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RESEARCH ARTICLE

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The effect of intramolecular hydrogen bond on the ultraviolet absorption of bi-aryl Schiff bases

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Abstract
Two kinds of Schiff bases, 85 samples of *N*-(benzylidene)-anilines (ZBAY) and 83 samples of *N*-(phenyl-ethylene)-anilines (ZAPEY), were used as model compounds, in which the ZBAY contains 13 compounds with 2-OH and the ZAPEY contains 35 compounds with 2-OH (synthesized by this work). The quantitative correlation analysis ultraviolet absorption spectra of ZBAY and ZAPEY were performed, and the effect of intramolecular hydrogen bond on their wave number ν_{max} (cm^{-1}) of the maximum absorption wavelength λ_{max} (nm) was investigated. The results show that (a) the factors affecting the ν_{max} of ZBAY and ZAPEY are roughly the same, but their intensities are different. (b) The ν_{max} move caused by intramolecular hydrogen bond is all red shift for both ZBAY and ZAPEY, but the red shift value (2,381) of the ZBAY is more than twice than that (850) of ZAPEY. (c) The effect of intramolecular hydrogen bond on ν_{max} is only dominated by the parent structure unit of Schiff base, rather than the substituents in the molecule. For those compounds with the same parent structure unit, their red shift values of ν_{max} are at fixed value, but their red shift values of λ_{max} are unequal. Generally, the red shift value caused by the intramolecular hydrogen bond is larger for the compound with a larger λ_{max} value. The above observed phenomena are discussed from the view of molecular coplanarity.

KEYWORDS
bi-aryl Schiff bases, intramolecular hydrogen bond, proton transfer, substituent effect, ultraviolet absorption spectra

1 | INTRODUCTION

Schiff bases, with their classical π-conjugated system, showed good ultraviolet (UV) absorption, and this photoelectric characteristic property has been used in many applications. The theoretical and experimental study on Schiff base molecular structure and the change regularity of its optical property is of great significance in the development of photoelectric functional materials.[1–6] The studied Schiff bases exhibit an intramolecular hydrogen bond between the OH group of the six-membered ring and the imine moiety linking the other aromatic ring, which contributes to the photoelectric properties of the bases. This phenomenon has widely attracted the attention of researchers.[7–13]

There is an enol–keto tautomeric equilibrium in solution for Schiff bases containing *N*-salicylideneaniline (NSA) structural unit,[7–9] as shown in Figure 1. The transformation of tautomer is realized by intramolecular hydrogen bond proton transfer, which has been observed in crystal structure, as shown in Figure 2.[10] This kind of intramolecular hydrogen bond in Schiff base can

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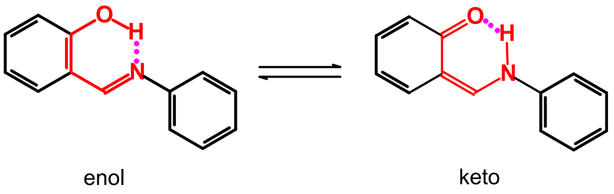


FIGURE 1 Tautomerization of *N*-salicylideneaniline between the enol–imine and keto–enamine tautomers

significantly transform the photoelectric properties of Schiff base via the proton transfer, such as, the UV absorptions and photoluminescences,[11–13] the fluorescent emissions in water induced the excited state intramolecular proton transfer (ESIPT),[14] solid-state photochromisms and thermochromisms,[15] and pH-responsive fluorescent sensors[16] and fluorescent probes of reaction[17].

As we know, both photoluminescence and photoelectric conversion are closely related to the light absorption properties of the compounds. Meanwhile, the light absorption property of compounds is intimately connected to their molecular structures. In previous studies of our research team,[18–25] the effect of substituents on UV absorption spectra of many compounds were analyzed in depth, in which these compounds involved stilbene (XSBY), benzylideneaniline (XBAY), and phenylethylaniline (XPEAY). The obtained results show that the effect of substituent on the wave number ν_{max} (cm^{-1}) of the longest wavelength maximum λ_{max} (nm) of UV has different modes due to different molecular skeletons. Recently, Cao et al.[22] explored the effect of hydroxyl groups, attached to different locations in aryl Schiff bases XArCH=NArY (XBAY), on the ν_{max} of the same series of compounds, and observed that hydroxyl groups at different locations have additional effect on the ν_{max}. For example, 2-position hydroxyl (2-OH), compared with 2′-position hydroxyl (2′-OH), declines the ν_{max} and contributes a red shift; maybe, the 2-OH, compared with 2′-OH, is easier to form a intramolecular hydrogen bond with the N atom of the bridging bond C=N; as a result, the intramolecular hydrogen bond contributes a red shift to the ν_{max} of the compounds. It implies that the UV absorption of aryl Schiff bases with 2-OH has a special performance. Therefore, we initiated the study of bi-aryl Schiff bases to figure out the influence of intramolecular hydrogen bond on the ν_{max} of them and the how the substituents attached to the aryl groups impact the ν_{max}. This study will contribute molecular design of optoelectronic materials with NAS structure.

In order to explore this topic, we select two kinds of Schiff bases *N*-(benzylidene)-anilines (ZBAY) and *N*-(phenyl-ethylene) aniline ZArC (Me) = NArY (ZAPEY) as model compounds to examine the effect of intramolecular hydrogen bonds on their ν_{max}.

2 | EXPERIMENTAL SECTION

2.1 | Synthesis of model compounds

The model compounds, substituted-*N*-(phenyl-ethylene) aniline ZArC (Me)=NArY (ZPEAY) were divided into two groups. The Group I is 2-H-XArC (Me)=NArY (Z=2-H, X; abbreviated as 2-H-XPEAY) without *ortho*-hydroxyl (2-OH), as shown in Figure 3. And the Group II is 2-OH-XArC (Me)=NArY (Z=2-OH, X; abbreviated as 2-OH-XPEAY) containing 2-OH. In this paper, the Group II was synthesized by using the method of the Cao et al.[26,27] as shown in Figure 4. The crude products were purified via column chromatography, and all the model compounds were characterized with nuclear magnetic resonance (NMR) spectra. Their ^{1}H NMR and ^{13}C NMR data and spectra can be seen in the supporting information.

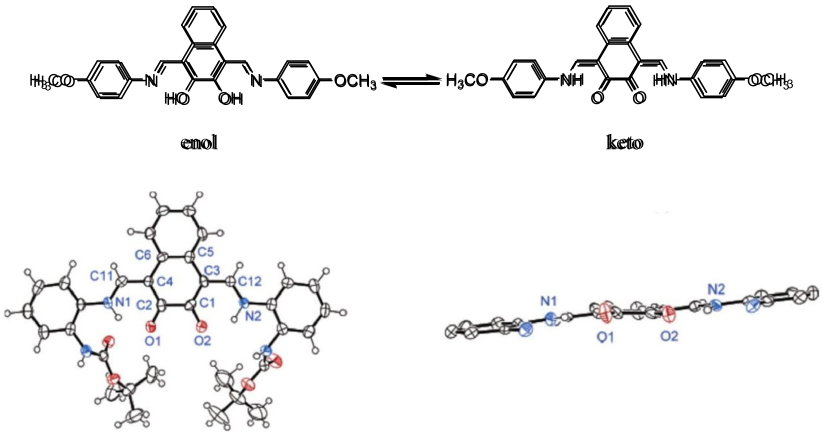


FIGURE 2 Tautomerization of Naphthalenediimines between the enol–imine and keto–enamine tautomers (up), and the crystal structure of keto–enamine tautomer (down) reported by Kukułka[10]

2.2 | Data preparation

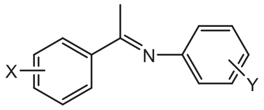
The UV absorption data of Group I (2-H-XPEAY) were taken from Luo et al.[23] (Table 1, Nos. 1–48). In this work, the model compound solutions with concentration 7.27×10^{-3} mol L^{-1} were prepared by dissolving the Group II (2-OH-XPEAY) of 7.27×10^{-5} mol in 10-ml anhydrous ethanol. And then the model compound solution of 5 μl was mixed with anhydrous ethanol in a sample cell (kept total volume 3 ml), and its UV absorption spectrum was tested with a UV-1800 (Shimadzu, Japan) spectrometer, scanning range 200–500 nm, and scanning speed 10 nm/s. The Group II UV spectra were recorded, and their λ_{max} were collected. The spectrum of each target compound was tested for three times (the absorption spectra can be seen in the supporting information), then the average value of the three λ_{max} was employed in this work. The λ_{max} values and the ν_{max} values ($\nu_{max} = 1 \times 10^7/\lambda_{max}$) of all target compounds were listed in Table 1 (Nos. 49–83).

3 | DATA ANALYSIS AND RESULTS DISCUSSION

3.1 | Data analysis

3.1.1 | Influence of intramolecular hydrogen bond on the ν_{max} of ZPEAY

Luo et al.[23] used a five-parameters equation to quantify the ν_{max} of Table 1 (Nos. 1–48) for 2-H-XPEAY (Figure 3) and obtained Equation 1 with 95% confidence levels.



Group I: Nos. 1-48;

X (*m*/*p*)=OMe, Me, H, Cl, F, CF_3, NO_2;

Y(*m*/*p*)=NMe_2, OMe, Me, H, Cl, F, CN

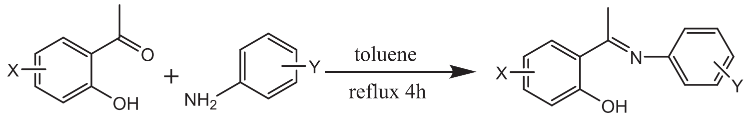
FIGURE 3 The molecular structure of model compounds 2-H-XPEAY (Group I). Group I: Nos. 1–48; X (*m*/*p*)=OMe, Me, H, Cl, F, CF_3, NO_2; Y(*m*/*p*)=NMe_2, OMe, Me, H, Cl, F, CN

$$\begin{gathered}\nu_{max} = 31{,}142 - 2{,}439.43\sigma(X) + 2{,}464.05\sigma(Y) - 308.60\Delta\sigma^2 \\ + 1{,}090.09\sum\sigma_{CC}^{ex} + 288.99\Delta\sigma_{CC}^{ex\ 2} \\ R = 0.9880, S = 317.96, F = 344.86, n = 48\end{gathered} \tag{1}$$

In which, σ(X) and σ(Y) are the ground-state electronic effect constants (Hammett constant) of X and Y substituent respectively. $\Delta\sigma^2 = [\sigma(X) - \sigma(Y)]^2$, expressing the substituent specific cross-interaction effect between X and Y. $\sum\sigma_{CC}^{ex} = \sigma_{CC}^{ex}(X) + \sigma_{CC}^{ex}(Y)$, expressing the sum of excited-state substituent constants of X and Y. $\Delta\sigma_{CC}^{ex\ 2} = [\sigma_{CC}^{ex}(X) - \sigma_{CC}^{ex}(Y)]^2$, expressing the substituent specific cross-interaction effect with excited-state substituent constant between X and Y. Adopting the same parameters of Equation 1, we carried out a regression analysis for the ν_{max} values of 83 samples of compounds in Table 1 (Groups I and II). Here, we took the items $\sum\sigma(X) = \sigma(X) + \sigma(2\text{-OH})$ and $\Delta\sigma^2(X,OH,Y) = [\sigma(X) + \sigma(2\text{-OH}) - \sigma(Y)]^2$ to replace the items σ(X) and $\Delta\sigma^2$ in Equation 1, due to the aromatic aldehydes of 2-OH-XPEAY compounds (Group II) containing 2-OH and X groups, and then obtained Equation 2 with 95% confidence levels.

$$\begin{gathered}\nu_{max} = 30{,}806 - 1{,}462.3X\sigma(X) + 2{,}142.29\sigma(Y) \\ + 455.43X\sigma_{CC}^{ex} - 1{,}420.19\Delta\sigma^2(X,OH,Y) + 23.14\Delta\sigma_{CC}^{ex\ 2} \\ R = 0.9437, S = 550.17, F = 125.22, n = 83\end{gathered} \tag{2}$$

The correlation of Equation 2 is not good. May be, it is that (a) there is intramolecular hydrogen bond effect between the 2-OH group of the six-membered ring and the imine moiety linking the other aromatic ring in the compounds of Group II; (b) the 2-OH group may influences the ν_{max} of compounds of Group II via its interacting with the Y group by way of the intramolecular hydrogen bond. And these two factors are not considered in Equation 2. To express the effect of above two factors on the ν_{max}, we dealt with them as following. (a) An indicator variable $I_{2\text{-OH}}$ of 2-OH was employed to express the contribution of the intramolecular hydrogen bond to the ν_{max}. Here, if the molecule contains 2-OH (Group II), $I_{2\text{-OH}} = 1$, otherwise (Group I), $I_{2\text{-OH}} = 0$. (b) The item $\Delta\sigma^2$(X,OH,Y) in Equation 2 was further divided into two terms, one expressing the interaction between X and Y, namely, $\Delta\sigma^2 = [\sigma(X) - \sigma(Y)]^2$; and the other expressing the interaction between 2-OH and Y, that is,



Group II: Nos.49-83;

X(*p*)=H, 4-OMe;

Y(*o*/*m*/*p*)=NMe_2, OMe, Me, H, Br, Cl, F, CF_3, NO_2, CN, OH

FIGURE 4 The synthetic route of model compounds 2-OH-XPEAY (Group II). Group II: Nos. 49–83; X(*p*)=H, 4-OMe; Y(*o*/*m*/*p*)=NMe_2, OMe, Me, H, Br, Cl, F, CF_3, NO_2, CN, OH

TABLE 1 The UV wavelength of absorption maximum λ_{max} (nm) and its wave number ν_{max} (cm^{-1}) for ZPEAY and substituent parameters

No.	X	Y	σ(2-OH)[a]	σ(X)[a]	σ(Y)[a]	$\sigma^{ex}_{CC}(X)$[b]	$\sigma^{ex}_{CC}(Y)$[b]	$\lambda_{max.\ exp}$[c]	$\nu_{max,\ exp.}$[c]
Group I (Z=2-H, X)									
1	4-OMe	4′-NMe$_2$	0	−0.27	−0.83	−0.50	−1.81	356.0	28,090
2	4-OMe	4′-OMe	0	−0.27	−0.27	−0.50	−0.50	330.0	30,303
3	4-OMe	4′-Me	0	−0.27	−0.17	−0.50	−0.17	320.0	31,250
4	4-OMe	4′-Cl	0	−0.27	0.23	−0.50	−0.22	316.0	31,646
5	4-OMe	4′-F	0	−0.27	0.06	−0.50	0.06	316.0	31,646
6	4-Me	4′-NMe$_2$	0	−0.17	−0.83	−0.17	−1.81	359.5	27,816
7	4-Me	4′-OMe	0	−0.17	−0.27	−0.17	−0.50	337.7	29,612
8	4-Me	4′-F	0	−0.17	0.06	−0.17	0.06	321.1	31,148
9	4-Me	4′-CN	0	−0.17	0.66	−0.17	−0.70	313.7	31,875
10	H	4′-OMe	0	0	−0.27	0	−0.50	330.0	30,303
11	H	H	0	0	0	0	0	324.7	30,802
12	H	4′-F	0	0	0.06	0	0.06	323.9	30,875
13	4-Cl	4′-NMe$_2$	0	0.23	−0.83	−0.22	−1.81	373.9	26,746
14	4-Cl	4′-OMe	0	0.23	−0.27	−0.22	−0.50	342.2	29,223
15	4-Cl	4′-Me	0	0.23	−0.17	−0.22	−0.17	332.6	30,066
16	4-Cl	4′-cl	0	0.23	0.23	−0.22	−0.22	328.0	30,492
17	4-Cl	4′-F	0	0.23	0.06	−0.22	0.06	327.0	30,581
18	4-Cl	4′-CN	0	0.23	0.66	−0.22	−0.70	315.1	31,740
19	4-F	4′-NMe$_2$	0	0.06	−0.83	0.06	−1.81	361.7	27,651
20	4-F	4′-OMe	0	0.06	−0.27	0.06	−0.50	337.7	29,616
21	4-F	4′-Me	0	0.06	−0.17	0.06	−0.17	329.1	30,391
22	4-F	H	0	0.06	0	0.06	0	322.0	31,056
23	4-F	4′-Cl	0	0.06	0.23	0.06	−0.22	322.8	30,984
24	4-F	4′-F	0	0.06	0.06	0.06	0.06	320.8	31,170
25	4-F	4′-CN	0	0.06	0.66	0.06	−0.70	313.5	31,896
26	4-CF$_3$	4′-NMe$_2$	0	0.54	−0.83	−0.12	−1.81	385.9	25,911
27	4-CF$_3$	4′-OMe	0	0.54	−0.27	−0.12	−0.50	351.5	28,453
28	4-CF$_3$	4′-Me	0	0.54	−0.17	−0.12	−0.17	340.8	29,340
29	4-CF$_3$	H	0	0.54	0	−0.12	0	335.0	29,850
30	4-CF$_3$	4′-Cl	0	0.54	0.23	−0.12	−0.22	335.7	29,793
31	4-CF$_3$	4′-F	0	0.54	0.06	−0.12	0.06	336.3	29,733
32	4-NO$_2$	4′-NMe$_2$	0	0.78	−0.83	−1.17	−1.81	432.8	23,108
33	4-NO$_2$	4′-OMe	0	0.78	−0.27	−1.17	−0.50	381.0	26,250
34	4-NO$_2$	4′-Me	0	0.78	−0.17	−1.17	−0.17	363.6	27,503
35	4-NO$_2$	H	0	0.78	0	−1.17	0	351.5	28,454
36	4-NO$_2$	4′-Cl	0	0.78	0.23	−1.17	−0.22	354.3	28,225
37	4-NO$_2$	4′-F	0	0.78	0.06	−1.17	0.06	353.4	28,301
38	3-Cl	4′-OMe	0	0.37	−0.27	0.02	−0.50	349.0	28,653
39	3-Cl	4′-Me	0	0.37	−0.17	0.02	−0.17	334.1	29,931
40	3-Cl	4′-F	0	0.37	0.06	0.02	0.06	329.5	30,349
41	4-Cl	3′-Me	0	0.23	−0.07	−0.22	−0.03	330.9	30,221
42	4-F	3′-Me	0	0.06	−0.07	0.06	−0.03	323.8	30,888

(Continues)

TABLE 1 (Continued)

No.	X	Y	σ(2-OH)[a]	σ(X)[a]	σ(Y)[a]	σ_{CC}^{ex}(X)[b]	σ_{CC}^{ex}(Y)[b]	$\lambda_{\text{max. exp}}$[c]	$\nu_{\text{max, exp.}}$[c]
43	4-NO$_2$	3′-Me	0	0.78	−0.07	−1.17	−0.03	355.0	28,173
44	4-Cl	3′-F	0	0.23	0.34	−0.22	0.02	321.0	31,158
45	4-F	3′-F	0	0.06	0.34	0.06	0.02	317.6	31,485
46	4-NO$_2$	3′-F	0	0.78	0.34	−1.17	0.02	344.3	29,049
47	H	3′-CN	0	0	0.56	0	0.56	301.5	33,173
48	4-F	3′-CN	0	0.06	0.56	0.06	0.56	295.3	33,870
Group II (Z=2-OH,X)									
49	H	4′-NMe$_2$	−0.38	0	−0.83	−0.10	−1.81	364.6	27,427
50	H	4′-OMe	−0.38	0	−0.27	−0.10	−0.50	332.2	30,102
51	H	4′-Me	−0.38	0	−0.17	−0.10	−0.17	326.6	30,618
52	H	H	−0.38	0	0	−0.10	0	324.4	30,826
53	H	4′-Br	−0.38	0	0.23	−0.10	−0.33	327.4	30,544
54	H	4′-Cl	−0.38	0	0.23	−0.10	−0.22	326.2	30,656
55	H	4′-F	−0.38	0	0.06	−0.10	0.06	332.0	30,120
56	H	4′-CF$_3$	−0.38	0	0.54	−0.10	−0.12	327.2	30,562
57	H	4′-CN	−0.38	0	0.66	−0.10	−0.70	325.6	30,713
58	H	4′-OH	−0.38	0	−0.37	−0.10	−0.19	333.8	29,958
59	H	3′-Me	−0.38	0	−0.07	−0.10	−0.03	326.0	30,675
60	H	3′-Br	−0.38	0	0.39	−0.10	−0.03	325.2	30,750
61	H	3′-Cl	−0.38	0	0.37	−0.10	0.02	325.4	30,731
62	H	3′-F	−0.38	0	0.34	−0.10	0.02	326.4	30,637
63	H	3′-CF$_3$	−0.38	0	0.43	−0.10	0.09	325.6	30,713
64	H	3′-NO$_2$	−0.38	0	0.71	−0.10	0.66	325.4	30,731
65	H	3′-CN	−0.38	0	0.56	−0.10	0.56	326.8	30,600
66	H	2′-OH	−0.38	0	−0.38	−0.10	−0.10	329.8	30,321
67	4-OMe	4′-OMe	−0.38	−0.27	−0.27	−0.60	−0.50	323.8	30,883
68	4-OMe	4′-Me	−0.38	−0.27	−0.17	−0.60	−0.17	318.6	31,387
69	4-OMe	H	−0.38	−0.27	0	−0.60	0	317.8	31,466
70	4-OMe	4′-Br	−0.38	−0.27	0.23	−0.60	−0.33	321.2	31,133
71	4-OMe	4′-Cl	−0.38	−0.27	0.23	−0.60	−0.22	321.6	31,095
72	4-OMe	4′-F	−0.38	−0.27	0.06	−0.60	0.06	318.4	31,407
73	4-OMe	4′-NO$_2$	−0.38	−0.27	0.78	−0.60	−1.17	329.6	30,340
74	4-OMe	4′-CF$_3$	−0.38	−0.27	0.54	−0.60	−0.12	322.0	31,056
75	4-OMe	4′-CN	−0.38	−0.27	0.66	−0.60	−0.70	324.2	30,845
76	4-OMe	4′-OH	−0.38	−0.27	−0.37	−0.60	−0.19	331.0	30,211
77	4-OMe	3′-Me	−0.38	−0.27	−0.07	−0.60	−0.03	317.0	31,546
78	4-OMe	3′-Br	−0.38	−0.27	0.39	−0.60	−0.03	321.2	31,133
79	4-OMe	3′-Cl	−0.38	−0.27	0.37	−0.60	0.02	321.4	31,114
80	4-OMe	3′-F	−0.38	−0.27	0.34	−0.60	0.02	320.0	31,250
81	4-OMe	3′-CF$_3$	−0.38	−0.27	0.43	−0.60	0.09	321.2	31,133
82	4-OMe	3′-NO$_2$	−0.38	−0.27	0.71	−0.60	0.66	323.0	30,960
83	4-OMe	3′-CN	−0.38	−0.27	0.56	−0.60	0.56	321.8	31,075

[a] The values were taken from other studies.[19–21]

[b] The values were taken from other studies.[28–31]

[c] $\nu_{\text{max}} = 1 \times 10^7/\lambda_{\text{max}}$. The values of Nos. 1–48 were from Luo et al.,[23] and those of Nos. 49–83 were determined by this work.

$\Delta\sigma^2(\mathrm{OH,Y}) = [\sigma(\text{2-OH}) - \sigma(\mathrm{Y})]^2$. The above three items $I_{\text{2-OH}}$, $\Delta\sigma^2$ and $\Delta\sigma^2(\mathrm{OH,Y})$ were introduced into Equation 2, removing the item $\Delta\sigma^2(\mathrm{X,OH,Y})$, and a regression analysis was carried out once again, then the Equation 3 with 95% confidence levels was obtained.

$$\begin{aligned} \nu_{\max} = {} & 31{,}058 - 2{,}613.13\sum\sigma(\mathrm{X}) + 2{,}611.31\sigma(\mathrm{Y}) \\ & + 660.77\sum\sigma_{\mathrm{CC}}^{\mathrm{ex}} + 101.26\Delta\sigma_{\mathrm{CC}}^{\mathrm{ex}\,2} - 456.02\Delta\sigma^2 \\ & - 1{,}956.30\Delta\sigma^2(\mathrm{OH,Y}) - 850.17I_{2-\mathrm{OH}} \\ & R = 0.9774, S = 355.97, F = 229.22, n = 83 \end{aligned} \tag{3}$$

The correlation of Equation 3 is much improved than that of Equation 2 and the value of *F*-stat of Equation 3 increases significantly, and the standard deviation of Equation 3 decreases significantly. It shows that the above treatment methods are reasonable. We want to know whether the five substituent parameters in Table 1 are all necessary. Thus, we carried out regression analysis with less five parameters for the $\nu_{\max}$ of Group II and got the results as shown in Table 2. The regression equations in Table 2 indicate that all models based on less the five parameters are weaker. Therefore, Equation 3 is recommended to express the variation of $\nu_{\max}$.

It can also be seen from Equation 3 that the influence of $\Delta\sigma^2$ and $\Delta\sigma^2(\mathrm{OH,Y})$ on the $\nu_{\max}$ are unequal. The intramolecular hydrogen bond ($I_{\text{2-OH}}$) has a fixed contribution to the $\nu_{\max}$, which reduces the $\nu_{\max}$ (about 850 cm^{-1}) and makes the $\lambda_{\max}$ a red shift.

3.1.2 | Influence of intramolecular hydrogen bond on the $\nu_{\max}$ of ZBAY

We notice that the molecular skeleton of compounds ZArCH=NArY (ZBAY) are very similar to that of ZPEAY. And the bridging bond is CH=N for the former and C (CH_3)=N for the latter. Chen et al.[24] and Cao et al.[22] investigated the $\nu_{\max}$ of 72 samples of XArCH=NArY compounds (abbreviated as 2-H-XBAY) and 13 samples of 2-OH-XArCH=NArY compounds (abbreviated as 2-OH-XBAY) respectively, and obtained their quantitative equations. However, the topic of “whether the influence of intramolecular hydrogen bond on the $\nu_{\max}$ of ZBAY and ZPEAY has difference” has not been studied, up to now. Based on the method of dealing with the compounds ZPEAY in Section 3.1.1, the $\nu_{\max}$ values of 85 samples of ZBAY compounds reported by Cao et al.[21] and Yuan and Cao[19] were regressed by adopting the same parameters of Equation 3, and then Equation 9 with 95% confidence levels was obtained.

TABLE 2 The regression equations with different substituent parameters

Equation no.	Regression equations	Parameters
(4)	$\nu_{\max} = 30{,}513 + 2{,}511.02\sigma(\mathrm{Y}) + 1{,}104.42\sum\sigma_{\mathrm{CC}}^{\mathrm{ex}} - 188.92\Delta\sigma_{\mathrm{CC}}^{\mathrm{ex}\,2} + 1{,}443.62\Delta\sigma^2(\mathrm{Y}) - 2{,}487.66\Delta\sigma^2(\mathrm{OH,Y}) + 1{,}215.21I_{\text{2-OH}}$ $R = 0.8629$, $S = 845.61$, $F = 36.94$, $n = 83$	$\sigma(\text{2-OH})$, $\sigma(\mathrm{Y})$, $\sigma_{\mathrm{CC}}^{\mathrm{ex}}(\mathrm{X})$, $\sigma_{\mathrm{CC}}^{\mathrm{ex}}(\mathrm{Y})$, $I_{\text{2-OH}}$ [delete $\sigma(\mathrm{X})$]
(5)	$\nu_{\max} = 31{,}170 - 2{,}263.52\sigma(\mathrm{X}) + 1{,}722.02\sigma(\mathrm{Y}) + 574.61\sum\sigma_{\mathrm{CC}}^{\mathrm{ex}} - 34.79\Delta\sigma_{\mathrm{CC}}^{\mathrm{ex}\,2} - 1{,}086.32\Delta\sigma^2 - 497.66I_{\text{2-OH}}$ $R = 0.9580$, $S = 480.12$, $F = 141.21$, $n = 83$	$\sigma(\mathrm{X})$, $\sigma(\mathrm{Y})$, $\sigma_{\mathrm{CC}}^{\mathrm{ex}}(\mathrm{X})$ $\sigma_{\mathrm{CC}}^{\mathrm{ex}}(\mathrm{Y})$, $I_{\text{2-OH}}$ [delete $\sigma(\text{2-OH})$]
(6)	$\nu_{\max} = 31{,}419 - 2{,}433.54\sum\sigma(\mathrm{X}) + 1{,}155.30\sum\sigma_{\mathrm{CC}}^{\mathrm{ex}} - 238.02\Delta\sigma_{\mathrm{CC}}^{\mathrm{ex}\,2} - 560.34\Delta\sigma^2 - 1{,}162.69I_{\text{2-OH}}$ $R = 0.8959$, $S = 738.50$, $F = 62.64$, $n = 83$	$\sigma(\mathrm{X})$, $\sigma(\text{2-OH})$, $\sigma_{\mathrm{CC}}^{\mathrm{ex}}(\mathrm{X})$, $\sigma_{\mathrm{CC}}^{\mathrm{ex}}(\mathrm{Y})$, $I_{\text{2-OH}}$ [delete $\sigma(\mathrm{Y})$]
(7)	$\nu_{\max} = 30{,}975 - 2{,}621.96\sum\sigma(\mathrm{X}) + 2{,}624.55\sigma(\mathrm{Y}) + 686.03\sigma_{\mathrm{CC}}^{\mathrm{ex}}(\mathrm{Y}) + 191.10\sigma_{\mathrm{CC}}^{\mathrm{ex2}}(\mathrm{Y}) - 862.86\Delta\sigma^2 - 1{,}798.35\Delta\sigma^2(\mathrm{OH,Y}) - 967.58I_{\text{2-OH}}$ $R = 0.9699$, $S = 410.30$, $F = 169.88$, $n = 83$	$\sigma(\mathrm{X})$, $\sigma(\text{2-OH})$, $\sigma(\mathrm{Y})$, $\sigma_{\mathrm{CC}}^{\mathrm{ex}}(\mathrm{Y})$, $I_{\text{2-OH}}$ [delete $\sigma_{\mathrm{CC}}^{\mathrm{ex}}(\mathrm{X})$]
(8)	$\nu_{\max} = 30{,}885 - 2{,}192.4\sum\sigma(\mathrm{X}) + 3{,}060.98\sigma(\mathrm{Y}) + 82.09\sigma_{\mathrm{CC}}^{\mathrm{ex}}(\mathrm{X}) - 459.52\sigma_{\mathrm{CC}}^{\mathrm{ex2}}(\mathrm{X}) - 838.86\Delta\sigma^2 - 1{,}980.16\Delta\sigma^2(\mathrm{OH,Y}) - 603.51I_{\text{2-OH}}$ $R = 0.9681$, $S = 421.83$, $F = 160.13$, $n = 83$	$\sigma(\mathrm{X})$, $\sigma(\text{2-OH})$, $\sigma(\mathrm{Y})$, $\sigma_{\mathrm{CC}}^{\mathrm{ex}}(\mathrm{X})$, $I_{\text{2-OH}}$ [delete $\sigma_{\mathrm{CC}}^{\mathrm{ex}}(\mathrm{Y})$]

$$
\begin{aligned}
\nu_{\max} = {} & 32{,}024 - 658.94\sum\sigma(\mathrm{X}) + 1{,}174.58\sigma(\mathrm{Y}) \\
& + 1{,}527.54\sum\sigma_{\mathrm{CC}}^{\mathrm{ex}} + 190.92\Delta\sigma_{\mathrm{CC}}^{\mathrm{ex}\,2} - 1{,}101.2\Delta\sigma^2 \\
& - 393.58\Delta\sigma^2(\mathrm{OH,Y}) - 2{,}381.78I_{2-\mathrm{OH}} \\
& R = 0.9807, S = 426.76, F = 276.03, n = 85
\end{aligned}
\tag{9}
$$

Equation 9 has good correlation, and it shows that the effect of item $\Delta\sigma^2$ on the $\nu_{\max}$ is different from that of $\Delta\sigma^2$(OH,Y) on the $\nu_{\max}$, and the intramolecular hydrogen bond ($I_{2\text{-OH}}$) has a fixed contribution to the $\nu_{\max}$, namely, which decreases the $\nu_{\max}$ (about 2,381 cm^{-1}), and makes the $\lambda_{\max}$ a red shift.

3.2 | Result discussion

When comparing Equation 3 with Equation 9, it can be seen that the influence factors of substituents on the $\nu_{\max}$ are by largely the same for the two kinds of Schiff bases ZBAY and ZPEAY. Because the bridging bond of ZBAY is different from that of ZPEAY, the influence intensities of variables on the $\nu_{\max}$ are different for these in Equations 3 and 9. The change regularities of the $\nu_{\max}$ of ZPEAY and ZBAY can be well expressed by Equations 3 and 9 respectively. Figure 5 is the plot of the calculated $\nu_{\max}$ values versus the experimental values.

It should be noted that the coefficient in front of the variable $I_{2\text{-OH}}$ in Equation 3 is −850.17, while the coefficient in front of $I_{2\text{-OH}}$ in Equation 9 is −2,318.79, the value of the latter is more than twice of the former. It indicates that the effect of intramolecular hydrogen bond on the $\nu_{\max}$ is only dominated by their parent molecular structure, rather than the substituent in the molecule. As to why the effect of intramolecular hydrogen bond on the $\nu_{\max}$ is much greater in ZBAY than in ZPEAY, it is perhaps caused by the difference of their molecular coplanarity. We obtained crystals of some compounds of 2-OH-XBAY and 2-OH-XPEAY and tested the crystals. Figure 6 shows the molecular configurations of 2-OH-HBACN-4′ (Cambridge Crystallographic Data Centre (CCDC)No. 2031443) and 2-OH-HPEACN-4′ (CCDC No. 1868713) in crystals, respectively. Their checkCIF files were reported in the supporting information. It can be seen, from Figure 6, that the two benzene rings in 2-OH-HBACN-4′ are almost coplanar and the two benzene rings in 2-OH-HPEACN-4′ are almost perpendicular to each other. Therefore, from which, we can infer that the coplanarity of molecule 2-OH-XBAY may be better than that of molecule 2-OH-XPEAY in solvent, which is more conducive to the proton transfer via intramolecular hydrogen bonds at a lower energy state.

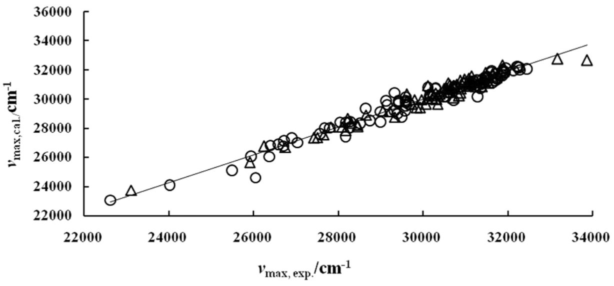


FIGURE 5 Plot of the calculated $\nu_{\max,\ \mathrm{cal.}}$ with Equations 3 and 9 versus the experimental $\nu_{\max,\ \mathrm{exp.}}$ (the symbols "o" and "Δ" represent the ZPEAY and ZBAY, respectively)

It should be pointed out that the intramolecular hydrogen bond has a fixed contribution to the $\nu_{\max}$ of ZBAY and ZPEAY, respectively, that is, reducing the $\nu_{\max}$ of ZBAY 2,381.78 cm^{-1} and that of ZPEAY 850.17 cm^{-1}. However, it does not mean that the $\lambda_{\max}$ of the compounds can move a fixed value. Because the $\nu_{\max} = 1\times10^7/\lambda_{\max}$, the red shift value of the $\lambda_{\max}$ caused by intramolecular hydrogen bond is related to the $\lambda_{\max}$ of the corresponding molecule. That is,

$$
aI_{2-\mathrm{OH}} = \frac{1\times10^7}{\lambda_{\max}} - \frac{1\times10^7}{\lambda'_{\max}} \tag{10}
$$

In Equation 10, the "a" is the coefficient in front of the variable $I_{2\text{-OH}}$ in Equation 3 or Equation 9, the $\lambda_{\max}$ is the measured value of the compound, and the $\lambda'_{\max}$ is the theoretical value of the corresponding compound without intramolecular hydrogen bond. From Equation 10 and the value of $I_{2\text{-OH}} = 1$, we can deduce Equation 11.

$$
\lambda'_{\max} = \frac{1\times10^7\lambda_{\max}}{1\times10^7 - a\lambda_{\max}} \tag{11}
$$

By employing Equation 11, we can calculate the $\lambda'_{\max}$, and further calculate the red shift value $\Delta\lambda$ of $\lambda_{\max}$, caused by the intramolecular hydrogen bond. That is, $\Delta\lambda = \lambda_{\max}\text{-}\lambda'_{\max}$. Figure 7 shows the relationship between the red shift values $\Delta\lambda$ and the $\lambda_{\max}$ of the

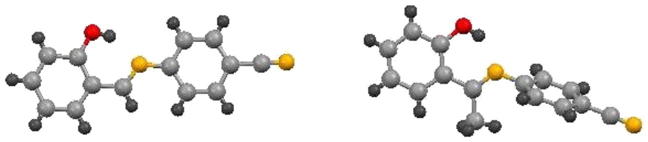


FIGURE 6 The molecular configurations of 2-OH-HBACN-4′ (left) and 2-OH-HPEACN-4′ (right) in crystals

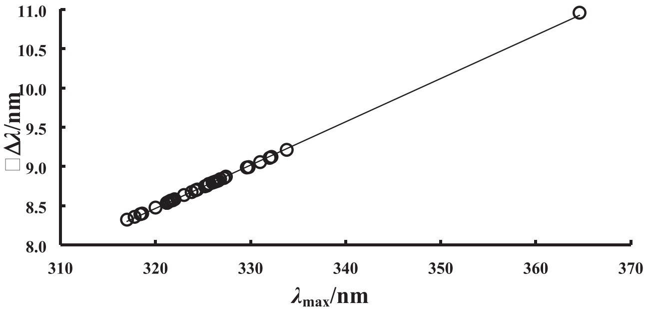


FIGURE 7 Plot of the $\Delta\lambda$ versus the λ_{max} of ZBAY in Table 1 (Nos. 49–83)

compounds in Table 1 (Nos. 49–83). It can be seen that the red shift $\Delta\lambda$ value of a compound with larger λ_{max} is also larger.

4 | CONCLUSION

On the basis of the above research results, we came to the conclusion that (a) the effects of substituents on the ν_{max} of ZPEAY and ZBAY are essentially the same, but their intensities of factors affecting the ν_{max} are different. (b) In the compounds 2-OH-XPEAY and 2-OH-XBAY, the effect of the cross-interaction between 2-OH and Y, that is, $\Delta\sigma^2$(OH,Y), on the ν_{max} is different from that of cross-interaction between X and Y (i.e., $\Delta\sigma^2$). (c) Maybe the coplanarity of molecule 2-OH-XBAY is better than that of 2-OH-XPEAY, and the red shift of the ν_{max} affected by intramolecular hydrogen bond in the former is greater than that in the latter. (d) The effect of intramolecular hydrogen bond on the ν_{max} is only dominated by the parent molecular structure unit, rather than the substituent in the molecules. For these compounds with a same parent structure, if the λ_{max} of the compound is larger, its red shift value $\Delta\lambda$ caused by intramolecular hydrogen bond is also larger. The phenomena observed in this work are helpful to not only understand the optical properties of Schiff bases containing intramolecular hydrogen bonds but also provide an important reference for the molecular design of using these compounds as optoelectronic materials.

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