



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 $p\text{-X-C}_6\text{H}_4\text{CH=NC}_6\text{H}_4\text{-}p\text{-Y}$ ($X = \text{NMe}_2, \text{OMe}, \text{Me}, \text{Cl}, \text{CN}, \text{or NO}_2, Y = \text{NMe}_2, \text{OMe}, \text{Me}, \text{Cl}, \text{CN}, \text{or NO}_2$) 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 ($\sin(\tau)$) is suitable to modify the substituent effects on the ν_{max} . However, the dihedral angle τ has a limited effect on the values of ^{13}C NMR chemical shifts $\delta_{\text{C}}(\text{C=N})$. The results indicate that the dihedral angle τ has a significant effect on UV spectra of Schiff bases with different parent structure although there is something different about the parameter metrics. While it has a relatively limited effect on the values of $\delta_{\text{C}}(\text{C=N})$ in both unsymmetrical and unsymmetrical Schiff bases. This study provides a 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 structure-property 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 ν_{max} . However, experimental investigations indicate that the dihedral angle τ has a limited effect on the values of $\delta_{\text{C}}(\text{C=N})$. 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 through-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 ^{13}C 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 ^{13}C NMR chemical shifts $\delta_{\text{C}}(\text{C}=\text{N})$ 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 (NMe_2) and the most electron-withdrawing one (NO_2). The effects of the molecular conformation on spectroscopic properties of **XBAY** were quantified.

2. Experimental methods

2.1. Sample preparation

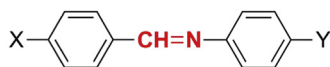
Compounds were all prepared by solid–solid reactions [27]. The pure *p*-substituted benzaldehyde and *p*-substituted aniline were mixed in a 1:1 M ratio, and then the mixture was heated and melted. The mixture was further stirred for several minutes before being cooled to room temperature and purified 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 CDCl_3 at 293 K. The ^1H NMR chemical shifts of the $\text{CH}=\text{N}$ groups are expressed in ppm relative to CDCl_3 (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 $K\alpha$ monochromated radiation ($\lambda = 0.71073 \text{ \AA}$). 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 NO_2 ;
Y = NMe_2 , OMe, Me, H, Cl, CN, or NO_2

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 $\text{C1–C7}=\text{N1–C1}'$.

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 $\text{C1–C7}=\text{N1}$, whereas the aniline ring is twisted significantly from the $\text{C7}=\text{N1–C1}'$. 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 $\text{C1–C7}=\text{N1–C1}'$. 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 $\text{C7}=\text{N1–C1}'$ 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 Me_2N , MeO, Me, H, Cl, CN and NO_2 , and substituent Y including Me_2N , MeO, Me, H, Cl, CN and NO_2 , the corresponding ν_{max} and $\delta_{\text{C}}(\text{C}=\text{N})$ 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 **NO₂BANMe₂** ($\tau = 172.9^\circ$), and the minimum is found in **HBAH** ($\tau = 126.7^\circ$). As seen in Table 1 (column 10 and 12), in case X is NO_2 , 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

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