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MCNDO/2 Calculation of the Radiative Lifetimes of the Triplet States of the Nucleic Acid Bases

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Synopsis. The radiative lifetimes of the lowest excited triplet states of the nucleic acid bases were calculated using a first-order perturbation treatment of the spin-orbit coupling. The calculated lifetimes were in the sequence of pyrimidines > purines; that of thymine was found to be largest. The relation between the radiative lifetimes and biological photodeactivation was discussed.

The electronic properties of the triplet states of the nucleic acid bases are of biological interest. A few experiments have suggested that the excited triplet states, in particular those of the pyrimidine bases, are responsible for the biological photodeactivation of the nucleic acids,[1–4] though the excited singlet states are also assumed to work as precursors in the energy-transfer process.[5] Taking notice of such characteristics of the triplet states, SCFCI and UHF calculations have been carried out for the energy states and electronic populations of the lowest triplets of the nucleic acid bases.[6]

Here, an attempt was made to estimate the radiative lifetimes of the lowest excited triplet states of the nucleic acid bases. That is, the singlet-triplet transition probability induced by spin-orbit coupling was calculated by a first-order perturbation method. The calculation was done according to the all-valence-electron SCF method of Jaffe *et al.*[7] The electric-dipole transition moment between the ground and lowest triplet states is given as:

$$\mathbf{M}(0,\Gamma_r)=\sum_k\{[\langle{}^1\Phi_k|H_{so}|{}^3\Phi_1^{\Gamma_r}\rangle^*/({}^3E_1-{}^1E_k)]\mathbf{M}({}^1\Phi_0,{}^1\Phi_k)\}$$
$$+\sum_m\{[\langle{}^3\Phi_m^{\Gamma_r}|H_{so}|{}^1\Phi_0\rangle/({}^1E_0-{}^3E_m)]\mathbf{M}({}^3\Phi_1^{\Gamma_r},{}^3\Phi_m^{\Gamma_r})\}$$

where Γ_r is the component of the triplet spin functions. It is chosen as:

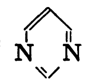
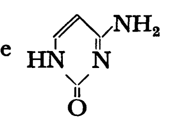
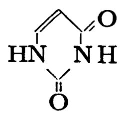
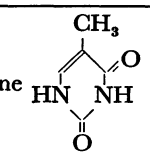
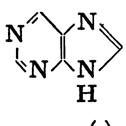
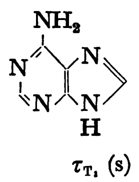
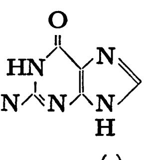
$$\Gamma_-:\ [\alpha(p)\alpha(q)-\beta(p)\beta(q)]$$
$$\Gamma_z:\ [\alpha(p)\beta(q)+\alpha(q)\beta(p)]$$
$$\Gamma_+:\ i[\alpha(p)\alpha(q)+\beta(p)\beta(q)]$$

The unperturbed wave function was calculated by the modified CNDO/2 method; the parameters used (in eV units) were as follows:

$-1/2(I_s+A_s)$: 7.176(H), 14.051(C), 19.316(N), 25.390(O)
$-1/2(I_p+A_p)$: 5.572(C), 7.275(N), 9.111(O)
γ_{AA}: 12.845(H), 11.089(C), 12.016(N), 13.599(O)
$\beta_A{}^0$: −12(H), −17(C), −26(N), −45(O)

The two-center Coulomb integral was calculated by the Ohno approximation.[8] The geometries of the heterocyclic rings were assumed as regular hexagon and pentagon, both with the ring-distance of 1.39 Å. The other bond-lengths were chosen as $R_{>\text{C-H}}=1.08$ Å, $R_{>\text{C-NH}_2}=1.34$ Å, $R_{>\text{N-H}}=1.03$ Å, $R_{>\text{C=O}}=1.20$ Å, $R_{>\text{C-CH}_3}=1.51$ Å, and $R_{>\text{C-H}}=1.12$ Å. The atomic

TABLE 1. CALCULATED RESULTS OF THE RADIATIVE LIFETIME OF THE LOWEST EXCITED TRIPLET OF THE NUCLEIC ACID BASES

	pyrimidine 		cytosine 		uracil 		thymine 	
spin state	$f_{T_1\to G}$	τ_{T_1} (s)	$f_{T_1\to G}$	τ_{T_1} (s)	$f_{T_1\to G}$	τ_{T_1} (s)	$f_{T_1\to G}$	τ_{T_1} (s)
Γ_-	0.19×10^{-9}	4.37	0.32×10^{-9}	2.72	0.70×10^{-9}	1.22	0.31×10^{-9}	3.32
Γ_z	0.13×10^{-9}	6.42	0.17×10^{-10}	52.75	0.20×10^{-10}	44.18	0.16×10^{-10}	62.23
Γ_+	0.59×10^{-9}	1.46	0.22×10^{-7}	0.04	0.11×10^{-8}	0.80	0.26×10^{-9}	3.95
		Av. 4.08		Av. 18.50		Av. 15.40		Av. 23.16
	9H-purine 		adenine 		guanine 			
spin state	$f_{T_1\to G}$	τ_{T_1} (s)	$f_{T_1\to G}$	τ_{T_1} (s)	$f_{T_1\to G}$	τ_{T_1} (s)		
Γ_-	0.35×10^{-8}	0.27	0.24×10^{-8}	0.36	0.33×10^{-8}	0.25		
Γ_z	0.25×10^{-8}	0.38	0.38×10^{-9}	2.28	0.10×10^{-8}	0.83		
Γ_+	0.62×10^{-9}	1.53	0.11×10^{-8}	0.81	0.62×10^{-8}	0.14		
		Av. 0.73		Av. 1.15		Av. 0.40		

parameters in the spin-orbit Hamiltonian (H_{SO}), which represent the effective electric field acting on the electron, were adopted from the atomic data;[9] 28 cm^{-1} for C, 70 cm^{-1} for N, and 152 cm^{-1} for O. The perturbation calculations were done by mixing the lowest 25 excited states.

The calculated results on the oscillator strength of the S–T transition and radiative lifetime of the lowest triplets are given in Table 1. The average value of the calculated lifetimes of the triplet components is largest in thymine. Admitting that the radiative lifetime does not necessarily play an important role in the photodimerization reaction, which proceeds under severe steric restrictions, this finding is of interest because thymine in irradiated nucleic acids undergoes an efficient dimerization. A low-temperature experiment at 77 K indicates that the lifetimes of the phosphorescence of adenine and guanine residues are 2.5 and 1.25 s respectively.[10] In this case, the agreement between the predicted and experimental data is considerably good. On the whole, this calculation shows that the radiative lifetimes of the triplet pyrimidine bases are rather longer than those of the triplet purine bases.

The numerical calculation was performed using a HITAC 5020–E and 8800/8700 Computers at the University of Tokyo. The authors wish to thank Dr. Fumihiko Hirota of Shizuoka University for his useful discussion and advice.

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