



The effect of solvent on electronic absorption bands of some Benzylideneanilines



Sagarika Panigrahi ^{a,*}, Pramila K. Misra ^{b,**}

^a Silicon Institute of Technology (Silicon West), Sason Sambalpur, 768200, Odisha, India

^b Centre of Studies in Surface Science and Technology, School of Chemistry, Sambalpur University, Jyoti Vihar, 768019, Odisha, India

ARTICLE INFO

Article history:

Received 9 May 2016

Received in revised form 17 August 2016

Accepted 12 September 2016

Available online 18 September 2016

Keywords:

Keto-enol tautomerism

Substituted benzylideneanilines

Solvent cage

Intramolecular H-bond

ABSTRACT

In the present investigation the effects of solvents of varied polarities on the UV–visible spectral bands of some substituted benzylideneanilines and their *o/p*-hydroxy derivatives were explored. The analyses of the electronic absorption bands indicated the long wavelength $\pi-\pi^*$ transition to be due to intramolecular charge transfer originating from the 4-methoxyaniline/aniline moiety as source and the $-\text{C}=\text{N}-$ unit as sink. The enol forms of *o/p* hydroxy benzylideneanilines were found to be more stable in neat solvents. The keto forms of these compounds on the other hand, predominated in some of the solvents in both acidic and basic conditions. A maximum of 84% keto form of *p*-hydroxybenzylideneaniline was observed in basic DMSO solutions at $[\text{NaOH}] = 0.002 \text{ M}$. The tautomerization constants (K_T 's) of *o/p*-hydroxybenzylideneanilines at 300 K were determined. A good correlation between the relative permittivities of solvents and K_T of *p*-hydroxybenzylideneaniline in the corresponding solvent with regression coefficient of 0.998 supported specific interactions between the solvent and the aldimines. But the occurrence of a scattering distribution of the relative permittivities of solvents with the K_T 's of *o*-hydroxybenzylideneaniline revealed no specific interaction of these molecules with the solvents. The oscillator strength of the charge transfer bands of the *o*-hydroxybenzylidene-4-methoxyaniline was found to be in the range $0.16\text{--}0.29 \text{ L mol}^{-1} \text{ cm}^{-2}$. The energy of the charge transfer band of the *o*-hydroxy substituted benzylideneanilines determined from experimental wavelength agreed very well with the theoretical values calculated by using Briegleb relation.

© 2016 Elsevier B.V. All rights reserved.

1. Introduction

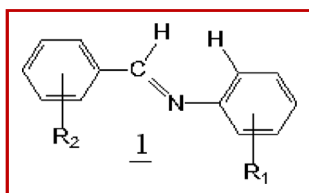
Benzylideneanilines belong to a class of compounds called aldimines having azomethine group ($-\text{CH}=\text{N}-$) as the characteristic functional moiety. The interests in the synthesis of aldimines and studies on their solution behaviour originate mostly due to their wide applications in various fields ranging from biological to analytical chemistry [1–5]. The exploitation of suitable structural properties of these compounds is easily accomplished due to their relatively simpler synthetic procedure and synthetic flexibility [6–7]. In addition, the presence of an ortho hydroxyl group with respect to azomethine linkage of the aldimines, facilitates the phenomena like intramolecular H-bonding ($\text{O}-\text{H}\cdots\text{N}$ and $\text{O}\cdots\text{H}-\text{N}$), tautomerism, thereby, promoting the formation of either enol-imino or keto-imino tautomers in those molecules

[8–11]. This phenomenon has also similarity with thermochromism [12, 13] and hence the tautomerization in salicylideneaniline and its analogues, has been receiving considerable attention. Acquiring characteristics spectral parameters of the aldimines through UV–visible technique is one of the expedient techniques that throw deeper insight into the tautomerism in salicylideneanilines and its *p*-hydroxy analogues. But pulling of spectral parameters, understanding the possible electronic transitions and assigning the UV–visible peaks in the absorption spectra are vital for these molecules. These depend meticulously on the structure of the aldimines and environments experienced by the aldimines in their immediate neighbourhoods. Particularly, significant differences in resolutions of spectra and transitions are exhibited as the polarity of the surrounding solvent changes. Therefore, the UV–visible spectra of these compounds have been studied in polar and non polar solvents in both acidic and basic media [14]. Usually, the manifestation of a new band at or beyond 400 nm for these compounds in the midst of some polar solvents containing acid/base is an indication of the formation of keto tautomer of the aldimine [8,10,11,15–16]. But these types of peaks emerge rarely or do not emerge at all in presence of some other nonpolar solvents even in acidic or basic conditions

* Correspondence to: S. Panigrahi, Department of Basic Science (Chemistry), Silicon Institute of Technology, Silicon West, Sason, Sambalpur, 768200, India.

** Correspondence to: P. K. Misra, Centre of Studies in Surface Science and Technology, School of Chemistry, Sambalpur University, Jyoti Vihar, 768019, India.

E-mail addresses: sagarika_panigrahi2003@yahoo.co.in (S. Panigrahi), pramila_61@yahoo.co.in (P.K. Misra).



- 1a:** $R_1 = p\text{-OCH}_3$, $R_2 = o\text{-OH}$; **1b:** $R_1 = p\text{-OCH}_3$, $R_2 = p\text{-OH}$ **1c:** $R_1 = \text{H}$, $R_2 = o\text{-OH}$;
1d: $R_1 = \text{H}$, $R_2 = p\text{-OH}$ **1e:** $R_1 = p\text{-OCH}_3$, $R_2 = \text{H}$; **1f:** $R_1 = \text{H}$, $R_2 = \text{H}$

Molecular Structure 1.

[14]. The studies on phenomena like solvatochromism, keto-enol tautomerism of the aldimine in organic solvents of varied polarity are, therefore, of considerable importance [17–18].

In the present study, we have synthesized a series of tailor made N-benzylideneaniline, *o/p*-hydroxy-benzylideneanilines, N-benzylidene-4-methoxyaniline and *o/p*-hydroxy-benzylidene-4-methoxyanilines and characterized them through spectral techniques comprising of IR, ^1H NMR and electronic absorption. The effects of both polar and nonpolar solvents on their electronic absorption bands were explored. DMSO affected the electronic transition of hydroxyl substituted aldimines to a greater extent promoting keto-enol tautomerism conspicuously. The percentages of keto and enol forms and the tautomerization constants of the *o/p*-OH substituted aldimines in DMSO were calculated.

2. Experimental

2.1. Synthesis of aldimines

The aldimines **1(a-f)** were synthesized by refluxing equimolar amount of aniline/*p*-anisidine with benzaldehyde/ salicylaldehyde/*p*-hydroxybenzaldehyde in minimum amount of ethanol [19–22]. These

compounds were recrystallized from ethanol three times to ensure the purity of the samples. The sharp melting point and distinct singular spot on TLC plate in each case indicate high purity of the samples. The generic structures of these aldimines are given in **Molecular structure 1**.

2.2. Characterization of the aldimines

The compounds were characterized by different spectral techniques such as FTIR and NMR spectroscopic analyses. FTIR spectra of these aldimines were recorded in the region $400\text{--}4000\text{ cm}^{-1}$ with the help of a Shimaduz IR Prestige-21 FTIR spectrophotometer using KBr disk. ^1H NMR spectra of the aldimines were recorded using 400 MHz FT NMR at SAIF, Madras IIT, Chennai. The FTIR and NMR plots for **1a** are provided in **Figs. 1 and 2** and supplementary Figs. S1–S9 (for the rest aldimines). The spectral data confirmed to their structures [23,24]. The FTIR spectral data are presented in supplementary Table S1.

2.3. Effect of solvents on UV–visible spectra of aldimines

The spectral parameters and electronic absorption spectra of the aldimines **1a** to **1f** were analyzed in presence of 13 organic solvents

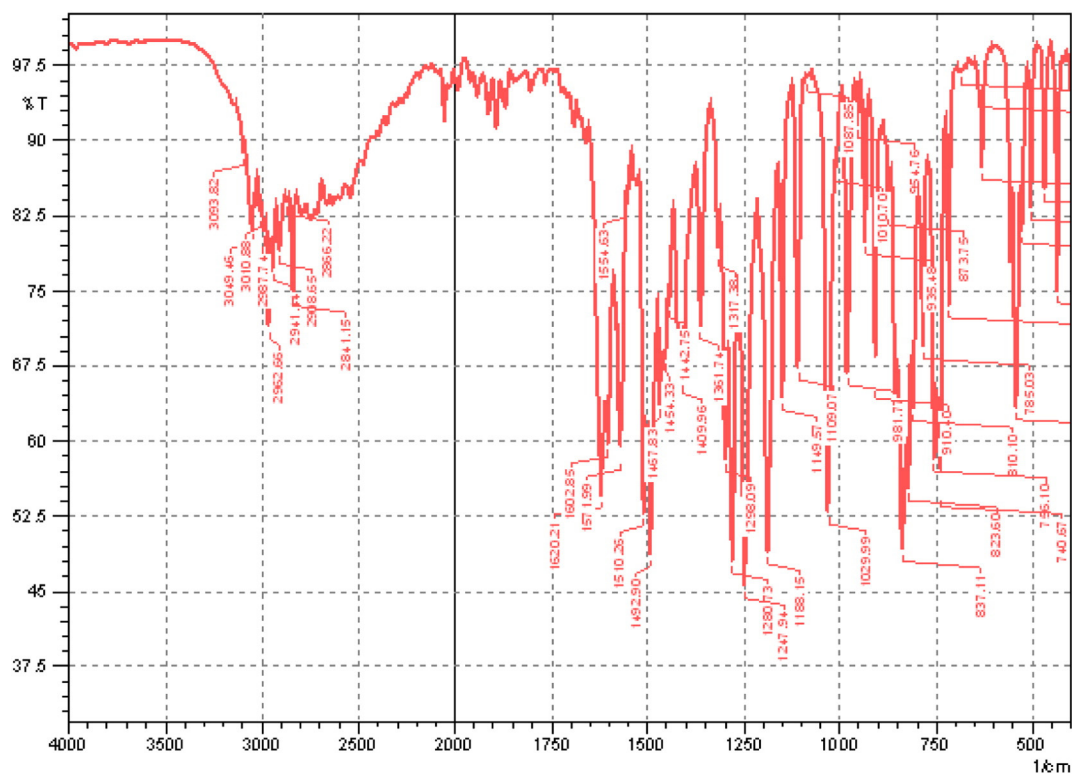


Fig. 1. IR spectrum of **1a** (KBr Disk).

Download English Version:

<https://daneshyari.com/en/article/5409311>

Download Persian Version:

<https://daneshyari.com/article/5409311>

[Daneshyari.com](https://daneshyari.com)