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Correlation analysis of UV spectral data of some phenylhydrazones and semicarbazones by the dual-parameter equation. Observation of three types of behaviors of the λ_{max} values induced by the polar effects of substituents

William Fa-Xiang Ding and Xi-Kui Jiang*

Shanghai Institute of Organic Chemistry, Academia Sinica, 354 Feng-Lin Lu, Shanghai, 200032, China

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ABSTRACT: The K-band λ_{max} values of the UV spectra of five types of *p*-Y-benzaldehyde derivatives, namely phenylhydrazones (**1**-Ys), 2,4-dinitrophenylhydrazones (**2**-Ys), 4-nitrophenylhydrazones (**3**-Ys), semicarbazones (**4**-Ys) and *N*-phenylsemicarbazones (**5**-Ys), were measured and the corresponding wavenumbers (ν_{max}) calculated. Correlation analyses of the ν_{max} values by the dual-parameter equation show that the ν_{max} values of these compounds are affected, albeit to different degrees, by both spin-delocalization effects ($\sigma^{\cdot}$) and polar effects (σ^{x}) of the substituents. The spin-delocalization effects of substituents always facilitate bathochromic shifts of the λ_{max} values ($\rho^{\cdot}$ negative). However, polar effects of the substituents on these λ_{max} data depend on the mode of polarization of these hydrazone or semicarbazone molecules, i.e. electron-pair acceptor substituents (Ys) facilitate bathochromic shifts for **1**-Ys (ρ^{x} negative), but hypsochromic shifts for **2**-Ys and **3**-Ys (ρ^{x} positive), and induce very small shifts for **4**-Ys and **5**-Ys. As expected, donor Ys facilitate hypsochromic shifts for **1**-Ys and bathochromic shifts for **2**-Ys and **3**-Ys and induce very small shifts for **4**-Ys and **5**-Ys. Possibly, a higher degree of polarization of the substrate molecule would demand a higher degree of polar assistance from the substituents at the transition states. © 1998 John Wiley & Sons, Ltd.

KEYWORDS: UV spectra; dual-parameter equation; correlation analysis; polar effect; spin-delocalization effect; *p*-Y-substituted benzaldehyde phenylhydrazones; *p*-Y-substituted benzaldehyde 2,4-dinitrophenylhydrazones; *p*-Y-substituted benzaldehyde 4-nitrophenylhydrazones; *p*-Y-substituted benzaldehyde *N*-phenylsemicarbazones; *p*-Y-substituted benzaldehyde semicarbazones.

INTRODUCTION

The importance of benzaldehyde phenylhydrazone and semicarbazone derivatives in analytical organic chemistry had led to many investigations of their ultraviolet spectra.[1–7] Notably, an interesting phenomenon of the substituent effect on the UV spectral data of benzaldehyde derivatives has been reported,[1] i.e. a *para*-positioned methoxy group at the benzene ring causes a bathochromic shift for 2,4-dinitrophenylhydrazones,[2] but induces a small hypsochromic shift for *N*,*N*-dimethylhydrazones. Furthermore, it leads to neither a bathochromic nor a hypsochromic shift for *N*-methylhydrazones. Correlation of the UV data of the above-mentioned studies by the dual-parameter equation (1), where $\rho^{x}\sigma^{x}$ and $\rho^{\cdot}\sigma^{\cdot}$ represent polar and spin-delocalization effects, respectively, had not been tried, although the single-parameter relationship [cf. Eqn (2)] had been applied to the correlation of UV data of nitro-, dinitro- and trinitrophenylhydrazones by plotting λ_{max} values against σ_{p} or $^{+2}$. However, no correlation coefficient (r) was reported,[8–10] hence reversion of the sign of ρ^{x} values for the aforesaid three types of phenylhydrazones could not have been rigorously demonstrated.

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

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

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

Our recent studies on the correlation analyses of UV data for styrenes, α-methylstyrenes, α,β,β-trifluorostyrenes,[11a] phenylacetylenes and acetophenones, all with a double or triple bond in conjugation with the *p*-Y-substituted benzene ring,[11b] by the single-parameter equation (3) with the spin-delocalization constant ($\sigma^{\cdot}$), have shown that the excited states of styrene-type aromatic compounds have radicaloid properties and the π–π^{*} transitions are mainly affected by the spin-delocalization effects of the substituents. Even though

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**Correspondence to:* X.-K. Jiang, Shanghai Institute of Organic Chemistry, Academia Sinica, 354 Feng-Lin Lu, Shanghai, 200032, China.

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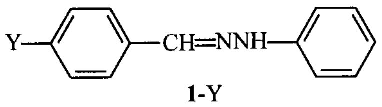
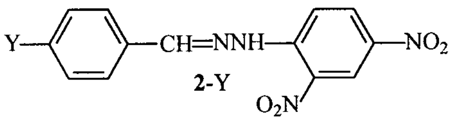


1-Y



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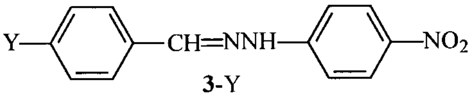

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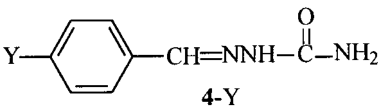
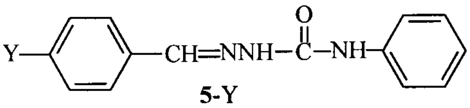


4-Y



5-Y

application of the dual-parameter equation (1) did not improve the correlation results of the UV spectral data of the above-mentioned styrene-type aromatic compounds, we still proposed that spectral and kinetic properties of radicaloid transition states (TSs) are always affected, albeit to different degrees, by both polar and spin-delocalization effects.[11b,12–15] In other words,in the correlation analysis of these properties,the applicability of the dual-parameter equation (1) should always be tested.[13] The $|\rho^{x}/\rho^{\cdot}|$ ratio, e.g. with $\rho^{x} = \rho_{mb}$ and $\rho^{\cdot} = \rho_{JJ}^{\cdot}$, may serve as a rough measure of the relative importance of the polar and the spin-delocalization effects of substituents.[16]

On the basis of the aforesaid correlation analysis of kinetic and spectral data, we came to realize that, in the absence of measurable steric effects, for correlation analyses in radical chemistry and some spectral data (e.g. UV, fluorescence, EPR and redox), four categories of possible circumstances might be visualized.[13,15] (I) When both polar and spin effects are important, the $|\rho_{mb}/\rho_{JJ}^{\cdot}|$ values might fall in the range (very) roughly 0.2–0.8, e.g. in electrophilic radical additions to, and fluorescence spectra of, styrenes.[14a,b,g] Under these circumstances, the necessity of using the dual-parameter equation (1) 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 H-atom abstraction reactions by electrophilic radicals,[14c,d] electrophilic radical addition reactions to phenylacetylenes[15a,b] and EPR data of some phenylnitroxides.[14e,f] Under these circumstances, using Eqn (1) instead of Eqn (2) may not much improve the correlation result, and the necessity of applying Eqn (1) cannot be established in a definitive manner. However, the existence of the spin effect can still be revealed by careful examination of the individual deviations of the data from the regression lines of Eqns (1) and (2). (III) When the spin-delocalization effect dominates, then Eqn (3) easily applies, and the use of Eqn (1) may not much improve the correlation result. Application of Eqn (1) might yield a $|\rho_{mb}/\rho_{JJ}^{\cdot}|$ ratio of less than 0.2. Recently discovered examples are the UV spectra of the aforesaid styrene-type compounds.[11] (IV) When there are other complicating and interacting factors or effects, then none of the three equations can be successfully applied.[8–11,15e]

To our knowledge, the UV data for benzaldehyde hydrazone derivatives have not been correlated by the dual-parameter equation (1), and therefore there has been insufficient understanding about how these spectral properties are affected by polar and spin-delocalization effects of the substituents. This paper is an attempt to correlate the UV absorption frequencies by the dual-parameter equation (1) with the wavenumber ν_{max} as the variable, and to show how the sign of ρ^{x} might be related to the mode of polarization of the substrate.

It has been well established that spin delocalization is a resonance effect which operates independently of the polar effects (including resonance polar effects) (see Ref. 13 and pertinent references cited therein). It has also been established that the spin-delocalization effect of *meta*-substituents is negligible or very small.[12b] Since one of the main objectives of our study was to evaluate the relative importance of the polar and spin-delocalization effects of the substituents, *meta*-substituted substrates were not included in all our previous studies.[13] Therefore, all the substrates chosen for our correlation analysis were *para*-substituted compounds, namely *p*-Y-substituted benzaldehyde phenylhydrazones (**1**-Ys), *p*-Y-substituted benzaldehyde 2,4-dinitrophenylhydrazones (**2**-Ys), *p*-Y-substituted benzaldehyde 4-nitrophenylhydrazones (**3**-Ys), *p*-Y-substituted benzaldehyde semicarbazones (**4**-Ys) and *p*-Y-substituted benzaldehyde *N*-phenylsemicarbazones (**5**-Ys).

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. Values of representative Hammett-type unresolved polar substituent constants (σ^{x}), i.e. σ_p, σ^{+} and σ_{mb}, were taken from Refs 17, 17 and 12a, respectively. Values of representative spin-delocalization constants ($\sigma^{\cdot}$), i.e. $\sigma_{JJ}^{\cdot}$, $\sigma_{C}^{\cdot}$ and $\sigma_{\alpha}^{\cdot}$, were

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

	1-Y			**2**-Y			**3**-Y		
Y	λ_{max}	ν_{max} ($\times 10^4$)	ε_{max} ($\times 10^4$)	λ_{max}	ν_{max} ($\times 10^4$)	ε_{max} ($\times 10^4$)	λ_{max}	ν_{max} ($\times 10^4$)	ε_{max} ($\times 10^4$)
H	354.4	2.822	2.24	376.8	2.654	2.97	400.7	2.496	4.88
CF_3	360.1	2.777	3.12	374.1	2.673	2.58	398.2	2.511	2.84
F	344.3	2.904	2.41	377.6	2.648	2.48	398.9	2.507	2.31
Br	354.3	2.822	1.04	379.0	2.639	2.88	400.7	2.496	2.98
Cl	352.8	2.834	3.28	378.9	2.639	3.43	400.4	2.498	3.26
Me	345.2	2.897	2.18	383.0	2.611	3.11	404.9	2.470	2.88
CO_2Me	371.7	2.690	3.02	380.6	2.627	2.91			
$SiMe_3$				377.9	2.646	3.69			
MeO	346.5	2.886	5.73	390.5	2.561	3.00	412.8	2.422	3.98
CN	379.4	2.636	2.91	377.8	2.647	3.01	408.9	2.446	3.08
NO_2	423.1	2.364	2.53	391.2	2.556	3.20	423.2	2.363	2.55
MeS	357.2	2.800	2.71	390.2	2.563	3.24	410.2	2.438	4.14
Me_2N	358.0	2.793	3.50	422.5	2.367	3.16	432.6	2.312	3.89

[a] Uncertainty: ±0.3 nm.

taken from Refs 12a, 18a and 18b, respectively. Results of correlation analyses in terms of ρ^x, $\rho^\cdot$, s,r or R, ψ and F values (cf. Ref. 11) by Eqns (1)–(3) are summarized in Table 3 (for **1**-Ys), 4 (for **2**-Ys), 5 (for **3**-Ys), 6 (for **4**-Ys) and 7 (for **5**-Ys). The identity of the substituents used in each entry is given in the footnotes to the tables. It should be noted that relative small differences in the r or R, ψ and F values of the different entries in the same table should not be taken too seriously because various complicating factors could affect the exact position of the UV absorption peaks.[8,9,10,11] The nitro group always seems to deviate from the regression lines much more than other substituents do,[2] possibly because it takes up a distinctively different geometric orientation in the excited state;[19] therefore, the nitro group was not included in our correlation. Also, as mentioned previously, a confidence level (CL) above 99.9% (based on $F_{0.001}$ values given in the the footnotes of the tables[11]) 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).

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

	4-Y			**5**-Y		
Y	λ_{max}	ν_{max} ($\times 10^4$)	ε_{max} ($\times 10^4$)	λ_{max}	ν_{max} ($\times 10^4$)	ε_{max} ($\times 10^4$)
H	281.9	3.547	2.48	293.7	3.405	3.97
CF_3	290.4	3.444	2.22	301.8	3.314	4.81
F	279.0	3.584	4.40	286.9	3.486	3.72
Br	287.4	3.479	4.97	300.7	3.326	4.81
Cl	286.6	3.489	2.68	298.6	3.349	3.72
Me	284.6	3.514	3.11	295.7	3.382	4.52
MeO	288.0	3.472	2.69	293.1	3.412	4.97
CN	303.2	3.298	2.06	315.4	3.171	3.72
NO_2	327.2	3.056	1.29	341.3	2.930	3.05
MeS	313.6	3.189	3.47	320.1	3.124	5.91
Me_2N	331.9	3.013	3.20	340.9	2.933	6.28

[a] Uncertainty: ±0.3 nm.

Results of single-parameter correlation of the wavenumbers (ν_{max}) of **1**-Ys by Eqn (2) or (3), summarized in Table 3, show that neither σ^x nor $\sigma^\cdot$ yields meaningful results, i.e. $r < 0.70$, $\psi > 0.80$, $F < 8.2$ ($n = 11$ or 9). In contrast, unlike the UV spectra of styrene-type compounds,[11] correlations by the dual-parameter equation (1) clearly yield much improved results (cf. Figs 1 and 2). It should be noted that the σ_{mb} scale is used in Fig. 1

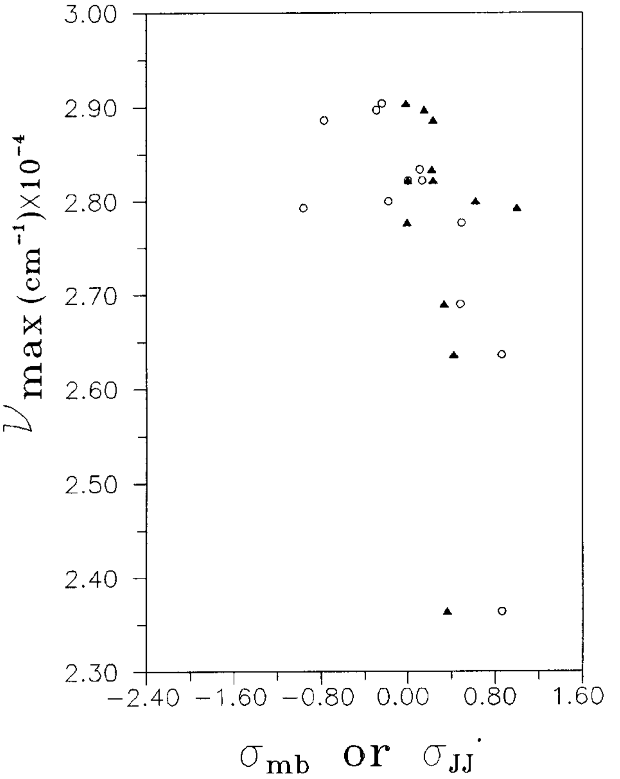


Figure 1. Plot of ν_{max} (cm^{-1}) vs σ_{mb} (○) or $\sigma_{JJ}^{\cdot}$ (▲) for **1**-Ys

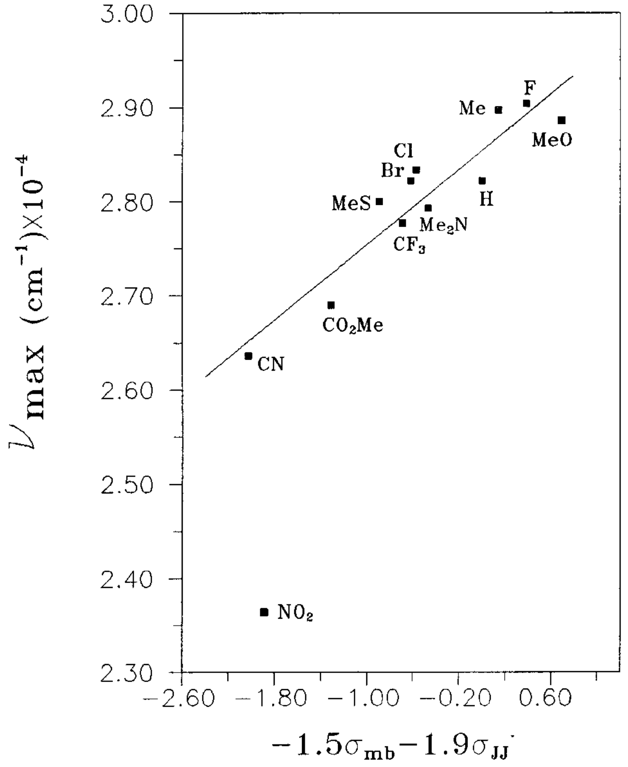


Figure 2. Plot of ν_{max} (cm^{-1}) vs $-1.5\sigma_{mb}$ $-1.9\sigma_{JJ}^{\cdot}$ for **1**-Ys

because it yields the best correlation among the three σ^x scales (cf. Table 3), while the (σ_{mb}, $\sigma_{JJ}^{\cdot}$) combination is used in Fig. 2 because it gives the $|\rho_{mb}/\rho_{JJ}^{\cdot}|$ value which is used as a rough measure of the relative importance of polar and spin-delocalization effects of substituents, as mentioned in the Introduction.[13] All the (σ^x, $\sigma^{\cdot}$) combinations, with the (σ_p, $\sigma_{JJ}^{\cdot}$) combination as the only exception, yield very good correlations (all CLs >99.9%), e.g. for (σ^+, $\sigma_{JJ}^{\cdot}$); $R = 0.929$, $\psi = 0.434$, $F = 25.23$, $n = 11$; for (σ_{mb}, $\sigma_{JJ}^{\cdot}$), $R = 0.937$, $\psi = 0.409$, $F = 28.82$, $n = 11$. Correlation results for other (σ^x, $\sigma^{\cdot}$) combinations are clearly summarized in Table 3 and are not discussed because of limited space. Therefore, judging by the $|\rho_{mb}/\rho_{JJ}^{\cdot}|$ value of 0.79 and by the fact that the dual-parameter correlation is clearly much better than the single-parameter correlation, the behavior of the UV spectral data of **1**-Ys may be classified as category I, i.e. the wavenumbers of **1**-Ys are affected to comparable extents by both polar and spin-delocalization effects. All $^{\cdot}$ values derived from the (σ^x, $\sigma^{\cdot}$) combinations are negative; this result demonstrates that all substituents induce bathochromic shifts by their spin-delocalization effects and is fully is harmony with the observations on styrenes, phenylacetylenes and acetophenones. On the other hand, all the ρ^x values derived from the (σ^x, $\sigma^{\cdot}$) combinations are negative; this result shows that an electron-pair acceptor substituent will facilitate a bathochromic shift, whereas a donor will facilitate a hypsochromic shift.

We may now ask the question, 'Can the sign of ρ^x be reversed when the mode of polarization of the substrate is changed or reversed?' A change in the polarity of **1**-Ys might be achieved by putting two nitro groups on the benzene ring attached to the nitrogen atom, i.e. by taking **2**-Ys as substrates. The correlation results summarized in Table 4 show that correlations with CLs greater than 99.9% can be achieved with either Eqn (2) or (3) with σ^+, $\sigma_{JJ}^{\cdot}$ or $\sigma_C^{\cdot}$, i.e. for σ^+, $r = 0.908$, $\psi = 0.459$, $F = 46.90$, $n = 12$; for $\sigma_{JJ}^{\cdot}$, $r = 0.852$, $\psi = 0.572$, $F = 26.53$, $n = 12$; for $\sigma_C^{\cdot}$, $r = 0.836$, $\psi = 0.601$, $F = 23.27$, $n = 12$. Notably, correlations by the dual-parameter equation (1) yield much improved results (cf. R or r and ψ values; Figs 3 and 4). The σ^+ scale is used in Fig. 3 because it yields the best correlation for **2**-Ys among the three σ^x scales. All the (σ^x, $\sigma^{\cdot}$) combinations yield very good correlations

Table 3. Values of ρ^x and $\rho^{\cdot}$ of Eqns (1), (2) and (3) and corresponding values of the correlation coefficient r or R, ψ, s and F-test for correlation of ν_{max} values of **1**-Ys with σ^x and $\sigma^{\cdot}$

σ^x or $\sigma^{\cdot}$ or (σ^x, $\sigma^{\cdot}$)	ρ^x (× 10^4)	$\rho^{\cdot}$ (× 10^4)	r or R	s (× 10^4)	ψ	F[a]	n[b]
σ_p	−0.11 ± 0.08		0.546	0.073	0.926	3.82	11
σ^+	−0.052 ± 0.052		0.438	0.079	0.994	2.14	11
σ_{mb}	−0.11 ± 0.08		0.689	0.063	0.801	8.14	11
$\sigma_{JJ}^{\cdot}$		−0.091 ± 0.088	0.334	0.083	1.042	1.13	11
$10\sigma_{\alpha}^{\cdot}$		−0.19 ± 0.11	0.521	0.084	0.968	2.61	9
$\sigma_C^{\cdot}$		−0.14 ± 0.09	0.469	0.077	0.977	2.53	11
σ_p, $\sigma_{JJ}^{\cdot}$	−0.19 ± 0.05	−0.23 ± 0.04	0.898	0.041	0.516	16.64	11
σ_p, $10\sigma_{\alpha}^{\cdot}$	−0.23 ± 0.05	−0.16 ± 0.04	0.953	0.033	0.373	29.40	9
σ_p, $\sigma_C^{\cdot}$	−0.18 ± 0.03	−0.26 ± 0.03	0.952	0.028	0.360	38.50	11
σ^+, $\sigma_{JJ}^{\cdot}$	−0.14 ± 0.02	−0.29 ± 0.04	0.929	0.034	0.434	25.23	11
σ^+, $10\sigma_{\alpha}^{\cdot}$	−0.15 ± 0.04	−0.23 ± 0.04	0.961	0.030	0.339	36.19	9
σ^+, $\sigma_C^{\cdot}$	−0.12 ± 0.01	−0.32 ± 0.03	0.975	0.021	0.263	75.54	11
σ_{mb}, $\sigma_{JJ}^{\cdot}$	−0.15 ± 0.03	−0.19 ± 0.03	0.937	0.032	0.409	28.82	11
σ_{mb}, $10\sigma_{\alpha}^{\cdot}$	−0.15 ± 0.03	−0.14 ± 0.04	0.960	0.030	0.344	34.98	9
σ_{mb}, $\sigma_C^{\cdot}$	−0.13 ± 0.02	−0.22 ± 0.03	0.973	0.021	0.269	72.13	11

[a] Critical F values:[20] $F_{0.10}$ (1,9) = 3.36; $F_{0.01}$ (2,8) = 8.65; $F_{0.001}$ (2,8) = 18.49; $F_{0.001}$ (2,6) = 27.00; $F_{0.25}$ (1,9) = 1.51; $F_{0.25}$ (1,7) = 1.57.

[b] $n = 11$, Y = H, CF_3, F, Br, Cl, CN, Me, CO_2Me, MeO, MeS and Me_2N; $n = 9$, Y = H, CF_3, F, Cl, CN, Me, CO_2Me, MeO and MeS.

Table 4. Values of ρ^x and $\rho^{\cdot}$ of Eqns (1),(2) and (3) and corresponding values of the correlation coefficient *r* or *R*, ψ, *s* and *F*-test for correlation of ν_{max} values of **2**-Ys with σ^x and $\sigma^{\cdot}$

σ^x or $\sigma^{\cdot}$ or (σ^x, $\sigma^{\cdot}$)	ρ^x (× 10^4)	$\rho^{\cdot}$ (× 10^4)	*r* or *R*	*s* (× 10^4)	ψ	F^a	n^b
σ_p	0.17 ± 0.06		0.811	0.051	0.641	19.22	12
σ^+	0.11 ± 0.02		0.908	0.036	0.459	46.90	12
σ_{mb}	0.12 ± 0.05		0.747	0.058	0.728	12.62	12
$\sigma_{JJ}^{\cdot}$		−0.24 ± 0.05	0.852	0.046	0.572	26.53	12
$10\sigma_{\alpha}^{\cdot}$		−0.095 ± 0.042	0.597	0.032	0.897	4.42	10
$\sigma_C^{\cdot}$		−0.26 ± 0.06	0.836	0.048	0.601	23.27	12
σ_p, $\sigma_{JJ}^{\cdot}$	0.10 ± 0.03	−0.17 ± 0.03	0.958	0.026	0.332	50.09	12
σ_p, $10\sigma_{\alpha}^{\cdot}$	0.078 ± 0.030	−0.11 ± 0.03	0.878	0.021	0.573	11.73	10
σ_p, $\sigma_C^{\cdot}$	0.12 ± 0.02	−0.19 ± 0.02	0.978	0.019	0.240	100.1	12
σ^+, $\sigma_{JJ}^{\cdot}$	0.076 ± 0.014	−0.13 ± 0.02	0.951	0.022	0.275	74.60	12
σ^+, $10\sigma_{\alpha}^{\cdot}$	0.059 ± 0.015	−0.078 ± 0.017	0.956	0.013	0.352	36.86	10
σ^+, $\sigma_C^{\cdot}$	0.080 ± 0.009	−0.15 ± 0.02	0.988	0.014	0.181	179.7	12
σ_{mb}, $\sigma_{JJ}^{\cdot}$	0.080 ± 0.021	−0.19 ± 0.02	0.972	0.022	0.273	75.98	12
σ_{mb}, $10\sigma_{\alpha}^{\cdot}$	0.063 ± 0.012	−0.12 ± 0.01	0.973	0.010	0.276	62.32	10
σ_{mb}, $\sigma_C^{\cdot}$	0.089 ± 0.011	−0.21 ± 0.01	0.991	0.012	0.154	250.1	12

[a] Critical *F* values:[20] $F_{0.001}(1,10) = 21.04$; $F_{0.01}(1,10) = 10.04$; $F_{0.001}(1,8) = 25.42$; $F_{0.01}(1,8) = 11.26$; $F_{0.001}(2,9) = 16.36$; $F_{0.001}(2,7) = 21.69$; $F_{0.01}(2,7) = 9.55$.

[b] $n = 12$, Y = H, CF_3, F, Br, Cl, CN, Me, CO_2Me, $SiMe_3$, MeO, MeS and Me_2N; $n = 10$, Y = H, CF_3, F, Cl, CN, Me, CO_2Me, $SiMe_3$, MeO and MeS.

(CLs > 99.9%), e.g. for (σ_p, $\sigma_{JJ}^{\cdot}$), $R = 0.958$, $\psi = 0.332$, $F = 50.09$, $n = 12$; for (σ^+, $\sigma_{JJ}^{\cdot}$), $R = 0.951$, $\psi = 0.275$, $F = 74.60$, $n = 12$; for (σ_{mb}, $\sigma_{JJ}^{\cdot}$), $R = 0.972$, $\psi = 0.273$, $F = 75.98$, $n = 12$. Judging by the $|\rho_{mb}/\rho_{JJ}^{\cdot}|$ value of 0.42 and the fact that the dual-parameter correlation is clearly better than the single-parameter correlation, the behavior of the UV spectral data of **2**-Ys may be classified as category I. Furthermore, similarly to the results for **1**-Ys, all the $\rho^{\cdot}$ values derived from the (σ^x, $\sigma^{\cdot}$) combinations are negative. Of particular interest, however, is the observation that, in contrast to the results for **1**-Ys, the ρ^x values now all become positive. In other words, the

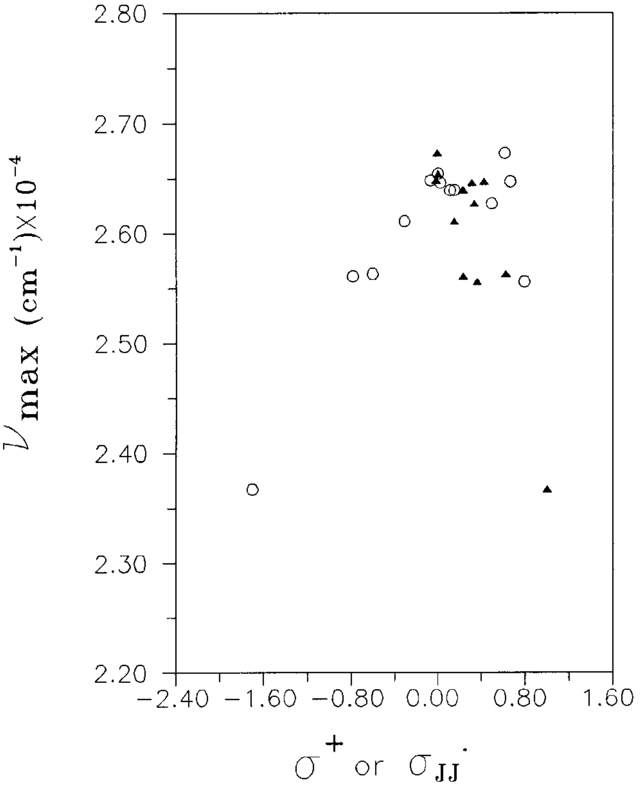


Figure 3. Plot of ν_{max} (cm^{-1}) vs σ^+ (○) or $\sigma_{JJ}^{\cdot}$ (▲) for **2**-Ys

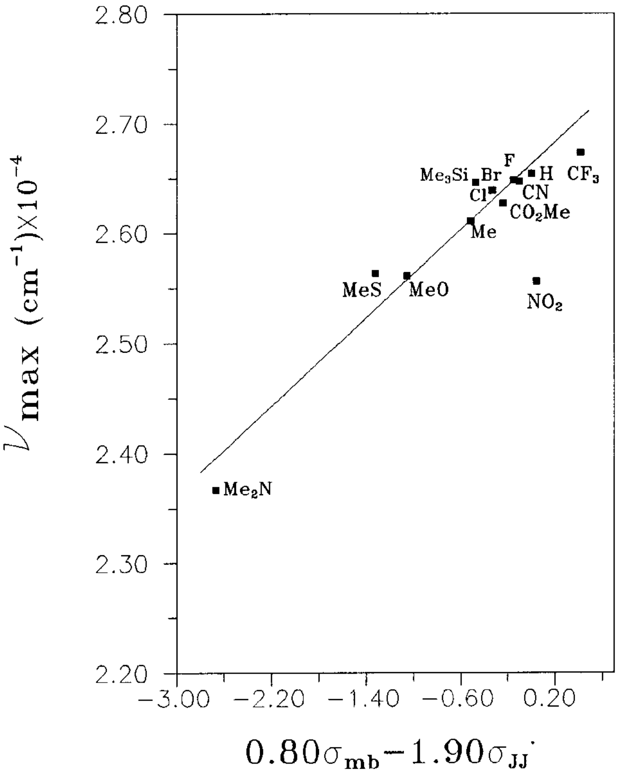


Figure 4. Plot of ν_{max} (cm^{-1}) vs $0.80\sigma_{mb} - 1.90\sigma_{JJ}^{\cdot}$ for **2**-Ys

Table 5. Values of ρ^{x} and $\rho^{\cdot}$ of Eqns (1), (2) and (3) and corresponding values of the correlation coefficient *r* or *R*, ψ, *s* and *F*-test for correlation of ν_{max} values of **3**-Ys with σ^{x} and $\sigma^{\cdot}$

σ^{x} or $\sigma^{\cdot}$ or (σ^{x}, $\sigma^{\cdot}$)	ρ^{x} ($\times 10^4$)	$\rho^{\cdot}$ ($\times 10^4$)	*r* or *R*	*s* ($\times 10^4$)	ψ	F[a]	n[b]
σ_p	0.11 ± 0.05		0.737	0.043	0.755	9.53	10
σ^{+}	0.072 ± 0.023		0.834	0.035	0.617	18.28	10
σ_{mb}	0.070 ± 0.048		0.621	0.050	0.877	5.01	10
$\sigma_{JJ}^{\cdot}$		-0.17 ± 0.03	0.904	0.027	0.478	35.79	10
$10\sigma_{\alpha}^{\cdot}$		-0.11 ± 0.03	0.784	0.023	0.718	9.536	8
$\sigma_C^{\cdot}$		-0.20 ± 0.03	0.933	0.023	0.403	53.62	10
σ_p, $\sigma_{JJ}^{\cdot}$	0.049 ± 0.026	-0.13 ± 0.02	0.949	0.022	0.377	31.71	10
σ_p, $10\sigma_{\alpha}^{\cdot}$	0.032 ± 0.034	-0.11 ± 0.03	0.838	0.022	0.690	5.91	8
σ_p, $\sigma_C^{\cdot}$	0.053 ± 0.013	-0.16 ± 0.01	0.986	0.011	0.196	126.3	10
σ^{+}, $\sigma_{JJ}^{\cdot}$	0.034 ± 0.014	-0.12 ± 0.02	0.947	0.022	0.383	30.64	10
σ^{+}, $10\sigma_{\alpha}^{\cdot}$	0.022 ± 0.027	-0.094 ± 0.030	0.846	0.022	0.674	6.31	8
σ^{+}, $\sigma_C^{\cdot}$	0.035 ± 0.008	-0.14 ± 0.01	0.984	0.012	0.214	105.4	10
σ_{mb}, $\sigma_{JJ}^{\cdot}$	0.034 ± 0.021	-0.15 ± 0.02	0.946	0.022	0.389	29.55	10
σ_{mb}, $10\sigma_{\alpha}^{\cdot}$	0.024 ± 0.025	-0.11 ± 0.03	0.855	0.021	0.656	6.80	8
σ_{mb}, $\sigma_C^{\cdot}$	0.039 ± 0.011	-0.17 ± 0.01	0.988	0.011	0.183	146.6	10

[a] Critical *F* values:[20] $F_{0.001}(1,8) = 25.42$; $F_{0.01}(1,8) = 11.26$; $F_{0.10}(1,8) = 3.46$; $F_{0.001}(2,7) = 21.69$; $F_{0.05}(2,5) = 5.79$.
[b] $n = 10$, Y = H, CF_3, F, Br, Cl, Me, CN, MeO, MeS and Me_2N; $n = 8$, Y = H, CF_3, F, Cl, Me, CN, MeO and MeS.

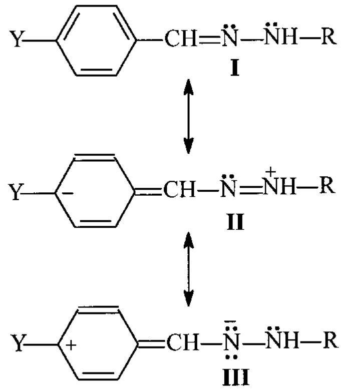
presence of two very strong acceptors (NO_2 groups) might have changed the degree and direction of polarization of the hydrazone molecules. Consequently, for **2**-Ys, acceptor Y-substituents will facilitate blue shifts and donor Y-substituents red shifts.

On the basis of the above-mentioned observations, we might expect that the mode of polarization of substrates with one NO_2 group, i.e. **3**-Ys, will be somewhere between those of **1**-Ys and **2**-Ys. In other words, the ρ^{x} values derived from Eqn (1) for **3**-Ys might lie in between the corresponding ρ^{x} values for **1**-Ys and **2**-Ys. This expectation has been realized, as shown by the correlation result presented in the next paragragh.

Single-parameter correlation results for **3**-Ys, summarized in Table 5, show that both $\sigma_{JJ}^{\cdot}$ and $\sigma_C^{\cdot}$ yield fairly good correlations whereas all the σ^{x}'s yield meaningless (σ_p and σ_{mb}) or not so good (σ^{+}) correlations. On the other hand, correlations by the dual-parameter equation (1) yield improved results with all CLs greater than 99.9% (cf. *R* or *r* and ψ values), e.g. for (σ_p, $\sigma_{JJ}^{\cdot}$), $R = 0.949$, $\psi = 0.377$, $F = 31.71$, $n = 10$; for (σ^{+}, $\sigma_{JJ}^{\cdot}$), $R = 0.947$, $\psi = 0.383$, $F = 30.64$, $n = 10$; for (σ_{mb}, $\sigma_{JJ}^{\cdot}$), $R = 0.946$, $\psi = 0.389$, $F = 29.55$, $n = 10$. As expected, the $\rho^{\cdot}$ values are all negative. Of particular interest is the fact that all the ρ^{x} values are between the corresponding values for **1**-Ys and **2**-Ys (see above), e.g. ρ_{mb} derived from the (σ_{mb}, $\sigma_{JJ}^{\cdot}$) pairing is 0.34×10^3, which is larger than -1.5×10^3 (for **1**-Ys) and smaller than 0.80×10^3 (for **2**-Ys). Judging by the $|\rho_{mb}/\rho_{JJ}^{\cdot}|$ value of 0.23 and the fact that the dual-parameter correlation is better than the single-parameter correlation, the behavior of the UV spectral data of **3**-Ys may also be classified as category I, although the contribution of the polar effect of substituents to the UV spectra of **3**-Ys is much smaller than those of **1**-Ys or **2**-Ys.

As experimentalists, we are hard put to interpret or rationalize our observations on the different behaviors of **1**-Ys, **2**-Ys and **3**-Ys, so we hope that some theoreticians might be interested in offering an explanation. However, we are still tempted to venture the following crude and simplistic speculation.

On the basis of their studies on the UV spectra of *p*-Y-substituted phenyl compounds, Katritzky *et al.*[21] had proposed that the long-distance interaction between a substituent and a heteroatom is qualitatively similar but is quantitatively much greater in the excited state than in the ground state. If this proposition were true, we could then envisage the following possible state of affairs. Resonance structures **I, II** and **III** are of pertinence to our discussion, and Katrizky *et al.*'s proposal might be transformed into the statement that polar structures **II** and **III** become more important in the excited states than they are in the ground states of **1**-Ys, **2**-Ys and **3**-Ys. Therefore, if R is an effective electron-pair releasing group, e.g. as in **1**-Ys, then **II** becomes more important in the excited state. Consequently, acceptor substituent Ys will lower the excited-state energy (cf. structure **II**) and facilitate bathochromic shifts. On the other hand, if R is a strong electron-pair withdrawing group, such as in **2**-Ys, then **III** becomes more important. Under these circumstances, donor Ys will lower the excited-state energy (cf. structure **III**) and facilitate red shifts. Naturally, the behavior of **3**-Ys should lie between those of **1**-Ys and **2**-Ys. In other words, structure **II** for **3**-Ys is less important than structure **II** for **1**-Ys, and structure **III** for **3**-Ys carries less weight than structure **III** for **2**-Ys. The aforesaid speculation seems to be in harmony with the relative magnitudes of the $|\rho_{mb}/\rho_{JJ}^{\cdot}|$ values, namely for **3**-Ys it is 0.23, which is smaller than either the value of 0.79 for **1**-Ys or the value of 0.42 for **2**-Ys.



Scheme 1

At this juncture, we may ask a second question, ‘Are there some hydrazone-type compounds whose spectra are mainly affected by the spin-delocalization effects of the substituents?’ In the behavior of **4**-Ys and **5**-Ys, where the carbonyl group interacts strongly with the lone-pair electrons on the nitrogen of the NH group, an answer of pertinence to the aforesaid question might be found. Therefore, we took the UV spectra of **4**-Ys and **5**-Ys. Correlation analysis of these UV data, summarized in Tables 6 and 7, shows the following results. (i) The $\nu_{\max}$ data for **4**-Ys and **5**-Ys are not related to the polar substituent constants σ^{x} by Eqn (2). (ii) Good correlations with CLs greater than 99.9% can be achieved by applying Eqn (3), i.e. for **4**-Ys for $\sigma_{JJ}^{\cdot}$, $r = 0.958$, $\psi = 0.321$, $F = 89.21$, $n = 10$; for $\sigma_{\alpha}^{\cdot}$, $r = 0.902$, $\psi = 0.498$, $F = 26.31$, $n = 8$; for $\sigma_{C}^{\cdot}$, $r = 0.965$, $\psi = 0.292$, $F = 109.6$, $n = 10$; and for **5**-Ys for $\sigma_{JJ}^{\cdot}$, $r = 0.937$, $\psi = 0.392$, $F = 57.14$, $n = 10$; for $\sigma_{\alpha}^{\cdot}$, $r = 0.847$, $\psi = 0.614$, $F = 15.24$, $n = 8$; for $\sigma_{C}^{\cdot}$, $r = 0.950$, $\psi = 0.351$, $F = 73.28$, $n = 10$. (iii) By using the dual-parameter equation (1), all the nine parings of (σ^{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 (3) already yields good results with CL >99.9%. (iv) The $|\rho^{x}|$ values are much smaller than $|\rho^{\cdot}|$, so the signs of ρ^{x} for **4**-Ys and **5**-Ys should not be taken too seriously. (v) Interestingly, the $|\rho^{\cdot}|$ values are much larger than those of **1**-Ys, **2**-Ys and **3**-Ys; in other words, the contributions of spin-delocalization effects of Y-substituents in **4**-Ys and **5**-Ys are much larger than those in **1**-Ys, **2**-Ys and **3**-Ys. This interesting phenomenon may be a reflection of the effect of Z group in the structure of p-YC$_6$H$_4$CH=NNHZ. Our speculative rationalization for the observed $\rho^{\cdot}$ values is that perhaps a larger spin effect and a smaller polar effect from Z might induce a smaller spin delocalization from the Y-substituents. Therefore, we might be able to assess very roughly the relative importance of these two effects by looking at their $\sigma^{\cdot}$ and σ^{x} values. For instance, for Z = Ph (**1**-Ys), $\sigma_{JJ}^{\cdot} = 0.47$,[12] $\sigma_{p} = -0.01$,[17] whereas for Z = CONH$_2$ (**4**-Ys), $\sigma_{JJ}^{\cdot} = 0.38$,[12] $\sigma_{p} = 0.36$.[17] In other words, the relative importance of the spin effect of Z in **1**-Ys (phenylhydrazone) is larger than that in **4**-Ys (semicarbazone). This might induce a smaller spin effect from the Y-substituents in **1**-Ys than the spin effect from Y-substituent in **4**-Ys. Judging by the $|\rho_{mb}/\rho_{JJ}^{\cdot}|$ value of 0.09 for **4**-Ys, and that of 0.15 for **5**-Ys, and the fact that dual-parameter correlation does not improve the correlation over the single-parameter correlation, the behavior of the UV spectral data of **4**-Ys and **5**-Ys can be classified as category III, i.e. the wavenumbers of **4**-Ys and **5**-Ys are mainly affected by the spin-delocalization effects of the substituents.

Table 6. Values of ρ^{x} and $\rho^{\cdot}$ of Eqns (1), (2) and (3) and corresponding values of the correlation coefficient r or R, ψ, s and F-test for correlation of $\nu_{\max}$ values of **4**-Ys with σ^{x} and $\sigma^{\cdot}$

σ^{x} or $\sigma^{\cdot}$ or (σ^{x}, $\sigma^{\cdot}$)	$\rho^{x}(\times10^{10})$	$\rho^{\cdot}(\times10^{4})$	r or R	$s(\times10^{4})$	ψ	F[a]	n[b]
σ_{p}	0.18 ± 0.20		0.418	0.170	1.016	1.69	10
σ^{+}	0.15 ± 0.11		0.584	0.160	0.908	4.14	10
σ_{mb}	0.088 ± 0.170		0.265	0.180	1.078	0.61	10
$\sigma_{JJ}^{\cdot}$		−0.54 ± 0.06	0.958	0.055	0.321	89.21	10
$10\sigma_{\alpha}^{\cdot}$		−0.48 ± 0.08	0.902	0.062	0.498	26.31	8
$\sigma_{C}^{\cdot}$		−0.61 ± 0.06	0.965	0.050	0.292	109.6	10
σ_{p}, $\sigma_{JJ}^{\cdot}$	−0.066 ± 0.062	−0.59 ± 0.06	0.967	0.053	0.306	49.86	10
σ_{p}, $10\sigma_{\alpha}^{\cdot}$	−0.13 ± 0.07	−0.48 ± 0.06	0.958	0.045	0.631	28.14	8
σ_{p}, $\sigma_{C}^{\cdot}$	−0.032 ± 0.061	−0.63 ± 0.06	0.968	0.052	0.302	51.29	10
σ^{+}, $\sigma_{JJ}^{\cdot}$	−0.043 ± 0.036	−0.60 ± 0.06	0.965	0.054	0.312	47.83	10
σ^{+}, $10\sigma_{\alpha}^{\cdot}$	−0.073 ± 0.065	−0.52 ± 0.07	0.942	0.053	0.424	19.72	8
σ^{+}, $\sigma_{C}^{\cdot}$	−0.013 ± 0.035	−0.63 ± 0.06	0.966	0.053	0.309	49.04	10
σ_{mb}, $\sigma_{JJ}^{\cdot}$	−0.050 ± 0.050	−0.57 ± 0.05	0.968	0.052	0.302	51.29	10
σ_{mb}, $10\sigma_{\alpha}^{\cdot}$	−0.073 ± 0.063	−0.47 ± 0.07	0.943	0.052	0.420	20.18	8
σ_{mb}, $\sigma_{C}^{\cdot}$	−0.022 ± 0.050	−0.62 ± 0.06	0.967	0.052	0.303	51.06	10

[a] Critical F values:[20] $F_{0.001}$ (1,8) = 25.42; $F_{0.10}$ (1,8) = 3.46; $F_{0.25}$(1,8) = 1.54; $F_{0.001}$ (2,7) = 21.69; $F_{0.001}$ (2,5) = 37.12; $F_{0.01}$(2,5) = 13.27

[b] $n = 10$, Y = H, CF$_3$, F, Br, Cl, Me, CN, MeO, MeS and Me$_2$N; $n = 8$, Y = H, CF$_3$, F, Cl, Me, CN, MeO and MeS.

Table 7. Values of ρ^x and $\rho^{\cdot}$ of Eqns (1), (2) and (3) and corresponding values of the correlation coefficient *r* or *R*, ψ, *s* and *F*-test for correlation of ν_{max} values of **5**-Ys with σ^x and $\sigma^{\cdot}$

σ^x, or $\sigma^{\cdot}$ or (σ^x, $\sigma^{\cdot}$)	$\rho^x(\times 10^4)$	$\rho^{\cdot}(\times 10^4)$	*r* or *R*	$s(\times 10^4)$	ψ	F^a	n^b
σ_p	0.13 ± 0.19		0.341	0.166	1.051	1.05	10
σ^+	0.12 ± 0.10		0.492	0.154	0.973	2.56	10
σ_{mb}	-0.048 ± 0.168		0.155	0.174	1.105	0.20	10
$\sigma_{JJ}^{\cdot}$		-0.48 ± 0.07	0.937	0.062	0.392	57.14	10
$10\sigma_{\alpha}^{\cdot}$		-0.42 ± 0.10	0.847	0.071	0.614	15.24	8
$\sigma_C^{\cdot}$		-0.55 ± 0.07	0.950	0.055	0.351	73.28	10
σ_p, $\sigma_{JJ}^{\cdot}$	-0.098 ± 0.062	-0.56 ± 0.06	0.959	0.053	0.338	40.34	10
σ_p, $10\sigma_{\alpha}^{\cdot}$	-0.18 ± 0.06	-0.42 ± 0.05	0.970	0.036	0.309	39.50	8
σ_p, $\sigma_C^{\cdot}$	-0.065 ± 0.062	-0.59 ± 0.06	0.960	0.053	0.333	41.56	10
σ^+, $\sigma_{JJ}^{\cdot}$	-0.075 ± 0.034	-0.60 ± 0.05	0.964	0.051	0.320	45.34	10
σ^+, $10\sigma_{\alpha}^{\cdot}$	-0.11 ± 0.05	-0.49 ± 0.06	0.962	0.040	0.346	30.98	8
σ^+, $\sigma_C^{\cdot}$	-0.044 ± 0.035	-0.62 ± 0.06	0.960	0.053	0.333	41.52	10
σ_{mb}, $\sigma_{JJ}^{\cdot}$	-0.083 ± 0.045	-0.54 ± 0.05	0.969	0.047	0.298	52.90	10
σ_{mb}, $10\sigma_{\alpha}^{\cdot}$	-0.12 ± 0.05	-0.41 ± 0.05	0.966	0.038	0.327	34.81	8
σ_{mb}, $\sigma_C^{\cdot}$	-0.057 ± 0.047	-0.58 ± 0.06	0.965	0.049	0.312	47.75	10

[a] Critical *F* values:[20] $F_{0.001}$ (1,8) = 25.42; $F_{0.01}$ (1,6) = 13.75; $F_{0.25}$ (1,8) = 1.54; $F_{0.001}$ (2,7) = 21.69; $F_{0.001}$ (2,5) = 37.12; $F_{0.01}$ (2,5) = 13.27.

[b] $n = 10$, Y = H, CF_3, F, Br, Cl, Me, CN, MeO, MeS and Me_2N; $n = 8$, Y = H, CF_3, F, Cl, Me, CN, MeO and MeS.

CONCLUSION

The UV spectra of **1**-Ys, **2**-Ys and **3**-Ys are clearly affected by both the polar and the spin-delocalization effects, whereas those of **4**-Ys and **5**-Ys are predominantly affected by the spin-delocalization effects of the substituents. In other words, in the former three cases, category I behavior has been observed, whereas in the latter two cases, category III bahavior has been found. In all cases, spin-delocalization effects of the substituents Ys will facilitate bathochromic shifts (all $\rho^{\cdot}$ values are negative). Most interestingly, it has now been demonstrated that the polar effect of the substituents (Ys) on the λ_{max} values depends on the mode of polarization of the substrates. Electron-pair acceptor Ys tend to induce bathochromic shifts for **1**-Ys, but hypsochromic shifts for **2**-Ys and **3**-Ys and very small shifts for **4**-Ys and **5**-Ys, because ρ^x values derived from the (σ^x, $\sigma^{\cdot}$) combinations are negative for **1**-Ys but positive for **2**-Ys and **3**-Ys, and the $|\rho^x|$ values are much smaller than $|\rho^{\cdot}|$ values for **4**-Ys and **5**-Ys. The fact that the sign of ρ^x values can be reversed suggests that the relative importance of the contribution of polar effects to the excited-state energy depends on the mode of polarization of the whole organic molecule. Possibly, a higher degree of polarization of the substrate molecule would demand a higher degree of polar assistance from the substituents at the transition states.

EXPERIMENTAL

All UV spectra were taken 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. IR spectra were recorded on Shimadzu IR-440 and Bio-Rad FTS-185 spectrometers. ^1H NMR spectra were recorded at 60 MHz on a Varian EM-360A and at 90 MHZ on an FX-90Q spectrometer with TMS as the external standard. ^{19}F NMR spectra were measured at 60 MHz on a Varian EM-360 spectrometer with trifluoroacetic acid as the external standard. Mass spectrometry (MS) were carried out using an HP 5989A MS instrument.

All **1**-Ys are known compounds. They were prepared by a known method[22] and were further identified by ^1H NMR (or ^{19}F NMR), MS and IR spectroscopy. Melting-points of **1**-Ys prepared in our laboratory are as follows: **1**-MeS, 136–137 °C (lit.[22] 137–138 °C); **1**-Me, 112–113 °C (lit.[23] 112–113 °C); **1**-Cl, 130–131 °C (lit.[23] 132 °C); **1**-NO_2, 153–154 °C (lit.[23] 154–155 °C); **1**-Me_2N, 146–147 °C (lit.[24] 148 °C); **1**-CN, 145–146 °C (lit.[24] 144 °C); **1**-MeO, 119–120 °C (lit.[24] 121 °C); **1**-CO_2Me, 140–142 °C (lit.[25] 142–144 °C); **1**-B, 113–114 °C (lit.[25] 112–113 °C); **1**-F, 138–140 °C (lit.[26] 147 °C); **1**-H, 154–155 °C (lit.[26] 154–155 °C); **1**-CF_3, 128–130 °C (lit.[27] 128–130 °C).

All **2**-Ys, except **2**-MeS and **2**-CO_2Me, are known compounds. They were prepared by a known method[6] and were further identified by ^1H NMR (or ^{19}F NMR), MS and IR spectroscopy. Melting-points of **2**-Ys prepared in our laboratory are as follows: **2**-H, 238–239 °C (lit.[6] 238–239 °C); **2**-NO_2, 317–318 °C (lit.[6] 319–320 °C); **2**-Cl, 263–264 °C (lit.[6] 264–265 °C); **2**-MeO, 250–251 °C (lit.[6] 251–252 °C); **2**-Me_2N, 233–234 °C (lit.[6] 233–234 °C); **2**-CF_3, 258–259 °C (lit.[28] 257 °C); **2**-Me_3Si, 221–222 °C (lit.[29] 220 °C); **2**-Me, 233–234 °C (lit.[30] 232.5–234.5 °C); **2**-Br, 260–261 °C (lit.[30] 260–261 °C); **2**-CN, 297–298 °C (lit.[30] 295–298 °C); **2**-F, 279–280 °C (lit.[31] 278 °C); The physical data for **2**-MeS and **2**-

CO_2Me are as follows: **2**-MeS, m.p. 253–254 °C (Found: C, 50.75; H, 3.34; N, 17.05. $C_{14}H_{12}N_4O_4S$ requires C, 50.60; H, 3.61; N, 16.87%); ^{1}H NMR, δ 7.30–9.00 (m, 7H, Ar), 11.70 (s, 1H, ArCH=), 2.50 (s, 3H, MeSAr); ν/cm^{-1} (KBr pellet), 3250, 1610, 1580, 1495, 1410, 1325, 1305, 1125; *m*/*z* (EI), 332 (M^+); **2**-CO_2Me, m.p. 272–274 °C (Found: C, 52.15; H, 3.41; N, 16.60. $C_{15}H_{12}N_4O_6$ requires C, 52.33; H, 3.49; N, 16.28%); 1H NMR, δ 7.90–8.90 (m, 7H, Ar), 11.80 (s, 1H, ArCH=), 3.90 (s, 3H, MeSAr); ν /cm^{-1} (KBr pellet), 3270, 1710, 1610, 1580, 1495, 1410, 1325, 1270, 1130, 1085; *m*/*z* (EI), 344 (M^+).

All **3**-Y substrates, except **3**-CF_3 and **3**-CN, are known compounds. They were prepared by a known method[6] and were further identified by ^{1}H NMR (or ^{19}F NMR), MS and IR spectroscopy. Melting-points of **3**-Ys prepared in our laboratory are as follows: **3**-H, 190–191 °C (lit.[23] 189–191 °C); **3**-Cl, 219–220 °C (lit.[32] 218–219 °C); **3**-F, 212–213 °C (lit.[26] 212 °C); **3**-MeS, 182–183 °C (lit.[22] 183 °C); **3**-MeO, 161–162 °C (lit.[33] 161 °C); **3**-Me_2N, 182–183 °C (lit.[33] 182°); **3**-Br, 207–208 °C (lit.[33] 207–208 °C); **3**-NO_2, 248–250 °C (lit.[33] 249 °C); **3**-Me, mp 196–197 °C (lit.[33] 196.5 °C); **3**-CF_3, 196–197 °C (Found: C, 54.27; H, 3.25; N, 13.42. $C_{14}H_{10}F_3N_3O_2$ requires C, 54.37; H, 3.24; N, 13.59%); ^{1}H NMR, δ 7.15–8.19 (m, 8H, Ar), 11.45 (s, 1H, ArCH=); ^{19}F NMR, δ −16.5 (s, $ArCF_3$); ν /cm^{-1} (KBr pellet) 3260, 1590, 1480, 1410, 1300, 1100, 840; *m*/*z* (EI), 309 (M^+); **3**-CN, m.p. 216–217 °C (Found: C, 62.96; H, 3.77; N, 21.53. $C_{14}H_{10}N_4O_2$ requires C, 63.16; H, 3.76; N, 21.05%); ^{1}H NMR, δ 7.16–8.18 (m, 8H, Ar), 11.53 (s, 1H, ArCH=), ν /cm^{-1} (KBr), 3250, 1580, 1470, 1310, 1271, 1100, 840; *m*/*z* (EI), 266 (M^+).

All **4**-Ys, except **4**-F and **4**-CN, are known compounds. They were prepared by a known method[34] and were further identified by ^{1}H NMR (or ^{19}F NMR), MS and IR spectroscopy. Melting-points of **4**-Ys prepared in our laboratory are as follows: **4**-H, 221–222 °C (lit.[34] 222 °C); **4**-Cl, 228–229 °C (lit.[34] 230 °C); **4**-Br, 226–227 °C (lit.[34] 228 °C); **4**-Me, 221–222 °C (lit.[34] 221 °C); **4**-MeO, 209–210 °C (lit.[34] 210–211 °C); **4**-MeS, 218–219 °C (lit.[35] 213 °C); **4**-CF_3, 195–196 °C (lit.[36] 193.5–194.5 °C); **4**-Me_2N, 220 °C (lit.[37] 219 °C); **4**-NO_2, 208–209 °C (lit.[37] 211 °C). The physical data for **4**-F and **4**-CN are as follows: for **4**-F, m.p. 224–225 °C (Found: C, 52.79; H, 4.34; N, 22.96. $C_8H_8FN_3O$ requires C, 53.04; H, 4.42; N, 23.20%); ^{1}H NMR, δ 7.04–7.83 (m, 5H, Ar and NNHCO), 10.26 (s, 1H, ArCH=), 6.51 (s, 2H, $CONH_2$); ^{19}F NMR, δ 35.0 (s, FAr); ν /cm^{-1} (KBr), 3490, 3200, 1720, 1670, 1600, 1500, 1440, 1360, 1300, 1240, 840; *m*/*z* (EI), 181 (M^+); **4**-CN, m.p. 266–268 °C (Found: C, 57.28; H, 4.27; N, 29.43. $C_9H_8N_4O$ requires C, 57.45; H, 4.26; N, 29.79%); ^{1}H NMR, δ 7.72–7.95 (m, 5H, Ar and NNHCO), 10.48 (s, 1H, ArCH=), 6.59 (s, 2H, $CONH_2$); ν /cm^{-1} (KBr), 3400, 3100, 1700, 1680, 1580, 1500, 1430, 1130, 920, 830, 760; *m*/*z* (EI), 188 (M^+).

All **5**-Y substrates are new compounds. They were prepared by a known method[38] and their physical data are as follows: for **5**-H, m.p. 180–181 °C (Found: C, 70.25; H, 5.43; N, 17.38. $C_{14}H_{13}N_3O$ requires: C, 70.30; H, 5.44; N, 17.57%); ^{1}H NMR, δ 6.96–7.92 (m, 10H, Ar), 8.82 (s, 1H, CONHPh), 10.75 (s, 1H, ArCH=N); ν /cm^{-1} (KBr), 3340, 1685, 1595, 1530, 1440, 1300, 1225, 1140, 940, 745, 680; *m*/*z* (EI), 239 (M^+); for **5**-Me, m.p. 184–186 °C (Found: C, 70.98; H, 5.90; N, 16.36. $C_{15}H_{15}N_3O$ requires C, 71.15; H, 5.93; N, 16.60%); ^{1}H NMR, δ 2.35 (s, 3H, MeAr); 6.92–7.94 (m, 9H, Ar); 8.85 (s, 1H, CONHPh); 10.65 (s, 1H, ArCH=N); ν /cm^{-1} (KBr), 3330, 1660, 1590, 1500, 1440, 1305, 1220, 1120, 805, 750; *m*/*z* (EI), 253 (M^+); for **5**-MeO, m.p. 177–179 °C (Found: C, 66.89; H, 5.63; N, 15.41. $C_{15}H_{15}N_3O_2$ requires C, 66.91; H, 5.58; N, 15.61%); ^{1}H, NMR, δ 3.80 (s, 3H, MeOAr), 6.91–7.89 (m, 9H, Ar), 8.81 (s, 1H, CONHPh), 10.56 (s, 1H, ArCH=N); ν /cm^{-1} (KBr), 3350, 1690, 1610, 1595, 1535, 1445, 1305, 1250, 1170, 1120, 1025; *m*/*z* (EI), 269 (M^+); for **5**-MeS, m.p. 181–182 °C (Found: C, 63.23; H, 5.26; N, 14.61. $C_{15}H_{15}N_3OS$ requires C, 63.16; H, 5.26; N, 14.74%); ^{1}H NMR, δ 2.45 (s, 3H, MeSAr), 6.90–7.88 (m, 9H, Ar), 8.83 (s, 1H, CONHPh), 10.66 (s, 1H, ArCH=N); ν /cm^{-1} (KBr), 3390, 1710, 1590, 1530, 1490, 1445, 1225, 1150, 820, 750, 690; *m*/*z* (EI), 285 (M^+); for **5**-Me_2N, m.p. 191–192 °C (Found: C, 67.97; H, 6.38; N, 19.64. $C_{16}H_{18}N_4O$ requires C, 68.09; H, 6.38; N, 19.86%); ^{1}H NMR, δ 2.93 (s, 6H, Me_2NAr), 6.63–7.81 (m, 9H, Ar), 8.71 (s, 1H, CONHPh), 10.46 (s, 1H, ArCH=N); ν /cm^{-1} (KBr), 3372, 1682, 1606, 1593, 1531, 1500, 1446, 1361, 1230, 1184, 748; *m*/*z* (EI), 282 (M^+); for **5**-F, m.p. 171–172 °C (Found: C, 65.10; H, 4.50; N, 16.05. $C_{14}H_{12}FN_3O$ requires C, 65.37; H, 4.67; N, 16.34%); ^{1}H NMR, δ 6.90–7.97 (m, 9H, Ar), 8.86 (s, 1H, CONHPh), 10.61 (s, 1H, ArCH=N); ^{19}F NMR, δ 35 (s); ν /cm^{-1} (KBr), 3380, 1670, 1595, 1500, 1440, 1300, 1220, 1130, 830, 750, 690; *m*/*z* (EI), 257 (M^+); for **5**-Cl, m.p. 198–199 °C (Found: C, 61.49; H, 4.20; N, 15.21. $C_{14}H_{12}ClN_3O$ requires C, 61.43; H, 4.39; N, 15.36%); ^{1}H NMR, δ 6.96–7.90 (m, 9H, Ar), 8.90 (s, 1H, CONHPh), 10.73 (s, 1H, ArCH=N); ν /cm^{-1} (KBr), 3380, 1700, 1595, 1530, 1445, 1330, 1230, 1150, 1085, 1010, 815, 740, 680; *m*/*z* (EI), 273 (M^+); 275 [M^+ +2, relative intensity: (M^+)/(M^++ 2) = 3:1]; for **5**-Br, m.p. 210–211 °C (Found: C, 52.64; H, 3.66; N, 13.16. $C_{14}H_{12}BrN_3O$ requires C, 52.83; H, 3.77; N, 13.21%); ^{1}H NMR, δ 6.90–7.93 (m, 9H, Ar), 8.94 (s, 1H, CONHPh), 10.74 (s, 1H, ArCH=N); ν/cm^{-1} (KBr), 3394, 1703, 1596, 1541, 1499, 1448, 1331, 1237, 1153, 1070, 1009, 741; *m*/*z* (EI), 317 (M^+); 319 [M^++2, relative intensity: M^+/(M^++2) = 1:1]; for **5**-CF_3, m.p. 209–210 °C (Found: C, 58.53; H, 3.78; N, 13.55. $C_{15}H_{12}F_3N_3O$ requires C, 58.63; H, 3.91; N, 13.68%); 1H NMR, δ 6.96–8.06 (m, 9H, Ar), 8.93 (s, 1H, CONHPh), 10.96 (s, 1H, ArCH=N); ^{19}F NMR, δ -15 (s); ν/cm^{-1} (KBr), 3370, 1700, 1595, 1530, 1445, 1320, 1250, 1100, 1065, 1010, 925, 840, 750; *m*/*z* (EI), 307 (M^+); for **5**-NO_2, m.p. 224–225 °C (Found: C, 59.03; H, 4.09; N, 19.37. $C_{14}H_{12}N_4O_3$ requires C, 59.15; H, 4.23; N, 19.72%); ^{1}H NMR, δ 7.00–8.19 (m, 9H, Ar), 8.93 (s, 1H, CONHPh), 11.06 (s, 1H, ArCH=N); ν/cm^{-1} (KBr), 3360, 1690, 1600, 1540, 1510, 1450, 1340, 1275, 1225, 1100; *m/z* (EI), 284 (M^+); for **5**-CN, m.p. 213–214 °C (Found: C, 68.00; H, 4.39; N, 20.97. $C_{15}H_{12}N_4O$ requires C, 68.18; H, 4.55; N, 21.21%); ^{1}H NMR, δ 7.00–8.08 (m, 9H, Ar), 8.99 (s, 1H, CONHPh), 10.98 (s, 1H, ArCH=N); ν/cm^{-1} (KBr), 3300, 1675, 1590, 1520, 1440, 1360, 1275, 1225, 1145, 830; *m/z* (EI), 264 (M^+).

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