$

where σ is the wave number corresponding to the transition between electronic states S_0 and T_1. The notation $\boldsymbol{B}_{S_0 \to T_1}$ refers to the Einstein transition probability between molecular states S_0 and T_1. This quantity is given by:

$$\boldsymbol{B}_{S_0 \to T_1} = = \frac{2\pi}{3\hbar^2} \sum_{p=-1}^{1} (\boldsymbol{P}^*_{S_0 \to T_{1P}} \cdot \boldsymbol{P}_{S_0 \to T_{1P}}), \tag{2}$$

$$\boldsymbol{P}_{S_0 \to T_{1P}} = e \langle {}^1\Phi_{S_0} | \Sigma \boldsymbol{r}_i | {}^3\Phi_{1P} \rangle, \tag{3}$$

where p is the eigenvalue of S_z. Neglecting the spin-spin interaction, the singlet-triplet ($S \to T$) transition is caused by the perturbation of the state wave function ${}^1\Phi_{S_0}$ and ${}^3\Phi_{T_1}$ due to the spin-orbit interaction, H_{so}.

Since the effect of H_{so} is very small, the transition moment $\boldsymbol{P}_{S_0 \to T_1}$ is given by the first-order perturbation theory [3, 10, 11].

Neglecting the interaction between the spin of the i-th electron and the orbital motion of the j-th electron ($i \neq j$), the matrix elements, $\langle {}^1\Phi_i | H_{so} | {}^3\Phi_{T_{1P}} \rangle$ and $\langle {}^3\Phi_{jP} | H_{so} | {}^1\Phi_{so} \rangle^*$ are not zero only when they differ by only one molecular orbital, so that Eq. (3) becomes now,

$$\begin{aligned} \boldsymbol{P}_{S_0 \to T_{1(lm)p}} = & - \sum_{k(\neq l)}^{\text{occ}} \frac{\langle {}^1\Phi_{km} | H_{so} | {}^3\Phi_{lm:p} \rangle \left\langle {}^1\Phi_{so} \middle| \sum_t \boldsymbol{r}_t \middle| {}^1\Phi_{km} \right\rangle}{{}^1E_{km} - {}^3E_{lm}} \\ & - \sum_{r}^{\text{occ}} \frac{\langle {}^3\Phi_{rm:p} | H_{so} | {}^1\Phi_{so} \rangle^* \left\langle {}^3\Phi_{rm:p} \middle| \sum_t \boldsymbol{r}_t \middle| {}^3\Phi_{lm:p} \right\rangle}{{}^3E_{rm} - {}^1E_{S_0}} \\ & - \sum_{n(\neq m)}^{\text{unocc}} \frac{\langle {}^1\Phi_{ln} | H_{so} | {}^3\Phi_{lm:p} \rangle \left\langle {}^1\Phi_{so} \middle| \sum_t \boldsymbol{r}_t \middle| {}^1\Phi_{ln} \right\rangle}{{}^1E_{ln} - {}^3E_{lm}} \\ & - \sum_{s}^{\text{unocc}} \frac{\langle {}^3\Phi_{ls:p} | H_{so} | {}^1\Phi_{so} \rangle^* \left\langle {}^3\Phi_{ls:p} \middle| \sum_t \boldsymbol{r}_t \middle| {}^3\Phi_{lm:p} \right\rangle}{{}^3E_{ls} - {}^1E_{S_0}}. \end{aligned} \tag{4}$$

In the matrix element, ${}^3\Phi_{lm:p}$, as an example, denotes the triplet excited state due to one electron excitation from the l-th MO to the m-th MO and the eigenvalue of S_z is p.

Since the spin operators are independent of the space coordinates, the integration over the spin coordinate can be performed immediately. Hence matrix elements $\langle {}^1\Phi_{lk} | H_{so} | {}^3\Phi_{ls:p} \rangle$ and $\langle {}^1\Phi_0 | H_{so} | {}^3\Phi_{ab:p} \rangle$ can be reduced to one of the integrals in Table 5a and Table 5b respectively, depending on which component of the spin-orbit operator is being used.

The transition moment is also reduced as follows:

$$\left\langle {}^1\Phi_0 \middle| \sum_t \boldsymbol{r}_t \middle| {}^1\Phi_{km} \right\rangle = \sqrt{2} \langle k | \boldsymbol{r} | m \rangle, \tag{5}$$

$$\left\langle {}^3\Phi_{rm:p} \middle| \sum_t \boldsymbol{r}_t \middle| {}^3\Phi_{lm:p} \right\rangle = \langle r | \boldsymbol{r} | l \rangle \quad (p = -1, 0, 1). \tag{6}$$

Table 5a. *Matrix element:* $\langle {}^1\Phi_{lk}|H_{so}|{}^3\Phi_{ls:p}\rangle$

Component of H_{so}	$\langle {}^1\Phi_{lk}\lvert H_{so}\rvert {}^3\Phi_{ls:1}\rangle$	$\langle {}^1\Phi_{lk}\lvert H_{so}\rvert {}^3\Phi_{ls:0}\rangle$	$\langle {}^1\Phi_{lk}\lvert H_{so}\rvert {}^3\Phi_{ls:-1}\rangle$
$(H_{so})_x$	$\frac{\hbar}{2\sqrt{2}}\langle k\lvert AL_x\rvert s\rangle$	0	$-\frac{\hbar}{2\sqrt{2}}\langle k\lvert AL_x\rvert s\rangle$
$(H_{so})_y$	$\frac{\hbar i}{2\sqrt{2}}\langle k\lvert AL_y\rvert s\rangle$	0	$\frac{\hbar i}{2\sqrt{2}}\langle k\lvert AL_y\rvert s\rangle$
$(H_{so})_z$	0	$-\frac{\hbar}{2}\langle K\lvert AL_z\rvert s\rangle$	0

where $AL_i = \frac{\hbar e^2}{2m^2c^2}\sum_k^N \frac{Z_k L_{ik}}{r_k^3}$, Z_k: Effective atomic charge of nucleus k.

Table 5b. *Matrix element:* $\langle {}^1\Phi_0|H_{so}|{}^3\Phi_{ls:p}\rangle$

Component of H_{so}	$\langle {}^1\Phi_0\lvert H_{so}\rvert {}^3\Phi_{ls+1}\rangle$	$\langle {}^1\Phi_0\lvert H_{so}\rvert {}^3\Phi_{ls:0}\rangle$	$\langle {}^1\Phi_0\lvert H_{so}\rvert {}^3\Phi_{ls:-1}\rangle$
$(H_{so})_x$	$\frac{\hbar}{2}\langle l\lvert AL_x\rvert s\rangle$	0	$-\frac{\hbar}{2}\langle l\lvert AL_x\rvert s\rangle$
$(H_{so})_y$	$\frac{\hbar i}{2}\langle l\lvert AL_y\rvert s\rangle$	0	$\frac{\hbar i}{2}\langle l\lvert AL_y\rvert s\rangle$
$(H_{so})_z$	0	$-\frac{\hbar}{\sqrt{2}}\langle l\lvert AL_z\rvert s\rangle$	0

The effect of three angular momentum operators L_i $(i=x, y, z)$ on the three p-orbitals is simply a clockwise rotation of the p-orbital around the i-axis by 90°.

In C_{2v} symmetry, R_x, R_y and R_z belong to the B_2, B_1 and A_2 representation respectively. For the element $\langle k|AL_i|l\rangle\langle m|\boldsymbol{r}|k\rangle$ $(i=x, y, z)$ is not equal to zero only when the direct product of the irreducible representation, $\Gamma(AL_i)\times\Gamma(\boldsymbol{r})$, is equal to $\Gamma(l)\times\Gamma(m)$. Therefore, the term $\langle k|AL_i|l\rangle\langle m|\boldsymbol{r}|k\rangle$ has a different direction of the transition moment for $i=x, y, z$. Accordingly, Eq. (2) is reduced as follows:

$$\begin{aligned} \boldsymbol{B}_{S_0\to T_{1(lm)}} = \frac{2\pi}{3\hbar^2}\frac{\hbar^2}{2}\sum_{i=x,y,z}\Bigg| & \sum_{k(\neq l)}\frac{\langle k|AL_i|l\rangle\langle m|\boldsymbol{r}|k\rangle}{{}^1E_{km}-{}^3E_{lm}} - \sum_r^{\text{occ}}\frac{\langle r|AL_i|m\rangle\langle l|\boldsymbol{r}|r\rangle}{{}^3E_{rm}-{}^1E_{S_0}} \\ & - \sum_{n(\neq m)}\frac{\langle n|AL_i|m\rangle\langle l|\boldsymbol{r}|n\rangle}{{}^1E_{ln}-{}^3E_{lm}} + \sum_s^{\text{unocc}}\frac{\langle s|AL_i|l\rangle\langle m|\boldsymbol{r}|s\rangle}{{}^3E_{ls}-{}^1E_{S_0}}\Bigg|^2 . \end{aligned} \tag{7}$$

As to the matrix element $\langle a|AL_i|b\rangle$ $(i=x, y, z)$, only one center terms are taken into account and the adopted ζ-values are;

$$\zeta_C = 27\ \mathrm{cm}^{-1}, \qquad \zeta_N = 56\ \mathrm{cm}^{-1}.$$

Spin-Orbit Coupling in Azabenzenes

Azabenzenes such as pyridine, pyrazine, pyrimidine and pyridazine are studied in the present paper. The molecular orbitals and their symmetries are given in Table 6. In the calculation of the oscillator strengths in $S\to T$ transitions,

Table 6. *Molecular orbitals and their symmetries*[a]

Molecule		occupied MO									unoccupied MO				
	MO	1...7	8	9	10	11	12	13	14	15	16	17	18	19	20...30
Pyridine	(C_{2v})	a_1	b_2	a_1	b_2	b_1	b_2	a_1	a_2	b_1	b_1	a_2	b_1	b_2	a_1
Pyrazine	(D_{2h})	a_g	b_{3u}	b_{2u}	b_{3u}	b_{2g}	b_{1u}	b_{1g}	b_{3g}	a_g	b_{2u}	a_u	b_{3g}	b_{3u}	a_g
Pyrimidine	(C_{2v})	a_1	b_2	a_1	b_2	b_1	a_1	b_1	a_2	b_2	a_2	b_1	b_1	a_1	b_2
Pyridazine	(C_{2v})	a_1	b_2	a_1	a_1	b_1	a_2	a_1	b_1	b_2	a_2	b_1	b_2	a_2	a_1

[a] The number 1 ... 30 shows MO. It is numberised from the lower orbital energy to the higher orbital energies.

we considered the contributions from 8 higher occupied MO's and 5 lower unoccupied MO's. The rest contributions from the other MO's are neglected because these contributions may be small for their higher excitation energies [24] and their smaller values of the *p* AO coefficients in these MO's.

The contributions to the singlet-triplet transition moment by the perturbing singlet configurations and the perturbing triplet configurations are listed in Table 7a for $^3A_1(\pi,\pi^*)\rightarrow S_0$ in pyridine, Table 7b for $^3B_1(n,\pi^*)\rightarrow S_0$ in pyridine, Table 8a for $^3B_{1u}(\pi,\pi^*)\rightarrow S_0$ in pyrazine, Table 8b for $^3B_{2u}(n,\pi^*)\rightarrow S_0$ in pyrazine, Table 9 for $^3B_1(n,\pi^*)\rightarrow S_0$ in pyrimidine and Table 10 for $^3B_1(n,\pi^*)\rightarrow S_0$ transition in pyridazine.

In C_{2v} symmetry (pyridine, pyrimidine, pyridazine), the components of the orbital parts of the operator H_{so}: $(\operatorname{grad} V_{ik}\times P_i)_x\cdot S_x$, $(\operatorname{grad} V_{ik}\times P_i)_y\cdot S_y$, and $(\operatorname{grad} V_{ik}\times P_i)_z\cdot S_z$, belong to the B_2, B_1 and A_2 irreducible representations, respectively.

Table 7a. *Pyridine* $^3A_1(\pi,\pi^*)$, $0.89\,\Phi(15\pi,16\pi^*)-0.46\,\Phi(14\pi,17\pi^*)$, $E_{T_1}\rightarrow E_{S_0}=3.45$ *eV*

Perturbing $^1\Phi_i$	$^1E_i-{}^3E_{T_1}$ (eV)	Direction of $\langle{}^1\Phi_{S_0}\|r\|{}^1\Phi_i\rangle$	$\frac{1}{\sqrt{2}}\langle{}^1\Phi_{S_0}\|r\|{}^1\Phi_i\rangle$ (Å)	$e\langle{}^1\Phi_i\|H_{so}\|{}^3\Phi_{T_1}\rangle$ (10^{-4} eV)	Contribution to $\sqrt{\frac{3\hbar^2}{2\pi}}B_{S_0\rightarrow T_1}$ (Å)
$^1B_1$ $(7\sigma,16\pi^*)$	5.43	x	0.004	16.27	0.0085
$^1B_1$ $(9\sigma,16\pi^*)$	4.28	x	0.095	13.74	0.2157
$^1B_1(13n,16\pi^*)$	1.05	x	−0.019	−36.54	0.4675
$^1B_1(15\pi,20\sigma^*)$	13.48	x	0.105	−20.91	−0.1152
$^1B_2(14\pi,16\pi^*)$	2.70	y	−0.680	0	0
$^1B_2(15\pi,17\pi^*)$	3.05	y	0.687	0	0
Perturbing $^3\Phi_j$	$^3E_j-{}^1E_{S_0}$ (eV)	Direction of $\langle{}^3\Phi_j\|r\|{}^3\Phi_{T_1}\rangle$	$\langle{}^3\Phi_j\|r\|{}^3\Phi_{T_1}\rangle$ (Å)	$\frac{e}{\sqrt{2}}\langle{}^3\Phi_j\|H_{so}\|{}^1\Phi_{S_0}\rangle$ (10^{-4} eV)	Contribution to $\sqrt{\frac{3\hbar^2}{2\pi}}B_{S_0\rightarrow T_1}$ (Å)
$^3B_1$ $(7\sigma,16\pi^*)$	8.84	x	0.029	− 0.01	−0.00002
$^3B_1$ $(9\sigma,16\pi^*)$	7.60	x	−0.074	−11.86	0.0817
$^3B_1(13n,16\pi^*)$	3.58	x	0.032	34.25	0.2165
$^3B_1(15\pi,20\pi^*)$	16.71	x	−0.129	25.37	−0.1385
$^3B_2(14\pi,16\pi^*)$	4.74	y	−0.019	0	0
$^3B_2(15\pi,17\pi^*)$	5.05	y	−0.066	0	0

Table 7b. *Pyridine* $^3B_1(n, \pi^*)$, $0.98\,\Phi(13n, 16\pi^*) - 0.21\,\Phi(13n, 18\pi^*)$, $^3E_{T_1} - {}^1E_{S_0} = 3.58$ *eV*

Perturbing $^1\Phi_i$	$^1E_i - {}^3E_T$ (eV)	Direction of $\langle ^1\Phi_{S_0}\|r\|^1\Phi_i\rangle$	$\frac{1}{\sqrt{2}}\langle ^1\Phi_{S_0}\|r\|^1\Phi_i\rangle$ (Å)	$e\langle ^1\Phi_i\|H_{so}\|^3\Phi_{T_1}\rangle$ (10^{-4} eV)	Contribution to $\sqrt{\frac{3\hbar^2}{2\pi} B_{S_0 \to T_1}}$ (Å)
$^1A_1(11\pi, 16\pi^*)$	4.49	z	0.398	20.88	1.3087
$^1A_1(13n, 20\pi^*)$	4.51	z	0.518	−20.91	−1.6982
$^1A_1(15\pi, 16\pi^*)$	2.96	z	−0.729	35.81	−6.2363
$^1B_2(13n, 19\sigma^*)$	7.28	y	0.512	23.62	1.1746
$^1B_2(14\pi, 16\pi^*)$	2.57	y	−0.680	4.55	−1.2039

Perturbing $^3\Phi_j$	$^3E_j - {}^1E_{S_0}$ (*eV*)	Direction of $\langle ^3\Phi_j\|r\|^3\Phi_{T_1}\rangle$	$\langle ^3\Phi_j\|r\|^3\Phi_{T_1}\rangle$ (Å)	$\frac{e}{\sqrt{2}}\langle ^3\Phi_j\|H_{so}\|^1\Phi_{S_0}\rangle^*$ (10^{-4} *eV*)	Contribution to $\sqrt{\frac{3\hbar^2}{2\pi} B_{S_0 \to T_1}}$ (Å)
$^3B_1$ $(7\sigma, 16\pi^*)$	8.84	z	0.196	− 0.01	−0.0002
$^3B_1$ $(9\sigma, 16\pi^*)$	7.60	z	0.638	−13.59	−0.8535
$^3B_1$ $(13n, 18\pi^*)$ $(13n, 16\pi^*)$	10.90	z	−0.136	21.27	−0.1868
$^3A_2$ $(8\sigma, 16\pi^*)$	8.71	y	0.338	13.79	0.5351
$^3A_2(10\sigma, 16\pi^*)$	7.08	y	−0.509	35.89	−2.5802
$^3A_2(12\sigma, 16\pi^*)$	5.94	y	−0.316	− 6.87	0.2584
$^3A_2(13n, 17\pi^*)$	4.24	y	−0.066	0.18	−0.0020

In D_{2h} symmetry (pyrazine), these components belong to the B_{3g}, B_{2g} and B_{1g} irreducible representations, respectively. Accordingly, for the $^3A_1(\pi, \pi^*) \to S_0$ transition in pyridine, the nonvanishing singlet states, $^1\Phi_i$, in the integral, $\langle ^1\Phi_i|H_{so}|^3\Phi_{T_1}\rangle$ and the nonvanishing triplet states, $^3\Phi_j$, in $\langle ^3\Phi_j|H_{so}|^1\Phi_{S_0}\rangle^*$ should belong to the following symmetry states;

$$^1\Phi_i : {}^1A_2, {}^1B_1, {}^1B_2\,, \qquad {}^3\Phi_j : {}^3A_2, {}^3B_1, {}^3B_2\,.$$

Table 8a. *Pyrazine* $^3B_{1u}(14\pi, 16\pi^*)$, $^3E_{T_1} - {}^1E_{S_0} = 3.55$ *eV*

Perturbing $^1\Phi_i$	$^1E_i - {}^3E_T$ (eV)	Direction of $\langle ^1\Phi_{S_0}\|r\|^1\Phi_i\rangle$	$\frac{1}{\sqrt{2}}\langle ^1\Phi_{S_0}\|r\|^1\Phi_i\rangle$ (Å)	$e\langle ^1\Phi_i\|H_{so}\|^3\Phi_{T_1}\rangle$ (10^{-4} eV)	Contribution to $\sqrt{\frac{3\hbar^2}{2\pi} B_{S_0 \to T_1}}$ (Å)
$^1B_{2u}$ $(7\sigma, 16\pi^*)$	4.83	y	−0.067	−20.29	0.1990
$^1B_{3u}(13\pi, 16\pi^*)$	2.41	x	−0.638	0	0
$^1B_{3u}(14\pi, 17\pi^*)$	3.00	x	0.667	0	0
$^1B_{2u}(15n, 16\pi^*)$	−0.11	y	−0.050	−36.59	−16.6318

Perturbing $^3\Phi_j$	$^3E_j - {}^1E_{S_0}$ (eV)	Direction of $\langle ^3\Phi_j\|r\|^3\Phi_{T_1}\rangle$	$\langle ^3\Phi_j\|r\|^3\Phi_{T_1}\rangle$ (Å)	$\frac{e}{\sqrt{2}}\langle ^3\Phi_j\|H_{so}\|^1\Phi_{S_0}\rangle^*$ (10^{-4} eV)	Contribution to $\sqrt{\frac{3\hbar^2}{2\pi} B_{S_0 \to T_1}}$ (Å)
$^3B_{3g}(12n, 16\pi^*)$	4.82	y	0.017	−54.52	−0.1360
$^3B_{3g}(14\pi, 20\sigma^*)$	17.56	y	0.328	−26.43	−0.3491

Table 8b. *Pyrazine* $^3B_{2u}(15n, 16\pi^*)$, $^3E_{T_1} - {}^1E_{S_0} = 2.83$ *eV*

Perturbing $^1\Phi_i$	$^1E_i - {}^3E_T$ (eV)	Direction of $\langle {}^1\Phi_{S_0}\|\boldsymbol{r}\|{}^1\Phi_i\rangle$	$\frac{1}{\sqrt{2}}\langle {}^1\Phi_{S_0}\|\boldsymbol{r}\|{}^1\Phi_i\rangle$ (Å)	$e\langle {}^1\Phi_i\|H_{so}\|{}^3\Phi_{T_1}\rangle$ (10^{-4} eV)	Contribution to $\sqrt{\frac{3\hbar^2}{2\pi}}\boldsymbol{B}_{S_0\to T_1}$ (Å)
$^1B_{3u}(15n, 19\sigma^*)$	7.54	x	0.326	−44.80	−1.3697
$^1B_{3u}(13\pi, 16\pi^*)$	3.13	x	−0.638	− 4.50	0.6486
$^1B_{1u}(14\pi, 16\pi^*)$	3.66	z	0.746	36.59	5.2736
Perturbing $^3\Phi_j$	$^3E_j - {}^1E_{S_0}$ (eV)	Direction of $\langle {}^3\Phi_j\|\boldsymbol{r}\|{}^3\Phi_{T_1}\rangle$	$\langle {}^3\Phi_j\|\boldsymbol{r}\|{}^3\Phi_{T_1}\rangle$ (Å)	$\frac{e}{\sqrt{2}}\langle {}^3\Phi_j\|H_{so}\|{}^1\Phi_{S_0}\rangle$ (10^{-4} eV)	Contribution to $\sqrt{\frac{3\hbar^2}{2\pi}}\boldsymbol{B}_{S_0\to T_1}$ (Å)
$^3B_{3g}(12n, 16\pi^*)$	4.82	z	−1.236	−54.52	9.8859
$^3B_{3g}(15n, 18\pi^*)$	9.23	z	1.104	−61.21	−5.1770
$^3B_{3g}(8\sigma, 16\pi^*)$	8.43	x	0.474	17.65	0.7018
$^3B_{3g}(10\sigma, 16\pi^*)$	6.21	x	−0.075	41.82	−0.3571

In the above symmetry states, those which satisfy the condition;

$$\langle {}^1\Phi_{S_0}|\Sigma \boldsymbol{r}_t|{}^1\Phi_i\rangle \neq 0\,, \qquad \langle {}^3\Phi_j|\Sigma \boldsymbol{r}_t|{}^3A_1(\pi,\pi^*)\rangle \neq 0$$

become

$$^1\Phi_i : {}^1B_1, {}^1B_2\,, \qquad {}^3\Phi_j : {}^3B_1, {}^3B_2\,.$$

The perturbing singlet configurations, $^1\Phi_i$, and the perturbing triplet configurations, $^3\Phi_j$, are listed in the first column in Table 7a. In the same way, the perturbing singlet configuration, $^1\Phi_i$, and the perturbing triplet configurations $^3\Phi_j$ which satisfy the condition:

$$\langle {}^1\Phi_i|H_{so}|{}^3\Phi_{T_1}\rangle \langle {}^1\Phi_{S_0}|\Sigma \boldsymbol{r}_t|{}^1\Phi_i\rangle \neq 0\,,$$
$$\langle {}^3\Phi_j|H_{so}|{}^1\Phi_{S_0}\rangle^* \langle {}^3\Phi_j|\Sigma \boldsymbol{r}_t|{}^3\Phi_{T_1}\rangle \neq 0$$

are reduced by the symmetry as follows.

For the $^3B_1(n,\pi^*)\to S_0$ transition in pyridine, pyrimidine and pyridazine.

$$^1\Phi_i : {}^1B_2, {}^1A_1\,, \qquad {}^3\Phi_j : {}^3A_2, {}^3B_1\,.$$

For the $^3B_{1u}(\pi,\pi^*)\to S_0$ transition in pyrazine,

$$^1\Phi_i : {}^1B_{2u}, {}^1B_{1u}\,, \qquad {}^3\Phi_j : {}^3B_{2g}, {}^3B_{3g}\,.$$

For the $^3B_{2u}(n,\pi^*)\to S_0$ transition in pyrazine,

$$^1\Phi_i : {}^1B_{1u}, {}^1B_{3u}\,, \qquad {}^3\Phi_j : {}^3B_{1g}, {}^3B_{3g}\,.$$

These perturbing configurations are listed in the first column of Tables 7a, 7b, 8a, 8b, 9 and 10 and their contributions to $\boldsymbol{P}_{S_0\to T_1}$ are listed in the last column.

Using the results of a semi-empirical SCF method for valence electron systems, we have calculated the oscillator strengths of $S_0\to T_1$ transitions considering the effects of σ-electrons. The effect of σ-electrons to the $S_0\to T_1$ transition is small in

Table 9. *Pyrimidine* $^3B_1(15n, 16\pi^*)$, $^3E_{T_1} - {}^1E_{S_0} = 3.39$ *eV*

Perturbing $^1\Phi_i$	$^1E_i - {}^3E_T$ (eV)	Direction of $\langle {}^1\Phi_{S_0} \lvert \boldsymbol{r} \rvert {}^1\Phi_i \rangle$	$\frac{1}{\sqrt{2}} \langle {}^1\Phi_{S_0} \lvert \boldsymbol{r} \rvert {}^1\Phi_i \rangle$ (Å)	$e\langle {}^1\Phi_i \lvert H_{so} \rvert {}^3\Phi_{T_1} \rangle$ (10^{-4} eV)	Contribution to $\sqrt{\frac{3\hbar^2}{2\pi} \boldsymbol{B}_{S_0 \to T_1}}$ (Å)
$^1B_2(15n, 19\sigma^*)$	8.59	y	0.577	26.37	1.2525
$^1B_2(13\pi, 16\pi^*)$	2.69	y	−0.717	−17.12	3.2267
$^1B_2(11\pi, 16\pi^*)$	3.88	y	0.053	−29.86	−0.2884
$^1A_1(14\pi, 16\pi^*)$	2.45	z	−0.692	8.63	−1.7236
$^1A_1(15n, 20\sigma^*)$	11.89	z	0.435	−27.91	−0.7220

Perturbing $^3\Phi_j$	$^1E_j - {}^1E_{S_0}$ (eV)	Direction of $\langle {}^1\Phi_j \lvert \boldsymbol{r} \rvert {}^3\Phi_{T_1} \rangle$	$\langle {}^3\Phi_j \lvert \boldsymbol{r} \rvert {}^3\Phi_{T_1} \rangle$ (Å)	$\frac{e}{\sqrt{2}} \langle {}^3\Phi_j \lvert H_{so} \rvert {}^1\Phi_{S_0} \rangle^*$ (10^{-4} eV)	Contribution to $\sqrt{\frac{3\hbar^2}{2\pi} \boldsymbol{B}_{S_0 \to T_1}}$ (Å)
$^3A_2(15n, 17\pi^*)$	4.39	y	0.070	−23.87	−0.2691
$^3A_2(15n, 18\pi^*)$	9.14	y	−1.369	−54.29	5.7500
$^3A_2(12n, 16\pi^*)$	3.96	y	−0.902	−19.44	3.1311
$^3A_2\ (9\pi, 16\pi^*)$	6.69	y	−0.455	32.65	−1.5702
$^3A_2\ (7\sigma, 16\pi^*)$	8.33	y	−0.143	7.97	−0.1368
$^3B_1\ (8\sigma, 16\pi^*)$	6.99	z	−0.047	18.79	−0.0893
$^3B_1(10\sigma, 16\pi^*)$	6.06	z	0.847	37.89	3.7448

Table 10. *Pyridazine* $^3B_1(15n, 16\pi^*)$, $^3E_{T_1} - {}^1E_{S_0} = 3.31$ *eV*

Perturbing $^1\Phi_i$	$^1E_i - {}^3E_T$ (eV)	Direction of $\langle {}^1\Phi_{S_0} \lvert \boldsymbol{r} \rvert {}^1\Phi_i \rangle$	$\frac{1}{\sqrt{2}} \langle {}^1\Phi_{S_0} \lvert \boldsymbol{r} \rvert {}^1\Phi_i \rangle$ (Å)	$e\langle {}^1\Phi_i \lvert H_{so} \rvert {}^3\Phi_{T_1} \rangle$ (10^{-4} eV)	Contribution to $\sqrt{\frac{3\hbar^2}{2\pi} \boldsymbol{B}_{S_0 \to T_1}}$ (Å)
$^1B_2(11\pi, 16\pi^*)$	4.26	y	−0.137	−11.60	0.2638
$^1B_2(14\pi, 16\pi^*)$	2.81	y	0.638	6.61	1.0612
$^1B_2(15n, 20\sigma^*)$	13.25	y	−0.394	−17.27	0.3217
$^1A_1(15n, 18\sigma^*)$	6.31	z	0.496	−26.93	−2.1168
$^1A_1(12\pi, 16\pi^*)$	3.23	z	−0.519	21.81	−2.4780

Perturbing $^3\Phi_j$	$^3E_j - {}^1E_{S_0}$ (eV)	Direction of $\langle {}^3\Phi_j \lvert \boldsymbol{r} \rvert {}^3\Phi_{T_1} \rangle$	$\langle {}^3\Phi_j \lvert \boldsymbol{r} \rvert {}^3\Phi_{T_1} \rangle$ (Å)	$\frac{e}{\sqrt{2}} \langle {}^3\Phi_j \lvert H_{so} \rvert {}^1\Phi_{S_0} \rangle$ (10^{-4} eV)	Contribution to $\sqrt{\frac{3\hbar^2}{2\pi} \boldsymbol{B}_{S_0 \to T_1}}$ (Å)
$^3A_2(15n, 17\pi^*)$	3.78	y	0.308	9.93	0.5721
$^3A_2(13n, 16\pi^*)$	4.32	y	−0.090	−42.18	0.6214
$^3A_2(10\sigma, 16\pi^*)$	6.29	y	0.488	−33.68	−1.8477
$^3A_2\ (9\sigma, 16\pi^*)$	6.97	y	0.306	9.51	0.2952
$^3B_1(15n, 19\pi^*)$	9.07	z	−1.018	35.27	−2.7992
$^3B_1\ (8\sigma, 16\pi^*)$	7.72	z	0.576	− 8.32	−0.4390

the cases of pyridine and pyrazine, but is not negligible in the cases of pyrimidine and pyridazine as seen in Table 7a–10. The oscillator strengths and the polarizations of the $S_0 \rightarrow T_1$ transitions are listed in Table 11. The polarizations of the $T_1 \rightarrow S_0$ emissions in pyrazine and pyrimidine [7, 14] which have been experimentally determined are along the z-axis in Fig. 2. The present theoretical treatment predicts that the polarizations for the $^3B_1(n, \pi^*) \rightarrow S_0$ transitions in pyrazine and pyrimidine are both mainly along the z-axes in agreement with experiment. The polarization of a $n \rightarrow \pi^*$ $S_0 \rightarrow T_1$ transition is in the molecular plane and the polarization of a $\pi \rightarrow \pi^*$ $S_0 \rightarrow T_1$ transition is perpendicular to the molecular plane. Generally, the (n, π^*) triplet state has stronger radiative power than a (π, π^*) triplet [4, 21, 16]. The small power of the (π, π^*) triplet state is mainly due to the small values of the transition moments of the (n, π^*) and (σ, π^*) transitions (Tables 7d, 8a). In spite of this fact, our calculated oscillator strength of the $^3B_{2u}(n, \pi^*) \rightarrow S_0$ transition in pyrazine is very large.

Table 11. *The oscillator strength, the life time and the polarization of the* $S_0 \rightarrow T_1$ *transition*

Molecule	Triplet state	Direction of $\langle \boldsymbol{r} \rangle$	$(f_{T_1 \rightarrow S_0})_i$	$f_{T_1 \rightarrow S_0}$ and life time: τ	Observed
Pyridine	$^3A_1(\pi, \pi^*)$	x	$0.16 \cdot 10^{-8}$	$0.16 \cdot 10^{-8}$ 1.5378 sec	
	$^3B_1(n, \pi^*)$	z	$18.04 \cdot 10^{-8}$	$19.08 \cdot 10^{-8}$	
		y	$1.04 \cdot 10^{-8}$	0.0120 sec	
Pyrazine	$^3B_{1u}(\pi, \pi^*)$	y	$88.91 \cdot 10^{-8}$	$88.91 \cdot 10^{-8}$ 0.0026 sec	
	$3B_{2u}(n, \pi^*)$	x	$0.04 \cdot 10^{-8}$	$24.72 \cdot 10^{-8}$	$f_{T_1 \rightarrow S_0} \sim 10^{-7}$ [a]
		z	$24.68 \cdot 10^{-8}$	0.0148 sec	$\tau = 0.02$ sec z-polalized
Pyrimidine	$^3B_1(n, \pi^*)$	y	$36.52 \cdot 10^{-8}$	$36.95 \cdot 10^{-8}$	$\tau = 0.01$ [b]
		x	$0.43 \cdot 10^{-8}$	0.0069 sec	0.02 y-polalized
Pyridazine	$^3B_1(n, \pi^*)$	z	$17.77 \cdot 10^{-8}$	$18.25 \cdot 10^{-8}$	$f_{T_1 \rightarrow S_0} > 5 \cdot 10^{-8}$ [c]
		y	$0.48 \cdot 10^{-8}$	0.0146 sec	$\tau < 0.05$ sec

[a] Goodman, L., and M. Kasha: J. molecular Spectroscopy **2**, 58 (1958).

[b] Shimada, R.: Spectrochim. Acta **17**, 30 (1961). — Goodman, L., and V. G. Krishna: Rev. Mod. Physics **35**, 541 (1963).

[c] Hochstrasser, R. M., and C. Marzzacco: J. chem. Physics **46**, 4155 (1967).

If this energy difference is 1.0 eV, the calculated oscillator strength, 88.91×10^{-8} becomes 1.12×10^{-8}. The life times are calculated to be 1.538 sec and 0.012 sec for the $^3A_1(\pi, \pi^*) \rightarrow {}^1A_1$ and the $^3B_1(n, \pi^*) \rightarrow {}^1A_1$ emission of pyridine, 0.003 sec and 0.015 sec for the $^3B_1(\pi, \pi^*) \rightarrow {}^1A_g$ and the $^3B_{2u}(n, \pi^*) \rightarrow {}^1A_g$ emission of pyrazine, 0.007 sec and 0.015 sec for the $^3B_1(n, \pi^*) \rightarrow {}^1A_1$ emission of pyrimidine and pyridazine, respectively. The life time (τ) is calculated by the equation [13]:

$$\tau = \frac{4.500}{\sigma^2 f_{T_1 \rightarrow S_0}} \quad \sigma\text{: wave number } (\mathrm{cm}^{-1}). \tag{8}$$

As to the oscillator strength $f_{T_1 \to S_0}$, the sum of the two components for the $^3B(n, \pi^*) \to S_0$ transition is used as is seen in Table 11. Goodman and Krishna [9] calculated the life times of the emission of the two components separately. As in these compounds, the spin-lattice relaxation time T_1 will be very small [2] in the usual experimental temperature range, so that one component of the emission vanishes, the other component of the emission vanishes, too. Accordingly, it will be fairly resonable to use $f_{T_1 \to S_0}$ consisting of the two components of the $^3B(n, \pi^*) \to S_0$ emission.

The calculations are carried out on a Hitac 5020 computer at the computation center of the University of Tokyo.

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Dr. T. Yonezawa
Department of Hydrocarbon Chemistry
Kyoto University
Kyoto, Japan