RESEARCH ARTICLE

Abnormal effect of hydroxyl on the longest wavelength maximum in ultraviolet absorption spectra for bis-aryl Schiff bases

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Abstract

Two sets of bis-aryl Schiff bases that contain 4(or 4')-OH and 2(or 2')-OH were synthesized. The first set consists of 4-HOArCH=NArY and XArCH=NArOH-4', and the second set consists of 2-HOArCH=NArY and XArCH=NArOH-2'. Their ultraviolet absorption spectra were measured and investigated. A very interesting phenomenon was observed by analyzing their wave number ν_{max} (cm⁻¹) of longest wavelength maximum λ_{max} (nm) of ultraviolet. Compared with the change regularity of the ν_{max} of XArCH=NArY (where the X and Y excluded OH), the 4'-position hydroxyl (4'-OH) and 2'-position hydroxyl (2'-OH) have abnormal performance. The details are the following: the 4'-OH contributes an additional red shift to the ν_{max} of XArCH=NArOH-4' (λ_{max} increase), whereas the 2'-OH contributes an additional blue shift to the ν_{max} of XArCH=NArOH-2' (λ_{max} decrease). In addition, there are ortho steric effects of all 2-OH and 2'-OH on the ν_{max} for 2-HOArCH=NArY and XArCH=NArOH-2', and the ortho steric effect contributes a red shift to their ν_{max} . These experimental facts can provide an important theoretical reference for us using aryl Schiff base compounds as optical materials and performing the molecular design.

KEYWORDS

hydroxyl, ortho steric effect, Schiff base, substituent effect, ultraviolet absorption spectra

1 | INTRODUCTION

Photoelectric material is a kind of functional materials,^[1–7] and its energy of light absorption is an important property for its application. Aryl Schiff bases that contain classical π -conjugated system have potential optoelectronic properties and were applied well in many fields of optical functional materials.^[8–11] The substituents at the aromatic rings of an aryl Schiff base molecule have important influence on the molecular photoelectric properties. Therefore, the clear understanding on the relationship between their molecular structure and optical property is the basis for the molecular design and application of optoelectronic materials of aryl Schiff bases.

Recently, Hasan Tanak^[12,13] investigated the energetic and structural properties of the Schiff base compounds, 2-methyl-6-[2-(trifluoromethy) phenylimino-methyl] phenol

and (E)-2-[(2-chlorophenyl) iminomethyl]-4-trifluoromethoxyphenol. He used density functional theory to calculate their optimized geometry and optical properties. The calculated results are in agreement with the experimental facts. Cao et al^[14,15] investigated systematically the relationship between the substituent effect and the longest wavelength maximum λ_{max} (nm) of ultraviolet (UV) absorption for some aryl Schiff bases, and obtained good results, where the used parameters included excited-state substituent parameter $\sigma_{CC}^{\text{ex} [14,15]}$ and ground-state substituent polarity parameter (ie, Hammett constant σ).^[16] The compounds involved are the following: 4,4'-disubstituted N-(benzylidene)-anilines p-XArCH=NArY-p,^[17] symmetrical Schiff bases derived from 1,4-phenylenediamines p-XArCH=NArN=CHArX-p,^[18] extended benzylidene anilines p-XArCH=NArCH=CHArYp,^[19] N-(4-substituted bezylidene) cyclohexylamines p- $XArCH=NC_{6}H_{11}$,^[20] N-(phenyl-ethylene)-anilines XArC

(CH3)=NArY, and N-phenyl- α -phenylnitrones XArCH=N (O)ArY.^[21] On the bases of Cao's works, Wang^[22] explored a molecular design and obtained 31 samples of 3,4'/4,3'disubstituted N-(benzylidene)-anilines 3/4-XArCH=NArY-4'/3' with specified λ_{max} . Then, the designed compounds were synthesized, and their UV absorption spectra were measured in anhydrous ethanol. Wang's^[22] results showed that the predicted λ_{max} values of the designed compounds were in agreement with the experimental ones. Recently, Wang^[23] further quantified the ν_{max} (ie, $\nu_{max} = 1/\lambda_{max}$) of disubstituted/ multi-substituted N-(benzylidene)-anilines XArCH=NArY (abbreviated XBAY) and proposed Equation 1 to express the ν_{max} change regularity for 167 samples of XBAY that contain 1 to 4 substituents.

$$\nu_{\max} = 32032.64 - 666.51\sigma(X_p) + 633.01\Sigma\sigma(Y_m) + 1262.32\sigma(Y_p) - 808.82\Sigma\sigma_{CC(m)}^{ex} + 1629.15\Sigma\sigma_{CC(p)}^{ex} - 931.08\Delta(\Sigma\sigma)^2 - 194.83\Delta(\Sigma\sigma_{CC}^{ex})^2$$
(1)

 $R = 0.9850, R^2 = 0.9702, S = 353.06, F = 739.20, n = 167,$

where the meanings of parameters are as follows:

The σ is Hammett electronic effect constant of X or Y substituent, the X_p and Y_p indicate the para-position of X and Y respectively, the X_m and Y_m stand for the meta-position of X and Y respectively; The σ_{CC}^{ex} is excited-state substituent parameter of X or Y substituent, the subscripts p and m express the para-position and meta-position of the interested group respectively; $\Delta(\Sigma\sigma)^2 = \{[\sigma(X_p) + \sigma(X_m)] - [\sigma(Y_p) + \sigma(Y_m)]\}^2;$ $\Delta(\Sigma\sigma_{CC}^{ex})^2 = \{[\sigma_{CC}^{ex}(X_p) + \sigma_{CC}^{ex}(X_m)] - [\sigma_{CC}^{ex}(Y_p) + \sigma_{CC}^{ex}(Y_m)]\}^2.$

Equation 1 was established by using 167 compounds, and the substituents X and Y distribute on the different positions of the benzene rings. It seems to clearly express the effects of substituents on the ν_{max} of aryl Schiff bases. However, we read carefully the relevant studies^[12–23] published in the past and noticed that the Schiff bases that contain hydroxyl were not systematically investigated. The reason is still unknown. To be able to test if Equation 1 is applicable to the aryl Schiff bases containing hydroxyl, we used Equation 1 to design the Schiff bases, 4-OHArCH=NArY (abbreviated 4-OHBAY) and XArCH=NArOH-4' (abbreviated XBAOH-4'), which have specified λ_{max} . And then we synthesized the designed compounds and measured their λ_{max} values. At first, several representative compounds were designed, and the experimental verification was performed. A very surprising "abnormal" phenomenon was observed, which can be seen in Table 1.

In Table 1, there are mono-substituted and disubstituted benzylideneanilines, and also the substituents distribute on meta- and para-position of the benzene rings. These compounds have certain representation. From the results of Table 1, we noticed that the predicted λ_{max} values by

TABLE 1 The longest wavelength maximum λ_{max} (nm) in UV spectra for some 4-HOBAY and XBAOH-4'

Compound	$\lambda_{\max, pred}^{a}$	$\lambda_{max, exp}^{b}$	$\Delta\lambda^{c}$
4-HOArCH=NArH	314.1	313.0	1.1
HArCH=NArOH-4'	321.3	336.0	-14.7
4-HOArCH=NArF-4'	312.9	316.0	-3.1
4-FArCH=NArOH-4'	321.2	335.0	-13.8
4-HOArCH=NArOMe-3'	315.2	314.0	1.2
3-MeOArCH=NArOH-4'	323.3	336.0	-12.7

Abbreviation: UV, ultraviolet.

^aThe predicted values with Equation 1.

^bThe experimental values of this work.

 $^{c}\Delta\lambda = \lambda_{max, pred} - \lambda_{max, exp}$.

Equation 1 are in a good agreement with the experimental ones for the 4-OHBAY, whereas the predicted λ_{max} deviates considerably the measured ones for the XBAOH-4'. The OH of 4-OHBAY distributes on the para-position of benzene ring that attaches to the carbon atom of bridging group CH=N, whereas the OH of XBAOH-4' distributes on the para-position of benzene ring of the nitrogen atom of CH=N. It is a very interesting phenomenon. We want to know whether the 4'-OH in XBAOH-4' has a universal red shift effect (wavelength increase) or not. To be able to explore this topic, we synthesized a series of model compounds, recorded their UV absorption spectra, and performed the correlation between their molecular structures and the ν_{max} values.

2 | EXPERIMENTAL SECTIONS

2.1 | Synthesis of model compounds

In this work, the model compounds were synthesized by using the methods from a number of studies,^[20,22–25] as shown in Figure 1. Substituted benzaldehyde (0.01 mol) was mixed with substituted aniline (0.01 mol) in ethanol (20 mL), and the reaction mixture was stirred for 15 minutes at room temperature. Then the reaction mixture was stood over 3 hours, and solid was precipitated. The crude product was obtained by filtering the reaction mixture, which was purified by recrystallization treatment in anhydrous ethanol. The products were vacuum dried for a whole day, and all the model compounds were characterized by ¹H NMR and ¹³C NMR (see supporting information).

2.2 | Data preparation

The UV absorption spectra of model compounds were recorded by UV-2550 (SHIMADZU, Japan), scanning range 200-500 nm, and scanning speed 10 nm/s in anhydrous ethanol. The spectrum of each target compound was tested for 3 times (see supporting information), and the mean value of λ_{max} was used for each sample. The λ_{max} and ν_{max} values ($\nu_{\text{max}} = 1/\lambda_{\text{max}}$) of all target compounds were collected and listed in Tables 2 and 4 (groups I and II), respectively.

Group I:



Group II:



FIGURE 1 Synthesis of 4-HOBAY versus XBAOH-4'(group I) and 2-HOBAY versus XBAOH-2'(group II)

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

TABLE 2 The longest wavelength maximum λ_{max} (nm) and wavenumber ν_{max} (cm⁻¹) of UV spectra for 4-HOBAY and XBAOH-4', and the substituent constant values of σ and σ_{CC}^{ex} for groups X and Y

No.	Х	Y	σ(X) ^a	$\sigma(\mathbf{Y})^{\mathbf{a}}$	$\sigma_{\rm CC}^{\rm ex}({\rm X})^{\rm b}$	$\sigma_{\rm CC}^{\rm ex}({ m Y})^{\rm b}$	$\lambda_{max, exp}^{c}$	ε	$\nu_{\rm max, \ exp}^{\rm \ c}$	$ u_{ m max,\ cal}{}^{ m d}$
1	4-OH	4'-OMe	-0.37	-0.27	-0.19	-0.50	330.0	34 700	30 303	30 825
2	4-OH	4'-Me	-0.37	-0.17	-0.19	-0.17	320.0	54 900	31 250	31 449
3	4-OH	Н	-0.37	0.00	-0.19	0.00	313.0	56 200	31 949	31 811
4	4-OH	4'-F	-0.37	0.06	-0.19	0.06	316.0	48 400	31 646	31 921
5	4-OH	4'-C1	-0.37	0.23	-0.19	-0.22	320.0	34 800	31 250	31 526
6	4-OH	4'-Br	-0.37	0.23	-0.19	-0.33	320.6	46 900	31 153	31 352
7	4-OH	4'-CF ₃	-0.37	0.54	-0.19	-0.12	315.0	47 700	31 746	31 563
8	4-OH	3'-OMe	-0.37	0.12	-0.19	0.10	314.0	60 800	31 847	31 994
9	4-OH	3'-Me	-0.37	-0.07	-0.19	-0.03	315.2	29 600	31 746	31 731
10	4-OH	3'-F	-0.37	0.34	-0.19	0.02	313.5	49 500	31 847	31 870
11	4-OH	3'-C1	-0.37	0.37	-0.19	0.02	315.1	40 000	31 746	31 860
12	4-OH	3'-Br	-0.37	0.39	-0.19	-0.03	315.8	40 700	31 646	31 780
13	4-OH	3'-CF ₃	-0.37	0.43	-0.19	0.09	312.9	50 400	31 949	31 936
14	4-OH	3'-CN	-0.37	0.56	-0.19	0.56	310.1	33 900	32 258	32 471
15	4-OMe	4'-OH	-0.27	-0.37	-0.50	-0.19	334.7	37 500	29 851	29 455
16	4-Me	4'-OH	-0.17	-0.37	-0.17	-0.19	334.3	33 300	29 940	29 891
17	Н	4'-OH	0.00	-0.37	0.00	-0.19	336.0	21 700	29 762	29 933
18	4-F	4'-OH	0.06	-0.37	0.06	-0.19	335.0	63 500	29 851	29 930
19	4-C1	4'-OH	0.23	-0.37	-0.22	-0.19	341.3	83 400	29 326	29 215
20	4-Br	4'-OH	0.23	-0.37	-0.33	-0.19	342.3	73 200	29 240	29 040
21	4-CF ₃	4'-OH	0.54	-0.37	-0.12	-0.19	347.7	47 700	28 736	28 667
22	4-CN	4'-OH	0.66	-0.37	-0.70	-0.19	360.0	58 900	27 778	27 386
23	$4-NO_2$	4'-OH	0.78	-0.37	-1.17	-0.19	381.0	55 700	26 247	26 141
24	3-OMe	4'-OH	0.12	-0.37	0.10	-0.19	336.0	35 200	29 762	29 889
25	3-Me	4'-OH	-0.07	-0.37	-0.03	-0.19	336.3	54 900	29 762	29 984
26	3-F	4'-OH	0.34	-0.37	0.02	-0.19	340.0	36 600	29 412	29 351
27	3-C1	4'-OH	0.37	-0.37	0.02	-0.19	339.7	23 200	29 412	29 285
28	3-Br	4'-OH	0.39	-0.37	-0.03	-0.19	344.1	89 700	29 070	29 167
29	3-CF ₃	4'-OH	0.43	-0.37	0.09	-0.19	343.2	65 000	29 155	29 247
30	3-CN	4'-OH	0.56	-0.37	0.56	-0.19	347.0	35 600	28 818	29 538

Abbreviation: UV, ultraviolet.

^aThe values were taken from the study of Hansch et al.^[16]

^bThe values were taken from the 2 different studies of Cao et al.^[14,15]

^cThe values were obtained by this work.

^dThe values were calculated by Equation 3.

3 | DATA ANALYSIS AND RESULT DISCUSSION

3.1 | Effects of substituents 4-OH and 4'-OH on the ν_{max}

Figure 2 is the UV absorption spectra of the 3 pairs of model compounds listed in Table 1.

We can observe from Table 1 and Figure 2 that the calculated λ_{max} value of XBAOH-4' is red shift about 8 nm than that of 4-HOBAY, in case that the groups X and Y are the same. In fact, their corresponding measured λ_{max} value is red shift over 20 nm. It implies that 4'-OH of bis-aryl Schiff bases have an additional red shift effect on the λ_{max} of the molecules. To be able to investigate the magnitude of this red shift effect, we performed the following quantitative correlation analysis.

First step: The 30 ν_{max} values of Table 1 and the 167 ν_{max} values of Wang's^[23] report were merged into one data set (all 197 samples of compounds), and then a regression analysis was performed by using the 7 variables of Equation 1. We got Equation 2.

$$\nu_{\max} = 31850.02 - 650.55\sigma(X_p) + 1012.77\Sigma\sigma(Y_m)$$
(2)
+1608.50 $\sigma(Y_p) - 700.12\Sigma\sigma_{CC(m)}^{ex} + 1530.24\Sigma\sigma_{CC(p)}^{ex}$
-1042.47 $\Delta(\Sigma\sigma)^2 - 119.24\Delta(\Sigma\sigma_{CC}^{ex})^2$

 $R = 0.9722, R^2 = 0.9452, S = 459.08, F = 465.68, n = 197.$

Second step: The 197 samples of compounds and the 7 variables used in the first step were still used. In addition, an indicator variable $I_{4'-OH}$ was used for expressing the additional contribution of 4'-OH to the ν_{max} . The value of $I_{4'-OH}$ is taken as 1 or 0, that is, when the molecule contains 4'-OH, $I_{4'-OH} = 1$; otherwise, $I_{4'-OH} = 0$. Once again, a regression analysis was performed by using total of above 8 variables, and Equation 3 was obtained.

$$\nu_{\max} = 32007.9 - 657.786\sigma(X_p) + 726.274\Sigma\sigma(Y_m)$$
(3)
+1273.314 $\sigma(Y_p) - 614.843\Sigma\sigma_{CC(m)}^{ex}$
+ 1625.72 $\Sigma\sigma_{CC(p)}^{ex} - 901.984\Delta(\Sigma\sigma)^2$
-199.603 $\Delta(\Sigma\sigma_{CC}^{ex})^2 - 1195.81I_{4'-OH}$

 $R = 0.9842, R^2 = 0.9687, S = 348.09, F = 726.32, n = 197.$

Comparing the result of the first step with that of the second step, we can see that the correlation coefficient R of Equation 3 is obviously improved than that of Equation 2 and the standard deviation S of Equation 3 reduces more than 100 cm^{-1} . Further, from Equations 1 to 3, we can get the following results: The correlation of Equation 2 is less than that of Equation 1, and the coefficients in front of variables of Equation 2 deviate greatly from those of corresponding items of Equation 1. Whereas the correlation coefficients R of Equations 1 and 3 are close to each other, the coefficients of corresponding items among Equations 1 and 3 are also close



FIGURE 2 The UV absorption spectra of 3 pairs of model compounds: a, 4-HOBAH versus HBAOH-4'; b, 4-HOBAF-4' versus 4-FBAOH-4'; and c, 4-HOBAOMe-3' versus 3-MeOBAOH-4'

to each other, and the standard deviation *S* of Equation 3 is smaller than that of Equation 1. The coefficient in front of indicator variable $I_{4'-OH}$ is negative (-1195.81), which indicates that the 4'-OH (by comparing with 4-OH) has a red shift effect on the ν_{max} : It decreases the ν_{max} and increases the λ_{max} value.

We calculated the ν_{max} of the 197 samples of compounds with Equation 3 and then converted them to λ_{max} . The mean absolute error of the calculated λ_{max} values versus the experimental ones is only 2.9 nm, the most absolute error is 11.4 nm, and the error distribution was listed in Table 3. Figure 3 is the plot of the calculated $\nu_{max, cal}$ versus the experimental $\nu_{max, exp}$ values.

The results of Table 3 and Figure 3 showed that Equation 3 expresses the ν_{max} change regularity of bis-aryl Schiff bases XBAY that involve 4-OH and 4'-OH.

3.2 | Effects of substituents 2-OH and 2'-OH on

the $\nu_{\rm max}$

On the basis of the action regularity of substituent conjugative effect, it is generally believed that the conjugative effect is similar for these substituents at 2-position and 4position of a benzene ring and only has a different intensity. From the results of Section 3.1, we think whether the ν_{max} change of 2-HOBAY versus XBAOH-2' is similar to that of 4-HOBAY versus XBAOH-4' or not. So we further synthesized a series of compounds listed in Table 4, measured their UV absorption spectra, and then made a quantitative molecular structure- ν_{max} values relationship analysis.

It should be noted that it is not appropriate to put the compounds of Table 4 into Equation 3 for regression analysis, because of the ortho steric effect of neighboring groups.^[28] Therefore, we performed regression analysis independently by using the data of Table 4. It was searched from the studyof Charton^[26] that the Hammett electronic effect constant of the ortho hydroxyl (o-OH) σ_o is -0.38. However, the excited-

 TABLE 3
 The distribution of mean absolute error between the calculated values and the experimental ones



FIGURE 3 The plot of the calculated $\nu_{max, cal}$ versus the experimental ν_{max} , exp (The data is from the study of Wang et al^[23] except for the data of Table 1.)

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state substituent constant σ_{CC}^{ex} of *o*-OH has not been reported and cannot be got. Thus, we obtained the λ_{max} value 214 nm of catechol (in anhydrous ethanol) from the study of Williams and Fleming,^[29] then calculated the excited-state substituent constant of *o*-OH by using the method from the study of Chen and Cao,^[27] and got the $\sigma_{CC(o)}^{ex} = -0.10$ for *o*-OH. After having the parameters σ_o and $\sigma_{CC(o)}^{ex}$ of *o*-OH, we performed the regressions for the ν_{max} data of Table 4 as follows:

First step: Equation 4 was obtained by regression analysis with 5 parameters, $\sigma(X)$, $\sigma(Y)$, $\Sigma \sigma_{CC}^{ex}$, $\Delta \sigma^2$, and $\Delta \sigma_{CC}^{ex}^2$.

$$\nu_{\max} = 30082.24 + 509.062\sigma(X) + 1920.48\sigma(Y) + 415.436\Sigma\sigma_{CC}^{ex} - 1794.72\Delta\sigma^2 - 291.725\Delta\sigma_{CC}^{ex}{}^2$$
(4)

 $R = 0.9863, R^2 = 0.9729, S = 177.31, F = 150.65, n = 27.$

Second step: The 5 variables used in Equation 4 and an indicator variable $I_{2'-OH}$ of *o*-OH were used, where the $I_{2'-OH}$ expresses the additional contribution of 2'-OH to the ν_{max} . The value of $I_{2'-OH}$ is taken as 1 or 0, that is, when the molecule contains 2'-OH, $I_{2'-OH} = 1$, otherwise, $I_{2'-OH} = 0$. Once again, a regression analysis was performed by using total of above 6 variables, and Equation 5 was obtained.

$$\nu_{\text{max}} = 29737.63 - 54.4102\sigma(\text{X}) + 1796.979\sigma(\text{Y}) + 422.9062\Sigma\sigma_{\text{CC}}^{\text{ex}} - 1515.46\Delta\sigma^2 - 389.994\Delta\sigma_{\text{CC}}^{\text{ex}\ 2}$$
(5)
+ 380.50*I*_{2'-OH}

 $R = 0.9927, R^2 = 0.9855, S = 132.94, F = 226.22, n = 27.$

It can be observed from Equations 4 and 5 that the correlation of Equation 5 is better than that of Equation 4 because of addition of the indicator variable $I_{2'-OH}$. We noted that the coefficient in front of $I_{2'-OH}$ is positive (380.50). It means that the 2'-OH (by comparing with 2-OH) contributes a blue shift (rather than a red shift) effect on the ν_{max} : It increases the ν_{max} and decreases the λ_{max} value. Compared with Equation 3, it can be seen that the intercept of Equation 5 is smaller than that of Equation 3. Maybe it results from the ortho steric effect of the 2/2'-OH.

3.3 | Interpretation of effects of 4'-OH and 2'-OH on the ν_{max}

From the results of Equations 3 and 5, we observed that 4'-OH (comparing with 4-OH) has a red shift effect on the ν_{max} , whereas 2'-OH (comparing with 2-OH) has a blue shift effect on the ν_{max} . The effect difference between 4'-OH and 2'-OH on the ν_{max} may be related to the following factors.

1. For molecules 4-HOBAY and XBAOH-4', there is a resonance structure of A and B in Figure 4, respectively.

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TABLE 4 The longest wavelength maximum λ_{max} (nm) and wavenumber ν_{max} (cm⁻¹) of UV spectra for 2-HOBAY and XBAOH-2', and the substituent constant values of σ and σ_{CC}^{ex} for groups X and Y

No.	X	Y	$\sigma(\mathbf{X})^{\mathbf{a}}$	$\sigma(\mathbf{Y})^{\mathbf{a}}$	$\sigma^{\rm ex}_{\rm CC}({\rm X})^{\rm b}$	$\sigma^{\rm ex}_{\rm CC}({\rm Y})^{\rm b}$	λ _{max exp} ^c	ε	$\nu_{\max exp}^{c}$
1	2-НО	4'-NMe ₂	-0.38	-0.83	-0.10	-1.81	384.0	45 700	26 042
2	2-HO	4'-OMe	-0.38	-0.27	-0.10	-0.50	348.0	67 000	28 736
3	2-HO	4'-Me	-0.38	-0.17	-0.10	-0.17	341.3	25 200	29 326
4	2-HO	Н	-0.38	0.00	-0.10	0.00	337.0	31 600	29 674
5	2-HO	4'-F	-0.38	0.06	-0.10	0.06	338.3	31 200	29 586
6	2-HO	4'-CN	-0.38	0.66	-0.10	-0.70	345.0	65 600	28 986
7	2-HO	4'-NO2	-0.38	0.78	-0.10	-1.17	354.7	37 500	28 169
8	2-HO	3'-OMe	-0.38	0.12	-0.10	0.10	339.7	45 500	29 412
9	2-HO	3'-Me	-0.38	-0.07	-0.10	-0.03	337.7	23 200	29 586
10	2-HO	3'-F	-0.38	0.34	-0.10	0.02	339.7	74 300	29 412
11	2-HO	3'-Br	-0.38	0.39	-0.10	-0.03	339.8	116 000	29 412
12	2-HO	3'-CF ₃	-0.38	0.43	-0.10	0.09	338.0	55 500	29 586
13	2-HO	3'-CN	-0.38	0.56	-0.10	0.56	340.7	22 200	29 326
14	4-NMe ₂	2′-НО	-0.83	-0.38	-1.81	-0.10	367.3	115 300	27 248
15	4-Me	2′-НО	-0.17	-0.38	-0.17	-0.10	343.0	54 900	29 155
16	Н	2′-НО	0.00	-0.38	0.00	-0.10	344.0	51 300	29 070
17	4-F	2′-НО	0.06	-0.38	0.06	-0.10	343.3	107 600	29 155
18	4-Cl	2′-НО	0.23	-0.38	-0.22	-0.10	348.7	34 800	28 653
19	4-Br	2′-НО	0.23	-0.38	-0.33	-0.10	349.0	58 000	28 653
20	4-CF ₃	2′-НО	0.54	-0.38	-0.12	-0.10	356.0	50 400	28 090
21	4-CN	2′-НО	0.66	-0.38	-0.50	-0.10	366.0	30 000	27 322
22	$4-NO_2$	2′-НО	0.78	-0.38	-1.17	-0.10	381.0	34 000	26 247
23	3-F	2′-НО	0.34	-0.38	0.02	-0.10	349.7	44 100	28 571
24	3-C1	2′-НО	0.37	-0.38	0.02	-0.10	349.7	83 400	28 571
25	3-Br	2'-HO	0.39	-0.38	-0.03	-0.10	348.3	42 800	28 736
26	3-CF ₃	2'-HO	0.43	-0.38	0.09	-0.10	351.0	38 500	28 490
27	3-CN	2'-HO	0.56	-0.38	0.56	-0.10	356.0	46 700	28 090

Abbreviation: UV, ultraviolet.

^aThe values of 2-OH and 2'-OH were taken from the study of Charton,^[26] others were taken from the work of Hansch et al.^[16]

^bThe values of 2-OH and 2'-OH were calculated by this work with the method form the study of Chen and Cao,^[27] others were taken from 2 different studies of Cao et al.^[14,15]

^cThe values were obtained by this work.



FIGURE 4 One of the resonance structures for (A) 4-HOBAY and (B) XBAOH-4' $\,$

The formation of resonance structures A and B is beneficial to the conjugative effect of OH. For the A, the negative charge distributes on the nitrogen atom of bridging group CH=N, whereas it does on the carbon atom of CH=N for the B. Since the electronegativity of N atom is larger than that of C atom, the A is more stable than the B. That is, the energy level of the highest occupied molecular orbital of the B is higher than that of the A, and the transition of electrons from



FIGURE 5 One of the resonance structures for (C) 2-HOBAY and (D) XBAOH-2' $\,$

highest occupied molecular orbital to lowest unoccupied molecular orbital is easier in the B than in the A. As a result, the 4'-OH contributes a red shift, ie, it reduces the ν_{max} and increases the λ_{max} .

2. For molecules 2-HOBAY and XBAOH-2', there is a resonance structure of C and D in Figure 5, respectively.

The resonance structures C and D in Figure 5 are more difficult to form than the A and B in Figure 4 to form, because their positive and negative charges are very close to each other and they require a larger energy supply.^[30,31] So the C and D contribute little to the conjugative effect of OH.

Besides the conjugative effect, perhaps the intramolecular hydrogen bond also has an important effect on the ν_{max} of 2-HOBAY and XBAOH-2'. Molecules 2-HOBAY and XBAOH-2' may form the intramolecular hydrogen bond, as shown in Figure 6.

In Figure 6, the intramolecular hydrogen bonding of E is a 6-numbered ring, whereas that of F is a 5-numbered ring, the E is easier to form than the F. Werner^[32] even testified experimentally that 2-(2'-hydroxy-5'-methylphenyl)benzotriazol (TIN) molecule formed the intramolecular hydrogen bonding of 6-numbered ring (not 5-numbered ring). He also confirmed that the intramolecular hydrogen bonding of the 6-numbered ring of like-TIN compounds was beneficial to form a planar molecule.^[33-36]

Gawinecki et al^[37] confirmed experimentally by ¹H, ¹³C, and ¹⁵N NMR spectra that the intramolecular hydrogen bonding of 6-numbered ring in *N*-Salicylideneanilines has aromaticity.

In addition, in this work we observed that the experimental ¹H NMR chemical shifts $\delta_{\rm H}$ are 10.15, 13.29, 9.53, and 8.74 for 4-HOBAH, 2-HOBAH, 4'-HOBAH, and 2'-HOBAH, respectively (see supporting information). Also we calculated the bond distance of the O-H bonds and the N...H hydrogen bonds of 2-HOBAH and 2'-HOBAH by using the quantum chemistry method M06 (6-311+ +g(2df,2p)) and got the results (in angstrom) O-H = 0.985 and N...H = 1.783 for 2-HOBAH and O-H = 0.970 and N...H = 2.083 for 2'-HOBAH. It implies that the O-H bond of the E is longer than that of the F, the N...H hydrogen bonds of the E is much shorter than that of the F. Above experimental ¹H NMR chemical shifts and quantum chemistry calculated results show that the intramolecular hydrogen bonding of 6-numbered ring (E of Figure 6) is more effective than the 5-numbered ring (F of Figure 6).

From the above analysis we can consider that the intramolecular hydrogen bonding of 2-HOBAY (E of Figure 6) is easier to form than that of XBAOH-2' (F of Figure 6). As a result, the 2'-OH (by comparing with 2-OH) contributes a blue shift effect on the ν_{max} .

To be able to verify that the 2-OH contributes a red shift effect, or the 2'-OH group makes a blue shift effect on the ν_{max} , we merged the 197 ν_{max} values used in Equation 3 and the 27 ν_{max} values of Table 4 into one data set (all 224



FIGURE 6 The intramolecular hydrogen bonding for molecules (E) 2-HOBAY and (F) XBAOH-2'

samples of compounds). Taking the symbol $S_{o(OH)}$ to represent the ortho steric effect of *o*-OH (including 2-OH and 2'-OH), using 2 indicator variables, $I_{2'-OH}$ and $S_{o(OH)}$, together with the 8 variables of Equation 3, we performed a regression analysis with 10 variables for the 224 ν_{max} values and obtained Equation 6.

$$\nu_{\max} = 31972.9 - 637.895\sigma(X_p) + 742.171\Sigma\sigma(Y_m) + 1325.56\sigma(Y_p) - 587.514\Sigma\sigma_{CC(m)}^{ex} + 1578.00\Sigma\sigma_{CC}^{ex}(p) - 946.896\Delta(\Sigma\sigma)^2 - 169.160\Delta(\Sigma\sigma_{CC}^{ex})^2 - 1146.72I_{4'-OH} + 245.542I_{2'-OH} - 2104.63S_{o(OH)}$$
(6)

 $R = 0.9840, R^2 = 0.9682, S = 350.10, F = 649.15, n = 224.$

Comparing Equation 6 with Equation 3, we observed that Equations 6 and 3 had same good correlation and their coefficients in front of corresponding variables were very close to each other. The coefficients of parameters $I_{4'-OH}$, $I_{2'-OH}$, and $S_{o(OH)}$ of Equation 6 indicate the following: Compared with the 4-OH, the 4'-OH decreases the ν_{max} and contributes a red shift effect; the 2'-OH, compared with the 2-OH, increases the ν_{max} and contributes a blue shift effect. The ortho steric effect $S_{o(OH)}$ of all 2-OH and 2'-OH decreases the ν_{max} and contributes a red shift effect. We can say that the 4'-OH has a red shift effect and the 2'-OH has a blue shift effect, because the ν_{max} of compounds 4-OHBAY and 2-OHBAY can be correlated well by using the equation in the work of Wang et al^[23] without any indicator variable, whereas the ν_{max} of 4'-OHBAY and 2'-OHBAY can be accepted by the equation in the work of Wang et al^[23] after adding indicator variables. Thus, the indicator variables express their additional contributions to the $\nu_{\rm max}$, respectively.

4 | CONCLUSIONS

There is an abnormal effect of hydroxyl on the ν_{max} of bisaryl Schiff bases (XArCH=NArY). From the above investigation, we can get the following conclusions: (1) Compared with the contribution of 4-hydroxyl to the ν_{max} of 4-hydroxyl substituted N-(benzylidene)-anilines 4-OHArCH=NArY, the 4'-hydroxyl contributes an additional red shift to the ν_{max} of XArCH=NArOH-4'. (2) Compared with the contribution of 2-hydroxyl to the ν_{max} of 2-hydroxyl substituted N-(benzylidene)-anilines 2-OHArCH=NArY, the 2'-hydroxyl contributes an additional blue shift to the ν_{max} of XArCH=NArOH-2'. (3) There are ortho steric effects of all 2-OH and 2'-OH on the ν_{max} for 2-HOArCH=NArY and XArCH=NArOH-2', and the ortho steric effect contributes a red shift to their ν_{max} . (4) When we take bis-aryl Schiff bases as the target molecules of UV absorption and perform the molecular design of optical materials, we should pay attention to the different effects of para-hydroxyl and ortho

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hydroxyl on the ν_{max} of the compounds. (5) The properties of aryl Schiff bases change very delicately, and we often meet the "abnormal" phenomenon. Therefore, we cannot predict their performance by our existing experience in some cases and must research on their properties in-depth and systematically.

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REFERENCES

- [1] L. C. Chen, K. C. Zhang, C. Q. Tang, Q. D. Zheng, Y. Xiao, J. Org. Chem. 2015, 80, 1871.
- [2] M. G. Han, Y. Tian, Z. Yuan, L. Zhu, B. W. Ma, Angew. Chem. Int. Ed. 2014, 53, 10908.
- [3] Z. Yuan, Y. Shu, Y. Tian, Y. Xin, B. W. Ma, Chem. Commun. 2015, 51, 16385.
- [4] D. M. Sun, Z. J. Ren, M. R. Bryce, S. K. Yan, J. Mater. Chem. C 2015, 3, 9496.
- [5] C. K. Zhou, Y. Tian, Z. Yuan, M. G. Han, J. M. Wang, L. Zhu, M. S. Tameh, C. Huang, B. W. Ma, Angew. Chem. Int. Ed. 2015, 54, 9591.
- [6] A. Rajendran, T. Tsuchiya, S. Hirata, J. Phys. Chem. A 2012, 116, 12153.
- [7] H. L. Zhong, E. J. Xu, D. L. Zeng, J. P. Du, J. Sun, S. J. Ren, B. Jiang, Q. Fang, Org. Lett. 2008, 10, 709.
- [8] C. J. Yang, S. A. Jenekhe, Chem. Mater. 1994, 6, 196.
- [9] F. S. Santos, T. M. H. Costa, V. Stefani, J. Phys. Chem. A 2011, 115, 13390.
- [10] L. Vukovic, C. F. Burmeister, P. Kral, J. Phys. Chem. Lett. 2013, 4, 1005.
- [11] Y. Jia, J. B. Li, Chem. Rev. 2015, 115, 1597.
- [12] H. Tanak, J. Mole. Struct: Theochem 2010, 950, 5.
- [13] H. Tanak, J. Phys. Chem. A 2011, 115, 13865.
- [14] C. Z. Cao, G. F. Chen, Z. Yin, J. Phys. Org. Chem 2008, 21, 808.
- [15] C. Z. Cao, B. Sheng, G. F. Chen, J. Phys. Org. Chem 2012, 25, 1315.
- [16] C. Hansch, A. Leo, R. W. Taft, Chem. Rev. 1991, 91, 165.
- [17] G. F. Chen, C. Z. Cao, J. Phys. Org. Chem 2012, 25, 327.

- [19] Z. J. Fang, C. Z. Cao, Spectrochim. Acta Part A 2013, 111, 62.
- [20] C. T. Cao, B. Y. Wei, C. Z. Cao, Acta Phys.-Chim. Sin. 2015, 31, 204.
- [21] Q. Q. Luo, C. T. Cao, Z. Z. Cao, C. Z. Cao, J. Phys. Org. Chem. 2016, 29, 406.
- [22] L. Y. Wang, C. T. Cao, C. Z. Cao, J. Phys. Org. Chem. 2014, 27, 818.
- [23] L. Y. Wang, C. T. Cao, C. Z. Cao, J. Phys. Org. Chem. 2016, 29, 299.
- [24] H. Neuvonen, K. Neuvonen, F. Fülöp, J. Org. Chem. 2006, 71, 3141.
- [25] C. Z. Cao, B. T. Lu, G. F. Chen, J. Phys. Org. Chem. 2011, 24, 335.
- [26] M. Charton, J. Am. Chem. Soc. 1964, 86, 2033.
- [27] G. F. Chen, C. Z. Cao, Chinese J. Chem. Phys. 2009, 22, 366.
- [28] G. Lin, Y.-C. Liu, Y.-G. Wu, Y.-R. Lee, J. Phys. Org. Chem. 2004, 17, 707.
- [29] D. H. Williams, I. Fleming, Spectroscopic Methods in Organic Chemistry, 5th ed., McGraw-Hill Book Co., England 1998 20.
- [30] R. W. Taft, Prog. Phys. Org. Chem. 1983, 14, 247.
- [31] C. T. Cao, Y. K. Bi, C. Z. Cao, Spectrochim. Acta Part A. 2016, 163, 96.
- [32] T. Werner, J. Phys. Chem. 1979, 83, 320.
- [33] G. Woessner, G. Goeller, P. Kollat, J. J. Stezowsk, M. Hauser, U. K. A. Klein, H. E. A. Kramer, J. Phys. Chem. 1984, 88, 5544.
- [34] G. Woessner, G. Goeller, J. Rieker, H. Hoier, J. J. Stezowski, E. Daltrozzo, M. Neureiter, H. E. A. Kramer, J. Phys. Chem. 1985, 89, 3629.
- [35] G. Goeller, J. Rieker, A. Maier, J. J. Stezowski, E. Daltrozzo, M. Neureiter, H. Port, M. Wiechmann, H. E. A. Kramer, J. Phys. Chem. 1988, 92, 1452.
- [36] J. Keck, H. E. A. Kramer, H. Port, T. Hirsch, P. Fischer, G. Rytz, J. Phys. Chem. 1996, 100, 14468.
- [37] R. Gawinecki, A. Kuczek, E. Kolehmainen, B. Ośmiałowski, T. M. Krygowski, R. Kauppinen, J. Org. Chem. 2007, 72, 5598.

SUPPORTING INFORMATION

Additional Supporting Information may be found online in the supporting information tab for this article.

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