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Substituent effect on the UV spectra of p-disubstituted compounds XPh(CH=CHPh)$_n$Y ($n = 0, 1, 2$)

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Three parameters, σ_{CC}^{ex}, $\sigma_{CC}^{ex}(XY)$ and $\upsilon_{max,parent}$, are developed to express the substituent effect and the effect of the parent molecular structure of p-disubstituted compounds XPh(CH=CHPh)$_n$Y ($n = 0, 1, 2$). The investigated result shows a good correlation between the UV absorption wavenumbers (υ_{max}) and the three parameters for a diverse set of title compounds, and the correlation equation can be used to predict the UV absorption energy of compounds with the mentioned structure. This approach provides a new insight for the quantitative structure-property relationship (QSPR) correlation of the UV absorption energy of p-disubstituted homologues. Copyright © 2010 John Wiley & Sons, Ltd.

Keywords: excited-state substituent parameter; p-disubstituted homologue; substituent effect; UV absorption energy

INTRODUCTION

The UV absorption spectrum is one of the basic properties of conjugated organic compounds. Perhaps, the UV absorption wavelength is known to be the more important parameter before one decides to use an optical compound specially.[1–3] Even in the design of a new optical compound, it is also necessary to predict its maximum of UV absorption wavelength for evaluating its application. The UV absorption energy of available organic compounds can be determined experimentally, but cannot be for the compounds designed. Generally, in order to obtain credible UV spectrum data of a new optical compound, people spend much time on synthesizing them and then measure their relevant optical characters. Hence, it is helpful for chemists that an appropriate quantitative structure–property relationship (QSPR) model is used to predict the optical property of the target compound. Up to now, there have been numerous attempts to calculate the UV absorption energy of conjugated organic compounds. For organic homologues, there was an in-depth study on the rule of UV spectra of different homologues by Jiang in 1980s.[4] Recently, Taherpour and Shafiei[5] studied the structural relationship between Randić indices, the determinants of the adjacency matrixes and distance matrixes to maximum wavelength of linear simple conjugated polyene compounds $H_2C{=}CH(HC{=}CH)_nH$ ($n = 1, 2, 3, \ldots, 24$). For substituted aromatic derivatives, now, there are three main kinds of parameters applied to study the substituent effect on UV spectra: (1) Polar substituent parameter,[6] such as Hammett constant σ_p; some workers[7–11] used two straight lines or the absolute values of polar substituent constant, $|\sigma_p|$ for a 'successful' correlation of UV data. (2) Free radical substituent parameter,[12–14] for example spin-delocalization substituent constant $\sigma_{JJ}^{\bullet}$; Jiang *et al.*[15,16] studied the correlation between free radical constant and the molecular UV absorption energy, and single-parameter (radical substituent parameter) equation or dual-parameter (polar and radical substituent parameters) equation. (3) Excited-state substituent parameter[17–19]; Cao *et al.*[19] recently proposed a new excited-state substituent parameter σ_{CC}^{ex}, and recommended the single-parameter equation (1) in terms of excited-state substituent parameter σ_{CC}^{ex}, or the dual-parameter equation (2) in terms of a combination of σ_p and σ_{CC}^{ex} to correlate the UV absorption wavenumbers (υ_{max}) of monosubstituted benzene derivatives, monosubstituted stilbene derivatives and monosubstituted ethene derivatives. Further, Cao and his co-workers[20] studied the substituent effect on the UV absorption energy of 1,4-disubstituted benzenes, and successfully obtained the QSPR equation.

For the monosubstituted conjugated organic compounds X—A (X denotes different substituents and A denotes the molecular structures of parents), Cao *et al.*[19] reported that their UV absorption energy could be well correlated with single-parameter equation (1) or dual-parameter equation (2). For p-disubstituted conjugated organic compounds X—A—Y (Y also denotes different substituents), Chen *et al.*[20] also studied the rule of the substituent effect on the UV absorption energy of 1,4-disubsituted benzenes and constructed the interaction item with $\sigma_{CC}^{ex}(XY)$, where $\sigma_{CC}^{ex}(XY) = \sigma_{CC}^{ex}(X) \cdot \sigma_{CC}^{ex}(Y)$. For the p-disubstituted organic compounds X—(A)$_n$—Y (n denotes the number of repeating unit A), there are three factors influencing

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their UV absorption energy, which are the substituents X, Y and the number of repeating unit. We want to know how the three factors affect the UV absorption energy of compounds X—(A)$_n$—Y. This topic was investigated in this paper.

$$\upsilon_{\max} = \rho^{\mathrm{ex}}\sigma^{\mathrm{ex}}_{\mathrm{CC}} + c \tag{1}$$

$$\upsilon_{\max} = \rho^{\mathrm{ex}}\sigma^{\mathrm{ex}}_{\mathrm{CC}} + \rho_{\mathrm{p}}\sigma_{\mathrm{p}} + c \tag{2}$$

DATASET

In order to organize the studied dataset, we synthesized a set of 4,4′-disubstituted stilbenes and measured their UV absorption wavelengths ($\lambda_{\max}$), and also collected the $\lambda_{\max}$ values of some 1,4-disubstituted benzenes, 4,4′-disubstituted stilbenes and 1,4-bis(p-Y-substituted phenylethenyl)benzenes measured in the same solvent.

Measured data

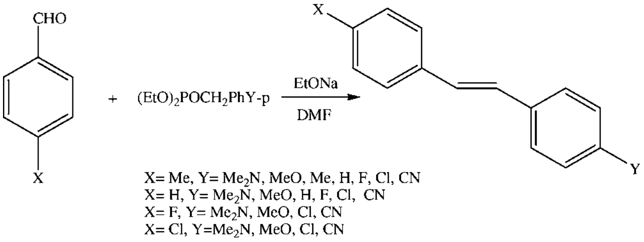
Twenty one samples of 4,4′-disubstituted stilbene derivatives including p-Y-substituted-p′-chlorostilbenes (YSBCls), p-Y-substituted-p′-fluorostilbenes (YSBFs), p-Y-substituted stilbenes (YSBs) and p-Y-substituted-p′-methylstilbenes (YSBMes) were synthesized with the Witting–Horner reaction[21] shown in Scheme 1, and all UV–Vis spectra of the above compounds were measured in ethanol, and the obtained absorption wavelengths are listed in Table 1.

Collected data

Experimental UV wavelengths of 80 samples of 1,4-disubstituted benzenes[15,16] including p-Y-substituted-styrenes (Y-STs), p-Y-substituted-acetophenones (Y-ATPs), p-Y-substituted-α-methylstyrenes (Y-MSTs), p-Y-substituted-phenylacetylenes (Y-PATs), l- (p-Y-substituted-phenyl)-3-butyn-l-ols (Y-PBOs), p-Y-substituted-α, β, β-trifluoromethylstyrenes (Y-TFSTs), 3-hydroxy-3-(p-Y-substituted-phenyl)propanates (Y-PPNs) were collected; six samples of p-Y-substituted-p′-methylsulphonylstilbenes (YSBSO$_2$Mes)[15] and six samples of 1,4-bis(p-Y-substituted phenylethenyl)benzenes (YSPBYs)[22] were collected (Table 1).

METHODS AND DISCUSSION

As we know, the UV absorption energy of conjugated compounds is affected by their structures. More specifically, the key factors causing their UV absorption wavenumber shift can be divided into two parts: one is the substituent effect and the other is the effect of parent molecular structure.[23] In our previous paper,[20] it was confirmed that the UV absorption energy of 1,4-disubstituted benzenes (XPhY) is well correlated with two parameters: one is the sum of effects of substituents X and Y ($\sum\sigma^{\mathrm{ex}}_{\mathrm{CC}}$) and the other is the interaction between substituents X and Y($\sigma^{\mathrm{ex}}_{\mathrm{CC}}$(XY)), with which the correlation Eqn (3) was obtained. Based on this reported work, here we also obtained Eqns (4) and (5) for 4,4′-disubstituted stilbenes and 1,4-bis(p-Y-substituted phenylethenyl)benzenes with the corresponding UV absorption wavenumbers ($\upsilon_{\max}$), $\sum\sigma^{\mathrm{ex}}_{\mathrm{CC}}$and $\sigma^{\mathrm{ex}}_{\mathrm{CC}}$(XY) shown in Table 2.



Scheme 1. Synthesis of samples of 4,4′-disubstituted stilbene derivatives

For 1,4-disubstituted benzenes (no. 1–80 of Table 2),

$$\upsilon_{\max} = 48828.75 + 7541.04\sum\sigma^{\mathrm{ex}}_{\mathrm{CC}} + 3209.85\sigma^{\mathrm{ex}}_{\mathrm{CC}}(\mathrm{XY}) \tag{3}$$

$$R = 0.9805,\ s = 672.27,\ F = 951.21,\ n = 80$$

For 4,4′-disubstituted stilbenes (no. 81–107 of Table 2),

$$\upsilon_{\max} = 32476.63 + 2043.63\sum\sigma^{\mathrm{ex}}_{\mathrm{CC}} - 1013.42\sigma^{\mathrm{ex}}_{\mathrm{CC}}(\mathrm{XY}) \tag{4}$$

$$R = 0.9860,\ s = 254.09,\ F = 421.05,\ n = 27$$

For 1,4-bis(substituted phenylethenyl)benzenes (no. 108–113 of Table 2),

$$\upsilon_{\max} = 28411.60 + 930.14\sum\sigma^{\mathrm{ex}}_{\mathrm{CC}} + 132.52\sigma^{\mathrm{ex}}_{\mathrm{CC}}(\mathrm{XY}) \tag{5}$$

$$R = 0.9981,\ s = 86.23,\ F = 392.15,\ n = 6$$

The results obtained from Eqns (4) and (5) showed that $\upsilon_{\max}$ values also have good correlations with parameters, $\sum\sigma^{\mathrm{ex}}_{\mathrm{CC}}$ and $\sigma^{\mathrm{ex}}_{\mathrm{CC}}$(XY)for 4,4′-disubstituted stilbenes and 1,4-bis(substituted phenylethenyl)benzenes. The above results showed that the double-parameter equation with $\sum\sigma^{\mathrm{ex}}_{\mathrm{CC}}$ and $\sigma^{\mathrm{ex}}_{\mathrm{CC}}$(XY)can be well employed to calculate the UV absorption wavenumbers of compounds with a same parent. For the above three equations, the coefficients in front of the $\sum\sigma^{\mathrm{ex}}_{\mathrm{CC}}$are all positive. It indicated that the effect of substituents on UV wavenumbers is additive and forces the UV wavelength red-shift for different systems. The result is consistent with the experimental phenomenon. However, surprisingly, cofficients in front of $\sigma^{\mathrm{ex}}_{\mathrm{CC}}$(XY)are different, i.e. those in Eqns (3) and (5) are positive, while it is negative in Eqn (4). The structures of benzene, stilbene and 1,4-bis(phenylethenyl)benzene show that they are homologues and can be expressed as Ph(CH═CHPh)$_n$H (n = 0, 1, 2). Combined with the operator changes of coefficients in front of $\sigma^{\mathrm{ex}}_{\mathrm{CC}}$(XY), we guessed that operators of coefficients in front of $\sum\sigma^{\mathrm{ex}}_{\mathrm{CC}}$could be related to the numbers of repeating unit (n) in Ph(CH═CHPh)$_n$H. When the n value is odd, the symbol in front of $\sigma^{\mathrm{ex}}_{\mathrm{CC}}$(XY)is negative; otherwise, it is positive.

It is interesting if the UV absorption wavenumbers of 1,4-disubstituted benzenes, 4,4′-disubstituted stilbenes and 1,4-bis(Y-substituted phenylethenyl)benzenes can be expressed with one QSPR equation; if the substituent effect can be scaled with $\sum\sigma^{\mathrm{ex}}_{\mathrm{CC}}$and $\sigma^{\mathrm{ex}}_{\mathrm{CC}}$(XY), then how to scale the effect of the parent molecular structure? Let us again see Eqns (3)–(5); there is a good linear relationship between the intercepts of the three equations and the experimental wavenumbers of the corresponding parent compounds (the $\upsilon_{\max}$ of benzene is 49140 cm^{-1},[24] 32485 cm^{-1} for stilbene and 28433 cm^{-1} for 1,4-bisphenylethenylbenzene[22]), so we recommended that the effect of the parent molecular structure on the UV absorption energy is scaled with the experimental wavenumber of the parent ($\upsilon_{\max,\mathrm{parent}}$). Furthermore, we also thought that the effect of two items $\sum\sigma^{\mathrm{ex}}_{\mathrm{CC}}$and $\sigma^{\mathrm{ex}}_{\mathrm{CC}}$(XY)on the UV absorption energy could be related to the $\upsilon_{\max,\mathrm{parent}}$ value. Fortunately, the investigation showed that the absolute values of coefficients

Table 1. The $\lambda_{\max}$ (nm) values of 1,4-disubstituted benzenes, 4,4′-disubstituted stilbenes and 1,4-bis(Y-substituted phenylethenyl) benzenes

No.	Compound	$\lambda_{\max}$	No.	Compound	$\lambda_{\max}$	No.	Compound	$\lambda_{\max}$
1	FST	246	39	COMePAT	269.2	77	MePPN	212.5
2	ST	247.2	40	CNPAT	262.6	78	PPN	209.3
3	Me(CO)OST	249	41	MeSOPAT	262	79	ClPPN	220.6
4	Me_3SiST	250	42	PAT	245	80	FPPN	206.9
5	MeST	251	43	CF_3PAT	248.8	81	Me_2NSBSO_2Me	376.7
6	t-BuST	251	44	$MeCO_2PAT$	258.2	82	$MeOSBSO_2Me$	332.0
7	ClST	252	45	MeOPAT	254.4	83	$MeSBSO_2Me$	323.1
8	BrST	254.6	46	t-BuPAT	250.2	84	$SBSO_2Me$	316.0
9	$MeSO_2ST$	257	47	NO_2PAT	272.8	85	$ClSBSO_2Me$	320.3
10	MeOST	258.5	48	$SiMe_3PAT$	253.4	86	$BrSBSO_2Me$	321.3
11	IST	260	49	MeSPAT	279.6	87	Me_2NSBMe	347.93
12	MeSOST	261	50	Me_2NPAT	285.4	88	MeOSBMe	321.24
13	$MeCO_2ST$	263.1	51	PBO	208.8	89	MeSBMe	314.91
14	CNST	263.5	52	MePBO	212.8	90	MeSB	311.21
15	MeCOST	274.5	53	MeOPBO	225.1	91	MeSBF	311.32
16	MeSST	282	54	ClPBO	220.7	92	MeSBCl	316.35
17	Me_2NST	294	55	FPBO	207.5	93	MeSBCN	326.57
18	FATP	239.3	56	FTFST	237.7	94	Me_2NSB	350.10
19	ClATP	249.7	57	TFST	239.7	95	MeOSB	318.20
20	BrATP	251.4	58	Me(CO)OTFST	242.8	96	SB	307.83
21	MeATP	244.4	59	$Me_3SiTFST$	246.4	97	FSB	307.35
22	ATP	242	60	MeTFST	243	98	ClSB	312.07
23	MeOATP	262.2	61	t-BuTFST	243	99	CNSB	320.47
24	t-BuATP	251.8	62	ClTFST	246.8	100	Me_2NSBF	349.32
25	MeSATP	303.6	63	BrTFST	248.9	101	MeOSBF	318.44
26	NMe_2ATP	307.1	64	$MeSO_2TFST$	255.1	102	ClSBF	312.32
27	FMST	242.2	65	MeOTFST	250.1	103	FSBCN	320.77
28	MST	242.5	66	MeSOTFST	260.2	104	Me_2NSBCl	354.29
29	MeMST	248.1	67	$MeCO_2TFST$	265	105	MeOSBCl	323.80
30	ClMST	249.7	68	CNTFST	261.5	106	ClSBCl	316.70
31	$MeCO_2MST$	267.9	69	MeCOTFST	272.5	107	ClSBCN	324.10
32	MeCOMST	277.7	70	CF_3TFST	242.1	108	SPB	351.7
33	MeSMST	276.7	71	c-propanylTFST	250	109	MeSPBMe	355.0
34	CF_3MST	247.4	72	HOOCTFST	258.6	110	t-BuSPBBu-t	357.5
35	FPAT	243.8	73	$NH_2COTFST$	260.1	111	FSPBF	356.7
36	ClPAT	252.4	74	PhTFST	270.5	112	ClSPBCl	363.3
37	BrPAT	254.6	75	Me_2NTFST	323.3	113	$Me_2NSPBNMe_2$	392.5
38	MePAT	249.6	76	OMePPN	225.4			

in front of variables in three equations are also in good linear relationships with the $\upsilon_{\max,\mathrm{parent}}$. For the absolute values of coefficients in front of $\sum\sigma^{ex}_{CC}$, the correlation coefficient R is 0.9996; for $\sigma^{ex}_{CC}(XY)$, R is 0.9954. Therefore, we used $\sum\sigma^{ex}_{CC}\cdot\upsilon_{\max,\mathrm{parent}}$ and $(-1)^n\sigma^{ex}_{CC}(XY)\cdot\upsilon_{\max,\mathrm{parent}}$ to scale the substituent effect for compounds XPh(CH=CHPh)$_n$Y. From the above-mentioned descriptors, a QSPR correlation equation was obtained.

$$\begin{aligned}\upsilon_{\max} = 7756.25 + 0.1065\sum\sigma^{ex}_{CC}\cdot\upsilon_{\max,\mathrm{parent}} + 0.0193\\ (-1)^n\sigma^{ex}_{CC}(XY)\cdot\upsilon_{\max,\mathrm{parent}} + 0.7919\upsilon_{\max,\mathrm{parent}}\end{aligned} \qquad (6)$$

$$R = 0.9824,\ s = 1003.14,\ F = 1008.57,\ n = 113$$

From the result of Eqn (6), it is seen that there is a good correlation between UV absorption wavenumbers and the variables, and the contributions of those parameters to UV absorption wavenumber are different. The contribution of $\upsilon_{\max,\mathrm{parent}}$ is largest among them, whereas it is smallest for $(-1)^n\sigma^{ex}_{CC}(XY)\cdot\upsilon_{\max,\mathrm{parent}}$. It is not difficult to understand that the effect of the parent molecular structure is dominant in the structure factors, and the substituent effect only plays a role of adjusting the UV absorption energy of compounds.[23] Furthermore, for the substituent effect, the additive effect of substituents X and Y decreases the UV absorption energy, generally, while the influence of the interaction between X and Y is related to the number of repeating unit.

Figure 1 shows the plot of the calculated wavenumbers with the experimental values of 113 kinds of XPh(CH=CHPh)$_n$Y (n = 0, 1, 2). Figure 1 shows that the calculated wavenumbers are in good agreement with the experimental values. Analysed from the residuals of title compounds in Table 2, the $\Delta\upsilon$ values of

Table 2. The employed parameters, experimental wavenumbers, calculated wavenumbers and residuals

No.	Compound	$\sum\sigma_{CC}^{ex}$	$\sigma_{CC}^{ex}(XY)$	$\upsilon_{max,parent}$	υ_{max} (exp)	υ_{max} (cal)[a]	$\Delta\upsilon$[a]	υ_{max} (cal)[b]	$\Delta\upsilon$[b]
1	FST	−1.07	−0.06	49140	40650	41017	−367	40860	−210
2	ST	−1.13	0.00	49140	40453	40760	−307	40623	−170
3	Me(CO)OST	−1.21	0.09	49140	40161	40427	−266	40302	−141
4	Me_3SiST	−1.26	0.14	49140	40000	40213	−213	40105	−105
5	MeST	−1.30	0.19	49140	39841	40051	−210	39941	−100
6	t-BuST	−1.30	0.19	49140	39841	40051	−210	39941	−100
7	ClST	−1.35	0.24	49140	39683	39836	−153	39744	−61
8	BrST	−1.46	0.37	49140	39277	39384	−107	39299	−22
9	$MeSO_2ST$	−1.56	0.49	49140	38911	38974	−63	38893	18
10	MeOST	−1.63	0.56	49140	38685	38674	11	38616	69
11	IST	−1.69	0.63	49140	38462	38427	35	38374	88
12	MeSOST	−1.73	0.68	49140	38314	38265	49	38211	103
13	$MeCO_2ST$	−1.82	0.78	49140	38008	37889	119	37850	158
14	CNST	−1.83	0.80	49140	37951	37855	96	37805	146
15	MeCOST	−2.26	1.28	49140	36430	36060	370	36080	350
16	MeSST	−2.53	1.59	49140	35461	34941	520	34992	469
17	Me_2NST	−2.94	2.05	49140	34014	33232	782	33346	668
18	FATP	−1.07	−0.06	49140	41789	41017	772	40860	929
19	ClATP	−1.35	0.24	49140	40048	39836	212	39744	304
20	BrATP	−1.46	0.37	49140	39777	39384	393	39299	478
21	MeATP	−1.30	0.19	49140	40917	40051	866	39941	976
22	ATP	−1.13	0.00	49140	41322	40760	562	40623	699
23	MeOATP	−1.63	0.56	49140	38139	38674	−535	38616	−477
24	t-BuATP	−1.30	0.19	49140	39714	40051	−337	39941	−227
25	MeSATP	−2.53	1.58	49140	32938	34932	−1994	34997	−2059
26	NMe_2ATP	−2.94	2.04	49140	32563	33222	−659	33351	−788
27	FMST	−0.92	−0.05	49140	41288	41811	−523	41360	−72
28	MST	−0.98	0.00	49140	41237	41544	−307	41129	108
29	MeMST	−1.15	0.17	49140	40306	40816	−510	40459	−153
30	ClMST	−1.20	0.21	49140	40048	40592	−544	40267	−219
31	$MeCO_2MST$	−1.67	0.67	49140	37327	38569	−1242	38419	−1092
32	MeCOMST	−2.11	1.11	49140	36010	36684	−674	36683	−673
33	MeSMST	−2.38	1.37	49140	36140	35518	622	35624	516
34	CF_3MST	−1.10	0.11	49140	40420	41021	−601	40661	−241
35	FPAT	−0.99	−0.06	49140	41017	41435	−418	41130	−113
36	ClPAT	−1.27	0.23	49140	39620	40245	−625	40019	−399
37	BrPAT	−1.38	0.35	49140	39277	39783	−506	39580	−303
38	MePAT	−1.22	0.18	49140	40064	40459	−395	40217	−153
39	COMePAT	−2.18	1.19	49140	37147	36393	754	36401	746
40	CNPAT	−1.75	0.74	49140	38081	38217	−136	38109	−28
41	MeSOPAT	−1.65	0.63	49140	38168	38636	−468	38509	−341
42	PAT	−1.05	0.00	49140	40816	41178	−362	40893	−77
43	CF_3PAT	−1.17	0.12	49140	40193	40664	−471	40420	−227
44	$MeCO_2PAT$	−1.74	0.72	49140	38730	38250	480	38154	576
45	MeOPAT	−1.55	0.52	49140	39308	39055	253	38909	399
46	t-BuPAT	−1.22	0.18	49140	39968	40459	−491	40217	−249
47	NO_2PAT	−2.22	1.23	49140	36657	36222	435	36243	414
48	$SiMe_3PAT$	−1.18	0.13	49140	39463	40621	−1158	40380	−917
49	MeSPAT	−2.45	1.47	49140	35765	35246	519	35330	435
50	Me_2NPAT	−2.86	1.90	49140	35039	33508	1531	33701	1338
51	PBO	−0.15	0.00	49140	47893[c]	45884	2009	—	—
52	MePBO	−0.32	0.03	49140	46992[c]	45024	1968	—	—
53	MeOPBO	−0.65	0.08	49140	44425[c]	43345	1080	—	—
54	ClPBO	−0.37	0.03	49140	45310[c]	44762	548	—	—

(*Continued*)

Table 2. (Continued)

No.	Compound	$\sum \sigma_{CC}^{ex}$	$\sigma_{CC}^{ex}(XY)$	$\upsilon_{max,parent}$	υ_{max} (exp)	υ_{max} (cal)[a]	$\Delta\upsilon$[a]	υ_{max} (cal)[b]	$\Delta\upsilon$[b]
55	FPBO	−0.09	−0.01	49140	48193[c]	46188	2005	—	—
56	FTFS	−0.86	−0.05	49140	42070	42125	−55	41562	508
57	TFS	−0.92	0.00	49140	41719	41858	−139	41332	387
58	Me(CO)OTFST	−1.00	0.08	49140	41186	41515	−329	41016	170
59	$Me_3SiTFST$	−1.05	0.12	49140	40584	41292	−708	40824	−240
60	MeTFST	−1.09	0.16	49140	41152	41120	32	40667	485
61	t-BuTFST	−1.09	0.16	49140	41152	41120	32	40667	485
62	ClTFST	−1.14	0.20	49140	40519	40897	−378	40475	44
63	BrTFST	−1.25	0.30	49140	40177	40416	−239	40047	130
64	$MeSO_2TFST$	−1.35	0.40	49140	39200	39987	−787	39652	−452
65	MeOTFST	−1.42	0.46	49140	39984	39678	306	39382	602
66	MeSOTFST	−1.52	0.55	49140	38432	39240	−808	38993	−561
67	$MeCO_2TFST$	−1.61	0.63	49140	37736	38845	−1109	38644	−908
68	CNTFST	−1.62	0.65	49140	38241	38812	−571	38599	−358
69	MeCOTFST	−2.05	1.04	49140	36697	36932	−235	36925	−228
70	CF_3TFST	−1.04	0.11	49140	41305	41334	−29	40864	441
71	c-propanylTFST	−1.26	0.31	49140	40000	40373	−373	40007	−7
72	HOOCTFST	−1.62	0.65	49140	38670	38812	−142	38599	71
73	$NH_2COTFST$	−1.53	0.56	49140	38447	39197	−750	38954	−507
74	PhTFST	−1.78	0.80	49140	36969	38117	−1148	37973	−1004
75	Me_2NTFST	−2.73	1.66	49140	30931[c]	33971	−3040	—	—
76	MeOPPN	−0.67	0.08	49140	44366[c]	43241	1125	—	—
77	MePPN	−0.34	0.03	49140	47059[c]	44919	2140	—	—
78	PPN	−0.17	0.00	49140	47778[c]	45779	1999	—	—
79	ClPPN	−0.39	0.04	49140	45331[c]	44667	664	—	—
80	FPPN	−0.11	−0.01	49140	48333[c]	46084	2249	—	—
81	Me_2NSBSO_2Me	−2.24	0.78	32485	26546	25251	1295	27667	−1121
82	$MeOSBSO_2Me$	−0.93	0.22	32485	30120	30128	−8	30376	−256
83	$MeSBSO_2Me$	−0.60	0.07	32485	30950	31362	−412	31055	−105
84	$HSBSO_2Me$	−0.43	0.00	32485	31646	31994	−348	31407	239
85	$ClSBSO_2Me$	−0.65	0.09	32485	31221	31177	44	30951	270
86	$BrSBSO_2Me$	−0.76	0.14	32485	31124	30766	358	30725	399
87	Me_2NSBMe	−1.98	0.31	32485	28741	26443	2298	28069	672
88	MeOSBMe	−0.67	0.09	32485	31129	31108	21	30906	223
89	MeSBMe	−0.34	0.03	32485	31755	32286	−531	31619	136
90	MeSB	−0.17	0.00	32485	32133	32892	−759	31987	146
91	MeSBF	−0.12	−0.01	32485	32121	33071	−950	32095	26
92	MeSBCl	−0.39	0.04	32485	31611	32107	−496	31512	99
93	MeSBCN	−0.87	0.12	32485	30621	30398	223	30472	149
94	Me_2NSB	−1.81	0.00	32485	28563	27224	1339	28331	232
95	MeOSB	−0.50	0.00	32485	31427	31752	−325	31251	176
96	SB	0.00	0.00	32485	32485	33480	−995	32366	119
97	FSB	0.06	0.00	32485	32536	33687	−1151	32500	36
98	ClSB	−0.22	0.00	32485	32044	32719	−675	31876	168
99	CNSB	−0.70	0.00	32485	31204	31060	144	30805	399
100	Me_2NSBF	−1.75	−0.11	32485	28627	27500	1127	28423	204
101	MeOSBF	−0.44	−0.03	32485	31403	31978	−575	31374	29
102	ClSBF	−0.16	−0.01	32485	32018	32933	−915	32006	12
103	FSBCN	−0.65	−0.04	32485	31175	31258	−83	30902	273
104	Me_2NSBCl	−2.02	0.40	32485	28225	26248	1977	28014	211
105	MeOSBCl	−0.71	0.11	32485	30883	30957	−74	30825	58
106	ClSBCl	−0.43	0.05	32485	31576	31962	−386	31426	150
107	ClSBCN	−0.92	0.15	32485	30855	30206	649	30372	483
108	SPB	0.00	0.00	28433	28433	30271	−1838	29430	−997

(*Continued*)

Table 2. (Continued)

No.	Compound	$\sum \sigma_{CC}^{ex}$	$\sigma_{CC}^{ex}(XY)$	$\upsilon_{max,parent}$	υ_{max} (exp)	υ_{max} (cal)[a]	$\Delta\upsilon$[a]	υ_{max} (cal)[b]	$\Delta\upsilon$[b]
109	MeSPBMe	−0.34	0.03	28433	28169	29259	−1090	28757	−588
110	t-BuSPBBu-t	−0.34	0.03	28433	27972	29259	−1287	28757	−785
111	FSPBF	−0.44	0.05	28433	28035	28967	−932	28555	−520
112	ClSPBCl	−1.00	0.25	28433	27525	27382	143	27396	129
113	$Me_2NSPBNMe_2$	−3.62	3.28	28433	25478[c]	21111	4367	—	—

[a] data came from the Eqn (6), $\Delta\upsilon = \upsilon_{max}$ (exp) $-$ υ_{max} (cal).

[b] data came from the Eqn (7), $\Delta\upsilon = \upsilon_{max}$ (exp) $-$ υ_{max} (cal).

[c] those experimental data of no. 51–55, no. 75–80 and no. 113 data were excluded from the group regressed with Eqn (7).

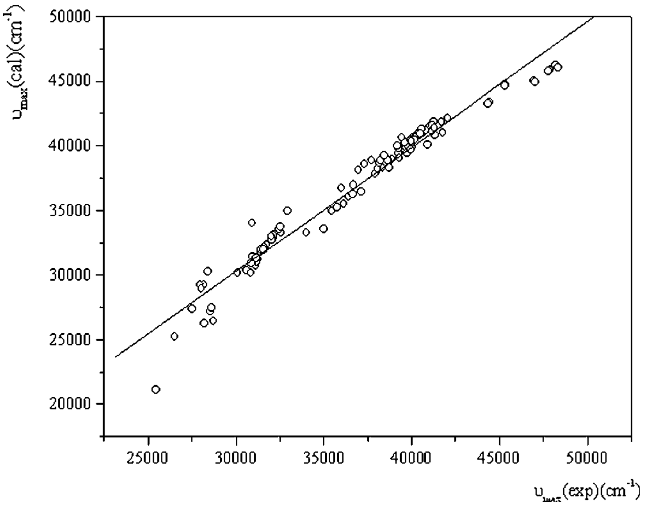


Figure 1. Plot of the calculated wavenumbers *vs.* the experiment ones of 113 kinds of p-disubstituted homologues Ph(CH═CHPh)$_n$H ($n = 0, 1, 2$)

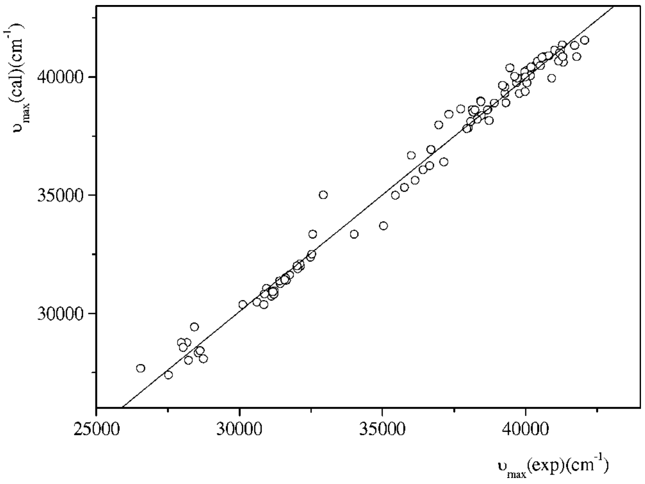


Figure 2. Plot of the calculated wavenumbers *vs.* the experiment ones of 101 kinds of p-disubstituted homologues Ph(CH═CHPh)$_n$H ($n = 0, 1, 2$) (without Y-PBOs, Y-PPNs, Me_2NTFST and $Me_2NSPBNMe_2$)

Me_2NTFST and $Me_2NSPBNMe_2$ are larger (value is 3040 cm^{-1} for Me_2NTFST and 4367 cm^{-1} for $Me_2NSPBNMe_2$), both of which are beyond 3000 cm^{-1}. The reason of this phenomenon was perhaps caused by the NMe_2 group. In the UV measurement of Me_2N-substituted stilbenes, we found that those compounds are sensitive to light in the solvent, so the measurement of 4,4′-disubstituted stilbenes synthesized was all done timely after the solutions were prepared. In Table 2, we even found that the $\Delta\upsilon$ values of Me_2N-substituted compounds are large, so we presumed that the UV values of Me_2NTFST and $Me_2NSPBNMe_2$ are perhaps less exact because of the measurement conditions. Meanwhile, analysing from the structures of all substituents, we considered that OH group of Y-PBOs and Y-PPNs can form the hydrogen bond with solvent ethanol, which could perhaps affect the result of correlation equation. If the above 12 points were excluded, then another correlation equation was obtained.

$$\begin{aligned}\upsilon_{max} = {} & 8827.27 + 0.0686 \sum \sigma_{CC}^{ex} \cdot \upsilon_{max,\,parent} \\ & - 0.0117\,(-1)^n \sigma_{CC}^{ex}(XY) \cdot \upsilon_{max,\,parent} \\ & + 0.7246\upsilon_{max,\,parent} \qquad (7)\end{aligned}$$

$$R = 0.9937,\ s = 506.22,\ F = 2559.63,\ n = 101$$

Compared with Eqn (6), the correlation of Eqn (7) was significantly improved. The correlation coefficient R of the equation is increased to 0.9937 and F values to 2559.63, and its standard deviation s is lowered to 506.22 cm^{-1}. The plot of the calculated wavenumbers with the experimental ones of 101 kinds of XPh(CH═CHPh)$_n$Y ($n = 0, 1, 2$) is shown in Fig. 2.

In order to further confirm the rationality of the equation with the three parameters, we continued to synthesize another four samples of p-Y-substituted-p′-ethylstilbenes (Y = Me, H, F, Cl) and measured their UV–Vis spectra in ethanol (Table 3). Since the σ_{CC}^{ex} of ethyl group (Et) was not reported in reference [19], here we calculated its σ_{CC}^{ex} with the method of reference [19]. From references [24,25], we got the λ_{max} values of K-band of benzene and ethylbenzene, 203.5 nm (i.e. 6.09 eV) and 208 nm (i.e. 5.96 eV), respectively. Thus the excited-state substituent constant σ_{CC}^{ex} of Et group is

$$\sigma_{CC}^{ex}(\mathrm{Et}) = 5.96 - 6.09 = -0.13 \qquad (8)$$

According to Eqn (6) and the $\sigma_{CC}^{ex}(\mathrm{Et})$ value, the predicted values of four p-Y-substituted-p′-ethylstilbenes (Y = Me, H, F, Cl) are 32429, 33030, 33243 and 32252 cm^{-1}, respectively. Compared with their experimental values in Table 3, the $\Delta\upsilon$ values are −705,

Table 3. The experimental data, calculated data and residuals of p-Y-substituted-p′-ethylstilbenes

Compound	λ_{max} (exp) (nm)	υ_{max} (exp) (cm^{-1})	υ_{max} (cal) (cm^{-1})[a]	$\Delta\upsilon$[a]	υ_{max} (cal) (cm^{-1})[b]	$\Delta\upsilon$[b]
MeSBEt	315.22	31724	32429	−705	31706	18
HSBEt	311.96	32055	33030	−975	32076	−21
FSBEt	311.51	32102	33243	−1141	32207	−105
ClSBEt	316.66	31580	32252	−672	31597	−17

[a] υ_{max} (cal) were calculated with Eqn (6), $\Delta\upsilon = \upsilon_{max}$ (exp) $-$ υ_{max} (cal).
[b] υ_{max} (cal) were calculated with Eqn (7), $\Delta\upsilon = \upsilon_{max}$ (exp) $-$ υ_{max} (cal).

−975, −1141 and −672 cm^{-1}, respectively. If the predicted values of four p-Y-substituted-p′-ethylstilbenes were calculated with Eqn (7), their $\Delta\upsilon$ values are less than 110 cm^{-1} (the corresponding errors, $\Delta\upsilon$ values are 18, −21, −105, −17 cm^{-1}). The results showed that the correlation Eqn (7) is more suitable to predict the UV absorption energy of conjugated compounds $XPh(CH{=}CHPh)_nY$ ($n = 0, 1, 2$).

However, it is worth to investigate further if the item $(-1)^n\sigma_{CC}^{ex}(XY)\cdot\upsilon_{max,parent}$ of the correlation Eqn (7) is still effective when the repeat unit (n) in the title compounds exceeds 2.

CONCLUSION

For the title compounds, their UV absorption energy is mainly influenced by the substituent effect and the effect of the parent molecular structure. For the effect of the parent molecular structure, it is scaled with the UV absorption wavenumber of the parent compound simply, i.e. $\upsilon_{max,parent}$; while for the substituent effect, it is related to not only the additive effect of substituents X and Y, but also the interaction between them, and it is scaled with $\sum\sigma_{CC}^{ex}\cdot\upsilon_{max,parent}$ and $(-1)^n\sigma_{CC}^{ex}(XY)\cdot\upsilon_{max,parent}$. The correlation Eqn (7) with the three parameters can be well used to calculate the UV absorption energy of title compounds. This approach provides a new insight for QSPR correlation of UV absorption energy of p-disubstituted homologues.

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