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Influence of the methyl group at C=C bridging bond of stilbene on the longest wavelength maximum in ultraviolet absorption spectra

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Abstract

The compounds stilbenes XArCH=CHArY(XSBY) and 1,2-diphenylpropylenes XArC(Me)=CHArY(XSMBY) have bridging groups CH=CH and C(CH₃)=CH, respectively, in which the C(CH₃)=CH has a side-group CH₃ at the carbon-carbon double bond. A series of XSMBY were synthesized, and their longest wavelength maximum λ_{max} (nm) in ultraviolet absorption spectra were measured in this work. We investigated the change regularity of the ν_{max} (cm⁻¹, $\nu_{max} = 1/\lambda_{max}$) of XSMBY and compared it with that of XSBY. The results indicate that (1) there is no good linear relationship between the ν_{max} of XSMBY and that of XSBY. (2) Because of the influence of the side-group CH₃, in case of the same couple of groups X and Y, the λ_{max} of XSMBY is shorter than that of XSBY, that is, it has a blue shift. (3) The cross-interaction between the side-group CH₃ and Y has an important effect on the ν_{max} and can be ignored. (4) The specific cross-interaction between X and Y has important effect on the ν_{max} of XSMBY.

KEYWORDS

diphenyl propylene, side-group, stilbene, substituent effect, wavelength of ultraviolet absorption

1 | **INTRODUCTION**

Stilbene molecule has a classic π -conjugated system in which 2 benzene rings are connected by a carbon-carbon double bond. It has good chemical properties and is widely used in medicines, foods, functional materials, dyes, and other industries.^[1–9] Especially because of its good 2-photon absorption effect,^[10] molecular adjustability, excellent fatigue resistance, photoelectric discoloration, and fluorescence adjustability,^[11] it is prospected wide applications in many fields of optical functional materials. Therefore, stilbene derivatives received significant attention and were a hot point of the optical study in the past decades.^[12,13]

Stilbene and its derivatives were taken as model molecules for the study of luminophores,^[14,15] in which a chemical modification of the parent molecule was performed.

Then the relationship between the molecular structures and optical properties of the compounds was theoretically and experimentally explored, to find out the change regularity of their optical property for instructing the synthesis of various functional materials.^[16–18]

To quantify the influence of substituents at aromatic ring on the chemical property of aromatic compounds, in 1937, Hammett^[19] proposed σ -constant to express the contribution of substituent electronic effect to the ground-state molecule. Hammett constant σ was widely used but was less successful in quantifying the UV absorption spectra of organic compounds. In 2008, Cao et al.^[20] proposed excited-state substituent constant σ_{cc}^{ex} to express the contribution of substituent electronic effect to the excited-state molecule, and then they used the σ_{cc}^{ex} to quantify the UV absorption spectra of many kinds of compounds.^[21–25] They observed that the wave number ν_{max} (cm⁻¹, $\nu_{\text{max}} = 1/\lambda_{\text{max}}$) of the longest wavelength maximum λ_{max} (nm) of UV were mainly affected by the excited-state substituent constant σ_{cc}^{ex} for substituted benzene,^[20] stilbene,^[25,26] and conjugated polyene.^[18] Whereas the $\nu_{\rm max}$ of Schiff bases were affected by both σ_{cc}^{ex} and σ because of having a polar bridging bond C=N.^[24] It should be noted that the bridging group CH=CH in stilbene XArCH=CHArY (abbreviated XSBY) is a symmetrical group (ie, its right and left ends all are the CH). The π electrons are evenly distributed on the C=C double bond, in which the bridging group is nonpolar. If a hydrogen on the carbon of the bridging group CH=CH is replaced by a methyl group the 1,2-diphenylpropylenes XArC(Me)=CHArY (Me), (abbreviated XSMBY) will be formed. Compared XSMBY with XSBY, there is an Me at the 2-position of XSMBY, and the Me must increase the steric effect among the groups at the bridging group. The bridging group C(Me)=CH is asymmetric and somewhat polar. Then what are the change characteristic of the λ_{max} of UV for XSMBY, and how is the regularity for the effect of substituents X and Y on their ν_{max} . It is an interesting and theoretical topic. Also, it must be a clear understanding theoretical topic for the application of optical materials of stilbene derivatives. Therefore, this paper studied on it and tried to find out the change regularity of λ_{max} of XSMBY.

2 | EXPERIMENTAL SECTIONS

2.1 | Synthesis of the model compounds

The target compounds were synthesized with Wittig-Honer reaction^[27] or Grignard reaction^[28] (as shown in Figure 1), and their molecular structures were characterized by nuclear magnetic resonance spectrum (The ¹H NMR and ¹³C NMR chemical shift data, spectra, and specific synthesis methods can be seen in Data S1).

2.2 | Determination of ultraviolet absorption spectrum

The anhydrous ethanol was fully dried with anhydrous $MgSO_4$ and used as the reference solution. The target

compounds were made solution (about 2.0 g/L) with anhydrous ethanol. Their UV-Vis spectra were recorded at room temperature (25°C), by UV-2550 (SHIMADZU, Japan), scanning range 200 to 500 nm and scanning speed of 10 nm/s. The spectrum of each target compound was tested for 3 times, and the mean value of λ_{max} was used for each sample. The λ_{max} (nm) and ν_{max} (cm⁻¹, $\nu_{max} = 1/\lambda_{max}$) values of all target compounds were collected and listed in Table 1. (The UV spectra can be seen in Data S1).

3 | EFFECT OF SUBSTITUENT ON THE ν_{MAX}

3.1 | Effect of substituent on the ν_{max} of XSMBY

Cao et al.^[30] used 2-parameter Equation 1 to quantify the ν_{max} of UV absorption for XSBY.

$$\begin{split} \nu_{\text{max}} &= 32418.29 + 2087.889 \ \Sigma \sigma_{cc}^{ex} + 697.1173 \ \sigma_{cc}^{ex}(\text{XY}), \\ \text{R} &= 0.9951, \text{S} = 130.41, \text{F} = 1111.00, \text{n} = 25, \end{split}$$

where $\Sigma \sigma_{cc}^{ex}$ is the sum of excited-state substituent constants of X and Y, that is, $\Sigma \sigma_{cc}^{ex} = \sigma_{cc}^{ex}(X) + \sigma_{cc}^{ex}(Y)$; $\sigma_{cc}^{ex}(XY)$ is the cross-interaction effect between X and Y expressed with σ_{cc}^{ex} , that is, $\sigma_{cc}^{ex}(XY) = \sigma_{cc}^{ex}(X) \times \sigma_{cc}^{ex}(Y)$; in which, R is the correlation coefficient, S is the standard deviation, F is the Fisher ratio, and n is the date points of the regression equation, respectively.

We also tried to quantify the ν_{max} of Table 1 by using the 2 parameters of Equation 1, and Equation 2 was obtained.

$$\begin{split} \nu_{\text{max}} &= 36750.23 + 3642.151 \ \Sigma \sigma_{cc}^{ex} + 1266.097 \ \sigma_{cc}^{ex}(\text{XY}), \\ \text{R} &= 0.9053, \text{S} = 506.29, \text{F} = 93.09, \text{n} = 44. \end{split}$$

Compared with Equation 1, Equation 2 has poor correlation. It implies that the factors affecting the ν_{max} of XSMBY are different from these of XSBY. To investigate the relationship between the ν_{max} of XSBY and XSMBY, we selected some



X=H, Me, Et, OMe, F, Cl, Br, CF₃; Y=H, Me, F, Cl, Br, CN, CF₃

FIGURE 1 Synthesis of 1,2diphenylpropylenes with A, Wittig-Honer reaction or B, Grignard reaction

TABLE 1 The λ_{max} (nm) and ν_{max} (cm⁻¹) of UV spectra for XSMBY and the substituent constants values σ and σ_{cc}^{ex} for groups X and Y

No.	X	Y	$\sigma(\mathbf{X})^{\mathbf{a}}$	$\sigma(Y)^{a}$	$\sigma^{ex}_{cc}(X)^b$	$\sigma^{ex}_{cc}(Y)^b$	$\lambda_{\max exp.}^{c}$	$\nu_{\rm max\ exp.}^{\rm c}$
1	<i>р</i> -Н	<i>р</i> -Н	0.00	0.00	0.00	0.00	273.6	36 550
2	<i>р</i> -Н	<i>p</i> -F	0.00	0.06	0.00	0.06	272.1	36 751
3	<i>р</i> -Н	p-Cl	0.00	0.23	0.00	-0.22	278.5	35 907
4	<i>р</i> -Н	<i>p</i> -CN	0.00	0.66	0.00	-0.70	303.0	33 003
5	<i>р</i> -Н	p-CF ₃	0.00	0.54	0.00	-0.12	280.1	35 702
6	<i>p</i> -Me	<i>р</i> -Н	-0.17	0.00	-0.17	0.00	276.4	36 179
7	<i>p</i> -Me	<i>p</i> -Me	-0.17	-0.17	-0.17	-0.17	280.1	35 702
8	<i>p</i> -Me	<i>p</i> -F	-0.17	0.06	-0.17	0.06	274.7	36 403
9	<i>p</i> -Me	<i>p</i> -Cl	-0.17	0.23	-0.17	-0.22	282.3	35 423
10	<i>p</i> -Me	<i>p</i> -Br	-0.17	0.23	-0.17	-0.33	283.9	35 224
11	<i>p</i> -Me	<i>p</i> -CN	-0.17	0.66	-0.17	-0.70	297.3	33 639
12	<i>p</i> -Me	<i>p</i> -CF ₃	-0.17	0.54	-0.17	-0.12	285.7	35 005
13	<i>p</i> -Et	<i>р</i> -Н	-0.15	0.00	-0.13	0.00	276.7	36 144
14	<i>p</i> -Et	<i>p</i> -F	-0.15	0.06	-0.13	0.06	274.7	36 403
15	<i>p</i> -Et	p-Cl	-0.15	0.23	-0.13	-0.22	282.6	35 386
16	<i>p</i> -Et	<i>p</i> -CN	-0.15	0.66	-0.13	-0.70	303.7	32 930
17	<i>p</i> -Et	<i>p</i> -CF ₃	-0.15	0.54	-0.13	-0.12	286.6	34 892
18	<i>p</i> -OMe	<i>р</i> -Н	-0.27	0.00	-0.50	0.00	283.3	35 298
19	<i>p</i> -OMe	<i>p</i> -Me	-0.27	-0.17	-0.50	-0.17	284.5	35 149
20	<i>p</i> -OMe	<i>p</i> -F	-0.27	0.06	-0.50	0.06	281.1	35 575
21	<i>p</i> -OMe	p-Cl	-0.27	0.23	-0.50	-0.22	288.3	34 686
22	<i>p</i> -OMe	<i>p</i> -Br	-0.27	0.23	-0.50	-0.33	284.5	35 149
23	<i>p</i> -OMe	<i>p</i> -CN	-0.27	0.66	-0.50	-0.70	313.5	31 895
24	p-OMe	<i>p</i> -CF ₃	-0.27	0.54	-0.50	-0.12	294.1	33 999
25	<i>p</i> -F	<i>р</i> -Н	0.06	0.00	0.06	0.00	271.8	36 792
26	<i>p</i> -F	<i>p</i> -Me	0.06	-0.17	0.06	-0.17	275.6	36 284
27	<i>p</i> -F	<i>p</i> -F	0.06	0.06	0.06	0.06	270.3	36 996
28	<i>p</i> -F	p-Cl	0.06	0.23	0.06	-0.22	276.5	36 166
29	<i>p</i> -F	<i>p</i> -Br	0.06	0.23	0.06	-0.33	277.5	36 040
30	<i>p</i> -F	<i>p</i> -CN	0.06	0.66	0.06	-0.70	296.5	33 730
31	p-Cl	<i>р</i> -Н	0.23	0.00	-0.22	0.00	277.3	36 062
32	p-Cl	<i>p</i> -Me	0.23	-0.17	-0.22	-0.17	281.2	35 562
33	p-Cl	<i>p</i> -F	0.23	0.06	-0.22	0.06	269.9	37 055
34	p-Cl	p-Cl	0.23	0.23	-0.22	-0.22	282.1	35 448
35	p-Cl	<i>p</i> -Br	0.23	0.23	-0.22	-0.33	282.7	35 369
36	P-Cl	<i>p</i> -CN	0.23	0.66	-0.22	-0.70	297.8	33 580
37	p-Cl	p-CF ₃	0.23	0.54	-0.22	-0.12	282.6	35 386
38	<i>p</i> -Br	<i>р</i> -Н	0.23	0.00	-0.33	0.00	278.5	35 907
39	<i>p</i> -Br	<i>p</i> -Me	0.23	-0.17	-0.33	-0.17	283.1	35 323
40	<i>p</i> -Br	<i>p</i> -F	0.23	0.06	-0.33	0.06	277.4	36 049

(Continues)

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No.	X	Y	$\sigma(X)^{a}$	$\sigma(Y)^{a}$	$\sigma^{ex}_{cc}(X)^b$	$\sigma^{ex}_{cc}(Y)^b$	λ _{max exp.} c	ν _{max exp.} c
41	<i>p</i> -Br	p-Cl	0.23	0.23	-0.33	-0.22	282.9	35 348
42	<i>p</i> -Br	<i>p</i> -CN	0.23	0.66	-0.33	-0.70	298.8	33 467
43	<i>p</i> -Br	<i>p</i> -CF ₃	0.23	0.54	-0.33	-0.12	283.7	35 245

-0.12

0.66

^aThe values were taken from Hansch et al.^[29]

^bThe values were taken from Cao et al.^[20]

 $p-CF_3$

^cThe values were obtained by this work.

XSBY and XSMBY compounds containing the same couple of groups X and Y and plotted the experimental ν_{max} of XSBY against that of corresponding XSMBY (eg, p-FSBCN-p versus *p*-FSMBCN-*p*); Figure 2 was obtained.

p-CN

0.54

It can be observed in Figure 2 that the ν_{max} of XSBY versus XSMBY has no good correlation. Maybe their ν_{max} are affected by different factors. Therefore, the change regularity of the ν_{max} of XSMBY cannot be quantified well by only using the 2 parameters of Equation 1.

By analyzing the t-Stat values (Table 2).of the coefficients in front of variables in Equation 2, we can see that the contribution of item $\sigma_{cc}^{ex}(XY)$ is relatively small and can be ignored. Considering the bridging group that connected the 2 benzene rings in XSMBY is C(Me)=CH, its left and right ends are asymmetric and has somewhat polar; we think that the ground-state polar electronic effect (Hammett constant σ) of substituents X and Y may also play a role. According to Cao's method^[31] of quantifying the ν_{max} of Schiff bases, we also tried to add the substituent specific cross-interaction effect ($\Delta \sigma^2$) between X and Y, ie, $\Delta \sigma^2 = [\sigma(X) - \sigma(Y)]^2$. In addition, there may be interactions between Me of the bridging group and the substituents X or Y to affect the $\nu_{\rm max}$ then increase the interaction items ω^2 and χ^2 of Me versus X and Y, where $\omega^2 = [\sigma_p(Me)]$ $-\sigma(\mathbf{X})]^2$ $[-0.17 - \sigma(X)]^2$, = χ^2 = $[\sigma_{\rm p}({\rm Me})]$ $-\sigma(Y)$ ² = $[-0.17 - \sigma(Y)]^2$. Thus, we use the 4 parameters $\Sigma \sigma_{cc}^{ex}, \Delta \sigma^2, \omega^2$, and χ^2 to correlate the ν_{max} , and the Equation 3 was obtained.

$$\nu_{\text{max}} = 36699.28 + 2254.936 \ \Sigma \sigma_{cc}^{ex} - 1028.2\Delta \sigma^{2} + 697.7103\omega^{2} - 1401.37\chi^{2}, \text{R} = 0.9759, \quad (3)$$

S = 266.60, F = 195.06, n = 44.



FIGURE 2 Plot of the $\nu_{max exp.}$ of XSBY vs that of XSMBY

34 122

It is observed that the correlation of Equation 3 is much better than that of Equation 2. The t-Stat values (Table 3).of the coefficients in front of variables in Equation 3 show that the interaction item of the Me versus X is smaller. It means that the effect of item ω^2 on the ν_{max} can be ignored. Thus, we removed the item ω^2 , performed a regression analysis once again, and obtained Equation 4.

293.1

-0.70

$$\nu_{\text{max}} = 36728.99 + 2184.583 \ \Sigma \sigma_{cc}^{ex} - 1315.19 \Delta \sigma^2 - 1242.26 \chi^2,$$

$$\mathbf{R} = 0.9750, \mathbf{S} = 267.98, \mathbf{F} = 256.96, \mathbf{n} = 44.$$
(4)

Comparing Equation 4 with Equation 3, there are no obvious changes of the correlation coefficient and standard deviation, whereas the F value of Equation 4 is much increased. Hence, Equation 4 is recommended to quantify the change regularity of the ν_{max} for XSMBY. To more intuitively observe if the fitting data of Equation 4 is reasonable, we plotted the calculated values of Equation 4 against the experimental ones (see Figure 3).

It can be obtained from Figure 3 that the calculated values $\nu_{\text{max cal.}}$ of Equation 4 agree with the experimental values $\nu_{max exp.}$ for XSMBY. We converted the calculated $\nu_{max cal.}$ to $\lambda_{max cal.}$ and observed that the average absolute error of $\nu_{\text{max cal.}}$ versus $\nu_{\text{max exp.}}$ was only 1.37 nm; the maximum absolute error was 6.89 nm. It indicates that Equation 4 expresses the change regularity of the ν_{max} of XSMBY better.

3.2 | Effect of substituent on the ν_{max} of XSMBY and XSBY

Both XSMBY and XSBY have the stilbene molecular skeleton with the bridging group of carbon-carbon double bond but for the Me of bridging group in XSMBY. Can we propose a general quantitative equation to express the change regularity of their ν_{max} ? Therefore, we merged the 44 ν_{max} of Table 1 and the 25 ν_{max} of values of Cao's report^[30] into 1 data set (all

TABLE 2 The t-Stat values of parameters in Equation 2

Parameter	$\Sigma \sigma^{ex}_{cc}$	$\sigma^{ex}_{cc}(\mathrm{XY})$
t-Stat	8.74	0.72

TABLE 3 The t-Stat values of parameters in Equation 3



FIGURE 3 Plot of the calculated $\nu_{max cal.}$ with Equation 4 versus the experimental ones for XSMBY

69 samples of compounds, see Data S1) and performed the following quantitative correlation analysis.

Firstly, the 69 ν_{max} values were quantified by using Equation 5:

$$\nu_{\text{max}} = 32445.37 + 4267.889I + 2131.555 \ \Sigma \sigma_{cc}^{ex} - 1320.99\chi^2 - 1414.72\Delta \sigma^2 + 725.0323 \ \sigma_{cc}^{ex}(\text{XY}), \text{R} = 0.9956, \quad (5)$$

S = 226.85, F = 1429.08, n = 69.

In Equation 5, *I* is an indicator variable used for expressing the contribution of Me at the bridging group to the ν_{max} . The value of *I* is taken as 1 or 0, that is, for C(Me)=CH, *I* = 1; for CH=CH, *I* = 0. The meanings of items $\sigma_{cc}^{ex}(XY)$, χ^2 , and $\Delta\sigma^2$ can be seen in Equations 3 and 4. It should be noted that both the values of χ^2 and $\Delta\sigma^2$ all are 0, because the bridging group CH=CH of XSBY has no Me and is nonpolar. Equation 5 with 5 parameters has good correlation and small standard deviation. By analyzing the t-Stat values (Table 4). of the coefficients of Equation 5, we can see that the contribution of the item $\sigma_{cc}^{ex}(XY)$ is relatively small and can be ignored.

TABLE 4 The t-Stat values of parameters in Equation 5

Secondly, we removed item $\sigma_{cc}^{ex}(XY)$ and performed regression analysis once again. Then Equation 6 was obtained.

$$\nu_{\text{max}} = 32424.58 + 4274.216I + 2046.107 \ \Sigma \sigma_{cc}^{ex} -1320.88 \chi^2 - 1360.92 \Delta \sigma^2, \text{R} = 0.9954, \quad (6)$$

S = 230.25, F = 1733.33, n = 69.

Compared with Equation 5, the correlation coefficient and standard deviation of Equation 6 are much closed to these of Equation 5, and the F value is much increased. Therefore, we recommend Equation 6 to express the change regularity of the ν_{max} of both XSMBY and XSBY. Figure 4 is the plot of calculated $\nu_{max cal.}$ values with Equation 6 versus the experimental ones, which shows that the calculated $\nu_{max cal.}$ values are in agreement with the experimental ν_{max} exp. values.

4 | **RESULT DISCUSSION**

4.1 | Comparison of factors affecting ν_{max} of XSMBY and XSBY

Equation 4 showed that the ν_{max} of 1,2-(4-substituted phenyl) propene was mainly affected by 3 factors: the excited-state substituent constants of X and Y (ie, $\sum \sigma_{cc}^{ex}$), the substituentspecific cross-interaction effect between X and Y (ie, $\Delta \sigma^2$), and the interaction between Me of bridging group and the substituent Y (ie, χ^2). To compare the contribution of the 3 factors to the ν_{max} of XSMBY in Equation 4, we calculated the relative contributions (Ψ_r) or fraction contributions (Ψ_f), using Equations 7 and 8, respectively.^[32,33]

$$\Psi_{\gamma}(i) = m_i \overline{X}_i, \tag{7}$$

$$\Psi_f(i) = \frac{R^2 |\Psi_{\gamma}(i)|}{\sum_i |\Psi_{\gamma}(i)|} \times 100\%, \tag{8}$$



where the m_i and \overline{X}_i are the coefficient and the average value of the parameters in Equation 4 and *R* is the correlation coefficient of Equation 4.



TABLE 5 The relative and fraction contributions $(\Psi_r \text{ and } \Psi_f)$ of $\Sigma \sigma_{cc}^{ex}$, $\Delta \sigma^2$, and χ^2 in Equation 4

Variant	$\Sigma \sigma^{ex}_{cc}$	$\Delta\sigma^2$	χ^2
Ψ_r	895.68	-223.58	-310.57
$\Psi_{f}(\%)$	59.55	14.86	20.65

TABLE 6 The relative and fraction contributions $(\Psi_r \text{ and } \Psi_f)$ of $\Sigma \sigma_{cc}^{ex}$ and $\sigma_{cc}^{ex}(XY)$ in Equation 1

Variant	$\Sigma \sigma^{ex}_{cc}$	$\sigma^{ex}_{cc}(XY)$
Ψ_r	-1315.37	34.86
$\Psi_{f}(\%)$	96.47	2.56

TABLE 7 The comparison of λ_{max} (nm) of XSMBY with that of XSBY

		ax			λ _{max}				
X	Y	XSMBY	XSBY	$\Delta\lambda^{\mathbf{a}}$	Х	Y	XSMBY	XSBY	$\Delta\lambda^{a}$
<i>р</i> -Н	<i>р</i> -Н	273.6	307.8	34.2	<i>p</i> -F	<i>р</i> -Н	271.8	307.4	35.6
	<i>p</i> -F	272.1	307.4	35.3		<i>p</i> -Me	275.6	311.3	35.7
	p-Cl	278.5	312.1	33.6		p-Cl	276.5	312.3	35.8
	<i>p</i> -CN	303.0	320.5	17.5		<i>p</i> -CN	296.5	320.8	24.3
<i>p</i> -Me	<i>p</i> -Me	280.1	314.9	34.8	<i>p</i> -Cl	<i>р</i> -Н	277.3	312.1	34.8
	<i>p</i> -F	274.7	311.3	36.6		<i>p</i> -Me	281.2	316.3	35.1
	p-Cl	282.3	316.3	34.0		<i>p</i> -F	269.9	312.3	42.4
	<i>p</i> -CN	297.3	326.6	29.3		p-Cl	282.1	316.7	34.6
<i>p</i> -OMe	<i>р</i> -Н	283.3	318.2	34.9		<i>p</i> -CN	297.8	324.1	26.3
	<i>p</i> -Me	284.5	321.2	36.7	<i>p</i> -Et	<i>р</i> -Н	276.7	312.0	35.3
	<i>p</i> -F	281.1	318.4	37.3		<i>p</i> -F	274.7	311.5	36.8
	p-Cl	288.3	323.8	35.5		p-Cl	282.6	316.7	34.1

 $^{a}\Delta\lambda = \lambda_{max}(XSBY)-\lambda_{max}(XSMBY).$

Table 5 shows that among the parameters in Equation 4, item $\Sigma \sigma_{cc}^{ex}$ makes the most contribution (59.55%). For items χ^2 and $\Delta \sigma^2$, the contribution of χ^2 is greater than that of $\Delta \sigma^2$, which maybe a result from the shorter distance between the Me and Y versus between the X and Y. The shorter distance between Me and Y results in a stronger interaction and a greater contribution to the ν_{max} . In Equation 4, both the negative coefficients in front of χ^2 and $\Delta \sigma^2$ indicate that they all decrease the ν_{max} value, that is, they make the λ_{max} of XSMBY red shift.

Also, we calculated the relative contributions and fraction contributions of the parameters to the ν_{max} of XSBY in Equation 1 reported by Cao et al.^[30] (Table 6).

Table 6 shows that the ν_{max} change of XSBY is mainly affected by item $\Sigma \sigma_{cc}^{ex}$ (96.47%). The contribution of item $\sigma_{cc}^{ex}(XY)$ is only 2.56%. This result also can be used to explain why Equation 6 still has good correlation as Equation 5 has, in spite of ignoring item $\sigma_{cc}^{ex}(XY)$. However, the addition of Me results in the bridging group asymmetric and somewhat polar. It enhances the importance of the contribution of item $\Delta \sigma^2$ to the ν_{max} . Thus, the addition of Me that forces the change regularity of the ν_{max} of XSMBY is different from that of XSBY.

4.2 | Effect of Me at the bridging group to the v_{max} of XSMBY

Analyzing the coefficients in front of variables of Equation 6 carefully, it can be observed that the coefficient in front of the indicator variable *I* is positive (4274.216). It indicates that the ν_{max} of XSMBY is larger than that of XSBY, that is, the λ_{max} of XSMBY decreases (blue shift). As a comparison, we selected some λ_{max} of XSMBY and XSBY and listed them in Table 7, in which the XSMBY and XSBY have the same couple of groups X and Y.

It can be observed in Table 7 that all the λ_{max} of XSMBY are shorter than that of the corresponding XSBY in case of the same couple of groups X and Y and are blue shift. Maybe it primarily results from the steric effect. The addition of methyl group to the bridging group makes the groups crowed at the ends of the C=C bridge bond. The 2 benzene rings at 1,2-position and the C=C double bond form less coplanarity for XSMBY than XSBY, which decreases the conjugative effect and result in a blue shift of λ_{max} . It should be noted that although all λ_{max} of XSMBY are blue shift than that of XSBY and the increment of ν_{max} resulting from the indicator variable *I* in Equation 6 is a fixed value (4274.216 cm⁻¹), the decrement of corresponding λ_{max} is not a fixed value because of the relationship of $\nu_{max} = 1/\lambda_{max}$.

5 | CONCLUSION

From the above quantitative correlation analysis of ν_{max} of XSMBY and comparing the change regularity of their ν_{max} with that of XSBY, we can obtain the following conclusions: (1) There is no linear relationship between the ν_{max} of XSMBY and that of XSBY, and the factors influencing the $\nu_{\rm max}$ of them are different. The addition of methyl group to the bridging group makes the ground-state polar electronic effect (σ) also has important effects on the ν_{max} of XSMBY, whereas the influence of the σ constants of X and Y on the $\nu_{\rm max}$ of XSBY is negligible. (2) For the compounds XSMBY and XSBY, their ν_{max} can be quantified by a general equation, and the equation has a good correlation. (3) The steric effect resulting from the methyl group at the bridging group contributes a blue shift effect to the λ_{max} of XSMBY, and this blue shift is not a fixed value. The observed results of this work can provide theoretical references for the application and molecular design of photoelectric materials of stilbene compounds.

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SUPPORTING INFORMATION

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