

# Substituent effects on the $^{13}\text{C}$ NMR chemical shifts of the imine carbon in *N*-(4-*X*-benzylidene)-4-(4-*Y*-styryl) anilines

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Long-range electronic substituent effects were targeted using the substituent dependence of  $\delta_{\text{C}}(\text{C}=\text{N})$ , and specific cross-interactions were explored extendedly. A wide set of *N*-(4-*X*-benzylidene)-4-(4-*Y*-styryl) anilines,  $p\text{-X-C}_6\text{H}_4\text{CH}=\text{NC}_6\text{H}_4\text{CH}=\text{CHC}_6\text{H}_4\text{-}p\text{-Y}$  (*X* = NMe<sub>2</sub>, OMe, Me, H, Cl, F, CN, or NO<sub>2</sub>; *Y* = NMe<sub>2</sub>, OMe, Me, H, Cl, or CN) were prepared for this study, and their  $^{13}\text{C}$  NMR chemical shifts  $\delta_{\text{C}}(\text{C}=\text{N})$  of C=N bonds were measured. The results show that both the inductive and resonance effects of the substituents *Y* on the  $\delta_{\text{C}}(\text{C}=\text{N})$  of  $p\text{-X-C}_6\text{H}_4\text{CH}=\text{NC}_6\text{H}_4\text{CH}=\text{CHC}_6\text{H}_4\text{-}p\text{-Y}$  are less than those of the substituents *Y* in  $p\text{-X-C}_6\text{H}_4\text{CH}=\text{NC}_6\text{H}_4\text{-}p\text{-Y}$ . Moreover, the sensitivity of the electronic character of the C=N function to electron donation/electron withdrawal by the substituent *X* or *Y* attenuates as the length of the conjugated chain is elongated. It was confirmed that the substituent cross-interaction is an important factor influencing  $\delta_{\text{C}}(\text{C}=\text{N})$ , not only when both *X* and *Y* are varied but also when either *X* or *Y* is fixed. The long-range transmission of the specific cross-interaction effects on  $\delta_{\text{C}}(\text{C}=\text{N})$  decreases with increasing conjugated distance between *X* and *Y*. The results of this study suggest that there is a long-range transmission of the substituent effects in  $p\text{-X-C}_6\text{H}_4\text{CH}=\text{NC}_6\text{H}_4\text{CH}=\text{CHC}_6\text{H}_4\text{-}p\text{-Y}$ . Copyright © 2012 John Wiley & Sons, Ltd. Supporting information may be found in the online version of this paper

**Keywords:**  $^{13}\text{C}$  NMR chemical shift; benzylidene aniline; long-range transmission; substituent effect

## INTRODUCTION

To use new liquid crystals and nonlinear optical materials optimally and design new candidates efficiently, it is necessary to understand the charge distribution of the molecules of mesogenic compounds, which is central to their optical and electronic characters.<sup>[1–3]</sup> It has been reported that when the electron density of the carbon nucleus increases, the field of resonance also increases.<sup>[4,5]</sup> Substituent effects on  $^{13}\text{C}$  NMR have been investigated.<sup>[6–8]</sup> Several  $^{13}\text{C}$  NMR studies have revealed that the overall electron distribution can be finely tuned through the electronic effects of remote substituents.<sup>[9–11]</sup>

Substituted benzylidene anilines are widely used structural units in liquid crystals and nonlinear optical materials.<sup>[12–15]</sup> Neuvonen and co-workers<sup>[16]</sup> demonstrated that changes of the substituents *X* and *Y* could finely control the electronic character, and the presence of the specific cross-interaction between *X* and *Y* in **M3** (Scheme 1) was verified. Cao *et al.*<sup>[17]</sup> further explored the substituent-specific cross-interaction effects in the same system and successfully proposed the new parameter  $\Delta\sigma^2$  ( $\Delta\sigma^2 = (\sigma_{\text{X}} - \sigma_{\text{Y}})^2$ ) to scale the effects, where the  $\sigma_{\text{X}}$  and  $\sigma_{\text{Y}}$  are Hammett constants of the substituents *X* and *Y*, respectively. It is known that the length of the conjugated chain can affect the inductive and resonance effects and thus might lead to changes in the electron distribution. Cao *et al.*<sup>[18]</sup> also investigated the substituent effects in **M2** (Scheme 1). Our observations of the substituent effects in **M2** encouraged us to prepare other type of benzylidene anilines, in which the conjugated chain in the aniline unit is elongated. The higher electronegativity of nitrogen, compared with carbon, and the presence of a lone pair of electrons in the nitrogen atom influence the electron distribution. Consequently, the substituent

effects on the  $^{13}\text{C}$  NMR chemical shifts  $\delta_{\text{C}}(\text{C}=\text{N})$  of C=N in **M1** (Scheme 1) are not quite the same as those in **M2**. Thus, it is worthwhile to provide more information on the substituent effects in **M1**.

In the present work, compounds **M1** are synthesized and chosen as the model compounds, and the  $^{13}\text{C}$  NMR chemical shifts of their imine carbons are used to analyze the substituent effects. Our primary interest is to study the long-range substituent effects in benzylidene anilines with elongated chains.

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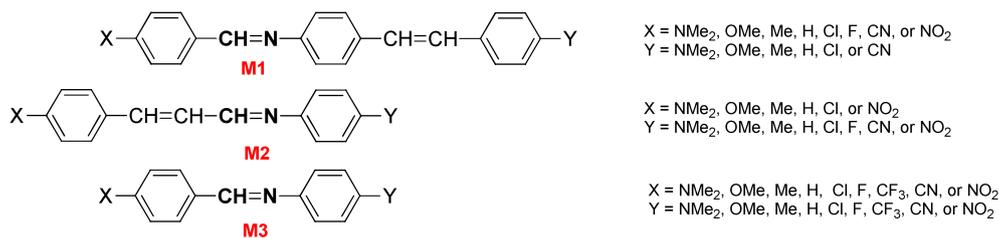
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**Scheme 1.** Structures of compounds **M1**, **M2**, and **M3**

## RESULTS

The <sup>13</sup>C NMR chemical spectra of the compounds **M1** in Scheme 1 were recorded in CDCl<sub>3</sub> at 293 K. The  $\delta_C(\text{C}=\text{N})$  of **M1** are reported in Table 1, and the chemical shifts are expressed in ppm relative to CDCl<sub>3</sub> (77.0 ppm).

## DISCUSSION

To give an insight into the changing regularity of the substituent effects of  $X$  and  $Y$  on  $\delta_C(\text{C}=\text{N})$  in **M1**, we focused on two aspects. One is the corresponding effect of the benzylidene substituent  $X$  and aniline substituent  $Y$  on  $\delta_C(\text{C}=\text{N})$  in **M1**, and the other is the specific cross-interaction effect between  $X$  and  $Y$ . Also, a distinction of the substituent effects between **M1** and **M2**, and **M1** and **M3** was investigated.

### Effect of substituents $X$ on $\delta_C(\text{C}=\text{N})$

For each substituent  $Y$  in **M1**, when the substituent  $X$  was varied, the  $\delta_C(\text{C}=\text{N})$  values in Table 1 were fitted using Eqns (1) and (2). The correlation results are listed in Table 2 (columns 2 to 8).

$$\delta_C(\text{C}=\text{N}) = \rho\sigma + \text{constant} \quad (1)$$

$$\delta_C(\text{C}=\text{N}) = \rho_F\sigma_F + \rho_R\sigma_R + \text{constant} \quad (2)$$

where  $\sigma$ ,  $\sigma_F$ , and  $\sigma_R$  are the Hammett parameters of substituents ( $\sigma = \sigma_F + \sigma_R$ ),  $\sigma_F$  and  $\sigma_R$  are the inductive parameter and resonance parameter, respectively, and  $\rho$ ,  $\rho_F$ , and  $\rho_R$  are the corresponding coefficients.

The <sup>13</sup>C NMR chemical shifts of the C=N carbon were first correlated with the  $\sigma$  parameter according to Eqn (1), and their results were poor (Table 2; columns 2 to 4). Significant improvements were obtained with Eqn (2) (Table 2; columns 5 to 8), suggesting that a dual substituent parameter approach provides

**Table 1.** <sup>13</sup>C NMR shifts of the C=N carbons in **M1**

X	Y					
	NMe <sub>2</sub>	OMe	Me	H	Cl	CN
NMe <sub>2</sub>	159.44	159.66	159.73	159.84	159.69	160.22
OMe	158.88	158.87	159.15	159.28	159.38	159.68
Me	159.40	159.69	159.77	159.90	159.86	160.33
H	159.42	159.72	159.82	159.94	160.03	160.40
Cl	157.55	157.89	158.00	158.31	158.25	158.75
F	157.83	158.13	158.23	158.36	158.43	158.77
CN	156.41	156.93	157.07	157.17	157.32	157.76
NO <sub>2</sub>	155.87	156.27	156.53	156.67	156.81	157.25

a more accurate description of the substituent effects of  $X$  in **M1**. This is because the dual substituent parameter approach allows for the different contributions of inductive and conjugative effects. Thus, this approach is suitable for the analysis of the effects of substituents  $X$  on  $\delta_C(\text{C}=\text{N})$ , in which the susceptibility of  $\delta_C(\text{C}=\text{N})$  is dissimilar greatly to the inductive and conjugative effects of  $X$ .

Both the signs in front of  $\rho_F(X)$  and  $\rho_R(X)$  are negative, indicating that electron-donating (ED) benzylidene substituents  $X$  cause deshielding, while electron-withdrawing (EW) ones cause shielding. This behavior can be understood by considering the resonance structures of **M1** shown in Scheme 2. The nitrogen atom is more electronegative than the carbon atom. Consequently, the nitrogen and carbon atoms of the C=N alternate with negative and positive charges, as the resonance form **M1-2** (Scheme 2). The ED substituents  $X$  inductively stabilize the form **M1-2**, increasing its relative contribution, and lead to the deshielding of the imine carbon. On the other hand, the EW substituents  $X$  inductively destabilize **M1-2**.

As seen in Table 2 (columns 5 to 6),  $\rho_F(X)$  or  $\rho_R(X)$  changes as the aniline substituent  $Y$  changes, suggesting that the contribution of the inductive and conjugative effects of the substituent  $X$  can be affected by the remote substituent  $Y$ . These phenomena are illustrated in Figs 1 and 2. Good linear correlations revealed that the electronic effects of  $X$  on  $\delta_C(\text{C}=\text{N})$  can be modified by  $Y$ . The values of  $\rho_F(X)$  and  $\rho_R(X)$  for **M2** and **M3** reported by Cao *et al.* and Neuvonen *et al.*<sup>[16,18]</sup> which were correlated with the dual substituent parameter approach, are also shown in Figs 1 and 2. In the comparison of the slopes of the lines in Figs 1 and 2, in each figure, the line for **M1** has the smallest slope, while the slope of the line corresponding to **M2** takes second place. It can be inferred that the sensitivity of the electronic character of the C=N function to electron donation/electron withdrawal by the substituent  $X$  attenuates as the length of the conjugated chain is elongated.

In our previous reports,<sup>[17,18]</sup> the parameter  $\Delta\sigma^2$  ( $\Delta\sigma^2 = (\sigma_X - \sigma_Y)^2 = \{[\sigma_F(X) + \sigma_R(X)] - [\sigma_F(Y) + \sigma_R(Y)]\}^2$ ) was used to evaluate the substituent cross-interaction effect when both  $X$  and  $Y$  were varied, and excellent correlations had been observed with Eqn (3). If  $Y$  is fixed, the second and the fourth terms in Eqn (3) are constant; thus,  $Y$  is fixed, and Eqn (3) can be simplified to Eqn (4).

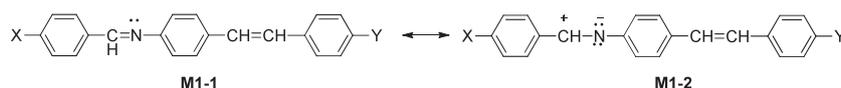
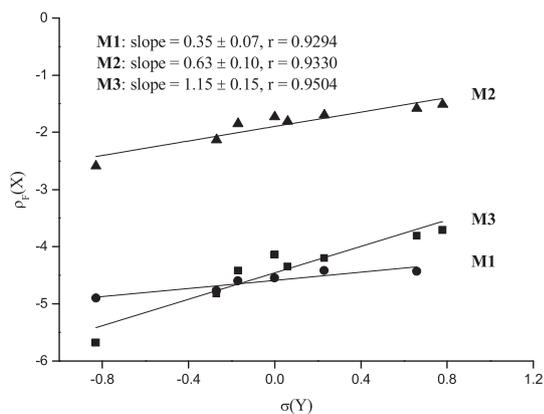
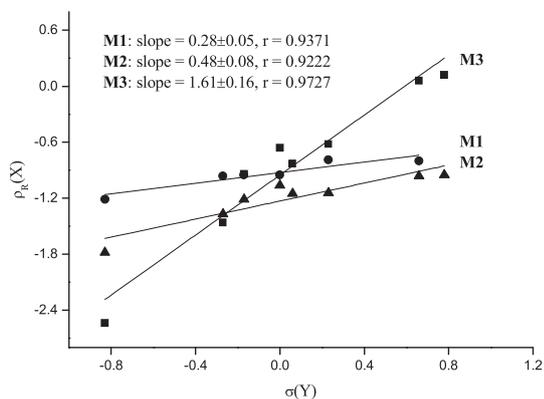
$$\delta_C(\text{C}=\text{N}) = \rho_F\sigma_F(X) + \rho_F\sigma_F(Y) + \rho_R\sigma_R(X) + \rho_R\sigma_R(Y) + \rho_{(\Delta\sigma^2)}\Delta\sigma^2 + \text{constant} \quad (3)$$

$$\delta_C(\text{C}=\text{N}) = \rho_F\sigma_F(X) + \rho_R\sigma_R(X) + \rho_{(\Delta\sigma^2)}\Delta\sigma^2 + \text{constant} \quad (4)$$

These preceding observations suggest that  $\Delta\sigma^2$  may be used to scale the interaction between  $X$  and  $Y$  in **M1** when  $Y$  was fixed. It is interesting that excellent correlations were observed with Eqn (4) (Table 2; columns 9 to 13), and the standard error was

**Table 2.** Correlation of  $\delta_C(\text{C}=\text{N})$  values for **M1** according to Eqns (1), (2), and (4)

Y	Correlation												n
	$\delta_C(\text{C}=\text{N})$ versus $\sigma(X)$			$\delta_C(\text{C}=\text{N})$ versus $\sigma_F(X)$ and $\sigma_R(X)$				$\delta_C(\text{C}=\text{N})$ versus $\sigma_F(X)$ , $\sigma_R(X)$ and $\Delta\sigma^2$					
	$\rho(X)$	R	s	$\rho_F(X)$	$\rho_R(X)$	R	s	$\rho_F(X)$	$\rho_R(X)$	$\rho(\Delta\sigma^2)$	R	s	
NMe <sub>2</sub>	-2.43 ± 0.52	0.8872	0.71	-4.90 ± 0.44	-1.21 ± 0.28	0.9876	0.26	-3.18 ± 0.50	-0.11 ± 0.30	-0.77 ± 0.19	0.9974	0.14	8
OMe	-2.23 ± 0.52	0.8694	0.71	-4.77 ± 0.31	-0.96 ± 0.20	0.9930	0.19	-4.15 ± 0.19	-0.79 ± 0.09	-0.56 ± 0.12	0.9990	0.08	8
Me	-2.17 ± 0.50	0.8718	0.68	-4.60 ± 0.34	-0.95 ± 0.21	0.9913	0.20	-4.09 ± 0.24	-0.89 ± 0.12	-0.56 ± 0.16	0.9979	0.11	8
H	-2.15 ± 0.49	0.8709	0.68	-4.55 ± 0.38	-0.95 ± 0.24	0.9887	0.23	-4.15 ± 0.19	-1.11 ± 0.11	-0.67 ± 0.14	0.9983	0.10	8
Cl	-2.00 ± 0.51	0.8476	0.69	-4.42 ± 0.44	-0.79 ± 0.28	0.9832	0.26	-4.34 ± 0.26	-1.30 ± 0.22	-0.74 ± 0.22	0.9954	0.15	8
CN	-2.01 ± 0.49	0.8577	0.67	-4.43 ± 0.32	-0.80 ± 0.20	0.9913	0.19	-4.84 ± 0.19	-1.67 ± 0.24	-0.55 ± 0.14	0.9983	0.09	8

**Scheme 2.** Resonance structures of **M1****Figure 1.** Plots of  $\rho_F(X)$  for three series of substituted benzylidene anilines (**M1**, **M2**, and **M3**) versus  $\sigma(Y)$ **Figure 2.** Plots of  $\rho_R(X)$  for three series of substituted benzylidene anilines (**M1**, **M2**, and **M3**) versus  $\sigma(Y)$ 

reduced to approximately half of that of the corresponding series obtained with Eqn (2). This confirmed that the effect of the interaction between X and Y is an important factor that could

not be ignored, even if Y is unchanged. To further demonstrate this statement, we correlated the  $\delta_C(\text{C}=\text{N})$  values of **M2** and **M3** reported in the literature,<sup>[16,18]</sup> using Eqn (4), and the results obtained are listed in Table 3 (columns 8 to 13). To make comparisons easier, the results of Eqn (2) for **M2** and **M3** are also given in Table 3 (columns 3 to 7). The results obtained show that the correlations obtained with Eqn (4) are much better than those obtained with Eqn (2) (Table 3). Thus, we can conclude that  $\Delta\sigma^2$  is suitable to evaluate the interaction effect between X and Y on  $\delta_C(\text{C}=\text{N})$  in different benzylidene anilines, even if Y is fixed.

As seen in Tables 2 and 3, the signs in front of  $\rho(\Delta\sigma^2)$  are the same in all cases, while their coefficients  $\rho(\Delta\sigma^2)$  are different, indicating that the relative magnitude of the interactions between X and Y is different for each substituent Y.

### Effect of substituents Y on $\delta_C(\text{C}=\text{N})$

A preferable correlation of the  $\delta_C(\text{C}=\text{N})$  with a dual substituent parameter approach (Eqn (2)) was achieved in the studying of the effect of substituents X for **M1**, **M2**, or **M3** than that with a single parameter treatment (Eqn (1)). Therefore, when substituent X was fixed and Y was varied, we correlated the  $\delta_C(\text{C}=\text{N})$  and the substituent parameters of Y according to Eqn (2) (Table 4; columns 2 to 5), and the correlation results were listed in Table 4 (columns 6 to 10).

Positive  $\rho_F$  and  $\rho_R$  values indicate that EW substituents Y cause deshielding, while ED ones cause shielding. The  $\delta_C(\text{C}=\text{N})$  behavior can also be explained by the resonance structure **M1-2** shown in Scheme 2. The EW substituents Y inductively stabilize the form **M1-2**. Consequently, the electron density of the imine carbon decreases, and the  $^{13}\text{C}$  NMR chemical shift of the  $\text{C}=\text{N}$  carbon increases. However, ED substituents have an opposite effect on **M1-2**, resulting in shielding of the imine carbon.

These effects are similar to the influence of X on  $\delta_C(\text{C}=\text{N})$ , where the corresponding coefficient  $\rho_F(Y)$  or  $\rho_R(Y)$  clearly changes with the variation of X (Table 4; columns 2 to 3). This behavior was depicted in the lines for **M1** in Figs 3 and 4. The plots of  $\rho_F(Y)$  or  $\rho_R(Y)$  versus  $\sigma(X)$  for **M3** (data from literature<sup>[16]</sup>) and **M2** (data from literature<sup>[18]</sup>) are also shown in Figs 3 and 4. As can be seen, the

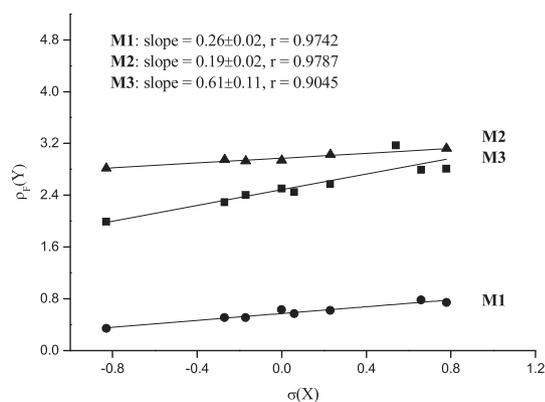
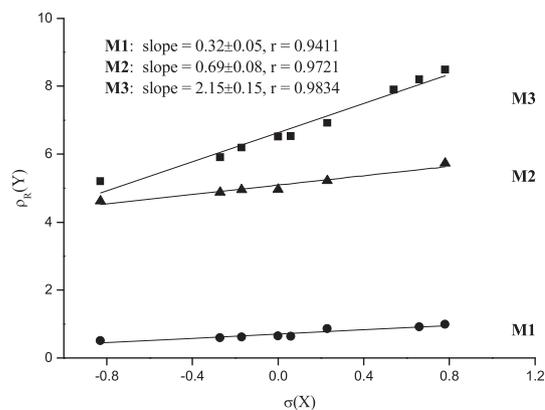
**Table 3.** Correlation of  $\delta_C(\text{C}=\text{N})$  values for **M2** and **M3** according to Eqns (2) and (4)

		Correlation											
		$\delta_C(\text{C}=\text{N})$ versus $\sigma_F(X)$ and $\sigma_R(X)$					$\delta_C(\text{C}=\text{N})$ versus $\sigma_F(X)$ , $\sigma_R(X)$ and $\Delta\sigma^2$						
Y		$\rho_F(X)$	$\rho_R(X)$	R	s	F	$\rho_F(X)$	$\rho_R(X)$	$\rho(\Delta\sigma^2)$	R	s	F	n
<b>M3<sup>a</sup></b>	NMe <sub>2</sub>	-3.67 ± 0.48	-0.65 ± 0.30	0.9939	0.31	133.16	-3.67 ± 0.48	-0.65 ± 0.30	-1.03 ± 0.19	0.9984	0.13	524.94	9
	OMe	-4.19 ± 0.21	-1.13 ± 0.10	0.9943	0.22	159.04	-4.19 ± 0.21	-1.13 ± 0.10	-0.73 ± 0.13	0.9987	0.09	661.91	9
	Me	-4.04 ± 0.17	-0.91 ± 0.08	0.9940	0.18	183.28	-4.04 ± 0.17	-0.91 ± 0.08	-0.58 ± 0.12	0.9987	0.08	620.25	9
	H	-4.01 ± 0.14	-0.87 ± 0.08	0.9948	0.14	232.30	-4.01 ± 0.14	-0.87 ± 0.08	-0.45 ± 0.11	0.9986	0.08	578.29	9
	Cl	-4.28 ± 0.13	-1.11 ± 0.11	0.9930	0.08	566.36	-4.28 ± 0.13	-1.11 ± 0.11	-0.54 ± 0.11	0.9985	0.08	566.36	9
	F	-4.24 ± 0.14	-1.09 ± 0.08	0.9939	0.17	184.57	-4.24 ± 0.14	-1.09 ± 0.08	-0.57 ± 0.11	0.9987	0.08	658.48	9
	CN	-4.19 ± 0.15	-0.95 ± 0.18	0.9893	0.14	166.76	-4.19 ± 0.15	-0.95 ± 0.18	-0.44 ± 0.11	0.9979	0.08	399.33	9
	NO <sub>2</sub>	-4.18 ± 0.17	-0.92 ± 0.22	0.9889	0.14	149.71	-4.18 ± 0.17	-0.92 ± 0.22	-0.41 ± 0.11	0.9980	0.08	334.20	9
<b>M2<sup>b</sup></b>	NMe <sub>2</sub>	-2.59 ± 0.31	-1.78 ± 0.19	0.9931	0.17	107.40	-1.30 ± 0.09	-1.10 ± 0.05	-0.54 ± 0.04	0.9999	0.02	5365.64	6
	OMe	-2.13 ± 0.27	-1.37 ± 0.17	0.9916	0.15	87.63	-1.53 ± 0.07	-1.30 ± 0.03	-0.47 ± 0.04	0.9999	0.02	2706.13	6
	Me	-1.85 ± 0.22	-1.21 ± 0.14	0.9926	0.12	99.73	-1.45 ± 0.12	-1.23 ± 0.05	-0.38 ± 0.08	0.9993	0.04	524.50	6
	H	-1.73 ± 0.18	-1.06 ± 0.11	0.9942	0.10	129.09	-1.51 ± 0.08	-1.17 ± 0.05	-0.30 ± 0.06	0.9995	0.03	705.77	6
	Cl	-1.70 ± 0.22	-1.14 ± 0.14	0.9915	0.12	87.12	-1.59 ± 0.06	-1.35 ± 0.04	-0.38 ± 0.06	0.9999	0.02	3846.93	6
	F	-1.81 ± 0.22	-1.15 ± 0.14	0.9924	0.12	97.50	-1.59 ± 0.03	-1.47 ± 0.03	-0.39 ± 0.03	0.9997	0.03	1010.06	6
	CN	-1.58 ± 0.29	-0.96 ± 0.17	0.9928	0.12	68.45	-1.72 ± 0.03	-1.53 ± 0.05	-0.32 ± 0.02	1.0000	0.01	4160.96	5
	NO <sub>2</sub>	-1.51 ± 0.21	-0.95 ± 0.13	0.9901	0.11	74.63	-1.79 ± 0.13	-1.59 ± 0.21	-0.33 ± 0.10	0.9985	0.05	215.13	6

<sup>a</sup>Data were taken from Cao *et al.*<sup>[18]</sup>.  
<sup>b</sup>Data were taken from Neuvonen *et al.*<sup>[16]</sup>.

**Table 4.** Correlation of  $\delta_C(\text{C}=\text{N})$  values for **M1** according to Eqns (2) and (5)

		Correlation									
		$\delta_C(\text{C}=\text{N})$ versus $\sigma_F(Y)$ and $\sigma_R(Y)$				$\delta_C(\text{C}=\text{N})$ versus $\sigma_F(Y)$ , $\sigma_R(Y)$ and $\Delta\sigma^2$					
X		$\rho_F(Y)$	$\rho_R(Y)$	R	s	$\rho_F(Y)$	$\rho_R(Y)$	$\rho(\Delta\sigma^2)$	R	s	n
NMe <sub>2</sub>		0.34 ± 0.30	0.51 ± 0.67	0.9084	0.14	-0.41 ± 0.67	-0.07 ± 0.33	0.35 ± 0.24	0.9564	0.11	6
OMe		0.51 ± 0.31	0.60 ± 0.31	0.9322	0.15	0.09 ± 0.31	0.54 ± 0.12	0.41 ± 0.21	0.9772	0.10	6
Me		0.51 ± 0.19	0.62 ± 0.20	0.9721	0.09	0.31 ± 0.20	0.63 ± 0.08	0.24 ± 0.15	0.9882	0.06	6
H		0.63 ± 0.09	0.65 ± 0.03	0.9943	0.04	0.56 ± 0.03	0.71 ± 0.02	0.15 ± 0.02	0.9998	0.01	6
Cl		0.62 ± 0.23	0.86 ± 0.17	0.9803	0.10	0.61 ± 0.17	1.10 ± 0.16	0.28 ± 0.02	0.9922	0.07	6
F		0.57 ± 0.08	0.64 ± 0.03	0.9957	0.04	0.53 ± 0.03	0.71 ± 0.02	0.13 ± 0.02	0.9997	0.01	6
CN		0.78 ± 0.08	0.92 ± 0.12	0.9979	0.04	0.80 ± 0.12	0.96 ± 0.16	0.02 ± 0.09	0.9980	0.04	6
NO <sub>2</sub>		0.74 ± 0.13	0.99 ± 0.12	0.9952	0.06	0.92 ± 0.12	1.33 ± 0.17	0.16 ± 0.08	0.9985	0.04	6

**Figure 3.** Plots of  $\rho_F(Y)$  for three series of substituted benzylidene anilines (**M1**, **M2**, and **M3**) versus  $\sigma(X)$ **Figure 4.** Plots of  $\rho_R(Y)$  for three series of substituted benzylidene anilines (**M1**, **M2**, and **M3**) versus  $\sigma(X)$

slopes of the lines in each figure decrease when the distance between the substituents X and Y increase, suggesting that the substituent effect of X on  $\rho_R(Y)$  and  $\rho_F(Y)$  becomes weaker with the elongation of the conjugated chain. In other words, the substituent effect of X on  $\delta_C(C=N)$  can be modified by substituent Y, but this influence decreases with the increasing distance between X and Y.

The behaviors observed in Figs 3 and 4 indicate the existence of mutual interference between X and Y in **M1**, when X is fixed. Here, we also used  $\Delta\sigma^2$  to evaluate the interaction between X and Y (Eqn (5)), obtaining only a slight improvement on the correlations for each series (Table 4; columns 6 to 10), although the improvement becomes greater as the absolute values of  $\rho_{(\Delta\sigma^2)}$  increase.

$$\delta_C(C=N) = \rho_F\sigma_F(Y) + \rho_R\sigma_R(Y) + \rho_{(\Delta\sigma^2)}\Delta\sigma^2 + \text{constant} \quad (5)$$

By comparing Tables 2–4, it can be observed that  $|\rho_{(\Delta\sigma^2)}|$  are smaller in the former, suggesting that the interaction effect between X and Y in case that X is fixed is smaller than Y is fixed. To further clarify this point, we correlated the  $\delta_C(C=N)$  values of **M3** and **M2** reported by Neuvonen *et al.* and Cao *et al.*<sup>[16,18]</sup> by using Eqn (5), and the results are listed in Table 5 (columns 8 to 13). Likewise, the results of Eqn (2) for **M2** and **M3**, with the use of the published data,<sup>[16,18]</sup> are given in Table 5 (columns 3 to 7). From the data in Tables 3 and 5, we can conclude that in substituted benzylidene anilines, the interaction effect between X and Y, when X is fixed, also affects the value of  $\delta_C(C=N)$ , but the influence is not as important as when Y is fixed.

To investigate the effects of Y in more detail, we evaluated the differences in  $\delta_C(C=N)$  between **M1** and **M3** ( $\Delta\delta_C(\mathbf{M1}-\mathbf{M3})$ ) (Table 6), as both substituents X and Y in **M1** correspond to those in **M3**. When Y belongs to an ED group, the value of  $\Delta\delta_C(\mathbf{M1}-\mathbf{M3})$  is positive; otherwise, the value is negative. The increasing value of  $|\Delta\delta_C$

**Table 6.** Differences in the  $\delta_C(C=N)$  between compounds **M1** and **M3** [ $\Delta\delta_C(\mathbf{M1}-\mathbf{M3}) = \delta_C(C=N)_{\mathbf{M1}} - \delta_C(C=N)_{\mathbf{M3}}$ ]<sup>a</sup>

Y	X							
	NMe <sub>2</sub>	OMe	Me	H	Cl	F	CN	NO <sub>2</sub>
NMe <sub>2</sub>	2.71	3.19	3.25	3.45	3.48	3.46	4.19	4.36
OMe	1.01	0.99	1.23	1.31	1.21	1.29	1.58	1.51
Me	0.16	0.21	0.19	0.23	0.06	0.23	0.22	0.21
H	-0.37	-0.36	-0.41	-0.40	-0.43	-0.40	-0.65	-0.66
Cl	-0.82	-0.61	-0.81	-0.68	-0.86	-0.68	-0.83	-0.84
CN	-1.64	-1.86	-1.96	-2.04	-2.15	-2.05	-2.45	-2.50

<sup>a</sup>The values of  $\delta_C(C=N)_{\mathbf{M3}}$  were taken from Neuvonen *et al.*<sup>[16]</sup>.

(**M1-M3**) is in line with the increasing ED or EW capability of Y. This suggests that for each substituent X in **M1**, when the aniline substituents Y become more ED, the shielding of the C=N carbon decreases relative to **M3**, and the deshielding of the imine carbon also decreases. In other words, the effect of the substituents Y on  $\delta_C(C=N)$  in **M1** decreases relative to that in **M3**. This is due to the fact that the distance between the substituents Y and the azomethine carbon center is different for **M1** and **M3**. For substituents Y, the number of chemical bonds far from the C=N carbon is 12 in **M1** and 6 in **M3**.

#### Specific cross-interaction effect between substituents X and Y on $\delta_C(C=N)$

In the preceding discussion concerning the effect of substituents X or Y on  $\delta_C(C=N)$ , it was demonstrated that substituent cross-interaction was an important factor influencing the  $\delta_C(C=N)$ , even if either X or Y was fixed. To further testify the relative importance of the parameter  $\Delta\sigma^2$  when X or Y was fixed, and the other

**Table 5.** Correlation of  $\delta_C(C=N)$  values for **M2** and **M3** according to Eqns (2) and (5)

X	Correlation												
	$\delta_C(C=N)$ versus $\sigma_F(Y)$ and $\sigma_R(Y)$					$\delta_C(C=N)$ versus $\sigma_F(Y)$ , $\sigma_R(Y)$ and $\Delta\sigma^2$							
	$\rho_F(Y)$	$\rho_R(Y)$	R	s	F	$\rho_F(Y)$	$\rho_R(Y)$	$\rho_{(\Delta\sigma^2)}$	R	s	F	n	
<b>M2</b> <sup>a</sup>	NMe <sub>2</sub>	2.81 ± 0.29	4.66 ± 0.18	0.9976	0.17	528.47	3.59 ± 0.55	5.16 ± 0.35	-0.35 ± 0.22	0.9986	0.15	462.97	8
	OMe	3.13 ± 1.27	4.71 ± 0.79	0.9973	0.19	463.08	3.42 ± 0.37	5.08 ± 0.18	-0.44 ± 0.23	0.9986	0.16	469.80	8
	Me	2.94 ± 0.32	4.90 ± 0.20	0.9971	0.19	464.30	3.33 ± 0.33	5.06 ± 0.16	-0.45 ± 0.23	0.9987	0.15	498.44	8
	H	2.94 ± 0.55	4.96 ± 0.33	0.9925	0.32	265.36	3.23 ± 0.37	5.04 ± 0.24	-0.51 ± 0.30	0.9981	0.20	256.14	7
	Cl	3.03 ± 0.38	5.22 ± 0.22	0.9964	0.23	359.19	3.08 ± 0.28	4.87 ± 0.24	-0.60 ± 0.24	0.9986	0.16	491.34	8
	NO <sub>2</sub>	3.12 ± 0.46	5.73 ± 0.27	0.9956	0.27	294.60	2.39 ± 0.44	4.52 ± 0.56	-0.71 ± 0.29	0.9983	0.20	400.62	8
<b>M3</b> <sup>b</sup>	NMe <sub>2</sub>	2.33 ± 0.28	3.78 ± 0.18	0.9966	0.17	364.95	3.21 ± 0.49	4.33 ± 0.31	-0.39 ± 0.20	0.9983	0.13	388.54	8
	OMe	2.66 ± 0.31	4.31 ± 0.19	0.9968	0.18	393.72	3.13 ± 0.34	4.44 ± 0.17	-0.42 ± 0.21	0.9984	0.14	418.08	8
	Me	2.77 ± 0.34	4.53 ± 0.21	0.9967	0.20	373.93	3.20 ± 0.33	4.58 ± 0.16	-0.47 ± 0.22	0.9984	0.15	413.14	8
	H	2.88 ± 0.34	4.77 ± 0.21	0.9969	0.20	399.78	3.16 ± 0.29	4.66 ± 0.17	-0.48 ± 0.23	0.9985	0.16	451.30	8
	Cl	2.98 ± 0.38	5.06 ± 0.23	0.9966	0.22	566.36	3.05 ± 0.27	4.67 ± 0.24	-0.55 ± 0.24	0.9986	0.16	465.34	8
	F	2.85 ± 0.35	4.77 ± 0.22	0.9966	0.21	369.89	3.08 ± 0.29	4.59 ± 0.19	-0.50 ± 0.23	0.9984	0.16	423.66	8
	CF <sub>3</sub>	3.32 ± 0.51	5.55 ± 0.28	0.9958	0.26	235.62	2.75 ± 0.49	4.61 ± 0.54	-0.67 ± 0.35	0.9981	0.20	263.81	7
	CN	3.29 ± 0.48	5.97 ± 0.30	0.9960	0.28	308.01	2.73 ± 0.37	4.81 ± 0.47	-0.75 ± 0.28	0.9986	0.19	468.69	8
NO <sub>2</sub>	3.33 ± 0.51	6.17 ± 0.32	0.9956	0.30	284.59	2.54 ± 0.43	4.71 ± 0.55	-0.81 ± 0.29	0.9986	0.20	460.31	8	

<sup>a</sup>Data were taken from Cao *et al.*<sup>[18]</sup>.  
<sup>b</sup>Data were taken from Neuvonen *et al.*<sup>[16]</sup>.

one was varied, we investigated the relative contributions ( $\psi_r$ ) or fraction contributions ( $\psi_f$ ) of the corresponding parameters in Eqns (4) and (5) to the  $\delta_C(\text{C}=\text{N})$ .<sup>[19,20]</sup>

$$\psi_r = m_i \bar{X}_i \quad (6)$$

$$\psi_f = \frac{R^2 |\psi_r(i)|}{\sum_i |\psi_r(i)|} \times 100\% \quad (7)$$

where the  $m_i$  and  $\bar{X}_i$  are the coefficient and the average value of the  $i$ th parameter in Eqn (4) or (5). The contribution results for the parameters of Eqns (4) and (5) are shown in Tables 7 and 8, respectively.

As seen in Table 7, for each different substituent Y, as the substituent X was varied, the relative contributions or fraction contributions of  $\Delta\sigma^2$  increased in parallel with the increasing ED or EW ability of the substituent Y. It means that  $\Delta\sigma^2$  plays more important role as Y become more ED or EW. The behavior can be understood by considering the average value of the  $\Delta\sigma^2$  parameter. The value increased as the ED or EW ability of the substituent Y improves. Thus, increasing the electron effect of substituent Y increased the contribution of  $\Delta\sigma^2$ .

Similarly, we could see from Table 8 that, when X was fixed, the relative contributions or fraction contributions of  $\Delta\sigma^2$  increased in parallel with the increasing ED or EW ability of the substituent X. It also can be explained by the increasing average value of the  $\Delta\sigma^2$  as X becomes more ED or EW.

We also studied the importance of the item  $\Delta\sigma^2$  in case both substituents X and Y in **M1** were varied. Firstly, the  $\delta_C(\text{C}=\text{N})$  values were correlated with  $\sigma_F$  and  $\sigma_R$  parameters, and Eqn (8) was obtained.

$$\begin{aligned} \delta_C(\text{C}=\text{N}) &= 159.87 - 4.61\sigma_F(\text{X}) + 0.59\sigma_F(\text{Y}) \\ &\quad - 0.94\sigma_R(\text{X}) + 0.73\sigma_R(\text{Y}) \quad (8) \\ R &= 0.9876, R^2 = 0.9753, s = 0.21, n = 48, F = 424.44 \end{aligned}$$

Then, the  $\delta_C(\text{C}=\text{N})$  values were correlated with  $\sigma_F$ ,  $\sigma_R$ , and  $\Delta\sigma^2$ , and Eqn (9) was obtained. The much better correlation of Eqn (9) than that of Eqn (8) demonstrated that  $\Delta\sigma^2$  was appropriate to

evaluate the substituent-specific cross-interaction effects between X and Y in **M1**, with the variation of both X and Y. The calculated results with Eqn (9) or (8) showed that  $\Delta\sigma^2$  was a factor affecting  $\delta_C(\text{C}=\text{N})$  of **M1** that should not be neglected, especially as the difference of electronic effect between X and Y increased; for example, when X was the  $\text{NO}_2$  group and Y was  $\text{NMe}_2$ , the deviation between the calculated and experimental  $\delta_C(\text{C}=\text{N})$  was only 0.07 ppm with Eqn (9), while it was 0.25 ppm with Eqn (8); in case X was the  $\text{NMe}_2$  group and Y was CN, the deviation was 0.11 ppm with Eqn (9) and 0.29 ppm with Eqn (8), respectively. The statistical data for the correlations are shown in the Supporting Information. To evaluate systematically the long-range effects of the substituent-specific cross-interaction, Eqns (10) and (11) reported in our previous works<sup>[17,18]</sup> are given as follows.

$$\begin{aligned} \text{For } \mathbf{M1}, \quad \delta_C(\text{C}=\text{N}) &= 159.86 - 4.47\sigma_F(\text{X}) + 0.66\sigma_F(\text{Y}) \\ &\quad - 0.96\sigma_R(\text{X}) + 0.62\sigma_R(\text{Y}) - 0.20\Delta\sigma^2 \quad (9) \\ R &= 0.9913, R^2 = 0.9827, s = 0.18, n = 48, F = 476.46 \end{aligned}$$

$$\begin{aligned} \text{For } \mathbf{M2}, \quad \delta_C(\text{C}=\text{N}) &= 161.56 - 1.63\sigma_F(\text{X}) + 3.18\sigma_F(\text{Y}) \\ &\quad - 1.40\sigma_R(\text{X}) + 5.01\sigma_R(\text{Y}) - 0.33\Delta\sigma^2 \quad (10) \\ R &= 0.9974, R^2 = 0.9948, s = 0.17, n = 53, F = 1794.53 \end{aligned}$$

$$\begin{aligned} \text{For } \mathbf{M3}, \quad \delta_C(\text{C}=\text{N}) &= 160.25 - 4.18\sigma_F(\text{X}) + 3.24\sigma_F(\text{Y}) \\ &\quad - 1.15\sigma_R(\text{X}) + 4.67\sigma_R(\text{Y}) - 0.59\Delta\sigma^2 \quad (11) \\ R &= 0.9975, R^2 = 0.9950, s = 0.17, n = 80, F = 2937.31 \end{aligned}$$

It can be seen in Eqns (9), (10), and (11) that the signs in front of  $\rho_F$  and  $\rho_R$  are alternated and they are in good agreement with the signs in front of the  $\rho_F$  and  $\rho_R$  shown in Tables 2–5 (except for the  $\rho_F(\text{Y})$  and  $\rho_R(\text{Y})$  in Table 4 when X =  $\text{NMe}_2$ ). The alternated signs suggest that the maximum interference occurs between the most ED and EW substituents; for example, the strongest effect was observed, or X was the  $\text{NMe}_2$  group and Y was  $\text{NO}_2$ . In contrast, there is minimum interaction in both X and Y being the most ED, or both being the most EW substituents; for

**Table 7.** The relative and fraction contribution ( $\psi_r$  and  $\psi_f$ ) of parameters  $\sigma_F(\text{X})$ ,  $\sigma_R(\text{X})$ , and  $\Delta\sigma^2$  to the  $\delta_C(\text{C}=\text{N})$  of **M1**, **M2**, and **M3**

	Y	$\sigma_F(\text{X})$		$\sigma_R(\text{X})$		$\Delta\sigma^2$		Y	$\sigma_F(\text{X})$		$\sigma_R(\text{X})$		$\Delta\sigma^2$		
		$\psi_r$	$\psi_f$ (%)	$\psi_r$	$\psi_f$ (%)	$\psi_r$	$\psi_f$ (%)		$\psi_r$	$\psi_f$ (%)	$\psi_r$	$\psi_f$ (%)	$\psi_r$	$\psi_f$ (%)	
<b>M1</b>	$\text{NMe}_2$	-0.9858	54.49	0.0278	1.54	-0.7860	43.45	<b>M3</b>	$\text{NMe}_2$	-1.1662	47.45	0.1343	5.46	-1.1494	46.77
	OMe	-1.2865	76.58	0.1995	11.88	-0.1906	11.35		OMe	-1.3315	72.21	0.2335	12.66	-0.2741	14.87
	Me	-1.2679	76.42	0.2247	13.54	-0.1595	9.61		Me	-1.2838	73.03	0.1881	10.70	-0.2814	16.01
	H	-1.2865	74.32	0.2803	16.19	-0.1584	9.15		H	-1.2743	76.32	0.1798	10.77	-0.2110	12.64
	Cl	-1.3454	71.35	0.3283	17.41	-0.1945	10.32		Cl	-1.3601	72.88	0.2294	12.29	-0.2712	14.53
<b>M2</b>	CN	-1.5004	66.46	0.4217	18.68	-0.3279	14.52	F	-1.3474	73.58	0.2253	12.30	-0.2538	13.86	
	$\text{NMe}_2$	-0.3293	29.41	0.3263	29.14	-0.4638	41.42	CN	-1.3315	65.23	0.1963	9.62	-0.5049	24.73	
	OMe	-0.3876	42.57	0.3857	42.36	-0.1370	15.05	$\text{NO}_2$	-1.2958	58.06	0.2323	10.41	-0.6947	31.13	
	Me	-0.3673	44.22	0.3649	43.93	-0.0973	11.71								
	H	-0.3825	47.63	0.3471	43.23	-0.0726	9.04								
	Cl	-0.4028	44.82	0.4005	44.56	-0.0953	10.60								
	F	-0.4028	41.86	0.4361	45.32	-0.1228	12.76								
	CN	-0.5229	39.56	0.5447	41.21	-0.2543	19.24								
$\text{NO}_2$	-0.4535	36.82	0.4717	38.29	-0.3029	24.59									

**Table 8.** The relative and fraction contribution ( $\psi_r$  and  $\psi_f$ ) of parameters  $\sigma_F(Y)$ ,  $\sigma_R(Y)$ , and  $\Delta\sigma^2$  to the  $\delta_C(C=N)$  of **M1**, **M2**, and **M3**

	X	$\sigma_F(Y)$		$\sigma_R(Y)$		$\Delta\sigma^2$		X	$\sigma_F(Y)$		$\sigma_R(Y)$		$\Delta\sigma^2$	
		$\psi_r$	$\psi_f$ (%)	$\psi_r$	$\psi_f$ (%)	$\psi_r$	$\psi_f$ (%)		$\psi_r$	$\psi_f$ (%)	$\psi_r$	$\psi_f$ (%)	$\psi_r$	$\psi_f$ (%)
<b>M1</b>	NMe <sub>2</sub>	-0.0943	21.91	0.0205	4.76	0.2789	64.80	NMe <sub>2</sub>	0.9951	39.88	-1.0933	43.82	-0.3981	15.96
	OMe	0.0207	7.00	-0.1584	53.56	0.1033	34.93	OMe	0.9703	43.29	-1.1211	50.01	-0.1430	6.38
	Me	0.0713	22.53	-0.1848	58.40	0.0529	16.72	Me	0.9920	43.32	-1.1565	50.51	-0.1339	5.85
	H	0.1288	34.88	-0.2083	56.41	0.0320	8.67	H	0.9796	43.03	-1.1767	51.69	-0.1135	4.99
	Cl	0.1403	25.31	-0.3227	58.22	0.0827	14.92	Cl	0.9455	41.55	-1.1792	51.82	-0.1446	6.35
	F	0.1219	33.90	-0.2083	57.92	0.0292	8.12	F	0.9548	29.46	-1.1590	35.76	-1.1166	34.45
<b>M2</b>	CN	0.1840	38.16	-0.2816	58.41	0.0146	3.03	CF <sub>3</sub>	0.7189	28.81	-1.4159	56.74	-0.3512	14.07
	NO <sub>2</sub>	0.2116	28.17	-0.3901	51.93	0.1473	19.61	CN	0.9863	37.14	-1.2145	45.74	-0.4471	16.84
	NMe <sub>2</sub>	1.1129	40.02	-1.3029	46.85	-0.3573	12.85	NO <sub>2</sub>	0.7874	30.34	-1.1893	45.82	-0.6116	23.56
	OMe	1.0602	42.41	-1.2827	51.31	-0.1498	5.99							
	Me	1.0323	42.23	-1.2777	52.27	-0.1282	5.24							
	H	0.9090	35.13	-1.5624	60.39	-0.1061	4.10							
<b>M3</b>	Cl	0.9548	40.66	-1.2297	52.37	-0.1571	6.69							
	CN	0.7409	30.53	-1.1413	47.03	-0.5361	22.09							

example, the weakest effect would be observed when X and Y all were NO<sub>2</sub> group, or all were NMe<sub>2</sub>.

The values of  $\rho_F(Y)$  and  $\rho_R(Y)$  were smaller in Eqn (9) than in Eqns (10) and (11), indicating that the inductive and resonance effects of the substituents Y on  $\delta_C(C=N)$  are less than those of the substituents Y in **M3**. This observation is in good agreement with the discussion concerning the influence of Y on  $\delta_C(C=N)$ .

Meanwhile, the coefficient  $\rho_{(\Delta\sigma^2)}$  decreased as the chemical bond numbers between X and Y increased in case that both X and Y are varied. Here, we try to describe the quantitative relationship between the coefficient  $\rho_{(\Delta\sigma^2)}$  and bond numbers ( $m$ ), in which  $m$  is the chemical bond number between X and Y. In **M1**, **M2**, and **M3**, their values of  $m$  are 17, 13 and 11, respectively, and their coefficients are 0.20, 0.33, and 0.59, respectively. It is not difficult to find that the  $\rho_{(\Delta\sigma^2)}$  is nearly inversely proportional to  $m^2$ .

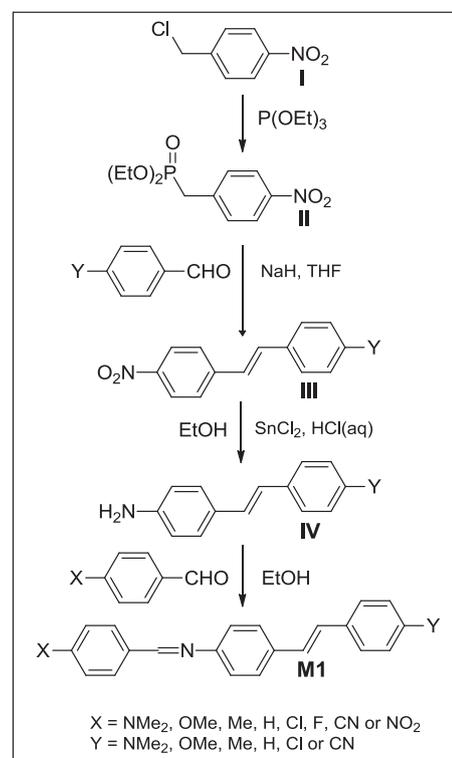
## CONCLUSION

Considering the respective effects of substituents X and Y in molecules **M1** together with **M2** and **M3**, we found that both X and Y act systematically on the imine carbon. By a comparison of the substituent effects on  $\delta_C(C=N)$  in **M1**, **M2**, and **M3**, it was observed that the inductive and resonance effects of substituents Y on  $\delta_C(C=N)$  attenuated with the increasing distance between Y and the imine carbon center, while as the length of the conjugated chain between X and the imine carbon center was elongated, the inductive effects of substituents X on  $\delta_C(C=N)$  decreased, and the change of the resonance effects was nearly ignorable. It is interesting that the correlations improved when  $\Delta\sigma^2$  was employed to quantify the effect of X or Y on  $\delta_C(C=N)$ , and the correlations are much better in the studying of the effect of X than that of Y on  $\delta_C(C=N)$ , and that  $\Delta\sigma^2$  plays a more important role as X or Y become more ED or EW. This shows that the interaction between X and Y cannot be neglected in case one of substituents X and Y is fixed. It was confirmed that  $\Delta\sigma^2$  was also suitable to evaluate the substituent cross-interaction effect on  $\delta_C(C=N)$  of **M1** in case both X and Y were varied, and the calculated  $\delta_C(C=N)$  is more close to the experimental values when the difference between the electronic effect of X and Y increased. The results showed that compared with the quantitative equation of **M1**, **M2**, and **M3**,

the coefficient in front of each parameter decreased as the length of the chain increases and the  $\rho_{(\Delta\sigma^2)}$  was inversely proportional to  $m^2$  ( $m$  represents the bond number between X and Y). This suggests that there is a long-range transmission effect of substituent effects as the distance between X and Y increases. Whether the quantitative relationship between  $\rho_{(\Delta\sigma^2)}$  and the bond numbers is a general rule is being investigated.

## EXPERIMENTAL SECTION

The compounds **M1** shown in Scheme 3 were synthesized according to published procedures, with slight modifications.<sup>[21–23]</sup> The detailed

**Scheme 3.** Synthetic procedures for the titled compounds **M1**

analytical data of the synthesized compounds are available in the Supporting Information.

### Preparation of compounds III

A mixture of *p*-nitrobenzyl chloride (4.53 g, 30 mmol) and triethyl phosphate (5.48 g, 33 mmol) was heated at 140 °C for 5 h before being cooled to room temperature, and the product was not further purified. Then, *p*-substituted benzaldehyde (30 mmol) by substituents Y (Y = NMe<sub>2</sub>, OMe, Me, H, Cl, or CN) was added, and the mixture was stirred in dry tetrahydrofuran (100 mL) containing NaH (2.16 g, 90 mmol) under a nitrogen atmosphere at 50 °C for 30 min. Colored solids were obtained after precipitation in water. The crude products were recrystallized from hot ethanol to give compounds III. The products were dried in vacuum at 60 °C for 18 h.

### Preparation of compounds IV

To a suspension of compounds III (25 mmol) in a mixture of ethanol (150 mL) and hydrochloric acid (36% concentration, 50 mL), SnCl<sub>2</sub>·2H<sub>2</sub>O (62.5 mmol) was used as an effective reducing agent, and the reduction of III by it could not be forced beyond the diphenylethene state. The reaction mixture was stirred for 1 h at room temperature, followed by refluxing for 6 h. Subsequently, the reaction solution was poured into ice water and controlled to pH ≈ 8 with sodium hydroxide solution. After extraction with ethyl acetate four times, the combined organic layer was dried over MgSO<sub>4</sub>, followed by evaporation and recrystallization from ethanol to afford pure compounds IV.

### Preparation of compounds M1

Equimolar amounts of compounds IV and *p*-substituted benzaldehydes by substituents X (X = NMe<sub>2</sub>, OMe, Me, H, Cl, F, CN, or NO<sub>2</sub>) were dissolved in ethanol, followed by stirring at 80 °C for 1 h. The solvent was removed by rotary evaporation and recrystallized from dichloromethane and ethanol to give compounds M1.

## SUPPORTING INFORMATION

SUPPORTING INFORMATION

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