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Effect of molecular conformation on spectroscopic properties of symmetrical Schiff bases derived from 1,4-phenylenediamine

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HIGHLIGHTS

► Seven crystals of bis-Schiff bases suitable for X-ray diffraction were obtained.

Form $\sin \tau$ is suitable to modify the substituent effects on the v_{max} .

► Dihedral angle τ has a limited effect on the values of $\delta_{C}(C=N)$.

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ABSTRACT

The relationship between the molecular conformation and spectroscopic properties of symmetrical bis-Schiff bases was explored experimentally. Seven samples of compounds p-X–C₆H₄CH=NC₆H₄N=CHC₆H₄-p-X (X = OMe, Me, Et, Cl, F, CF₃, or CN) were prepared for this study, and their crystal structures were measured by X-ray diffraction. Their λ_{max} values in ethanol, acetonitrile, chloroform and cyclohexane solvents were measured, and their δ_{c} (C=N) values in chloroform-d were determined. The results show that the v_{max} is dependent on the substituents at the benzylidene ring and the dihedral angle τ of the titled molecules, and the term $sin(\tau)$ is suitable to modify the substituent effects on the v_{max} . However, experimental investigations indicate that the dihedral angle τ has a limited effect on the values of δ_{c} (C=N). This study provides a new understanding for the molecular conformation on spectroscopic properties of symmetrical Schiff bases.

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1. Introduction

Schiff bases have recently gained much attention in the design of catalysts in various chemical processes [1-4], as models for of biological systems [5-8], and as effective ligands in metal complexes in the preparation of dyes [9,10]. Most importantly, they have been shown to have potential applications in optical communications, and many of them have nonlinear optical behavior [11-13].

Most recent studies have suggested that the UV absorption wavelength of mesogenic compounds plays an important role in the design of new materials for nonlinear optical purposes [14,15]. It is known that the UV maximum absorption wavelength (λ_{max}) of a planar conjugated molecule is longer than that of the nonplanar one

with a same conjugated chain. Surprisingly, we have recently observed a bathochromic shift of the λ_{max} of benzylideneaniline compared with stilbene, which is in an almost planar conformation [16]. Nevertheless, the effects of molecular non-planarity on the λ_{max} of Schiff bases have rarely been experimentally studied.

Charge distribution of the molecules is central to the optical and electronic characters of mesogens [17,18]. Several ¹³C NMR studies have revealed that the overall electron distribution can be fine-tuned through the electronic effects of remote substituents [19,20]. By means of computational study, Neuvonen and coworkers [21] have proposed that the twist of the aniline ring with respect of the plane of the C=N unit may affect the ¹³C NMR chemical shifts of imine carbon in benzylideneanilines. However, Neuvonen's conjecture has not been experimentally explored and still remains complicated.

To clarify the effects of molecular conformation on the λ_{max} and ¹³C NMR chemical shifts $\delta_C(C=N)$ of Schiff bases, we synthesized seven samples of symmetrical bis-Schiff bases *p***-XBAX-***p* (Fig. 1)

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Fig. 1. General structures of compounds a-g.

in this work. In *p***-XBAX-***p*, the substituents X include electrondonating groups (X = OMe, Me, or Et) and electron-withdrawing ones (X = Cl, F, CF₃, or CN). Their crystal structures and spectroscopic properties were measured experimentally, and the effects of the molecular conformation on spectroscopic properties of **a**-**g** were quantified.

2. Experimental methods

2.1. Sample preparation

Compounds **a**–**g** were all prepared by solid–solid reactions [22]. The pure *p*-substituted benzaldehyde and *p*-phenylenediamine 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 recrystal-lization from absolute ethanol.

2.2. X-ray crystallography

Crystals of bis-Schiff bases *p***-XBAX-***p* suitable for X-ray diffraction were obtained by slow evaporation from a binary solvent mixture of methanol–chloroform (3:1). Colored crystals were obtained

Table 1 Values of λ_{max} (cm) and v_{max} (cm⁻¹) for compounds **a–g**.

| No | Compounds | $\sigma_{ m P}$ | $\sigma^{ m ex}_{ m cc}$ | λ_{max} | v_{max} | Solvent |
|----|-----------|-----------------|--------------------------|-----------------|-----------|--------------|
| 1 | a | -0.27 | -0.50 | 354.23 | 28230 | Ethanol |
| 2 | b | -0.17 | -0.17 | 350.90 | 28498 | Ethanol |
| 3 | с | -0.15 | -0.13 | 350.75 | 28510 | Ethanol |
| 4 | d | 0.23 | -0.22 | 354.38 | 28218 | Ethanol |
| 5 | d | 0.06 | 0.06 | 348.14 | 28724 | Ethanol |
| 6 | f | 0.54 | -0.12 | 359.14 | 27844 | Ethanol |
| 7 | g | 0.66 | -0.70 | 371.54 | 26915 | Ethanol |
| 8 | a | -0.27 | -0.50 | 354.52 | 28207 | Acetonitrile |
| 9 | b | -0.17 | -0.17 | 350.83 | 28504 | Acetonitrile |
| 10 | с | -0.15 | -0.13 | 350.70 | 28514 | Acetonitrile |
| 11 | d | 0.23 | -0.22 | 354.09 | 28241 | Acetonitrile |
| 12 | d | 0.06 | 0.06 | 348.45 | 28699 | Acetonitrile |
| 13 | f | 0.54 | -0.12 | 358.35 | 27906 | Acetonitrile |
| 14 | g | 0.66 | -0.70 | 370.38 | 26999 | Acetonitrile |
| 15 | a | -0.27 | -0.50 | 357.73 | 27954 | Chloroform |
| 16 | b | -0.17 | -0.17 | 354.34 | 28221 | Chloroform |
| 17 | с | -0.15 | -0.13 | 354.69 | 28194 | Chloroform |
| 18 | d | 0.23 | -0.22 | 357.81 | 27948 | Chloroform |
| 19 | d | 0.06 | 0.06 | 351.02 | 28488 | Chloroform |
| 20 | f | 0.54 | -0.12 | 361.93 | 27630 | Chloroform |
| 21 | g | 0.66 | -0.70 | 375.96 | 26599 | Chloroform |
| 22 | a | -0.27 | -0.50 | 357.88 | 27942 | Cyclohexane |
| 23 | b | -0.17 | -0.17 | 355.52 | 28128 | Cyclohexane |
| 24 | с | -0.15 | -0.13 | 356.05 | 28086 | Cyclohexane |
| 25 | d | 0.23 | -0.22 | 360.10 | 27770 | Cyclohexane |
| 26 | d | 0.06 | 0.06 | 354.70 | 28193 | Cyclohexane |
| 27 | f | 0.54 | -0.12 | 364.90 | 27405 | Cyclohexane |
| 28 | g | 0.66 | -0.70 | 374.94 | 26671 | Cyclohexane |

after a few days. For compound **a**, crystallographic analyses were performed on a Rigaku Saturn 724 CCD diffractometer; for b, X-ray diffraction was performed with a Bruker Smart CCD Apex II platform diffractometer; for **c**, **d**, **e**, **f**, and **g**, X-ray diffraction were performed with a Gemini S Ultra, Oxford platform diffractometer. The crystals **a**, **b**, **c**, **e**, **f**, and **g** were measured with Mo Kα monochromated radiation (λ = 0.71073 Å), and crystal **d** was measured with Cu K α monochromated radiation (λ = 1.54184 Å). An empirical absorption correction was applied. The structures were solved using the direct method and refined by the full-matrix leastsquares method on F^2 using the SHELXL-97 software [23]. 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 **a-g** is available in the Supporting Information.

CCDC 885615, 885616, 885617, 892132, 892515, 892516 and 892517 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).

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 λ_{max} and the maximum absorption wavenumber v_{max} for compounds **a**-**g** are listed in Table 1. The NMR chemical spectra of compounds **a**-**g** were recorded in CDCl₃ at 293 K. The ¹³C NMR chemical shifts of the C=N groups are reported in Table 3, expressed in ppm relative to CDCl₃ (77.0 ppm). The detailed analytical data of compounds **a**-**g** 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 **a–g** (Fig. 2). Compounds **a**, **b**, **e**, and **g** crystallized in the monoclinic space groups P2(1), $P2_1/n$, $P2_1/n$ and $P2_1/n$, respectively, while **c**, **d**, and **f** all crystallized in the triclinic space group P-1. The CF₃ groups in compound **f** were observed to be disordered over many sites. The results are in good agreement with the previous results [24,25]. The high symmetry of the CF₃ group, coupled with the relatively low energy barrier for rotation about the 3-fold symmetry axis, was suggested to be the reason for the high level of disorder observed over many positions [24].

In all seven cases, the conformation observed for the molecules is the *anti*-form with respect to the C=N bond. As shown in Fig. 2, the benzylidene ring of each compound is nearly co-planar with the C4–C7=N1 or C15–C14=N2, whereas the aniline ring is twisted significantly from the C7=N1–C8 or C11–N2=C14. Because of the slight deviation of the benzylidene ring from the C4–C7=N1 or C15–C14=N2 plane, we discuss below the twist of the aniline ring with respect of the plane of the C=N unit only. The dihedral angle τ is defined by atoms C7=N1–C8–C9 or C14=N2–C11–C10. The values of τ in **a**–**g** are reported in Fig. 2. The value of τ = 180° corresponds to the co-planarity of the aniline ring and the C7=N1–C8 or C11–N2=C14 plane. It should be noted that τ is clearly affected by the substitution of the aromatic ring.

Table 2 Correlation results for **a**-**g**, in acetonitrile, chloroform and cyclohexane.

| Solvent | $v_{max} = \rho_{cc}^{ex} \sigma_{cc}^{ex} + \rho_p \sigma_p + \text{constant}$ $v_{max} = \rho_{cc}^{ex} \sigma_{cc}^{ex} \sin(\tau) + \rho_p \sigma_p \sin(\tau) + \text{constant}$ | | | | | | | | | | |
|--------------|---|--------------|----------|--------|--------|--------|--------|---|------|--|--|
| | $\rho_{\rm cc}^{\rm ex}$ | $ ho_{ m p}$ | Constant | R | R^2 | S | F | n | Eqs. | | |
| Ethanol | 1451.91 | -1030.3 | 28636.01 | 0.9904 | 0.9810 | 102.50 | 103.10 | 7 | | | |
| | 3476.75 | -1816.19 | 28627.64 | 0.9976 | 0.9952 | 51.56 | 413.41 | 7 | | | |
| Acetonitrile | 1415.12 | -936.17 | 28633.11 | 0.9919 | 0.9838 | 89.00 | 121.36 | 7 | (4) | | |
| | 3343.64 | -1655.12 | 28621.65 | 0.9967 | 0.9935 | 56.52 | 303.88 | 7 | (5) | | |
| Chloroform | 1552.13 | -993.24 | 28384.33 | 0.9879 | 0.9759 | 117.63 | 81.03 | 7 | (6) | | |
| | 3776.59 | -1689.74 | 28380.29 | 0.9970 | 0.9941 | 58.37 | 335.15 | 7 | (7) | | |
| Cyclohexane | 1067.63 | -1078.39 | 28152.23 | 0.9934 | 0.9868 | 76.55 | 149.20 | 7 | (8) | | |
| - | 2582.79 | -1952.50 | 28145.88 | 0.9965 | 0.9929 | 55.97 | 280.86 | 7 | (9) | | |

Table 3

¹³C NMR shifts (ppm) of the C=N carbons in compounds a-g.

| No | Х | $\sigma_{ m F}$ | $\sigma_{ m R}$ | $_{\delta C}(C=N)$ | No | Х | $\sigma_{ m F}$ | $\sigma_{ m R}$ | $_{\delta C}(C=N)$ |
|----|-----|-----------------|-----------------|--------------------|----|--------|-----------------|-----------------|--------------------|
| 1 | OMe | 0.29 | -0.56 | 158.93 | 5 | F | 0.45 | -0.39 | 158.22 |
| 2 | Me | 0.01 | -0.18 | 159.63 | 6 | CF_3 | 0.38 | 0.16 | 158.08 |
| 3 | Et | 0.00 | -0.15 | 159.65 | 7 | CN | 0.51 | 0.15 | 157.79 |
| 4 | Cl | 0.42 | -0.19 | 158.19 | | | | | |

Table 4

Correlation results of $_{\delta C}(C=N)$ for **a-g**.

| Regression equation | R | R^2 | S | F | п | No |
|--|--------|--------|--|--------|---|------|
| $_{\delta C}$ (C=N) = 159.53-3.63 σ_{F} -0.83 σ_{R} | 0.9989 | 0.9978 | $\textbf{4.74}\times \textbf{10}^{-2}$ | 906.00 | 7 | (10) |
| $\delta C(C=N) = 159.61 - 3.93$ $\sigma_F + 96.01 \sigma_R \sin(\tau)$ | 0.9903 | 0.9807 | 0.14 | 101.67 | 7 | (11) |
| $_{\delta C}(C=N) = 158.05 + 948.98$ $\sigma_{F} \sin(\tau) - 7.34 \sigma_{R}$ | 0.8352 | 0.6976 | 0.56 | 4.61 | 7 | (12) |
| $\sigma_{\rm F} \sin(\tau) = 159.53 - 89.07$ $\sigma_{\rm F} \sin(\tau) - 24.01 \sigma_{\rm R}$ $\sin(\tau)$ | 0.1508 | 0.0228 | 1.00 | 0.05 | 7 | (13) |

Among the seven compounds, the maximum value of τ occurs in **a** (τ = 163.25°) and **d** (τ = 163.49°), and the minimum is found in **c** (τ = 136.08°).

3.2. Absorption spectra

Table 1 summarizes the λ_{max} (column 5) and the corresponding v_{max} (column 6) of **a–g** in protic solvent (ethanol), electron pair donating solvent (acetonitrile), and those with no specific solvent–solute interactions (chloroform, cyclohexane). The absorption spectra of **a–g** 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 [26,27]. The maximum absorption bands at about 2.6– 2.9×10^4 cm⁻¹ are assigned to the intramolecular charge transfer band of the azomethine C=N group. It is noted that a bathochromic shift is observed with the increasing electron-withdrawing or electron-donating ability of *X*. Compound **g** had the highest λ_{max} , followed by compound **f**, **d**, **a**, **b**, **c**, and **e** in order of increasing λ_{max} . This observation is in accordance with our previous study [16]. In our previous research, it was verified that substituent effects had obvious impacts on the v_{max} of molecules, and the v_{max} was correlated with the excited-state parameter (σ_{cc}^{ex}) and Hammett parameter (σ_{P}) for substituted benzenes. The equation is as

follows (Eq. (1)) [28], where $\rho_{\rm cc}^{\rm ex}$ and $\rho_{\rm p}$ are the corresponding coefficients.

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

Therefore, in this work, we tried to correlate the v_{max} of **a**–**g** in ethanol with Eq. (1), and obtained Eq. (2). The results are good, and the correlation coefficient was as high as 0.9904.

$$v_{\text{max}} = 28636.01 + 1451.91\sigma_{\text{cc}}^{\text{ex}} - 1030.3\sigma_{\text{p}}$$

$$R = 0.9904, \ R^2 = 0.9810, \ s = 102.50, \ n = 7, \ F = 103.10$$
(2)

It is interesting to note that the dihedral angle τ of compounds changes with the substituent X. Does the dihedral angle have an impact on the UV absorption energy of molecules? Recently, we observed that the correlation results of benzylideneanilines with Eq. (1) were somewhat worse, presumably because of the twist of the benzylidene ring [16]. Thus, in this study, we want to consider the effects of τ on the v_{max} of **a–g**. When the C=N unit and the aniline ring are co-planar ($\tau = 0^{\circ}$ or 180°) there prevails conjugation between them. However, when they are in the orthogonal orientation ($\tau = 90^{\circ}$) the conjugation is the weakest. Therefore, we can take a sine function of τ to describe the interaction. Applying the term $\sin(\tau)$ to modify the parameters $\sigma_{\rm cc}^{\rm ex}$ and $\sigma_{\rm p}$, we carried out a correlation analysis once again (Eq. (3)). The correlation of Eq. (3) is much better than that of Eq. (2), and its standard error is only 51.56 cm $^{-1}$, which is approximately half of Eq. (2). This confirms that the effect of the twist of the aniline ring with respect of the plane of the C=N unit is also an important factor influencing the substituent effects on the λ_{max} , though it is not as important to the λ_{max} as the effects of conjugation unity or the substituents on the compound.

$$v_{\text{max}} = 28627.64 + 3476.75\sigma_{\text{cc}}^{\text{ex}}\sin(\tau) - 1816.19\sigma_{\text{p}}\sin(\tau)$$

$$R = 0.9976, \ R^2 = 0.9952, \ s = 51.56, \ n = 7, \ F = 413.41$$
(3)

To further verify this result, the absorbance spectra of **a-g** were experimentally measured in acetonitrile, chloroform and cyclohexane. We correlated the v_{max} of **a-g** in acetonitrile, chloroform and cyclohexane, respectively, and obtained Eqs. (4)–(9) (Table 2). The results of Eqs. (5), (7) and (9) are excellent. This is further proof that the substituent effects upon the λ_{max} are affected by the twist of the aniline ring with respect to the rest of the molecules, and the term $\sin(\tau)$ is available to scale the effects.

3.3. NMR spectra

By computational study, Neuvonen et al. proposed that the dihedral angle τ affected the $\delta_{C}(C=N)$ of benzylideneanilines [21]. To experimentally validate this claim, we examined the effects of τ on the $\delta_{C}(C=N)$ of **a**–**g**.

Table 3 summarizes the $\delta_C(C=N)$ values of **a–g**. As shown in Table 3, the $\delta_C(C=N)$ of compounds range from 157.79 to



Fig. 2. Representative solid state molecular structures of a-g. 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 **a**-**g** in ethanol.

159.65 ppm. When substituent *X* is electron-withdrawing, the $\delta_{\rm C}$ (C=N) decreases with increasing electron-withdrawing capability. This indicates that electron-withdrawing substituents *X* cause shielding of the imine carbon. The electron-donating ones also behave in the same way: with the increasing capability of electron donating, there is also a decreasing $\delta_{\rm C}$ (C=N). The experimental re-

sults are not in accordance with the previous research [19,29,30], perhaps because compounds **a**–**g** are symmetrical in structure.

To give insight into the substituent effects on $\delta_{\rm C}({\rm C=N})$ in symmetrical bis-Schiff bases, the $\delta_{\rm C}({\rm C=N})$ values 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. (10) was obtained. The results are shown in Table 4. The correlation results are excellent, and the deviation is only 4.74×10^{-2} .

Is the twist of the aniline ring a factor influencing the $\delta_{C}(C=N)$ in symmetrical bis-Schiff bases? We modified the parameters σ_{F} and σ_{R} with the parameter $\sin(\tau)$. However, good to poor correlations were observed when the term $\sin(\tau)$ was used to modify σ_{R} (Eq. (11)), σ_{F} (Eq. (12)), or both σ_{F} and σ_{R} (Eq. (13)) (Table 4). This suggests the effects of the twist of aniline ring on the $\delta_{C}(C=N)$ values of symmetrical bis-Schiff bases are not obvious.

The behaviors described above can be understood by the properties of λ_{max} and $\delta_C(C=N)$. λ_{max} depends on the HOMO–LUMO gap, and a larger conjugation generally leads to a lesser gap. The smaller the torsion of the C=N unit and the aniline ring is the greater conjugation is. Thus, the absorbance energy is affected by the twist of an aniline ring. However, the $\delta_C(C=N)$ value depends on the charge properties of imine carbon. The charge of imine carbon depends on the whole molecular orbitals of molecules, not just the frontier molecular orbitals. Therefore, the effects of aniline ring torsion on electronic density of imine carbon are limited. This rationalization about the $\delta_C(C=N)$ is supported by several studies concerning

the investigation of substituent effects on the $\delta_{C}(C=N)$ [31–33], in which the $\delta_{C}(C=N)$ values are well correlated with the parameters $\sigma_{\rm F}$ and $\sigma_{\rm R}$.

4. Conclusion

A comparison of the crystal structures of compounds **a-g** shows that the dihedral angle τ is clearly affected by the substituents on the aromatic ring. The dihedral angles τ influences the electronic effects of substituents on the v_{max} , and the term $sin(\tau)$ is suitable to modify the effect. Surprisingly, the twist of the aniline ring with respect to the plane of the C=N unit has a limited role on the $\delta_{\rm C}({\rm C=N})$ in **a–g**, and a good correlation between the $\delta_{\rm C}({\rm C=N})$ and the substituent parameters is obtained. The results of this investigation indicate the importance of the molecular conformation effects upon the absorbance spectra. The spectral behavior resulting from molecular conformation must be considered to fully understand the spectroscopic properties of these potential optical materials.

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Appendix A. Supplementary data

Supplementary data associated with this article can be found, in the online version, at http://dx.doi.org/10.1016/j.molstruc.2012. 12.014. These data include MOL files and InChiKeys of the most important compounds described in this article.

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