JOURNAL OF PHYSICAL ORGANIC CHEMISTRY
J. Phys. Org. Chem. **12**, 392–400 (1999)

Dual-parameter correlation analysis of UV spectral data for 1-methyl-2-formyl-5-Y-substituted pyrroles and their hydrazones. First observation of a dominant polar effect

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Received 23 August 1998; accepted 14 October 1998

ABSTRACT: By using 1-methyl-2-formyl-5-Y-substituted pyrroles (**1-Ys**), 1-methyl-2-formyl-5-Y-substituted pyrrole phenylhydrazones (**2-Ys**) and 1-methyl-2-formyl-5-Y-substituted pyrrole (4-nitrophenyl)hydrazones (**3-Ys**) as models for nitrogen-containing heterocyclic aromatic compounds, the *K*-band $\lambda_{\max}$ values of their UV spectra were measured. Correlation analysis of the $\nu_{\max}$ values by a dual-parameter equation shows that the $\nu_{\max}$ values of these compounds are affected, albeit to different degrees, by both the polar (σ^x) and spin-delocalization effects ($\sigma^{\cdot}$) of the substituents. Interestingly, the UV spectra of **3-Ys** are mainly affected by the polar effects. The correlation results are in accord with a previous speculation that a higher degree of polarization of the substrate molecule would demand a higher degree of polar assistance from the substituent at the transition states. Copyright © 1999 John Wiley & Sons, Ltd.

KEYWORDS: UV spectra; correlation analysis; polar effect; spin-delocalization effect; 1-methyl-2-formyl-5-Y-substituted pyrroles; 1-methyl-2-formyl-5-Y-substituted pyrrole phenylhydrazones; 1-methyl-2-formyl-5-Y-substituted pyrrole (4-nitrophenyl)hydrazones

INTRODUCTION

We have recently reported the correlation analysis of UV data for styrenes, α-methylstyrenes, α,β,β-trifluorostyrenes,[1a] phenylacetylenes and acetophenones[1b] by a dual-parameter equation [Eqn. (1)] with the polar constant (σ^x) and the spin-delocalization constant ($\sigma^{\cdot}$), and also by single-parameter equations [Eqns (2) and (3)].

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

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

$$\text{variable} = \rho^{\cdot}\sigma^{\cdot} \quad (3)$$

Our results showed 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. We proposed, however, that the UV spectral properties of radicaloid transition states (TSs) are always affected, albeit to different degrees, by both polar and spin-delocalization effects. In other words, in the correlation analysis of these properties, the applicability of the dual-parameter Eqn. (1) should always be tested and compared with the correlation results based on application of the single-parameter Eqns (2) and (3).[2–5] The $|\rho^x/\rho^{\cdot}|$ ratio, e.g. with $\rho^x = \rho_{\mathrm{mb}}$ and $\rho^{\cdot} = \rho_{\mathrm{JJ}}^{\cdot}$, may serve as a rough measure of the relative importance of the polar and the spin-delocalization effects of substituents.[6]

On the basis of our studies, we came to realize that, in the absence of measurable steric effects, four categories of possible circumstances might be visualized.[3,5] (i) When both polar and spin effects are important, the $|\rho_{\mathrm{mb}}/\rho_{\mathrm{JJ}}^{\cdot}|$ values might fall in the range of (very) roughly 0.2–0.8, e.g. in radical additions to styrenes. Under these circumstances, the necessity to use the dual-parameter Eqn. (1) can be easily established because it yields much better correlation results than those from Eqn. (2). Correlation results of the fluorescence spectral data of substituted styrenes and α-methylstyrenes[7] have also been found to fall in this category. (ii) When polar effects dorminate, this ratio might be around or greater than unity, e.g. in H-atom abstraction reactions by electrophilic radicals,[4c,4d] phenylacetylene addition reactions by electrophilic radicals[5a,5b] and EPR data for some phenylnitroxides.[4e,4f] Under these circumstances, using

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Contract/grant sponsor: National Natural Science Foundation of China.
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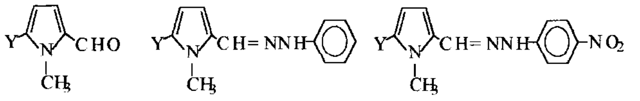
CCC 0894–3230/99/050392–09 $17.50

Table 1. λ_{max} (nm), wavenumber (ν_{max}, cm^{-1}) and ε_{max} ($l\ mol^{-1}\ cm^{-1}$) values for **1-Ys**, **2-Ys** and **3-Ys** (solvent, 95% EtOH; uncertainty of λ_{max}, ±0.3 nm)

	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	288.0	3.472	1.588	336.0	2.976	2.592	429.6	2.328	3.429
CH_3	297.0	3.367	2.014	343.2	2.914	2.760	439.2	2.277	2.499
Cl	292.0	3.425	2.337	344.4	2.904	2.812	424.8	2.354	3.234
CN	289.2	3.458	1.917	377.5	2.649	3.814	413.2	2.420	4.115
$COCH_3$	306.0	3.268	2.046	388.8	2.572	3.579	426.0	2.347	4.184
NO_2	331.2	3.019	1.207	451.2	2.216	2.675	450.0	2.222	4.085
COOH	299.0	3.344	2.139	363.6	2.750	3.513	426.0	2.347	3.405
SCH_3	319.0	3.135	1.968	369.8	2.704	3.349	439.6	2.275	3.063
$COOCH_3$	297.6	3.360	2.375	368.4	2.714	3.878	421.2	2.374	3.892
$Si(CH_3)_3$	296.4	3.374	1.979	348.0	2.874	2.762	432.0	2.315	3.005
Br	294.0	3.401	1.838	345.6	2.894	2.795	426.0	2.347	3.304
OCH_3	307.2	3.255	2.738	337.4	2.964	2.911	450.0	2.222	2.745

Eqn. (1) instead of Eqn. (2) may not improve the correlation results much, 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 and total deviations of the experimental 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 improve the correlation results much. Application of Eqn. (1) might yield a $|\rho_{mb}/\rho_{JJ}^{\cdot}|$ ratio of less than 0.2. A small $|\rho_{mb}/\rho_{JJ}^{\cdot}|$ value suggests the dominance of the spin effect, but it does not necessarily signify the absence of the polar effect. (iv) When there are other complicating and interacting factors, then none of the three equations can be successfully applied.[1b,5d,8–10]

The importance of benzaldehyde phenylhydrazone and semicarbazone derivatives in analytical organic chemistry has led to many investigations of their ultraviolet spectra.[11–16] Although the single-parameter relationship [cf. Eqn. (2)] has been applied to the correlation of UV data for nitro-, dinitro- and trinitrophenylhydrazones,[8–10] correlation analysis of the UV data for these compounds by the dual-parameter Eqn. (1) has been tried only recently and the results show that the UV data are clearly affected by both the polar and the spin-delocalization effects.[17] However, there is no report about the correlation analysis by the dual-parameter Eqn. (1) of the UV spectral data of heteroaromatic compounds, e.g. pyrroles. Will the correlation result for the UV spectral data of pyrroles conform to categeory (i), (ii) or (iii) behavior? The purpose of this paper is to answer this question. The compounds chosen for our analysis were 1-methyl-2-formyl-5-Y-substituted pyrroles (**1-Ys**), 1-methyl-2-formyl-5-Y-substituted pyrrole phenylhydrazones (**2-Ys**) and 1-methyl-2-formyl-5-Y-substituted pyrrole (4-nitrophenyl)hydrazones (**3-Ys**). *N*-Methylpyrrole derivatives were chosen instead of pyrrole derivatives in order to avoid possible side-reactions of the reactive *N*-hydrogen during the synthetic steps.[18]



1-Y **2-Y** **3-Y**

Y = H, CH_3, Cl, CN, $COCH_3$, NO_2, COOH,

SCH_3, $COOCH_3$, $Si(CH_3)_3$, Br and OCH_3

RESULTS AND DISCUSSION

Measured λ_{max} values of **1-Ys, 2-Ys** and **3-Ys,** together with their corresponding wavenumbers (ν_{max}) and molar absorption coefficients (ε), are summarized in Table 1. Values of representative Hammett-type unresolved polar substituent constants (σ^x), i.e. σ_{mb}, σ_p and σ^+, were taken from Refs 2, 18 and 18, respectively, and values of representative spin-delocalization constants ($\sigma^{\cdot}$), i.e. $\sigma_{JJ}^{\cdot}$, $\sigma_c^{\cdot}$ and $\sigma_\alpha^{\cdot}$, were taken from Refs 2, 19 and 20, respectively. Results of correlation analysis in terms of ρ^x, $\rho^{\cdot}$, s, r or R, ψ and F values by Eqns (1–3) are summarized in Tables 2 (for **1-Ys**), 3 (for **2-Ys**) and 4 (for **3-Ys**). 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 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.[1,8–10] For reasons unclear to us, the nitro group always seems to deviate from the regression lines much more than other substituents do (cf. Figs 2–4),[1b,11] therefore, the nitro group is not included in our correlation analysis. As mentioned previously, a confidence level (CL) above 99.9% (based on $F_{0.001}$ values given in the footnotes to the tables; cf. Ref. 1) is considered good, even though the r (or R) value is <0.95,

Table 2. Values of ρ^x and $\rho^{\cdot}$ in Eqns (1), (2) and (3) and the 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 ($\sigma^x + \sigma^{\cdot}$)	ρ^x ($\times 10^4$)	$\rho^{\cdot}$ ($\times 10^4$)	*r* or *R*	*s* ($\times 10^4$)	ψ	F^a	n^b
σ_p	0.08602		0.2662	0.1005	1.066	0.6862	11
σ^+	0.1470		0.6831	0.07755	0.8165	6.999	10
σ_{mb}	0.08821		0.3962	0.09568	1.015	1.676	11
$\sigma_{JJ}^{\cdot}$		−0.3807	0.6769	0.07670	0.8137	7.613	11
10 $\sigma_\alpha^{\cdot}$		−0.3173	0.6557	0.08794	0.8561	5.280	9^c
$\sigma_c^{\cdot}$		−0.3116	0.4636	0.1004	1.005	1.916	9^d
$\sigma_p + \sigma_{JJ}^{\cdot}$	0.2237	−0.5503	0.9201	0.04331	0.4594	22.06	11
$\sigma^+ + \sigma_{JJ}^{\cdot}$	0.1509	−0.3963	0.9511	0.03505	0.3691	33.20	10
$\sigma_{mb} + \sigma_{JJ}^{\cdot}$	0.1649	−0.5324	0.9666	0.02833	0.3005	56.91	11
$\sigma_p + 10\ \sigma_\alpha^{\cdot}$	0.2785	−0.5248	0.9701	0.03052	0.2971	47.98	9^c
$\sigma^+ + 10\ \sigma_\alpha^{\cdot}$	0.1711	−0.3557	0.9826	0.02468	0.2351	69.86	8
$\sigma_{mb} + 10\ \sigma_\alpha^{\cdot}$	0.1774	−0.4733	0.9830	0.02310	0.2248	86.02	9^c
$\sigma_p + \sigma_c^{\cdot}$	0.3100	−0.5991	0.8987	0.05371	0.5372	12.59	9^d
$\sigma^+ + \sigma_c^{\cdot}$	0.1861	−0.3962	0.9381	0.04242	0.4243	21.99	9^d
$\sigma_{mb} + \sigma_c^{\cdot}$	0.1947	−0.5239	0.9124	0.05013	0.5014	14.89	9^d

[a] Critical *F* values: $F_{0.05}$ (1, 9) = 5.12; $F_{0.001}$ (2, 8) = 18.49; $F_{0.001}$ (2, 7) = 21.69; $F_{0.001}$ (2, 6) = 27.00; $F_{0.001}$ (2, 5) = 37.12.

[b] *n* = 11, **Y = H, CH_3, Cl, CN, $COCH_3$, COOH, SCH_3, $COOCH_3$, $Si(CH_3)_3$, Br, OCH_3**; *n* = 10, all 11 substituted groups except **$COCH_3$**; *n* = 8, all 11 substituted groups except **$COCH_3$, COOH** and **Br**.

[c] *n* = 9, all 11 substituted groups except **COOH** and **Br**.

[d] *n* = 9, all 11 substituted groups except **$COCH_3$** and **COOH**.

because the *r* value does not take into account the number of substituents (*n*).

Results of single-parameter correlation of the wavenumbers (ν_{max}) of **1-Ys** by Eqn. (2) or (3), summarized in Table 2, show that neither σ^x nor $\sigma^{\cdot}$ yields meaningful results, i.e. $r < 0.70$, $\psi > 0.80$, $F < 8.0$ (*n* = 11, 10 or 9). Unlike the UV spectra of styrene-type compounds,[1] correlations by the dual-parameter Eqn. (1) clearly yield much improved results (cf. Figs 1 and 2). All the (σ^x or $\sigma^{\cdot}$) combinations, except for (σ_p, $\sigma_c^{\cdot}$), (σ^+, $\sigma_c^{\cdot}$) and (σ_{mb}, $\sigma_c^{\cdot}$) combinations, yield very good correlations (all CLs >99.9%), e.g. for (σ_p, $\sigma_{JJ}^{\cdot}$), $R = 0.9201$, $\psi = 0.4594$, $F = 22.06$, $n = 11$; for (σ_{mb}, $\sigma_{JJ}^{\cdot}$), $R = 0.9666$, $\psi = 0.3005$, $F = 56.91$, $n = 11$; for (σ_{mb}, $10\sigma_\alpha^{\cdot}$), $R = 0.9830$, $\psi = 0.2248$, $F = 86.02$, $n = 9$. Therefore, judging from the $|\rho_{mb}/\rho_{JJ}^{\cdot}|$ value of 0.31 and 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 $\rho^{\cdot}$ values derived from the (σ^x, $\sigma^{\cdot}$) combinations are negative; this result demonstrate that all substituents induce bathochromic shifts by their spin-delocalization effects and is fully in harmony with the observations on styrenes, phenylacetylenes and acetophenones. On the

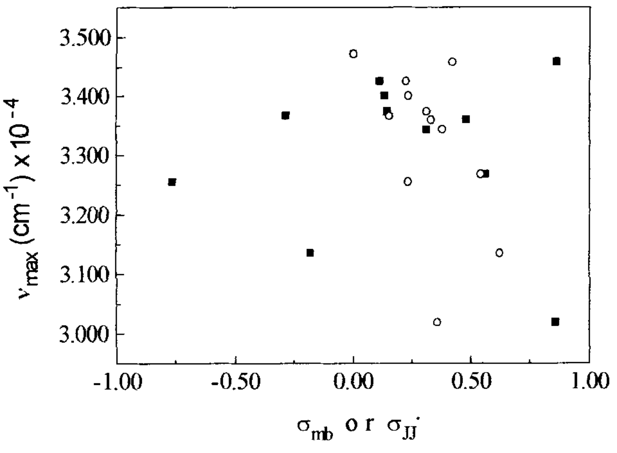


Figure 1. Plot of ν_{max} vs σ_{mb} (■) or $\sigma_{JJ}^{\cdot}$ (○) for **1-Ys**

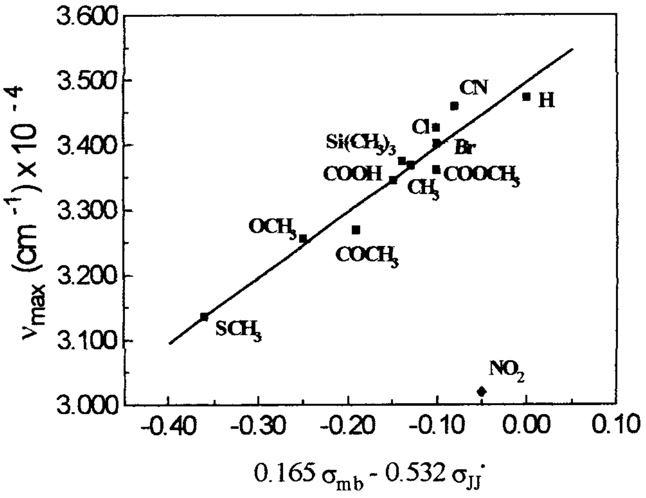


Figure 2. Plot of ν_{max} vs [0.165 σ_{mb} − 0.532 $\sigma_{JJ}^{\cdot}$] for **1-Ys**

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

σ^x or $\sigma^{\cdot}$ or $(\sigma^x + \sigma^{\cdot})$	ρ^x ($\times 10^4$)	$\rho^{\cdot}$ ($\times 10^4$)	r or R	s ($\times 10^4$)	ψ	F^a	n^b
σ_p	−0.3411		0.7580	0.09418	0.7191	12.27	11
σ^+	−0.1267		0.4980	0.1089	0.9695	2.638	10
σ_{mb}	−0.2213		0.7155	0.1012	0.7723	9.442	11
$\sigma_{JJ}^{\cdot}$		−0.6701	0.8575	0.07450	0.5688	24.99	11
$10\ \sigma_{\alpha}^{\cdot}$		−0.6042	0.9121	0.06536	0.4648	34.66	9^c
$\sigma_c^{\cdot}$		−0.6991	0.9069	0.05476	0.4777	32.43	9^d
$\sigma_p + \sigma_{JJ}^{\cdot}$	−0.2140	−0.5080	0.9588	0.04363	0.3331	45.56	11
$\sigma^+ + \sigma_{JJ}^{\cdot}$	−0.1210	−0.5755	0.9531	0.04063	0.3617	34.71	10
$\sigma_{mb} + \sigma_{JJ}^{\cdot}$	−0.1438	−0.5378	0.9607	0.04266	0.3257	47.84	11
$\sigma_p + 10\ \sigma_{\alpha}^{\cdot}$	−0.1999	−0.4553	0.9862	0.02853	0.2029	106.33	9^c
$\sigma^+ + 10\ \sigma_{\alpha}^{\cdot}$	−0.1169	−0.5327	0.9909	0.02045	0.1703	135.4	8
$\sigma_{mb} + 10\ \sigma_{\alpha}^{\cdot}$	−0.1301	−0.4898	0.9929	0.02039	0.1450	210.9	9^c
$\sigma_p + \sigma_c^{\cdot}$	−0.1423	−0.5671	0.9578	0.04034	0.3519	33.34	9^d
$\sigma^+ + \sigma_c^{\cdot}$	−0.08448	−0.6607	0.9626	0.03801	0.3316	37.91	9^d
$\sigma_{mb} + \sigma_c^{\cdot}$	−0.1013	−0.5886	0.9745	0.03153	0.2751	56.46	9^d

[a] Critical F values: $F_{0.05}$ (1, 9) = 5.12; $F_{0.001}$ (1, 9) = 10.56; $F_{0.001}$ (1, 9) = 22.86; $F_{0.001}$ (1, 7) = 29.25; $F_{0.001}$ (2, 8) = 18.49; $F_{0.001}$ (2, 7) = 21.69; $F_{0.001}$ (2, 6) = 27.00; $F_{0.001}$ (2, 5) = 37.12.

[b] n = 11, **Y = H, CH_3, Cl, CN, $COCH_3$, COOH, SCH_3, $COOCH_3$, $Si(CH_3)_3$, Br, OCH_3**; n = 10, all 11 substituted groups except **$COCH_3$**; n = 8, all 11 substituted groups except **$COCH_3$, COOH** and **Br**.

[c] n = 9, all 11 substituted groups except **COOH** and **Br**.

[d] n = 9, all 11 substituted groups except **$COCH_3$** and **COOH**.

other hand, all the ρ^x values derived from the (σ^x, $\sigma^{\cdot}$) combinations are positive; this shows that an electron-pair acceptor substituent will facilitate a hypsochromic shift, while a donor will facilitate a bathochromic shift.

Single-parameter correlation results for **2-Ys**, summarized in Table 3, show that correlations with CLs >99.9% can be achieved by Eqn. (3) with $\sigma_{JJ}^{\cdot}$, 10 $\sigma_{\alpha}^{\cdot}$ or $\sigma_c^{\cdot}$, i.e. for $\sigma_{JJ}^{\cdot}$, $r = 0.8575$, $\psi = 0.5688$, $F = 24.99$, $n = 11$; for $10\sigma_{\alpha}^{\cdot}$, $r = 0.9121$, $\psi = 0.4648$, $F = 34.66$, $n = 9$; for $\sigma_c^{\cdot}$, $r = 0.9069$, $\psi = 0.4777$, $F = 32.43$, $n = 9$. However, single-parameter correlation analyses with all the σ^x yield meaningless (σ^+, σ_{mb}) or not very good (σ_p) results.

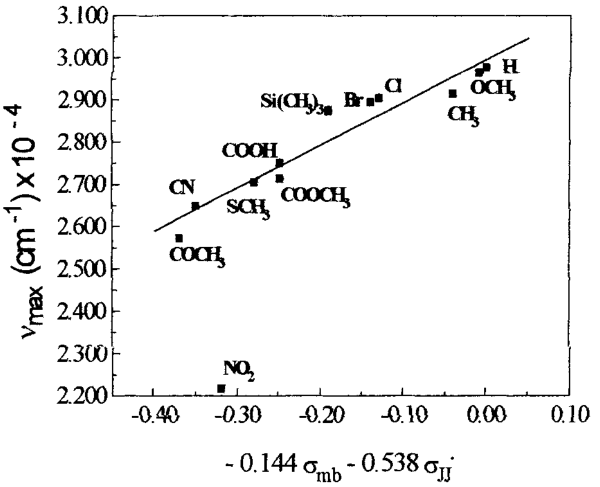


Figure 3. Plot of $\nu_{\max}$ (cm^{-1}) vs [− 0.144 σ_{mb} − 0.538 $\sigma_{JJ}^{\cdot}$] for **2-Ys**

Notably, correlations by the dual-parameter Eqn. (1) yield much improved results (cf. R or r and ψ values; Fig. 3). All the (σ^x, $\sigma^{\cdot}$) combinations give very good correlation results (CLs >99.9%), e.g. for (σ_p, $\sigma_{JJ}^{\cdot}$), $R = 0.9588$, $\psi = 0.3331$, $F = 45.56$, $n = 11$; for (σ_{mb}, $\sigma_{JJ}^{\cdot}$), $R = 0.9607$, $\psi = 0.3257$, $F = 47.84$, $n = 11$. Judging from the $|\rho_{mb}/\rho_{JJ}^{\cdot}|$ value of 0.27 and the fact that the dual-parameter correlation is better than the single-parameter correlation, the behavior of the UV spectral data of **2-Ys** may be classified as category (i), although the contribution of the polar effect of substituents to the UV spectra of **2-Ys** appears to be smaller than the contribution of the spin-delocalization effect of substituents.

Single-parameter correlation results for **3-Ys,** summarized in Table 4, show that correlations with CLs >99.9% can be achieved by Eqn. (2) with σ_p, σ^+ or σ_{mb}, i.e, for σ_p, $r = 0.8984$, $\psi = 0.4856$, $F = 37.64$, $n = 11$; for σ^+, $r = 0.9603$, $\psi = 0.3119$, $F = 94.81$, $n = 10$; for σ_{mb}, $r = 0.9485$, $\psi = 0.3501$, $F = 80.76$, $n = 11$. However, single-parameter correlation analyses with all the $\sigma^{\cdot}$ yield meaningless results (cf. Fig 4). By using the dual-parameter Eqn. (1), all the nine parings of ($\sigma^x + \sigma^{\cdot}$) yield good correlations with CLs >99.9%. No meaningful improvement can be claimed for the use of the dual-parameter correlation because application of the single-parameter Eqn. (2) already yields good results with CLs >99.9%. Interestingly, the $|\rho^{\cdot}|$ values of **3-Ys** are much smaller than those of **2-Ys**; in other words, the contributions of spin-delocalization effects of Y-substituents in **3-Ys** are much smaller than those of **2-Ys**. Judging from the $|\rho_{mb}/\rho_{JJ}^{\cdot}|$ value of 1.71 for **3-Ys** and the fact that the dual-parameter correlation does not improve

Table 4. Values of ρ^x and $\rho^{\cdot}$ in Eqns (1), (2) and (3) and the 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 ($\sigma^x + \sigma^{\cdot}$)	ρ^x ($\times 10^4$)	$\rho^{\cdot}$ ($\times 10^4$)	*r* or *R*	*s* ($\times 10^4$)	ψ	F^a	n^b
σ_p	0.1586		0.8984	0.02500	0.4856	37.64	11
σ^+	0.1166		0.9603	0.01672	0.3119	94.81	10
σ_{mb}	0.1153		0.9485	0.01802	0.3501	80.76	11
$\sigma_{JJ}^{\cdot}$		0.04238	0.1379	0.05637	1.095	0.1746	11
$10\ \sigma_{\alpha}^{\cdot}$		0.05024	0.1904	0.06237	1.113	0.2632	9^c
$\sigma_c^{\cdot}$		0.8445	0.2241	0.06192	1.105	0.3703	9^d
$\sigma_p + \sigma_{JJ}^{\cdot}$	0.1826	−0.0959	0.9414	0.02037	0.3956	31.14	11
$\sigma^+ + \sigma_{JJ}^{\cdot}$	0.1164	0.02399	0.9629	0.01729	0.3225	44.59	10
$\sigma_{mb} + \sigma_{JJ}^{\cdot}$	0.1259	−0.0734	0.9743	0.01360	0.2641	74.87	11
$\sigma_p + 10\ \sigma_{\alpha}^{\cdot}$	0.2010	−0.0995	0.9651	0.01797	0.3207	40.76	9^c
$\sigma^+ + 10\ \sigma_{\alpha}^{\cdot}$	0.1226	0.02823	0.9787	0.01527	0.2597	56.79	8
$\sigma_{mb} + 10\ \sigma_{\alpha}^{\cdot}$	0.1266	−0.0611	0.9770	0.01462	0.2609	63.09	9^c
$\sigma_p + \sigma_c^{\cdot}$	0.2148	−0.1147	0.9775	0.01449	0.2586	64.31	9^d
$\sigma^+ + \sigma_c^{\cdot}$	1.217	0.0291	0.9778	0.01439	0.2569	65.20	9^d
$\sigma_{mb} + \sigma_c^{\cdot}$	0.1327	−0.0603	0.9815	0.01312	0.2343	79.00	9^d

[a] Critical *F* values: $F_{0.001}$ (1, 9) = 22.86; $F_{0.001}$ (1, 8) = 25.42; $F_{0.001}$ (2, 8) = 18.49; $F_{0.001}$ (2, 7) = 21.69; $F_{0.001}$ (2, 6) = 27.00; $F_{0.001}$ (2, 5) = 37.12.

[b] *n* = 11, **Y = H, CH_3, Cl, CN, $COCH_3$, COOH, SCH_3, $COOCH_3$, $Si(CH_3)_3$, Br, OCH_3;** *n* = 10, all 11 substituted groups except **$COCH_3$**; *n* = 8, all 11 substituted groups except **$COCH_3$**, **COOH** and **Br**.

[c] *n* = 0, all 11 substituted groups except **COCH** and **Br**.

[d] *n* = 9, all 11 substituted groups except of **$COCH_3$** and **COOH**.

the correlation over that of the single-parameter correlation, the behavior of the UV spectral data of **3-Ys** can be classified as category (ii), i.e. wavenumbers of **3-Ys** are mainly affected by the polar effects of the substituents. This appears to be the first category (ii) example for the correlation analysis of our UV data.

On the basis of the correlation analysis of **2-Ys** and **3-Ys** (cf. Tables 3 and 4), we may conclude that both the polar and spin-delocalization effects are important for **2-Ys**, whereas the polar effects dominate for **3-Ys**. This may be rationalized by making a comparison of their resonance structures. With a powerful electron-withdrawing nitro group attached to the phenyl ring, the resonance structure **B** of **3-Ys** is greatly stabilized by the nitro group and becomes more important than the resonance structure **B** of **2-Ys**. Therefore, the degree of the polarization of **3-Ys** is much larger than that of **2-Ys**. Consequently, the polar effects on UV data become dominant for **3-Ys**. This result accords with our recent proposition that a higher degree of polarization of the substrate molecule would demand a higher degree of polar assistance from the substituents at the transition state.[17]

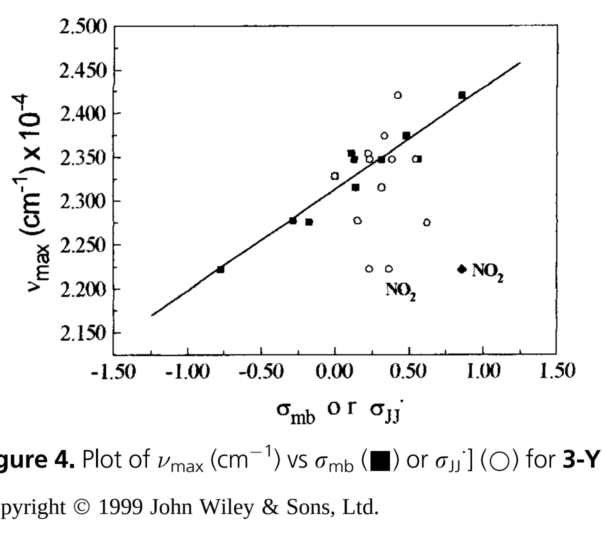
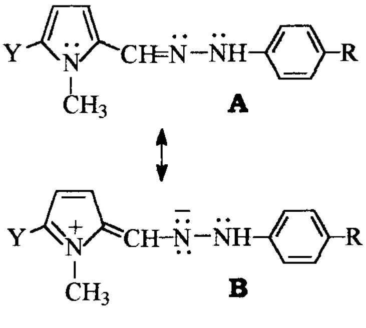


Figure 4. Plot of ν_{max} (cm^{-1}) vs σ_{mb} (■) or $\sigma_{JJ}^{\cdot}$] (○) for **3-Ys**



R = H (**2-Ys**); NO$_2$ (**3-Ys**)

CONCLUSION

The UV spectra of **1-Ys** and **2-Ys** are clearly affected by both the polar and the spin-delocalization effects, whereas those of **3-Ys** are predominantly affected by the polar effects of the substituents. In other words, the behavior of the UV spectral data of **1-Ys** and **2-Ys** can be classified as category (i), whereas that of **3-Ys** can be classified as category (ii). This appears to be the first category (ii) example for the correlation analysis of our UV data. The correlation results are in accord with our former speculation, i.e. a higher degree of polarization of the substrate molecule would demand a higher degree of polar assistance from the substituent at the transition states.

EXPERIMENTAL

All UV spectra were measured at room temperature in 95% EtOH on a Perkin-Elmer Lambda 2 instrument with a wavelength accuracy of $\pm$0.3 nm and a reproducibility of $\pm$0.1 nm. Melting-points were recorded on a Buchi-535 instrument and are uncorrected. IR, ^{1}H NMR and mass spectra were recorded on a Shimadzu IR-440, a Varian FX-90Q or Bruker 300 MHz (TMS as internal standard) and an HP 5989A instrument, respectively. Elemental analyses were performed on a Carlo Erba EA-1108 instrument.

Synthetic methods for 1-methyl-2-formyl-5-Y-substituted pyrroles (**1-Ys**), 1-methyl-2-formyl-5-Y-substituted pyrrole phenylhydrazones (**2-Ys**) and 1-methyl-2-formyl-5-Y-substituted pyrrole (4-nitrophenyl) hydrazones (**3-Ys**) have been reported elsewhere.[18]

All the **1-Ys**, except **1-COCH$_3$, 1-COOH, 1-COOCH$_3$, 1-Br** and **1-OCH$_3$**, are known compounds. They were prepared by the known methods and were further identified by ^{1}H NMR, IR and MS methods. Boiling- or melting-points of **1-Ys** prepared in our laboratory are as follows: **1-H**, b.p. 63 °C/6 Torr (lit.[19] 76 °C/11 Torr), UV (95% EtOH) $\lambda_{max} = 288.0$ nm, $\varepsilon = 1.588 \times 10^4$ l mol^{-1} cm^{-1}; **1-CH$_3$**, b.p. 97 °C/10 Torr (lit.[20] no report of b.p.), UV (95% EtOH) $\lambda_{max} = 297.0$ nm, $\varepsilon = 2.014 \times 10^4$ l mol^{-1} cm^{-1}; **1-CH**, no b.p. obtained,[21] UV (95% EtOH) $\lambda_{max} = 292.0$ nm, $\varepsilon = 2.337 \times 10^4$ l mol^{-1} cm^{-1}; **1-CN**, m.p. 67 °C (lit.[22] 67 °C), UV (95% EtOH) $\lambda_{max} = 289.2$ nm, $\varepsilon = 1.917 \times 10^4$ l mol^{-1} cm^{-1}; **1-NO$_2$**, m.p. 71 °C (lit.[23] 71 °C), UV (95% EtOH) $\lambda_{max} = 331.2$ nm, $\varepsilon = 1.207 \times 10^4$ l mol^{-1} cm^{-1}; **1-SCH$_3$**, b.p. 89 °C/3 Torr (lit.[24] 130 °C/14 Torr), UV (95% EtOH) $\lambda_{max} = 319.0$ nm, $\varepsilon = 1.968 \times 10^4$ l mol^{-1} cm^{-1}; **1-Si(CH$_3$)$_3$**, b.p. 94 °C/1 Torr (lit.[25] 79 °C/ 0.4 Torr), UV (95% EtOH) $\lambda_{max} = 296.4$ nm, $\varepsilon = 1.979 \times 10^4$ l mol^{-1} cm^{-1}.

1-COCH$_3$, 1-COOH, 1-COOCH$_3$, 1-Br and 1-OCH$_3$ are new compounds and were confirmed by the following data.

1-COCH$_3$. M.p. 78 °C (found: C, 63.62; H, 5.93; N, 9.39. $C_8H_9NO_2$ requires C, 63.55; H, 6.01; N, 9.27%); ^{1}H NMR ($CDCl_3$, δ ppm), 9.76 (s, 1H, CHO), 6.87 (m, 2H, C_3H and C_4H), 4.24 (s, 3H, NCH_3), 2.51 (s, 3H, $COCH_3$); ν (KBr pellet, cm^{-1}), 1683 (CO), 1658(CO), 1368, 1220, 1182, 784; MS [EI, *m/z* (%)], 151 (M$^+$, 100.0), 136 (M$^+$ – CH$_3$, 75.1); UV (95% EtOH), $\lambda_{max} = 306.0$ nm, $\varepsilon = 2.046 \times 10^4$ l mol^{-1} cm^{-1}.

1-COOH. M.p. 179 °C (found: C, 54.85; H, 4.52; N, 9.07. $C_7H_7NO_3$ requires C, 54.90; H, 4.62; N, 9.15%); ^{1}H NMR (CD_3COCD_3, δ ppm), 9.75 (s, 1H, CHO), 7.00 (d, 1H, C_4H, $J_{3,4} = 4.0$ Hz), 6.91 (d, 1H, C_3H, $J_{3,4} = 4.0$ Hz), 4.21 (s, 3H, NCH_3); ν (KBr pellet, cm^{-1}), 3500–2500 (COOH), 1699 (COO), 1665 (CO), 1512, 1459, 1378, 1252, 1182; MS [EI, *m/z* (%)], 153 [M$^+$, 100.0), 152 (M$^+$ – H, 60.9), 108 (M$^+$ – COOH, 10.9); UV (95% EtOH), $\lambda_{max} = 299.0$ nm, $\varepsilon = 2.139 \times 10^4$ l mol^{-1} cm^{-1}.

1-COOCH$_3$. M.p. 109 °C (found: C, 57.40; H, 5.33; N, 8.28. $C_8H_9NO_3$ requires C, 57.47; H, 5.44; N, 8.38%); ^{1}H NMR ($CDCl_3$, δ ppm), 9.71 (s, 1H, CHO), 6.89 (m, 2H, C_3H and C_4H), 4.27 (s, 3H, NCH_3), 3.87 (s, 3H, $COOCH_3$); ν (KBr pellet, cm^{-1}), 1715 (COO), 1673, 1242; MS [EI, *m/z* (%)], 167 (M$^+$, 100.0), 152 (M$^+$ – CH$_3$, 39.4), 136 (M$^+$ – CH$_3$O, 66.2), 122 (34.9); UV (95% EtOH), $\lambda_{max} = 297.6$ nm, $\varepsilon = 2.375 \times 10^4$ l mol^{-1} cm^{-1}.

1-Br. M.p. 64 °C (found: C, 38.36; H, 3.12; N, 7.33. C_6H_6BrNO requires C, 38.32; H, 3.22; N, 7.45%); ^{1}H NMR ($CDCl_3$, δ ppm), 9.35 (s, 1H, CHO), 6.83 (d, 1H, C_3H, $J_{3,4} = 4.0$ Hz), 6.27 (d, 1H, C_4H, $J_{3,4} = 4.0$ Hz), 3.94 (s, 3H, NCH_3); ν (KBr pellet, cm^{-1}), 1654 (CO), 1465, 1421, 1359, 1031, 778, 763; MS [EI, *m/z* (%)], 190 (7.5), 189 (100.0), 188 (M$^+$, 92.0), 187 (90.4), 186 (79.0); UV (95% EtOH), $\lambda_{max} = 294.0$ nm, $\varepsilon = 1.838 \times 10^4$ l mol^{-1} cm^{-1}.

1-OCH$_3$. M.p. 60 °C (found: C, 60.32; H, 6.47; N, 9.98. $C_7H_9NO_2$ requires C, 60.41; H, 6.53; N, 10.06%); ^{1}H NMR ($CDCl_3$, δ ppm), 9.20 (s, 1H, CHO), 6.76 (d, 1H, C_3H, $J_{3,4} = 4.5$ Hz), 5.48 (d, 1H, C_4H, $J_{3,4} = 4.5$ Hz), 3.89 (s, 3H, NCH_3), 3.72 (s, 3H, OCH_3); ν (KBr pellet, cm^{-1}), 1639 (CO), 1544, 1366, 1029 (C—O—C); MS [EI, *m/z* %)], 139 (M$^+$, 100.0), 124 (M$^+$ – CH$_3$, 31.1), 114 (M$^+$ – CHO, 6.2), 96 (15.2), 68 (35.9); UV (95% EtOH), $\lambda_{max} = 307.2$ nm, $\varepsilon = 2.738 \times 10^4$ l mol^{-1} cm^{-1}.

All the **2-Ys** are new compounds and were confirmed by the following data.

2-H. M.p. 130 °C (found: C, 72.44; H, 6.59; N, 21.07. $C_{12}H_{13}N_3$ requires C, 72.34; H, 6.58; N, 21.09%); ^{1}H NMR (CD_3COCD_3, δ ppm), 9.14 (broad s, <1 H, =NNH—), 7.84 (s, 1H, —CH=N—), 7.25–6.73 (m, 5H, phenyl-H), 6.73 (m, 1H, C_3H), 6.26 (m, 1H, C_4H), 6.03 (m, 1H, C_5H), 3.93 (s, 3H, NCH_3); ν (KBr pellet, cm^{-1}), 3302 (NH), 1602 (C=N), 1506, 1463, 1296, 1254, 752, 722, 694; MS [EI, *m/z* (%)], 200 (M$^+$ + H, 33.1), 199 (M$^+$, 100.0), 93 (10.4), 82 (13.5), 53 (7.3); UV (95% EtOH), $\lambda_{max} = 336.0$ nm, $\varepsilon = 2.592 \times 10^4$ l mol^{-1} cm^{-1}.

2-CH$_3$. M.p. 129 °C (found: C, 73.18; H, 6.99; N, 19.73. $C_{13}H_{15}N_3$ requires C, 73.21; H, 7.09; N, 19.70%); ^{1}H NMR (CD_3 $COCD_3$, δ ppm), 7.80 (s, 1H,—CH=N—), 7.28–6.70 (m, 5H, phenyl-H), 6.15 (d, 1H, C_3H,

$J_{3,4}$ = 3.0 Hz), 5.79 (d, 1H, C_4H, $J_{3,4}$ = 3.0 Hz), 3.78 (s, 3H, NCH_3), 2.25 (s, 3H, CH_3); ν (KBr pellet, cm^{-1}), 3276 (NH), 1597 (C═N), 1497, 1294, 1255, 778, 747, 691; MS [EI, *m/z* (%)], 214 ($M^+ + H$, 23.1), 213 (M^+, 100.0), 121 (14.3), 96(16.8), 53(9.6); UV (95% EtOH), λ_{max} = 343.2 nm, ε = 2.760 × 10^4 l mol^{-1} cm^{-1}.

2-Cl. Decomposes at 170 °C (found: C, 61.78; H, 5.17; N, 18.12, $C_{12}H_{12}ClN_3$ requires C, 61.67; H, 5.18; N, 17.98%); ^{1}H NMR (CD_3 $COCD_3$, δ ppm), 7.80 (s, 1H, —CH═N—), 7.29–6.74 (m, 5H, phenyl-H), 6.30 (d, 1H, C_3H, $J_{3,4}$ = 3.2 Hz), 6.09 (d, 1H, C_4H, $J_{3,4}$ = 3.2 Hz), 3.95 (s, 3H, NCH_3); ν (KBr pellet, cm^{-1}), 3307 (NH), 1599 (C═N), 1504, 1450, 1255, 747, 692; MS [EI, *m/z* (%)], 235 ($M^+ + H$, 36.4, 234 (M^+, 17.9), 233 ($M^+ - H$, 100.0), 199 ($M^+ - Cl$, 71.9), 91 (43.7), 78 (32.4), 65 (21.0); UV (95% EtOH), λ_{max} = 344.4 nm, ε = 2.812 × 10^4 l mol^{-1} cm^{-1}.

2-CN. M.p. 145 °C (found: C, 69.48; H, 5.32; N, 24.92, $C_{13}H_{12}N_4$ requires C, 69.62; H, 5.39; N, 24.98%); ^{1}H NMR (CD_3COCD_3, δ ppm), 9.71 (s, <1 H, ═NNH—), 7.88 (s, 1H, —CH═N—), 7.33–6.78 (m, 5H, phenyl-H), 6.72 (d, 1H, C_3H, $J_{3,4}$ = 4.2 Hz), 6.40 (d, 1H, C_4H, $J_{3,4}$ = 4.2 Hz), 4.02 (s, 3H, NCH_3); ν (KBr pellet, cm^{-1}), 3290 (NH), 2216 (CN), 1604 (C—N), 1595, 1493, 1261, 767, 690; MS [EI, *m/z* (%)], 225 ($M^+ + H$, 38.9), 224 (M^+, 100.0), 118 (8.4), 105 (10.9), 77 (7.0), 65(14.5); UV (95% EtOH), λ_{max} = 377.5 nm, ε = 3.814 × 10^4 l mol^{-1} cm^{-1}.

2-COCH$_3$. M.p. 148 °C (found: C, 69.63; H, 6.30; N, 17.34. $C_{14}H_{15}N_3O$ requires C, 69.68; H, 6.28; N, 17.41%); ^{1}H NMR (CD_3COCD_3, δ ppm), 7.92 (s, 1H, —CH═N—), 7.32–6.78 (m, 5H, phenyl-H), 7.01 (d, 1H, C_3H, $J_{3,4}$ = 4.0 Hz), 6.45 (d, 1H, C_4H, $J_{3,4}$ = 4.0 Hz), 4.17 (s, 3H, NCH_3), 2.40 (s, 3H, $COCH_3$); ν (KBr pellet, cm^{-1}), 3242 (NH), 1626 (C═N), 1593, 1488, 1371, 1266, 747, 693; MS [EI, *m/z* (%)], 242 ($M^+ + H$, 39.1), 241 (M^+, 100.0), 124 (15.7), 106 (14.8), 91 (18.0), 65 (17.0); UV (95% EtOH), λ_{max} = 388.8 nm, ε = 3.579 × 10^4 l mol^{-1} cm^{-1}.

2-NO$_2$. M.p. 174 °C (found: C, 59.10; H, 4.80; N, 23.08. $C_{12}H_{12}N_4O_2$ requires C, 59.01; H, 4.95; N, 22.94%); ^{1}H NMR (CD_3COCD_3, δ ppm): 7.96 (s, 1H, —CH═N—), 7.37–6.82 (m, 5H, phenyl-H), 7.19 (d, 1H, C_4H, $J_{3,4}$ = 4.0 Hz), 6.57 (d, 1H, C_3H, $J_{3,4}$ = 4.0 Hz), 4.22 (s, 3H, NCH_3); ν (KBr pellet, cm^{-1}), 3257 (NH), 1603 (C═N), 1545, 1496, 1349, 1334, 1280, 746, 729, 689; MS [EI, *m/z* (%)], 245 ($M^+ + H$, 46.5), 244 (M^+, 100.0), 106 (5.7), 92 (12.6), 65 (9.2); UV (95% EtOH), λ_{max} = 451.2 nm, ε = 2.675 × 10^4 l mol^{-1} cm^{-1}.

2-COOH. M.p. 163 °C (found: C, 64.18; H, 5.27; N, 17.47. $C_{13}H_{13}N_3O_2$ requires C, 64.19; H, 5.39; N, 17.27%); ^{1}H NMR (CD_3COCD_3, δ ppm), 7.92 (s, 1H, —CH═N—), 7.32–6.71 (m, 5H, phenyl-H), 6.92 (d, 1H, C_3H, $J_{3,4}$ = 3.8 Hz), 6.40 (d, 1H, C_4H, $J_{3,4}$ = 3.8 Hz), 4.19 (s, 3H, NCH_3); ν (KBr pellet, cm^{-1}), 3304 (NH), 3300–2400 (COOH), 1662 (C═N), 1602, 1488, 1388, 1255, 747, 690; MS [EI, *m/z* (%)], 245 ($M^+ + 2$ H, 46.5), 244 ($M^+ + H$, 100.0), 243 (M^+, 52.4), 106 (18.3), 91 (78.8), 65 (28.7); UV (95% EtOH), λ_{max} = 363.6 nm, ε = 3.513 × 10^4 l mol^{-1} cm^{-1}.

2-SCH$_3$. M.p. 91 °C (found: C, 63.48; H, 6.12, N, 17.24. $C_{13}H_{15}N_3S$ requires C, 63.64; H, 6.16; N, 17.13%);^{1}H NMR (CD_3COCD_3, δ ppm), 7.84 (s, 1H—CH═N—), 7.28–6.72 (m, 5H, phenyl-H), 6.30 (dd, 2H, C_3H and C_4H, $J_{3,4}$ = 3.0 Hz), 4.00 (s, 3H, NCH_3), 2.33 (s, 3H, SCH_3); ν (KBr pellet, cm^{-1}), 3308 (NH), 1597 (C═N), 1525, 1485, 1290, 762, 753, 695; MS [EI, *m/z* (%)], 246 ($M^+ + H$, 35.9), 245 (M^+, 100.0), 230 (49.6), 127 (19.3), 106 (19.8), 92 (9.0), 65 (8.7); UV (95% EtOH), λ_{max} = 369.8 nm, ε = 3.349 × 10^4 l mol^{-1} cm^{-1}.

2-COOCH$_3$. M.p. 119 °C (found: C, 65.34; H, 5.88; N, 16.48. $C_{14}H_{15}N_3O_2$ requires C, 65.35; H, 5.89; N, 16.34%); ^{1}H NMR (CD_3COCD_3, δ ppm), 9.65 (s, <1H, ═NNH—), 7.93 (s, 1 H, —CH═N—), 7.33–6.74 (m, 5H, phenyl-H), 6.89 (d, 1H, C_3H, $J_{3,4}$ = 4.0 Hz), 6.41 (d, 1H, C_4H, $J_{3,4}$ = 4.0 Hz), 4.18 (s, 3H, NCH_3), 3.79 (s, 3H, $COOCH_3$); ν (KBr pellet, cm^{-1}), 3304 (NH), 1690 (COO), 1679 (C═N), 1598, 1487, 1382, 1264, 751, 745, 690; MS [EI, *m/z* (%)], 258 ($M^+ + H$, 32.7), 257 (M^+, 100.0), 224 (8.0), 140 (15.4), 91 (22.3), 65 (12.0). UV (95% EtOH), λ_{max} = 368.4 nm, ε = 3.878 × 10^4 l mol^{-1} cm^{-1}.

2-Si(CH$_3$)$_3$. M.p. 96 °C (found: C, 66.51; H, 7.76; N, 15.47. $C_{15}H_{21}N_3Si$ requires C, 66.37; H, 7.80; N, 15.48); ^{1}H NMR (CD_3COCD_3, δ ppm), 7.90 (s, 1H, —CH═N—), 7.27–6.73 (m, 5H, phenyl-H), 6.30 (dd, 2H, C_3H and C_4H, $J_{3,4}$ = 3.0 Hz), 4.05 (s, 3H, NCH_3), 0.35 [s, 9H, $Si(CH_3)_3$]; ν (KBr pellet, cm^{-1}), 3305(NH), 1599 (C═N), 1523, 1498, 1252, 751, 692; MS [EI, *m/z* (%)], 272 ($M^+ + H$, 30.4), 271 (M^+, 100.0), 256 (9.8), 138 (21.9), 73 (22.6), 65 (4.6); UV (95% EtOH), λ_{max} = 348.0 nm, ε = 2.762 × 10^4 l mol^{-1} cm^{-1}.

2-Br. M.p. 163 °C (found: C, 51.92; H, 4.27; N, 14.97. $C_{12}H_{12}N_3Br$ requires C, 51.82; H, 4.35; N, 15.11%); ^{1}H NMR (CD_3COCD_3, δ ppm), 7.73 (s, 1H, —CH═N—), 7.28–6.71 (m, 5H, phenyl-H), 6.30 (d, 1H, C_3H, $J_{3,4}$ = 4.0 Hz), 6.15 (d, 1H, C_4H, $J_{3,4}$ = 4.0 Hz), 3.90 (s, 3H, NCH_3); ν (KBr pellet, cm^{-1}), 3296 (NH), 1599 (C═N), 1527, 1448, 1254, 747, 692; MS [EI, *m/z* (%)], 279 ($M^+ + H$, 5.5), 278 (M^+, 1.6), 277 ($M^+ - H$, 6.0), 276 ($M^+ - 2H$, 3.7), 199 (29.7), 93 (100.0), 82 (95.8), 66(28.9); UV (95% EtOH), λ_{max} = 345.6 nm, ε = 2.795 × 10^4 l mol^{-1} cm^{-1}.

2-OCH$_3$. M.p. 105 °C (found: C, 67.92; H, 6.59; N, 18.24.

$C_{13}H_{15}N_3O$ requires C, 68.09; H, 6.61; N, 18.33%); ^{1}H NMR (CD_3COCD_3, δ ppm), 7.73 (s, 1H,—CH═N—), 7.21–6.71 (m, 5H, phenyl-H), 6.14 (d, 1H, C_3H, $J_{3,4} = 3.8$ Hz), 5.30 (d, 1H, C_4H, $J_{3,4} = 3.8$ Hz), 3.76 (s, 3H, NCH_3), 3.67 (s, 3H, OCH_3); ν (KBr pellet, cm^{-1}), 3313 (NH), 1602 (C═N), 1551, 1427, 1298, 1169, 1118, 1044 (C—O—C), 744, 692; MS [EI, *m/z* (%)], 230 ($M^+ + H$, 39.5), 229 (M^+, 100.0), 214 (63.2), 121(11.5), 106 (41.6), 92 (14.7), 67 (14.7); UV (95% EtOH), $\lambda_{max} = 337.4$ nm, $\varepsilon = 2.911 \times 10^4$ l mol^{-1} cm^{-1}.

All the **3-Ys** are new compounds and were confirmed by the following data.

3-H. M.p. 199 °C (found: C, 59.13; H, 4.87; N, 23.02. $C_{12}H_{12}N_4O_2$ requires C, 59.01; H, 4.95; N, 22.94%); ^{1}H NMR (CD_3COCD_3, δ ppm), 8.16 (s, 1H, —CH═N—), 8.03, 8.00, 7.17, 7.07 (each 1H, 4H, phenyl-H), 6.87 (m, 1H, C_3H), 6.42 (m, 1H, C_4H), 6.12 (m, 1H, C_5H), 3.99 (s, 3H, NCH_3H); ν (KBr pellet, cm^{-1}), 3261 (NH), 1614 (C═N), 1599, 1471, 1295, 1271, 839, 748; MS [EI, *m/z* (%)], 245 ($M^+ + H$, 25.7), 244 (M^+, 100.0), 107 (17.7), 94 (5.8), 82 (13.5), 53 (7.3); UV (95% EtOH), $\lambda_{max} = 429.6$ nm, $\varepsilon = 3.429 \times 10^4$ l mol^{-1} cm^{-1}.

3-CH$_3$. M.p. 204 °C (found: C, 60.47; H, 5.59; N, 21.54. $C_{13}H_{14}N_4O_2$ requires C, 60.45; H, 5.46; N, 21.69%); ^{1}H NMR (CD_3COCD_3, δ ppm), 8.11 (s, 1H, —CH═N—), 8.07, 7.94, 7.10, 7.07 (each 1H, 4H, phenyl-H), 6.30 (d, 1H, C_3H, $J_{3,4} = 4.0$ *Hz*), 5.89 (d, 1H, C_4H, $J_{3,4} = 4.0$ Hz), 3.87 (s, 3H, NCH_3), 2.24 (s, 3H, CH_3); ν (KBr pellet, cm^{-1}), 3275 (NH), 1614 (C═N), 1600, 1477, 1292, 1270, 835, 748; MS [EI, *m/z* (%)], 259 ($M^+ + H$, 16.9), 258 (M^+, 100.0), 121 (66.8), 95 (23.7), 53(6.9); UV (95% EtOH), $\lambda_{max} = 439.2$ nm, $\varepsilon = 2.499 \times 10^4$ l mol^{-1} cm^{-1}.

3-Cl. Decomposes at 160 °C (found: C, 51.90; H, 3.83; N, 20.12. $C_{12}H_{11}ClN_4O_2$ requires C, 51.72; H, 3.98; N, 20.10%); ^{1}H NMR (CD_3COCD_3, δ ppm), 8.19 (s, 1H, —CH═N—), 8.09, 7.99, 7.20, 7.10 (each 1H, 4H, phenyl-H), 6.46 (d, 1H, C_3H, $J_{3,4} = 4.0$ Hz), 6.16 (d, 1H, C_4H, $J_{3,4} = 4.0$ Hz), 3.99 (s, 3H, NCH_3); MS [EI, *m/z* (%)], 280 ($M^+ + H$, 39.8), 279 (M^+, 26.6), 278 ($M^+ - H$, 100.0), 244 ($M^+ - Cl$, 10.2), 115 (41.4), 92 (17.4), 65 (17.1); ν (KBr pellet, cm^{-1}), 3271 (NH), 1598 (C═N), 1479, 1297, 1271, 1105, 836, 750; UV (95% EtOH), $\lambda_{max} = 424.8$ nm, $\varepsilon = 3.234 \times 10^4$ l mol^{-1} cm^{-1}.

3-CN. M.p. 219 °C (found: C, 57.85; H, 4.12; N, 26.07. $C_{13}H_{11}N_5O_2$ requires C, 57.99; H, 4.12; N, 26.01%); ^{1}H NMR (CD_3COCD_3, δ ppm), 8.13 (s, 1H, —CH═N—), 8.01 (m, 2H, phenyl-H) 7.19, 7.08 (each 1H, 2H, phenyl-H), 6.82 (d, 1H, C_3H, $J_{3,4} = 4.0$ Hz), 6.49 (d, 1H, C_4H, $J_{3,4} = 4.0$ Hz), 4.03 (s, 3H, NCH_3); MS [EI, *m/z* (%)], 270 ($M^+ + H$, 22.9), 269 (M^+, 100.0), 136 (29.1), 107 (24.9), 90 (10.6), 64 (22.5); ν (KBr pellet, cm^{-1}), 3257 (NH), 2211 (CN), 1614 (C═N), 1593, 1498, 1274, 1109, 840, 751; UV (95% EtOH), $\lambda_{max} = 413.2$ nm, $\varepsilon = 4.115 \times 10^4$ l mol^{-1} cm^{-1}.

3-COCH$_3$. M.p. 232 °C (found: C, 58.66; H, 4.83; N, 19.70. $C_{14}H_{14}N_4O_3$ requires C, 58.74; H, 4.93; N, 19.57%); ^{1}H NMR (CD_3COCD_3, δ ppm), 8.26 (s, 1H, —CH═N—), 8.12 (d, 2H, phenyl-H), 7.30, 7.16 (each 1H, 2H, phenyl-H), 7.09 (d, 1H, C_3H, $J_{3,4} = 4.0$ Hz), 6.63 (d, 1H, C_4H, $J_{3,4} = 4.0$ Hz), 4.17 (s, 3H, NCH_3), 2.47 (s, 3H, $COCH_3$); MS [EI, *m/z* (%)], 287 ($M^+ + H$, 54.1), 286 (M^+, 100.0), 271(4.8), 149 (35.0), 107 (21.3), 92 (10.2), 53 (6.0); ν (KBr pellet, cm^{-1}), 3297 (NH), 1646 (C═N), 1592, 1483, 1382, 1298, 1108, 840, 750; UV (95% EtOH), $\lambda_{max} = 426.0$ nm, $\varepsilon = 4.184 \times 10^4$ l mol^{-1} cm^{-1}.

3–NO$_2$. M.p. 249 °C (found: C, 49.85; H, 3.77; N, 24.40. $C_{12}H_{11}N_5O_4$ requires C, 49.82, H, 3.84, N, 24.22%); ^{1}H NMR (CD_3COCD_3, δ ppm), 8.23 (s, 1H, —CH═N—), 8.14, 8.10, 7.34, 7.30 (each 1H, 4H, phenyl-H), 7.20 (d, 1H, C_4H, $J_{3,4} = 3.8$ Hz), 6.65 (d, 1H, C_3H, $J_{3,4} = 3.8$ Hz), 4.20 (s, 3H, NCH_3); MS [EI, *m/z* (%)], 290 ($M^+ + H$, 18.4), 289 (M^+, 100.0), 151 (15.4), 110 (17.7), 92 (40.6), 64 (41.0); ν (KBr pellet, cm^{-1}), 3261 (NH), 1609 (C═N), 1594, 1497, 1301, 1262, 1108, 848, 752; UV (95% EtOH), $\lambda_{max} = 450.0$ nm, $\varepsilon = 4.085 \times 10^4$ l mol^{-1} cm^{-1}.

3-COOH. M.p. 238 °C (found: C, 54.10; H, 4.18; N, 19.34. $C_{13}H_{12}N_4O_4$ requires C, 54.17; H, 4.20; N, 19.44%); ^{1}H NMR (CD_3COCD_3, δppm), 8.20 (s, 1H, —CH═N—), 8.11 (s, 2H, phenyl-H), 7.26, 7.16 (each 1H, 2H, phenyl-H), 6.94 (d, 1H, C_3H, $J_{3,4} = 4.0$ Hz), 6.59 (d, 1H, C_4H, $J_{3,4} = 4.0$ Hz), 4.21 (s, 3H, NCH_3); MS [EI, *m/z* (%)], 289 ($M^+ + H$, 46.5), 288 (M^+, 100.0), 244 (24.0), 151 (10.0), 105 (15.7), 92 (12.0), 64 (11.5); ν (KBr pellet, cm^{-1}), 3273 (NH), 3200–2500 (COOH), 1664 (C═N), 1595, 1473, 1298, 1269, 840, 751; UV. (95% EtOH), $\lambda_{max} = 426.0$ nm, $\varepsilon = 3.405 \times 10^4$ l mol^{-1} cm^{-1}.

3-SCH$_3$. M.p. 204 °C (found: C, 53.66; H, 4.86; N, 19.41. $C_{13}H_{14}N_4O_2S$ requires C, 53.78; H, 4.86; N, 19.30%);^{1}H NMR (CD_3COCD_3, δppm), 8.19 (s, 1H, —CH═N—), 8.10, 8.03, 7.22, 7.11 (each 1H, 4H, phenyl-H), 6.48 (d, 1H, C_3H, $J_{3,4} = 4.0$ Hz), 6.34 (d, 1H, C_4H, $J_{3,4} = 4.0$ Hz), 4.03 (s, 3H, NCH_3), 2.35 (s, 3H, SCH_3); MS [EI, *m/z* (%)], 291 ($M^+ + H$, 28.0), 290 (M^+, 100.0), 275 (26.5), 127 (21.6), 111 (13.8), 96 (15.0), 64 (11.6); ν (KBr pellet, cm^{-1}), 3259 (NH), 1600 (C═N), 1471, 1300, 1271, 838, 750; UV (95% EtOH), $\lambda_{max} = 439.6$ nm, $\varepsilon = 3.063 \times 10^4$ l mol^{-1} cm^{-1}.

3-COOCH$_3$. M.p. 213 °C (found: C, 55.75; H, 4.74; N, 18.48. $C_{14}H_{14}N_4O_4$ requires C, 55.63; H, 4.67; N, 18.53%); ^{1}H NMR (CD_3COCD_3, δppm), 8.25 (s, 1H, —CH═N—), 8.11, 8.08, 7.28, 7.13 (each 1H, 4H, phenyl-H), 6.93 (d, 1H, C_3H, $J_{3,4} = 4.5$ Hz), 6.56 (d, 1H,

C_4H, $J_{3,4} = 4.5$ Hz), 4.23 (s, 3H, NCH_3), 3.80 (s, 3H, $COOCH_3$); MS [EI, *m/z* (%)], 303 ($M^+ + H$, 31.0), 302 (M^+, 100.0), 286 (4.4), 133 (14.2), 108 (20.4), 92 (9.0), 64 (9.8); ν (KBr pellet, cm^{-1}), 3261 (NH), 1699 (COO), 1591 (C═N), 1481, 1296, 1109, 844, 754; UV (95% EtOH), $\lambda_{max} = 421.2$ nm, $\varepsilon = 3.892 \times 10^4$ l mol^{-1} cm^{-1}.

3-Si(CH$_3$)$_3$. M.p. 175 °C (found: C, 56.88; H, 6.22; N, 17.85. $C_{15}H_{20}N_4O_2Si$ requires C, 56.94; H, 6.37; N, 17.71%); ^1H NMR (CD_3COCD_3, δppm), 8.13 (s, 1H, —CH═N—), 8.00 (2H, phenyl-H), 7.18, 7.01 (each 1H, 2H, phenyl-H), 6.42 (d, 1H, C_3H, $J_{3,4} = 4.0$ Hz), 6.28 (d, 1H, C_4H, $J_{3,4} = 4.0$ Hz), 4.02 (s, 3H, NCH_3), 0.31 [s, 9H, $Si(CH_3)_3$]; MS [EI, *m/z* (%)], 317 ($M^+ + H$, 24.9), 316 (M^+, 100.0), 301 (6.3), 163 (18.5), 138 (35.2), 73 (61.2), 59 (9.0); ν (KBr pellet, cm^{-1}), 3281 (NH), 1599 (C═N), 1477, 1321, 1294, 1272, 836, 750; UV (95% EtOH), $\lambda_{max} = 432.0$ nm, $\varepsilon = 3.005 \times 10^4$ l mol^{-1} cm^{-1}.

3-Br. Decomposes at 170 °C (found: C, 44.76; H, 3.32; N, 17.20. $C_{12}H_{11}N_4O_2Br$ requires C, 44.60; H, 3.43; N, 17.34%); ^1H NMR (CD_3COCD_3, δppm), 8.17 (s, 1H, —CH═N—), 8.07, 7.97, 7.19, 7.09 (each 1H, 4H, phenyl-H), 6.49 (d, 1H, C_3H, $J_{3,4} = 4.0$ Hz), 3.99 (s, 3H, NCH_3); MS [EI, *m/z* (%)], 324 ($M^+ + H$, 4.5), 323 (M^+, 30.0), 322 ($M^+ - H$, 6.5), 321 ($M^+ - 2H$, 30.3), 244 (33.9), 159 (20.9), 138 (100.0), 108 (83.4), 80 (62.8), 65 (43.1); ν (KBr pellet, cm^{-1}), 3277 (NH), 1615 (C═N), 1598, 1474, 1269, 835, 750; UV (95% EtOH), $\lambda_{max} = 426.0$ nm, $\varepsilon = 3.304 \times 10^4$ l mol^{-1} cm^{-1}.

3-OCH$_3$. M.p. 197 °C (found: C, 56.96; H, 5.18; N, 20.53. $C_{13}H_{14}N_4O_3$ requires C, 56.93; H, 5.14; N, 20.43); ^1H NMR (CD_3COCD_3, δppm), 8.07 (s, 1H,—CH═N—), 7.98, 7.77, 7.03, 6.93 (each 1H, 4H, phenyl-H), 6.22 (d, 1H, C_3H, $J_{3,4} = 4.0$ Hz), 5.40 (d, 1H, C_4H, $J_{3,4} = 4.0$ Hz), 3.87 (s, 3H, NCH_3), 3.77 (s, 3H, OCH_3); MS [EI, *m/z* (%)], 275 ($M^+ + H$, 30.5), 274 (M^+, 100.0), 259 (73.7), 122 (17.9), 109 (17.2), 96 (7.7), 67 (12.2); ν (KBr pellet, cm^{-1}), 3259 (NH), 1606 (C═N), 1544, 1479, 1279, 1112, 1044 (C—O—C), 839, 750; UV (95% EtOH), $\lambda_{max} = 450.0$ nm, $\varepsilon = 2.745 \times 10^4$ l mol^{-1} cm^{-1}.

Acknowledgements

We thank the National Science Foundation of China and the China Postdoctoral Science Foundation for financial support.

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