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Influence of the side-group at C=N bridging bond of bis-aryl Schiff bases on the wavelength of absorption maximum of ultraviolet absorption spectra

Qingqing Luo[a], Chao-Tun Cao[a], Zhongzhong Cao[a] and Chenzhong Cao[b]*

The compounds N-(benzylidene)-anilines XArCH=NArY (XBAY), N-(phenyl-ethylene)-anilines XArC(CH_3)=NArY (XPEAY) and N-phenyl-α-phenylnitrones XArCH=N(O)ArY (XPNY) have bridging group CH=N, C(CH_3)=N and CH=N(O) respectively, in which the C(CH_3)=N has a side-group methyl CH_3 at carbon end and the CH=N(O) has a side-group O atom at nitrogen end. In this work, a series of XPEAY and XPNY were synthesized, and their longest wavelength maximum λ_{max} (nm) of ultraviolet absorption spectra were measured. Then the change regularity of the ν_{max} (cm^{-1}, $\nu_{max}=1/\lambda_{max}$) of XPEAY and XPNY were investigated, and they were compared with that of XBAY (reported by ref.26). The results indicate: (1) There are no good linear relationships between the ν_{max} of XBAYs and XPEAYs or XPNYs. (2) In case of a same set of X-Y group couples, the distribution of λ_{max} of XPEAYs is larger than that of XPNYs. (3) The side-group CH_3 makes the effect of σ(X) larger than that of σ(Y) on the ν_{max} of XPEAYs, whereas the O atom makes the effect of σ(Y) larger than that of σ(X) on the ν_{max} of XPNYs. (4) The cross-interaction between X and Y has important effect on the all ν_{max}. However, the cross-interaction between CH_3 and X/Y has not important effect on the ν_{max} of XPEAY, and the cross-interaction between O and X/Y has not important effect on the ν_{max} of XPNY. Copyright © 2016 John Wiley & Sons, Ltd.

Keywords: cross-interaction effect; N-phenyl-α-phenylnitrone; N-(phenyl-ethylene)-aniline; side-group; Ultraviolet absorption spectra

INTRODUCTION

In recent years, optoelectronic materials have attracted extensive attention as a new type of functional material.[1–9] Some organic compounds, such as Schiff bases, which contains classical π conjugate system are applied well in many fields of optical functional materials due to their potential optoelectronic properties.[10–12] Recently, Hasan Tanak[13,14] investigated the energetic and structural properties of the Schiff base compounds, 2-methyl-6-[2-(trifluorometh y)phenyliminomethyl]phenol and (E)-2-[(2-chlorophenyl)iminomethyl]-4-trifluoromethoxyphenol. Also, he calculated the optimized geometry, vibration spectra and assignments, statistical thermodynamic parameters, electronic absorption spectra and nonlinear optical properties by using density functional theory. The calculated results are in agreement with the experimental facts. His valuable works provide an insight into the molecular properties of Schiff base compounds. The aryl Schiff bases with a classic π-conjugated molecular system have been employed in investigating the substituent effects as an important parent-structure. The properties of parent-structure can be easily influenced by the different factors including chemical environment around and change of substituents in molecules.

Ultraviolet (UV) absorption spectra are usually used to study the relationship between molecular structure and property (or activity),[15–19] which is also an important method in the tests of optical properties. Cao et al.[20–23] have successfully quantified the UV absorption energy ν_{max} (cm^{-1}) of wavelength of absorption maximum λ_{max} (nm) by applying the excited-state substituent parameter σ_{cc}^{ex} [22–24] for the disubstituted stilbenes XArCH=CHArY (abbreviated XSBY). Their research shows that the ν_{max} of XSBYs can be quantified well by only employing the σ_{cc}^{ex} parameter without Hammett constant σ.[25]

The correlations between the ν_{max} of aryl-Schiff bases and substituent effects were also reported. Chen et al.[26] investigated the substituent effects on the ν_{max} of 4,4′-disubstituted N-(benzylidene)-anilines *p*-XArCH=NArY-*p* (abbreviated *p*-XBAY-*p*). Fang et al.[27–29] reported the substituent effects on the ν_{max} of extended benzylidene anilines and the effects of molecular conformation on the ν_{max} of symmetrical Schiff bases. Cao et al.[30] studied the effect of substituents on the ν_{max} of *N*-(4-substituted benzylidene) anilines and *N*-(4-substituted benzylidene) cyclohexylamines. These studies of substituent effects on the ν_{max} of aryl-Schiff bases show that not only the excited-state substituent parameter σ_{cc}^{ex}, but also Hammett constant σ were employed in the quantitative correlations of the ν_{max}. Wang[31] even made an attempt of molecular design and synthesis of 3,4′/4,3′-disubstituted benzylidene anilines with

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* *Correspondence to: Chenzhong Cao, School of Chemistry and Chemical Engineering, Hunan University of Science and Technology, Xiangtan 411201,China. Email: czcao@hnust.edu.cn*

a *Q. Luo, C.-T. Cao, Z. Cao*
Key Laboratory of Theoretical Organic Chemistry and Function Molecule, Ministry of Education, Key Laboratory of QSAR/QSPR of Hunan Provincial University

b *C. Cao*
School of Chemistry and Chemical Engineering, Hunan University of Science and Technology, Xiangtan 411201, China

specified λ_{max}, on the basis of Chen's report,[26] in which the predicted λ_{max} values are in agreement with the experimental ones for these designed compounds.

Comparing with the C=C non-polar bond in XSBY, there is a polar C=N bridging group in the disubstituted benzylideneanilines XArCH=NArY (abbreviated XBAY). By investigating 72 samples of XBAY, Chen et al.[26] proposed a penta-parameter equation to quantify the ν_{max} well. On the basis of the study on XBAY, we come up with another two series of compounds: one is the disubstituted N-(phenyl-ethylene)-anilines XArC(Me)=NArY (abbreviated XPEAY) in which the H atom in CH=N is replaced by a methyl CH_3 (abbreviated Me); another is the disubstituted N-phenyl-α-phenylnitrone XArCH=N(O)ArY (abbreviated XPNY) in which an O atom is attached to the N in CH=N. The compounds XPEAY and XPNY have C(Me)=N and CH=N(O) bridging group carrying a side-group respectively, which are different from the XBAY with a CH=N bridging group. What we want to know is how their ν_{max} are influenced by the substituents X and Y, and what the differences of change regularities of the ν_{max} are for above mentioned three kinds of compounds. This is an interesting topic and is worthy of being studied. For this purpose, two series of compounds, XPEAYs and XPNYs were synthesized, next, their wavelength of absorption maximum λ_{max} (nm) in the UV spectra were measured, and then, the correlations between the ν_{max}, (cm^{-1}, $\nu_{max}=1/\lambda_{max}$) and the substituent effects of X and Y were carried out for the compounds XPEAYs and XPNYs, also the different effect of substituents on the ν_{max} of the three kinds of compounds XBAY, XPEAY and XPNY were investigated in this work. Maybe it can provide us with a valuable reference for designing and using these three kinds of compounds as optical materials.[31]

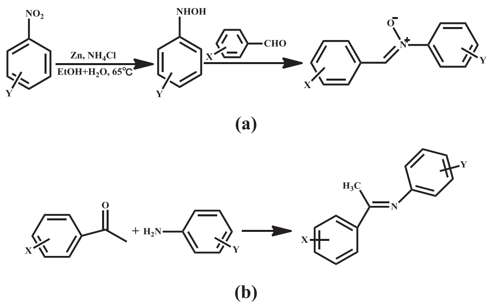
EXPERIMENTAL SECTIONS

Materials prepared

In this work, the XPNY and XPEAY were synthesized according to the reports of Liu[32] and Barluenga[33] as shown in scheme 1. All the compounds were characterized by ^1H NMR, in which the confirmation of XPEAYs were carried out by employing the method of our previous work.[34]

Date preparation.

The products were vacuum dried for a whole day before measurement. Their spectra were recorded by UV-2550 (SHIMADZU, Japan), scanning range 200-500 nm, and scanning speed 10 nm/s in anhydrous ethanol. The spectrum of each target compound was tested for three times (the absorption spectra of XPNYs can be seen in the supporting information, the λ_{max} values of XPEAYs come from the Cao's master thesis[35]), then the mean value of λ_{max} for each sample was employed in this work, The λ_{max} values of all target compounds were collected and their λ_{max} as well as ν_{max} values ($\nu_{max}=1/\lambda_{max}$) were listed in Tables 1 and 2. The ν_{max} values of XBAYs were employed from Chen's report.[26]



X (*p* or *m*) =CN, NO_2, CF_3, F, Cl, H, Me, NMe_2 or OMe

Y (*p* or *m*) =CN, NO_2, CF_3, F, Cl, H, Me, NMe_2 or OMe

Scheme 1. The synthesis of samples of (a) XPNYs and (b) XPEAYs

EFFECT OF SUBSTITUENT ON THE ν_{MAX} OF XPEAYS AND XPNYS

Chen[26] investigated the effects of substituents on the ν_{max} of XBAYs and obtained the correlation equation (1).

$$\nu_{max}(XBAY) = 32120 - 718.51\sigma(X) + 1197.18\sigma(Y) - 1017.23\Delta\sigma^2 + 1632.49\Sigma\sigma_{cc}^{ex} - 229.53\Delta\sigma_{cc}^{ex2} \quad (1)$$

Where σ is Hammett constant, $\Delta\sigma^2$ is the substituent specific cross-interaction effect expressed with Hammett constant between X and Y,[36] that is $\Delta\sigma^2$=[σ(X)-σ(Y)]^2={[σ_F(X)+σ_R(X)]- [σ_F(Y) +σ_R(Y)]}^{2}; $\Sigma\sigma_{cc}^{ex}$ is the sum of excited-state substituent constants $\sigma_{cc}^{ex}(X)$ of X and $\sigma_{cc}^{ex}(Y)$ of Y; $\Delta\sigma_{cc}^{ex2}$ is the substituent specific cross-interaction effect expressed with excited-state substituent constants between X and Y, namely $\Delta\sigma_{cc}^{ex2} = \left[\sigma_{cc}^{ex}(X) - \sigma_{cc}^{ex}(Y)\right]^2$.

The parent molecular skeletons of XPEAY and XPNY are similar to that of XBAY, whether the change regularities of ν_{max} of XPEAYs and XPNYs are also in keeping with that of XBAYs or not. Thus we plotted the experimental ν_{max} of XBAYs against that of corresponding XPEAYs (e.g., *p*-MeBAF-*p* versus *p*-MePEAF-*p*) and that of corresponding XPNYs (e.g., *p*-MeBAF-*p* versus *p*-MePNF-*p*) respectively, and obtained Figure 1.

It can be observed in Figure 1 that the ν_{max} of XBAYs versus XPEAYs and XBAYs versus XPNYs all have no good correlation. It implies that the factors affecting the ν_{max} of XPEAYs and XPNYs are different from these of XBAYs. In order to probe their differences, we still employed the 5 parameters in equation (1) to correlate the ν_{max} of XPEAYs and XPNYs, and got the equations (2) and (3), respectively.

$$\nu_{max}(XPEAY) = 31142 - 2439.43\sigma(X) + 2464.05\sigma(Y) - 308.60\Delta\sigma^2 + 1090.09\Sigma\sigma_{cc}^{ex} + 288.99\Delta\sigma_{cc}^{ex2} \quad (2)$$

$$R = 0.9880, S = 317.96, F = 344.86, n = 48$$

$$\nu_{max}(XPNY) = 31781 + 86.41\sigma(X) - 1123.55\sigma(Y) - 461.32\Delta\sigma^2 + 2029.93\Sigma\sigma_{cc}^{ex} - 583.96\Delta\sigma_{cc}^{ex2} \quad (3)$$

$$R = 0.9893, S = 241.31, F = 431.48, n = 53$$

In which, R is the correlation coefficient, S is the standard deviation, and F is the Fisher ratio, n is the date-points of regression equation respectively. The correlations of equations (2) and (3) show that the parameters of equation (1) can also be used to quantify the ν_{max} of XPEAYs and XPNYs, but their contributions

Table 1. The wavelength of absorption maximum λ_{max}(nm) and its wavenumber ν_{max}(cm^{-1}) of UV spectrum for XPEAYs and the substituent constants values σ_F, σ_R and σ_{cc}^{ex} for groups X and Y

No.	X	Y	σ_F(X) [a]	σ_F(Y)[a]	σ_R(X)[a]	σ_R(Y)[a]	σ_{cc}^{ex}(X)[b]	σ_{cc}^{ex}(Y)[b]	$\lambda_{max\ exp.}$ [c]	$\nu_{max\ exp.}$ [d]	$\nu_{max.cal.}$ [e]
1	*p*-OMe	*p*-NMe$_2$	0.29	0.15	-0.56	-0.98	-0.50	-1.81	356.00	28090	27637
2	*p*-OMe	*p*-OMe	0.29	0.29	-0.56	-0.56	-0.50	-0.50	330.00	30303	30046
3	*p*-OMe	*p*-Me	0.29	0.01	-0.56	-0.18	-0.50	-0.17	320.00	31250	30680
4	*p*-OMe	*p*-Cl	0.29	0.42	-0.56	-0.19	-0.50	-0.22	316.00	31646	31528
5	*p*-OMe	*p*-F	0.29	0.45	-0.56	-0.39	-0.50	0.06	316.00	31646	31526
6	*p*-Me	*p*-NMe$_2$	0.01	0.15	-0.18	-0.98	-0.17	-1.81	359.50	27816	27996
7	*p*-Me	*p*-OMe	0.01	0.29	-0.18	-0.56	-0.17	-0.50	337.70	29612	30190
8	*p*-Me	*p*-F	0.01	0.45	-0.18	-0.39	-0.17	0.06	321.05	31148	31584
9	*p*-Me	*p*-CN	0.01	0.51	-0.18	0.15	-0.17	-0.70	313.73	31875	32103
10	H	*p*-OMe	0.00	0.29	0.00	-0.56	0.00	-0.50	330.00	30303	29982
11	H	H	0.00	0.00	0.00	0.00	0.00	0.00	324.65	30802	31142
12	H	*p*-F	0.00	0.45	0.00	-0.39	0.00	0.06	323.89	30875	31355
13	*p*-Cl	*p*-NMe$_2$	0.42	0.15	-0.19	-0.98	-0.22	-1.81	373.89	26746	26707
14	*p*-Cl	*p*-OMe	0.42	0.29	-0.19	-0.56	-0.22	-0.50	342.20	29223	29077
15	*p*-Cl	*p*-Me	0.42	0.01	-0.19	-0.18	-0.22	-0.17	332.60	30066	29689
16	*p*-Cl	*p*-Cl	0.42	0.42	-0.19	-0.19	-0.22	-0.22	327.95	30492	30668
17	*p*-Cl	*p*-F	0.42	0.45	-0.19	-0.39	-0.22	0.06	327.00	30581	30568
18	*p*-Cl	*p*-CN	0.42	0.51	-0.19	0.15	-0.22	-0.70	315.06	31740	31214
19	*p*-F	*p*-NMe$_2$	0.45	0.15	-0.39	-0.98	0.06	-1.81	361.65	27651	27809
20	*p*-F	*p*-OMe	0.45	0.29	-0.39	-0.56	0.06	-0.50	337.66	29616	29908
21	*p*-F	*p*-Me	0.45	0.01	-0.39	-0.18	0.06	-0.17	329.05	30391	30456
22	*p*-F	H	0.45	0.00	-0.39	0.00	0.06	0.00	322.00	31056	31061
23	*p*-F	*p*-Cl	0.45	0.42	-0.39	-0.19	0.06	-0.22	322.75	30984	31402
24	*p*-F	*p*-F	0.45	0.45	-0.39	-0.39	0.06	0.06	320.82	31170	31275
25	*p*-F	*p*-CN	0.45	0.51	-0.39	0.15	0.06	-0.70	313.52	31896	31980
26	*p*-CF$_3$	*p*-NMe$_2$	0.38	0.15	0.16	-0.98	-0.12	-1.81	385.93	25911	25922
27	*p*-CF$_3$	*p*-OMe	0.38	0.29	0.16	-0.56	-0.12	-0.50	351.46	28453	28323
28	*p*-CF$_3$	*p*-Me	0.38	0.01	0.16	-0.18	-0.12	-0.17	340.83	29340	28935
29	*p*-CF$_3$	H	0.38	0.00	0.16	0.00	-0.12	0.00	335.01	29850	29608
30	*p*-CF$_3$	*p*-Cl	0.38	0.42	0.16	-0.19	-0.12	-0.22	335.65	29793	29994
31	*p*-CF$_3$	*p*-F	0.38	0.45	0.16	-0.39	-0.12	0.06	336.33	29733	29846
32	*p*-NO$_2$	*p*-NMe$_2$	0.65	0.15	0.13	-0.98	-1.17	-1.81	432.75	23108	23264
33	*p*-NO$_2$	*p*-OMe	0.65	0.29	0.13	-0.56	-1.17	-0.50	380.95	26250	26543
34	*p*-NO$_2$	*p*-Me	0.65	0.01	0.13	-0.18	-1.17	-0.17	363.60	27503	27370
35	*p*-NO$_2$	H	0.65	0.00	0.13	0.00	-1.17	0.00	351.45	28454	28172
36	*p*-NO$_2$	*p*-Cl	0.65	0.42	0.13	-0.19	-1.17	-0.22	354.30	28225	28459
37	*p*-NO$_2$	*p*-F	0.65	0.45	0.13	-0.39	-1.17	0.06	353.35	28301	28455
38	*m*-Cl	*p*-OMe	0.37	0.29	0.00	-0.56	0.02	-0.50	349.00	28653	29003
39	*m*-Cl	*p*-Me	0.37	0.01	0.00	-0.18	0.02	-0.17	334.10	29931	29578
40	*m*-Cl	*p*-F	0.37	0.45	0.00	-0.39	0.02	0.06	329.50	30349	30446
41	*p*-Cl	*m* -Me	0.42	-0.07	-0.19	0.00	-0.22	-0.03	330.90	30221	30119
42	*p*-F	*m* -Me	0.45	-0.07	-0.39	0.00	0.06	-0.03	323.75	30888	30853
43	*p*-NO$_2$	*m* -Me	0.65	-0.07	0.13	0.00	-1.17	-0.03	354.95	28173	27912
44	*p*-Cl	*m* -F	0.42	0.34	-0.19	0.00	-0.22	0.02	320.95	31158	31214
45	*p*-F	*m* -F	0.45	0.34	-0.39	0.00	0.06	0.02	317.61	31485	31897
46	*p*-NO$_2$	*m* -F	0.65	0.34	0.13	0.00	-1.17	0.02	344.25	29049	29173
47	H	*m* -CN	0.00	0.56	0.00	0.00	0.00	0.56	301.45	33173	33126
48	*p*-F	*m* -CN	0.45	0.56	-0.39	0.00	0.06	0.56	295.25	33870	33047

[a] The values were taken from Reference.[25]

[b] The values were taken from Reference.[22]

[c] The values were obtained by this work, which were presented in Cao's master thesis[35] and were not yet published.

[d] $\nu_{max\ exp}=1/\lambda_{max\ exp}$.

[e] Calculated values with Eqn(2).

Table 2. The wavelength of absorption maximum λ_{max}(nm) and its wavenumber ν_{max}(cm^{-1}) of UV spectrum for XPNYs and the substituent constants values σ_F, σ_R and σ_{cc}^{ex} for groups X and Y

No.	X	Y	$\sigma_F(X)$[a]	$\sigma_F(Y)$[a]	$\sigma_R(X)$[a]	$\sigma_R(Y)$[a]	$\sigma_{cc}^{ex}(X)$[b]	$\sigma_{cc}^{ex}(Y)$[b]	$\lambda_{max.exp.}$[c]	$\nu_{max\ exp.}$[d]	$\nu_{max\ cal.}$[e]
1	*P*-MeO	H	0.29	0.00	-0.56	0.00	-0.50	0.00	330.93	30218	30563
2	*P*-Me	H	0.01	0.00	-0.18	0.00	-0.17	0.00	316.71	31575	31391
3	H	H	0.00	0.00	0.00	0.00	0.00	0.00	312.01	32050	31781
4	*P*-Cl	H	0.42	0.00	-0.19	0.00	-0.22	0.00	321.92	31064	31301
5	*P*-F	H	0.45	0.00	-0.39	0.00	0.06	0.00	315.79	31667	31904
6	*P*-CF_3	H	0.38	0.00	0.16	0.00	-0.12	0.00	318.92	31356	31441
7	*P*-Me_2N	H	0.15	0.00	-0.98	0.00	-1.81	0.00	381.92	26183	25804
8	*P*-CN	H	0.51	0.00	0.15	0.00	-0.70	0.00	331.87	30132	29930
9	*P*-NO_2	H	0.65	0.00	0.13	0.00	-1.17	0.00	355.73	28111	28393
10	*P*-MeO	*P*-Cl	0.29	0.42	-0.56	-0.19	-0.50	-0.22	337.18	29658	29876
11	*P*-Me	*P*-Cl	0.01	0.42	-0.18	-0.19	-0.17	-0.22	324.86	30782	30641
12	H	*P*-Cl	0.00	0.42	0.00	-0.19	0.00	-0.22	318.37	31410	31023
13	*P*-Cl	*P*-Cl	0.42	0.42	-0.19	-0.19	-0.22	-0.22	324.64	30803	30649
14	*P*-F	*P*-Cl	0.45	0.42	-0.39	-0.19	0.06	-0.22	318.72	31376	31144
15	*P*-CF_3	*P*-Cl	0.38	0.42	0.16	-0.19	-0.12	-0.22	320.47	31204	30829
16	*P*-CN	*P*-Cl	0.51	0.42	0.15	-0.19	-0.70	-0.22	335.13	29839	29492
17	*P*-Me_2N	*P*-Cl	0.15	0.42	-0.98	-0.19	-1.81	-0.22	393.13	25437	25335
18	*P*-NO_2	*P*-Cl	0.65	0.42	0.13	-0.19	-1.17	-0.22	360.23	27760	28102
19	*P*-MeO	*P*-Me	0.29	0.01	-0.56	-0.18	-0.50	-0.17	331.28	30186	30520
20	*P*-Me	*P*-Me	0.01	0.01	-0.18	-0.18	-0.17	-0.17	320.69	31183	31267
21	*P*-Cl	*P*-Me	0.42	0.01	-0.19	-0.18	-0.22	-0.17	320.69	31183	31125
22	*P*-F	*P*-Me	0.45	0.01	-0.39	-0.18	0.06	-0.17	315.16	31730	31698
23	*P*-CF_3	*P*-Me	0.38	0.01	0.16	-0.18	-0.12	-0.17	318.27	31420	31196
24	*P*-Me_2N	*P*-Me	0.15	0.01	-0.98	-0.18	-1.81	-0.17	381.94	26182	26109
25	H	*P*-Me	0.00	0.01	0.00	-0.18	0.00	-0.17	315.74	31672	31596
26	*P*-CN	*P*-Me	0.51	0.01	0.15	-0.18	-0.70	-0.17	334.51	29894	29781
27	*P*-NO_2	*P*-Me	0.65	0.01	0.13	-0.18	-1.17	-0.17	358.09	27926	28319
28	*P*-MeO	*P*-F	0.29	0.45	-0.56	-0.39	-0.50	0.06	331.40	30175	30564
29	*P*-Me	*P*-F	0.01	0.45	-0.18	-0.39	-0.17	0.06	319.67	31282	31420
30	*P*-NO_2	*P*-F	0.65	0.45	0.13	-0.39	-1.17	0.06	355.07	28163	28405
31	*P*-Cl	*P*-F	0.42	0.45	-0.19	-0.39	-0.22	0.06	320.67	31185	31349
32	H	*P*-F	0.00	0.45	0.00	-0.39	0.00	0.06	314.13	31834	31831
33	*P*-F	*P*-F	0.45	0.45	-0.39	-0.39	0.06	0.06	314.67	31779	31962
34	*P*-MeO	*m*-Cl	0.29	0.37	-0.56	0.00	-0.50	0.02	337.27	29650	30021
35	*P*-NO_2	*m*-Cl	0.65	0.37	0.13	0.00	-1.17	0.02	357.20	27996	28194
36	*P*-CN	*m*-Cl	0.51	0.37	0.15	0.00	-0.70	0.02	333.53	29982	29700
37	*P*-Cl	*m*-Cl	0.42	0.37	-0.19	0.00	-0.22	0.02	323.87	30877	30936
38	*P*-Me	*m*-Cl	0.01	0.37	-0.18	0.00	-0.17	0.02	324.13	30852	30890
39	*m*-Cl	*P*-Cl	0.37	0.42	0.00	-0.19	0.02	-0.22	320.13	31237	31106

(*Continues*)

Table 2. (Continued)

No.	X	Y	$\sigma_F(X)^a$	$\sigma_F(Y)^a$	$\sigma_R(X)^a$	$\sigma_R(Y)^a$	$\sigma_{cc}^{ex}(X)^b$	$\sigma_{cc}^{ex}(Y)^b$	$\lambda_{max.exp.}{}^c$	$\nu_{max\ exp.}{}^d$	$\nu_{max\ cal.}{}^e$
40	*m*-F	*P*-Cl	0.34	0.42	0.00	-0.19	0.02	-0.22	319.73	31276	31107
41	*m*-MeO	*P*-Cl	0.12	0.42	0.00	-0.19	0.10	-0.22	321.47	31107	31224
42	H	*P*-MeO	0.00	0.29	0.00	-0.56	0.00	-0.50	319.53	31296	30890
43	*P*-MeO	*P*-MeO	0.29	0.29	-0.56	-0.56	-0.50	-0.50	334.33	29911	30031
44	*P*-CN	*P*-MeO	0.51	0.29	0.15	-0.56	-0.70	-0.50	340.27	29388	29283
45	*P*-Cl	*P*-MeO	0.42	0.29	-0.19	-0.56	-0.22	-0.50	325.33	30738	30481
46	*P*-MeO	*P*-CN	0.29	0.51	-0.56	0.15	-0.50	-0.70	352.27	28387	28158
47	H	*m*-F	0.00	0.34	0.00	0.00	0.00	0.02	317.87	31459	31386
48	*P*-CF_3	*m*-F	0.38	0.34	0.16	0.00	-0.12	0.02	320.13	31237	31213
49	*P*-F	*m*-F	0.45	0.34	-0.39	0.00	0.06	0.02	317.87	31459	31529
50	*P*-Cl	*m*-F	0.42	0.34	-0.19	0.00	-0.22	0.02	323.40	30921	30973
51	*P*-NO_2	*m*-F	0.65	0.34	0.13	0.00	-1.17	0.02	354.87	28179	28216
52	*P*-MeO	*m*-F	0.29	0.34	-0.56	0.00	-0.50	0.02	336.87	29685	30072
53	*P*-CN	*m*-F	0.51	0.34	0.15	0.00	-0.70	0.02	335.40	29815	29725

[a] The values were taken from Reference.[25]

[b] The values were taken from Reference.[22]

[c] The values were obtained by this work.

[d] $\nu_{max\ exp}=1/\lambda_{max\ exp.}$

[e] Calculated values with Eqn(3).

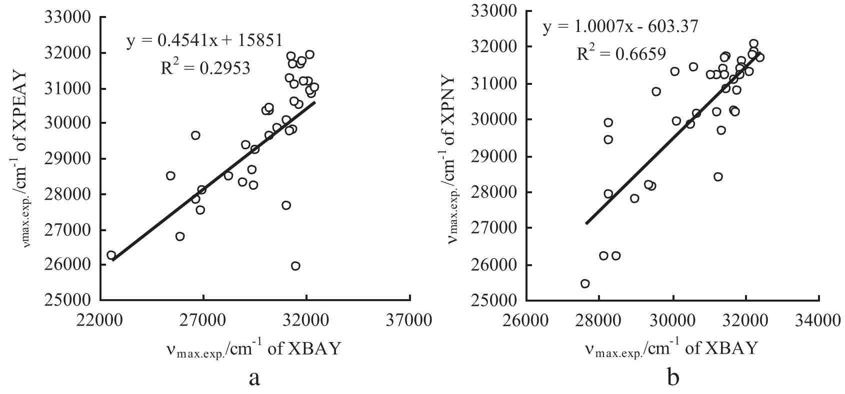


Figure 1. Plot of the $\nu_{max.exp}$ of XBAYs vs that of XPEAYs, and the $\nu_{max.exp}$ of XBAYs vs that of XPNYs a: XBAYs vs XPEAYs (38 couples); b: XBAYs vs XPNYs (38 couples)

are different from that to the ν_{max} of XBAYs. For purpose of comparison, the coefficients in front of each parameter of equations (1), (2) and (3) were all collected in Table 3.

It can be observed in Table 3 that: (i) In compound XPEAYs, the parameters σ(X), σ(Y), $\Delta\sigma^2$ and $\Sigma\sigma_{cc}^{ex}$ have similar effect on the ν_{max} as they do in XBAYs, whereas the $\Delta\sigma_{cc}^{ex2}$ item has an opposite action as it does in XBAYs. (ii) In XPNYs, the effect of $\Delta\sigma^2$, $\Sigma\sigma_{cc}^{ex}$ and $\Delta\sigma_{cc}^{ex2}$ on the ν_{max} have a similar effect as they do in XBAYs, whereas the σ(X) and σ(Y) have opposite action as they do in XBAYs. It is to say that the introduction of a side-group to the C=N bridging bond in XBAYs will lead to a different change regularity of the ν_{max} for XPEAYs and XPNYs.

RESULT DISCUSSION

The change of λ_{max} in XBAY, XPEAY and XPNY

The intercepts of equations (1), (2) and (3) are 32120, 31142 and 31781 cm^{-1}, which correspond to the λ_{max} values 311.33, 321.11 and 314.66 nm of the parent molecules HBAH, HPEAH and HPNH respectively. It shows that the side-group Me at the carbon end and O atom at the nitrogen end of C=N bond all increase the wavelength of λ_{max} for the parent molecules. However this increment is not a constant between XBAYs and XPEAYs or XPNYs due to the different coefficients in front of parameters in equations (1), (2) and (3). In general, the λ_{max}(XPNY) and λ_{max}(XPEAY) are longer than that of λ_{max}(XBAY) in case that the molecules of XPNYs, XPEAYs and XBAYs carry a same couple of X-Y groups, which can be seen in Table 4.

An interesting phenomenon has been observed from Table 4 that if keep Y group fixed and change X group, the variation of λ_{max} is least for XBAY, namely $\Delta\lambda_{max}$(XBAY) $<$ $\Delta\lambda_{max}$(XPNY), and $\Delta\lambda_{max}$(XBAY) $<$ $\Delta\lambda_{max}$(XPEAY). Whereas the $\Delta\lambda_{max}$(XBAY) is largest in case of X group fixed and Y group changing, that is, $\Delta\lambda_{max}$(XBAY) $>$ $\Delta\lambda_{max}$(XPNY), and $\Delta\lambda_{max}$(XBAY) $>$ $\Delta\lambda_{max}$(XPEAY). These experimental facts can be used to design UV absorption materials, from which we can employ these three kinds of compounds, XBAYs, XPEAFYs and XPNYs to obtain a series of materials with more distribution of λ_{max} in UV spectra. For examples, when X=MeO, F, Cl, CF_3 and NO_2, Y=Cl (Table 4), the λ_{max} is from 313.6 (FBACl) to 360.2 nm (NO_2PNCl), in which their λ_{max} gap is 46.6 nm, and in case of the same set of X groups and Y=Me (Table 4), their λ_{max} gap is 48.4 nm between NO_2PEAMe and FPNMe.

The action of side-group

For the parameters in equations (1), (2) and (3), their relative contributions (Ψ_r) and fraction contributions (Ψ_f) can be calculated by equations (4) and (5),[37,38] and the calculated results were listed in Table 5.

$$\psi_r = m_i \overline{X}_i \tag{4}$$

$$\psi_{f(i)} = \frac{R^2\left|\psi_{r(i)}\right|}{\sum_i \left|\psi_{r(i)}\right|} \times 100\% \tag{5}$$

Where the m_i and $\overline{X}_i$ are the coefficient and the average value of the parameters and the R is the correlation coefficients of the equations, respectively. The sum is over the parameters in the equations.

Table 5 shows that among the 5 parameters in equations (1), (2) and (3), which correspond to the compounds XBAYs, XPEAYs and XPNYs, the item $\Sigma\sigma_{cc}^{ex}$ made the most contribution, and the total contribution of excited-state substituent constant (items $\Sigma\sigma_{cc}^{ex}$ and $\Delta\sigma_{cc}^{ex2}$) is more than 50% for these three kinds of compounds. It is interesting that the introduction of the side-group CH_3 makes the effect of σ(X) larger than that of σ(Y) on the ν_{max}

Table 3. The coefficients in front of the parameters in equations (1), (2) and (3)

Equation	compound	coefficient				
		σ(X)	σ(Y)	$\Delta\sigma^2$	$\Sigma\sigma_{cc}^{ex}$	$\Delta\sigma_{cc}^{ex2}$
(1)	XBAY	-718.51	1197.18	-1017.23	1632.49	-229.53
(2)	XPEAY	-2439.43	2464.05	-308.60	1090.09	288.99
(3)	XPNY	86.41	-1123.55	-461.32	2029.93	-583.96

Table 4. Some examples of λ_{max}(nm) of XBAY, XPEAY and XPNY with same couple of X-Y groups

X	Y	XBAY[a]	XPEAY[b]	XPNY[b]	X	Y	XBAY[a]	XPEAY[b]	XPNY[b]
F	Cl	313.6	322.8	318.7	MeO	F	314.9	316.0	331.4
Cl		317.4	328.0	324.6		Cl	318.8	316.0	337.2
MeO		318.8	316.0	337.2		Me	319.9	320.0	331.3
CF_3		319.9	335.7	320.5		MeO	331.5	330.0	334.3
NO_2		345.0	354.3	360.2	$\Delta\lambda_{max}$		16.6	14.0	5.9
$\Delta\lambda_{max}$		31.4	38.3	41.5	Cl	F	313.8	327.0	320.7
F	Me	317.4	329.1	315.2		H	315.2	327.0	321.9
MeO		319.9	320.0	331.3		Cl	317.4	328.0	324.6
Cl		321.9	332.6	320.7		Me	321.9	332.6	320.7
CF_3		326.5	340.8	318.3		MeO	337.9	342.2	325.3
NO_2		353.8	363.6	358.1	$\Delta\lambda_{max}$		24.1	15.2	4.6
$\Delta\lambda_{max}$		36.4	43.6	42.9	NO_2	H	339.1	351.5	355.7
H	F	310.0	323.9	314.1		F	340.3	353.4	355.1
F		310.3	320.8	314.7		Cl	345.0	354.3	360.2
Me		311.3	321.1	319.7		Me	353.8	363.6	358.1
Cl		313.8	327.0	320.7	$\Delta\lambda_{max}$		14.7	12.1	5.1
MeO		314.9	316.0	331.4					
NO_2		340.3	354.3	355.1					
$\Delta\lambda_{max}$		30.3	38.3	41.0					

[a]The values of ν_{max} were taken from Reference.[26]
[b]The values of λ_{max} were measured in this work.

Table 5. The relative and fraction contribution (Ψ_r and Ψ_f) of σ(X), σ(Y), $\Delta\sigma^2$, $\Sigma\sigma_{cc}^{ex}$ and $\Delta\sigma_{cc}^{ex}2$ in equations (1), (2) and (3).

Compound	Equation	variable	σ(X)	σ(Y)	$\Delta\sigma^2$	$\Sigma\sigma_{cc}^{ex}$	$\Delta\sigma_{cc}^{ex2}$
XBAY	(1)	Ψ_r	-89.82	32.93	-440.97	-1650.61	-155.58
		Ψ_f (%)	3.71	1.37	18.16	67.93	4.41
XPEAY	(2)	Ψ_r	-559.04	-134.50	-110.56	-723.77	153.15
		Ψ_f (%)	32.46	7.81	6.42	42.03	8.89
XPNY	(3)	Ψ_r	13.11	-114.43	-103.24	-1124.12	228.07
		Ψ_f (%)	0.81	7.08	6.38	69.50	14.10

of XPEAYs, whereas the introduction of an O atom makes the effect of σ(Y) larger than that of σ(X) on the ν_{max} of XPNYs.

Attentions should be paied to the substituent specific cross-interaction effects between X and Y groups, namely $\Delta\sigma^2$ and $\Delta\sigma_{cc}^{ex2}$ items also play an important role in quantifying the ν_{max} for all three kinds of compounds, XBAYs, XPEAYs and XPNYs. What we want to know is whether the cross-interactions between the Me and X or Y have important contribution to the ν_{max} of XPEAYs, and whether the cross-interactions between the O^- and X or Y have important contribution to the ν_{max} of XPNYs. Thus we put the corresponding items, $\omega^2=[\sigma(Me)-\sigma(X)]^2= [-0.17-\sigma(X)]^2$ and $\chi^2=[\sigma(Me)-\sigma(Y)]^2=[-0.17-\sigma(Y)]^2$ into equation (2), and put items $\gamma^2= [\sigma(O^-)-\sigma(X)]^2=[-0.81-\sigma(X)]^2$ and $\beta^2=[\sigma(O^-)-\sigma(Y)]^2=[-0.81-\sigma(Y)]^2$ into the equation (3), then carried out the regression analysis respectively. The obtained results showed that the contributions of cross-interactions ω^2 and χ^2 to the ν_{max} of XPEAYs are so little that can be ignored, and so do the contributions of γ^2 and β^2 to the ν_{max} of XPNYs.

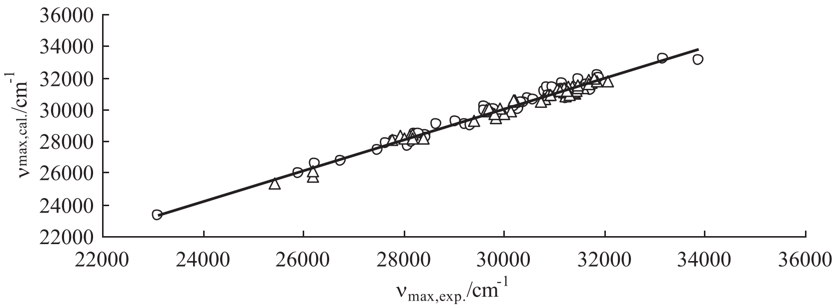


Figure 2. Plot of the calculated wavenumbers versus the experimental ones for XPEAY in Table 1 and XPNY in Table 2 (the symbols 'o' and 'Δ' represent the XPEAY and XPNY respectively)

Figure 2 is the plot of the calculated wavenumbers $\nu_{\max,\ \mathrm{cal.}}$ versus the experimental ones $\nu_{\max,\ \mathrm{exp.}}$ for XPEAYs and XPNYs. It can be seen in Figure 2 that the calculated wavenumbers are in good agreement with the experimental values for XPEAYs and XPNYs, and the distribution of $\nu_{\max}$ of XPEAYs in Table 1 is wider than that of XPNYs in Table 2.

We noted that, in case of a set of same X-Y group couples, the XPEAYs has more distribution of $\nu_{\max}$ than XPNYs has. For a calculation example, the biggest $\nu_{\max}$ is 33870 cm^{-1} (*p*-FPEACN-*m*) (corresponding to $\lambda_{\max}$ 295.25 nm) and the least $\nu_{\max}$ is 23108 cm^{-1} (*p*-NO$_2$PEANMe$_2$-*p*) (corresponding to $\lambda_{\max}$ 432.75 nm) for the 48 samples of XPEAYs in Table 1, and its gap ($\Delta\lambda_{\max}$) of $\lambda_{\max}$ is 137.50 nm. If these X-Y group couples in XPEAYs are attached to the XPNYs, we can calculate their corresponding $\nu_{\max}$ with equation (3). The obtained results are as the following: the biggest $\nu_{\max}$ is 32154 cm^{-1} ($\lambda_{\max}$ 311.00 nm) of *p*-FPNCN-*m*, and the least $\nu_{\max}$ is 25297 cm^{-1} ($\lambda_{\max}$ 395.31 nm) of *p*-NO$_2$PNNMe$_2$-*p*, in which the gap ($\Delta\lambda_{\max}$) of $\lambda_{\max}$ is only 84.31 nm, and is much less than that of XPEAYs. Here we also calculated the $\nu_{\max}$ of 72 samples of XBAY reported by Chen[26] with equations (2) and (3) respectively, and obtained the gap ($\Delta\lambda_{\max}$) 123.46 nm and 101.55 nm respectively. It also shows that the side-group Me at carbon end increases the distribution of $\lambda_{\max}$. Maybe, this difference is due to the interaction between the polarity of C=N bond and the electron donating effect of the side-group. Because the C=N bond is a polar double bond, the electronegativity of N atom is bigger than that of C atom, the π-electron density is transferred along the C to N, and the Me is an electron-donating group. Thus, when the electron-donating group Me connects with the carbon atom end of C=N, its electron donating effect is in agreement with the transfer direction of the π-electron density of C=N. Whereas, for the O atom at the nitrogen atom end of C=N, its unshared *p* electron pairs will transfer electron density to the N of C=N, which is opposite to the transfer direction of the π-electron density of C=N. As a result, the Me group is more effective than O atom to promote the conjugate effect in the interested molecules. That is to say, if there are a same set of X-Y group couples in hand, one expect to get a set of compounds with more distribution of $\lambda_{\max}$, it is better to employ the XPEAYs rather than the XPNYs molecule series.

CONCLUSIONS

From the above investigation, we can get the following conclusions. After the side-groups Me and O atom were introduced to the C=N bridging bond of the disubstituted aryl Schiff base XBAY, the XPEAY and XPNY compounds were formed. However there is no linear relationship between the $\nu_{\max}$ of XBAYs and XPEAYs or XPNYs. There are different change regularities of $\nu_{\max}$ for the three kinds of compounds, XBAYs, XPEAYs and XPNYs. In case of a same set of X-Y group couples, the distribution of $\lambda_{\max}$ of XPEAYs with the C(Me)=N bridging group is larger than that of XPNYs with CH=N(O) bridging group, which is due to the Me being at the carbon end of C=N and its electron donating effect being in agreement with the transfer direction of π-electron density of C=N. The contributions of cross-interactions between the Me and X or Y to the $\nu_{\max}$ of XPEAYs are so little that can be ignored, and so do the contributions of cross-interactions between the O$^-$ and X or Y to the $\nu_{\max}$ of XPNYs. Maybe the results of this work can provide a theoretical refference for designing those optical materials involving aryl-Schiff base molecules.

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