



Effects of styrene unit on molecular conformation and spectral properties of CN–PhCH=NPhCH=CHPh–CN

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ABSTRACT

Compound CN–PhCH=NPhCH=CHPh–CN with both stilbene and benzylidene aniline units was synthesized, and studied from the viewpoint of molecular conformation and spectroscopic property by a combined use of experimental and computational methods. The maximum UV absorption wavelength (λ_{\max}) of the compound in ethanol, acetonitrile, chloroform and cyclohexane solvents were measured, and the ^{13}C NMR chemical shift value $\delta_{\text{C}}(\text{C}=\text{N})$ in chloroform-*d* was determined. The crystal structure of the compound was determined by X-ray diffraction. The frontier molecular orbital was calculated by density functional theory method. The results show that the UV absorption spectrum of the titled compound is similar to those of Schiff bases, while there is a larger red shift of λ_{\max} comparing to that of CN–PhCH=NPh–CN. Moreover, the molecular configuration of the titled compound relative to C=N is *anti*-form, having a more obvious twisted structure. The spectral and structural behaviors are further supported by the results of frontier molecular orbital analyses, NBO, electrostatic potentials and TD-DFT calculations. The study provides deeper insights into the molecular conformation of Schiff bases.

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1. Introduction

For the design and optimal use of new materials for optical purposes, special attention has been devoted to the relationship between structure and property of newly derived compounds [1–3]. As potentially applicable materials in optical communications, substituted Schiff bases with C=N bridge bond have received much attention and many of them have nonlinear optical behavior [4–6].

Recent studies have suggested that the spectra of mesogenic compounds are informative in the design of new materials for nonlinear optical purposes [7–9]. It is known that the maximum UV absorption wavelength (λ_{\max}) of a conjugated molecule is sensitive to the degree of coplanarity [10–12]. Thus, an understanding of the molecular conformation and spectral behaviors is critical for the design of new compounds of this kind.

Researches have revealed that stilbenes X–PhCH=CHPh–Y are

nearly coplanar, whereas Schiff bases X–PhCH=NPh–Y are non-coplanar and the aniline ring is significantly twisted [13–15]. Cao et al. [16] observed a bathochromic λ_{\max} shift of benzylideneaniline compared to that of stilbene with the same substituents X and Y, and proposed different quantitative models for stilbenes X–PhCH=CHPh–Y and Schiff bases X–PhCH=NPh–Y.

The unique conformations and spectroscopic behaviors of stilbenes and Schiff bases propelled us to explore the effects of a stilbene unit on a new conceptual framework CN–PhCH=NPhCH=CHPh–CN (SB-styrene, Fig. 1), which can be considered a simple combination of benzylidene aniline with a stilbene unit. The purpose is to determine whether the spectroscopic behavior of a SB-styrene compound is stilbene-like, Schiff base-like, stilbene-unlike or Schiff base-unlike, as well as to identify the difference and similarity in terms of molecular conformation between SB-Styrene and the simple Schiff base compound CN–PhCH=NPh–CN (SB, Fig. 1). The structure of CN–PhCH=CHPh–CN is also listed in Fig. 1.

We report herein the conformation and spectral behavior of SB-styrene. Endowed with a styryl group, the titled compound displays effects uncommon to those of SB.

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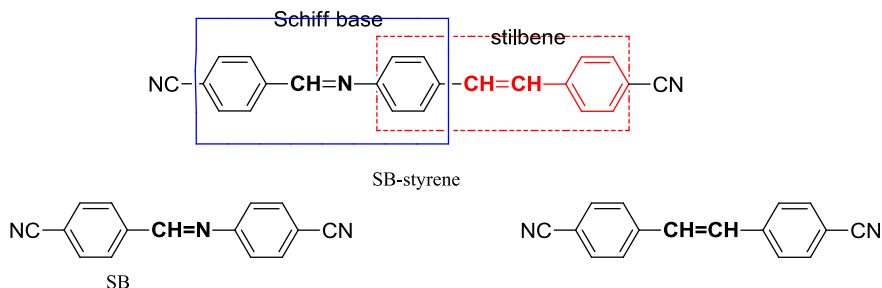


Fig. 1. General structure of compounds SB-styrene, SB and CN-PhCH=CHPh-CN.

2. Experimental

2.1. Sample preparation

The compound SB-styrene showed in Scheme 1 was synthesized according to published procedures but with two slight modifications. One is related to the purification of products **II** and **III**, and the other is the order of adding materials during the synthesis of compound **III**.

Compound II diethyl 4-nitrobenzylphosphonate [17,18]. A mixture of 4-nitrobenzyl chloride **I** (2.57 g, 15 mmol) and triethoxyphosphine (2.66 g, 16 mmol) was heated at 140 °C for 6 h before being cooled to room temperature. There was no need to separate or purify the product.

Compound III (E)-4-(4-nitrostyryl)benzonitrile [17,18]. 4-Cyanobenzaldehyde (1.97 g, 15 mmol) was added to compound **II** and the mixture was stirred in dry THF (50 ml) containing NaH (1.08 g, 45 mmol) under a nitrogen atmosphere at 60 °C for 30 min. Yellow substances were obtained after precipitation in water. The crude product was recrystallized with solvent (Ethyl acetate:Petroleum ether = 1:3) to give compound **III**. The product was dried in vacuum at 60 °C for 18 h. The yield was 76%.

Compound IV (E)-4-(4-aminostyryl)benzonitrile [18]. To a suspension of compound **III** (10 mmol) in a mixture of ethanol (100 ml) and hydrochloric acid (36% concentration, 25 ml), SnCl₂·2H₂O (20 mmol) was added as an effective reducing agent. The reaction mixture was stirred for 1 h at room temperature, followed by refluxing for 6 h. Subsequently, the reaction solution was poured into ice water and controlled to pH ≈ 8 with a solution of sodium hydroxide. After extraction with ethyl acetate four times, the combined organic layer was dried over MgSO₄, followed by evaporation and recrystallization from ethanol to afford pure

compound **IV**. The yield was 62%.

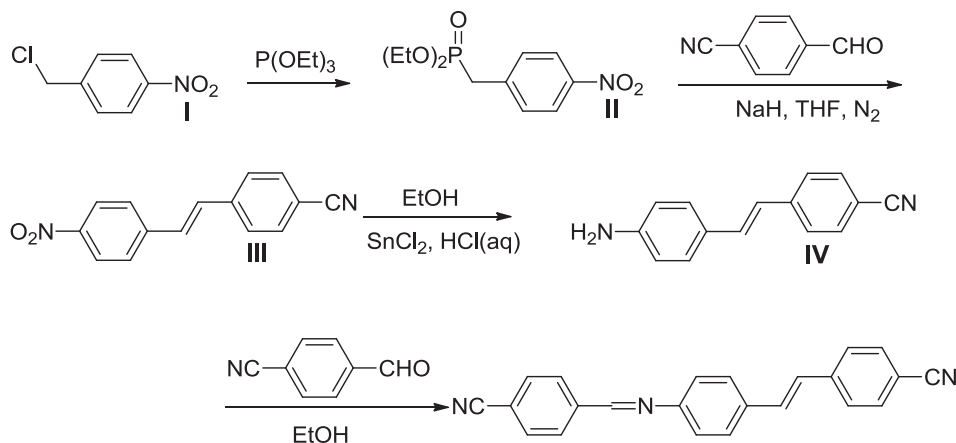
Compound 4-((E)-4-((4-cyanobenzylidene)amino)styryl)benzonitrile [19]. Equimolar amounts of compound **IV** and 4-cyanobenzaldehyde were dissolved in ethanol, followed by stirring at 80 °C for 1 h. The solvent was removed by rotary evaporation and the harvested product was recrystallized from dichloromethane and ethanol to give the titled compound. The yield was 95%.

2.2. Spectral measurement

Absorbance spectra were collected on a LAMBDA-35 UV–vis spectrometer in a concentration range of 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 ¹H NMR and ¹³C NMR spectra of compound were recorded at 293 K on a Bruker AV-500 spectrometer using CDCl₃ as solvent and TMS as internal standard.

2.3. X-ray crystallography

Crystals of SB-styrene suitable for X-ray diffraction were obtained through slow evaporation of a methanol–chloroform mixture (vol:vol = 3:1) of the compound. Yellow crystals were obtained after a few days. Crystallographic analyses were performed on a Gemini S Ultra, Oxford platform diffractometer using Mo K α monochromatic radiation ($\lambda = 0.71073 \text{ \AA}$) with the application of empirical absorption correction. The structure was solved using the direct method and refined by the full-matrix least-squares method on F^2 using the SHELXL-97 software [20,21]. The non-hydrogen atoms were refined anisotropically whereas the hydrogen atoms were refined isotropically as a riding mode using



Scheme 1. Route for the synthesis of the title compound.

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