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SUCCESSFUL APPLICATION OF THE SPIN-DELOCALIZATION SUBSTITUENT CONSTANTS $\sigma^{\cdot}$ TO THE CORRELATION OF THE UV SPECTRA OF SOME MODEL COMPOUNDS WITH *PARA*-Y-SUBSTITUTED PHENYL GROUPS

XI-KUI JIANG,* GUO-ZHEN JI, DANIEL ZE-RONG WANG AND JOHN RONG-YUAN XIE
Shanghai Institute of Organic Chemistry, 354 Feng-Lin Lu, Shanghai 200032, China

UV spectra of 16 *p*-Y-substituted phenylacetylenes (1-Ys), nine *p*-Y-substituted acetophenones (2-Ys) and six *p*-Y-substituted-*p*′-methylsulphonylstilbenes (3-Ys) were measured and correlated against spin-delocalization substituent constants ($\sigma^{\cdot}$) with confidence levels above 99·9%. UV spectra of five ethyl 3-hydroxy-3-(*p*-Y-substituted-phenyl)-propanates (4-Ys) and five 1-(*p*-Y-substituted-phenyl)-3-butyn-1-ols (5-Ys) were also measured. Correlation analysis results are discussed. Some literature UV data were also successfully correlated by the dual-parameter equation.

INTRODUCTION

Searching for a good correlation of UV data on simple aromatic compounds with a certain scale of substituent constants has been an intriguing but not very successful endeavour for many interested workers. It seems that a useful and conclusive generalization for this subject has not yet been achieved.[1–3] For instance, Brownlee and Topsom[2] made a comment that 'previously claimed simple relationships between UV frequency or wavelength shifts and substituent electronic properties are mostly unfounded,' and Shorter[3] was of the opinion that 'the achievements of correlation analysis in UV spectroscopy are somewhat limited.' It is also particularly noteworthy that most all previous workers have only used polar (including resonance polar) substituent constants (designated here as σ^{X}) or *ad hoc* excited-state substituent constants (designated as σ^{ex}) for their correlation analyses by a single-parameter equation such as equation (1), with variable = ν_{max}.[4–6] Therefore, for a number of years, we have been intrigued by the puzzle of why no-one has reported an attempt to correlate the UV data on simple aromatic compounds by equation (2) in terms of spin-delocalization substituent constants (designated as $\sigma^{\cdot}$), or by equation (3) in terms of a combination of σ^{X} and $\sigma^{\cdot}$, while knowing that the excited state should possess radicaloid character because it possesses two half-occupied molecular orbitals.[7,8]

$$\text{variable} = \rho^{X}\sigma^{X}\ (\text{or } \rho^{ex}\sigma^{ex}) + C \qquad (1)$$

$$\text{variable} = \rho^{\cdot}\sigma^{\cdot} + C \qquad (2)$$

$$\text{variable} = \rho^{X}\sigma^{X} + \rho^{\cdot}\sigma^{\cdot} + C \qquad (3)$$

Furthermore, the 'necessity' of using two straight lines (sometimes with slopes of opposite signs) or the absolute values of σ^{X} (i.e. $|\sigma^{X}|$) for a 'successful' correlation of UV data, as claimed by some workers,[9] suggests to us that at least another factor is operating in addition to the polar factor (σ^{X}). The radicaloid nature of the excited state mentioned above would certainly suggest that this other factor could be the spin-delocalizing abilities of the substituents ($\sigma^{\cdot}$).[8]

On the basis of the above-mentioned considerations, we adopted the following approach to test our proposition, namely, to use a simple model with an easily identified UV absorption for the correlation study. Forty-five *p*-Y-substituted styrenes were therefore used as model molecules and the λ_{max} values of their K-bands were measured.[8a] Correlation analysis of the corresponding ν_{max} values by equations (1), (2) and (3) yielded an astonishing result, namely that the ν_{max} values cannot be correlated by equation (1) with any of the Hammett-type polar substituent constants (σ^{X}), but can be correlated with a >99·9% confidence level[10] (CL) by using equation (2) with the spin-delocalization substituent constants ($\sigma^{\cdot}$). This result clearly indicates

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* Author for correspondence.

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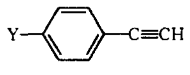
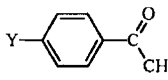
that the dominant factor which decides the magnitude of the energy difference between the first excited state and the ground state of styrene-type molecules is the spin-delocalizing ability of the substituent. Evidently, our next important task is to find out whether other molecules structurally related to styrenes also behave in a similar manner.

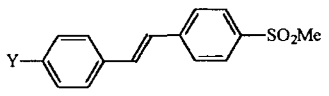
This paper reports the correlation analysis of the UV data for three types of benzene derivatives with π-bonds directly conjugated with the substituent Y, namely *p*-Y-substituted-phenylacetylenes (**1**-Y), *p*-Y-substituted-acetophenones (**2**-Y) and *p*-Y-substituted-*p*'-methylsulphonylstilbenes (**3**-Y). Preliminary UV data on ethyl 3-hydroxy-3-(*p*-Y-substituted-phenyl)-propanates (**4**-Y) and 1-(*p*-Y-substituted-phenyl)-3-butyn-1-ols (**5**-Y) are also discussed.



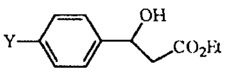
1-Y



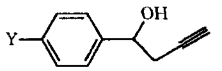
2-Y



3-Y



4-Y



5-Y

RESULTS AND DISCUSSION

Measured λ_{max} values of **1**-Ys, **2**-Ys, **3**-Ys, **4**-Ys and **5**-Ys, together with their corresponding wavenumbers (ν_{max}) and molar absorption coefficients (ε), are summarized in Tables 1 and 2 (cf. Ref. 8a). Values of representative Hammett-type unresolved polar substituent constants (σ^X), i.e. σ_p, σ^+ and σ_{mb}, were taken from Refs 11, 11 and 12, respectively, and values of representative spin-delocalization constants, i.e. $\sigma^{\cdot}_{JJ}$, $\sigma^{\cdot}_C$ and $\sigma^{\cdot}_{\alpha}$, were taken from Refs 12, 13a and 13b, respectively. Results of correlation analysis in terms of ρ^X, $\rho^{\cdot}$, s^2, r or R, Ψ and F values (cf. Refs 8a and 14) by equations (1)—(3) are summarized in Tables 3 (for **1**-Y), 4 (**2**-Y), 5 (**3**-Y), 6 (**4**-Y) and 7 (**5**-Y). The identity of the substituents used in each entry is given in the footnotes to the tables. It should be noted that relatively small differences in the r, Ψ and F values of the different entries in the same table should not be taken seriously because various complicating factors could affect the exact position of the UV absorption peaks (cf. Refs 1–3 and 8a). Also, as mentioned previously,[8a] a confidence level (CL) above 99·9% (based on $F_{0 \cdot 001}$ values given in the footnotes of the tables; cf. Refs 10 and 14) is considered good, even though the r (or R) value is smaller than 0·95, because the r value does not take into account the number of substituents (n).

A striking similarity is revealed if the correlation results for phenylacetylenes (**1**-Ys), as summarized in Table 3 and shown in Figure 1, are compared with those for the styrenes (cf. Ref. 8a). In other words, for both of the above-mentioned systems with multiple bonds at positions *para* to the substituents, three observations stand out in vivid contrast to all those previously

Table 1. Wavenumbers (ν_{max}, cm^{-1}), λ_{max} (nm)[a] and ε_{max} (l mol^{-1}cm^{-1}) values for **1**-Ys and **2**-Ys

	1-Y			**2**-Y		
Y	λ_{max}	ν_{max}	$\varepsilon_{max}(\times 10^4)$	λ_{max}	ν_{max}	$\varepsilon_{max}(\times 10^4)$
F	243·8	41017	1·39	239·3	41788	1·24
Cl	252·4	39620	1·70	249·7	40048	1·74
Br	254·6	39277	1·84	251·4	39777	1·88
Me	249·6	40064	1·80	244·4	40916	1·63
COMe	269·2	37147	2·50			
CN	262·6	38081	1·71			
MeSO	262·0	38168	2·25			
H	245·0	40816	1·52	242·0	41322	1·32
CF_3	248·8	40193	1·61			
CO_2Me	258·2	38730	2·44			
OMe	254·4	39308	2·16	262·2	38139	1·94
t-Bu	250·2	39968	1·92	251·8	39713	1·71
NO_2	272·8	36657	1·25			
$SiMe_3$	253·4	39463	1·61			
SMe	279·6	35765	1·89	303·6	32938	1·86
NMe_2	285·4	35038	2·47	307·1	32563	2·55

Table 2. Wavenumbers (ν_{max}, cm^{-1}), λ_{max} (nm)[a] and ε_{max} (l mol^{-1} cm^{-1}) values for **3**-Ys, **4**-Ys and **5**-Ys

	3-Y			4-Y			5-Y		
Y	λ_{max}	ν_{max}	$\varepsilon_{max}(\times 10^4)$	λ_{max}	ν_{max}	$\varepsilon_{max}(\times 10^4)$	λ_{max}	ν_{max}	$\varepsilon_{max}(\times 10^4)$
H	316·0	31646	3·16	209·3	47778	0·80	208·8	47893	0·83
CH_3	323·1	30950	3·09	212·5	47059	1·08	212·8	46992	0·98
OCH_3	332·0	30120	3·01	225·4	44366	1·67	225·1	44425	1·05
Cl	320·3	31221	3·12	220·6	45331	1·25	220·7	45310	1·04
Br	321·3	31124	3·11						
NMe_2	376·7	26546	2·65						
F				206·9	48333	0·81	207·5	48193	0·79

[a] Uncertainty ±0·3 nm

Table 3. Correlation results for **1**-Ys

σ^X or $\sigma^{\cdot}$ or $\sigma^X + \sigma^{\cdot}$	ρ^X $(\times 10^3)$	$\rho^{\cdot}$ $(\times 10^3)$	s^2 $(\times 10^3)$	r or R	Ψ	F[a]	n
σ_{mb}	0·026		1·83	0·008	1·07	0·001	16[b]
σ^+	1·03		1·78	0·370	1·00	1·90	14[c]
σ_p	0·223		1·83	0·053	1·07	0·039	16[b]
$\sigma^{\cdot}_{JJ}$		−6·23	0·703	0·923	0·410	81·0	16[b]
$10\sigma^{\cdot}_{\alpha}$		−5·79	0·606	0·922	0·421	62·3	13[d]
$\sigma^{\cdot}_C$		−6·54	0·705	0·924	0·410	76·2	15[e]
$\sigma_{mb} + \sigma^{\cdot}_{JJ}$	−0·617	−6·47	0·647	0·940	0·378	49·5	16[b]
$\sigma_{mb} + 10\sigma^{\cdot}_{\alpha}$	0·0347	−5·81	0·635	0·922	0·442	28·3	13[d]
$\sigma_{mb} + \sigma^{\cdot}_C$	0·006	−6·54	0·734	0·924	0·427	35·2	15[e]
$\sigma^+ + \sigma^{\cdot}_{JJ}$	−0·652	−7·22	0·668	0·942	0·377	43·7	14[c]
$\sigma^+ + 10\sigma^{\cdot}_{\alpha}$	0·171	−5·99	0·566	0·938	0·406	29·4	11[f]
$\sigma^+ + \sigma^{\cdot}_C$	0·112	−6·54	0·677	0·941	0·382	42·4	14[c]
$\sigma_p + \sigma^{\cdot}_{JJ}$	−0·902	−6·62	0·617	0·946	0·360	55·2	16[b]
$\sigma_p + 10\sigma^{\cdot}_{\alpha}$	−0·382	−5·65	0·622	0·925	0·432	29·8	13[d]
$\sigma_p + \sigma^{\cdot}_C$	−0·224	−6·60	0·727	0·926	0·423	36·0	15[e]

[a] Critical F values:[10] $F_{0.001}$ (1, 14) = 17·14, $F_{0.001}$ (1, 13) = 17·81, $F_{0.001}$ (1, 12) = 18·64, $F_{0.001}$(1, 11) = 19·69, $F_{0.001}$ (1, 9) = 22·86, $F_{0.001}$ (2, 13) = 12·31, $F_{0.001}$ (2, 12) = 12·97, $F_{0.001}$ (2, 12) = 13·81, $F_{0.001}$(2, 10) = 14·91, $F_{0.001}$ (2, 8) = 18·49, $F_{0.05}$ (1, 14) = 4·60, $F_{0.05}$ (1, 12) = 4·75.
[b] Y = F, Cl, Br, Me, COMe, CN, SOMe, H, CF_3, CO_2Me, OMe, t-Bu, NO_2, Me_3Si, SMe and NMe_2.
[c] Y = F, Cl, Br, Me, CN, H, CF_3, CO_2Me, OMe, t-Bu, NO_2, Me_3Si, SMe and NMe_2.
[d] Y = F, Cl, Me, COMe, CN, SOMe, H, CF_3, CO_2Me, OMe, t-Bu, Me_3Si and SMe.
[e] Y = F, Cl, Br, Me, CN, SOMe, H, CF_3, CO_2Me, OMe, t-Bu, NO_2, Me_3Si, SMe and NMe_2.
[f] Y = F, Cl, Me, CN, H, CF_3, CO_2Me, OMe, t-Bu, Me_3Si and SMe.

reported,[4–6,9] namely (i) the ν_{max} data for **1**-Ys are not related to the polar substituent constants σ^X ($\sigma^X = \sigma_{mb}$, σ^+ and σ_p, $r = 0{\cdot}01$, 0·37 and 0·05; $n = 16$, 14 and 16) by using equation (1); (ii) good correlations, all with F values which correspond to confidence levels greater than 99·9%, can be obtained by applying equation (2) ($\sigma^{\cdot} = \sigma^{\cdot}_{JJ}$, $\sigma^{\cdot}_{\alpha}$ and $\sigma^{\cdot}_C$; $F = 81$, 62 and 76; $n = 16$, 13 and 15); and (iii) by using the dual-parameter equation (3), all the nine pairings of ($\sigma^X + \sigma^{\cdot}$) yield good correlations with CL > 99·9%. Naturally, no meaningful improvement can be claimed for the use of the dual-parameter correlation over that of the single-parameter correlation because application of the single-parameter equation (2) already yields good results with CL > 99·9%. All the above-mentioned facts demonstrate persuasively that, as expected, the UV absorption processes of styrenes and phenylacetylenes are very much alike.

At this juncture we may ask, 'What will happen if a carbonyl group takes the place of the multiple bond?' The acetophenones (**2**-Ys) and styrenes or phenylacetylenes all possess a pair of π-electrons in conjugation with the p-Y-substituted benzene ring, thus similar UV spectral behaviours might be expected. The correlation results for **2**-Ys summarized in Table 4 are certainly in accord with the aforesaid expectation. There is no meaningful correlation between ν_{max} and σ^X ($r = 0{\cdot}55$–$0{\cdot}80$, $n = 9$), but there are good correlations with F values that correspond to confidence levels above 99·9% for all the three spin-delocalization constants (for $\sigma^{\cdot}_{JJ}$, $F = 59$, $n = 9$; for $\sigma^{\cdot}_{\alpha}$, $F = 61$, $n = 7$; for $\sigma^{\cdot}_C$, $F = 38$, $n = 9$). Again, application of the

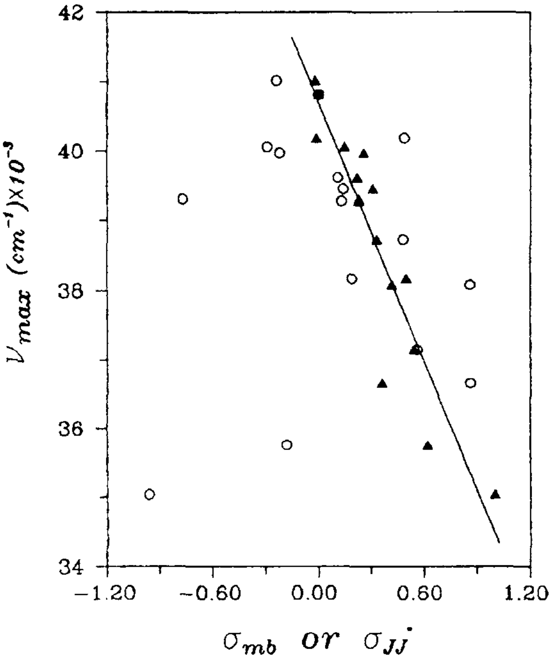


Figure 1. Plot of ν_{max}, vs σ_{mb} (○) and, $\sigma^{\cdot}_{JJ}$ (▲) for **1**-Y

dual-parameter equation (3) does not improve the correlation. Therefore, the carbonyl group does seem to behave similarly to a carbon–carbon double or triple bond during UV absorption.

We also looked at six substituted stilbenes (**3**-Ys) to see whether similar spectral behaviour would again be observed. Table 5 shows that among the three polar scales (σ^X), only σ^+ yields a correlation with a CL greater than 99% ($r = 0{\cdot}955$, $n = 6$), whereas σ_{mb} and σ_p yield confidence levels of only >95%. In contrast, for correlations with the spin-delocalization scales ($\sigma^{\cdot}$) by the single-parameter equation (2), both $\sigma^{\cdot}_{JJ}$ ($r = 0{\cdot}98$, $n = 6$, $F = 82$) and $\sigma^{\cdot}_c$ ($r = 0{\cdot}99$, $n = 6$, $F = 348$) yield correlations with confidence levels >99·9%. Correlations using the $\sigma^{\cdot}_\alpha$ scale here may not be so reliable because the number of substituents is too small ($n = 4$). It is noteworthy that three of the ($\sigma^X + \sigma^{\cdot}$) combinations yield excellent correlations, namely for ($\sigma^+ + \sigma^{\cdot}_{JJ}$), $r = 0{\cdot}999$, $\Psi = 0{\cdot}045$, $F = 1488$, CL > 99·9%; for ($\sigma_p + \sigma^{\cdot}_{JJ}$), $r = 0{\cdot}998$, $\Psi = 0{\cdot}089$, $F = 382$, CL > 99.9%; and for ($\sigma_{mb} + \sigma^{\cdot}_{JJ}$), $r = 0{\cdot}998$, $\Psi = 0{\cdot}098$, $F = 309$, CL > 99·9%. Evidently, the stilbene system (**3**-Y) is not very different from the styrene-like systems (styrenes, **1**-Y and **2**-Y), except that the polar effect is now beginning to make itself visible. This is clearly indicated by the $|\rho^X_{mb}/\rho^{\cdot}_{JJ}|$ value of 0·28, which is sizable. This observation seems to support our previous proposition that for the UV absorption by styrenes, polar effects are not non-existent even though the spin-delocalization effect predominates.[8a]

We also made a preliminary examination of *p*-substituted benzenes without a double bond in conjugation with the ring, namely **4**-Ys and **5**-Ys. Correlation results are summarized in Tables 6 and 7. As a whole, correlation results are far from being as clear cut as the results for styrenes, **1**-Ys, **2**-Ys and **3**-Ys. However, it is

Table 4. Correlation results for **2**-Ys

σ^X or $\sigma^{\cdot}$ or $\sigma^X + \sigma^{\cdot}$	ρ^X (×10³)	$\rho^{\cdot}$ (×10³)	s^2 (×10³)	*r* or *R*	Ψ	F^a	*n*
σ_{mb}	5·15		3·09	0·554	0·944	3·11	9^b
σ^+	4·78		2·20	0·804	0·674	12·8	9^b
σ_p	6·30		3·00	0·588	0·917	3·71	9^b
$\sigma^{\cdot}_{JJ}$		−10·2	1·21	0·946	0·369	59·2	9^b
$10\sigma^{\cdot}_\alpha$		−12·5	0·918	0·961	0·326	60·7	7^c
$\sigma^{\cdot}_C$		−10·9	1·46	0·920	0·445	38·4	9^b
$\sigma_{mb} + \sigma^{\cdot}_{JJ}$	−0·0678	−10·3	1·30	0·946	0·398	25·4	9^b
$\sigma_{mb} + 10\sigma^{\cdot}_\alpha$	0·934	−12·4	0·977	0·965	0·347	27·0	7^c
$\sigma_{mb} + \sigma^{\cdot}_C$	−1·48	−12·2	1·50	0·927	0·460	18·3	9^b
$\sigma^+ + \sigma^{\cdot}_{JJ}$	0·0741	−10·1	1·30	0·946	0·398	25·4	9^b
$\sigma^+ + 10\sigma^{\cdot}_\alpha$	1·12	−11·5	0·966	0·966	0·343	27·7	7^c
$\sigma^+ + \sigma^{\cdot}_C$	−1·13	−13·0	1·54	0·923	0·471	17·3	9^b
$\sigma_p + \sigma^{\cdot}_{JJ}$	−1·56	−11·3	1·23	0·951	0·377	28·6	9^b
$\sigma_p + 10\sigma^{\cdot}_\alpha$	0·129	−12·5	1·03	0·961	0·365	24·3	7^c
$\sigma_p + \sigma^{\cdot}_C$	−3·73	−14·2	1·32	0·944	0·402	24·8	9^b

[a] Critical *F* values:[10] $F_{0{\cdot}001}$ (1, 7) = 29·25, $F_{0{\cdot}001}$ (1, 5) = 47·18, $F_{0{\cdot}001}$ (2, 6) = 27·00, $F_{0{\cdot}001}$ (2, 4) = 61·25, $F_{0{\cdot}01}$ (1, 7) = 12·25, $F_{0{\cdot}01}$ (1, 5) = 16·26, $F_{0{\cdot}01}$ (2, 6) = 10·92, $F_{0{\cdot}01}$(2, 4) = 18·00, $F_{0{\cdot}05}$ (1, 7) = 5·59.

[b] Y = F, Cl, Br, Me, H, OMe, t-Bu, SMe and NMe_2.

[c] Y = F, Cl, Me, H, OMe, t-Bu and SMe.

Table 5. Correlation results for **3**-Ys

σ^{X} or $\sigma^{\cdot}$ or $\sigma^{\mathrm{X}}+\sigma^{\cdot}$	ρ^{X} ($\times 10^3$)	$\rho^{\cdot}$ ($\times 10^3$)	s^2 ($\times 10^3$)	r or R	Ψ	F^{a}	n
σ_{mb}	3·37		1·16	0·8356	0·497	9·26	6^{b}
σ^{+}	2·52		0·627	0·9550	0·363	41·50	6^{b}
σ_{p}	4·36		0·857	0·9141	0·673	20·32	6^{b}
$\sigma^{\cdot}_{\mathrm{JJ}}$		−5·25	0·457	0·9763	0·265	81·50	6^{b}
$10\sigma^{\cdot}_{\alpha}$		−3·49	0·0944	0·9928	0·169	137·4	4^{c}
$\sigma^{\cdot}_{\mathrm{C}}$		−5·70	0·225	0·9943	0·131	347·9	6^{b}
$\sigma_{\mathrm{mb}}+\sigma^{\cdot}_{\mathrm{JJ}}$	1·17	−4·15	0·170	0·9976	0·0983	308·9	6^{b}
$\sigma_{\mathrm{mb}}+10\sigma^{\cdot}_{\alpha}$	0·115	−3·26	0·130	0·9932	0·233	36·28	4^{c}
$\sigma_{\mathrm{mb}}+\sigma^{\cdot}_{\mathrm{C}}$	−0·145	−5·88	0·256	0·9945	0·148	134·8	6^{b}
$\sigma^{+}+\sigma^{\cdot}_{\mathrm{JJ}}$	1·15	−3·22	0·0775	0·9995	0·0449	1487·8	6^{b}
$\sigma^{+}+10\sigma^{\cdot}_{\alpha}$	0·133	−3·22	0·128	0·9933	0·230	37·18	4^{c}
$\sigma^{+}+\sigma^{\cdot}_{\mathrm{C}}$	0·204	−5·28	0·254	0·9946	0·147	137·1	6^{b}
$\sigma_{\mathrm{p}}+\sigma^{\cdot}_{\mathrm{JJ}}$	1·69	−3·70	0·153	0·9980	0·0885	381·5	6^{b}
$\sigma_{\mathrm{p}}+10\sigma^{\cdot}_{\alpha}$	0·177	−3·35	0·124	0·9938	0·222	40·03	4^{c}
$\sigma_{p}+\sigma^{\cdot}_{\mathrm{C}}$	0·586	−5·07	0·223	0·9958	0·129	178·2	6^{b}

[a] Critical F values:[10] $F_{0\cdot001}$ (1, 4) = 74·14, $F_{0\cdot01}$ (1, 4) = 21·20, $F_{0\cdot05}$ (1, 4) = 7· 71, $F_{0\cdot01}$ (1, 2) = 98·5 $F_{0\cdot001}$ (2, 3) = 148·5, $F_{0\cdot01}$ (2, 3) = 30·82, $F_{0\cdot05}$ (2, 1) = 199·5.
[b] R = H, CH_3, OCH_3, Cl, Br and NMe_2.
[c] R = H, CH_3, Cl and OCH_3.

Table 6. Correlation results for **4**-Ys[a]

σ^{X} or $\sigma^{\cdot}$ or $\sigma^{\mathrm{X}}+\sigma^{\cdot}$	ρ^{X} ($\times 10^3$)	$\rho^{\cdot}$ ($\times 10^3$)	s^2 ($\times 10^3$)	r or R	Ψ	F^{b}
σ_{mb}	2·22		1·75	0·4461	1·16	0·746
σ^{+}	2·67		1·62	0·5601	1·07	1·37
σ_{p}	2·24		1·88	0·2605	1·25	0·218
$\sigma^{\cdot}_{\mathrm{JJ}}$		−13·2	0·722	0·9290	0·478	18·91
$10\sigma^{\cdot}_{\alpha}$		−11·5	1·13	0·8162	0·746	5·99
$\sigma^{\cdot}_{\mathrm{C}}$		−12·9	0·693	0·9347	0·459	20·75
$\sigma_{\mathrm{mb}}+\sigma^{\cdot}_{\mathrm{JJ}}$	0·779	−12·4	0·810	0·9408	0·536	7·70
$\sigma_{\mathrm{mb}}+10\sigma^{\cdot}_{\alpha}$	0·711	−10·7	1·34	0·8267	0·890	2·16
$\sigma_{\mathrm{mb}}+\sigma^{\cdot}_{\mathrm{C}}$	−0·470	−13·6	0·828	0·9381	0·548	7·33
$\sigma^{+}+\sigma^{\cdot}_{\mathrm{JJ}}$	0·781	−12·1	0·814	0·9402	0·538	7·63
$\sigma^{+}+10\sigma^{\cdot}_{\alpha}$	0·638	−10·4	1·36	0·8234	0·897	2·106
$\sigma^{+}+\sigma^{\cdot}_{\mathrm{C}}$	−0·828	−14·6	0·795	0·9430	0·526	8·03
$\sigma_{\mathrm{p}}+\sigma^{\cdot}_{\mathrm{JJ}}$	0·489	−13·0	0·874	0·9307	0·578	6·47
$\sigma_{\mathrm{p}}+10\sigma^{\cdot}_{\alpha}$	−1·52	−12·7	1·33	0·8307	0·880	2·23
$\sigma_{p}+\sigma^{\cdot}_{\mathrm{C}}$	−2·51	−14·9	0·601	0·9678	0·398	14·80

[a] R = H, CH_3, OCH_3, Cl and F.
[b] Critical F values:[10] $F_{0\cdot05}$ (1, 3) = 10·13, $F_{0\cdot1}$ (1, 3) = 5·54, $F_{0\cdot1}$ (2, 2) = 9·00.

still noteworthy that all the polar constants (σ^{X}) do not correlate the data, whereas both $\sigma^{\cdot}_{\mathrm{JJ}}$ and $\sigma^{\cdot}_{\mathrm{C}}$ can correlate the data, albeit poorly, with confidence levels greater than 95%. Therefore, the spin effect is still an important factor in affecting UV absorption processes of these aromatic molecules (**4**-Ys and **5**-Ys).

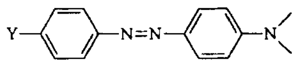
The value or significance of new observations or generalizations depends on their applicability to some other data reported in the literature. As pointed out by other workers[1-3] and in the Introduction, previously claimed 'successful' correlations are devoid of meaning if straight lines of different slopes (sometimes of opposite signs), or absolute values of substituent constants ($|\sigma^{\mathrm{X}}|$), have to be used for the correlations. The above-mentioned point will be illustrated by the following examples in which correlations with σ^{X} by equation (1) are compared either with correlations with $\sigma^{\cdot}$ by equation (2) or with correlations by the dual-parameter equation (3).

Mustroph[9a] reported the UV spectra of four kinds of *p*-Y-substituted charge transfer chromophores, namely

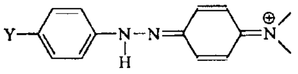
Table 7. Correlation results for **5**-Ys[a]

σ^X or $\sigma^{\bullet}$ or $\sigma^X+\sigma^{\bullet}$	ρ^X ($\times10^3$)	$\rho^{\bullet}$ ($\times10^3$)	s^2 ($\times10^3$)	r or R	Ψ	F[b]
σ_{mb}	2·14		1·70	0·445	1·16	0·739
σ^+	2·56		1·58	0·552	1·08	1·32
σ_p	2·04		1·84	0·244	1·25	0·190
$\sigma^{\bullet}_{JJ}$		−12·9	0·645	0·9401	0·440	22·82
$10\sigma^{\bullet}_{\alpha}$		−11·1	1·10	0·8121	0·753	5·81
$\sigma^{\bullet}_{C}$		−12·4	0·701	0·9289	0·478	18·87
$\sigma_{mb}+\sigma^{\bullet}_{JJ}$	0·727	−12·2	0·718	0·9508	0·490	9·43
$\sigma_{mb}+10\sigma^{\bullet}_{\alpha}$	0·690	−10·3	1·32	0·8226	0·899	2·09
$\sigma_{mb}+\sigma^{\bullet}_{C}$	−0·445	−13·1	0·840	0·9321	0·573	6·62
$\sigma^++\sigma^{\bullet}_{JJ}$	0·683	−12·0	0·730	0·9491	0·498	9·08
$\sigma^++10\sigma^{\bullet}_{\alpha}$	0·582	−10·1	1·33	0·8185	0·908	2·03
$\sigma^++\sigma^{\bullet}_{C}$	−0·835	−14·1	0·804	0·9379	0·549	7·31
$\sigma_p+\sigma^{\bullet}_{JJ}$	0·309	−12·8	0·786	0·9408	0·536	7·70
$\sigma_p+10\sigma^{\bullet}_{\alpha}$	−1·63	−12·4	1·29	0·8299	0·882	2·21
$\sigma_p+\sigma^{\bullet}_{C}$	−2·59	−14·5	0·596	0·9664	0·406	14·13

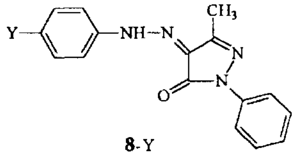
[a] R = H, CH_3, OCH_3, Cl and F.
[b] Critical F values:[10] $F_{0.05}$ (1, 3) = 10.13, $F_{0.1}$ (1, 3) = 5.54, $F_{0.1}$ (2, 2) = 9.00.



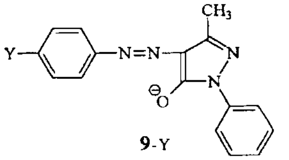
6-Y



7-Y



8-Y

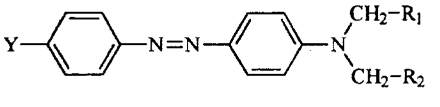


9-Y

4-dimethylaminoazobenzenes (**6**-Ys) and their protonated salts (**7**-Ys), the hydrazones of phenylazopyrazolones (**8**-Ys) and anions of the hydrazones of phenylazopyrazolones (**9**-Ys). Their plots of UV absorption wavenumbers of **6**-Y, **7**-Y, **8**-Y and **9**-Y against σ_p gave two crossing lines. The ν_{max} data on **6**-Ys cannot be correlated with σ^X by equation (1), i.e. for σ_p, $r=0{\cdot}75$, $n=8$, for σ^+, $r=0{\cdot}61$, $n=7$; and for σ_{mb}, $r=0{\cdot}79$, $n=8$. Similarly, the data cannot be correlated by equation (2). However, correlation by the dual-parameter equation (3) yields some good results with CL>99·9%., e.g. for $(\sigma_p+10\sigma^{\bullet}_{\alpha})$, $R=0.995$, $n=6$, $\Psi=0{\cdot}14$, $F=157$, $\rho^X=-2100$, $\rho^{\bullet}=-2080$, $|\rho^X/\rho^{\bullet}|=1{\cdot}01$; for $(\sigma_p+\sigma^{\bullet}_C)$, $R=0{\cdot}99$, $n=7$, $\Psi=0{\cdot}20$, $F=81$, $\rho^X=-2190$, $\rho^{\bullet}=-3070$, $|\rho^X/\rho^{\bullet}|=0{\cdot}71$, for $(\sigma^++\sigma^{\bullet}_C)$, $R=0{\cdot}99$, $n=7$, $\Psi=0{\cdot}21$, $F=80$, $\rho^X=-1480$, $\rho^{\bullet}=-3720$, $|\rho^X/\rho^{\bullet}|=0{\cdot}40$. For the protonated salts **7**-Ys, among the three σ^X scales and also the three $\sigma^{\bullet}$ scales, only σ^+ can correlate the data with a CL above 99% ($r=0{\cdot}91$, $n=7$, $F=24$). However, four pairings of $(\sigma^X+\sigma^{\bullet})$ yield correlations with CL>99·9%, namely for $(\sigma_p+\sigma^{\bullet}_{JJ})$, $R=0{\cdot}99$, $n=8$, $\Psi=0{\cdot}18$, $F=125$, $\rho^X=1850$, $\rho^{\bullet}=-2820$, $|\rho^X/\rho^{\bullet}|=0{\cdot}66$; for $(\sigma^++\sigma^{\bullet}_{JJ})$, $R=0{\cdot}997$, $n=7$, $\Psi=0{\cdot}096$, $F=378$, $\rho^X=1200$, $\rho^{\bullet}=-2500$, $|\rho^X/\rho^{\bullet}|=0{\cdot}48$; for $(\sigma^++\sigma^{\bullet}_C)$, $R=0{\cdot}995$, $n=7$, $\Psi=0{\cdot}13$, $F=202$, $\rho^X=1460$, $\rho^{\bullet}=-2170$, $|\rho^X/\rho^{\bullet}|=0{\cdot}67$; and for $(\sigma_p+\sigma^{\bullet}_C)$, $R=0{\cdot}995$, $n=7$, $\Psi=0{\cdot}13$, $F=200$, $\rho^X=2160$, $\rho^{\bullet}=-2820$, $|\rho^X/\rho^{\bullet}|=0{\cdot}76$. Similar results are obtained for the hydrazones **8**-Ys. Of the three σ^Xs and three $\sigma^{\bullet}$s, only σ^+ correlates the data with a CL>99% ($r=0{\cdot}89$, $n=7$, $F=19$), but three combinations of $(\sigma^X+\sigma^{\bullet})$ give correlations with CL>99·9%, namely for $(\sigma_p+\sigma^{\bullet}_{JJ})$, $R=0{\cdot}97$, $n=8$, $\Psi=0{\cdot}30$, $F=43$, $\rho^X=2070$, $\rho^{\bullet}=-3290$, $|\rho^X/\rho^{\bullet}|=0{\cdot}63$; for $(\sigma_p+\sigma^{\bullet}_C)$, $R=0{\cdot}99$, $n=7$, $\Psi=0{\cdot}17$, $F=127$, $\rho^X=2390$, $\rho^{\bullet}=-3460$, $|\rho^X/\rho^{\bullet}|=0{\cdot}69$; and for $(\sigma^++\sigma^{\bullet}_C)$, $R=0{\cdot}99$, $n=7$, $\Psi=0{\cdot}16$, $F=141$, $\rho^X=1620$, $\rho^X=-2750$, $|\rho^X/\rho^{\bullet}|=0{\cdot}59$. Finally, for the anions of the hydrazones **9**-Ys, the six correlations with σ^Xs and $\sigma^{\bullet}$s by equations (1) and (2) are again poor, but the dual-parameter correlations with $(\sigma^X+\sigma^{\bullet})$ yield good or fair results, i.e. for $(\sigma_p+10\sigma^{\bullet}_{\alpha})$, $R=0{\cdot}999$, $n=6$, $\Psi=0{\cdot}075$, $F=539$, CL>99·9%, $\rho^X=-2230$,

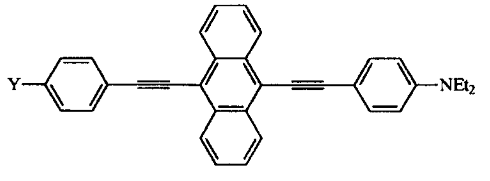
$\rho^{\cdot} = -4060$, $|\rho^{X}/\rho^{\cdot}| = 0{\cdot}55$; for $(\sigma_{p} + \sigma^{\cdot}_{JJ})$, $R = 0{\cdot}94$, $n = 8$, $\Psi = 0{\cdot}42$, $F = 20$, CL > 99%, $\rho^{X} = -3420$, $\rho^{\cdot} = -3900$, $|\rho^{X}/\rho^{\cdot}| = 0{\cdot}88$; and for $(\sigma_{p} + \sigma^{\cdot}_{C})$, $R = 0{\cdot}98$, $n = 7$, $\Psi = 0{\cdot}29$, $F = 40$, CL > 99%, $\rho^{X} = -2960$, $\rho^{\cdot} = -4130$, $|\rho^{X}/\rho^{\cdot}| = 0{\cdot}72$.

Mustroph and Epperlein[9b] also studied the UV spectra of 4-dialkylaminoazobenzenes (**10**-Ys), and reported absorption increments ε which are derived from the excitation-energy difference between azobenzene and monosubstituted azobenzenes. They found that the ε values could be correlated by two crossing lines. Actually, we have found that among the correlation results of ε with three σ^{X}s, only σ^{+} yields a CL > 99% whereas the correlation with $\sigma^{\cdot}$ ($\sigma^{\cdot}_{JJ}$ and $\sigma^{\cdot}_{C}$) gives CL > 99% (for $\sigma^{\cdot}_{JJ}$, $r = 0{\cdot}82$, $n = 12$, $F = 20$; for $\sigma^{\cdot}_{C}$, $r = 0{\cdot}84$, $n = 11$, $F = 21$). However, correlation by the dual-parameter equation (3) yields better results with CL > 99·9%, e.g. for $(\sigma^{+} + \sigma^{\cdot}_{JJ})$, $R = 0{\cdot}96$, $n = 10$, $\Psi = 0{\cdot}33$, $F = 40$, $\rho^{X} = -1{\cdot}18$, $\rho^{\cdot} = 4{\cdot}48$, $|\rho^{X}/\rho^{\cdot}| = 0{\cdot}26$; for $(\sigma^{+} + \sigma^{\cdot}_{C})$, $R = 0{\cdot}99$, $n = 10$, $\Psi = 0{\cdot}20$, $F = 125$, $\rho^{X} = -1{\cdot}56$, $\rho^{\cdot} = 4{\cdot}28$, $|\rho^{X}/\rho^{\cdot}| = 0{\cdot}36$; for $(\sigma_{p} + \sigma^{\cdot}_{C})$, $R = 0{\cdot}97$, $n = 11$, $\Psi = 0{\cdot}28$, $F = 65$, $\rho^{X} = -2{\cdot}02$, $\rho^{\cdot} = 4{\cdot}94$, $|\rho^{X}/\rho^{\cdot}| = 0{\cdot}41$.



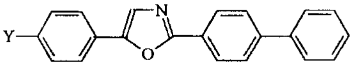
10-Y

Nakatsuji *et al.*[9f] has measured the ν_{max} of the UV spectra of *p*-Y-phenylethynyl-p′-diethylaminophenylethynyl-9,10-anthracenes (**11**-Ys) and found a correlation with σ_{p} by two crossing lines. Actually, correlation with any of the three σ^{X}s is poor ($r < 0{\cdot}55$, $n = 5$), but correlation with $\sigma^{\cdot}_{C}$ is good, i.e. $r = 0{\cdot}99$, $n = 5$, CL > 99·9%, while the other two $\sigma^{\cdot}$s ($\sigma^{\cdot}_{JJ}$ and $\sigma^{\cdot}_{\alpha}$) both yield correlations with CL > 99%. Application of the dual-parameter equation (3) does not improve the correlation.

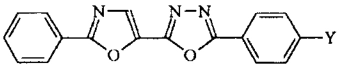


11-Y

Zhou and co-workers[9h,9i] found that absolute values of σ^{+} ($|\sigma^{+}|$) have to be used in order to correlate the UV data for 2-*p*-biphenyl-5-phenyloxazoles (12-Ys) and 5-phenyl-2-(2′-phenyloxazol-5′-yl)1,3,4-oxadiazoles (**13**-Ys). Actually, for **12**-Y, the ν_{max} values do not correlate with any of the three σ^{X}s, but they do correlate with $\sigma^{\cdot}_{C}$ by equation (2) with CL > 99·9% ($r = 0{\cdot}92$, $n = 9$, $\Psi = 0{\cdot}44$, $F = 39$). Furthermore, all of the following three pairs of $(\sigma^{X} + \sigma^{\cdot})$ correlations by equation (3) yield results with CL > 99·9%, i.e. for $(\sigma_{mb} + \sigma^{\cdot}_{C})$, $R = 0{\cdot}96$, $n = 9$, $\Psi = 0{\cdot}34$, $F = 36$, $\rho^{X} = -756$, $\rho^{\cdot} = -3726$, $|\rho^{X}/\rho^{\cdot}| = 0{\cdot}20$; for $(\sigma_{p} + \sigma^{\cdot}_{C})$, $R = 0{\cdot}97$, $n = 9$, $\Psi = 0{\cdot}29$, $F = 49$, $\rho^{X} = -1141$, $\rho^{\cdot} = -3712$, $|\rho^{X}/\rho^{\cdot}| = 0{\cdot}31$; and for $(\sigma^{+} + \sigma^{\cdot}_{C})$, $R = 0{\cdot}97$, $n = 9$, $\Psi = 0{\cdot}30$, $F = 47$, $\rho^{X} = -791$, $\rho^{\cdot} = -3996$, $|\rho^{X}/\rho^{\cdot}| = 0{\cdot}20$. The correlation results for **13**-Y are very similar. Application of equation (1) with any of the three σ^{X}s leads to no correlation, but application of equation (2) with either $\sigma^{\cdot}_{JJ}$ or $\sigma^{\cdot}_{C}$ leads to correlation with CL > 99·9%, i.e. for $\sigma^{\cdot}_{JJ}$, $r = 0{\cdot}93$, $n = 9$, $\Psi = 0{\cdot}41$, $F = 47$; for $\sigma^{\cdot}_{C}$, $r = 0{\cdot}97$, $n = 9$, $\Psi = 0{\cdot}28$, $F = 112$. The dual-parameter correlations with $(\sigma^{X} + \sigma^{\cdot})$ are equally successful (CL > 99·9%), i.e. for $(\sigma_{mb} + \sigma^{\cdot}_{C})$, $R = 0{\cdot}98$, $n = 9$, $\Psi = 0{\cdot}26$, $F = 62$, $\rho^{X} = 277$, $\rho^{\cdot} = -3508$, $|\rho^{X}/\rho^{\cdot}| = 0{\cdot}08$; for $(\sigma^{+} + \sigma^{\cdot}_{C})$, $R = 0{\cdot}98$, $n = 9$, $\Psi = 0{\cdot}27$, $F = 60$, $\rho^{X} = 214$, $\rho^{\cdot} = -3368$, $|\rho^{X}/\rho^{\cdot}| = 0{\cdot}06$; and for $(\sigma_{p} + \sigma^{\cdot}_{C})$, $R = 0{\cdot}97$, $n = 9$, $\Psi = 0{\cdot}28$, $F = 55$, $\rho^{X} = -233$, $\rho^{\cdot} = -3488$, $|\rho^{X}/\rho^{\cdot}| = 0{\cdot}07$.



12-Y



13-Y

On the basis of all the above-mentioned observations on our data and the data of previous workers, we are inclined to formulate our views as follows. In the absence of measurable steric effects, the chemical and spectral properties of radical or radicaloid species are always affected, albeit to different degrees, by both polar and spin-delocalization effects. Therefore, in correlation analyses of these properties [designated as variable in equations (1)–(3)], the applicability of the dual-parameter equation (3) should always be tested. The $|\rho^{X}/\rho^{\cdot}|$ ratio may serve as a rough measure of the relative importance of the polar effect and spin effect. For safety, it might be preferable to use the same ρ^{X} and $\rho^{\cdot}$ in this ratio, e.g. only $|\rho^{X}_{mb}/\sigma^{\cdot}_{JJ}|$ values are compared with each other. In general, four categories of possible circumstances may be considered. (i) When both polar and spin effects are important, the $|\rho^{X}/\rho^{\cdot}|$ values might fall in the range (very) roughly 0·2–0·8, e.g. in radical additions to[15a,15b] and fluorescence spectra, of styrenes.[8b,8c] Under these circumstances, the necessity for using the dual-parameter equation (3) can be easily established because it yields much better correlation results than those of single-parameter equations. (ii) When polar effects dominate, this ratio might be around or greater than unity, e.g. in hydrogen-atom abstraction reactions and EPR data of some phenyl nitroxides.[15c,15d] Under these circumstances, using equation (3) instead of equation (1) may not improve, or only slightly improve, the correlation result, and the necessity for applying equation (3) cannot be established in a definitive manner. However, the existence of the spin effect can still be revealed by careful examination of the individual and total deviations of the data from the regression lines of equations (1) and (3).[15c,15d] (iii) When the spin-delocalization effect dominates, then equation (2) easily applies, and the use of equation (3) does not improve or does not greatly improve the correlation result. (iv) When there are other complicating and interacting factors or effects, as pointed out by previous workers for some of the UV studies, then none of the three equations may be applicable.[1–3,9d,e,j] Finally, it should be pointed out that all $\rho^{\cdot}$ values of meaningful correlations reported in this and previous work[8a] are negative, and that this is certainly not a consequence of fortuity. This observation suggests that the Y-substituents can delocalize or stabilize the spin in the higher half-occupied orbital of the excited state and lower its energy, and that the extents of this excited-state stabilization by the substituents parallel their stabilizing abilities in the ground state. Therefore, up to now there seems to be no rigorously established justification for the use of excited-state substituent constants (σ^{ex}).[8b]

It is particularly noteworthy (as pointed out by a referee) that our data seem to reveal an interesting 'heteroatom effect'. That is, for compounds with a carbon atom in a position α to the ring and *para* to the Y substituent, e.g. compounds **1–5** and **11–13**, the single-parameter equation (2) suffices to correlate the UV data. However, for compounds with an α-nitrogen atom *para* to Y, e.g. compounds **6–10**, the dual-parameter equation (3) is needed for a good correlation. In other words, the behaviour of the former class of compounds falls into the third category of our discussions mentioned above, whereas the behaviour of the latter class of compounds belongs to the first category. It is hoped that this observation will lead to new research efforts in the future.

Naturally, the applicability of the $\sigma^{\cdot}$ scales and the dual-parameter equation (3) will be limited to the UV spectra of only certain types of compounds. It is not difficult to find cases where they do not apply in a simple manner, e.g. the data reported by Toma and coworkers[9d,9e] and Nakatsuji *et al.*[9j] However, on the basis of the present and preceding work,[8a] we can still conclude that spin delocalization is an important factor affecting the UV absorption processes of aromatic compounds.

EXPERIMENTAL

All UV spectra were measured at room temperature in 95% EtOH on a Perkin-Elmer Lambda 2 instrument with a wavelength accuracy of ±0·3 nm and a reproducibility of ±0·1 nm. ^{1}H NMR spectra were obtained at 90 MHz on a Varian EM-90C or at 60 MHz on a Varian EM-360A spectrometer with TMS as the external standard. Mass spectra were measured on a Hewlett-Packard Model 5989A spectrometer. IR spectra were recorded on Perkin-Elmer Model 983 or a Shimadzu IR-440 spectrometer.

Phenylacetylene (**1**-H) was purchased from Fluka and vacuum distilled before use (50–52 °C/30 Torr). Acetylenes **1**-Ys with Y = Cl, Br, t-Bu, Me, OMe, CN, F were prepared according to a previously described method.[16] Acetylenes **1**-Ys with Y = SiMe$_3$, NO$_2$, COMe, SMe, NMe$_2$, CF$_3$, CO$_2$Me were prepared by procedures[17,18] derived from the well known Heck reaction.[19] The sulphoxide **1**-SOMe was prepared from **1**-MeS by NaIO$_4$ oxidation.[20].

All **1**-Y substrates are known compounds and were further identified by ^{1}H NMR, IR and mass spectrometry. Boiling points or melting points of **1**-Ys prepared in our laboratory are as follows: **1**-Cl, m.p. 42–44 °C (lit.[21] 43·5–44 °C), **1**-Br, m.p. 64–65 °C (lit.[21] 63·5–63·7 °C); **1**-t-Bu, b.p. 68–69 °C/2 Torr (lit.[22] 67 °C/1·7 Torr); **1**-Me, b.p. 164–166 °C (lit.[21] 168 °C); **1**-OMe, b.p. 86–88 °C/9 Torr (lit.[23] 73–74 °C/2 Torr); **1**-CN, m.p. 154–155 °C (lit.[23] 153 °C); **1**-F, b.p. 45–49 °C/6·5 Torr (lit.[24] 34–35 °C/10 Torr); **1**-SiMe$_3$, b.p. 72–75 °C/4 Torr (lit.[25] 65–66 °C/2·5 Torr); **1**-NO$_2$, m.p. 148–149 °C (lit.[24] 149–150 °C); **1**-C(O)Me, m.p. 67·5–68·5 °C (lit.[18] 69–70 °C); **1**-CF$_3$, b.p. 58–60 °C/30 Torr (lit.[23] 47–48 °C/20 Torr); **1**-CO$_2$Me, m.p. 92–93 °C (lit.[17] 92·5–93·5 °C). (**1**-SMe[23] and **1**-SOMe were viscous compounds which could not be vacuum distilled.)

Acetophenone (**2**-H) and *p*-methoxyl acetophenone (**2**-OMe) are commercially available reagents. They were further purified by vacuum-distillation or recrystallization before use (**2**-H, b.p. 93–95 °C/20 Torr; **2**-OMe, m.p. 37–38 °C). Acetophenones **2**-Ys with Y = Cl, Br, F, Me, t-Bu, SMe, NMe$_2$ were prepared according to the well known Friedel–Crafts condensation of PhY with AcCl.[26]

All **2**-Y substrates are known compounds and were further identified by ^{1}H NMR, IR and mass spectrometry. Boiling points or melting points of **2**-Ys prepared in our laboratory are as follows: **2**-Cl, b.p. 110–111 °C/10 Torr (lit.[27] 232 °C), **2**-Br, m.p. 51–52·5 °C (lit.[28] 50–52 °C); **2**-F, b.p. 85–87 °C/20 Torr (lit.[29] 196 °C); **2**-Me, b.p. 103–105 °C/10 Torr (lit.[30] 224–225 °C); **2**-t-Bu, b.p. 130–132 °C/10 Torr (lit.[31] 262 °C/750 Torr); **2**-SMe, m.p. 81–82 °C (lit.[32] 80·6–81·4 °C); **2**-NMe$_2$, m.p. 124–125 °C (lit.[33] 125–126 °C).

All **3**-Ys, except **3**-NMe$_2$, are new compounds and were prepared by a known method.[34] The identities of **3**-Ys were further confirmed by the following data. For Y = H, ^{1}H NMR (90 MHz, CDCl$_3$), δ (ppm) 7·84 (AB, 4H, J_{AB} = 8·2 Hz), 7·43 (AB, 4H, J_{AB} = 8·1 Hz), 7·35 (AB, 2H, J_{AB} = 17·2 Hz), 3·03 (s, 3H); MS, m/z (relative intensity, %), 258 (M^{+}, 74·45), 195 (13·17), 178 (100·00), 179 (69·92), 155 (35·29), 91 (83·60);

IR, 3434·0, 3018·0, 2929·0, 1634·0, 1591·0, 1495·0, 1454·0, 1408·0, 1307·0, 876·0, 826·0 cm^{-1}. For $Y = CH_3$, ^1H NMR (90 MHz, $CDCl_3$), δ (ppm) 7·85 (AB, 4H, J_{AB} = 8·4 Hz), 7·37 (AB, 4H, J_{AB} = 8·4 Hz), 7·30 (AB, 2H, J_{AB} = 15·0 Hz), 2·97 (s, 3H), 2·40 (s, 3H); MS, m/z (relative intensity, %), 272 (M^+, 30·12), 273 (5·63), 274(1·93), 188(1·29), 178(36·00), 170(40·59), 155(44·73), 115(2·12), 107(32·53), 91(100·00); IR, 3438·0, 3011·0, 2974·0, 2926·0, 2284·0, 1922·0, 1630·0, 1593·0, 1513·0, 1458·0, 1408·0, 1385·0, 1323·0, 1304·0, 1293·0, 1226·0, 857·0 cm^{-1}. For $Y = CH_3O$[35], ^1H NMR (90 MHz, $CDCl_3$), δ (ppm) 7·81 (AB, 4H, J_{AB} = 8·5Hz), 7·40(AB, 4H, J_{AB} = 8·4Hz), 66·97(AB, 2H, J_{AB} = 16·4Hz), 3·90(s, 3H), 3·10(s, 3H); MS, m/z (relative intensity, %), 288 (M^+, 100·00), 289 (18·10), 290 (14·73), 257 (2·92), 225 (10·61), 209 (17·47), 194 (17·07), 178 (17·86); IR, 3458·0, 3009·0, 2926·0, 2844·0, 1632·0, 1604·0, 1590·0, 1575·0, 1513·0, 1456·0, 1445·0, 1424·0, 1407·0, 1300·0, 1261·0, 874·0 cm^{-1}. For Y = Cl, ^1H NMR (90 MHz, $CDCl_3$), δ (ppm) 7·83 (AB, 4H, J_{AB} = 8·4 Hz), 7·45 (AB, 2H, J_{AB} = 15·9 Hz), 7·37 (AB, 4H, J_{AB} = 8·2 Hz), 3·07 (s, 3H); MS, m/z (relative intensity, %), 292 (M^+, 84·03), 293 (16·43), 294 (32·48), 295 (5·80), 257 (5·99), 229 (22·50), 213 (33·12), 178 (98·88), 69 (100·00); IR, 3442·0, 3021·0, 2925·0, 1633·0, 1588·0, 1494·0, 1411·0, 1308·0, 1300·0, 1194·0, 873·0, 839·0 cm^{-1}. For Y = Br, ^1H NMR (90 MHz, $CDCl_3$), δ (ppm) 7·82 (AB, 4H, J_{AB} = 8·3 Hz), 7·17–7·48 (multiple, 6H), 3·08 (s, 3H); MS, m/z (relative intensity, %), 336 (50·62), 338 (51·42), 339 (9·15), 273 (8·31), 257 (12·83), 259 (10·60), 178 (100·00), 179 (15·39), 166 (17·40); IR, 3458·0, 3012·0, 2926·0, 1908·0, 1633·0, 1594·0, 1582·0, 1487·0, 1411·0, 1308·0, 1192·0, 808·0 cm^{-1}. For $Y = NMe_2$,[33,34] ^1H NMR (90 MHz, $CDCl_3$), δ (ppm) 7·75 (AB, 4H, J_{AB} = 8·4 Hz), 7·35 (AB, 4H, J_{AB} = 8·4 Hz), 7·45 (AB, 2H, J_{AB} = 16·5 Hz), 3·08 (s, 3H), 3·04 (s, 3H); MS, m/z (relative intensity, %), 301 (M^+, 100·00), 302 (20·46), 303 (6·79), 300 (21·51), 222 (21·56), 178 (17·50); IR, 2925·0, 1686·0, 1587·0, 1525·0, 1485·0, 1447·0, 1407·0, 1364·0, 1301·0, 1226·0, 870·0, 830·0 cm^{-1}.

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