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Comparison of the substituent effects on the ¹³C NMR with the ¹H NMR chemical shifts of CH=N in substituted benzylideneanilines

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Fifty-two samples of substituted benzylideneanilines XPhCH=NPhYs (XBAYs) were synthesized, and their NMR spectra were determined in this paper. Together with the NMR data of other 77 samples of XBAYs quoted from literatures, the ¹H NMR chemical shifts ($\delta_{H}(CH=N)$) and ¹³C NMR chemical shifts ($\delta_{C}(CH=N)$) of the CH=N bridging group were investigated for total of 129 samples of XBAYs. The result shows that the $\delta_{H}(CH=N)$ and $\delta_{C}(CH=N)$ have no distinctive linear relationship, which is contrary to the theoretical thought that declared the $\delta_{H}(CH=N)$ values would increase as the $\delta_{C}(CH=N)$ values increase. With the in-depth analysis, we found that the effects of σ_{F} and σ_{R} of X/Y group on the $\delta_{H}(CH=N)$ and the $\delta_{C}(CH=N)$ are opposite; the effects of the substituent specific cross-interaction effect between X and Y ($\Delta\sigma^{2}$) on the $\delta_{H}(CH=N)$ and the $\delta_{C}(CH=N)$ are different; the contributions of parameters in the regression equations of the $\delta_{H}(CH=N)$ and the $\delta_{C}(CH=N)$ [Eqns (4 and 7), respectively] also have an obvious difference. Copyright © 2015 John Wiley & Sons, Ltd.

Keywords: benzylideneanilines; substituent effects; ¹H NMR chemical shifts; ¹³C NMR chemical shifts; substituent specific cross-interaction

Introduction

The benzylideneanilines XPhCH=NPhYs (abbreviated XBAYs) are a kind of typical compounds with π conjugate system and have been applied extensively in the fields of liquid crystal and nonlinear optical material.^[1-3] In the molecule of XBAY, CH=N is a bridge linking two aromatic rings, in which one ring carries substituent X and another ring carries substituent Y. The substituents X and Y can act as electron donors and/or electron acceptors. Changes of X and Y in XBAY can affect its molecular overall electron distribution and the properties of optoelectronic materials containing the molecule of XBAY. Therefore, the substituent effects on the performance of the CH=N bridging group attained great interest in recent years.^[4–11]

As we know, the NMR shielding is affected by the electron density, and the field of resonance increases with the increasing electron density of the protons and carbon nucleus in the molecule.^[12,13] So the NMR chemical shifts of CH=N (δ_{H} (CH=N) and $\delta_{C}(CH=N)$) were always applied by many researchers to study the substituent effects on the molecules in the past years.^[4–6,8,14,15] Echevarria et al.^[14] have made sketchy studies about the ¹H NMR and ¹³C NMR of CH=N by employing 24 samples of substituted benzylideneanilines and discussed the linear relationship between the δ_H (CH=N) values or δ_C (CH=N) values and the Hammett substituent constant σ_p . They obtained results: the δ_H (CH=N) presented linear relation with σ_p of the benzaldehyde ring substituents but did not present linear relation with the σ_p of the aniline ring substituents; in addition, the effects of the aniline ring substituents on the $\delta_{C}(CH=N)$ were larger than that of the benzaldehyde ring substituents. Afterwards, the substituent effects on the $\delta_{C}(CH=N)$ of some title compounds were analyzed by employing several different single and dual substituent parameter approaches, and the relatively best equation [Eqn (1)] was attained by Neuvonen et al.^[7,16] In their research, they pointed out that the presence of the substituent specific cross-interaction between X and Y could be verified. Although they did not quantify the cross-interaction, their works strongly promotes the research of the substituent effects on the $\delta_C(CH=N)$ of title compounds. In our recent work,^[17] the substituent specific cross-interaction effects was quantified with the item $\Delta\sigma^2 (\Delta\sigma^2 = (\sigma_X - \sigma_Y)^2)$ and a more effective five-parameter equation [Eqn (2)] was proposed to quantify the $\delta_C(CH=N)$ of substituted benzylideneanilines by adding $\Delta\sigma^2$ item to Eqn (1). σ_F is the inductive effect; σ_R is the conjugative effect; $\Delta\sigma^2$ is the substituent specific cross-interaction effect; ρ is the coefficient of corresponding parameter.

$$\begin{split} \delta_{\mathsf{C}}(\mathsf{CH} = \mathsf{N}) &= \mathsf{constant} + \rho_{\mathsf{F}}(\mathsf{X})\sigma_{\mathsf{F}}(\mathsf{X}) + \rho_{\mathsf{F}}(\mathsf{Y})\sigma_{\mathsf{F}}(\mathsf{Y}) \\ &+ \rho_{\mathsf{R}}(\mathsf{X})\sigma_{\mathsf{R}}(\mathsf{X}) + \rho_{\mathsf{R}}(\mathsf{Y})\sigma_{\mathsf{R}}(\mathsf{Y}) \end{split} \tag{1}$$

$$\delta_{\mathsf{C}}(\mathsf{CH} = \mathsf{N}) = \text{constant} + \rho_{\mathsf{F}}(\mathsf{X})\,\sigma_{\mathsf{F}}(\mathsf{X}) + \rho_{\mathsf{F}}(\mathsf{Y})\,\sigma_{\mathsf{F}}(\mathsf{Y}) + \rho_{\mathsf{R}}(\mathsf{X})\,\sigma_{\mathsf{R}}(\mathsf{X}) + \rho_{\mathsf{R}}(\mathsf{Y})\,\sigma_{\mathsf{R}}(\mathsf{Y}) + \rho_{(\Delta\sigma^{2})}\Delta\sigma^{2}$$
(2)

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Now that the ¹H NMR and ¹³C NMR chemical shifts are all affected by the electron density, and it was generally believed that the $\delta_{H}(CH=N)$ values should increase as the $\delta_{C}(CH=N)$ values increase in a same set of compounds. Is it true? Based on a wide set of 129 samples of substituted benzylideneanilines (as shown in Scheme 1), the plot of $\delta_{C}(CH=N)$ values *versus* $\delta_{H}(CH=N)$ values was carried out (Fig. 1).

Figure 1 shows a surprising result that there is a bad correlation between the δ_H (CH=N) and δ_C (CH=N) of XBAYs, the correlation coefficient is only 0.6347. It implies that the effects of substituents X and Y on the δ_H (CH=N) and on the δ_C (CH=N) are different. What are the reasons bringing out the aforementioned phenomenon? In this paper, we made an investigation on this topic using the 129 samples of title compounds and attained a meaningful result.

Results and discussions

The $\delta_C(CH=N)$ values and $\delta_H(CH=N)$ values of title compounds were collected and listed in Table 1. Some of them were measured in this work, and the rest were quoted from the literatures. The substituents X and Y in molecules of title compounds are of electron-withdrawing substituents (e.g. NO₂ and CN) and electron-donating substituents (e.g. NMe₂ and OMe); in addition, X and Y are of parasubstituted and meta-substituted. Taking Eqns (1 and 2) as models, corresponding regression equations were attained [Eqns (3 and 4)] for the 129 $\delta_C(CH=N)$ values in Table 1.

$$\delta_{\rm C}({\rm CH}={\rm N}) = 160.25 - 4.68\,\sigma_{\rm F}({\rm X}) + 3.19\,\sigma_{\rm F}({\rm Y}) - 0.86\,\sigma_{\rm R}({\rm X}) + 5.04\,\sigma_{\rm R}({\rm Y})$$
(3)

$$R = 0.9860, R^2 = 0.9722, S = 0.37, F = 1084.48, n = 129$$

$$\begin{split} \delta_{\mathsf{C}}(\mathsf{CH} = \mathsf{N}) &= 160.30 - 4.38\,\sigma_{\mathsf{F}}(\mathsf{X}) + 3.07\,\sigma_{\mathsf{F}}(\mathsf{Y}) \\ &- 1.11\,\sigma_{\mathsf{R}}(\mathsf{X}) + 4.63\,\sigma_{\mathsf{R}}(\mathsf{Y}) - 0.61\Delta\sigma^2 \end{split} \tag{4}$$

$$R = 0.9938, R^2 = 0.9877, S = 0.25, F = 1968.77, n = 129$$

One can observe that Eqn (4) is superior to Eqn (3) obviously. The correlation coefficient *R* of Eqn (4) is larger than that of Eqn (3), and the standard error *S* of Eqn (4) is smaller than that of Eqn (3). Equation (4) shows that the $\sigma_{\rm F}$ and $\sigma_{\rm R}$ of X group decrease



X (p or m)= NMe₂, OMe, Me, H, F, Cl, CF₃, CN, NO₂ or Br Y (p or m)= NMe₂, OMe, Me, H, F, Cl, CN, NO₂ or Br





Figure 1. The plot of $\delta_{H}(CH{=}N)$ values versus $\delta_{C}(CH{=}N)$ values of title compounds.

the $\delta_C(CH=N)$, while the σ_F and σ_R of Y group increase the $\delta_C(CH=N)$. What we want to know is how do the X and Y groups affect the $\delta_H(CH=N)$. We made discussions as follows.

Based on 129 samples of title compounds, the regression analysis of the $\delta_{\rm H}(\rm CH=N)$ values of Hammett constant $\sigma_{p/m}$ of X and Y was carried out in this paper, and Eqn (5) was obtained (Table 2). In Eqn (5), the ration of $|\rho(X)/\rho(Y)|$ is 2.00, which means that the effect of X on the $\delta_{\rm H}(\rm CH=N)$ is 2.00 times higher than Y on $\delta_{\rm H}(\rm CH=N)$, and the effect of Y on the $\delta_{\rm H}(\rm CH=N)$ is not ignorable. On the other hand, Eqn (5) shows that the $\sigma_{p/m}$ of X group increases the $\delta_{\rm H}(\rm CH=N)$, while the $\sigma_{p/m}$ of Y group decreases the $\delta_{\rm H}(\rm CH=N)$. It is just opposite with the effects of substituents on the $\delta_{\rm C}(\rm CH=N)$.

As we know, $\sigma = \sigma_F + \sigma_R$. In the report of Cao *et al.*,^[17] the regression equation of the $\delta_C(CH=N)$ became better when Hammett constant σ was divided to the inductive constant σ_F and conjugative constant σ_R ; therefore, the different contributions of inductive and conjugative effects were taken into account in the regression analysis of the $\delta_H(CH=N)$ values in this paper, and Eqn (6) was obtained (Table 2). Comparing the correlation coefficient (*R*), the standard errors (*S*), and *F* value of Eqn (6) with these of Eqn (5), the results show that Eqn (6) has no improvement after dividing σ to σ_F and σ_R . That is to say, the inductive and conjugative effects of substituents on δ_H (CH=N) are almost the same intensity, and they can be merged in the correlation equation. It is different from the results of regression analysis of the $\delta_C(CH=N)$ by Cao *et al.*^[17]

It is known that the substituent specific cross-interaction effects $\Delta\sigma^2$ between X and Y is a necessary item in quantifying $\delta_C(CH=N),^{[17]}$ additionally for the comparison with Eqn (4), so this item was also added into Eqn (6) to carry out the regression analysis against the $\delta_H(CH=N)$ values, then Eqn (7) was obtained (Table 2).

The results of Table 2 show that the correlation coefficient (*R*) and the standard errors (*S*) of Eqns (5 and 7) are almost the same; but the *F* value of Eqn (5) is larger than that of Eqn 7. Also, the average absolute errors between the calculated values and experimental values of the two equations are all equal to 0.03 ppm. In conclusion, the Eqn (5) is enough to quantify the substituent effects on the $\delta_{\rm H}$ (CH=N), and the substituent specific cross-interaction effects $\Delta\sigma^2$ on the $\delta_{\rm H}$ (CH=N) is negligible, which is different from the effect of $\Delta\sigma^2$ on the $\delta_{\rm C}$ (CH=N).^[17] In the report of Cao *et al.*,^[17] the substituent specific cross-interaction effect on the $\delta_{\rm C}$ (CH=N) is indispensable. The reason leading to the difference of substituent effects on the $\delta_{\rm C}$ (CH=N) and $\delta_{\rm H}$ (CH=N) may be the deviation of hydrogen atom from the conjugated main chain in the molecules of XBAYs.

In addition, the parameter effects on the $\delta_C(CH=N)$ and $\delta_H(CH=N)$ are different. For that, Eqns (4 and 7) have the same parameters and the regression results of Eqn (7) are close to that of Eqn (5). So here the relative importance of parameters in Eqns (4 and 7) are investigated from the relative contributions (ψ_γ) or fraction contributions (ψ_f) of the corresponding parameters to the $\delta_C(CH=N)$ and $\delta_H(CH=N).^{[20,21]}$

$$\psi_{\gamma} = m_i \overline{X_i} \tag{8}$$

$$\psi_{\rm f}(i) = \frac{R^2 \left| \psi_{\gamma}(i) \right|}{\sum_{i} \left| \psi_{\gamma}(i) \right|} \times 100\% \tag{9}$$

The m_i and $\overline{X_i}$ are the coefficient and the average value of the *i*th parameter in Eqn (4 or 7), respectively, and the *R* are the correlation coefficients of Eqn (4 or 7). The sum is over the parameters in the equations. The contribution results for the corresponding parameters of Eqns (4 and 7) are all shown in Table 3.

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Table 1. The data of $\delta_C(CH=N)$ and $\delta_H(CH=N)$ of 129 samples of title compounds											
Number	Х	Y	σ_{F} (X) ^a	$\sigma_{F}\left(Y\right)^{a}$	$\sigma_{R}\left(X ight)^{a}$	$\sigma_{R}\left(Y ight)^{a}$	$\Delta\sigma^{2a}$	$\delta_{C}{}^{b}$	$\delta_{H}{}^{c}$	$\delta_{\text{C.calcd.}}{}^{d}$	$\delta_{\text{H.calcd.}}^{\text{e}}$
1	<i>m</i> -F	p-NMe ₂	0.34	0.15	0.00	-0.98	1.37	153.99	8.49	153.89	8.51
2	<i>m</i> -F	<i>p</i> -OMe	0.34	0.29	0.00	-0.56	0.37	156.66	8.46	156.88	8.48
3	<i>m</i> -F	<i>p</i> -Me	0.34	0.01	0.00	-0.18	0.26	158.00	8.45	157.85	8.47
4	<i>m</i> -F	p-Cl	0.34	0.42	0.00	-0.19	0.01	159.17	8.41	159.22	8.44
5	<i>m</i> -Br	<i>p</i> -NMe ₂	0.39	0.15	0.00	-0.98	1.49	153.58	8.45	153.60	8.52
6	<i>m</i> -Br	<i>p</i> -OMe	0.39	0.29	0.00	-0.56	0.44	156.28	8.42	156.62	8.48
7	<i>m</i> -Br	<i>p</i> -Me	0.39	0.01	0.00	-0.18	0.31	157.61	8.41	157.60	8.48
8	<i>m</i> -Br	<i>p</i> -F	0.39	0.45	0.00	-0.39	0.11	158.23	8.38	158.10	8.46
9	<i>m</i> -Br	p-Cl	0.39	0.42	0.00	-0.19	0.03	158.84	8.37	158.98	8.45
10	<i>m</i> -CN	<i>p</i> -NMe ₂	0.56	0.15	0.00	-0.98	1.93	151.96	8.51	152.58	8.54
11	<i>m</i> -CN	<i>p</i> -OMe	0.56	0.29	0.00	-0.56	0.69	154.93	8.48	155.72	8.50
12	<i>m</i> -CN	<i>p</i> -Me	0.56	0.01	0.00	-0.18	0.53	156.38	8.47	156.72	8.50
13	<i>m</i> -CN	p-Cl	0.56	0.42	0.00	-0.19	0.11	157.66	8.44	158.19	8.47
14	<i>m</i> -CN	<i>p</i> -CN	0.56	0.51	0.00	0.15	0.01	159.69	8.43	160.10	8.44
15	<i>m</i> -OMe	<i>p</i> -NMe ₂	0.12	0.15	0.00	-0.98	0.90	155.83	8.49	155.14	8.48
16	<i>p</i> -NMe ₂	<i>m</i> -Me	0.15	-0.07	-0.98	0.00	0.58	160.06	8.33	160.16	8.32
17	<i>p</i> -OMe	<i>m</i> -Me	0.29	-0.07	-0.56	0.00	0.04	159.50	8.35	159.41	8.39
18	<i>p</i> -Cl	<i>m</i> -Me	0.42	-0.07	-0.19	0.00	0.09	158.60	8.42	158.40	8.45
19	p-CF ₃	<i>m</i> -Me	0.38	-0.07	0.16	0.00	0.37	158.32	8.51	158.02	8.49
20	<i>p</i> -CN	<i>m</i> -Me	0.51	-0.07	0.15	0.00	0.53	157.63	8.49	157.36	8.50
21	<i>p</i> -NO ₂	<i>m</i> -Me	0.65	-0.07	0.13	0.00	0.72	157.10	8.55	156.65	8.52
22	<i>p</i> -NMe ₂	<i>m</i> -F	0.15	0.34	-0.98	0.00	1.37	160.98	8.32	160.94	8.30
23	<i>p</i> -OMe	<i>m</i> -F	0.29	0.34	-0.56	0.00	0.37	160.51	8.36	160.47	8.36
24	<i>p</i> -Me	m-F	0.01	0.34	-0.18	0.00	0.26	161.19	8.40	161.34	8.38
25	p-Cl	<i>m</i> -F	0.42	0.34	-0.19	0.00	0.01	159.71	8.40	159.71	8.42
26	<i>p</i> -CN	<i>m</i> -F	0.51	0.34	0.15	0.00	0.10	158.83	8.47	158.88	8.48
27	<i>p</i> -NO ₂	m-F	0.65	0.34	0.13	0.00	0.19	158.35	8.53	158.24	8.49
28	<i>p</i> -NMe ₂	<i>m</i> -Br	0.15	0.39	-0.98	0.00	1.49	161.06	8.27	161.02	8.29
29	<i>p</i> -OMe	<i>m</i> -Br	0.29	0.39	-0.56	0.00	0.44	160.60	8.38	160.58	8.36
30	<i>p</i> -Me	<i>m</i> -Br	0.01	0.39	-0.18	0.00	0.31	161.30	8.40	161.46	8.37
31	p-Cl	<i>m</i> -Br	0.42	0.39	-0.19	0.00	0.03	159.81	8.38	159.85	8.42
32	p-CN	<i>m</i> -Br	0.51	0.39	0.15	0.00	0.07	158.92	8.46	159.06	8.47
33	$p-NO_2$	<i>m</i> -Br	0.65	0.39	0.13	0.00	0.15	158.44	8.52	158.42	8.49
34	<i>p</i> -NMe ₂	<i>m</i> -OMe	0.15	0.12	-0.98	0.00	0.90	160.16	8.33	160.55	8.31
35	p-CN	<i>m</i> -Oivie	0.51	0.12	0.15	0.00	0.29	158.09	8.49	158.09	8.49
36	p-NO ₂	<i>m</i> -OMe	0.65	0.12	0.13	0.00	0.44	157.54	8.55	157.41	8.50
3/	p-Cl	m-CN	0.42	0.50	-0.19	0.00	0.11	160.77	8.39	160.33	8.41
38	p-CN	m-CN	0.51	0.50	0.15	0.00	0.01	162.15	8.48	159.01	8.40
39	<i>m</i> -Oivie	<i>m</i> -CN	0.12	0.56	0.00	0.00	0.19	162.15	8.38	161.38	8.40
40	m Me	m Ma	-0.07	0.12	0.00	0.00	0.04	160.20	0.44	160.95	0.40
41	m Me	m E	-0.07	-0.07	0.00	0.00	0.00	161 52	0.44	161 55	0.41
42	m-ivie	m-r	-0.07	0.34	0.00	0.00	0.17	101.52	8.40	101.55	8.39
45	m F	m E	0.34	-0.07	0.00	0.00	0.17	150.59	0.45	150.49	0.40
44	m F	m Pr	0.34	0.34	0.00	0.00	0.00	150.00	0.41	159.60	0.44
45	m CN	m OMo	0.54	0.59	0.00	0.00	0.00	157.55	0.59	159.10	0.45
40	m-CN	m-Mo	0.50	0.12	0.00	0.00	0.19	157.55	8.40 8.46	156.10	0.40 8.40
47	m-CN	m E	0.50	-0.07	0.00	0.00	0.40	150 22	0.40	157.59	0.49
40	m-CN	m CN	0.50	0.54	0.00	0.00	0.05	150.52	0.44	150.00	0.40 0.45
49 50	m_Br	m-Mo	0.20	0.00	0.00	0.00	0.00	150 24	0.45 8 20	128.21	0.45 Q /17
51	111-DI m_Pr	m_CN	0.39	-0.07	0.00	0.00	0.21	150.24	0.37 0.27	120.20	0.4/ 0.10
57	III-DI	m_Br	0.29	0.20	0.00	0.00	0.05	150 51	0.50	150 70	0.45 Q //
53	m_Mo		0.39	0.09	0.00	0.00	0.00	150 7/	0.33 Q //E	1 J7.17 150 Q0	0.44 Q /17
55	m C	p-Oivie	-0.07	0.29	0.00	-0.50	0.04	156./4	0.40	156.00	0.45
54 55		p-Oivie	0.37	0.29	0.00	0.50	0.41	150.45	0.43	150./3	0.4ð 0 50
55 56	m C	p-Oivie	0.71	0.29	0.00	-0.50	0.90	154.70	0.27	124.90	0.52
50		p-COUEt	0.3/	0.34	0.00	0.11	0.01	100.00	0.40	100.23	0.45
57	$III-INO_2$	p-COUET	0.71	0.34	0.00	0.11	0.07	120.00	0.54	138./0	ö.4ŏ

(Continues)

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Table 1. (Continued)											
Number	Х	Y	$\sigma_{F}\left(X\right)^{a}$	$\sigma_{F}\left(Y\right)^{a}$	$\sigma_{R}\left(X ight)^{a}$	$\sigma_{R}\left(Y\right)^{a}$	$\Delta\sigma^{2a}$	${\delta_{C}}^{b}$	$\delta_{H}{}^{c}$	$\delta_{\text{C.calcd.}}^{} d$	$\delta_{\text{H.calcd.}}^{\text{e}}$
58	<i>m</i> -Me	p-COOEt	-0.07	0.34	0.00	0.11	0.27	161.92	8.41	162.00	8.38
59	<i>p</i> -CN	p-COOEt	0.51	0.34	0.15	0.11	0.04	159.33	8.50	159.43	8.47
60	p-CF ₃	p-COOEt	0.38	0.34	0.16	0.11	0.01	159.93	8.50	160.01	8.45
61	<i>p</i> -F	p-COOEt	0.45	0.34	-0.39	0.11	0.15	160.05	8.41	160.23	8.40
62	<i>p</i> -Cl	p-COOEt	0.42	0.34	-0.19	0.11	0.05	160.11	8.41	160.20	8.42
63	<i>p</i> -Me	p-COOEt	0.01	0.34	-0.18	0.11	0.38	161.56	8.40	161.78	8.37
64	$p-NO_2$	p-COOEt	0.65	0.34	0.13	0.11	0.11	158.86	8.55	158.80	8.48
65	H	p-COOEt	0.00	0.34	0.00	0.11	0.20	161.6/	8.44	161./3	8.39
60 67	p-INIVIe ₂	p-COOEt	0.15	0.34	-0.98	0.11	1.64	161.30	8.30	161.28	8.29
69	p-Ome	p-COOEt	0.29	0.34	-0.50	0.11	0.52	160.84	8.30	160.89	8.30 9.47
60	$p = NO_2$	p-CN	0.05	0.51	0.13	0.15	0.01	156.06	0.JZ 8.56	156.57	0.47 8 51
70	$p = NO_2$	p-r n-Cl	0.05	0.45	0.13	-0.39	0.32	157.64	8.50 8.54	150.57	8.50
70	$p \operatorname{NO}_2$ $p \operatorname{NO}_2$	рсі Н	0.05	0.42	0.13	0.00	0.50	157.33	8.56	156.94	8 51
72	<i>p</i> -NO ₂	<i>n</i> -Me	0.65	0.01	0.13	-0.18	0.90	156.32	8.56	155.95	8.52
73	p-NO ₂	p-OMe	0.65	0.29	0.13	-0.56	1.10	154.76	8.48	154.93	8.53
74	p-NO ₂	p-NMe ₂	0.65	0.15	0.13	-0.98	2.59	151.51	8.60	151.64	8.56
75	p-CN	p-CN	0.51	0.51	0.15	0.15	0.00	160.21	8.46	160.16	8.46
76	, p-CN	, <i>р</i> -F	0.51	0.45	0.15	-0.39	0.36	157.48	8.49	157.26	8.49
77	p-CN	p-Cl	0.51	0.42	0.15	-0.19	0.18	158.14	8.48	158.20	8.48
78	<i>p</i> -CN	н	0.51	0.00	0.15	0.00	0.44	157.82	8.50	157.63	8.50
79	<i>p</i> -CN	<i>p</i> -Me	0.51	0.01	0.15	-0.18	0.69	156.85	8.51	156.67	8.51
80	<i>p</i> -CN	<i>p</i> -OMe	0.51	0.29	0.15	-0.56	0.86	155.35	8.52	155.67	8.51
81	<i>p</i> -CN	<i>p</i> -NMe ₂	0.51	0.15	0.15	-0.98	2.22	152.22	8.55	152.46	8.55
82	<i>p</i> -F	<i>p</i> -CN	0.45	0.51	-0.39	0.15	0.36	160.82	8.37	160.80	8.38
83	<i>p</i> -F	<i>p</i> -F	0.45	0.45	-0.39	-0.39	0.00	158.57	8.41	158.34	8.42
84	<i>p</i> -F	p-Cl	0.45	0.42	-0.39	-0.19	0.03	159.11	8.39	159.16	8.41
85	p-F	н.,	0.45	0.00	-0.39	0.00	0.00	158.76	8.42	158.76	8.42
86	<i>р</i> -н	<i>p</i> -Me	0.45	0.01	-0.39	-0.18	0.05	158.00	8.42	157.93	8.44
8/	<i>р</i> -г	<i>p</i> -Oivie	0.45	0.29	-0.39	-0.56	0.11	156.81	8.44	156.99	8.44
88	p-r	p-inivie ₂	0.45	0.15	-0.39	-0.98	0.79	154.37	8.48 9.27	154.20	8.48 9.40
09 00	p-Cl	p-CN	0.42	0.51	-0.19	0.15	0.10	158 52	0.37 Q /1	100.02	0.40 8.47
90	p-Cl	р-1 р-СІ	0.42	0.45	-0.19 -0.19	-0.39 -0.19	0.05	150.52	8.40	150.25	8.43
92	p-Cl	РСI	0.42	0.00	-0.19	0.00	0.00	158.74	8.41	159.66	8.45
93	p-Cl	<i>n</i> -Me	0.42	0.01	-0.19	-0.18	0.16	157.94	8.42	157.77	8.46
94	p-Cl	p-OMe	0.42	0.29	-0.19	-0.56	0.25	156.68	8.44	156.82	8.46
95	p-Cl	p-NMe ₂	0.42	0.15	-0.19	-0.98	1.12	154.07	8.47	153.91	8.50
96	, H	, p-F	0.00	0.45	0.00	-0.39	0.00	160.16	8.46	159.88	8.41
97	Н	p-Cl	0.00	0.42	0.00	-0.19	0.05	160.71	8.43	160.68	8.40
98	Н	Н	0.00	0.00	0.00	0.00	0.00	160.34	8.45	160.30	8.42
99	Н	Me	0.00	0.01	0.00	-0.18	0.03	159.59	8.47	159.48	8.43
100	Н	<i>p</i> -OMe	0.00	0.29	0.00	-0.56	0.07	158.41	8.48	158.55	8.43
101	Н	<i>p</i> -NMe ₂	0.00	0.15	0.00	-0.98	0.69	155.97	8.52	155.80	8.47
102	<i>p</i> -Me	<i>p</i> -CN	0.01	0.51	-0.18	0.15	0.69	162.29	8.36	162.29	8.36
103	<i>p</i> -Me	<i>p</i> -F	0.01	0.45	-0.18	-0.39	0.05	160.15	8.40	160.00	8.39
104	<i>p</i> -Me	p-Cl	0.01	0.42	-0.18	-0.19	0.16	160.67	8.38	160.77	8.38
105	<i>p</i> -Me	Н	0.01	0.00	-0.18	0.00	0.03	160.30	8.42	160.44	8.40
106	<i>p</i> -Me	<i>p</i> -Me	0.01	0.01	-0.18	-0.18	0.00	159.58	8.43	159.65	8.41
107	<i>p</i> -Me	<i>p</i> -OMe	0.01	0.29	-0.18	-0.56	0.01	158.46	8.44	158.75	8.41
108	<i>p</i> -Me	p-NMe ₂	0.01	0.15	-0.18	-0.98	0.44	156.15	8.48	156.11	8.45
109	p-OMe	p-CN	0.29	0.51	-0.56	0.15	0.86	161.54	8.33	161.39	8.34 0.20
110	p-ONe	p-r	0.29	0.45	-0.50	-0.39	0.11	159.49	0.4U	159.10	ö.3ö حد ہ
117	p-OMe	<i>р-</i> Сі ц	0.29	0.42	-0.50	-0.19	0.25	159.99	0.35 0.20	159.91 150.61	0.3/ 0.20
112	p-OMe	n-Me	0.29	0.00	-0.50	0.00	0.07	152.04	0.20	129.01	0.30 8 10
115	POME	PINE	0.29	0.01	-0.50	-0.10	0.01	130.24	0.57	10.00	0.40

(Continues)

Table 1. (Continued)											
Number	х	Y	$\sigma_F \left(X \right)^a$	$\sigma_F \left(Y \right)^a$	$\sigma_{R}\left(X\right)^{a}$	$\sigma_{R}\left(Y\right)^{a}$	$\Delta\sigma^{2a}$	${\delta_{C}}^{b}$	$\delta_{H}{}^{c}$	$\delta_{\text{C.calcd.}}{}^d$	$\delta_{\text{H.calcd.}}^{\text{e}}$
114	<i>p</i> -OMe	<i>p</i> -OMe	0.29	0.29	-0.56	-0.56	0.00	157.88	8.43	157.95	8.40
115	<i>p</i> -OMe	<i>p</i> -NMe ₂	0.29	0.15	-0.56	-0.98	0.31	155.69	8.44	155.39	8.44
116	<i>p</i> -NMe ₂	<i>p</i> -CN	0.15	0.51	-0.98	0.15	2.22	161.86	8.26	161.63	8.28
117	<i>p</i> -NMe ₂	<i>p</i> -F	0.15	0.45	-0.98	-0.39	0.79	160.08	8.30	159.82	8.31
118	<i>p</i> -NMe ₂	<i>p</i> -Cl	0.15	0.42	-0.98	-0.19	1.12	160.51	8.29	160.46	8.30
119	<i>p</i> -NMe ₂	Н	0.15	0.00	-0.98	0.00	0.69	160.21	8.32	160.31	8.32
120	<i>p</i> -NMe ₂	<i>p</i> -Me	0.15	0.01	-0.98	-0.18	0.44	159.57	8.33	159.66	8.33
121	<i>p</i> -NMe ₂	<i>p</i> -OMe	0.15	0.29	-0.98	-0.56	0.31	158.65	8.34	158.84	8.33
122	<i>p</i> -NMe ₂	<i>p</i> -NMe ₂	0.15	0.15	-0.98	-0.98	0.00	156.73	8.37	156.66	8.37
123	p-CF ₃	<i>p</i> -CN	0.38	0.51	0.16	0.15	0.01	160.76	8.46	160.71	8.44
124	p-CF ₃	<i>p</i> -F	0.38	0.45	0.16	-0.39	0.23	158.22	8.50	157.89	8.48
125	p-CF ₃	<i>p</i> -Cl	0.38	0.42	0.16	-0.19	0.10	158.85	8.49	158.81	8.47
126	p-CF ₃	Н	0.38	0.00	0.16	0.00	0.29	158.51	8.51	158.28	8.48
127	p-CF ₃	<i>p</i> -Me	0.38	0.01	0.16	-0.18	0.50	157.62	8.52	157.35	8.49
128	p-CF ₃	<i>p</i> -OMe	0.38	0.29	0.16	-0.56	0.66	156.24	8.54	156.35	8.50
129	p-CF ₃	p-NMe ₂	0.38	0.15	0.16	-0.98	1.88	153.39	8.56	153.23	8.53

^aThe values of parameters were taken from Hansch *et al.*^[18] $\Delta \sigma^2 = (\sigma_X - \sigma_Y)^2$.

^b δ_C is the δ_C (CH=N). The δ_C (CH=N) of numbers 1–52 were measured in this work; the δ_C (CH=N) of numbers 53–67 were taken from our previous work;^[17] the δ_C (CH=N) of 68–129 were taken from Neuvonen *et al.*^[7]

 $^{c}\delta_{H}$ is the δ_{H} (CH=N).The δ_{H} (CH=N) of numbers 1–52 were measured in this work; the δ_{H} (CH=N) of numbers 53–67 were taken from our previous work;^[17] the δ_{H} (CH=N) of 68–129 were taken from our unpublished work (the master's dissertation of B. Lu).^[19]

 ${}^{d}\delta_{C,calcd}$ is the $\delta_{C}(CH=N)$ values calculated in Eqn (4).

 ${}^{e}\delta_{H,calcd.}$ is the $\delta_{H}(CH=N)$ values calculated in Eqn (5).

Table 2. The correlation equations between the $\delta_{H}(CH{=}N)$ values and the substituent effect constants for compounds XBAYs							
$\delta_{\rm H}(\rm CH = N) = 8.42 + 0.12\sigma(X) - 0.06\sigma(Y)$	Eqn (5)						
$R = 0.8811, R^2 = 0.7764, S = 0.03, F = 218.77, n = 129$							
$\delta_{\rm H}(\rm CH = N) = 8.44 + 0.09\sigma_{\rm F}(\rm X) - 0.07\sigma_{\rm F}(\rm Y) +$	Eqn (6)						
$0.14\sigma_{\rm R}({\rm X}) - 0.06\sigma_{\rm R}({\rm Y})$							
$R = 0.8879, R^2 = 0.7884, S = 0.03, F = 115.53, n = 129$							
$\delta_{\rm H}(\rm CH = N) = 8.43 + 0.08\sigma_{\rm F}(\rm X) - 0.07\sigma_{\rm F}(\rm Y) +$	Eqn (7)						
$0.14\sigma_{\rm R}({\rm X}) - 0.05\sigma_{\rm R}({\rm Y}) + 0.008\Delta\sigma^2$							
$R = 0.8895, R^2 = 0.7913, S = 0.03, F = 93.25, n = 129$							
XBAYs, XPhCH=NPhYs.							

Table 3. The relative and fraction contribution (ψ_{γ} and ψ_{f}) of parameters to the $\delta_{C}(CH=N)$ and $\delta_{H}(CH=N)$ of XBAYs

Paramet	er	σ(X)	σ($\Delta\sigma^2$	
		σ _F (X)	σ _R (X)	σ _F (Y)	$\sigma_{R}\left(Y ight)$	
Eqn (4)	Ψγ	-1.4997	0.1736	0.7975	-0.9623	-0.2398
Eqn (7)	ψ _f (90) Ψ _γ	40.33 0.0274	-0.0182	_0.0219	0.0104	0.45
	ψ _f (%)	33.82	22.45	27.02	12.83	3.88

One can observe in Table 3 that the contributions of parameters to the changes of $\delta_C(CH=N)$ and $\delta_H(CH=N)$ are very different. $\sigma_R(X)$ contributes more to $\delta_H(CH=N)$ than $\delta_C(CH=N)$, while $\sigma_R(Y)$ and $\Delta\sigma^2$ contribute more to $\delta_C(CH=N)$ than $\delta_H(CH=N)$. On the whole, for the contributions to the change of $\delta_C(CH=N)$, the σ of Y is somewhat

larger than the σ of X, while to the change of $\delta_{\text{H}}(\text{CH}{=}\text{N})$, the σ of X is much more than the σ of Y.

On the other hand, the plots of the $\delta_C(CH=N)$ and $\delta_H(CH=N)$ values calculated by Eqns ((4) and (5)), respectively, *versus* the corresponding experimental ones were made, shown as in Figs 2 and 3 (all the values were listed in Table 1). As seen from the figures, good relevance in Fig. 2 was presented, and relatively poor relevance in Fig. 3 could be accepted because the range of the experimental $\delta_H(CH=N)$ values is only 0.34 ppm.







Figure 3. The plot of the $\delta_{H}(CH=N)$ values calculated in Eqn (5) versus the experimental $\delta_{H}(CH=N)$ values of title compounds.

Conclusions

In contrast to empirical prediction, there is no distinctive linear relationship between the $\delta_{H}(CH=N)$ and $\delta_{C}(CH=N)$ of title compounds. Equations (4 and 5) show that the $\delta_{C}(CH=N)$ and $\delta_{H}(CH=N)$ are dominated by different substituent effects. As seen in Eqn (4), the σ_{F} and σ_{R} of X group decrease the $\delta_{C}(CH=N)$, while the σ_{F} and σ_{R} of Y group increase the $\delta_{C}(CH=N)$. However, the effects of X and Y groups on the $\delta_{H}(CH=N)$ have opposite behaviors [Eqn (5)]. In addition, the result shows that the effect of substituent specific cross-interaction effects between X and Y ($\Delta\sigma^{2}$) on the $\delta_{H}(CH=N)$ is negligible, while it is indispensable on the $\delta_{C}(CH=N)$. Finally, the contributions of parameters to the change of $\delta_{C}(CH=N)$ and $\delta_{H}(CH=N)$ are different, for the change of $\delta_{H}(CH=N)$, the contribution of $\sigma(X)$ is much larger than that of $\sigma(Y)$; while for the change of $\delta_{C}(CH=N)$.

Why substituents X and Y present the different effects on the δ_{H} (CH=N) and δ_{C} (CH=N) of title compounds is still an interesting topic and need to be further investigated deeply.

Dataset

The substituted benzylideneanilines were all synthesized with the solvent-free method according to Scheme 1.^[17,22] They were purified with anhydrous alcohol and were confirmed with ¹H NMR and ¹³C NMR. The NMR spectra were recorded with Bruker AV 500 MHz in CDCl₃ at room temperature at an approximate concentration. The NMR chemical shifts are expressed in parts per million relative to TMS (0.00 ppm), which is used as an internal reference. The detailed data of the synthesized compounds are available in the Supporting Information.

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Supporting information

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