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Calculations of Singlet and Triplet States of Some Azabenzenes by Modified INDO – CI*

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Transition energies, ionization potentials, dipole moments and oscillator strengths have been calculated for pyridine, pyrazine, pyrimidine, pyridazine, 3-cyanopyridine and 4-cyanopyridine by modified INDO-CI. Triplet radiative lifetimes have been calculated for these molecules.

Key words: Ionization potential – Oscillator strength – Spin-orbit coupling – Azabenzenes

1. Introduction

Semi-empirical SCF all-valence-electron calculations to estimate transition energies of nitrogen-containing heterocyclic compounds have been performed by several authors. Del Bene and Jaffé's CNDO – CI calculations [1, 2] does not provide $S-T$ splitting for $n \rightarrow \pi^*$ transitions. Giessner-Prettre and Pullman [3] have used the INDO method with original parameterization [4] to calculate the transition energies of pyridine. The INDO method does give the $S-T$ splitting, although the calculated values were too large. Yonezawa *et al.* [5] performed semi-empirical calculations on some azabenzenes taking all overlap integrals into account explicitly. *Ab initio* SCF MO calculations for the ground state of pyridine and pyrazine have been made by Clementi [6, 7] and by Petke *et al.* [8]. In the present work, using a modified INDO – CI method, the transition energies, oscillator strengths, ionization potentials and dipole moments are calculated and compared with existing experimental data.

Previous treatments of spin-orbit interaction in the singlet-triplet forbidden transitions of azines [9 – 12] always took the lone pair (n) orbital as a localized hybrid orbital at the nitrogen atom. Yonezawa *et al.* [5] have studied the azabenzenes considering both of σ and π MO's explicitly. In the present work, using the spin-orbit coupling (SOC) perturbation on the INDO – CI wavefunctions, the singlet-triplet transition probabilities, the major sources of its intensity and the lifetimes of the triplet states are studied.

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2. Calculations

Ground State

The INDO method in its original parameterization was unable to give good transition energies without some refinement, and some (σ, π) transitions were inserted between the different (π, π^*) states. Our INDO calculations with some modifications of the original parameterization give improved results. These modifications are described as follows:

The monocenter coulombic integrals are the same those used by Yamaguchi and Fueno [13]. The parameters (γ_{AA}) for hydrogen, carbon and nitrogen are 12.845, 11.715 and 12.860 respectively.

To evaluate the two-center coulombic integrals, γ_{AB}, we use a modified Mataga and Nishimoto type algorithm. The formula is

$$\gamma_{AB} = \langle \mu\mu | \nu\nu \rangle = \frac{e^2}{R_{AB}/0.529167 + a \cdot \exp(-bR^c_{AB})}$$

where e is the electronic charge; R_{AB} is in Å units; the factor $\exp(-bR^c_{AB})$ is added to cause the integral curve to fall off with increasing distance R_{AB}; b and c are determined for different atomic centers of A and B and are listed in Table 1. Parameter a is determined using the valence state ionization potential I_μ and electron affinity A_μ in the same valence state as follows:

(i) For the case of homonuclear interaction, we use a as did Mataga and Nishimoto.

(ii) For the case of heteronuclear interaction, we take the weighted average value,

$$\frac{e^2}{a} = \frac{\delta_A \gamma_{AA} + \delta_B \gamma_{BB}}{\delta_A + \delta_B}$$

where δ's are the atomic orbital exponents by Slater's rule.

The resonance integrals are taken the same as formulated by Jaffe [1].

$$\tfrac{1}{2} k \, (\beta^0_A + \beta^0_B) \, S_{\mu\nu}$$

where the factor k is used to separate the σ and π type overlap integrals. For σ levels the value of k is unity, for π levels the value of k found more suitable in our calculation is 0.595. The bonding parameters β^0_A are 9 eV for hydrogen (the original CNDO value), 17 eV and 26 eV for carbon and nitrogen (the Jaffé's values) respectively.

The terms, $-\frac{1}{2}(I_\mu + A_\mu)$, of the core integrals are taken from Hinze and Jaffe's valence state data, except that the $2p_z$ integral was decreased to decrease the stability of π-bonding; see Table 2.

Table 1. The constants in the exponential factor $\exp(-bR^c)$ for computation of γ_{AB}

Atomic center constants	N−N	N−C	N−H	C−C	C−H	H−H
b	0.8250	0.7964	0.8125	0.7713	0.7843	0.9730
c	0.7	0.68	0.7	0.7	0.7	0.5

Table 2. Some parameters in the INDO matrix elements (eV)

Atom	$-1/2\,(I_\mu+A_\mu)$			G^1	F^2
	s	$p_{x,y}$	p_z		
C Original INDO	14.051	5.572	5.572	7.284	4.727
This work	14.960	5.805	5.000	6.180	3.886
N Original INDO	19.316	7.275	7.275	9.416	5.961
This work	19.536	7.550	6.250	7.750	5.070

Early attempts to utilize INDO with Jaffé's parameterization and the values of G^1 and F^2 given in original INDO paper [4] placed the n orbital higher than occupied π orbitals in pyridine molecule. This disagrees with the non-empirical results [6, 8] and the measured ionization potential definitely favours the π nature of the first ionization [19]. To overcome this difficulty, we used smaller values of G^1 and F^2 to increase the delocalization of n electrons and to get better results in spectroscopic properties. The values of G^1 and F^2 are given in Table 2.

Excited State Transitions and Intensities

The excited states are generated by CI [14] among configurations formed by single electron excitation from occupied MO's into unoccupied or virtual orbitals determined in the ground state calculation. The number of configurations to be treated in the CI matrix is limited by a preset energy criterion. The energy criterion is usually between 9 and 10 eV or high enough to contain some (σ, π) transitions. Good agreement of calculated excited state energies with experiment is the criterion used to optimize the parametrization in the ground state basis functions.

The effect of SOC in organic systems is small enough to be treated by the first-order perturbation theory. McClure's [15, 16] central-field approximation is used in which the spin-orbit interaction for light atoms is expressed as:

$$H_{so}=\sum_i A_i l_i \cdot s_i$$

In the present treatment we shall need the expectation values of the spin-orbit interaction over the radial part of the $2p$ atomic orbitals. The integral is:

$$\xi_k=\hbar^2\langle A_{ik}\rangle_{av}\,.$$

The values of ξ_k for carbon and nitrogen are taken from Hartree-Fock atomic parameters [17] and are $\xi_C=31.95\,\mathrm{cm}^{-1}$ and $\xi_N=75.59\,\mathrm{cm}^{-1}$ respectively.

3. Results and Discussion

Orbital Energies and Ionization Potentials

The molecular orbital energies, bond orders and charge densities calculated by the present method are listed and discussed in the Chapter IV of Ref. [18]. The predicted molecular vertical ionization potentials (IP) via Koopmans'

Table 3. Calculated and observed dipole moments (Debyes)

Molecule	Calc.			Obs.
	D_{ch}	D_A	D_t	
Pyridine	0.91	1.73	2.64	2.21[a]
Pyrazine	0.0	0.0	0.0	0.0
Pyrimidine	0.96	1.79	2.75	2.40[b]
Pyridazine	1.83	3.27	5.10	3.97[b]
3-cyanopyridine	$2.33x$	$2.06x$	$4.39x$	—
	$-0.37y$	$0.83y$	$0.46y$	
4-cyanopyridine	1.58	0.28	1.86	—

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theorem are in reasonable agreement with the experimental data. The IP's of non-bonding electron for pyridine, pyrazine, pyrimidine and pyridazine are 10.89, 11.01, 10.76 and 11.00 eV comparing with the observed values 10.45, 10.15, 9.42 and 8.91 eV respectively. The IP's of non-bonding electron for 3-cyano and 4-cyano pyridines are 11.26 and 11.24 eV respectively.

Dipole Moments

The total electronic dipole moments are divided into two parts,

$$D_t = D_{ch} + D_a$$

where the term D_{ch} represents the contribution due to the formal charges and the term D_A is the one form atomic polarization resulting from mixing of the $2s$ and $2p$ orbitals in same atom.

Our calculated values agree satisfactorily with the experimental data, and have the same relative ordering as obtains experimentally; see Table 3.

Excitation Energies

Table 4 represents the calculated results for some lower excitation energies ΔE and oscillator strengths f. The calculated lower $n \rightarrow \pi^*$ and $\pi \rightarrow \pi^*$ transition energies are in good agreement with experimental data except for the lowest $n \rightarrow \pi^*$ transitions in pyrazine and pyridazine. The calculated singlet-triplet splitting in the lowest $n \rightarrow \pi^*$ and $\pi \rightarrow \pi^*$ transitions are reasonable in comparison with observed values.

Recently, Hoover and Kasha [20] concluded that the lowest triplet of pyridine is in fact $n \rightarrow \pi^*$ and not $\pi \rightarrow \pi^*$, and from the phosphorescence in ethanol glass at 77° K, the lowest triplet was assigned to be $^3A_1(\pi, \pi^*)$ for 3-cyanopyridine and $^3B_1(n, \pi^*)$ for 4-cyanopyridine. This is in agreement with the results obtained in this work.

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

	Calc.		Obs.			Calc.		Obs.	
	ΔE	f	ΔE	f		ΔE	f	ΔE	f
Pyridine					Pyrazine				
$^1\underline{B}_1$	4.22	0.045	4.31	0.003^{a}	$^1\underline{B}_{3u}$	3.28	0.08	3.83	0.01^{c,a}
$^1B_2$	5.00	0.013	4.75	0.04^{a}	$^1B_{2u}$	4.61	0.05	4.69	0.1^{a}
$^1A_1$	5.61	0.001	6.17	0.2^{b,c}	$^1B_{1u}$	5.39	0.0003	4.81	weak^{a}
$^1A_1$	7.26	0.01			$^1\underline{\underline{B}}_{1u}$	7.06	0.016	6.31	0.15^{e,a}
$^1B_2$	7.68	0.55	6.82	1.3^{b,c}	$^1B_{2u}$	7.65	0.514	7.52	1.0^{e}
$^1\underline{\underline{B}}_1$	7.69	0.083			$^3\underline{B}_{3u}$	2.82		3.32^{f}	
$^3\underline{B}_1$	3.58		3.68^{d}		$^3B_{2u}$	3.41			
$^3A_1$	3.66				$^3B_{1u}$	3.43			
$^3B_2$	4.12								
Pyrimidine					Pyridazine				
$^1\underline{B}_1$	3.89	0.076	3.85	0.0069^{e,c}	$^1\underline{B}_1$	3.92	0.115	3.30	0.0058^{e,c}
$^1\underline{A}_2$	5.19	0.0002			$^1A_1$	5.50	0.008	4.90	0.02^{c}
$^1B_2$	5.21	0.01	5.00	0.052^{c}	$^1\underline{\underline{B}}_1$	5.65	0.019		
$^1A_1$	5.81	0.01	6.34	0.005^{f}	$^1B_2$	5.78	0.0038	6.2	0.10^{c}
$^1\underline{B}_1$	6.06	0.0031	6.49	0.016^{c}	$^1B_2$	7.52	0.22	7.10	1.0^{f}
$^1A_1$	7.47	0.13	7.25	1.0^{f}	$^1A_1$	7.58	0.06		
$^1B_2$	7.50	0.0054			$^3\underline{B}_1$	3.39		3.01^{h}	
$^3\underline{B}_1$	3.56		3.63^{g}		$^3B_2$	3.81			
$^3\underline{A}_2$	3.98				$^3\underline{A}_2$	3.93			
$^3A_1$	4.02								
3-Cyanopyridine					4-Cyanopyridine				
$^1\underline{A}''$	4.36	0.029	4.4^{a}	weak	$^1\underline{B}_1$	4.03	0.028	3.99	—
$^1\underline{A}''$	4.93	0.0002			$^1B_2$	4.98	0.027	4.6^{b}	(2840)
$1A'$	5.01	0.019	4.7^{i}	(2230)	$^1A_1$	6.88	0.27		
$^1A'$	7.14	0.37			$^1B_2$	7.40	0.33		
$^1A'$	7.31	0.39			$^1\underline{\underline{B}}_1$	7.46	0.052		
$^3A'$	3.68		3.34^{j}		$^3\underline{B}_1$	3.66	3.30^{j}		
$^3\underline{A}''$	3.85				$^3A_1$	3.72			
$^3A'$	4.13				$^3B_2$	3.99			

Underline denotes $n \rightarrow \pi^*$ type state; double underline denotes $\sigma \rightarrow \pi^*$ type state; the rest are $\pi \rightarrow \pi^*$ type states

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Spin-orbit Coupling Mechanism

The contributions to the singlet-triplet transition moment by the perturbing singlet and triplet states are obtained by a spin-orbit coupling (SOC) perturbation calculation between singlet and triplet manifolds after CI and summed [18].

For the transition of ${}^3B_1(n,\pi^*)\rightarrow S_0$ in the molecules having symmetry of the C_{2v} point group, such as pyridine, pyrimidine, pyridazine and 4-cyanopyridine, the perturbing singlet and triplet states are in the symmetry of ${}^1B_2$, ${}^1A_1$, ${}^3A_2$ and ${}^3B_1$.

In D_{2h} symmetry (pyrzaine), the perturbing states for ${}^3B_{3u}$ $(n,\pi^*)\rightarrow S_0$ are ${}^1B_{1u}$, ${}^1B_{3u}$, ${}^3B_{3g}$ and ${}^3B_{1g}$. For the ${}^3A'$ $(\pi,\pi^*)\rightarrow S_0$ in 3-cyanopyridine, which has the symmetry of C_s point group, the perturbing states are ${}^1A''$ and ${}^3A''$.

As is to be expected, the polarization of the transition ${}^3(\pi,\pi^*)\rightarrow S_0$ is perpendicular to the molecular plane, while the polarization of ${}^3(n,\pi^*)\rightarrow S_0$ is parallel to the molecular plane. For pyrazine and pyrimidine the transitions are polarized mainly along the N−N axes in agreement with experimental results [21, 22].

It is interesting to note that the contribution to the singlet-triplet transition is found to be from the component, $r=+1$ and $r=-1$, of the triplet state wavefunction. No contribution to $T_1\rightarrow S_0$ is found from $r=0$ component of triplet states.

The Radiative Lifetimes of Triplet State

The radiative lifetimes of triplet states are calculated by using the Mulliken approximation [23],

$$\tau=\frac{4.5}{v^2\sum_r f^r}\qquad (r=+1,\ -1\ \text{or}\ 0)$$

and are given in Table 5 along with experimental estimated values.

It is generally known that the values calculated from this approximation are not directly comparable to the observed values. Competing radiationless processes usually will cause the observed lifetime to be shorter than the calculated lifetime.

Table 5. Radiative lifetimes of the triplet states

Molecule	Triplet states	Calc. (sec.)	Obs. (sec.)
Pyridine	${}^3B_1(n,\pi^*)$	0.054 y	—
Pyrazine	${}^3B_{3u}(n,\pi^*)$	0.052 y	0.02[a]
Pyrimidine	${}^3B_1(n,\pi^*)$	0.072 y	0.01 – 0.02[b]
Pyridazine	${}^3B_1(n,\pi^*)$	0.050 y	0.05[c]
3-Cyanopyridine	${}^3A'(\pi,\pi^*)$	53.5 z	3.3[d]
4-Cyanopyridine	${}^3B_1(n,\pi^*)$	0.038 y	0.004[d]

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