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Effects of molecular conformation on the spectroscopic properties of 4,4'-disubstituted benzylideneanilines



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ABSTRACT

The relationship between the molecular conformation and spectroscopic properties of unsymmetrical 4,4'-disubstituted benzylideneanilines, was explored by the combination of experiment and reference data. Crystal structure information and spectroscopic behaviors of the seventeen samples p-X–C₆H₄CH= NC₆H₄–p-Y (X = NMe₂, OMe, Me, Cl, CN, or NO₂, Y==NMe₂, OMe, Me, Cl, CN, or NO₂) were provided for this study. Among these seventeen compounds, nine ones were synthesized firstly, and five crystal structures were determined and analyzed. It was observed that the twist angle of the aniline ring with respect to the rest of the molecule (τ) is systematically controlled by the substituent at the aromatic ring. The correlation results show that the UV maximum absorption in wavenumbers (ν_{max}) is dependent on the substituent at the aromatic ring and the dihedral angle τ of the titled molecules, and a sine function of τ (sin(τ)) is suitable to modify the substituent effects on the ν_{max} . However, the dihedral angle τ has a limited effect on the values of ¹³C NMR chemical shifts δ_C (C=N). The results indicate that the dihedral angle τ has a relatively limited effect on the values of δ_C (C=N) in both unsymmetrical and unsymmetrical Schiff bases. This study provides an sufficient evidence of the molecular conformation on spectroscopic properties of Schiff bases.

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1. Introduction

The spectroscopic behavior is known to be an important factor for the optimal use of the optical materials and the design of new candidates [1-5]. Understanding the quantitative structureproperty relationship (QSPR) helps to predict the optical properties of the target compounds [6,7]. Therefore, much attention has been focused on the QSPR of the spectroscopic properties of conjugated organic compounds [8–10], including disubstituted benzenes [11], disubstituted stilbenes [12,13], and disubstituted benzylidene anilines [14].

Schiff bases are receiving increasing attention in view of their potential application as effective ligands for complexation [15,16]. Most importantly, they are used in the design of liquid crystals [17–19] and nonlinear optical materials [20–23].

Recently, we have verified that the molecular conformation has

an important role on the UV energy of symmetrical Schiff bases derived from 1,4-Phenylenediamine and 1,4-Phthalaldehyde [24,25]. The UV energy is dependent on the substituent at the aniline ring and the dihedral angle τ , and the term $sin(\tau)$ is suitable to modify the substituent effects on the UV maximum absorption in wavenumbers umax. However, experimental investigations indicate that the dihedral angle τ has a limited effect on the values of $\delta_{\rm C}({\rm C}=$ N). These studies provide an evidence of molecular conformation effects on spectroscopic properties of symmetrical bis-Schiff bases. However, research samples of these investigations are structurally symmetrical, and in these samples the group at one end is identical with that at the opposite end. It is known that the polarity is offset in symmetrical systems, and in which the though-bond electronic communication is different from that in unsymmetrical ones. Therefore, a suggestion that the evidence of molecular conformation effects on spectroscopic properties in Schiff bases is insufficient if it only comes from symmetrical Schiff bases. Consequently, it is a worthwhile work to explore the conformation effects in unsymmetrical Schiff bases and provide a further proof for the effects of molecular conformation on spectroscopic properties of Schiff



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bases.

We report herein the results of our systematic studies on the conformation effects upon the Schiff bases. 4,4'-disubstituted benzylideneanilines(i.e. **XBAY**, shown in Fig. 1) have simple structure and are representative, so they are applicable to fully prove the effects of molecular conformation on spectroscopic properties of Schiff bases if the samples are sufficient.

By means of computational study, Neuvonen and co-workers [26] 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 **XBAY**, we provided seventeen samples of unsymmetrical Schiff bases **XBAY** in this work, and their crystal structures information and spectroscopic properties were obtained from the experimental values of our work or the Cambridge Crystallographic Data Centre (CCDC). In **XBAY**, the substituents X or Y include the most electron-donating group (NMe₂) and the most electron-withdrawing one (NO₂). The effects of the molecular conformation on spectroscopic properties of **XBAY** were quantified.

2. Experimental methods

2.1. Sample preparation

Compounds were all prepared by solid—solid reactions [27]. The pure *p*-substituted benzaldehyde and *p*-substituted aniline were mixed in a 1:1 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. 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. Ethanol used in absorption experiments were of spectroscopic grade and were used as purchased. The NMR chemical spectra of compounds were recorded in CDCl₃ at 293 K. The ¹H NMR chemical shifts of the CH—N groups are expressed in ppm relative to CDCl₃ (7.26 ppm). The detailed analytical data of compounds are available in the Supporting Information.

2.3. X-ray crystallography

Crystals suitable for X-ray diffraction were obtained by slow evaporation from a binary solvent mixture of petroleum ether – chloroform (3:1). Colored crystals were obtained after a few days. For compounds **MeOBAH**, **MeOBAOMe**, **CNBACN**, **CIBACI** and **NO₂BAOMe**, crystallographic analyses were performed on a Gemini S Ultra, Oxford platform diffractometer. The crystals of them were measured with Mo K α monochromated radiation ($\lambda = 0.71073$ Å). An empirical absorption correction was applied. The structures were solved using the direct method and refined by the full-matrix



 $X = NMe_2$, OMe, Me, H, Cl, CN, or NO₂; Y = NMe₂, OMe, Me, H, Cl, CN, or NO₂

Fig. 1. General structures of compounds XBAY.

least-squares method on F^2 using the SHELXL–97 software [28]. 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 the five compounds is available in the Supporting Information.

3. Results and discussion

3.1. Description of the crystal structures

The reliability of the dihedral angle τ values is necessary for research work in this paper. Experimental data available in the literature were obtained in the different conditions, such as condition of crystal test or cultivation. In addition, an analysis reveals that the difference is relatively obvious between the calculated and the experimental value of the same molecule (Table 1, column 10 and 11). Thus, to verify whether ambient conditions make a difference on the τ value, we prepared five compounds including two compounds whose experimental data not available in the literature and obtained their crystals. Crystal structures of them are shown in Fig. 2.

A comparison of the X-ray crystal structures revealed a possible role for the conformation of compounds 1-5 (Fig. 2). Compounds 1, 2 and 5 crystallized in the monoclinic space groups P2(1), while 3 and 4 crystallized in the orthorhombic space group Pbca. The C and N elements in compounds 3 and 4 were observed to be disordered because of the pseudo-symmetry in the structure of them. The results are in good agreement with the reference results [29–31]. The dihedral angle τ is defined by atoms C1–C7=N1–C1'.

3.2. Results of the conformation and spectra of compounds

Crystal structure informations of compounds come from our works and CCDC. In all cases, the conformation observed for the molecules is the *anti*-form with respect to the C=N bond. The benzylidene ring of each compound is nearly co-planar with the C1–C7=N1, whereas the aniline ring is twisted significantly from the C7=N1-C1'. Because of the slight deviation of the benzylidene ring from the C1–C7=N1 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 C1–C7=N1–C1'. The values of τ in **XBAY** are listed in Table 1 (column 10 and 12). The value of $\tau = 180^{\circ}$ corresponds to the co-planarity of the aniline ring and the C7=N1-C1' plane. As seen in Table 1, the dihedral angle τ values of compounds 1, 2 and 4 in our works are in accordance with the experimental data available in the literature. This shows that the data of τ has a high reliability and it isn't restricted by the condition of crystal test or cultivation.

For the seventeen samples of **XBAY**, substituent X including Me₂N, MeO, Me, H, Cl, CN and NO₂, and substituent Y including Me₂N, MeO, Me, H, Cl, CN and NO₂, the corresponding v_{max} and δ_C (C=N) in model compounds are listed in Table 1, which come from previous or this work [32,33].

3.3. Effects of substituents on the molecular conformation

It should be noted that τ is clearly affected by the substitution of the aromatic ring. Among the seventeen compounds, the maximum value of τ occurs in **NO₂BANMe**₂ ($\tau = 172.9^{\circ}$), and the minimum is found in **HBAH** ($\tau = 126.7^{\circ}$). As seen in Table 1 (column 10 and 12), in case X is NO₂, the twist of the ring increases (value of τ decreases) as the electron-withdrawing ability of the substituent Y improves. In case Y is OMe, τ decreases as the electron-withdrawing ability of the substituent X improves. While the regularity is not obvious in

Table 1

Values of λ_{max}	(cm). Umay	(cm^{-1})) and $\tau(\circ)$	for com	pounds XBAY.
values of Amax	(cm), omax	(em)	fund of f	ioi com	poundo monte.

Colum	n												
1	2	3	4	5	6	7	8	9	10	11	12	13	14
No	x	Y	$\sigma_{cc}^{ex}(X)$	$\overline{\sigma_{cc}^{ex}(Y)}$	$\sigma_{F}(X)$	$\sigma_{R}(X)$	$\sigma_F(Y)$	$\sigma_{R}(Y)$	τ^{a}	$\tau^{\mathbf{b}}$	τ ^c	v_{max}^{d}	$\delta_C(C=N)^e$
1	OMe	Н	-0.50	0.00	0.29	-0.56	0.00	0.00	141.6	143.6	149.5	30113	159.64
2	CN	CN	-0.70	-0.70	0.51	0.15	0.51	0.15		142.9	168.5	30149	160.21
3	OMe	OMe	-0.50	-0.50	0.29	-0.56	0.29	-0.56	165.8	147.8	163.7	30162	157.88
4	Cl	Cl	-0.22	-0.22	0.42	-0.19	0.42	-0.19	141.4	145.3	141.6	31505	159.11
5	NO ₂	OMe	-1.17	-0.5	0.65	0.13	0.29	-0.56		152.7	152.8	30211	154.76
6	NMe ₂	OMe	-1.81	-0.50	0.15	-0.98	0.29	-0.56	166.3	147.1		27026	158.65
7	NMe_2	Н	-1.81	0.00	0.15	-0.98	0.00	0.00	137.7	143.2		26580	160.21
8	NMe_2	Cl	-1.81	-0.22	0.15	-0.98	0.42	-0.19	140.5	144.0		25934	160.51
9	NMe_2	CN	-1.81	-0.70	0.15	-0.98	0.51	0.15	137.1	142.3		24013	161.86
10	Me	OMe	-0.17	-0.50	0.01	-0.18	0.29	-0.56	162.1	148.2		31257	158.46
11	Me	Me	-0.17	-0.17	0.01	-0.18	0.01	-0.18	140.3	145.3		31452	159.58
12	Н	Н	0.00	0.00	0.00	0.00	0.00	0.00	126.7	143.9		32276	160.34
13	Cl	OMe	-0.22	-0.50	0.42	-0.19	0.29	-0.56	160.7	149.5		31373	156.68
14	CN	Н	-0.70	0.00	0.51	0.15	0.00	0.00	149.5	146.1		31634	157.82
15	NO ₂	NMe_2	-1.17	-1.81	0.65	0.13	0.15	-0.98	172.9	160.4		26954	151.51
16	NO ₂	Me	-1.17	-0.17	0.65	0.13	0.01	-0.18	152.1	148.4		30581	156.32
17	NO ₂	Н	-1.17	0	0.65	0.13	0	0	142.5	146.6		31646	157.33

 σ_{qc}^{ex} , σ_F and σ_R are the excited-state parameter, inductive parameter and resonance parameter, respectively. ω_{max} is UV maximum absorption in wavenumbers. $\delta_C(C=N)$ is the value of ¹³C NMR chemical shifts of C=N.

^a The values were obtained via http://www. ccdc.cam.ac.uk/conts/retrieving.html (or from CCDC).

^b The values were taken from Ref. [26].

^c The experimental values of our work.

^d The values were taken from Ref. [32].

^e The values were taken from Ref. [33].







2. **CNBACN**







CIBACI 4.



Fig. 2. Representative solid state molecular structures of compounds 1-5. Displacement ellipsoids are drawn at the 50% probability level, and H atoms are shown as small spheres of arbitrary radii. Dihedral angle τ is defined by atoms C1–C7=N1–C1'.

case X is NMe₂ or Y is H. This behavior can be understood by the correlations of τ versus σ_F and σ_R parameters (σ_F and σ_R are the inductive parameter and resonance parameter, respectively). The correlation results are shown in Table 2. Good linear correlations reveal that substituents have a remarkable and systematic electronic effect on the dihedral angle τ in **XBAY**. It can be seen in Table 2, the signs in front of ρ_F and ρ_R are the same in case X is NO₂ and Y is OMe, while in case X is NMe₂ and Y is H, the signs are alternated. Both ρ_F and ρ_R values are bigger in case X is NO₂ than those in other three cases. From these preceding observations, it can be inferred that the electronic effects on the molecular conformation are different for the four cases, and the twist of the aniline ring is more sensitive in case X is NO₂.

3.4. Effects of molecular conformation on the absorption spectra

To give insight into the effects of molecular conformation on the absorption spectra in 4,4'-disubstituted benzylideneanilines, the v_{max} values in Table 1 (column 13) were first correlated with $\sigma_{\text{cc}}^{\text{ex}}$ and σ_P parameters (σ_{cc}^{ex} and σ_P are the excited-state parameter and Hammett parameter parameter, respectively; $\sigma_P = \sigma_R + \sigma_F$), and Eqn (1) was obtained. The results are shown in Table 3. The results are average, and the correlation coefficient is 0.9719. In our previous researches, it was found that the ν_{max} was dependent on the substituents at the benzylidene ring and the dihedral angle τ of symmetrical bis-Schiff bases, and the term $sin(\tau)$ was suitable to modify the substituent effects on the v_{max} [24,25]. Therefore, applying the term $sin(\tau)$ to modify both σ_{cc}^{ex} and σ_{p} , we carried out a correlation analysis once again (Eqn (2)). Surprisingly, the correlation of Eqn (2) is much worse than that of Eqn (1), and its correlation coefficient is only 0.9059. As further proof, the term $sin(\tau)$ was used to modify σ_p (Eqn (3)) and σ_{cc}^{ex} (Eqn (4)), respectively. However, the correlation of Eqn (3) is much better than that of Eqn (1), and its standard error is only 268 cm⁻¹, which is half of Eqn (1). Correlation coefficient is only 0.8949 when $sin(\tau)$ was used to only modify σ_{cc}^{ex} only (Table 3). This suggests that in 4,4'-disubstituted benzylideneanilines, the effect of the twist of the aniline ring with respect of the plane of the C=N unit is an important factor influencing the substituent effects on the λ_{max} , and the effects can be scaled by modified the parameter σ_p with the term $\sin(\tau)$. The results are not in accordance with our previous studies [24,25].

The behaviors can be understood by the physical meaning of σ_p and σ_{cc}^{ex} . The parameter σ_p expresses the electronic effects of groups and reflects the degree of electronic communication. While the parameter σ_{cc}^{ex} is applied to measure the relative stability of free radicals. It is known that the smaller the torsion of the C=N unit and the aniline ring is beneficial to the communication of electrons. Thus, the twist of the aniline ring with respect of the plane of the C=N unit has greater impact on the σ_p than that on the σ_{cc}^{ex} , and $\sin(\tau)$ is suitable to modify the parameter σ_p .

To further verify this result, Leave-One-Out method was applied [34,35]. For the seventeen compounds, there are seventeen predicted v_{max} values. The predicted v_{max} and the error between the experimental and the predicted value are available in the Supporting Information.

Fig. 3 represents the correlation between the predicted and the experimental v_{max} , and it indicates that the predicted v_{max} of **XBAY**

Table 2 Correlation results of τ versus σ_F and σ_R parameters are in good agreement with their experimental values. To allow comparison, the errors of v_{max} have been converted to λ_{max} . The deviation ranges of the experimental and the predicted values are shown in Fig. 4, in which the predicted λ_{max} of seventeen samples, the percentage of data points within 4.0 nm is 70.5%, within 6.0 nm is 82.3%, with the maximum error being 9.8 nm. Both Figs. 3 and 4 confirm the reliability of Eqn (3). This demonstrates that molecular conformation of benzylideneanilines with different parent structure has an significant effect on their absorption spectra, but there is something different about the parameters of metrics.

3.5. Effects of molecular conformation on the NMR spectra

Table 1 summarizes the $\delta_{C}(C=N)$ values of **XBAY**. As shown in Table 1(column 14), the $\delta_{C}(C=N)$ of compounds range from 151.51 to 161.86 ppm.

To investigate the effects of molecular conformation on the NMR spectra in 4,4'-disubstituted benzylideneanilines, the $\delta_C(C=N)$ values in Table 1 were first correlated with σ_F and σ_R parameters, and Eqn (5) was obtained. The results are shown in Table 4. The correlation results are excellent, and the deviation is only 0.44 ppm. Is the twist of the aniline ring a factor influencing the $\delta_C(C=N)$ in unsymmetrical 4,4'-disubstituted benzylideneanilines? We modified the parameters σ_F and σ_R with the parameter $\sin(\tau)$. However, unsatisfactory correlations were observed when the term $\sin(\tau)$ was used to modify σ_F (Eqn. (6)), σ_R (Eqn. (7)), or both σ_F and σ_R (Eqn. (8)) (Table 4).

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 [24].

Further, to verify this result, LOO method was adopted [34,35]. The seventeen predicted $\delta_C(C=N)$ values and the error between the experimental and the predicted are available in the Supporting Information.

Fig. 5 represents the correlation between the predicted and the experimental $\delta_{C}(C=N)$, and it indicates that the predicted $\delta_{C}(C=N)$ of **XBAY** are in good agreement with their experimental values. The deviation ranges of the experimental and the predicted values are shown in Fig. 6, in which the predicted $\delta_{C}(C=N)$ of seventeen samples, the percentage of data points within 0.5 ppm is 76.4%, within 0.75 ppm is 88.2%, with the maximum error being 1.41 ppm. Both Figs. 5 and 6 confirm the reliability of Eqn (5). This confirms that the effects of the twist of aniline ring on the $\delta_{C}(C=N)$ values of unsymmetrical 4,4'-disubstituted benzylideneanilines are not obvious.

4. Conclusion

Substituents have a remarkable and systematic electronic effects on the dihedral angle τ , but the effects are not the same for

correlation	Areadon results of v versus of and or parameters.												
	$\tau = Intercept + \rho_F(Y)\sigma_F(Y) + \rho_R(Y)\sigma_R(Y)$							$\tau = Intercept + \rho_{F}(X)\sigma_{F}(X) + \rho_{R}(X)\sigma_{R}(X)$					
Х	Intercept	$\rho_F(Y)$	$\rho_R(Y)$	R	S	n	Y	Intercept	$\rho_F(X)$	$\rho_R(X)$	R	S	n
NMe ₂ NO ₂	137.93 144.1	3.4 -40.1	-42.8 -35.9	0.9338 0.9934	8.6 2.5	4 4	H OMe	128.3 161.2	30.8 8.7	-5.1 -8.4	0.8669 0.9361	5.8 2.7	5 5

Table 3

Correlation results of υ_{max} for model compounds.

Regression equation	R	R^2	S	F	n	Eqns.
$\upsilon_{max} = 2269 \sigma_{cc}^{ex}(X) + 2476 \sigma_{cc}^{ex}(Y) + 1705 \sigma_p(X) - 1031 \sigma_p(Y) + 32426$	0.9719	0.9643	539	81	17	(1)
$\upsilon_{max} = 2889 \sigma_{cc}^{ex}(X) \sin(\tau) + 8309 \sigma_{cc}^{ex}(Y) \sin(\tau) + 3351 \sigma_p(X) \sin(\tau) + 2648 \sigma_p(Y) \sin(\tau) + 31867$	0.9059	8207	1210	130	17	(2)
$\upsilon_{max} = 2154\sigma_{cc}^{ex}(X) + 1739\sigma_{cc}^{ex}(Y) + 3416\sigma_{p}(X)sin(\tau) - 2158\sigma_{p}(Y)sin(\tau) + 32230$	0.9956	0.9912	268	338	17	(3)
$\upsilon_{max} = 3360\sigma_{cc}^{ex}(X)sin(\tau) + 8642\sigma_{cc}^{ex}(Y)sin(\tau) + 1254\sigma_{p}(X) - 1414\sigma_{p}(Y) + 32091$	0.8949	0.8008	1276	12	17	(4)



Fig. 3. Plots of the predicted υ_{max} using LOO method versus experimental values of the XBAY compounds.



Fig. 4. Deviation ranges of the experimental and the predicted λ_{max} values.



Fig. 5. . Plots of the predicted δ_C (C=N) using LOO method versus experimental values of the XBAY compounds.



Fig. 6. . Deviation ranges of the experimental and the predicted $\delta_{C}(C=N)$ values.

Table 4

Correlation results of $\delta_C(C=N)$ for **XBAY**.

Regression equation	R	R^2	S	F	n	Eqs.
$\delta_{C}(C=N) = 160.51 - 5.05\sigma_{F}(X) - 0.67\sigma_{R}(X) + 2.84\sigma_{F}(Y) + 5.33\sigma_{R}(Y)$	0.9880	0.9760	0.44	122.02	17	(5)
$\delta_{\rm C}({\rm C=\!N}) = 159.17 - 4.96\sigma_{\rm F}({\rm X}) \sin(\tau) - 2.45\sigma_{\rm R}({\rm X}) + 5.00\sigma_{\rm F}({\rm Y}) \sin(\tau) + 12.89\sigma_{\rm R}({\rm Y})$	0.7546	0.5700	1.89	3.97	17	(6)
$\delta_{\rm C} \left({\rm C=N} \right) = 160.78 - 6.09 \sigma_{\rm F}({\rm X}) - 0.08 \sigma_{\rm R}({\rm X}) \sin(\tau) + 5.97 \sigma_{\rm F}({\rm Y}) + 13.03 \sigma_{\rm R}({\rm Y}) \sin(\tau)$	0.8810	0.7761	1.36	10.40	17	(7)
$\delta_{C}(C=N) = 160.22 - 7.95\sigma_{F}(X)sin(\tau) - 1.86\sigma_{R}(X)sin(\tau) + 2.18\sigma_{F}(Y) + 6.21\sigma_{R}(Y)$	0.9378	0.8794	1.00	21.87	17	(8)

different substituent. The v_{max} or $\delta_C(C=N)$ values of 4,4'-disubstituted benzylideneanilines were correlated with corresponding parameter, and the reliability of the obtained equations were confirmed by LOO method. The molecular conformation of unsymmetrical 4,4'-disubstituted benzylideneanilines has significant effects on their absorption spectra. While unlike that of symmetrical bis-Schiff bases, the dihedral angles τ in 4.4'-disubstituted benzylideneanilines only influences the polar electronic effects on the v_{max} , and the term $sin(\tau)$ is suitable to modify the effect. Namely, molecular conformation of benzylideneanilines with different parent structure has an important effect on their absorption spectra, but there is something different about the parameters of metrics. The correlation results indicate that the twist of the aniline ring with respect to the plane of the C=N unit has a limited role on the $\delta_{C}(C=N)$ in 4,4'-disubstituted benzylideneanilines. The results of this investigation indicate the importance of the molecular conformation effects upon the absorbance spectra of unsymmetrical 4,4'-disubstituted benzylideneanilines.

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Appendix A. Supplementary data

Supplementary data related to this article can be found at http:// dx.doi.org/10.1016/j.molstruc.2015.09.035.

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