ELSEVIER

Should the dual-parameter equation be used in the correlation analysis of fluorescence spectral data of substituted styrenes and α-methylstyrenes?

Yu-Huang Zhang *, Gary Hong-Xun Guo, Xiang-Shan Jin, Benjamin Bin Jiang, Yao-Hong Fu, Xi-Kui Jiang *

Shanghai Institute of Organic Chemistry, Academia Sinica, 354 Fenglin Lu, Shanghai 200032, People's Republic of China

Abstract

The fluorescence spectra of 13 para-substituted styrenes (Y-STs) and ten para-substituted α-methylstyrenes (Y-MSTs) were recorded and correlation analysed by both the dual-parameter equation and the single-parameter equation. Very good correlations of the fluorescence energy (ΔE) can be obtained by using the dual-parameter equation with the σ_{jj} scale in combination with either σ_{mb} or σ^+. Our results suggest that the singlet excited states of styrenes are diradical in nature as expected, and there is no need to use excited state substituent constants for this type of molecular species.

Keywords: Correlation analysis; Fluorescence spectra; Styrenes; Dual-parameter equation

1. Introduction

Although Hammett-type polar σ^x scales have been extensively applied successfully to ground state chemistry, it is not known whether they are equally applicable to excited state chemistry. For instance, Baldry [1] and Shim [2] have proposed new sets of substituent constants, i.e. σ_{ex} and σ^*, for excited state chemistry, and, more recently, McEwen and Yates [3] suggested that existing ground state σ scales are not applicable to the photoreactions of substituted styrenes and phenylacetylenes, and proposed a σ^{hv} scale for use in photochemical reactions. Very recently, Mai et al. [4] reported a successful correlation analysis of fluorescence spectral data, and showed that the exciplex energies of para-substituted *trans*-stilbenes and 3-substituted phenanthrenes can be correlated linearly with the Hammett constants.

In this work, we aim to tackle this problem. We propose that, for a particular molecular system, e.g. styrene, if the singlet excited state is radical in nature because it possesses two half-occupied molecular orbitals [5,6], it might be possible to correlate the fluorescence emission energy (ΔE) by a combination of

* Corresponding authors.

ground state polar and spin delocalization constants, σ^x and σ, as shown by Eq. (1)

$$\Delta E(Y) = \rho^x \sigma^{x+} \rho \cdot \sigma \cdot + C \qquad (1)$$

$$\Delta E(Y) = \rho^x \sigma^x + C \qquad (2)$$

We report the fluorescence spectra of 13 *p*-Y-substituted styrenes (Y-STs) (with Y ≡ NMe$_2$, F, Cl, Br, OMe, SMe, Me, tert-Bu, H, CN, SiMe$_3$, CF$_3$ and MeSO$_2$) and ten *p*-Y-substituted α-methylstyrenes (Y-MSTs) (Y ≡ F, Cl, Br, SMe, Me, H, CN, SiMe$_3$, CF$_3$ and CO$_2$Me). The results of correlation analysis are discussed.

2. Experimental section

2.1. Apparatus

Fluorescence spectra were measured on a Perkin–Elmer LS-50 luminescence spectrometer. Nuclear magnetic resonance (NMR) spectra were recorded on a Varian XL-200 spectrometer, with tetramethylsilane (TMS) as external standard. IR spectra were taken on a Shimadzu IR 440 instrument.

2.2. Reagents and substrates

Analytical grade acetonitrile was purified using alkali ($KMnO_4$) followed by fractional distillation from CaH_2 [7]. Analytical grade and freshly fractionated (boiling point (b.p.), 56–58 °C/30 Torr) styrene was used. p-SO_2Me-ST was a gift from Mr. Daniel Z.R. Wang [8]. Other Y-STs were prepared by previously reported methods [9]. The Y-MSTs were donated by Dr. Wayne W.Z. Liu [10].

2.3. Measurement of fluorescence spectra

A 1 cm quartz cell was used for fluorescence measurements. The cell was capped with a septum and degassed with nitrogen. The concentrations of the solutions were adjusted to $(0.1-1) \times 10^{-5}$ M for spectroscopic measurements. The spectra were recorded at room temperature.

3. Results and discussion

Thirteen Y-STs and ten Y-MSTs (see above) were examined. Their spin delocalization substituent constants $\sigma^{\cdot}$ and polar substituent constants σ^x are summarized in Table 1. When a solution of Y-ST or Y-MST is excited at an excitation wavelength of λ_{ex} (see Table 2) at room temperature in the cell, a fluorescence emission spectrum with maxima $\lambda_{max(em)}$ in the 300–380 nm region is obtained. A typical fluorescence spectrum is shown in Fig. 1. The spectral parameters $\lambda_{max(em)}$

Table 1
Polar and spin delocalization substituent constants of substituents Y

Y	$\sigma_{JJ}^{\cdot}$ [a]	$\sigma_\alpha^{\cdot}$ [b]	$\sigma_C^{\cdot}$ [c]	σ_{mb} [a]	σ_P [d]	σ^+ [d]
NMe_2	1.00			-0.96	-0.83	-1.70
F	-0.02	-0.011	-0.08	-0.24	0.06	-0.07
Cl	0.22	0.011	0.12	0.11	0.23	0.11
Br	0.23		0.13	0.13	0.23	0.15
OMe	0.23	0.018	0.24	-0.77	-0.27	-0.78
SMe	0.62	0.063	0.43	-0.18	0.00	-0.60
Me	0.15	0.015	0.11	-0.29	-0.17	-0.31
tert-Bu	0.26	0.008	0.13	-0.22	-0.20	-0.26
H	0	0	0	0	0	0
CN	0.42	0.040	0.46	0.86	0.66	0.66
$SiMe_3$	0.31	0.017	0.17	0.14	-0.07	0.02
CF_3	-0.01	-0.009	0.07	0.49	0.54	0.61
SO_2Me [e]	0.41	0.005		0.64	0.72	
CO_2Me	0.33	0.043		0.48	0.45	0.49

[a] Data taken from Ref. [11].
[b] Data taken from Ref. [12a].
[c] Data taken from Ref. [12b].
[d] Data taken from Ref. [13].
[e] The $\sigma_{JJ}^{\cdot}$ and σ_{mb} values given for the SO_2Me group in Ref. [11] are slightly in error. The $\sigma_{JJ}^{\cdot}$ values should be 0.41 ± 0.04 instead of 0.38 ± 0.03, and the σ_{mb} value should be 0.64 instead of 0.55.

Table 2
Maximum fluorescence emission wavelengths ($\lambda_{max(em)}$) for Y-STs and Y-MSTs

Y	Y-ST			Y-MST		
	$\lambda_{max(em)}$ [a]	ΔE [b]	λ_{ex} [c]	$\lambda_{max(em)}$ [a]	ΔE [b]	λ_{ex} [c]
NMe_2	370	77.3	294			
F	304	94.1	244	310	92.3	244
Cl	312	91.7	248	317	90.2	249
Br	316	90.5	248	317	90.2	294
OMe	324	88.3	257			
SMe	344	83.1	285	344	83.1	284
Me	309	92.6	247	316	90.5	248
tert-Bu	316	90.5	248			
H	303	94.4	279	308	92.9	247
CN	313	91.4	262	318	89.9	265
$SiMe_3$	310	92.3	248	318	89.9	249
CF_3	298	96.0	250	308	92.9	250
SO_2Me	311	92.0	250			
CO_2Me				316	90.5	266

[a] In nanometres.
[b] $\Delta E = 2.86 \times 10^4 / \lambda_{max(em)}$ (kcal mol^{-1}).
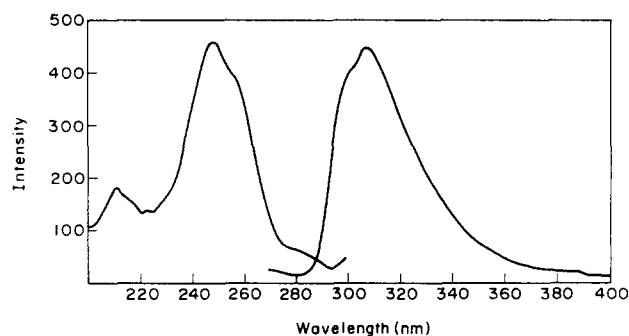[c] Excitation wavelength (in nm) used.

Fig. 1. Fluorescence excitation and emission spectra of p-$SiMe_3$-ST in acetonitrile at room temperature ($[p$-$SiMe_3$-ST] $= 2.06 \times 10^{-6}$ M).

and λ_{ex} of the Y-STs and Y-MSTs are listed in Table 2.

The fluorescence energy (ΔE) values were correlated by Eq. (2) using Hammett-type polar substituent constants as well as excited state substituent constants, i.e. σ_{mb}, σ_P, σ^+, σ_{ex}, σ^* and $\sigma^{h\nu}$. They were also correlated by the dual-parameter equation (Eq. (1)) using polar constants σ^x together with various spin delocalization constants $\sigma^{\cdot}$, i.e. $\sigma_{JJ}^{\cdot}$, $\sigma_\alpha^{\cdot}$ and $\sigma_C^{\cdot}$. The results of these attempted correlations are summarized in Tables 3 and 4. The correlations of the ΔE values with the polar or excited state substituent constants by the single-parameter equation (Eq. (2)) are poor or very poor ($r = 0.848$–0.286). The only "satisfactory" correlation (by $\sigma^{h\nu}$) cannot be regarded as reliable because the confidence level is only about 95% ($n = 4$) [15]. In contrast, however, application of the dual-parameter equation (Eq. (1)) yielded excellent correlations for some combinations of $\sigma^{\cdot}$ and σ^x. Particularly noteworthy is the fact that the $(\sigma_{JJ}^{\cdot} + \sigma_{mb})$ and $(\sigma_{JJ}^{\cdot} + \sigma^+)$ com-

Table 3
Correlation analysis of ΔE values of Y-STs by Eq. (1) with $\sigma^x + \sigma$ and by Eq. (2) with σ^x

σ	ρ^x	$\rho^{\cdot}$	C	$\rho^x/\rho^{\cdot}$	R	ψ	F^a	n
σ_{mb}	6.01		90.5		0.614	0.86	6.64	13
σ_P	7.72		89.8		0.645	0.83	7.86	13
σ^+	6.95		91.4		0.848	0.58	25.6	12
σ_{ex}	1.83		91.0		0.286	1.07	0.71	10
σ^*	1.50		91.9		0.396	1.12	0.74	6
$\sigma^{h\nu}$	4.46		94.0		0.961	0.39	24.3	4
$\sigma_{JJ}{}^{\cdot} + \sigma_{mb}$	3.54	−14.4	94.7	−0.25	0.982	0.22	126.3	13
$\sigma_{JJ}{}^{\cdot} + \sigma_P$	3.83	−14.1	94.2	−0.27	0.964	0.30	66.1	13
$\sigma_{JJ}{}^{\cdot} + \sigma^+$	3.06	−12.3	94.2	−0.25	0.983	0.22	125.2	12
$10\sigma_\alpha{}^{\cdot} + \sigma_{mb}$	2.69	−13.8	93.3	−0.19	0.930	0.43	25.7	11
$10\sigma_\alpha{}^{\cdot} + \sigma_P$	2.57	−13.6	93.1	−0.19	0.894	0.52	16.0	11
$10\sigma_\alpha{}^{\cdot} + \alpha^+$	3.58	−11.9	93.5	−0.30	0.962	0.33	43.4	11
$\sigma_C{}^{\cdot} + \sigma_{mb}$	4.65	−18.2	94.3	−0.26	0.907	0.49	18.5	11
$\sigma_C{}^{\cdot} + \sigma_P$	5.86	−17.6	93.7	−0.33	0.868	0.58	12.2	11
$\sigma_C{}^{\cdot} + \sigma^+$	4.63	−14.3	93.9	−0.32	0.927	0.44	24.4	11

[a] Critical F values (data taken from Ref. [14]): $F_{0.001}(2,10) = 14.91$, $F_{0.001}(2,9) = 16.39$, $F_{0.001}(2,8) = 18.49$, $F_{0.5}(1,11) = 4.84$, $F_{0.5}(1,10) = 4.96$, $F_{0.5}(1,8) = 5.32$, $F_{0.5}(1,4) = 7.71$, $F_{0.5}(1,2) = 18.51$.

Table 4
Correlation analysis of ΔE values of Y-MSTs by Eq. (1) with $\sigma^x + \sigma$ and by Eq. (2) with σ^x

σ	ρ^x	$\rho^{\cdot}$	C	$\rho^x/\rho^{\cdot}$	R	ψ	F^a	n
σ_{mb}	1.56		90.0		0.195	1.11	0.28	10
σ_P	2.03		89.9		0.203	1.11	0.30	10
σ^+	3.89		89.8		0.557	0.93	3.60	10
σ_{ex}	0.90		90.0		0.168	1.14	0.17	8
σ^*	−1.83		91.7		0.510	1.11	1.05	5
$\sigma^{h\nu}$	2.99		92.2		0.883	0.81	3.53	3
$\sigma_{JJ}{}^{\cdot} + \sigma_{mb}$	2.82	−13.0	92.7	−0.22	0.968	0.30	51.4	10
$\sigma_{JJ}{}^{\cdot} + \sigma_P$	2.75	−12.4	92.5	−0.22	0.937	0.42	25.2	10
$\sigma_{JJ}{}^{\cdot} + \sigma^+$	2.68	−11.0	92.4	−0.24	0.971	0.28	58.4	10
$10\sigma_\alpha{}^{\cdot} + \sigma_{mb}$	2.86	−10.7	91.8	−0.27	0.920	0.48	16.6	9
$10\sigma_\alpha{}^{\cdot} + \sigma_P$	3.07	−10.3	91.6	−0.30	0.897	0.54	12.3	9
$10\sigma_\alpha{}^{\cdot} + \sigma^+$	2.94	−9.00	91.6	−0.33	0.939	0.42	22.4	9
$\sigma_C{}^{\cdot} + \sigma_{mb}$	5.24	−17.1	92.3	−0.31	0.956	0.36	31.8	9
$\sigma_C{}^{\cdot} + \sigma_P$	5.30	−15.0	91.7	−0.35	0.891	0.56	11.6	9
$\sigma_C{}^{\cdot} + \sigma^+$	4.37	−12.5	91.9	−0.35	0.957	0.36	32.6	9

[a] Critical values (data taken from Ref. [14]): $F_{0.001}(2,7) = 21.69$, $F_{0.001}(2,6) = 27.00$, $F_{0.5}(1,8) = 5.32$, $F_{0.5}(1,6) = 5.99$, $F_{0.5}(1,3) = 10.13$, $F_{0.5}(1,1) = 161.4$.

binations yield the best correlations, i.e. $r = 0.982$ and 0.983 for Y-STs and $r = 0.968$ and 0.971 for Y-MSTs. These results confirm that the singlet excited state of these molecules may be diradical in nature possessing two half-occupied orbitals [5,6]. When one electron in the higher half-occupied orbital returns to the lower half-occupied orbital, the molecule emits fluorescence [5]. Apparently, the frequency of this transition is directly affected by both the spin delocalization effect and the polar effect of the substituent. Therefore our results

suggest that there may be no justification for the use of excited state substituent constants (such as σ_{ex}, σ^* and $\sigma^{h\nu}$) for correlation analysis of properties related to the excited states of this type of molecule. (We have found that the Stern–Volmer constants of the reaction of the excited states of Y-STs and Y-MSTs with the quencher tetramethylethene can only be correlated by Eq. (1) with $\sigma_{JJ}{}^{\cdot}$ and σ_{mb} [16].) Finally, it is of special interest to note that, although the fluorescence emission data of Nakatsuji et al. [17] on 9,10-bis(phenylethynyl)anthracenes could not be correlated by a single-parameter equation, successful correlation by the dual-parameter equation with either the $(\sigma_{JJ}{}^{\cdot} + \sigma_P)$ or $(\sigma_{JJ}{}^{\cdot} + \sigma_{mb})$ combination was achieved with r values of greater than 0.99 $(n = 6)$.

Turro and Kraeutler [18] have remarked that, although the existence of triplet diradicals can be observed and examined in many cases, there seems to be no direct proof for the existence of singlet diradicals. This work appears to support the existence of excited state singlet diradicals. Recently, a cogent piece of evidence for the diradical nature of the singlet excited state has been reported by Hasler et al. [6]. They observed a perinaphthadiyl singlet biradical intermediate on picosecond flash photolysis of either 2,7-dihydro-2,2,7,7-tetramethylpyrene or 2,2,7,7-tetramethyldicyclopropa-[a,g]-pyracene.

Acknowledgement

References

[1] P.J. Baldry, J. Chem. Soc., Perkin Trans. 2, (1979) 951.

[2] (a) S.C. Shim, J.W. Park and H.S. Ham, Bull. Korean Chem. Soc., 3 (1982) 13. (b) S.C. Shim, J.W. Park, H.S. Ham and J.S. Chung, Bull. Korean Chem. Soc., 4 (1983) 45.

[3] J. McEwen and K. Yates, J. Phys. Org. Chem., 4 (1991) 193.

[4] (a) J.C. Mai, Y.C. Lin and T.I. Ho, J. Photochem. Photobiol. A: Chem., 54 (1990) 299. (b) J.C. Mai, J.Y. Cheng and T.I. Ho, J. Photochem. Photobiol. A: Chem., 62 (1992) 53.

[5] (a) N.J. Turro, Modern Molecular Photochemistry, Benjamin/Cummings, Menlo Park, 1978. (b) N.S. Isaacs, Physical Organic Chemistry, Longman, London, 1987, p. 778.

[6] E. Hasler, A. Hormann, G. Persy, H. Platsch and J. Wirz, J. Am. Chem. Soc., 115 (1993) 5400.

[7] D.D. Perrin, W.L. Armarego and D.R. Perrin, Purification of Laboratory Chemicals, Pergamon, Oxford, 2nd edn., 1980, p. 79.

[8] X.K. Jiang, G.Z. Ji and Z.R. Wang, J. Fluorine Chem., 66 (1994) 187.

[9] G.H.X. Guo, S.S.X. Sun, G.Z. Ji and X.K. Jiang, J. Chem. Res. (S), (1993) 166; (M), (1993) 1123–1143.

[10] (a) X.K. Jiang, W.W.Z. Liu and S.H. Wu, J. Phys. Org. Chem., 7 (1994) 96. (b) X.K. Jiang, W.W.Z. Liu and S.H. Wu, Tetrahedron, 50 (1994) 7503.

[11] X.K. Jiang and G.Z. Ji, *J. Org. Chem.*, *57* (1992) 6053.
[12] (a) D.R. Arnold, in R. Mereny, Z. Jamousek and H.G. Viche (eds.), *Substituent Effects in Radical Chemistry*, Reidel, Dordrecht, 1986, p. 171. (b) X. Creary, in R. Mereny, Z. Jamousek and H.G. Viche (eds.), *Substituent Effects in Radical Chemistry*, Reidel, Dordrecht, 1986, p. 245.
[13] A. Leo and R.W. Tafts, *Chem. Rev.*, *91* (1991) 165.
[14] G.E. Box, W.G. Hunter and J.S. Hunter, *Statistics for Experimenters, An Introduction to Design, Data Analysis and Model Building*, Wiley, New York, 1979.

[15] J. Shorter, *Correlation Analysis of Organic Reactivity*, Research Studies Press, Chichester, 1982, p. 16.
[16] Y.-H. Zhang, B.B. Jiang, and X.-K. Jiang, *J. Photochem. Photobiol. A: Chem.*, submitted for publication.
[17] S. Nakatsuji, K. Matsuda, Y. Uesugi, K. Nakashima, S. Akiyama and W. Fabian, *J. Chem. Soc., Perkin Trans. 1*, (1992) 755.
[18] N.J. Turro and B. Kraeutler, in W.T. Borden (ed.), *Diradicals*, Wiley, New York, 1982, p. 256.