

ARTICLE

Effect of Excited-state Substituent Constant on the UV Spectra of 1,4-disubstituted Benzenes

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A correlation equation between the UV absorption wavenumbers of 1,4-disubstituted benzenes and the excited-state substituent constant was obtained. For 80 sorts of 1,4-disubstituted benzenes, the correlation coefficient was 0.9805, and the standard deviation was only 672.27 cm^{-1} . The results imply that the excited-state substituent constant can be used productively for research on UV energy of 1,4-disubstituted benzenes. The present method provides a new avenue to study the UV absorption spectra of aromatic systems with the excited-state substituent constant, and it is helpful to understand the effect of substituent electrostatic effects on the chemical and physical properties of conjugated compounds with multiple substituents in excited state.

Key words: Excited-state substituent constant, 1,4-disubstituted benzene, UV absorption wavenumber, Interaction of substituent

I. INTRODUCTION

The UV spectrum is an important property of conjugated compounds, and the quantitative correlation between the substituent effects and the UV energy has been said to be one of the most important and difficult problems in chemistry [1–4]. For a conjugated compound, generally both electron-donating (ED) and electron-withdrawing (EW) substituent make the molecular UV wavelength red-shift compared with the parent compound.

According to the perturbation theory of quantum chemistry, the effect of a substituent on UV absorption energy of substituted compound can be materially considered as the perturbation of the substituent on the HOMO-LUMO gap of the parent compound. To estimate this effect, many researchers have used the absolute values of polar substituent constant σ^X (*i.e.* $|\sigma^X|$) or two straight lines for a “successful” correlation of UV energy [5–15]. Jiang *et al.* considered that the excited state of compounds should possess diradicaloid character, and recommended the single-parameter Eq.(1) or the dual-parameter Eq.(2) to be used in the correlation of the UV spectra of compounds [16]. Jiang *et al.* used the equations to correlate the UV absorption wavenumber of different series of conjugated compounds, and

obtained good results [16–18].

$$v_{\max} = \rho' \sigma' + C \quad (1)$$

$$v_{\max} = \rho' \sigma' + \rho^X \sigma^X + C \quad (2)$$

v_{\max} is the UV absorption wavenumber, σ^X is polar substituent constant, ρ^X is the coefficient in front of polar parameter, ρ' and σ' are the radical substituent constant and its coefficient, respectively.

Recently, the authors developed an excited-state constant σ_{CC}^{ex} , and used it successfully to correlate the UV absorption energy of some substituted conjugated compounds [19].

It should be noted that the preceding studies focused mostly on the UV absorption energy of the substituted compounds in which only one substituent is to be changed. Now, what we want to know is how the UV absorption energy is affected by the substituents in disubstituted compounds. Therefore, the relation of the UV wavenumbers of *para*-disubstituted benzenes with σ_{CC}^{ex} was investigated, and an interaction item between two substituents which affects the UV wavenumbers of model compounds was proposed in this work. A new equation relating UV absorption wavenumbers of 1,4-disubstituted benzenes to σ_{CC}^{ex} was obtained.

II. DATASET

Experimental UV wavelengths of 80 sorts of 1,4-disubstituted benzenes were collected in Table I [16,17],

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TABLE I The λ_{\max} and ν_{\max} values of 1,4-disubstituted benzene [16,17].

Compound	λ_{\max}/nm	$\nu_{\max}/\text{cm}^{-1}$	Compound	λ_{\max}/nm	$\nu_{\max}/\text{cm}^{-1}$	Compound	λ_{\max}/nm	$\nu_{\max}/\text{cm}^{-1}$
FST	246	40650	MST	242.5	41237	FPBO	207.5	48193
ST	247.2	40453	MeMST	248.1	40306	FTFST	237.7	42070
Me(CO)OST	249	40161	CIMST	249.7	40048	TFST	239.7	41719
Me ₃ SiST	250	40000	MeCO ₂ MST	267.9	37327	Me(CO)OTFST	242.8	41186
MeST	251	39841	MeCOMST	277.7	36010	Me ₃ SiTFST	246.4	40584
<i>t</i> -BuST	251	39841	MeSMST	276.7	36140	MeTFST	243	41152
CIST	252	39683	CF ₃ MST	247.4	40420	<i>t</i> -BuTFST	243	41152
BrST	254.6	39277	FPAT	243.8	41017	CITFST	246.8	40519
MeSO ₂ ST	257	38911	CIPAT	252.4	39620	BrTFST	248.9	40177
MeOST	258.5	38685	BrPAT	254.6	39277	MeSO ₂ TFST	255.1	39200
IST	260	38462	MePAT	249.6	40064	MeOTFST	250.1	39984
MeSOST	261	38314	COMePAT	269.2	37147	MeSOTFST	260.2	38432
MeCO ₂ ST	263.1	38008	CNPAT	262.6	38081	MeCO ₂ TFST	265	37736
CNST	263.5	37951	MeSOPAT	262	38168	CNTFST	261.5	38241
MeCOST	274.5	36430	PAT	245	40816	MeCOTFST	272.5	36697
MeSST	282	35461	CF ₃ PAT	248.8	40193	CF ₃ TFST	242.1	41305
Me ₂ NST	294	34014	MeCO ₂ PAT	258.2	38730	<i>c</i> -propanylTFST	250	40000
FATP	239.3	41789	MeOPAT	254.4	39308	HOCTFST	258.6	38670
CIATP	249.7	40048	<i>t</i> -BuPAT	250.2	39968	NH ₂ COTFST	260.1	38447
BrATP	251.4	39777	NO ₂ PAT	272.8	36657	PhTFST	270.5	36969
MeATP	244.4	40917	SiMe ₃ PAT	253.4	39463	Me ₂ NTFST	323.3	30931
ATP	242	41322	MeSPAT	279.6	35765	OMePPN	225.4	44366
MeOATP	262.2	38139	Me ₂ NPAT	285.4	35039	MePPN	212.5	47059
<i>t</i> -BuATP	251.8	39714	PBO	208.8	47893	PPN	209.3	47778
MeSATP	303.6	32938	MePBO	212.8	46992	CIPPN	220.6	45331
NMe ₂ ATP	307.1	32563	MeOPBO	225.1	44425	FPPN	206.9	48333
FMST	242.2	41288	CIPBO	220.7	45310			

which included *p*-Y-substituted-styrenes (Y-STs), *p*-Y-substituted-acetophenones (Y-ATPs), *p*-Y-substituted- α -methylstyrenes (Y-MSTs), *p*-Y-substitutedphenylacetylenes (Y-PATs), 1-(*p*-Y-substituted-phenyl)-3-butyn-1-ols (Y-PBOs), *p*-Y-substituted- α , β , β -trifluoromethyl styrenes (Y-TFSTs), and 3-hydroxy-3-(*p*-Y-substituted-phenyl)-propanates (Y-PPNs).

III. METHOD AND DISCUSSION

In our previous work [19], an σ_{CC}^{ex} was developed and it was confirmed that there were good correlations between the σ_{CC}^{ex} and the UV absorption wavenumbers of conjugated compounds where one substituent is to be altered. For the 1,4-disubstituted benzenes (XPhYs), we believe the substituent effect on the UV absorption wavelengths should be affected by their two substituents. In general, it is proposed that the UV absorption wavelengths of aromatic compounds should be a certain additivity of their substituent effects. For instance, the wavelength of benzene is 203.5 nm [20], and that of benzonitrile is 231 nm [20], and that of

styrene is 247.2 nm [16], whereas that of 4-cyanostyrene is 263.5 nm [16]. Therefore, the parameter $\sum \sigma_{CC}^{\text{ex}}$ was first tried to scale the total contributions of the corresponding substituents X and Y in XPhY, *i.e.*

$$\sum \sigma_{CC}^{\text{ex}} = \sigma_{CC}^{\text{ex}}(\text{X}) + \sigma_{CC}^{\text{ex}}(\text{Y}) \quad (3)$$

and the σ_{CC}^{ex} values of substituents X and Y were taken from the literature [19]. With the ν_{\max} of Table I and $\sum \sigma_{CC}^{\text{ex}}$ (see Table II), the correlation Eq.(4) was obtained.

$$\begin{aligned} \nu_{\max} &= 46881.90 + 5067.02 \sum \sigma_{CC}^{\text{ex}} \quad (4) \\ R &= 0.9605, \quad s = 943.96, \quad F = 930.85, \quad n = 80 \end{aligned}$$

Eq.(4) showed that there was a good correlation between the absorption energy of 1,4-disubstituted benzene and the $\sum \sigma_{CC}^{\text{ex}}$ values. The coefficient in front of the $\sum \sigma_{CC}^{\text{ex}}$ value is positive, which indicates that collective effect of substituents caused the UV wavelength red-shift, compared with benzene. The result is consistent with the experimental phenomenon.

TABLE II The employed parameters, experimental wavenumbers, calculated wavenumbers, and residuals of Eq.(9).

Compound	$\sum \sigma_{CC}^{ex}$	σ_{CC}^{ex}	$\nu_{max}(exp)$	$\nu_{max}(cal)$	$\Delta\nu$	Compound	$\sum \sigma_{CC}^{ex}$	σ_{CC}^{ex}	$\nu_{max}(exp)$	$\nu_{max}(cal)$	$\Delta\nu$
FST	-1.07	-0.06	40650	40567	83	MeSOPAT	-1.65	0.63	38168	38408	-240
ST	-1.13	0.00	40453	40307	146	PAT	-1.05	0.00	40816	40911	-95
Me(CO)OST	-1.21	0.09	40161	39993	168	CF ₃ PAT	-1.17	0.12	40193	40391	-198
Me ₃ SiST	-1.26	0.14	40000	39776	224	MeCO ₂ PAT	-1.74	0.72	38730	38018	712
MeST	-1.30	0.19	39841	39635	206	MeOPAT	-1.55	0.52	39308	38809	499
<i>t</i> -BuST	-1.30	0.19	39841	39635	206	<i>t</i> -BuPAT	-1.22	0.18	39968	40206	-238
CIST	-1.35	0.24	39683	39419	264	NO ₂ PAT	-2.22	1.23	36657	36036	621
BrST	-1.46	0.37	39277	39006	271	SiMe ₃ PAT	-1.18	0.13	39463	40348	-885
MeSO ₂ ST	-1.56	0.49	38911	38638	273	MeSPAT	-2.45	1.47	35765	35072	693
MeOST	-1.63	0.56	38685	38334	351	Me ₂ NPAT	-2.86	1.90	35039	33360	1679
IST	-1.69	0.63	38462	38107	355	PBO	-0.15	0.00	47893	47698	195
MeSOST	-1.73	0.68	38314	37965	349	MePBO	-0.32	0.03	46992	46512	480
MeCO ₂ ST	-1.82	0.78	38008	37608	400	MeOPBO	-0.65	0.08	44425	44184	241
CNST	-1.83	0.80	37951	37597	354	CIPBO	-0.37	0.03	45310	46135	-825
MeCOST	-2.26	1.28	36430	35895	535	FPBO	-0.09	-0.01	48193	48118	75
MeSST	-2.53	1.59	35461	34854	607	FTFS	-0.86	-0.05	42070	42183	-113
Me ₂ NST	-2.94	2.05	34014	33238	776	TFS	-0.92	0.00	41719	41891	-172
FATP	-1.07	-0.06	41789	40567	1222	Me(CO)OTFST	-1.00	0.08	41186	41544	-358
ClATP	-1.35	0.24	40048	39419	629	Me ₃ SiTFST	-1.05	0.12	40584	41296	-712
BrATP	-1.46	0.37	39777	39006	771	MeTFST	-1.09	0.16	41152	41123	29
MeATP	-1.30	0.19	40917	39635	1282	<i>t</i> -BuTFST	-1.09	0.16	41152	41123	29
ATP	-1.13	0.00	41322	40307	1015	CITFST	-1.14	0.20	40519	40874	-355
MeOATP	-1.63	0.56	38139	38334	-195	BrTFST	-1.25	0.30	40177	40365	-188
<i>t</i> -BuATP	-1.30	0.19	39714	39635	79	MeSO ₂ TFST	-1.35	0.40	39200	39932	-732
MeSATP	-2.53	1.58	32938	34821	-1883	MeOTFST	-1.42	0.46	39984	39597	387
NMe ₂ ATP	-2.94	2.04	32563	33206	-643	MeSOTFST	-1.52	0.55	38432	39132	-700
FMST	-0.92	-0.05	41288	41730	-442	MeCO ₂ TFST	-1.61	0.63	37736	38710	-974
MST	-0.98	0.00	41237	41439	-202	CNTFST	-1.62	0.65	38241	38699	-458
MeMST	-1.15	0.17	40306	40702	-396	MeCOTFST	-2.05	1.04	36697	36708	-11
CIMST	-1.20	0.21	40048	40454	-406	CF ₃ TFST	-1.04	0.11	41305	41339	-34
MeCO ₂ MST	-1.67	0.67	37327	38386	-1059	<i>c</i> -propanylTFST	-1.26	0.31	40000	40322	-322
MeCOMST	-2.11	1.11	36010	36480	-470	HOCTFST	-1.62	0.65	38670	38699	-29
MeSMST	-2.38	1.37	36140	35279	861	NH ₂ COTFST	-1.53	0.56	38447	39088	-641
CF ₃ MST	-1.10	0.11	40420	40887	-467	PhTFST	-1.78	0.80	36969	37974	-1005
FPAT	-0.99	-0.06	41017	41171	-154	Me ₂ NTFST	-2.73	1.66	30931	33570	-2639
CIPAT	-1.27	0.23	39620	39990	-370	OMePPN	-0.67	0.08	44366	44033	333
BrPAT	-1.38	0.35	39277	39546	-269	MePPN	-0.34	0.03	47059	46361	698
MePAT	-1.22	0.18	40064	40206	-142	PPN	-0.17	0.00	47778	47547	231
COMePAT	-2.18	1.19	37147	36209	938	CIPPN	-0.39	0.04	45331	46016	-685
CNPAT	-1.75	0.74	38081	38007	74	FPPN	-0.11	-0.01	48333	47967	366

It should be noted that when the $\sum \sigma_{CC}^{ex}$ term in the Eq.(4) was replaced by polar constants ($\sum \sigma_{mb}$, $\sum \sigma^+$, and $\sum \sigma_p$) or free radical constants ($\sum \sigma_{JJ}^*$ and $\sum \sigma_C^*$) respectively, the correlation of the equations was reduced (see Table III). The results of Table III showed that the σ_{CC}^{ex} has better capability

than both the radical substituent constants and polar substituent constants to correlate the UV absorption energy of 1,4-disubstituted benzenes.

Further, the insight into Eq.(4) showed us some disadvantages: (i) Eq.(4) had a good correlation, but still had larger standard deviation; (ii) Its intercept was 46881.90 cm⁻¹ (that is 213.30 nm), which deviated far from the UV absorption wavelength of benzene (by

TABLE III The correlation results of 1,4-disubstituted benzenes by polar substituent constants, radical substituent constants and the excited-state substituent constant.

Parameter	$v_{\max}=a+b\sum\sigma$ (or $\sum\sigma^*$ or $\sum\sigma_{CC}^{\text{ex}}$)		R	$s\times 10^3$	F	n
	$a\times 10^3$	$b\times 10^3$				
σ_{mb} [23]	38.24	2.094	0.3143	2.708	2.96	29
σ^+ [24]	38.85	0.932	0.2973	1.797	2.52	28
σ_{p} [24]	38.45	0.975	0.1716	2.171	1.46	50
σ_{JJ}^* [23]	46.27	-6.714	0.7210	1.977	29.24	29
σ_{C}^* [25]	44.86	-7.121	0.9133	0.803	95.55	21
$\sigma_{\text{CC}}^{\text{ex}}$	46.88	5.067	0.9605	0.944	930.85	80

For the σ_{mb} and σ_{JJ}^* , the researched systems are Y-ATPs and Y-TFSTs; for the σ^+ , the researched systems are Y-STs and Y-PATs; for the σ_{p} , the researched systems are Y-STs, Y-ATPs, Y-MSTs, and Y-PATs; for the σ^* , the researched systems are Y-STs and Y-MSTs.

203.5 nm [20]). Suresh and Gadre also pointed out that the simple additivity rule with the values of substituent constants has serious drawbacks [21]. The above facts remind us that it must be an interaction factor between substituents X and Y to be not counted.

As the title compounds are all conjugated compounds, there should be an interaction between their substituents X and Y attached in the 1,4-position. According to the research of Guo *et al.* [22], the substituent interaction energy (SIE) was recommended,

$$\text{SIE}(X, Y) = -k\sigma_X\sigma_Y \quad (5)$$

where k was a constant dependent on the system and was a certain scale of electronic substituent constant. Here, we also employed the formula to scale the interaction term between substituents X and Y.

$$\sigma(\text{XY}) = \sigma(\text{X})\sigma(\text{Y}) \quad (6)$$

Firstly, the Hammett constants $\sigma_{\text{p}}(\text{X})$ and $\sigma_{\text{p}}(\text{Y})$ were tried to express the interaction term, *i.e.*

$$\sigma_{\text{p}}(\text{XY}) = \sigma_{\text{p}}(\text{X})\sigma_{\text{p}}(\text{Y}) \quad (7)$$

Using the parameters $\sum\sigma_{\text{CC}}^{\text{ex}}$ and $\sigma_{\text{p}}(\text{XY})$, we carried out a correlation with the v_{\max} of the compounds in Table II. Unfortunately, the obtained correlation was less than that of Eq.(4). It showed that the $\sigma_{\text{p}}(\text{XY})$ is unable to scale the interaction between X and Y accurately. Next, the product of $\sigma_{\text{CC}}^{\text{ex}}(\text{X})$ and $\sigma_{\text{CC}}^{\text{ex}}(\text{Y})$ was employed to scale the interaction term, and Eq.(9) was obtained (see Table II).

$$\sigma_{\text{CC}}^{\text{ex}}(\text{XY}) = \sigma_{\text{CC}}^{\text{ex}}(\text{X})\sigma_{\text{CC}}^{\text{ex}}(\text{Y}) \quad (8)$$

$$v_{\max} = 48828.75 + 7541.04 \sum\sigma_{\text{CC}}^{\text{ex}} + 3209.85 \sigma_{\text{CC}}^{\text{ex}}(\text{XY}) \quad (9)$$

$$R = 0.9805, \quad s = 672.27, \quad F = 956.05, \quad n = 80$$

In Eq.(9), the values of two variables, $\sum\sigma_{\text{CC}}^{\text{ex}}$ and $\sigma_{\text{CC}}^{\text{ex}}(\text{XY})$ were 24.64 and 8.76, respectively, and all variables were significant in $P < 10^{-13}$. Compared

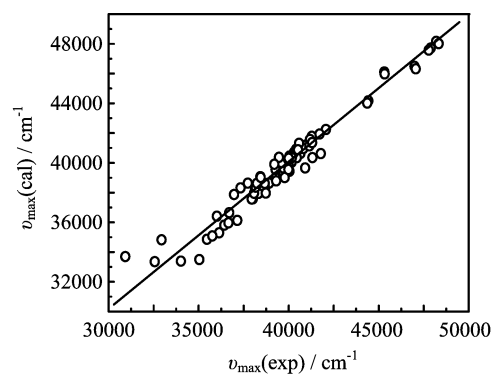


FIG. 1 Plot of the calculated wavenumbers *vs.* the experimental ones of 80 sorts of 1,4-disubstituted benzenes.

with Eq.(4), the correlation of Eq.(9) was greatly improved. In particular, the intercept of Eq.(9) was 48828.75 cm^{-1} , which is equal to 204.80 nm and is near the UV absorption wavelength of benzene (203.5 nm). Seen from the UV wavelengths of benzene, XPh, YPh, and XPhY, the total contribution of X and Y in disubstituted benzene is greater than either of them in monosubstituted benzene, and smaller than the sum of individual X and individual Y in mono-substituted benzene. This implies that when the second substituent is introduced into the monosubstituted benzene, the effect of the second substituent on the UV wavelength will be influenced by the primary substituent. Therefore a modification term $\sigma_{\text{CC}}^{\text{ex}}(\text{XY})$ was introduced into Eq.(9) and the correlation of Eq.(9) was greatly improved.

The results above indicate that including Eq.(9) the double-parameter can be employed to calculate the absorption energy of 1,4-disubstituted benzenes well.

The plot of the calculated wavenumbers with the experimental ones of 80 sorts of 1,4-disubstituted benzenes is shown in Fig.1. Seen from Fig.1, the calculated wavenumbers were in good agreement with the experimental values. Analyzed from Δv in Table II, the residuals of some points were still larger, such as

MeSATP, Me₂NPAT, and Me₂NTFST, which deviated from the straight line and whose residuals all were beyond 1500 cm⁻¹. The reason for this phenomenon is still unknown. If the above three points are excluded, the correlation coefficient *R* of the double-parameter equation is raised to 0.9859 and *F* values to 1282.35, and its standard deviation *s* is lowered to 530.95 cm⁻¹.

IV. CONCLUSION

The above correlation analyses showed that the σ_{CC}^{ex} is a better constant than the radical substituent constants and the polar substituent constants for correlating with the UV absorption energy of 1,4-disubstituted aromatic compounds. The correlation equation between the UV absorption wavenumbers (ν_{max}) of the title compounds and the σ_{CC}^{ex} was obtained, where the $\sigma_{CC}^{ex}(XY)$ can be used to scale accurately the interaction between substituents X and Y in the research on UV absorption energies of XPhYs. It is expected that the σ_{CC}^{ex} can be applied in QSPR study on other sorts of disubstituted or multi-substituted compounds in excited state.

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