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COMPARISON ON EMISSION SPECTRA OF DI-PYRIDYL-KETONE AND DI-PYRIDYL-AMINE

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ABSTRACT

It has been well understood that presence of heteroatom influences the photophysical and photochemical behaviour of aromatic molecules. Different rate constants of aromatic molecules changes due to presence of different nπ and ππ* interactions. Increased spin-orbit coupling due to the heavy atom effect or the occurrence of an* $^3n\pi^* \rightarrow S_0$ *transition will enhance the value of non radiative rate constant.*

Keywords: *Spin-orbit coupling, Phosphorescence spectra, heavy atom effect, triplet state life time.*

Introduction

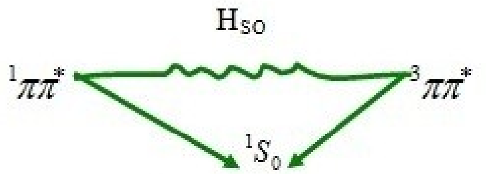
A molecule undergoes transitions from the ground electronic state to higher electronic excited singlet states. The deactivation of the molecule takes place either via radiative or via radiationless pathways. The transition to the ground state by radiative pathway is called fluorescence and non radiative pathway called internal conversion. The non radiative transition from singlet to triplet state is called intersystem crossing. The radiative deactivation from the lowest triplet state to the ground state is called Phosphorescence [1-7].

Phosphorescence:

Different mechanisms through which phosphorescence occur are discussed below**.**

Mechanism-I:

$$\left\langle {}^3\pi\pi^* \left| \overline{M} \right| {}^1S_0 \right\rangle = \frac{\left\langle {}^3\pi\pi^* \left| H_{SO} \right| {}^1\pi\pi^* \right\rangle}{\left| E\left({}^3\pi\pi^*\right) - E\left({}^1\pi\pi^*\right) \right|} \left\langle {}^1\pi\pi^* \left| \overline{M} \right| {}^1S_0 \right\rangle$$



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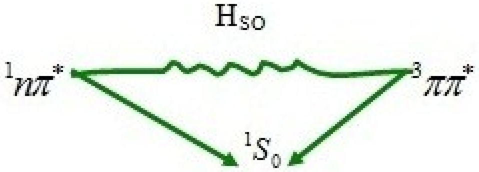
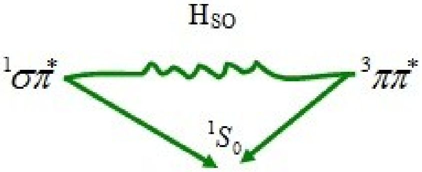
Mechanism-II:

$$\left\langle {}^{3}\pi\pi^{*}\left|\vec{M}\right|{}^{1}S_{0}\right\rangle = \frac{\left\langle {}^{3}\pi\pi^{*}\left|H_{SO}\right|{}^{1}n\pi^{*}\right\rangle}{\left|E\left({}^{3}\pi\pi^{*}\right)-E\left({}^{1}n\pi^{*}\right)\right|}\left\langle {}^{1}n\pi^{*}\left|\vec{M}\right|{}^{1}S_{0}\right\rangle$$



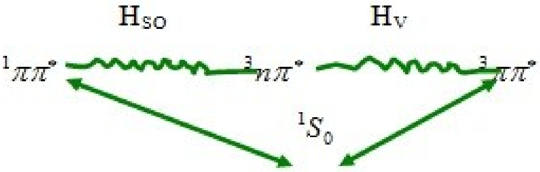
Mechanism-III:

$$\left\langle {}^{3}\pi\pi^{*}\left|\vec{M}\right|{}^{1}S_{0}\right\rangle = \frac{\left\langle {}^{3}\pi\pi^{*}\left|H_{SO}\right|{}^{1}\sigma\pi^{*}\right\rangle}{\left|E\left({}^{3}\pi\pi^{*}\right)-E\left({}^{1}\sigma\pi^{*}\right)\right|}\left\langle {}^{1}\sigma\pi^{*}\left|\vec{M}\right|{}^{1}S_{0}\right\rangle$$



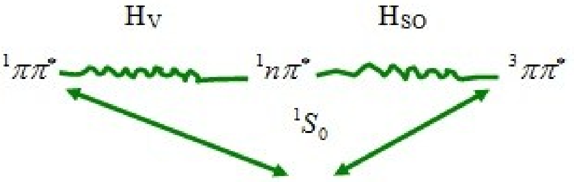
Mechanism-IV:

$$\left\langle {}^{3}\pi\pi^{*}\left|\vec{M}\right|{}^{1}S_{0}\right\rangle = \frac{\left\langle {}^{3}\pi\pi^{*}\left|H_{V}\right|{}^{3}n\pi^{*}\right\rangle\left\langle {}^{3}n\pi^{*}\left|H_{SO}\right|{}^{1}\pi\pi^{*}\right\rangle}{\left|E\left({}^{3}\pi\pi^{*}\right)-E\left({}^{3}n\pi^{*}\right)\right|\left|E\left({}^{3}\pi\pi^{*}\right)-E\left({}^{1}\pi\pi^{*}\right)\right|}\left\langle {}^{1}\pi\pi^{*}\left|\vec{M}\right|{}^{1}S_{0}\right\rangle$$



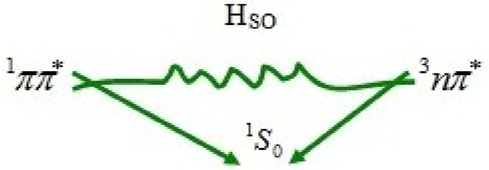
Mechanism-V:

$$\left\langle {}^{3}\pi\pi^{*}\left|\vec{M}\right|{}^{1}S_{0}\right\rangle = \frac{\left\langle {}^{3}\pi\pi^{*}\left|H_{SO}\right|{}^{1}n\pi^{*}\right\rangle\left\langle {}^{1}n\pi^{*}\left|H_{V}\right|{}^{1}\pi\pi^{*}\right\rangle}{\left|E\left({}^{3}\pi\pi^{*}\right)-E\left({}^{1}n\pi^{*}\right)\right|\left|E\left({}^{3}\pi\pi^{*}\right)-E\left({}^{1}\pi\pi^{*}\right)\right|}\left\langle {}^{1}\pi\pi^{*}\left|\vec{M}\right|{}^{1}S_{0}\right\rangle$$



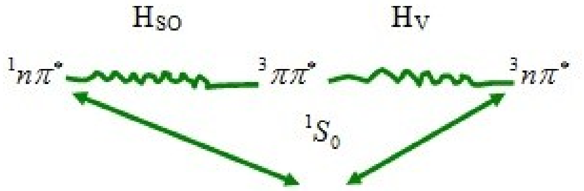
Mechanism-VI:

$$\left\langle {}^{3}n\pi^{*}\left|\overline{M}\right|{}^{1}S_{0}\right\rangle = \frac{\left\langle {}^{3}n\pi^{*}\left|H_{SO}\right|{}^{1}\pi\pi^{*}\right\rangle}{\left|E\left({}^{3}n\pi^{*}\right)-E\left({}^{1}\pi\pi^{*}\right)\right|}\left\langle {}^{1}\pi\pi^{*}\left|\overline{M}\right|{}^{1}S_{0}\right\rangle$$



Mechanism VII:

$$\left\langle {}^{3}n\pi^{*}\left|\overline{M}\right|{}^{1}S_{0}\right\rangle = \frac{\left\langle {}^{3}n\pi^{*}\left|H_{V}\right|{}^{3}\pi\pi^{*}\right\rangle\left\langle {}^{3}\pi\pi^{*}\left|H_{SO}\right|{}^{1}n\pi^{*}\right\rangle}{\left|E\left({}^{3}n\pi^{*}\right)-E\left({}^{3}\pi\pi^{*}\right)\right|\left|\left({}^{3}n\pi^{*}\right)-E\left({}^{1}n\pi^{*}\right)\right|}\left\langle {}^{1}n\pi^{*}\left|\overline{M}\right|{}^{1}S_{0}\right\rangle$$



Discussion

In the present work phosphorescence spectra of Di-pyridyl-ketone and Di-pyridyl-amine have been compared.

Phosphorescence Life Time, Quantum Yield and Different Rate Constants

Molecule	In EtOH solution			
	T_p (in ms)	Φ_p	K_p in s^{-1}	K_{np} in s^{-1}
DPK	6.36	0.20	31	126

On the assumption of $\varphi_T = 1$ and $K_s = K_{ns} = 0$, above constants are determined from the well known formulae $K_p = 1/\tau_p^{o} = \varphi_p/\varphi_T \,.\, \tau_p$ and $K_{np} = (1 - \varphi_p)/\varphi_T \,.\, \tau_p$. Here K_s and K_{ns} are the fluorescence radiative and non radiative rate constants, K_p and K_{np} are the phosphorescence radiative and non radiative rate constants, φ_T and φ_p are triplet state and phosphorescence quantum yields, τ_p is the phosphorescence life time and τ_p^{o} is the intrinsic phosphorescence life time that is the life time when the only depleting process is phosphorescence radiative emission

Phosphorescence Life Time, Quantum Yield and Different Rate Constants

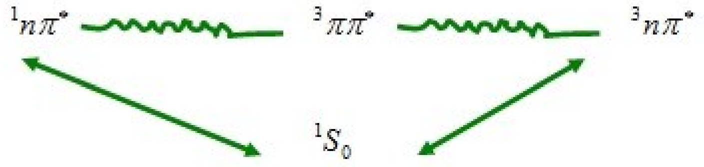
Molecule	In ETOH solution			
	T_p(in s)	Φ_p	K_p in s^{-1}	K_{np} in s^{-1}
DPyA	1.1	0.5	.76	0.15

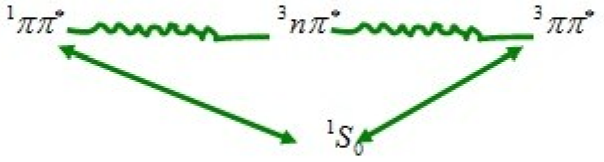
The triplet state life time T_p suggests that in case of DPK the lowest triplet state and lowest singlet state are nπ* whereas these are ππ* for DpyA [8]. Also it has been revealed that intermediate states are nπ* for DpyA and ππ* for DPK [9].

Conclusion

Therefore energy level diagram for DpyA and DPK are of opposite in nature. The heavy atom effects are dominant since $n\pi^*$ transitions play important role in both the atoms. Moreover non bonding electrons in Di-pyridyl-ketone make extra energy states which are absent in Di-pyridyl-amine.

Therefore possible mechanisms for phosphorescence spectra of Di-pyridyl-ketone and Di-pyridyl-amine are following.





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