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# Substituent effects on the stretching vibration of C=N in multi-substituted benzylideneanilines

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**1** | INTRODUCTION

# Abstract

Forty-nine samples of 3,4'/4,3'/3,3'-disubstituted benzylideneanilines (XBAYs) and 52 samples of multi-substituted XBAYs were synthesized, and their infrared absorption spectra were recorded in this paper. On the basis of the stretching vibration frequencies  $v_{C=N}$  of C=N bridging bond of 158 samples of substituted XBAYs (including 57 samples of 4,4'-disubstituted XBAYs from reference and 101 samples of substituted XBAYs synthesized in this paper), an extensional research of substituent effects on the  $v_{C=N}$  values from 4,4'-disubstituted XBAYs to multi-substituted XBAYs was made. A modified equation for quantifying the  $\nu_{C=N}$  values of multi-substituted XBAYs was obtained (shown as Equation (3)). Equation (3) indicates that the excitedstate substituent constant of Y and the substituent specific cross-interaction effect between X and X cannot be ignored for the quantitative regression analysis of the  $v_{C=N}$  values of multi-substituted XBAYs. Compared with Equation (1), Equation (3) has a wider application and more accuracy in quantifying the  $v_{C=N}$  values of substituted XBAYs.

## **KEYWORDS**

excited-state substituent constant, multi-substituted benzylideneanilines, stretching vibration frequencies, substituent effects, substituent specific cross-interaction effect

Benzylideneanilines (XBAYs) are a kind of typical compounds with  $\pi$  conjugate system and have been applied extensively in the fields of liquid crystal and nonlinear optical material.<sup>[1–3]</sup> Their molecular structure-property relationships were explored widely in past years.<sup>[4-8]</sup> Among the researches, infrared spectroscopy (IR) is a very important method in the molecular structure

identification and component analysis of compounds, and it is always used to study the structure-property relationships.

In 1969, Molnar and Orchin<sup>[9]</sup> analyzed the infrared spectra of some XBAY derivatives and related complexes. The results showed the coordination of XBAYs to palladium always resulted in a shift of the C=N to a lower frequency. In 1991, Figueroa et al<sup>[10]</sup> found that a donor group in para position of the benzylidene ring in molecule of XBAY had a significant effect on the skeletal vibrations. And the interpretations for the vibrational spectra of the XBAY and 4,4'-disubstituted XBAY were given. In 1993, Kozhevina et al<sup>[11]</sup> explored the vibrational spectra of XBAY and its fluoroderivatives, and they found that the fluorination of the aniline or benzylidene rings did not exercise much influence on the  $v_{(C=N)}$  bond position but caused a significant change in the intensity. In 2002, Güner and Bavari<sup>[8]</sup> discussed the interpretation of the substituent effect on the infrared data of XBAYs. The correlation between Hammett constant  $\sigma_R$  and the infrared data of XBAYs in which the para position of the benzylidene ring was substituted by an electrondonating or electron-withdrawing group was found, but the Hammett relation was not obtained for the p-aniline ring substituent. In 2013, Sek et al<sup>[12]</sup> analyzed the influence of the chemical structure of azines and their azomethine analogues on the IR spectra. In the IR spectra of investigated compounds, the band characteristic for the HC=N stretching vibration was detected in each case in the spectral range of 1608 to 1633 cm<sup>-1</sup>. Compared with the isolated C=N group, the band frequency is strongly reduced by the conjugation of the C=N group with phenyl ring because of the energy diminishing of the C=N bond and the delocalization of nitrogen pair into the imine double bond.

Given all that, the molecular structure makes a significant influence on the IR spectrum. In other words, the change of substituents in the molecules can also affect the IR spectra. But in previous researches, the substituent effects on IR spectra have not been studied systematically. Until recently, Cao et al<sup>[13]</sup> explored the substituent effects on the stretching vibration frequencies of C=N bridging bond ( $\nu_{C=N}$ ) of 4,4'-disubstituted XBAYs systematically, and they obtained a quantitative equation shown as Equation (1). In Equation (1),  $\sigma_p(X)$ ,  $\sigma_p(Y)$ , and  $\Delta\sigma^2$  are Hammett polar constants.<sup>[14]</sup>  $\sigma_{CC}^{ex}(X)$  is the excited-state substituent constant,<sup>[15,16]</sup> which has good applications in the quantitative researches of the spectra and reduction potential properties of XBAY derivatives.<sup>[17-21]</sup>  $\Delta\sigma^2 = (\sigma(X) - \sigma(Y))^2$ .

$$\nu_{\rm C=N} = 1624.78 + 7.68840\sigma_p(X) + 2.11844\sigma_p(Y) + 5.22127\sigma_{cc}^{ex}(X) - 3.20243\Delta\sigma^2$$
(1)

 $R = 0.9107, R^2 = 0.8294, S = 3.13, n = 57, F = 63.18.$ 

Through the analysis of the factors affecting  $\nu_{C=N}$ , they proposed three modes in the stretching vibration of C=N bond: (I) polar double bond-form C=N, (II) single bond-ion-form C<sup>+</sup>—N<sup>-</sup>, and (III) single bond-diradical form-C<sup>•</sup>—N<sup>•</sup>. The three modes are shown as Figure 1. In Cao et al,<sup>[13]</sup> the effects of the three modes on  $\nu_{C=N}$  of 4,4'-disubstituted XBAYs were analyzed, and the



FIGURE 1 The possible modes of C=N stretching vibration

results showed that the largest contribution of the three forms was the form (III); the next was the form (II).

In Cao et al,<sup>[13]</sup> the  $\sigma_p(X)$  and  $\sigma_p(Y)$  items were considered to express the contribution of polar double bond-form C=N to the change of  $\nu_{C=N}$ ;  $\Delta\sigma^2$  expressed the contribution of single bond-ion-form C<sup>+</sup>—N<sup>-</sup>; and  $\sigma_{CC}^{ex}(X)$  expressed the contribution of single bonddiradical-form C<sup>•</sup>—N<sup>•</sup>.

Since the effects of substituents or three modes on the  $\nu_{C=N}$  of 4,4'-disubstituted XBAYs has been studied, how do they affect the  $\nu_{C=N}$  values of 3,4'/4,3'/3,3'-disubstituted and multi-substituted XBAYs? To explore this problem and study the substituent effects on the  $\nu_{C=N}$  values of substituted XBAYs more systematically, 49 samples of 3,4'/4,3'/3,3'-disubstituted XBAYs and 52 samples of multi-substituted XBAYs shown in Scheme 1 were synthesized, and the substituent effects on their  $\nu_{C=N}$  values were explored.

# 2 | RESULTS AND DISCUSSIONS

The  $\nu_{C=N}$  values of 49 samples of 3,4'/4,3'/3,3'disubstituted XBAYs and 52 samples of multi-substituted XBAYs measured in this work were collected and listed in Table 1.

In Cao et al,<sup>[13]</sup> the parameters of  $\sigma(X)$ ,  $\sigma(Y)$ ,  $\sigma_{CC}^{ex}(X)$ , and  $\Delta \sigma^2$  were used to quantify the  $\nu_{C=N}$  values of 4,4'-disubstituted XBAYs (shown as Equation (1)). In molecules of multi-substituted XBAYs, the benzylidene ring and/or the aniline ring can be substituted by more than one group, so the respective parameters of the sum of  $\sigma(X)$ ,  $\sigma(Y)$ ,  $\sigma_{CC}^{ex}(X)$ , and  $\sigma_{CC}^{ex}(Y)$  (expressed by the symbols  $\Sigma\sigma(X)$ ,  $\Sigma\sigma(Y)$ ,  $\Sigma\sigma_{CC}^{ex}(X)$ , and  $\Sigma\sigma_{CC}^{ex}(Y)$ ) were used in this paper.  $\Delta(\Sigma\sigma)^2$  and  $\Delta(\Sigma\sigma_{CC}^{ex})^2$  were used to expressed the substituent specific cross-interaction



**SCHEME 1** 3,3'/4,3'/disubstituted and multi-substituted

benzylideneanilines (XBAYs) synthesized in this paper

 $\textbf{TABLE 1} \quad \text{The } \nu_{C=N} \text{ values of model compounds and the correlative parameters for X and Y}$ 

No.	X	Y	$\Sigma \sigma(X)^{a}$	$\Sigma \sigma(Y)^a$	$\boldsymbol{\Sigma\sigma^{ex}_{CC}(X)^{b}}$	$\Sigma \sigma^{ex}_{CC}(Y)^{\mathbf{b}}$	$\nu_{C=N\cdot exp}^{ \  c}$	$\nu_{C=N\cdot cal} (1)^d$	$\nu_{C=N\cdot cal} (2)^d$
1	3-F	4'-Me <sub>2</sub> N	0.34	-0.83	0.02	-1.81	1619	1620	1620
2	3-F	4'-MeO	0.34	-0.27	0.02	-0.50	1621	1625	1625
3	3-F	4'-Me	0.34	-0.17	0.02	-0.17	1627	1626	1626
4	3-F	4'-Cl	0.34	0.23	0.02	-0.22	1628	1627	1627
5	3-Br	4'-Me <sub>2</sub> N	0.39	-0.83	-0.03	-1.81	1615	1619	1620
6	3-Br	4'-MeO	0.39	-0.27	-0.03	-0.50	1621	1625	1625
7	3-Br	4'-Me	0.39	-0.17	-0.03	-0.17	1625	1626	1626
8	3-Br	4'-F	0.39	0.06	-0.03	0.06	1626	1627	1627
9	3-Br	4'-Cl	0.39	0.23	-0.03	-0.22	1626	1627	1627
10	3-CN	4'-NMe <sub>2</sub>	0.56	-0.83	0.56	-1.81	1619	1618	1619
11	3-CN	4'-OMe	0.56	-0.27	0.56	-0.50	1626	1625	1625
12	3-CN	4'-Me	0.56	-0.17	0.56	-0.17	1622	1626	1626
13	3-CN	4'-Cl	0.56	0.23	0.56	-0.22	1628	1627	1628
14	3-CN	4'-CN	0.56	0.66	0.56	-0.70	1629	1628	1628
15	3-MeO	4'-Me <sub>2</sub> N	0.12	-0.83	0.10	-1.81	1618	1620	1620
16	4-Me <sub>2</sub> N	3'-Me	-0.83	-0.07	-1.81	-0.03	1607	1608	1608
17	4-MeO	3'-Me	-0.27	-0.07	-0.50	-0.03	1621	1622	1621
18	4-Cl	3'-Me	0.23	-0.07	-0.22	-0.03	1629	1626	1626
19	4-CF <sub>3</sub>	3'-Me	0.54	-0.07	-0.12	-0.03	1618	1626	1626
20	4-CN	3'-Me	0.66	-0.07	-0.70	-0.03	1625	1625	1624
21	4-NO <sub>2</sub>	3'-Me	0.78	-0.07	-1.17	-0.03	1628	1623	1623
22	4-Me <sub>2</sub> N	3'-F	-0.83	0.34	-1.81	0.02	1618	1607	1607
23	4-MeO	3'-F	-0.27	0.34	-0.50	0.02	1630	1622	1622
24	4-Me	3'-F	-0.17	0.34	-0.17	0.02	1627	1624	1624
25	4-Cl	3'-F	0.23	0.34	-0.22	0.02	1629	1627	1627
26	4-CN	3'-F	0.66	0.34	-0.70	0.02	1627	1626	1626
27	4-NO <sub>2</sub>	3'-F	0.78	0.34	-1.17	0.02	1629	1625	1625
28	4-Me <sub>2</sub> N	3'-Br	-0.83	0.39	-1.81	-0.03	1602	1606	1607
29	4-MeO	3'-Br	-0.27	0.39	-0.50	-0.03	1624	1622	1622
30	4-Me	3'-Br	-0.17	0.39	-0.17	-0.03	1620	1624	1624
31	4-Cl	3'-Br	0.23	0.39	-0.22	-0.03	1625	1627	1627
32	4-CN	3'-Br	0.66	0.39	-0.70	-0.03	1625	1626	1626
33	4-NO <sub>2</sub>	3'-Br	0.78	0.39	-1.17	-0.03	1628	1625	1625
34	4-Me <sub>2</sub> N	3'-MeO	-0.83	0.12	-1.81	0.10	1605	1607	1608
35	4-CN	3'-MeO	0.66	0.12	-0.70	0.10	1626	1626	1626
36	4-NO <sub>2</sub>	3'-MeO	0.78	0.12	-1.17	0.10	1628	1624	1624
37	4-Cl	3'-CN	0.23	0.56	-0.22	0.56	1627	1628	1628
38	4-CN	3'-CN	0.66	0.56	-0.70	0.56	1624	1628	1628
39	3-MeO	3'-CN	0.12	0.56	0.10	0.56	1630	1628	1628
40	3-Me	3'-Me	-0.07	-0.07	-0.03	-0.03	1629	1625	1625
41	3-F	3'-Me	0.34	-0.07	0.02	-0.03	1630	1627	1627

(Continues)

No.	Х	Y	$\Sigma \sigma(X)^{a}$	$\Sigma \sigma(Y)^{a}$	$\Sigma \sigma^{ex}_{CC}(X)^{\mathbf{b}}$	$\Sigma \sigma^{ex}_{CC}(Y)^{\mathbf{b}}$	$\nu_{C=N\cdot exp}^{c}$	$\nu_{C=N\cdot cal} (1)^d$	$\nu_{C=N\cdot cal} (2)^d$
42	3-F	3'-F	0.34	0.34	0.02	0.02	1632	1628	1628
43	3-F	3'-Br	0.34	0.39	0.02	-0.03	1628	1628	1628
44	3-CN	3'-Me	0.56	-0.07	0.56	-0.03	1633	1627	1627
45	3-CN	3'-F	0.56	0.34	0.56	0.02	1631	1628	1629
46	3-CN	3'-CN	0.56	0.56	0.56	0.56	1630	1630	1630
47	3-Br	3'-Me	0.39	-0.07	-0.03	-0.03	1628	1627	1627
48	3-Br	3'-CN	0.39	0.56	-0.03	0.56	1633	1629	1629
49	3-Br	3'-Br	0.39	0.39	-0.03	-0.03	1630	1628	1628
50	3,4-Me	Н	-0.24	0.00	-0.20	0.00	1627	1623	1622
51	3,4-Me	4'-Me	-0.24	-0.17	-0.20	-0.17	1621	1622	1622
52	3,5-Me	Н	-0.14	0.00	-0.06	0.00	1627	1624	1624
53	Н	3',4'-Me	0.00	-0.24	0.00	-0.20	1627	1625	1625
54	Н	3′,5′-Me	0.00	-0.14	0.00	-0.06	1628	1625	1625
55	3,4-MeO	Н	-0.15	0.00	-0.40	0.00	1628	1623	1623
56	3,4-MeO	4'-NMe <sub>2</sub>	-0.15	-0.83	-0.40	-1.81	1618	1618	1618
57	3,4-MeO	4'-Me	-0.15	-0.17	-0.40	-0.17	1623	1623	1623
58	3,4-MeO	4'-F	-0.15	0.06	-0.40	0.06	1620	1624	1623
59	3,4-MeO	4'-Cl	-0.15	0.23	-0.40	-0.22	1621	1623	1623
60	3,4-MeO	4'-CN	-0.15	0.66	-0.40	-0.70	1629	1622	1622
61	3,5-MeO	Н	0.24	0.00	0.20	0.00	1627	1627	1627
62	3,5-MeO	4'-Me	0.24	-0.17	0.20	-0.17	1625	1626	1626
63	3,5-MeO	4'-Cl	0.24	0.23	0.20	-0.22	1623	1627	1627
64	3,5-MeO	4'-CN	0.24	0.66	0.20	-0.70	1630	1627	1627
65	3,4-Cl	Н	0.60	0.00	-0.20	0.00	1623	1626	1626
66	3,4-Cl	4'-NMe <sub>2</sub>	0.60	-0.83	-0.20	-1.81	1617	1618	1618
67	3,4-Cl	4'-Me	0.60	-0.17	-0.20	-0.17	1625	1625	1625
68	3,4-Cl	4'-F	0.60	0.06	-0.20	0.06	1625	1626	1626
69	3,4-Cl	4'-Cl	0.60	0.23	-0.20	-0.22	1626	1627	1627
70	3,4-Cl	4'-CN	0.60	0.66	-0.20	-0.70	1626	1627	1627
71	Н	3',4'-Cl	0.00	0.60	0.00	-0.20	1628	1626	1626
72	4-Me	3',4'-Cl	-0.17	0.60	-0.17	-0.20	1625	1623	1623
73	4-F	3',4'-Cl	0.06	0.60	0.06	-0.20	1627	1626	1626
74	4-Cl	3',4'-Cl	0.23	0.60	-0.22	-0.20	1621	1627	1627
75	3-Cl	3',4'-Cl	0.37	0.60	0.02	-0.20	1621	1628	1628
76	3,5-Cl	Н	0.74	0.00	0.04	0.00	1627	1625	1625
77	3,5-Cl	4'-NMe <sub>2</sub>	0.74	-0.83	0.04	-1.81	1621	1616	1617
78	3,5-Cl	4'-Me	0.74	-0.17	0.04	-0.17	1623	1624	1624
79	3,5-Cl	4'-Cl	0.74	0.23	0.04	-0.22	1628	1626	1626
80	Н	3′,5′-Cl	0.00	0.74	0.00	0.04	1629	1626	1626
81	4-NMe <sub>2</sub>	3′,5′-Cl	-0.83	0.74	-1.81	0.04	1601	1605	1605
82	4-F	3',5'-Cl	0.06	0.74	0.06	0.04	1627	1627	1627

(Continues)

5 of 7

No.	X	Y	$\Sigma \sigma(X)^{a}$	$\Sigma \sigma(Y)^{a}$	$\Sigma \sigma^{ex}_{CC}(X)^{\mathbf{b}}$	$\Sigma \sigma^{ex}_{CC}(Y)^{\mathbf{b}}$	$\nu_{C=N\cdot exp}^{c}$	$\nu_{C=N\cdot cal} (1)^d$	$\nu_{C=N\cdot cal} (2)^d$
83	4-Cl	3′,5′-Cl	0.23	0.74	-0.22	0.04	1625	1628	1628
84	3,4-F	4'-NMe <sub>2</sub>	0.40	-0.83	0.08	-1.81	1621	1619	1620
85	3,4-F	4'-Cl	0.40	0.23	0.08	-0.22	1630	1627	1627
86	3,5-F	Н	0.68	0.00	0.04	0.00	1626	1626	1626
87	3,4-Br	Н	0.62	0.00	-0.36	0.00	1626	1626	1626
88	3,5-Br	Н	0.78	0.00	-0.06	0.00	1625	1625	1625
89	3-F-4-Me	Н	0.17	0.00	-0.15	0.00	1620	1626	1626
90	3-Br-4-Me	Н	0.22	0.00	-0.20	0.00	1623	1627	1626
91	Н	3'-F-4'-Me	0.00	0.17	0.00	-0.15	1633	1625	1626
92	Н	3'-Cl-4'-Me	0.00	0.20	0.00	-0.15	1625	1625	1626
93	Н	3'-Br-4'-Me	0.00	0.22	0.00	-0.20	1620	1625	1625
94	3,4-MeO	3',5'-Me	-0.15	-0.14	-0.40	-0.06	1625	1623	1623
95	3,4-Cl	3',4'-Cl	0.60	0.60	-0.20	-0.20	1622	1628	1628
96	3,4-Cl	3'-Cl-4'-Me	0.60	0.20	-0.20	-0.15	1624	1627	1627
97	3,4-Cl	3′,5′-Cl	0.60	0.74	-0.20	0.04	1626	1628	1628
98	3-F-4-Me	3',4'-Cl	0.17	0.60	-0.15	-0.20	1626	1627	1627
99	3-F-4-Me	3'-Cl-4'-Me	0.17	0.20	-0.15	-0.15	1623	1627	1627
100	3,5-Br	3'-Cl-4'-Me	0.78	0.20	-0.06	-0.15	1624	1625	1626
101	3,5-Br	3',5'-Cl	0.78	0.74	-0.06	0.04	1626	1628	1628

 ${}^{a}\Sigma\sigma(X/Y) = \sigma(X_m/Y_m) + \sigma(X_p/Y_p)$ ; the  $\sigma$  values of X and Y were taken from Hansch et al.<sup>[14]</sup>

 ${}^{\mathrm{b}}\Sigma \sigma_{CC}^{ex}(X/Y) = \sigma_{CC}^{ex}(X_m/Y_m) + \sigma_{CC}^{ex}(X_p/Y_p); \text{ the } \sigma_{CC}^{ex} \text{ values of X and Y were taken from previous studies.}$ 

<sup>c</sup>Experimental values of this work.

 $^{d}\nu_{C=N\cdot cal}$  (1) was calculated by Equation (2);  $\nu_{C=N\cdot cal}$  (2) was calculated by Equation (3).

effect between X and Y.  $\Delta(\sum \sigma)^2 = (\Sigma \sigma(X) - \Sigma \sigma(Y))^2$ ;  $\Delta(\sum \sigma_{CC}^{ex})^2 = (\Sigma \sigma_{CC}^{ex}(X) - \Sigma \sigma_{CC}^{ex}(Y))^2$ . In addition, there would be the substituent specific cross-interaction effect between X (or Y) and X (or Y). Therefore,  $(\sum \sigma(X))^2$  and  $(\sum \sigma(Y))^2$  were tentatively used as the substituent specific cross-interaction effect between X (or Y) and X (or Y) respectively in following research.  $(\sum \sigma(X))^2 = \sum \sigma(X) \times \sum \sigma(X)$ ;  $(\sum \sigma(Y))^2 = \sum \sigma(Y) \times \sum \sigma(Y)$ .

On the basis of the above,  $\Sigma\sigma(X)$ ,  $\Sigma\sigma(Y)$ ,  $\Sigma\sigma_{CC}^{ex}(X)$ ,  $\Sigma$  $\sigma_{CC}^{ex}(Y)$ ,  $\Delta(\Sigma\sigma)^2$ ,  $\Delta(\Sigma\sigma_{CC}^{ex})^2$ ,  $(\Sigma\sigma(X))^2$ , and  $(\Sigma\sigma(Y))^2$  were first used to quantify the  $\nu_{C=N}$  values of 158 samples of substituted XBAYs, including 57 samples of 4,4'disubstituted XBAYs from Cao et al,<sup>[13]</sup> 49 samples of 3,4'/4,3'/3,3'-disubstituted XBAYs, and 52 samples of multi-substituted XBAYs. Then, Equation (2) was obtained.

$$\nu_{C=N} = 1625.46 + 8.43339 \sum \sigma(X) + 1.68677 \sum \sigma(Y) + 1.15540 \sum \sigma_{CC}^{ex}(X) + 1.68330 \sum \sigma_{CC}^{ex}(Y) - 2.11501 \Delta (\sum \sigma)^2 - 0.24799 \Delta (\sum \sigma_{CC}^{ex})^2 - 9.68756 (\sum \sigma(X))^2 + 0.79001 (\sum \sigma(Y))^2 R = 0.8680, R^2 = 0.7535, S = 3.34, n = 158, F = 56.93.$$

As seen from Equation (2), the correlation coefficient Ris good, and the standard deviation S is only  $3.34 \text{ cm}^{-1}$ . The  $v_{C=N}$  values calculated by Equation (2) were listed in Table 1. The average absolute error between the calculated values and the experimental ones is  $2.50 \text{ cm}^{-1}$  for all the 158 samples of XBAYs. But we thought that the Fischer ratio F could be improved. Moreover, the coefficients of  $\sum \sigma_{CC}^{ex}(X)$  and  $\sum \sigma_{CC}^{ex}(Y)$  are close, that is to say the two parameters can be merged. Besides, in the regression process, we found that the statistics t values of  $\Delta(\sum \sigma_{CC}^{ex})^2$  and  $(\sum \sigma(Y))^2$  were -0.67 and 0.32, respectively. It indicated that their contributions were relatively unimportant, and they should be removed from the correlation equation. It is worth noting that the statistics t value of  $(\sum \sigma(X))^2$  is -4.26, which indicates that it is especially important for the regression analysis of the  $\nu_{C=N}$  values of multi-substituted XBAYs. The t values of the parameters used in Equation (2) were listed in Table 2.

After removing  $\Delta (\sum \sigma_{CC}^{ex})^2$  and  $(\sum \sigma(Y))^2$  and merging  $\sum \sigma_{CC}^{ex}(X)$  and  $\sum \sigma_{CC}^{ex}(Y)$ , the regression was made again. And Equation (3) was obtained. In Equation (3),  $\sum \sigma_{CC}^{ex} = \sum \sigma_{CC}^{ex}(X) + \sum \sigma_{CC}^{ex}(Y)$ .

**TABLE 2** The *t* values of the parameters used in Equation (2)

Param	$\sum \sigma(X)$	$\sum \sigma(Y)$	$\sum \sigma_{CC}^{ex}(X)$	$\sum \sigma_{CC}^{ex}(Y)$	$\Delta(\sum \sigma)^2$	$\Delta \left(\sum \sigma_{CC}^{ex}\right)^2$	$(\sum \sigma(X))^2$	$(\sum \sigma(Y))^2$
t	9.23	1.60	1.29	1.53	-2.96	-0.67	-4.26	0.32

$$\nu_{\text{C=N}} = 1625.42 + 8.45777 \sum \sigma(X) + 2.09814 \sum \sigma(Y)$$

+ 1.37082
$$\sum \sigma_{CC}^{ex}$$
 - 2.26407 $\Delta (\sum \sigma)^2$  (3)  
- 9.61173 $(\sum \sigma(X))^2$ 

 $R = 0.8675, R^2 = 0.7525, S = 3.32, n = 158, F = 92.43.$ 

Compared with Equation (2), Equation (3) also has good correlation, and its Fischer ratio (F) is improved from 56.93 to 92.43. So, Equation (3) is recommended to express the change regularity of the C=N stretching vibration frequencies ( $v_{C=N}$ ) for multi-substituted XBAYs. The  $v_{C=N}$  values calculated by Equation (3) were listed in Table 1. The average absolute error between the calculated values and the experimental ones is 2.53 cm<sup>-1</sup> for all the 158 samples of XBAYs.

In Equation (3), the coefficients of  $\sum \sigma(X)$ ,  $\sum \sigma(Y)$ , and  $\sum \sigma_{CC}^{ex}$  are positive, that is to say  $\sum \sigma(X)$ ,  $\sum \sigma(Y)$ , and  $\sum \sigma_{CC}^{ex}$  present positive correlation with the  $v_{C=N}$  value. The coefficients of  $\Delta(\sum \sigma)^2$  and  $(\sum \sigma(X))^2$  are negative, which demonstrates that  $\Delta(\sum \sigma)^2$  and  $(\sum \sigma(X))^2$  present negative correlation with the  $v_{C=N}$  value. Because the values of items  $\Delta(\sum \sigma)^2$  and  $(\sum \sigma(X))^2$  are greater than or equal to 0, the substituent specific cross-interaction effects always decrease the  $v_{C=N}$  values of the XBAYs.

As seen from Equation (1) and Equation (3), their results are consistent in some ways. When X and Y are H, the  $v_{C=N}$  values of HBAH obtained by Equation (1) and Equation (3) are 1624.78 and 1625.42  $\text{cm}^{-1}$ , respectively. Both of them are roughly 1625 cm<sup>-1</sup>. It indicates the two quantitative equations are reasonable. Moreover, the coefficients of  $\sum \sigma(X)$ ,  $\sum \sigma(Y)$ ,  $\sum \sigma_{CC}^{ex}$ , and  $\Delta(\sum \sigma)^2$  in Equation (3) have the same positive or negative sign with the corresponding parameters in Equation (1), that is to say their influences on the  $v_{C=N}$  values are also consistent. The biggest difference between Equation (1) and Equation (3) is the addition of  $\sum \sigma_{CC}^{ex}(Y)$  and  $(\sum \sigma(X))^2$ . Because the benzylidene ring and/or the aniline ring in molecules of multi-substituted XBAYs can be substituted by more than one group and the number of studied compounds increases, the effects of  $\sum \sigma_{CC}^{ex}(Y)$  and  $(\sum \sigma(X))^2$ show out. And they cannot be ignored for the quantitative regression analysis of multi-substituted XBAYs.

# 3 | CONCLUSIONS

An extensional research of substituent effects on the  $v_{C=N}$  values from 4,4'-disubstituted XBAYs to multi-substituted

XBAYs was made in this paper. And a modified equation for quantifying the  $v_{C=N}$  values of multi-substituted XBAYs was obtained (shown as Equation (3)). The results show that the excited-state substituent constant of Y  $\sum \sigma_{CC}^{ex}(Y)$  and the substituent specific cross-interaction effect between X and X  $(\sum \sigma(X))^2$  cannot be ignored for the quantitative regression analysis of multi-substituted XBAYs, especially  $(\sum \sigma(X))^2$ . Compared with Equation (1), Equation (3) has a wider application and more accuracy in quantifying the  $v_{C=N}$  values of substituted XBAYs.

Because of the addition of 3,4'/4,3'/3,3'-disubstituted XBAYs and multi-substituted XBAYs (most of them are trisubstituted XBAYs) to the research, the effects of  $\sum \sigma_{CC}^{ex}(Y)$  and  $(\sum \sigma(X))^2$  cannot be ignored for the quantitative regression analysis of the  $v_{C=N}$  values. If more multi-substituted XBAYs were added into the research, there may be other parameters needed to be considered. It is worthy of further research.

# 4 | DATASET

The substituted XBAYs were all synthesized by the solvent-free method according to Scheme  $1.^{[23,24]}$  They were purified with anhydrous alcohol and confirmed with <sup>1</sup>H NMR and <sup>13</sup>C NMR. The NMR spectra were recorded by Bruker AV 500 MHz in CDCl<sub>3</sub> at room temperature at an approximate concentration. The NMR chemical shifts were expressed in ppm relative to TMS (0.00 ppm) used as an internal reference. The infrared spectra of the model compounds were recorded by the infrared spectrometer (Nicolet 6700) with potassium bromide (KBr) disc. The detailed data of the synthesized compounds are available in the Supporting Information.

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Journal of Physical Organic Chemistry

7 of 7

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# SUPPORTING INFORMATION

Additional supporting information may be found online in the Supporting Information section at the end of the article.

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