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# An extending evidence of molecular conformation on spectroscopic properties of symmetrical bis-Schiff bases



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### HIGHLIGHTS

# G R A P H I C A L A B S T R A C T

- Extending evidence was provided to clarify the conformation effect upon the spectra.
- UV spectrum is dependent on the substituents and the dihedral angle *τ*.
- Dihedral angle τ has a limited effect on the δ<sub>c</sub>(C=N) of symmetrical bis-Schiff bases.



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# ABSTRACT

The relationship between the molecular conformation and spectroscopic properties of symmetrical bis-Schiff bases, was explored experimentally. The synthesis, crystal structures, and spectroscopic behaviors of symmetrical bis-Schiff bases derived from 1,4-Phthalaldehyde, p-Y—C<sub>6</sub>H<sub>4</sub>N=CHC<sub>6</sub>H<sub>4</sub>CH=NC<sub>6</sub>H<sub>4</sub>—p-Y (Y = OMe, Me, H, Cl, or F) were reported. The results show when the effect of distance between X or Y and the imine carbon was considered, a good correlation between the  $v_{max}$  or  $\delta_c$ (C=N) of symmetrical bis-Schiff bases and the substituent parameters was obtained. The correlation results indicate that for both symmetrical bis-Schiff bases derived from 1,4-Phenylenediamine and 1,4-Phthalaldehyde, the UV absorption spectrum is dependent on the substituent at the aniline ring and the dihedral angle  $\tau$ , and the term sin( $\tau$ ) is suitable to modify the substituent effects on the  $v_{max}$ . However, experimental investigations indicate that the dihedral angle  $\tau$  has a limited effect on the values of  $\delta_c$ (C=N). This study provides an extending evidence of molecular conformation effects on spectroscopic properties of symmetrical bis-Schiff bases.

Dihedral angle  $\tau$  displays important effects on their  $v_{\text{max}}$ , and  $\sin(\tau)$  is suitable to modify the effects.

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# 1. Introduction

Schiff bases with conjugated  $\pi$ -electron system carrying an electron acceptor group at one end and a donor group at the oppo-

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site end, are receiving increasing attention in view of their potential application as effective ligands for complexation [1–3]. Most importantly, they are used in the design of liquid crystals [4–9] and nonlinear optical materials [10–17].

The UV spectrum behavior is known to be an important factor for the optimal use of the optical materials and the design of new candidates [18–20]. The marked difference in the UV spec-



trum of N-benzylideneaniline from its isoelectronic molecules, (*E*)stilbene [21–25] and azobenzene [26,27], has led to a great number of theoretical and experimental studies and arguments in the past three decades [28,29]. However, the effects of molecular non-planar conformation on the  $\lambda_{max}$  of Schiff bases have rarely been experimentally studied. Recently, we have verified that the molecular conformation has an important role on the UV spectra of symmetrical Schiff bases derived from 1,4-Phenylenediamine (*p*-**XAAX-p**, Fig. 1a) [30]. Nevertheless, the evidence of the molecular conformation effects on UV spectra of Schiff bases is still scare.

Charge distribution of the molecules is central to the optical and electronic characters of mesogens [31,32]. Several <sup>13</sup>C NMR studies have revealed that the overall electron distribution can be finetuned through the electronic effects of remote substituents [33-36]. By means of computational study, Neuvonen and co-workers [37] have proposed that the twist of the aniline ring respect to the plane of the C=N unit may affect the <sup>13</sup>C NMR chemical shifts of imine carbon in benzylideneanilines. However, the investigation of the molecular conformation effects on NMR spectra of *p*-XAAX**p** shows that the dihedral angle  $\tau$  has a limited effect on the values of  $\delta_{C}(C=N)$ . Our observations of the conformation effects in symmetrical Schiff bases *p*-XAAX-*p* encouraged us to prepare the other type of symmetrical Schiff bases derived from 1,4-Phthalaldehyde (**p-YBBY-p**, Fig. 1b). When X=Y, **p-XAAX-p** and **p-YBBY-p** are isomers. However, the two kinds of symmetrical Schiff bases have different central moiety: in *p*-XAAX-*p*, it is central diimine moiety, in **p-YBBY-p**, it is central dimethylene moiety. The higher electronegativity of nitrogen, compared to carbon, and the presence of a lone pair of electrons in the nitrogen atom, influence the electron distribution. Consequently, it is a worthwhile work to explore the conformation effects in *p***-YBBY**-*p* and provide a further proof for the effects of molecular conformation on NMR spectrum of symmetrical bis-Schiff bases. These five compounds have been reported by Iwan et al. [28], Choi et al. [38] and Das et al. [39], but there are short of their crystal structure.

To provide an extending evidence of molecular conformation effects on the  $\lambda_{max}$  and <sup>13</sup>C NMR chemical shifts  $\delta_{C}(C=N)$  of symmetrical Schiff bases, we synthesized five samples of symmetrical bis-Schiff bases **p-YBBY-p** (Fig. 1b) in this work. In **p-YBBY-p**, the substituents Y include H atom, electron-donating groups (Y = OMe, or Me) and electron-withdrawing ones (Y = Cl, or F). Their crystal structures and spectroscopic properties were measured experimentally, and the effects of the molecular conformation on spectroscopic properties of **Ya-Ye** (Fig. 1b) were quantified.

#### 2. Experimental methods

#### 2.1. Sample preparation

Compounds **Ya–Ye** were all prepared by solid–solid reactions [40]. The pure *p*-substituted aniline and 1,4-Phthalaldehyde were mixed in a 2:1 M ratio, and then the mixture was heated and melted. The mixture was further stirred for several minutes before

being cooled to room temperature and purified by recrystallization from absolute ethanol.

#### 2.2. X-ray crystallography

For X-ray diffraction, suitable crystals of bis-Schiff bases compounds (*p***-YBBY-***p*) were obtained by slow evaporation from a binary solvent mixture of methanol-chloroform (3:1). Colored crystals were obtained after a few days. For compound Ya-Ye, crystallographic analyses were performed on a Gemini S Ultra, Oxford platform diffractometer. The crystals Ya, Yb and Yc were measured with Mo K $\alpha$  monochromated radiation ( $\lambda$  = 0.71073 Å), while crystals Yd and Ye were measured with Cu Ka monochromated radiation ( $\lambda = 1.54184$  Å). An empirical absorption correction was applied. The structures were solved using the direct method and refined by the full-matrix least-squares method on  $F^2$  using the SHELXL-97 software [41]. All of the non-hydrogen atoms were refined anisotropically, whereas all hydrogen atoms were refined isotropically as a riding mode using the default SHELXL parameters. A summary of the crystal data and the structure refinements for Ya-Ye is available in the Supporting Information.

# 2.3. Spectral measurement

Absorbance spectra were collected on a LAMBDA-35 UV-vis spectrometer in a concentration range from  $10^{-3}$  to  $10^{-5}$  mol/L. The solvents used in absorption experiments (ethanol, acetonitrile, chloroform and cyclohexane) were of spectroscopic grade and were used as purchased. The values of  $\lambda_{max}$  and the maximum absorption wavenumber  $v_{max}$  for compounds **Ya**-**Ye** are listed in Table 1. The NMR chemical spectra of compounds **Ya**-**Ye** were recorded in CDCl<sub>3</sub> at 293 K. The <sup>13</sup>C NMR chemical shifts of the C=N groups are reported in Table 3, expressed in ppm relative to CDCl<sub>3</sub> (77.0 ppm). The detailed analytical data of compounds **Ya**-**Ye** are available in the Supporting Information.

# 3. Results and discussion

#### 3.1. Description of the crystal structures

A comparison of the X-ray crystal structures revealed a possible role for the conformation of **Ya–Ye** (Fig. 2). Compound **Ya** crystallized in the orthorhombic space group Pbca, while **Yb**, **Yc**, **Yd**, and **Ye** all crystallized in the monoclinic space group  $P2_1/n$ .

As shown in Fig. 2, the benzylidene ring of each compound is nearly co-planar with the N1=C7–C8 or N1A=C7A–C8A, whereas the aniline ring is twisted significantly from the C4–N1=C7 or C4A–N1A=C7A. Because of the slight deviation of the benzylidene ring from the N1=C7–C8 or N1A=C7A–C8A plane, we discuss below the twist of the aniline ring respect to the plane of the C=N unit only. The dihedral angle  $\tau$  is defined by atoms C7=N1–C4–C3 or C7A=N1A–C4A–C3A. The values of  $\tau$  in Ya–Ye are reported in



Fig. 1. General structures of compounds *p*-XAAX-*p*(a) and *p*-YBBY-*p*(b).

**Table 1** Values of  $\lambda_{max}$  (nm) and  $v_{max}$  (cm<sup>-1</sup>) for compounds *p***-XAAX-***p* and *p***-YBBY-***p*.

Compound	m	6-	(rex	1	D	Solvent
compound	ш	ΟP	0 <sub>cc</sub>	<sup>A</sup> max	Umax	Solvent
Ya	6	-0.27	-0.50	375.5	26630	Ethanol
Yb	6	-0.17	-0.17	354.1	28237	Ethanol
Yc	6	0.00	0.00	346.9	28828	Ethanol
Yd	6	0.23	-0.22	347.7	28763	Ethanol
Ye	6	0.06	0.06	343.3	29132	Ethanol
Xa	5	-0.27	-0.50	354.2	28230	Ethanol
Xb	5	-0.17	-0.17	350.9	28498	Ethanol
Xc	5	-0.15	-0.13	350.8	28510	Ethanol
Xd	5	0.23	-0.22	354.4	28218	Ethanol
Xe	5	0.06	0.06	348.1	28724	Ethanol
Xf	5	0.54	-0.12	359.1	27844	Ethanol
Xg	5	0.66	-0.70	371.5	26915	Ethanol
Ya	6	-0.27	-0.50	373.7	26759	Acetonitrile
Yb	6	-0.17	-0.17	353.0	28329	Acetonitrile
Yc	6	0.00	0.00	345.1	28977	Acetonitrile
Yd	6	0.23	-0.22	345.8	28923	Acetonitrile
Ye	6	0.06	0.06	341.1	29319	Acetonitrile
Xa	5	-0.27	-0.50	354.5	28207	Acetonitrile
Xb	5	-0.17	-0.17	350.8	28504	Acetonitrile
Xc	5	-0.15	-0.13	350.7	28514	Acetonitrile
Xd	5	0.23	-0.22	354.1	28241	Acetonitrile
Xe	5	0.06	0.06	348.5	28699	Acetonitrile
Xf	5	0.54	-0.12	358.4	27906	Acetonitrile
Xg	5	0.66	-0.70	370.4	26999	Acetonitrile
Ya	6	-0.27	-0.50	378.2	26445	Chloroform
Yb	6	-0.17	-0.17	356.8	28024	Chloroform
Yc	6	0.00	0.00	350.0	28574	Chloroform
Yd	6	0.23	-0.22	352.8	28345	Chloroform
Ye	6	0.06	0.06	346.1	28894	Chloroform
Xa	5	-0.27	-0.50	357.7	27954	Chloroform
Xb	5	-0.17	-0.17	354.3	28221	Chloroform
Xc	5	-0.15	-0.13	354.7	28194	Chloroform
Xd	5	0.23	-0.22	357.8	27948	Chloroform
Xe	5	0.06	0.06	351.0	28488	Chloroform
Xf	5	0.54	-0.12	361.9	27630	Chloroform
Xg	5	0.66	-0.70	376.0	26599	Chloroform
Ya	6	-0.27	-0.50	378.4	26431	Cyclohexane
Yb	6	-0.17	-0.17	358.9	27866	Cyclohexane
Yc	6	0.00	0.00	351.0	28492	Cyclohexane
Yd	6	0.23	-0.22	352.0	28412	Cyclohexane
Ye	6	0.06	0.06	346.5	28858	Cyclohexane
Xa	5	-0.27	-0.50	357.9	27942	Cyclohexane
Xb	5	-0.17	-0.17	355.5	28128	Cyclohexane
Xc	5	-0.15	-0.13	356.1	28086	Cyclohexane
Xd	5	0.23	-0.22	360.1	27770	Cyclohexane
Xe	5	0.06	0.06	354.7	28193	Cyclohexane
Xf	5	0.54	-0.12	364.9	27405	Cvclohexane
Xg	5	0.66	-0.70	374.9	26671	Cvclohexane
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Fig. 2, in which  $\tau = 180^{\circ}$  corresponds to the co-planarity of the aniline ring and the C4–N1=C7 or C4A–N1A=C7A plane.

#### 3.2. Absorption spectra

Table 1 summarizes the  $\lambda_{max}$  (column 5) and the corresponding  $v_{max}$  (column 6) of *p***-XAAX-***p* and *p***-YBBY-***p* in protic solvent (ethanol), electron pair donating solvent (acetonitrile), and those with no specific solvent–solute interactions (chloroform, cyclohexane). The absorption spectra of **Ya–Ye** in ethanol are shown in Fig. 3. For comparison, the maximum absorbance is normalized to 1 for all measurements.

As can be seen from Fig. 3, all spectra show four bands. These values are similar to those observed in related Schiff base compounds [42,43]. The maximum absorption bands at about 2.6– $3.0 \times 10^4$  cm<sup>-1</sup> are assigned to the intramolecular charge transfer band of the azomethine C=N group.

In our previous research, it is verified that substituent effects have obvious impacts on the  $v_{max}$  of molecules, and the  $v_{max}$  is

$$\rho_{\rm max} = {\rm constant} + \rho_{\rm cc}^{\rm ex} \sigma_{\rm cc}^{\rm ex} + \rho_{\rm p} \sigma_{\rm p} \tag{1}$$

Therefore, in this work, we tried to correlate the  $v_{max}$  of **p-YBBY-p** in ethanol with Eq. (1), and obtained Eq. (2). The results are good, and the correlation coefficient was as high as 0.9891.The correlation equation about the **p-XAAX-p** in ethanol was also shown as Eq. (3). In comparison to the Eq. (2),  $\rho_p$  in Eq. (3) is negative, and both the values of  $\rho_{cc}^{ex}$  and  $\rho_p$  are smaller in Eq. (3) than those in Eq. (2). The behavior observed above may be understood by considering the distance between the imine carbon and X or Y. It can be observed that the chemical bond numbers (*m*) between X and the imine carbon in **p-XAAX-p** is 5, while the bond numbers (*m*) between Y and the imine carbon in **p-YBBY-p** is 6.

For ***p*-YBBY-*p***: 
$$v_{max} = 28908 + 3168\sigma_{cc}^{ex} + 2139\sigma_{p}$$
  
 $R = 0.9891, R^2 = 0.9784, s = 207, n = 5, F = 45.28$  (2)

For **p-XAAX-p**: 
$$v_{\text{max}} = 28636 + 1452\sigma_{\text{cc}}^{\text{ex}} - 1030\sigma_{\text{p}}$$
  
 $R = 0.9904, R^2 = 0.9810, s = 103, n = 7, F = 103.10$  (3)

To understand the effect of molecular conformation on absorption spectra of symmetrical Schiff bases, we try to propose a quantitative model to express the substituent dependence of the  $v_{max}$  of **p-XAAX-p** and **p-YBBY-p**. Firstly, we used Eq. (1) to correlate the  $v_{max}$  of **p-XAAX-p** and **p-YBBY-p** in ethanol, and Eq. (4) was obtained.

$$\upsilon_{\text{max}} = 28781 + 2487\sigma_{\text{cc}}^{\text{ex}} - 283\sigma_{\text{p}}$$
  

$$R = 0.8316, R^2 = 0.6916, s = 448, n = 12, F = 10.09$$
(4)

The results are poor, and the standard deviation is as high as 448 cm<sup>-1</sup>. It suggests that owing to the different structure of *p*-**XAAX**-*p* and *p*-**YBBY**-*p*, the distance between the imine carbon and X or Y must be considered. In Eq. (2), both the absolute values of  $\rho_{cc}^{ex}$  and  $\rho_p$  are about two times higher than those in Eq. (3). Furthermore,  $\rho_p$  in Eq. (2) is opposite to that in Eq. (3); i.e., odd chemical bond number causes negative  $\rho_p$ . Thus, we attempt to employ the item  $(-1)^m(1/m)^4$  to express the effect of distance between X or Y and the imine carbon. The parameters  $\sigma_{cc}^{ex}$  and  $\sigma_p$  in Eq. (1) were modified by the item  $(-1)^m(1/m)^4$ , and we carried out a correlation analysis for the twelve  $v_{max}$  and got Eq. (5).

$$v_{\text{max}} = 28724 + 1743100(-1)^{m}(1/m)^{4}\sigma_{\text{cc}}^{\text{ex}} + 1397700(-1)^{m}(1/m)^{4}\sigma_{\text{p}}$$
  

$$R = 0.9732, R^{2} = 0.9472, s = 185, n = 12, F = 80.75$$
(5)

The correlation results are good, and the standard deviation is reduced to 185 cm<sup>-1</sup> when the item  $(-1)^m(1/m)^4$  is used (Eq. (5)). Does the dihedral angle have an impact on the UV absorption energy of symmetrical Schiff bases? In *p***-XAAX-***p*, the  $v_{max}$  is depend on the dihedral angle  $\tau$ , and the term  $\sin(\tau)$  is suitable to modify the substituent effects on the  $v_{max}$  [30]. Thus, applying the term  $\sin(\tau)$  to modify the parameters  $\sigma_{cc}^{ex}$  and  $\sigma_p$  in Eq. (5), we carried out a correlation analysis once again (Eq. (6)). The correlation of Eq. (6) is much better than that of Eq. (5), and its standard error is only 141 cm<sup>-1</sup>. This confirms that the effect of the twist of the aniline ring respect to the plane of the C=N unit is an important factor influencing the substituent effects on the  $\lambda_{max}$ of symmetrical bis-Schiff bases, though it is not as important to the  $\lambda_{max}$  as the effects of conjugation extent or the substituents.

#### Table 2

Correlation results for *p*-XAAX-*p* and *p*-YBBY-*p* in acetonitrile, chloroform and cyclohexane.

 $v_{\text{max}} = (-1)^m (1/m)^4 \rho_{cc}^{\text{ex}} \sigma_{cc}^{\text{ex}} + (-1)^m (1/m)^4 \rho_{\text{p}} \sigma_{\text{p}} + \text{constant}$ 

 $v_{\text{max}} = (-1)^m (1/m)^4 \rho_{cc}^{\text{ex}} \sigma_{cc}^{\text{ex}} \sin(\tau) + (-1)^m (1/m)^4 \rho_n \sigma_p \sin(\tau) + \text{constant}$ 

	$ ho_{ m cc}^{ m ex}$	$ ho_{ m p}$	Constant	R	$R^2$	S	F	n	Eqs.
Ethanol	1743100	1397700	28724	0.9732	0.9472	185	80.75	12	(5)
	5466100	2468900	28708	0.9847	0.9696	141	143.49	12	(6)
Acetonitrile	1811000	1433100	28794	0.9638	0.9290	224	58.84	12	(7)
	5801900	2360900	28781	0.9716	0.9441	199	75.98	12	(8)
Chloroform	1920500	1264200	28474	0.9708	0.9425	196	73.81	12	(9)
	5898000	2198500	28450	0.9884	0.9770	124	191.18	12	(10)
Cyclohexane	1588000	1458400	28326	0.9652	0.9316	207	61.26	12	(11)
	4994000	2665100	28311	0.9710	0.9429	189	74.35	12	(12)

 Table 3

 <sup>13</sup>C NMR shifts (ppm) of the C=N carbons in compounds p-XAAX-p and p-YBBY-p.

p-YBBY-p					p-XAAX-p						
No	Y	т	$\sigma_{ m F}$	$\sigma_{ m R}$	$\delta_{C}(C=N)$	No	Х	т	$\sigma_{ m F}$	$\sigma_{ m R}$	$\delta_{C}(C=N)$
1	OMe	6	0.29	-0.56	157.37	1	OMe	5	0.29	-0.56	158.93
2	Me	6	0.01	-0.18	158.59	2	Me	5	0.01	-0.18	159.63
3	Н	6	0.00	0.00	159.40	3	Et	5	0.00	-0.15	159.65
4	Cl	6	0.42	-0.19	159.61	4	Cl	5	0.42	-0.19	158.19
5	F	6	0.45	-0.39	159.04	5	F	5	0.45	-0.39	158.22
						6	CF <sub>3</sub>	5	0.38	0.16	158.08
						7	CN	5	0.51	0.15	157.79

$$v_{\max} = 28708 + 5466100(-1)^m (1/m)^4 \sigma_{cc}^{ex} \sin(\tau) + 2468900(-1)^m (1/m)^4 \sigma_p \sin(\tau) R = 0.9847, R^2 = 0.9696, s = 141, n = 12, F = 143.49$$
(6)

To further clarify the influence of  $\sin(\tau)$  on  $v_{max}$ , we correlated the  $v_{max}$  of **p-XAAX-p** and **p-YBBY-p** in acetonitrile, chloroform and cyclohexane with  $(-1)^m(1/m)^4\sigma_{cx}^{ex}$  and  $(-1)^m(1/m)^4\sigma_p$  or with  $(-1)^m(1/m)^4\sigma_{cx}^{ex}\sin(\tau)$  and  $(-1)^m(1/m)^4\sigma_p\sin(\tau)$ , respectively, and obtained Eqs. (7)–(12) (Table 2). The correlations of Eqs. (8), (10) and (12) are better than those of Eqs. (7), (9) and (11), respectively. This is further proof that the substituent effects upon the  $\lambda_{max}$  are affected by the twist of the aniline ring respect to the rest of the molecules, and the term  $\sin(\tau)$  is available to scale the effects.

#### 3.3. NMR spectra

Table 3 summarizes the  $\delta_C(C=N)$  values of **p-XAAX-p** and **p-YBBY-p**. As shown in Table 3, the  $\delta_C(C=N)$  of **p-YBBY-p** range from 157.37 to 159.61 ppm. The  $\delta_C(C=N)$  increases with increasing electron-withdrawing capability of substituent Y. This indicates that electron-withdrawing substituents Y cause deshielding of the imine carbon, while electron-donating ones behave in the opposite way: with the increasing capability of electron donating, there is a decreasing  $\delta_C(C=N)$ .

To investigate the substituent effects on  $\delta_{\rm C}({\rm C=N})$  in *p***-YBBY-***p* in more detail, we evaluated the substituent effects on  $\delta_{\rm C}({\rm C=N})$ . The  $\delta_{\rm C}({\rm C=N})$  values of *p***-YBBY-***p* in Table 3 were first correlated with  $\sigma_{\rm F}$  and  $\sigma_{\rm R}$  parameters ( $\sigma_{\rm F}$  and  $\sigma_{\rm R}$  are the inductive parameter and resonance parameter, respectively), and Eq. (13) was obtained. The correlation of Eq. (13) is good, and the deviation is 0.19. The correlation equation about the  $\delta_{\rm C}({\rm C=N})$  of *p***-XAAX-***p* was also shown as Eq. (14). It is noted that the correlation coefficients are positive. This indicates that aniline substituents Y display a normal effect on  $\delta_{\rm C}(\rm C=N)$ ; i.e., electron-withdrawing substituents cause deshielding, while electron-donating ones cause shielding. However, the signs are negative in the study concerning the effects of benzylidene substituents X on  $\delta_{\rm C}(\rm C=N)$  in *p***-XAAX-***p*, in which benzylidene substituents X exhibit an opposite effect to the normal one; i.e., electron-withdrawing substituents cause shielding, while electron-donating ones cause deshielding. This suggests that the substituent effects on  $\delta_{\rm C}(\rm C=N)$  in *p***-YBBY-***p* are different with those in *p***-XAAX-***p*.

For ***p*-YBBY-*p*** : 
$$\delta_{\rm C}({\rm C=N}) = 159.41 + 3.10\sigma_{\rm F} + 5.04\sigma_{\rm R}$$
  
 $R = 0.9876, R^2 = 0.9754, s = 0.19, n = 5, F = 39.60$  (13)

For ***p*-XAAX-*p*** : 
$$\delta_{\rm C}({\rm C=N}) = 159.53 - 3.63\sigma_{\rm F} - 0.83\sigma_{\rm R}$$
  
 $R = 0.9989, R^2 = 0.9978, s = 4.74 \times 10^{-2}, n = 7, F = 906.00$ 
(14)

Furthermore, the coefficient of  $\sigma_R$  in Eq. (13) is nearly 6 times higher than that in Eq. (14). Thus, we tried to apply Eq. (15) to express the effects of substituents X and Y on the  $\delta_C(C=N)$  of symmetrical bis-Schiff bases *p***-XAAX-***p* and *p***-YBBY-***p*.

$$\delta_{\rm C}({\rm C=}{\rm N}) = (-1)^m \sigma_{\rm F} + (-1)^m {\rm e}^{(6/5)} \sigma_{\rm R} + {\rm constant} \tag{15}$$

The results are shown in Table 4 (Eq. (16)). The results are excellent, and the correlation coefficient is as high as 0.9915 and the standard deviation is only 0.11 ppm. Is the twist of the aniline ring a influencing factor on the  $\delta_{\rm C}$ (C=N) in symmetrical bis-Schiff bases? We modified the parameters  $\sigma_{\rm F}$  and  $\sigma_{\rm R}$  with the parameter  $\sin(\tau)$ . However, good to poor correlations were observed when the term  $\sin(\tau)$  was used to modify  $\sigma_{\rm F}$  (Eq. (18)),  $\sigma_{\rm R}$  (Eq. (19)), or both



Fig. 2. Representative solid state molecular structures of Ya–Ye. The dihedral angle  $\tau$  is defined by atoms C7=N1–C4–C3 or C7A=N1A–C4A–C3A. Displacement ellipsoids are drawn at the 50% probability level, and H atoms are shown as small spheres of arbitrary radii.



Fig. 3. Normalized absorbance spectra for Ya-Ye in ethanol.

 $\sigma_{\rm F}$  and  $\sigma_{\rm R}$  (Eq. (17)) (Table 4). This suggests the effects of the twist of aniline ring on the  $\delta_{\rm C}$ (C=N) values of symmetrical bis-Schiff bases are not obvious.

# 4. Conclusion

Different actions of polar Hammett parameter on the  $v_{max}$  and  $\delta_C(C=N)$  in *p***-XAAX-***p* and *p***-YBBY-***p* lead to different substituent effects of the two types of compounds. The effect of distance betweem X or Y the the imine carbon must be considered in the

**Table 4** Correlation results of  $\delta_C(C=N)$  for *p***-XAAX-***p* and *p***-YBBY-***p***.** 

quantitative model expressing the substituent dependence of  $v_{max}$ or  $\delta_{\rm C}({\rm C=N})$  of *p***-XAAX-***p* and *p***-YBBY-***p*. The dihedral angle  $\tau$  influences the electronic effects of substituents on the  $v_{max}$  of *p***-XAAX***p* and *p***-YBBY-***p*, and the term  $\sin(\tau)$  is suitable to modify the effect. Surprisingly, due to the different substituent effects on  $\delta_{\rm C}({\rm C=N})$ , the twist of the aniline ring respect to the plane of the C=N unit has a limited role on the  $\delta_{\rm C}({\rm C=N})$  in *p***-XAAX-***p* and *p***-YBBY-***p*. The results of this investigation indicate the importance of the molecular conformation effects upon the absorbance spectra.

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# Appendix A. Supplementary material

CCDC 892133, 892134, 892518, 917039 and 917040 contain the supplementary crystallographic data for this paper. These data can be obtained free of charge via http://www.ccdc.cam.ac.uk/conts/ retrieving.html (or from the Cambridge Crystallographic Data Centre, 12, Union Road, Cambridge CB2 1EZ, UK; fax: +44 1223 336033). Supplementary data associated with this article can be found, in the online version, at http://dx.doi.org/10.1016/j.mol-

Regression equation	R	$R^2$	S	F	n	Eqs.
$\delta_{\rm C}({\rm C=N}) = 159.46 + 3.22 \ (-1)^m \sigma_{\rm F} + 0.66 \ (-1)^m \ e^{(6/5)} \ \sigma_{\rm R}$	0.9915	0.9830	0.11	260.96	12	(16)
$\delta_{\rm C}({\rm C=N}) = 159.36 + 6.44 \ (-1)^m \sigma_{\rm F} \sin(\tau) + 1.39 (-1)^m \ {\rm e}^{(6/5)} \sigma_{\rm R} \sin(\tau)$	0.8925	0.7965	0.39	17.61	12	(17)
$\delta_{\rm C}({\rm C=N}) = 159.40 + 5.91(-1)^m \sigma_{\rm F} \sin(\tau) + 0.56 (-1)^m e^{(6/5)} \sigma_{\rm R}$	0.9090	0.8326	0.36	21.41	12	(18)
$\delta_{C}(C=N) = 159.19 + 2.45(-1)^{m}\sigma_{F} + 1.12(-1)^{m}e^{(6/5)}\sigma_{R}\sin(\tau)$	0.8095	0.6553	0.51	8.56	12	(19)

struc.2014.01.073. These data include MOL files and InChiKeys of the most important compounds described in this article.

#### References

- [1] Y.F. Han, H. Li, L.H. Wenga, G.X. Jin, Chem. Commun. 46 (2010) 3536.
- [2] H. Li, Y.F. Han, G.X. Jin, Dalton Trans. 40 (2011) 4982.
- [3] B. Bilgin-Eran, Ç. Yörür, C. Tschierske, M. Prehmb, U. Baumeisterc, J. Mater. Chem. 17 (2007) 2319.
- [4] A. Iwan, H. Janeczekb, A. Hreniaka, M. Palewiczac, D. Pociechad, Liq. Cryst. 37 (2010) 1021.
- [5] A. Iwan, H. Janeczekb, B. Jarzabekc, P. Rannoud, Matererials 2 (2009) 38.
- [6] H. Nádasi, W. Weissflog, A. Eremin, G. Pelzl, S. Diele, B. Dasb, S. Grande, J. Mater. Chem. 12 (2002) 1316.
- [7] M. Šepelj, A. Lesac, U. Baumeister, S. Diele, H.L. Nguyenc, D.W. Bruce, J. Mater. Chem. 17 (2007) 1154.
- [8] P.A. Henderson, C.T. Imrie, Macromolecules 38 (2005) 3307.
- [9] T. Donaldson, P.A. Henderson, M.F. Achard, C.T. Imrie, Liq. Cryst. 38 (2011) 1331.
- [10] A. Iwan, D. Sek, Prog. Polym. Sci. 33 (2008) 289.
- [11] A. Iwan, H. Janeczeka, P. Rannoub, R. Kwiatkowskic, J. Mol. Struct. 148 (2009) 77.
- [12] A. Iwan, H. Janeczekb, P. Rannoud, Spectrochim. Acta, Part: A. 72 (2009) 72.
- [13] C.J. Yang, S.A. Jenekhe, Macromolecules 24 (2009) 1180.
- [14] W. Mormann, C. Kuckertz, M. Bröcher, Macromol. Symp. 290 (2010) 70.
- [15] V. Saheb, I. Sheikhshoaie, Spectrochim. Acta Part A Mol. Biomol. Spectrosc. 81 (2011) 144.
- [16] I. Sheikhshoaie, V. Saheb, Spectrochim. Acta Part A Mol. Biomol. Spectrosc. 77 (2010) 1069.
- [17] A. Iwan, P. Bilskib, H. Janeczekb, B. Jarzabekc, M. Domanskic, P. Rannoud, A. Sikoraa, D. Pociechae, B. Kaczmarczykc, J. Mol. Struct. 963 (2010) 175.
- [18] C.E. Silva, H.F.Dos Santos, N.L. Speziali, R. Diniz, L.F.C. de Oliveira, J. Phys. Chem. A 114 (2010) 10097.
- [19] X.G. Guo, M.D. Watson, Org. Lett. 10 (2008) 5333.

- [20] H.P. Jia, S.X. Liu, L. Sanguinet, E. Levillain, S. Decurtins, J. Org. Chem. 74 (2009) 5727.
- [21] S. Zamir, J. Bernstein, A. Loffe, J. Brunovll, M. Kolonits, I. Hargittai, J. Chem. Soc. Perkin Trans. 2 (1994) 895.
- [22] R.D. Curtis, G.H. Penner, W. Power, R.E. Wasylishen, J. Phys. Chem. 94 (1990) 400.
- [23] P. Bao, Z.H. Yu, J. Comput. Chem. 27 (2006) 809.
- [24] J. Scott, M. Asami, K. Tanaka, New J. Chem. 26 (2002) 1822.
- [25] R. Montalvo, Gonzalez, A. Ariza, Castolo, J. Mol. Struct. 655 (2003) 375.
- [26] J. Harada, M. Harakawa, K. Ogawa, Acta Crystallogr., Sect. B 60 (2004) 578.
- [27] H.B. Brügi, J.D. Dunitz, J. Chem. Soc., Chem. Commun. (1969) 472.
- [28] A. Iwan, B. Kaczmarczyka, H. Janeczeka, D. Sek, S. Ostrowskib, Spectrochim. Acta Part A Mol. Biomol. Spectrosc. 66 (2007) 1030.
- [29] B. Kaczmarczyk, A. Iwan, D. Sek, Spectrochim. Acta Part A Mol. Biomol. Spectrosc. 68 (2007) 369.
- [30] Z.J. Fang, C.Z. Cao, J. Mol. Struct. 1036 (2013) 447.
- [31] W. Hu, L.P. Zhang, H. Cao, L. Song, H.Y. Zhao, Z. Yang, Z.H. Cheng, H. Yang, L. Guo, Phys. Chem. Chem. Phys. 12 (2010) 2632.
- [32] S. Köber, M. Salvador, K. Meerholz, Adv. Mater. 23 (2011) 4725.
- [33] C.Z. Cao, B.T. Lu, G.F. Chen, J. Phys. Org. Chem. 24 (2011) 335.
- [34] G.F. Chen, C.Z. Cao, B. Sheng, Y. Zhu, Z.X. Wu, X.S. Wu, J. Phys. Org. Chem. 25 (2012) 828.
- [35] Z.J. Fang, C.Z. Cao, G.F. Chen, J. Phys. Org. Chem. 25 (2012) 1343.
  [36] G.F. Chen, C.Z. Cao, Y. Zhu, Z.X. Wu, X.S. Wu, Spectrochim. Acta Part A Mol. Biomol. Spectrosc. 99 (2012) 218.
- [37] H. Neuvonen, K. Neuvonen, A. Koch, E. Kleinpeter, J. Mol. Struct. Theochem. 815 (2007) 95.
- [38] C.S. Choi, K.S. Jeon, K.H. Lee, J. Photosci. 11 (2004) 71.
- [39] S. Das, V.K. Das, L. Saikia, A.J. Thakur, Green Chem. Lett. Rev. 5 (2012) 457.
- [40] J. Schmeyers, F. Toda, J. Boy, G. Kaupp, J. Chem. Soc., Perkin Trans. 2 (4) (1998) 989.
- [41] G.M. Sheldrick, SHELXTL-97, University of Göttingen, 1997.
- [42] H. Tanak, A. Agar, M. Yavuz, J. Mol. Model. 16 (2010) 577.
- [43] S.H. Alarcon, D. Pagani, J. Bacigalupo, A.C. Olivieri, J. Mol. Struct. 475 (1999) 233.