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RESEARCH ARTICLE

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Determination and application of the excited-state substituent constants of pyridyl and substituted phenyl groups

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Abstract

Thirty six 1-pyridyl-2-arylethenes XCH=CHArY (abbreviated XAEY) were synthesized, in which, X is 2-pyridyl, 3-pyridyl and 4-pyridyl and Y is OMe, Me, H, Br, Cl, F, CF_3, and CN. Their ultraviolet absorption spectra were measured in anhydrous ethanol, and their wavelengths of absorption maximum λ_{max} were recorded. Also, the 234 λ_{max} values of 1-substituted phenyl-2-arylethylene compounds (XAEY, where X is substituted phenyl) were collected. The excited-state substituent constants $\sigma^{ex}_{CC(p)}(X)$ of three pyridyl groups and 23 substituted phenyl groups (total of 26) were obtained by means of curve-fitting method. Taking the λ_{max} values of 358 samples of bi-arylethene derivatives as a data set and 126 samples of bi-aryl Schiff bases (including nine compounds synthesized by this work) as another data set, quantitative correlation analyses were performed by employing the obtained $\sigma^{ex}_{CC(p)}(X)$ as a parameter, and good results were obtained for the two data sets. The reliability of the obtained $\sigma^{ex}_{CC(p)}(X)$ values was verified. The results of this paper can provide excited-state substituent constants for the study and application of optical properties of conjugated organic compounds containing aryl groups.

KEYWORDS

bi-arylethene, excited-state substituent constant, pyridyl, substituted phenyl, UV absorption spectrum

1 | INTRODUCTION

Pyridyl is a common organic group, therefore the organic compounds containing pyridyl have been widely studied and applied in Medicine,[1–3] photochemistry,[4–6] and electrochemistry.[7,8] For example, pyridyl disulfide functionalized polymers were applied to nanotherapeutic platforms,[9] the kinase inhibitors based on an o-aminopyridyl alkynyl scaffold were took as potential treatment for inflammatory disorders,[10] pyridyl-benzimidazoles were used as chemical tools to probe cancer,[11] and the complexes formed via pyridyl derivatives and different metals were applied to biological antibacterial activity[12,13] and catalysis.[14] Also pyridyl is an aromatic group and has good optical activity.[4–6] If an aromatic group is connected with a second substituted phenyl ring through the vinylene linkage, the molecule with long chain-conjugated system (such as stilbene and 1-furyl/thienyl-2-arylethylene derivatives) will be formed, which plays an important role in photochemistry.[15–17]

Up to now, there are mainly three kinds of parameters describing the electronic effects of substituents attached to the aromatic ring[18]: the ground state substituent constant (e.g., Hammett constant σ[19]), the free radical state substituent constant (e.g., spin delocalization effect constant $\sigma^{\bullet}_{JJ}$,[20]) and the excited-state substituent

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constant (e.g., σ_{CC}^{ex} [21–25]). Hammett constant σ and spin delocalization effect constant $\sigma_{JJ}^{\bullet}$ were applied well in the molecules being in the ground state and radical state respectively,[26–28] but they were less successful in the molecular excited state. Therefore, Cao et al.[21] proposed an excited-state substituent constant σ_{CC}^{ex} to distinguish from the substituent constants of the ground state and the free radical state. The constant σ_{CC}^{ex} together with constant σ were successfully applied to quantify the ultraviolet (UV) absorption wavelength,[29–32] nuclear magnetic resonance (NMR) chemical shift,[33–35] reduction potential (E_{red}),[36,37] and infrared (IR) absorption frequency[38,39] of substituted stilbenes, bi-aryl Schiff bases, and other kinds of conjugated organic compounds.

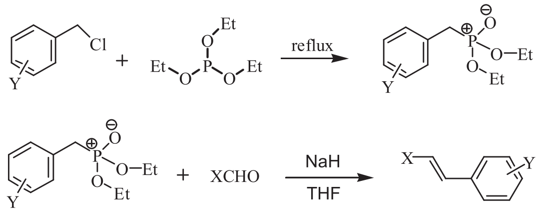
As regarding a successful quantitative structure property relationship of organic molecule involving the excited state, the key is acquisition of the excited-state substituent constant. However, it is an arduous work for the acquisition of the excited-state substituent constants of numerous substituents. A lot of efforts have been made for this goal. Cao et al.[21–23] extracted the excited-state substituent constants of some meta- and para-substituents via synthesizing a series of substituted stilbene derivatives and recording their UV spectra. Qu et al.[24] synthesized 1-furanyl/thienyl-2- arylethene compounds and formed a data set by employing the UV data of their synthesized compounds and the other compounds reported in the literature.[40–42] Then they obtained the excited-state substituent constants of furanyl and thienyl groups by means of curve-fitting method. Recently, Cao et al.[25] extracted the excited-state substituent constants of seven ortho-substituents by using 2,4′-disubstituted stilbenes as model compounds, in which the influence of steric effects of ortho-substituents on UV spectra were deducted. It is noteworthy that Dobrowolski et al.[43,44] recently performed a meaningful theoretical exploration in studying on excited-state substituent effect. They, using quantum chemistry method, calculated the electron donor–acceptor effect of some substituents on the first excited state (singlet and triplet states) of mono-substituted benzenes. Their works provide a new way for studying excited-state substituent effect.

It is known that there are many organic compounds containing pyridyl or substituted phenyl, which are widely used, especially in the fields of photochemistry and photophysics. However, now there are no available excited-state substituent constants of pyridyl and substituted phenyl. The lack of excited-state substituent constants of pyridyl and substituted phenyl brings difficulty of studying the properties, involving the excited state (e.g., photo electric conversion, UV absorption, and fluorescence emission), of these molecules containing pyridyl or substituted phenyl. Therefore, in this work, authors intend to synthesize a series of 1-pyridyl-2-arylethenes XCH=CHArY (XAEY, X = 2-pyridyl, 3-pyridyl, or 4-pyridyl) and try to extract the excited-state substituent constants of pyridyl by measuring their wavelength of UV absorption maximum λ_{max}. In addition, basing on the λ_{max} values of bi-arylethenes and the extracting method of excited-state substituent constants reported by Cao et al.,[21–23,25] this work also intends to collect the λ_{max} values of 1-substituted phenyl-2-arylethenes $ZC_6H_4CH{=}CHArY$ (XAEY, where X indicates the substituted phenyl, ZC_6H_4) dispersing in the literature,[22–24,40–42] and to extract the excited-state substituent constants of substituted phenyl via treating the substituted phenyl moiety as an independent group, then to verify the obtained excited-state substituent constants of pyridyl and substituted phenyl. It is expected to provide molecular structure parameters for the quantitative correlation of optical properties of conjugated organic compounds containing aryl.

2 | EXPERIMENTAL SECTIONS

2.1 | Synthesis of 1-pyridyl-2-arylethene

The model compounds were synthesized by the method of Qu et al.,[24] as shown in Figure 1. In a 100-ml flask, triethyl phosphite (15 mmol) and substituted benzyl chloride (15 mmol) were mixed and continuously stirred for 4 h at reflux temperature. After cooling reaction solution to room temperature without separating the intermediate product (substituted benzyl triethyl phosphate), pyridyldehyde (12 mmol) and tetrahydrofuran (THF, 20 ml) were added in successively, and then NaH (45 mmol) was added in slowly under ice water bath conditions. The reaction mixture was heated to reflux for 1 h. Stop heating, the reaction mixture was cooled to room temperature and poured into a beaker containing 100 ml of ice water with constant stirring. If there are



X = 2-pyridyl, 3-pyridyl or 4-pyridyl
Y (*m* or *p*) = OMe, Me, H, Br, Cl, F, CF_3, or CN

FIGURE 1 X = 2-pyridyl, 3-pyridyl or 4-pyridyl. Y (*m* or *p*) = OMe, Me, H, Br, Cl, F, CF_3, or CN. Synthesis of model compounds XCH=CHArY (XAEY) immediately precipitated solids, the solids was collected by filter and then recrystallized in anhydrous ethanol. If not, the reaction mixture was extracted with ethyl acetate, and then solids were precipitated successively by evaporating solvent. Their E-isomers were obtained by means of chromatographic column separation and confirmed by the magnitude of ^{1}H–^{1}H coupling constant in NMR. The molecular structures of model compounds were characterized by NMR spectrum (^{1}H NMR and ^{13}C NMR) and mass spectrum (Ms). Their NMR data and spectra can be seen in supporting information.

2.2 | Determination of UV spectrum of 1-pyridyl-2-arylethene

Employ anhydrous ethanol as solvent; the model compounds were dissolved (concentration about 6×10^{-3} mol·L^{-1}), and all solutions were prepared freshly. For each compound, add first a 3-ml anhydrous ethanol to three sample cells, respectively, and then add 5, 10, and 15 μl of compound solutions to the cells; in turn, their UV absorption spectra were recorded by UV-1800 (SHIMADZU, Japan), scanning range 200 to 500 nm. Take anhydrous ethanol as reference, and the mean value of wavelength of absorption maximum $\lambda_{\max}$ (nm) was used for each sample. Then the $\lambda_{\max}$ values were converted to the wavenumber $\nu_{\max}$ (cm^{-1}, $\nu_{\max} = 1 \times 10^7/\lambda_{\max}$) values, which were listed in Table 1.

3 | DETERMINING THE $\sigma_{\mathrm{CC}}^{\mathrm{EX}}$ VALUES OF PYRIDYL AND SUBSTITUTED PHENYL

3.1 | Determining the $\sigma_{\mathrm{cc}}^{\mathrm{ex}}$ values of pyridyl

Qu et al.[24] investigated systematically the $\nu_{\max}$ change regularity of UV absorption for substituted styrene derivatives (XAEY) and established a correlation Equation 1.

$$\begin{aligned}\nu_{\max} = {} & 40278.6 + 320.99\sigma(\mathrm{Y}) + 12041.65\sigma_{(p)}(\mathrm{X}) + 3325.01\sigma_{\mathrm{CC}}^{\mathrm{ex}}(\mathrm{Y}) \\ & + 9002.15\sigma_{\mathrm{CC}(p)}^{\mathrm{ex}}(\mathrm{X}) - 4431.1\Delta\sigma^2 + 1881.9\sigma_{\mathrm{CC}}^{\mathrm{ex}}(\mathrm{XY}) \\ & \mathrm{R} = 0.9963, \mathrm{S} = 302.90, \mathrm{F} = 1878.39, \mathrm{n} = 90\end{aligned} \tag{1}$$

In Equation 1, $\sigma_{(p)}(\mathrm{X})$ and $\sigma(\mathrm{Y})$ are Hammett constants of X and Y, respectively. $\sigma_{\mathrm{CC}(p)}^{\mathrm{ex}}(\mathrm{X})$ and $\sigma_{\mathrm{CC}}^{\mathrm{ex}}(\mathrm{Y})$ are excited-state substituent constants of X and Y, respectively. $\Delta\sigma^2$ is the substituent specific cross-interaction effect expressed with σ between X and Y, that is, $\Delta\sigma^2 = [\sigma(\mathrm{Y})-\sigma_{(p)}(\mathrm{X})]^2$, and, based on Qu's report,[24] $\Delta\sigma^2 = 0$ in case of X being H or Ph group. $\sigma_{\mathrm{CC}}^{\mathrm{ex}}(\mathrm{XY})$ is the cross-interaction effect expressed with $\sigma_{\mathrm{CC}}^{\mathrm{ex}}$ between X and Y, that is, $\sigma_{\mathrm{CC}}^{\mathrm{ex}}(\mathrm{XY}) = \sigma_{\mathrm{CC}(p)}^{\mathrm{ex}}(\mathrm{X}) \times \sigma_{\mathrm{CC}}^{\mathrm{ex}}(\mathrm{Y})$. The correlation of Equation 1 is very good, in which the correlation coefficient (R) is 0.9963, the standard deviation (S) is only 302.90, and Fisher ratio (F) is 1878.39. Thus, we use Equation 1 as the original reference equation to simulate the $\sigma_{\mathrm{CC}(p)}^{\mathrm{ex}}$ values of 2-pyridyl, 3-pyridyl and 4-pyridyl in Table 1. Take the determining $\sigma_{\mathrm{CC}(p)}^{\mathrm{ex}}$ of substituent 2-pyridyl for an example; the $\nu_{\max}$ values of compounds 2-pyridyl-AEY (Table 1, nos. 1–12) have been measured. In Equation 1, the values of $\sigma(\mathrm{Y})$ and $\sigma_{\mathrm{CC}}^{\mathrm{ex}}(\mathrm{Y})$ of substituents CN, CF_3, F, Cl, Br, H, OMe, and Me all are known, and the value of $\sigma_{(p)}(\mathrm{X})$ of substituent 2-pyridyl is also known, while the $\sigma_{\mathrm{CC}(p)}^{\mathrm{ex}}$ value of substituent 2-pyridyl must be a fixed value in the compounds 2-pyridyl-AEY. Further, by introducing the $\sigma(\mathrm{Y})$, $\sigma_{\mathrm{CC}}^{\mathrm{ex}}(\mathrm{Y})$, $\sigma_{(p)}(\mathrm{X})$ values and the measured values of $\nu_{\max}$ into Equation 1, the method of curve fitting was used to simulate the most appropriate $\sigma_{\mathrm{CC}(p)}^{\mathrm{ex}}$ value of substituent 2-pyridyl. With above stated way, we obtained 3 para-substituent constants $\sigma_{\mathrm{CC}(p)}^{\mathrm{ex}}$ of 2-pyridyl, 3-pyridyl, and 4-pyridyl for the E-isomers XAEY, as shown in Table 2 (nos. 1–3).

3.2 | Determining the $\sigma_{\mathrm{cc}}^{\mathrm{ex}}$ values of substituted phenyl

In order to obtain the excited-state substituent constants of substituted phenyl, we collected the $\nu_{\max}$ values of 234 samples of 1-substituted phenyl-2-arylethenes (XAEY, here X indicates substituted phenyl) reported in the literature[22–24,40–42] (see nos. 125–358 of Table S1). As we did in Section 3.1, fixing the X group, using Equation 1 as the original reference equation, and introducing the $\sigma(\mathrm{Y})$ and $\sigma_{\mathrm{CC}}^{\mathrm{ex}}(\mathrm{Y})$ values and the measured values of $\nu_{\max}$ into Equation 1, we simulate the most appropriate $\sigma_{\mathrm{CC}(p)}^{\mathrm{ex}}$ value of each substituted phenyl. The obtained $\sigma_{\mathrm{CC}(p)}^{\mathrm{ex}}$ values of substituted phenyls were listed in Table 2 (nos. 4–26).

4 | RESULT DISCUSSION

4.1 | The reliability of the $\sigma_{\mathrm{CC}(\boldsymbol{p})}^{\mathrm{ex}}$ values

The $\sigma_{\mathrm{CC}(p)}^{\mathrm{ex}}$ values of Table 2 were obtained by employing each series of XAEY compounds via fixing X group and changing Y group. Whether these $\sigma_{\mathrm{CC}(p)}^{\mathrm{ex}}$ values are applicable in a wider range of compounds should also be verified. To verify the reliability of the $\sigma_{\mathrm{CC}(p)}^{\mathrm{ex}}$ values in

TABLE 1 The wavelength of absorption maximum λ_{max} (nm) and its wavenumber ν_{max} (cm^{-1}) of UV absorption spectra for XAEY and the substituent constants for substituents X and Y

No.	X	Y	$\sigma(Y)$[a]	$\sigma_p(X)$[a]	$\sigma^{ex}_{CC}(Y)$[b]	$\sigma^{ex}_{CC}(X)$[b]	λ_{max}[c]	ν_{max}[d]
1	2-pyridyl	*p*-CN	0.66	0.17	−0.70	−1.10	320.0	31,250
2	2-pyridyl	*p*-CF_3	0.54	0.17	−0.12	−1.10	309.3	32,331
3	2-pyridyl	*p*-F	0.06	0.17	0.06	−1.10	310.9	32,165
4	2-pyridyl	*p*-Cl	0.23	0.17	−0.22	−1.10	315.0	31,746
5	2-pyridyl	*p*-Br	0.23	0.17	−0.33	−1.10	312.4	32,010
6	2-pyridyl	H	0	0.17	0	−1.10	310.5	32,206
7	2-pyridyl	*p*-CH_3	−0.17	0.17	−0.17	−1.10	316.0	31,646
8	2-pyridyl	*p*-OCH_3	−0.27	0.17	−0.50	−1.10	326.8	30,600
9	2-pyridyl	*m*-CN	0.56	0.17	0.56	−1.10	305.4	32,744
10	2-pyridyl	*m*-F	0.34	0.17	0.02	−1.10	309.5	32,310
11	2-pyridyl	*m*-Cl	0.37	0.17	0.02	−1.10	309.2	32,342
12	2-pyridyl	*m*-CH_3	−0.07	0.17	−0.03	−1.10	312.4	32,010
13	3-pyridyl	*p*-CN	0.66	0.25	−0.70	−1.17	316.9	31,556
14	3-pyridyl	*p*-CF_3	0.54	0.25	−0.12	−1.17	305.5	32,733
15	3-pyridyl	*p*-F	0.06	0.25	0.06	−1.17	306.0	32,680
16	3-pyridyl	*p*-Cl	0.23	0.25	−0.22	−1.17	310.8	32,175
17	3-pyridyl	*p*-Br	0.23	0.25	−0.33	−1.17	312.6	31,990
18	3-pyridyl	H	0	0.25	0	−1.17	305.8	32,701
19	3-pyridyl	*p*-CH_3	−0.17	0.25	−0.17	−1.17	311.7	32,082
20	3-pyridyl	*p*-OCH_3	−0.27	0.25	−0.50	−1.17	323.1	30,950
21	3-pyridyl	*m*-CN	0.56	0.25	0.56	−1.17	300.7	33,256
22	3-pyridyl	*m*-F	0.34	0.25	0.02	−1.17	305.9	32,690
23	4-pyridyl	*p*-CN	0.66	0.44	−0.70	−1.39	313.8	31,867
24	4-pyridyl	*p*-CF_3	0.54	0.44	−0.12	−1.39	304.8	32,808
25	4-pyridyl	*p*-F	0.06	0.44	0.06	−1.39	308.2	32,446
26	4-pyridyl	*p*-Cl	0.23	0.44	−0.22	−1.39	312.2	32,031
27	4-pyridyl	*p*-Br	0.23	0.44	−0.33	−1.39	313.4	31,908
28	4-pyridyl	H	0	0.44	0	−1.39	307.6	32,510
29	4-pyridyl	*p*-CH_3	−0.17	0.44	−0.17	−1.39	314.4	31,807
30	4-pyridyl	*p*-OCH_3	−0.27	0.44	−0.50	−1.39	327.0	30,581
31	4-pyridyl	*m*-CN	0.56	0.44	0.56	−1.39	293.3	34,095
32	4-pyridyl	*m*-CF_3	0.43	0.44	0.09	−1.39	294.7	33,933
33	4-pyridyl	*m*-F	0.34	0.44	0.02	−1.39	306.0	32,680
34	4-pyridyl	*m*-Cl	0.37	0.44	0.02	−1.39	300.0	33,333
35	4-pyridyl	*m*-CH_3	−0.07	0.44	−0.03	−1.39	309.1	32,352
36	4-pyridyl	*m*-OCH_3	0.12	0.44	0.10	−1.39	300.7	33,256

[a] The values were taken from Hansch et al.[45]

[b] The values were taken from other studies.[21–24]

[c] The λ_{max} were obtained by this work.

[d] $\nu_{max} = 1 \times 10^7/\lambda_{max}$.

Table 2, we collected the ν_{max} values of 358 compounds with the same parent structural unit, which involve 36 compounds synthesized in this work and 322 compounds reported in the literature (see Table S1), and got a complex ν_{max} data set. Then we performed a regression analysis via using the ν_{max} of 358 compounds

TABLE 2 The $\sigma^{ex}_{CC(p)}$ values of pyridyl and substituted phenyl groups

No.	Substituent	$\sigma^{ex}_{CC(p)}$	No.	Substituent	$\sigma^{ex}_{CC(p)}$	No.	Substituent	$\sigma^{ex}_{CC(p)}$
1	2-pyridyl	−1.10	10	m-C≡CHC$_6$H$_4$	−1.00	19	p-MeC$_6$H$_4$	−0.82
2	3-pyridyl	−1.37	11	m-MeOC$_6$H$_4$	−0.86	20	p-FC$_6$H$_4$	−0.87
3	4-pyridyl	−1.39	12	m-MeC$_6$H$_4$	−0.85	21	p-ClC$_6$H$_4$	−1.04
4	m-NO$_2$C$_6$H$_4$	−0.96	13	m-FC$_6$H$_4$	−0.95	22	p-NMe$_2$C$_6$H$_4$	−1.13
5	m-IC$_6$H$_4$	−0.90	14	m-ClC$_6$H$_4$	−0.95	23	p-MeOC$_6$H$_4$	−0.85
6	m-CH=CH$_2$C$_6$H$_4$	−1.04	15	m-BrC$_6$H$_4$	−0.95	24	p-EtC$_6$H$_4$	−0.87
7	m-PhC$_6$H$_4$	−1.05	16	m-CF$_3$C$_6$H$_4$	−0.95	25	p-CNC$_6$H$_4$	−1.46
8	m-EtC$_6$H$_4$	−1.07	17	m-CNC$_6$H$_4$	−0.95	26	p-CF$_3$C$_6$H$_4$	−1.26
9	m- NMe$_2$C$_6$H$_4$	−0.99	18	m-PhOC$_6$H$_4$	−1.10			

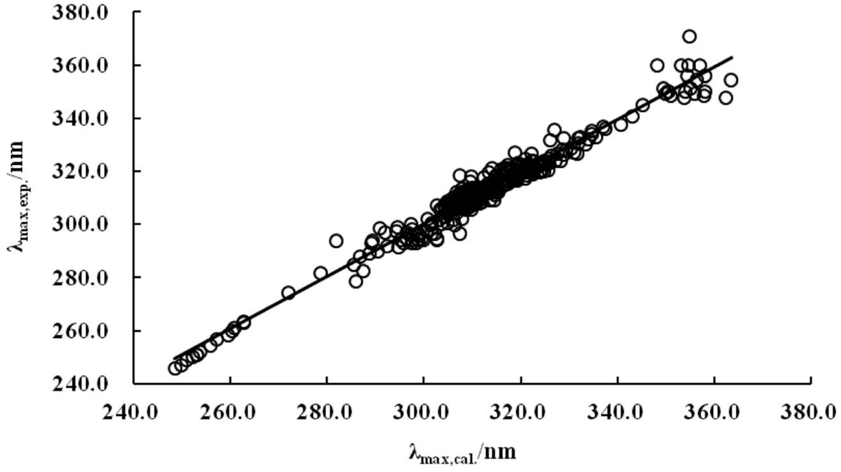


FIGURE 2 Plot of the experimental $\lambda_{max,exp.}$ versus the calculated $\lambda_{max,cal}$. By Equation 2 for the 358 compounds of Tables 2 and S1

against Hammett constants σ and the excited-state substituent constants σ^{ex}_{CC} of substituents X and Y and obtained Equation 2.

$$\begin{aligned}\nu_{max} &= 40034.61 + 147.20\sigma(\mathrm{Y}) + 12382.88\sigma_{(p)}(\mathrm{X}) + 2960.17\sigma^{ex}_{CC}(\mathrm{Y}) \\ &\quad + 9069.64\sigma^{ex}_{CC(p)}(\mathrm{X}) - 1887.36\Delta\sigma^2 + 1387.62\sigma^{ex}_{CC}(\mathrm{XY}) \\ &R = 0.9862, S = 334.23, F = 2083.33, n = 358\end{aligned} \tag{2}$$

It can be observed that the correlation of Equation 2 is good. Therefore, we recommend Equation 2 to express the ν_{max} change regularity of the 358 compounds XAEY. Calculating ν_{max} values with Equation 2 and converting them to λ_{max}, the result shows the average absolute error only 2.4 nm between the calculated and the experimental λ_{max} values, which is within the experimental error. To observe the calculation results of Equation 2 more intuitively, we plotted the experimental values against the calculated ones and obtained Figure 2. It can be seen that the experimental $\lambda_{max,exp.}$ values are in good agreement with the calculated $\lambda_{max,cal.}$ values by Equation 2. It should be noted that the compounds used in Equation 2 far exceed those compounds used to determine the $\sigma^{ex}_{CC(p)}$ values of pyridyl and substituted phenyl in Table 2 and the quantitative correlation result of Equation 2 still is good. It shows that the excited-substituent constants of pyridyl and substituted phenyl groups in Table 2 are reliable.

4.2 | Comparing σ^{ex}_{CC} with σ

For the convenience of the readers, we collected the σ^{ex}_{CC} values existing in the literature[21–25,46] and the σ^{ex}_{CC} values of this work (Table 2) and listed them in Table 3. There are total of 70 different groups (involving 93 σ^{ex}_{CC} values) in Table 3, which can provide the excited-state substituent constants for the quantitative structure-optical property relationship study of organic compounds. Further, we plotted the σ^{ex}_{CC} of substituents in Table 3 against Hammett constants σ[45] of the corresponding substituents and obtained Figure 3. Figure 3 shows no good linear relationship between the σ^{ex}_{CC} and σ, indicating that σ^{ex}_{CC} and σ express different electronic effects of substituents.

TABLE 3 Excited-state constant σ^{ex}_{CC} values of substituents

No.	Substituent	$\sigma^{ex}_{CC(o)}$ [a]	$\sigma^{ex}_{CC(m)}$ [b]	$\sigma^{ex}_{CC(p)}$ [c]	No.	Substituent	$\sigma^{ex}_{CC(o)}$ [a]	$\sigma^{ex}_{CC(m)}$ [b]	$\sigma^{ex}_{CC(p)}$ [c]
1	NH_2			−0.88	36	Ph		0.01	−0.86
2	OH		0.47	−0.19	37	NMe_2		0.17	−1.81
3	SH			−0.82	38	PhO		0	−1.52
4	CHO			−1.09	39	2-furyl			−0.97
5	NEt_2			−1.31	40	3-furyl			−0.46
6	H		0	0	41	2-thienyl			−1.09
7	NO_2		0.66	−1.17	42	3-thienyl			−0.66
8	$CHCH_2$		0.08	−1.13	43	2′-methyl2-furyl			−1.25
9	NHEt			−1.06	44	2′-methyl2-thienyl			−1.08
10	CCH		0.18	−1.05	45	2-pyridyl			−1.10
11	SO_2NH_2			−0.39	46	3-pyridyl			−1.37
12	COOH			−0.7	47	4-pyridyl			−1.39
13	$CF{=}CF_2$			−0.92	48	*m*-$NO_2C_6H_4$			−0.96
14	C (Me)$=CH_2$			−0.98	49	*m*-IC_6H_4			−0.90
15	CH (OH)CH_2COOPr			−0.17	50	*m*-$CH{=}CH_2C_6H_4$			−1.04
16	CH (OH)CH_2CCH			−0.15	51	*m*-PhC_6H_4			−1.05
17	Et		−0.06	−0.13	52	*m*-EtC_6H_4			−1.07
18	OMe	−0.74	0.10	−0.5	53	*m*- $NMe_2C_6H_4$			−0.99
19	F	0.06	0.02	0.06	54	*m*-$C{\equiv}CHC_6H_4$			−1.00
20	Cl	−0.28	0.02	−0.22	55	*m*-$MeOC_6H_4$			−0.86
21	Br	−0.43	−0.03	−0.33	56	*m*-MeC_6H_4			−0.85
22	I		0.05	−0.56	57	*m*-FC_6H_4			−0.95
23	CN		0.56	−0.7	58	*m*-ClC_6H_4			−0.95
24	MeCO			−1.13	59	*m*-BrC_6H_4			−0.95
25	$SiMe_3$			−0.13	60	*m*-$CF_3C_6H_4$			−0.95
26	t-Bu			−0.17	61	*m*-CNC_6H_4			−0.95
27	$MeSO_2$			−0.43	62	*m*-$PhOC_6H_4$			−1.10
28	MeSO			−0.6	63	*p*-MeC_6H_4			−0.82
29	Me	0.03	−0.03	−0.17	64	*p*-FC_6H_4			−0.87
30	COOMe			−0.69	65	*p*-ClC_6H_4			−1.04
31	OCOMe			−0.08	66	*p*-$NMe_2C_6H_4$			−1.13
32	SMe			−1.4	67	*p*-$MeOC_6H_4$			−0.85
33	CF_3	−0.11	0.09	−0.12	68	*p*-EtC_6H_4			−0.87
34	*c*-propanyl			−0.34	69	*p*-CNC_6H_4			−1.46
35	$CONH_2$			−0.61	70	*p*-$CF_3C_6H_4$			−1.26

[a] $\sigma^{ex}_{CC(o)}$ is the excited-state substituent constant of *ortho*-substituent. The $\sigma^{ex}_{CC(o)}$ values were taken from Cao et al.[25]

[b] $\sigma^{ex}_{CC(m)}$ is the excited-state substituent constant of *meta*-substituent. The $\sigma^{ex}_{CC(m)}$ values were taken from other studies.[22,23,46]

[c] $\sigma^{ex}_{CC(p)}$ is the excited-state substituent constant of *para*-substituent. The $\sigma^{ex}_{CC(p)}$ values of nos. 1–44 were taken from other studies[21,24]; the rest of $\sigma^{ex}_{CC(p)}$ values were obtained by this work.

4.3 | Application of $\sigma^{ex}_{CC(p)}$ in quantifying the λ_{max} of bi-aryl Schiff bases

Further, to test the availability of $\sigma^{ex}_{CC(p)}$ values in Table 2, we synthesized nine samples of bi-aryl Schiff bases (XCH=NArY-*p*, where X is 2-pyridyl, 3-pyridyl, or 4-pyridyl) and measured their λ_{max} of UV absorption in anhydrous ethanol (Table 4). In addition, we also collected the λ_{max} values of 117 samples of bi-aryl Schiff bases (XCH=NArY, where the X is substituted phenyl groups) reported in the literature[24,29–31] (Table S2, nos. 10–126). Converting the λ_{max} values of above 126 compounds into ν_{max} values, then we made a regression analysis of the ν_{max} values against Hammett constants and excited-state substituent constants of X and Y groups, and obtained Equation 3.

$$\nu_{max} = 35144.99 + 2678.85\sigma_{(p)}(X) + 1019.54\sum\sigma_F(Y) + 2222.80\sum\sigma_R(Y) + 3773.36\sigma^{ex}_{CC}(X) + 889.49\sum\sigma^{ex}_{CC}(Y) - 2167.88\Delta\sigma^2$$
$$R = 0.9723, S = 396.49, F = 343.50, n = 126 \tag{3}$$

In Equation 3, the parameters $\Sigma\sigma_F(Y)$ and $\Sigma\sigma_R(Y)$ indicate the sum of induced and conjugated effect constants of groups Y at the aniline ring, respectively, that is, $\Sigma\sigma_F(Y) = \sigma_F(Y_1) + \sigma_F(Y_2)$, $\Sigma\sigma_R(Y) = \sigma_R(Y_1) + \sigma_R(Y_2)$. $\sum\sigma^{ex}_{CC}(Y)$ indicates the sum of excited-state

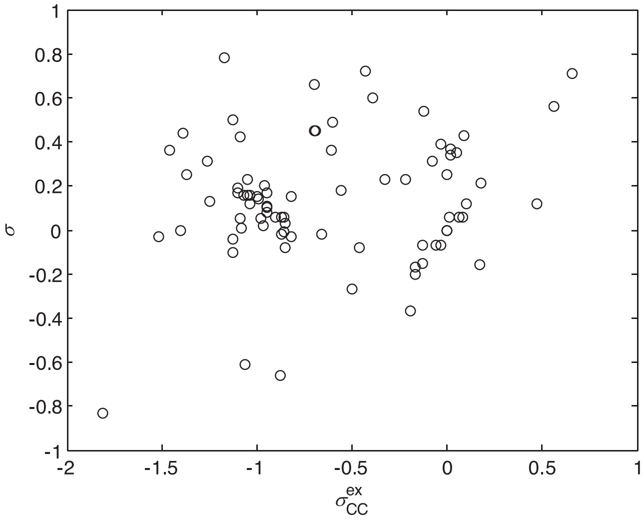


FIGURE 3 Plot of Hammett constants (σ) versus excited-state substituent constants (σ^{ex}_{CC})

TABLE 4 Experimental and calculated λ_{max} (nm) and ν_{max} (cm^{-1}) values of pyridyl-CH=NArY

No.	Pyridyl	Y	$\lambda_{max,exp.}$[a]	$\nu_{max,exp.}$[a]	$\lambda_{max,cal.}$[b]	$\nu_{max,cal.}$[b]	$\Delta\lambda_{max}$[c]
1	2-pyridyl	*p*-F	320.0	31,250	322.0	31,058	−2.0
2	2-pyridyl	*p*-Cl	322.0	31,056	320.1	31,242	1.9
3	2-pyridyl	*p*-OMe	341.5	29,283	337.5	29,626	4.0
4	3-pyridyl	*p*-Cl	318.6	31,387	320.4	31,216	−1.8
5	3-pyridyl	*p*-OMe	341.4	29,291	339.8	29,426	1.6
6	4-pyridyl	*p*-Cl	325.4	30,731	324.5	30,812	0.9
7	4-pyridyl	H	322.0	31,056	326.0	30,678	−4.0
8	4-pyridyl	*p*-Me	331.8	30,139	336.1	29,750	−4.3
9	4-pyridyl	*p*-OMe	348.1	28,727	349.5	28,611	−1.4

[a] The values were obtained by this work.

[b] The $\nu_{max,cal.}$ values were calculated by Equation 3. $\lambda_{max,cal.} = 1 \times 10^7/\nu_{max,cal.}$.

[c] $\Delta\lambda_{max} = \lambda_{max,exp.} - \lambda_{max,cal.}$.

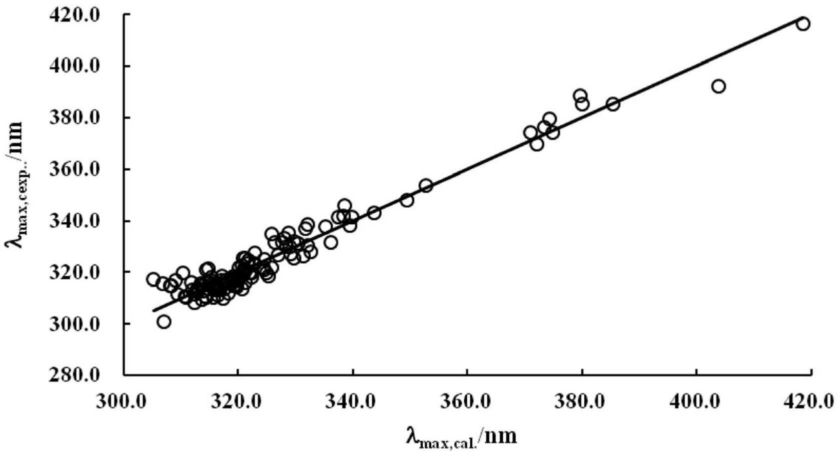


FIGURE 4 Plot of the experimental $\lambda_{max,exp.}$ versus the calculated $\lambda_{max,cal.}$ by Equation 3 for the 126 bi-aryl Schiff bases (XCH=NArY) of Tables 4 and S2

substituent constants of groups Y, that is, $\sum\sigma^{ex}_{CC}(Y)=\sigma^{ex}_{CC}(Y_1)+\sigma^{ex}_{CC}(Y_2)$. We calculated ν_{max} values with Equation 3 and converted them to λ_{max}. The result indicates that the average absolute error between the calculated wavelength values and the experimental ones of the 126 compounds was only 3.2 nm. Figure 4 is the plot of calculated $\lambda_{max,cal.}$ values by Equation 3 versus the experimental ones, which shows that the calculated λ_{max} values are in good agreement with the experimental ones. It should be noted that the parent molecular skeleton of styrene is XCH=CHArY, while that of Schiff bases is XCH=NArY; their molecular skeletons are different from each other. That is, the former has a nonpolar bridge bond CH=CH connecting two aromatic rings, while the latter has a polar bridge bond CH=N connecting two aromatic rings. However, the $\sigma^{ex}_{CC(p)}(X)$ values in Table 2 are still well applied in quantifying the ν_{max} of Schiff bases, which further verified that the obtained $\sigma^{ex}_{CC(p)}$ values are reliable.

5 | CONCLUSION

A series of 1-pyridyl-2-arylethylene compounds (XCH=CHArY) were synthesized, and their λ_{max} values of UV absorption were recorded in anhydrous ethanol. In addition, the λ_{max} values[22–24,40–42] of UV absorption wavelengths of 234 samples of 1-substituted phenyl-2-arylethenes were collected. Using Equation 1 (reported by Qu et al.[24]) as the original reference equation, 26 constants $\sigma^{ex}_{CC(p)}$ values of X groups (including three pyridyl and 23 substituted phenyl groups) were determined by means of curve-fitting method. These obtained $\sigma^{ex}_{CC(p)}$ values were verified by the ν_{max} quantitative correlation of 358 bi-arylethene derivatives. Further, nine samples of bi-aryl Schiff bases (XCH=NArY, here X = pyridyl) were synthesized. Using the synthesized nine compounds of this work and the 117 bi-aryl Schiff bases reported in the literature,[24,29–31] a quantitative correlation analysis of the ν_{max} (total of 126 compounds) was performed, and the result was good and further verified that the obtained $\sigma^{ex}_{CC(p)}$ values are reliable. The acquisition of $\sigma^{ex}_{CC(p)}$ values of pyridyl and substituted phenyl groups expanded the range of excited-state substituent constants of para-substituent in organic chemistry, which will provide substituent parameters for the study or application of the optical properties and the molecular design of optical materials for those organic conjugated compounds containing pyridyl and substituted phenyl.

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