

Dual-parameter Correlation Analysis of the Fluorescence Data of 1-Methyl-2-formyl-5-substituted Pyrrole (4-nitrophenyl)hydrazones

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Abstract: By using 1-methyl-2-formyl-5-Y-substituted pyrrole (4-nitrophenyl)hydrazones as a model for nitrogen-containing heterocyclic aromatic compounds, the emission wavelength [$\lambda_{\max(\text{em})}$] values of their fluorescence spectra have been measured. Correlation results show that the ΔE_{em} values are mainly affected by polar effects, but spin-delocalization effects also exist.

Keywords: Fluorescence spectra, correlation analysis, dual-parameter equation, spin-delocalization effect, polar effect, 1-methyl-2-formyl-5-Y-substituted pyrrole (4-nitrophenyl)hydrazones.

On the basis of the magnitudes of evaluated $|\rho_{\text{mb}}/\rho_{\text{JJ}}^{\bullet}|$ values of Eq.1, in which $\rho^{\text{x}}\sigma^{\text{x}}$ (or $\rho_{\text{mb}}/\sigma_{\text{mb}}$) and $\rho^{\bullet}\sigma^{\bullet}$ (or $\rho_{\text{JJ}}^{\bullet}/\sigma_{\text{JJ}}^{\bullet}$) represent the polar and spin-delocalization effect, we have recently proposed that there are four categories of possible circumstances for correlation analysis of radical reactivities and spectral properties¹. **I** Both polar and spin-delocalization effects are important, and $|\rho_{\text{mb}}/\rho_{\text{JJ}}^{\bullet}|$ falls in-between 0.2 and 0.8. **II** Polar effects predominate, $|\rho_{\text{mb}}/\rho_{\text{JJ}}^{\bullet}| > 1.0$. **III** The spin-delocalization effect predominates, $|\rho_{\text{mb}}/\rho_{\text{JJ}}^{\bullet}| < 0.2$. **IV** No correlation can be achieved.

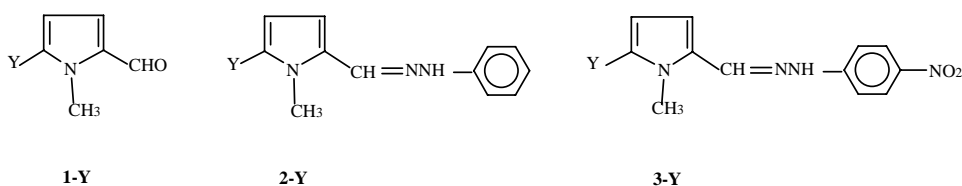
$$\text{variable} = \rho^{\text{x}}\sigma^{\text{x}} + \rho^{\bullet}\sigma^{\bullet} + C \quad (1)$$

$$\text{variable} = \rho^{\text{x}}\sigma^{\text{x}} + C \quad (2)$$

$$\text{variable} = \rho^{\bullet}\sigma^{\bullet} + C \quad (3)$$

Correlation results for the fluorescence spectral data of substituted styrenes and α -methylstyrenes have been found to fall in category-**I** in harmony with the diradicaloid character of the singlet excited states^{2,3}. We have also found that the behavior of the fluorescence spectral data of ethylene acetals and 4-nitrophenyl hydrazones can be classified as category-**III** and category-**II**, respectively⁴. However, there is no report on the correlation analysis of fluorescence spectral data of heterocyclic aromatic compounds, *e.g.*, pyrroles. Will the correlation results for the fluorescence spectral data of pyrroles conform to category-**I**, category-**II** or category-**III** behavior? The purpose of this paper is to answer this question. The compounds chosen for our analysis are

1-methyl-2-formyl-5-Y-substituted pyrroles **1-Y**, 1-methyl-2-formyl-5-Y-substituted pyrrole phenylhydrazones **2-Y** and 1-methyl-2-formyl-5-Y-substituted pyrrole (4-nitrophenyl)hydrazones **3-Y**⁵, but only **3-Y** possess fluorescence spectra (*cf* **Table 1**).



Y = H, CH₃, Cl, CN, COCH₃, NO₂, COOH, SCH₃, COOCH₃, Si(CH₃)₃, Br and OCH₃

Single-parameter correlation results for **3-Y** summarized in **Table 2** show that correlations with confidence level (CL) greater than 99.9% can be achieved by eqn. (2), *e.g.*, for σ_p : $r = 0.974$, $\Psi = 0.246$, $F = 188$, $n = 12$. However, single-parameter correlation analysis with all the σ^* constants yield meaningless results ($r < 0.62$). By using the dual-parameter eqn. (1), all the six pairings of ($\sigma^x + \sigma^*$) yield good correlations with CL > 99.9%, *e.g.*, for (σ_p, σ_{JJ}^*): $R = 0.974$, $\psi = 0.259$, $F = 84.6$, $n = 12$; for ($\sigma_{mb}, \sigma_{JJ}^*$): $R = 0.943$, $\Psi = 0.383$, $F = 36.3$, $n = 12$.

Table 1. λ_{ex} (nm), $\lambda_{max(em)}$ (nm) and their energies for the fluorescence spectra of **3-Y**^a

Y	λ_{ex} (nm)	ΔE_{ex} (eV) ^b	$\lambda_{max(em)}$ (nm)	ΔE_{em} (eV) ^b	D_{mb-1} ^c	D_{mJ-2} ^d
H	392.04	3.165	530.31	2.340	-0.017	-0.005
CH ₃	396.97	3.126	542.94	2.285	-0.022	-0.017
Cl	394.06	3.149	522.67	2.374	-0.002	0.002
CN	378.64	3.277	495.21	2.506		-0.010
					0.041	
COCH ₃	391.52	3.169	498.48	2.489	0.035	0.028
NO ₂	403.32	3.076	499.11	2.486	-0.049	-0.017
COOH	392.23	3.163	507.08	2.447	0.037	0.034
SCH ₃	392.13	3.164	537.25	2.310	-0.046	-0.021
COOCH ₃	383.27	3.237	503.19	2.466	0.056	0.027
Si(CH ₃) ₃	394.89	3.142	534.63	2.321	-0.060	-0.060
Br	390.11	3.181	521.61	2.379	-0.003	0.003
OCH ₃	397.00	3.125	548.88	2.261	0.037	0.035
				$\Sigma D $	0.41	0.26

a. Solvent: EtOH

b. ΔE (eV) = $1240.8/\lambda$ (nm)

c. Individual and total deviations of the experimental data from the regression line ($\Delta E_{em} \sim \sigma_{mb}$).

d. Individual and total deviations of the experimental data from the regression line [$\Delta E_{em} \sim (\sigma_{mb}, \sigma_{JJ}^*)$].

Although application of the dual-parameter eqn. (1) seems to improve the correlation results, this improvement cannot be considered meaningful unless we look into our data more closely¹. It would be good practice to examine the individual deviations (D_{mb-1} , D_{mJ-2}) as well as the sum of the deviations $\Sigma|D|$ (*cf* footnotes of **Table 1**). Notably, the D_{mb-1} of CN, SCH₃ and COOCH₃ is 0.041, -0.046 and 0.056 respectively, but the D_{mJ-2} of CN, SCH₃ and COOCH₃ is -0.01, -0.021 and 0.027 respectively. Furthermore, the $\Sigma|D_{mJ-2}|$ value (0.26) is much smaller than the $\Sigma|D_{mb-1}|$ value (0.41). Therefore, we believe that the above-mentioned improvement by application of the dual-parameter equation is genuine and that the spin-delocalization effect is in operation even though it is overshadowed by the polar effect. Judging by the $|\rho_{mb}/\rho_{JJ}^{\bullet}|$ value of 3.95 and by the aforesaid examination of the deviations, the behavior of fluorescence spectral data of **3-Y** can be classified as category-**II**, i.e., fluorescence spectra of **3-Y** are mainly affected by the polar effects of the substituents, but spin-delocalization effects also exist.

Table 2 Correlation results for the fluorescence spectral data of **3-Y** in EtOH

σ^x or σ^{\bullet} or ($\sigma^x + \sigma^{\bullet}$)	ρ^x	ρ^{\bullet}	r or R	s	ψ	F ^a	n ^b
σ_p	0.2501		0.9744	0.02050	0.2462	187.9	12
σ^+	0.1604		0.9425	0.02995	0.3696	71.51	11
σ_{mb}	0.1725		0.9402	0.03107	0.3732	76.17	12
$\sigma_p + \sigma_{JJ}^{\bullet}$	0.2493	0.00358	0.9744	0.02160	0.2594	84.64	12
$\sigma^+ + \sigma_{JJ}^{\bullet}$	0.1570	0.1197	0.9689	0.02352	0.2904	61.22	11
$\sigma_{mb} + \sigma_{JJ}^{\bullet}$	0.1671	0.04227	0.9433	0.03192	0.3834	36.32	12
$\sigma_p + \sigma_c^{\bullet}$	0.2542	-0.04150	0.9811	0.01896	0.2312	90.00	10
$\sigma^+ + \sigma_c^{\bullet}$	0.1401	0.1247	0.9708	0.02349	0.2866	57.39	10
$\sigma_{mb} + \sigma_c^{\bullet}$	0.1532	0.04852	0.9556	0.02887	0.3521	36.82	10

a. Critical F values: $F_{0.001}(1, 10) = 21.04$; $F_{0.001}(1, 9) = 22.86$; $F_{0.001}(2, 9) = 16.39$, $F_{0.001}(2, 8) = 18.49$; $F_{0.001}(2, 7) = 21.69$.

b. n = 12, Y = H, CH₃, Cl, CN, COCH₃, NO₂, COOH, SCH₃, COOCH₃, Si(CH₃)₃, Br, OCH₃;
n = 11, all of 12 substituted groups except for COCH₃;
n = 10, all of 12 substituted groups except for COCH₃ and COOH.

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References

1. X. K. Jiang, *Acc. Chem. Res.*, **1997**, *30*, 283.
2. Y. H. Zhang, G. H. X. Guo, X. S. Jin, B. B. Jiang, Y. H. Fu, X. K. Jiang, *J. Photochem. Photobiol. A: Chem.*, **1995**, *88*, 11.
3. H. Zhang, B. Jiang, X. K. Jiang, *Chin. J. Chem.*, **1997**, *15*, 395.
4. W. F. X. Ding, X. K. Jiang, *Chin. Chem. Lett.*, **1998**, *9*, 385
5. H. Y. He, X. K. Jiang, *Chin. J. Chem.*, **1998**, accepted.

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