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Excited-state substituent constants σ_{CC}^{ex} from substituted benzenes

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In this work, 13 compounds of 4,4′-disubstituted stilbenes and 5 compounds of 3-methyl-4′-substituted stilbenes were prepared and their UV spectra were measured. A new substituent effect constant, namely excited-state substituent constant, was proposed, which was calculated directly from the UV absorption energy data of substituted benzenes. The investigation result shows that the proposed constant is different from the existing polar substituent constants and radical substituent constants in nature. The availability of the new constant was confirmed by the good correlations with the UV absorption energy of four kinds of compounds, 1,4-disubstituted benzenes, 4,4′-disubstituted stilbenes, substituted ethenes, and *m*-Y-substituted aromatic compounds. It is expected that the excited-state substituent constant can be applied in QSPR study on organic compounds at the excited state. Copyright © 2008 John Wiley & Sons, Ltd.

Keywords: excited-state substituent constant; substituted benzene; substituent effect; substituted ethene; UV absorption energy

INTRODUCTION

Substituent electronic effect is a very important concept in organic chemistry for understanding molecular physico-chemical properties, predicting chemical reactivity, and analyzing reaction mechanism. Hammett[1] first proposed a set of substituent constants in 1937, namely σ-constants. Up to now these substituent constants have been deeply investigated and widely applied in organic chemistry, which can be seen in the review written by Hansch *et al.*[2] Taft[3] and Topsom[4] discussed and analyzed the nature of substituent electronic effects in detail. By means of experimental measurement and theoretical studies, they quantified four kinds of substituent electronic effects: (i) field effect σ_F; (ii) electronegativity effect σ_x; (iii) polarizability effect σ_α; (iv) resonance (π-electron transfer) effect σ_R. These electronic effect constants can be used well to explain the chemical activities of organic compounds in gas phase. Recently, Cherkasov[5] proposed an additive model to calculate the inductive effect. Cao[6] developed a polarizability effect index (PEI) to scale the polarizability effect of substituent groups. The mentioned parameters can be classified into the type of polar substituent constants.

It was believed that there are spin-delocalization effects in the ground state organic radicals. In order to quantify the abilities of various groups to stabilize radicals, a number of probes have been developed to evaluate radical-stabilizing effects on benzylic-type radicals, and various free radical substituent constants or spin-delocalization substituent constants (designated as $\sigma^{\cdot}$) scales have been established,[7] such as the $\sigma_F^{\cdot}$ scale developed by Fisher,[8] the $\sigma_J^{\cdot}$ scale developed by Jackson,[9] the $\sigma_{JJ}^{\cdot}$ scale developed by Jiang and Ji,[10] the $\sigma_\alpha^{\cdot}$ scale developed by Arnold,[11] the $\sigma_C^{\cdot}$ scale developed by Creary,[12] and the Adam[13] zero-field splitting parameter *D* of triplet biradicals. These meaningful parameters, we think, should be classified into the type of radical substituent constants.

It should be noted that the above two classes of substituent constants, namely polar substituent constants and radical substituent constants, were all determined at molecular ground state. Of course, they express the effect of substituents on the properties of molecule at ground state. In general, the properties of molecule at excited state cannot be correlated well with the polar substituent constants. Because the singlet excited state has two half-occupied molecular orbitals and may thus be diradicaloid in nature,[14] Jiang and Ji[15,16] employed the spin-delocalization substituent constants $\sigma_{JJ}^{\cdot}$ to correlate with the UV spectra of some model aromatic compounds, and developed single-parameter (radical substituent constant) equation and dual-parameter (polar and radical substituent constants) equation.

According to our knowledge, up to now, none of the existing substituent constants has been directly measured from the molecule being in the excited state with two half-occupied molecular orbitals. The UV spectra are direct measures of the excitation energy absorbed by molecules and it is easy to be measured. In this work, we attempt to develop an excited-state substituent constant (designated as σ_{CC}^{ex}), based on the UV spectra absorption energies of substituted aromatic compounds.

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Table 1. Excited-state substituent constant σ_{CC}^{ex} values of some substituents (**Y**)

No.	Y[a]	σ_{CC}^{ex}	No.	Y[a]	σ_{CC}^{ex}
1	NH_2	−0.88	19	F	0.06
2	OH	−0.19	20	Cl	−0.22
3	SH	−0.82	21	Br	−0.33
4	CHO	−1.09	22	I	−0.56
5	NEt_2	−1.31	23	CN	−0.70
6	H	0.00	24	MeCO	−1.13
7	NO_2	−1.17	25	$SiMe_3$	−0.13
8	$CH{=}CH_2$	−1.13	26	*t*-Bu	−0.17
9	NHEt	−1.06	27	$MeSO_2$	−0.43
10	CCH	−1.05	28	MeSO	−0.60
11	SO_2NH_2	−0.39	29	Me	−0.17
12	COOH	−0.70	30	COOMe	−0.69
13	$CF{=}CF_2$	−0.92	31	OCOMe	−0.08
14	$C(Me){=}CH_2$	−0.98	32	SMe	−1.40
15	$CH(OH)CH_2COOPr$	−0.17	33	CF_3	−0.12
16	$CH(OH)CH_2CCH$	−0.15	34	*c*-propanyl	−0.34
17	NMe_2	−1.81	35	$CONH_2$	−0.61
18	OMe	−0.50	36	Ph	−0.86

[a] For Y 1–16, their σ_{CC}^{ex} values are calculated from substituted benzenes, and the UV data were taken from Reference [17]; the σ_{CC}^{ex} values for Y 17–36 are based on the data of *p*-Y-substituted styrenes by using Eqn 4, and the UV data were taken from Reference [15].

EXCITED-STATE SUBSTITUENT CONSTANT σ_{CC}^{ex}

The UV absorption energy of a conjugated molecule reflects the energy discrepancy between molecular ground state and excited state. The λ_{max} values of conjugated molecular K-bands are easily identified and measured, which is dominated by the energy difference between the bonding π molecular orbital and anti-bonding π^* molecular orbital. Since the molecular orbital energies of ground state and excited-state (namely, in two half-occupied molecular orbitals of π and π^*) all are to be affected by the substituent in molecule, we can directly employ the K-band λ_{max} values of their UV absorption spectra to scale the excited-state substituent constants, from which the corresponding wavenumbers (ν_{max}) were calculated. Here, substituted benzenes and *p*-Y-substituted styrenes (**Y-ST**s) were used as model molecules, and their UV absorption energy was expressed by the unit eV (i.e., $1\ cm^{-1} = 1.23981 \times 10^{-4}$ eV).

The investigation of Jiang and Ji[15] showed that the contribution of the polar substituent constant to the UV absorption energy of *p*-**Y-ST**s is very little and it can be ignored. Further, authors observed that there is an excellent correlation between the UV absorption energy of substituted benzenes and that of *p*-**Y-ST**s for the substituents, OMe, Me, H, Cl, CN, F, and COOMe. Thus, we take benzene as a reference and use Eqn 1 to calculate the excited-state substituent constants σ_{CC}^{ex}:

$$\sigma_{CC}^{ex} = E_{UV(Y)} - E_{UV(H)} \tag{1}$$

where $E_{UV(H)}$ and $E_{UV(Y)}$ are the UV absorption energies (unit: eV) of K-bands of benzene and Y-substituted benzene, respectively.

Take OH group for a calculation example. It is known that the λ_{max} values of K-bands of HPh and HOPh are 203.5 and 210 nm,[17] namely, 6.09 (eV) and 5.90 (eV). Thus the excited-state substituent constant σ_{CC}^{ex} of OH group is

$$\sigma_{CC}^{ex} = 5.90 - 6.09 = -0.19 \tag{2}$$

It should be pointed out that Jiang and Ji[15] prepared many **Y-ST**s and measured their UV λ_{max} values. If the UV data of **Y-ST**s could be used to calculate σ_{CC}^{ex}, the number of substituent with σ_{CC}^{ex} value will be rapidly extended. When styrene is to be used as a reference, another excited-state substituent constant $\sigma_{CC(Y-ST)}^{ex}$ of **Y** group in **Y-ST** molecules will be obtained by

$$\sigma_{CC(Y-ST)}^{ex} = E_{UV(Y\text{-}ST)} - E_{UV(H\text{-}ST)} \tag{3}$$

where $E_{UV(H\text{-}ST)}$ and $E_{UV(Y\text{-}ST)}$ are the UV absorption energies(unit: eV) of K-bands of styrene and *p*-**Y-ST**, respectively. Here the groups, OMe, Me, H, Cl, CN, F, and COOMe, were taken as samples to establish the correlation between σ_{CC}^{ex} and $\sigma_{CC(Y-ST)}^{ex}$, and the correlation expression was obtained, as shown in

$$\sigma_{CC}^{ex} = 2.26\ \sigma_{CC(Y\text{-}ST)}^{ex} \tag{4}$$

$$r = 0.9913,\ s = 0.0397,\ n = 7,\ F = 340.63$$

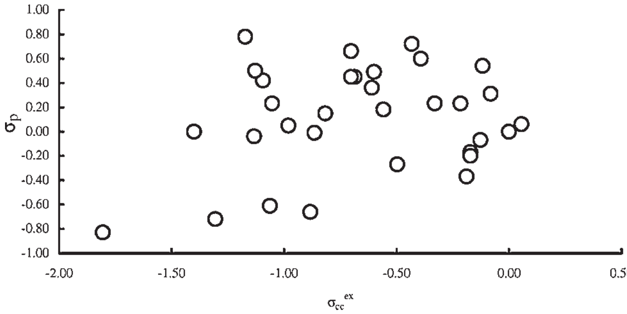

Figure 1. Plot of σ_{CC}^{ex} *versus* Hammett constants σ_p

Table 2. UV data, λ_{max} (nm) and wavenumber (ν_{max}, cm^{-1}) values for **1-Y**, **2-Y**, **3-Y**, and **4-Y**

	1-Y		**2-Y**		**3-Y**		**4-Y**	
Y	λ_{max}	ν_{max}	λ_{max}	ν_{max}	λ_{max}	ν_{max}	λ_{max}	ν_{max}
NMe_2	285.4	35 038	307.1	32 563				
OMe	254.4	39 308	262.2	38 139	225.4	44 366	225.1	44 425
Me	249.6	40 064	244.4	40 916	212.5	47 059	212.8	46 992
H	245.0	40 816	242.0	41 322	209.3	47 778	208.8	47 893
Cl	252.2	39 620	249.7	40 048	220.6	45 331	220.7	45 310
CN	262.6	38 081						
NO_2	272.8	36 657						
Br	254.6	39 277	251.4	39 777				
SMe	279.6	35 765	303.6	32 938				
F	243.8	41 017	239.3	41 788	206.9	48 333	207.5	48 193
COOMe	258.2	38 730						
MeCO	269.2	37 147						
CF_3	248.8	40 193						
$SiMe_3$	253.4	39 463						
t-Bu	250.2	39 968	251.8	39 713				
MeSO	262.0	38 168						

Table 3. Correlation equations for **1-Y**, **2-Y**, **3-Y**, and **4-Y**

	$\nu_{max} = a + b\ \sigma_{CC}^{ex}$						
Compound	a ($\times 10^3$)	b ($\times 10^3$)	r	s ($\times 10^3$)	F	n	Equation
1-Y	40.50	3.164	0.9844	0.3226	437.0	16	7
2-Y	41.22	5.251	0.9860	0.6177	245.6	9	8
3-Y	47.79	7.331	0.9492	0.6080	27.30	5	9
4-Y	47.75	7.171	0.9478	0.6039	26.48	5	10

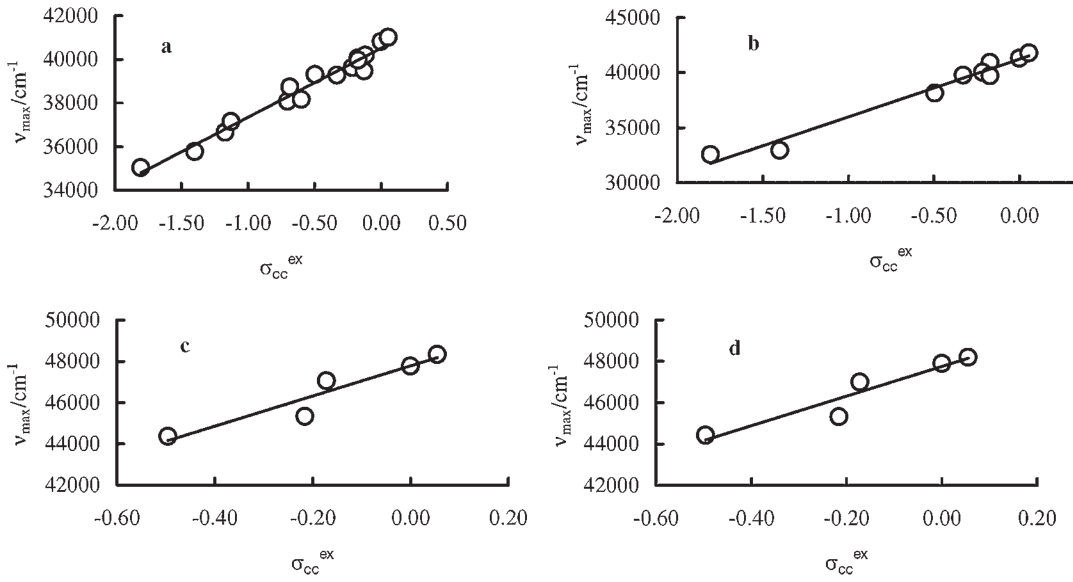

Figure 2. Plots of σ_{CC}^{ex} *versus* UV absorption energies (wavenumber: ν_{max}, cm^{-1}) of (a) **1-Y**, (b) **2-Y**, (c) **3-Y,** and (d) **4-Y**

Table 4. Correlation results obtained by Jiang[16] and this work

	1-Y			**2-Y**			**3-Y**			**4-Y**		
Parameter[a]	*r*	*F*	*n*	*r*	*F*	*n*	*r*	*F*	*n*	*r*	*F*	*n*
σ_{mb}	0.008	0.001	16	0.554	3.11	9	0.4461	0.746	5	0.445	0.739	5
σ^{+}	0.370	1.90	14	0.804	12.8	9	0.5601	1.37	5	0.552	1.32	5
σ_{p}	0.053	0.039	16	0.588	3.71	9	0.2605	0.218	5	0.244	0.190	5
$\sigma^{\bullet}_{JJ}$	0.923	81.0	16	0.946	59.2	9	0.9290	18.91	5	0.9401	22.82	5
$10\sigma^{\bullet}_{\alpha}$	0.922	62.3	13	0.961	60.7	7	0.8162	5.99	5	0.8121	5.81	5
$\sigma^{\bullet}_{C}$	0.924	76.2	15	0.920	38.4	9	0.9347	20.75	5	0.9289	18.87	5
$\sigma_{mb}+\sigma^{\bullet}_{JJ}$	0.940	49.5	16	0.946	25.4	9	0.9408	7.70	5	0.9508	9.43	5
$\sigma_{mb}+10\sigma^{\bullet}_{\alpha}$	0.922	28.3	13	0.965	27.0	7	0.8267	2.16	5	0.8226	2.09	5
$\sigma_{mb}+\sigma^{\bullet}_{C}$	0.924	35.2	15	0.927	18.3	9	0.9381	7.33	5	0.9321	6.62	5
$\sigma^{+}+\sigma^{\bullet}_{JJ}$	0.942	43.7	14	0.946	25.4	9	0.9402	7.63	5	0.9491	9.08	5
$\sigma^{+}+10\sigma^{\bullet}_{\alpha}$	0.938	29.4	11	0.966	27.7	7	0.8234	2.106	5	0.8185	2.03	5
$\sigma^{+}+\sigma^{\bullet}_{C}$	0.941	42.4	14	0.923	17.3	9	0.9430	8.03	5	0.9379	7.31	5
$\sigma_{p}+\sigma^{\bullet}_{JJ}$	0.946	55.2	16	0.951	28.6	9	0.9307	6.47	5	0.9408	7.70	5
$\sigma_{p}+10\sigma^{\bullet}_{\alpha}$	0.925	29.8	13	0.961	24.3	7	0.8307	2.23	5	0.8299	2.21	5
$\sigma_{p}+\sigma^{\bullet}_{C}$	0.926	36.0	15	0.944	24.8	9	0.9678	14.80	5	0.9664	14.13	5
σ_{CC}^{ex}[b]	0.9844	437.0	16	0.9860	245.6	9	0.9492	27.30	5	0.9478	26.48	5

[a] Taken from Reference [16], unless the noted parameter.

[b] This work.

Equation 4 shows that there is an excellent correlation between σ_{CC}^{ex} and $\sigma_{CC(Y-ST)}^{ex}$. It is to say, when the UV data of substituted benzene are unavailable, we can use the UV data of *p*-**Y-STs** to calculate the σ_{CC}^{ex} values of group **Y** by means of Eqn 4. Using the above calculation method (Eqn 2 together with Eqn 4), some σ_{CC}^{ex} values were obtained and they are listed in Table 1.

To investigate the correlation between σ_{CC}^{ex} and Hammett constants σ_p, the plot of σ_{CC}^{ex} against Hammett constants σ_p was

Table 5. Correlation equations with dual-parameter for **3-Y** and **4-Y**

	$\nu_{max}=a+b\sigma_{p}+c\sigma_{CC}^{ex}$							
Compound	a ($\times 10^3$)	b ($\times 10^3$)	c ($\times 10^3$)	*r*	*s* ($\times 10^3$)	*F*	*n*	Equation
3-Y	47.95	−3.123	8.858	0.9979	0.1536	236.5	5	11
4-Y	47.91	−3.166	8.720	0.9999	0.0344	4537	5	12

Table 6. UV data, λ_{max} (nm) and ν_{max} (cm^{-1}) values of **5-Y**, **6-Y**, and **7-Y**

	5-Y[a]		**6-Y**[b]		**7-Y**[b]	
Y	λ_{max}	ν_{max}	λ_{max}	ν_{max}	λ_{max}	ν_{max}
NMe_2	376.7	26 546	351.83	28 423	351.01	28 489
OMe	332.0	30 120	317.42	31 504	320.67	31 185
Me	323.1	30 950	311.26	32 127	315.17	31 729
H	316.0	31 646	307.14	32 558	311.26	32 127
F			306.93	32 581	311.08	32 146
Cl	320.3	31 221	311.62	32 090	315.36	31 710
CN			319.02	31 346	325.13	30 757
Br	321.3	31 124				

[a] Taken from Reference [16].

[b] Measured by this work.

Table 7. Correlation equations for **5-Y**, **6-Y**, and **7-Y**

Compound	$\nu_{max} = a + b\ \sigma^{ex}_{CC}$ a ($\times 10^3$)	 b ($\times 10^3$)	r	s ($\times 10^3$)	F	n	Equation
5-Y	31.65	2.807	0.9915 (0.9943)[a]	0.2710 (0.225)[a]	233.0 (347.9)[a]	6	13
6-Y	32.58	2.230	0.9941 (0.9680)	0.1718 (0.3971)	419.0 (74.39)	7	14
7-Y	32.11	1.986	0.9993 (0.9844)	0.0540 (0.2465)	3366 (156.8)	7	15

[a] The values in parentheses are the results correlated with the σ_C constant. For the **5-Y** system, the result was taken from Reference [16].

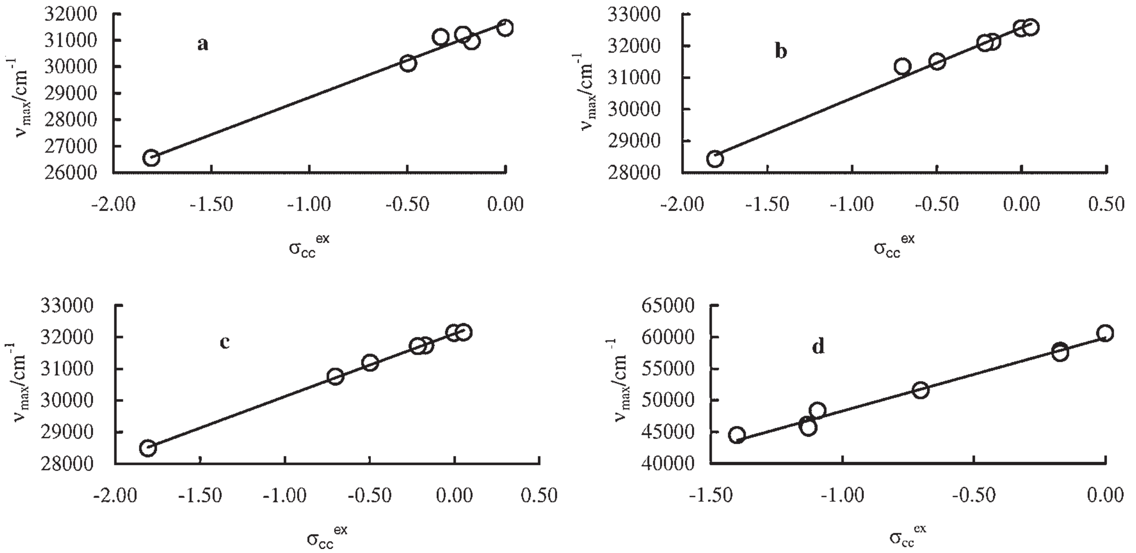

Figure 3. Plots of σ^{ex}_{CC} *versus* UV absorption energies (wavenumber: ν_{max}, cm^{-1}) of (a) **5-Y**, (b) **6-Y**, (c) **7-Y,** and (d) **8-Y**

made (as shown in Fig. 1). Figure 1 shows a bad correlation between σ^{ex}_{CC} and σ_p values, which indicates that σ^{ex}_{CC} is different from σ_p in nature.

APPLICATION OF σ^{ex}_{CC}

Correlation of the UV absorption energy for some 1,4-disubstituted benzenes

Jiang and Ji[16] investigated the correlation of the UV spectra of some 1,4-disubstituted benzenes with the polar substituent constants (σ^x) and radical substituent constants ($\sigma^{\bullet}$), and they obtained the meaningful result 'that all the polar constants (σ^x) do not correlate the data'. Furthermore they proposed the single-parameter Eqn 5 and the dual-parameter Eqn 6 to correlate the UV data:

Table 8. UV data, λ_{max} (nm) and ν_{max} (cm^{-1}) values of **8-Y**[18]

Y	λ_{max}	ν_{max}
H	165	60 606
Me	173	57 803
t-Bu	174	57 471
$CH{=}CH_2$	217	46 083
$CH{=}O$	207	48 309
$COCH_3$	219	45 662
COOH	193.9	51 573
SMe	225	44 444

$$\nu_{max} = \rho^{\bullet}\sigma^{\bullet} + c \tag{5}$$

$$\nu_{max} = \rho^x\sigma^x + \rho^{\bullet}\sigma^{\bullet} + c \tag{6}$$

Jiang and Ji's work[16] was an important progress in the correlation analysis of UV data of aromatic compounds. To test the availability of σ^{ex}_{CC} constants, the same model molecules, namely *p*-Y-substituted-phenylacetylenes (**1-Y**), *p*-Y-substituted-acetophenones (**2-Y**), ethyl 3-hydroxy-3-(*p*-Y-substituted-phenyl)-propanates (**3-Y**), and 1-(*p*-Y-substituted-phenyl)-3-butyn- 1-ols (**4-Y**), investigated by Jiang and Ji[16] were employed to carry out the correlation between their UV data (as shown in Table 2) and σ^{ex}_{CC} constants.

Using the single parameter σ^{ex}_{CC} to correlate the wavenumbers of **1-Y**, **2-Y**, **3-Y**, and **4-Y**, we obtained the correlation Eqns 7–10, as shown in Table 3. The plots of σ^{ex}_{CC} against UV absorption energy of **1-Y**, **2-Y**, **3-Y**, and **4-Y** are shown in Fig. 2.

Jiang and Ji[16] finished the correlation analysis of UV wavenumbers of compounds **1-Y**, **2-Y**, **3-Y**, and **4-Y** with Eqns 5 and 6. As comparison with the results obtained from the constants σ^x and $\sigma^{\bullet}$, the results reported by Jiang[16] and obtained by this work are all listed in Table 4.

Table 9. Correlation equations for **8-Y**

	$\nu_{max} = a + b\ \sigma_{CC}^{ex}$ (or $\sigma_C^{\bullet}$)						
σ_{CC}^{ex} or σ_C	a ($\times 10^3$)	b ($\times 10^3$)	r	s ($\times 10^3$)	F	n	Equation
σ_{CC}^{ex}	59.91	11.61	0.9923	0.8480	385.7	8	16
σ_C	60.37	−23.29	0.9006	2.979	25.74	8	17

Table 10. UV data, λ_{max} (nm) and ν_{max} (cm^{-1}) values of **9-Y**

Y	λ_{max}	ν_{max}
Me	312.73	31 976
OMe	319.28	31 320
Cl	313.83	31 864
CF$_3$	311.64	32 088
CN	322.90	30 969

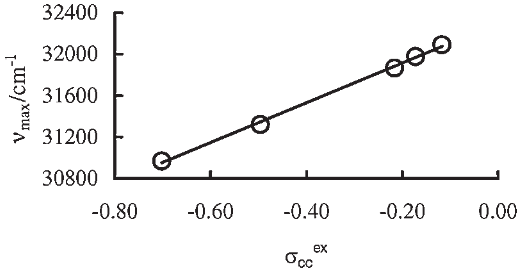

Figure 4. Plot of σ_{CC}^{ex} *versus* UV absorption energy (wavenumber: ν_{max}, cm^{-1}) of **9-Y**

Table 4 shows that the equation with σ_{CC}^{ex} constant has the best correlation among those single-parameter correlations. For the **1-Y**s and **2-Y**s systems, the correlations of equations with the single-parameter (σ_{CC}^{ex}) are even better than those of the corresponding dual-parameter (σ^X and $\sigma^{\bullet}$) equations. As regards the systems **3-Y**s and **4-Y**s, the correlations of equations with the single-parameter (σ_{CC}^{ex}) also approximate to those of the corresponding dual-parameter (σ^X and $\sigma^{\bullet}$) equations. These results indicate that the excited-state substituent constant σ_{CC}^{ex} has better capability than the radical substituent constants $\sigma^{\bullet}$ to correlate the UV absorption energy of 1,4-disubstituted benzenes. It should be noted that the correlations of Eqns 9 and 10 are less than those of Eqns 7 and 8. Perhaps, we think, it is resulted from the difference of the conjugated system, that is, in the systems **1-Y**s and **2-Y**s, both of two substituents in the molecule are conjugated with the benzene ring, whereas only one of them is conjugated with the benzene ring in the systems **3-Y**s and **4-Y**s. According to Jiang's[16] suggestion, the dual-parameter equation should be employed to correlate the UV absorption spectra for the systems **3-Y**s and **4-Y**s. Here, two parameters σ_p and σ_{CC}^{ex} were employed to correlate their UV data, and Eqns 11 and 12 were obtained (as shown in Table 5).

The correlations of Eqns 11 and 12 are much better than those of dual-parameter equations in Table 4 for **3-Y**s and **4-Y**s systems.

Correlation of the UV absorption energy for some 4,4′-disubstituted stilbenes

Further, some 4,4′-disubstituted stilbenes were used as model molecules to test the application of σ_{CC}^{ex}, which are *p*-Y-substituted-*p*′-methylsulphonylstilbenes (**5-Y**), *p*-Y- substituted-stilbenes (**6-Y**), and *p*-Y-substituted-*p*′-methylstilbenes (**7-Y**). Here, the K-band λ_{max} (ν_{max}) values of UV absorption spectra of **5-Y**s were taken directly from Jiang's work.[16] The compounds **6-Y**s and **7-Y**s were prepared by author's research group and their K-band λ_{max} values of UV absorption spectra were measured, from which the corresponding wavenumber (ν_{max}) was calculated. The λ_{max} and ν_{max} values of **5-Y**s, **6-Y**s, and **7-Y**s are all listed in Table 6.

Using the measured UV wavenumber (ν_{max}) values of **5-Y**s, **6-Y**s, and **7-Y**s in Table 6, we carried out the correlations between their ν_{max} values and σ_{CC}^{ex} constants, and obtained Eqns 13–15, as shown in Table 7.

Jiang's[16] report shows that σ_C has the best correlation with ν_{max} of **5-Y**s among those radical substituent constants. Thus, $\sigma_C^{\bullet}$ was employed to correlate with the ν_{max} values of **6-Y**s and **7-Y**s in this work, and the obtained results are presented in Table 7 (see the values in parentheses). It can be seen from Table 7

Table 11. Correlation equations for **9-Y**

	$\nu_{max} = a + b\ \sigma_{CC}^{ex}$ (or $\sigma_C^{\bullet}$)						
σ_{CC}^{ex} or $\sigma_C^{\bullet}$	a ($\times 10^3$)	b ($\times 10^3$)	r	s ($\times 10^3$)	F	n	Equation
σ_{CC}^{ex}	32.30	1.918	0.9991	0.02335	1678	5	18
$\sigma_C^{\bullet}$	32.23	−2.787	0.9625	0.1500	37.74	5	19

Table 12. UV data, λ_{max} (nm) and ν_{max} (cm^{-1}) values of **10-Y**[19]

Y	λ_{max}	ν_{max}
H	219	45 662
Me	222	45 045
OMe	222	45 045
Cl	219	45 662
NO_2	265	37 736

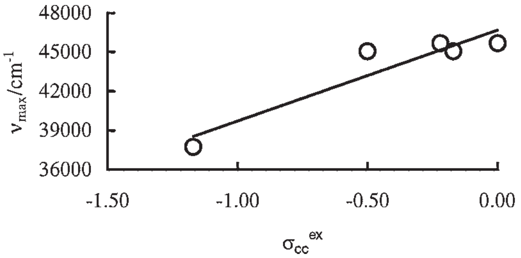

Figure 5. Plot of σ_{CC}^{ex} *versus* UV absorption energy (wavenumber: ν_{max}, cm^{-1}) of **10-Y**

Table 13. Correlation equations for **10-Y**

σ_{CC}^{ex} or $\sigma_{C}^{\bullet}$	$\nu_{max} = a + b\,\sigma_{CC}^{ex}$ (or $\sigma_{C}^{\bullet}$)						
	a ($\times 10^3$)	b ($\times 10^3$)	r	s ($\times 10^3$)	F	n	Equation
σ_{CC}^{ex}	46.70	6.977	0.9389	1.360	22.31	5	20
$\sigma_{C}^{\bullet}$	47.06	−14.54	0.9243	1.507	17.60	5	21

that the correlation of $\sigma_{C}^{\bullet}$ is somewhat better than that of σ_{CC}^{ex} for **5-Y**s, and is less than σ_{CC}^{ex} for **6-Y**s and **7-Y**s. The plots of σ_{CC}^{ex} against UV absorption energies of **5-Y**, **6-Y**, and **7-Y** are shown in Fig. 3 (see **a**, **b**, and **c**, respectively).

Correlation of the UV absorption energy for some substituted ethenes

The above UV analysis shows that the σ_{CC}^{ex} constants can be used to correlate well with the UV absorption energy of *p*-Y-substituted aromatic compounds. What we want to know is whether it can be used to correlate with the UV absorption energy[18] of substituted ethenes $CH_2{=}CH{-}Y$ (**8-Y**). Here, we used some substituted ethenes as model molecules, and carried out correlations between σ_{CC}^{ex} or $\sigma_{C}^{\bullet}$ and their UV wavenumbers (ν_{max}, as shown in Table 8). The obtained equations are listed in Table 9. The plot of σ_{CC}^{ex} against the UV data of **9-Y** is shown in Fig. 3(d).

The results in Table 9 show that the correlation of σ_{CC}^{ex} is better than that of $\sigma_{C}^{\bullet}$ constant.

Correlation of the UV absorption energy for some m-Y-substituted aromatic compounds

It has been found that *p*-Y-substituted stilbenes have a good correlation with σ_{CC}^{ex}. How about meta-substituted stilbenes? To test the application of σ_{CC}^{ex} in meta-substituted stilbenes, some model molecules (3-methyl-4′-substituted stilbenes, **9-Y**) were prepared and their K-band λ_{max} values of UV absorption spectra were measured in this work. The measured UV data are listed in Table 10. Here, σ_{CC}^{ex} and $\sigma_{C}^{\bullet}$ constants were also employed to correlate with the UV data of Table 10, respectively. The obtained regression equations are presented in Table 11. It can be seen from Table 11 that the correlation of σ_{CC}^{ex} is better than that of $\sigma_{C}^{\bullet}$ constant. Figure 4 is the plot of σ_{CC}^{ex} against the UV data of 3-methyl-4′-substituted stilbenes (**9-Y**).

Another example is *m*-Y-substituted phenylmercuric chlorides *m*-YC_6H_4HgCl (**10-Y**). Chen *et al.*[19] prepared a set of **10-Y**s and measured their UV spectra. This work employed σ_{CC}^{ex} and $\sigma_{C}^{\bullet}$ constants to correlate with the UV data of **10-Y** (as shown in Table 12). The obtained results are listed in Table 13, which shows a better correlation for σ_{CC}^{ex} than $\sigma_{C}^{\bullet}$. The plot of σ_{CC}^{ex} *versus* UV absorption energy of **10-Y** was obtained as shown in Fig. 5.

CONCLUSION

The above correlation analysis shows that the excited-state substituent constant σ_{CC}^{ex} is different from the polar substituent constants σ^{X} and radical substituent constants $\sigma^{\bullet}$. The σ_{CC}^{ex} should be measured as the difference of ground state and excited state, and σ^{X} and $\sigma^{\bullet}$ are measured in the molecular ground state. The correlation result is better for the σ_{CC}^{ex} to be used to correlate with the UV absorption energy than the σ^{X} or $\sigma^{\bullet}$ to be used for the four kinds of systems, 1,4′-disubstituted benzenes, 4,4′-disubstituted stilbenes, substituted ethenes, and *m*-Y-substituted aromatic compounds. It is expected that the excited-state substituent constant σ_{CC}^{ex} can be applied in QSPR study on organic compounds at the excited state. In addition, the σ_{CC}^{ex} constant is easy to be measured. Therefore we recommend using the σ_{CC}^{ex} constant to scale the substituent effect in the molecular excited state.

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