Journal of Molecular Liquids 224 (2016) 53–61

Contents lists available at ScienceDirect

Journal of Molecular Liquids

journal homepage: www.elsevier.com/locate/molliq

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

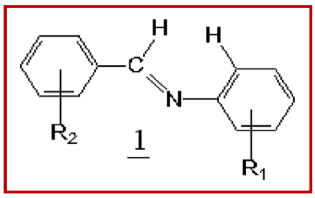
In the present investigation the effects of solvents of varied polarities on the UV–visible spectral bands of some substituted benzylideneanilines and their *o*/*p*-hydroxy derivatives were explored. The analyses of the electronic absorption bands indicated the long wavelength π-π* transition to be due to intramolecular charge transfer originating from the 4-methoxyaniline/aniline moiety as source and the —C═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 [NaOH] = 0.002 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 0.16–0.29 L mol^{-1} 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.

1. Introduction

Benzylideneanilines belong to a class of compounds called aldimines having azomethine group (—CH═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 (O—H….N and O….H—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).

http://dx.doi.org/10.1016/j.molliq.2016.09.036
0167-7322/



1a: R_1 = *p*-OCH_3, R_2 = *o*-OH; **1b**: R_1 = *p*-OCH_3, R_2 = *p*-OH **1c**: R_1 = H , R_2 = *o*-OH;
1d :R_1 = H, R_2 = *p*-OH **1e**: R_1 = *p*-OCH_3, R_2 = H; **1f**: R_1 = H, R_2 = H

Molecular Structure 1.

[14]. The studies on phenomena like solvatochrosim, 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, ^{1}H 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 spectroscoscopic analyses. FTIR spectra of these aldimines were recorded in the region 400–4000 cm^{-1} with the help of a Schimaduz IR Prestige-21 FTIR spectrophotometer using KBr disk. ^{1}H 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

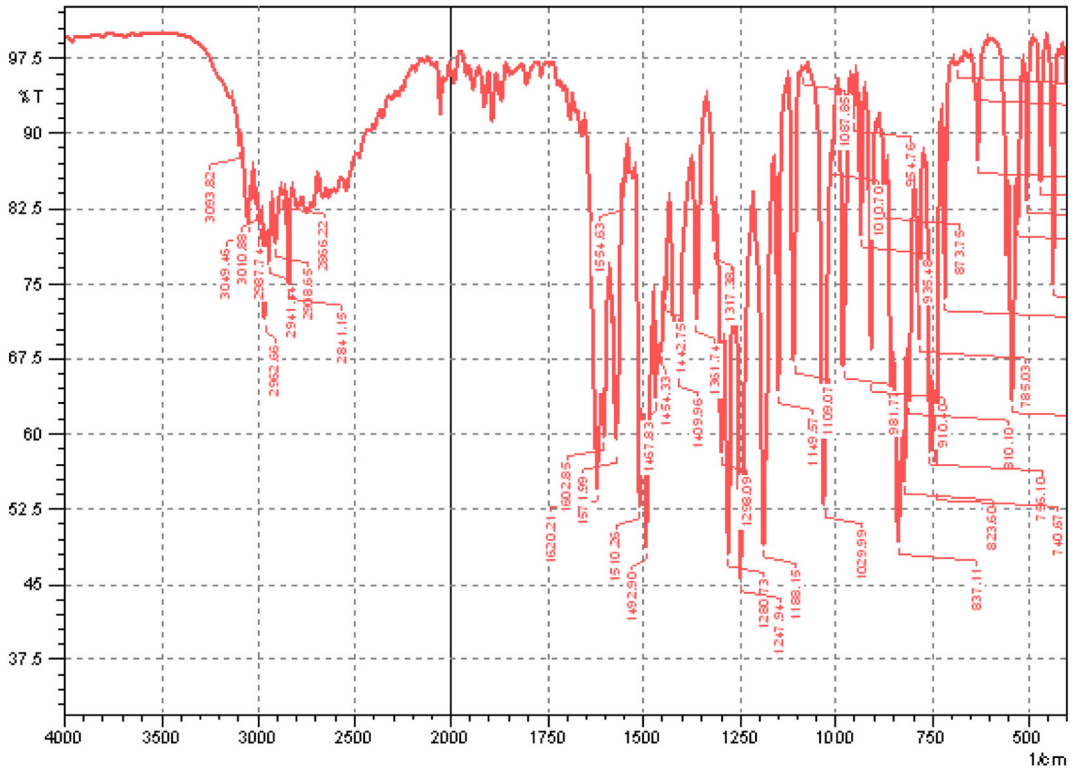


Fig. 1. IR spectrum of **1a** (KBr Disk).

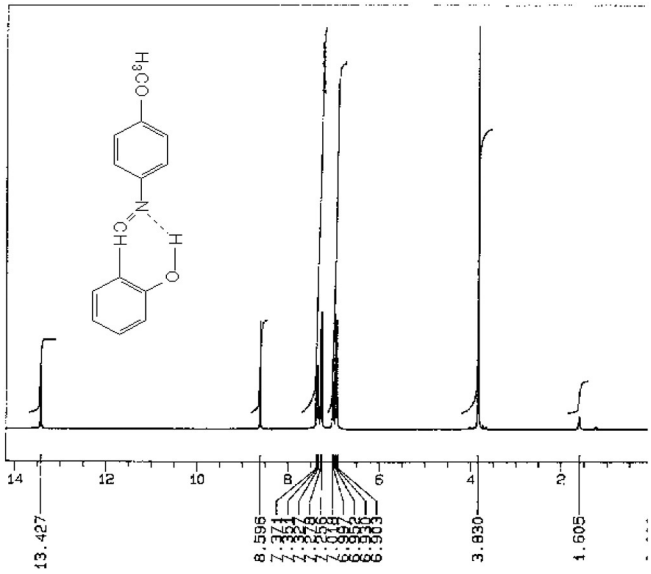


Fig. 2. ^{1}H NMR Spectrum of **1a** (Resolution: 399.65 MHz, Solvent: $CDCl_3$).

of varied polarities namely, methanol, ethanol, 1-propanol, 1-butanol 2-propanol, DMSO, DMF, chloroform, THF, 1,4-dioxane, toluene, hexane, cyclohexane using Shimadzu UV-2450 UV–vis spectrophotometer. All reagents used were of spectroscopic grade and distilled prior to the measurements.

The occurrence of keto-enol tautomerism in hydroxy-substituted aldimines, **1a** to **1d** was investigated in presence of both polar and nonpolar solvents. The aldimines, **1e** and **1f** did not exhibit keto-enol taotomerism due to the absence of –OH group in their skeletal moiety. HCl and NaOH in the range 10^{-4} M to 2×10^{-3} M were added to uphold acidic and basic conditions whenever necessary. The aldimines of 5×10^{-5} M was used throughout the experiments. The tautomerization constants, K_T's were calculated theoretically.

3. Result and discussions

3.1. Electronic absorption spectra in organic solvents

The nitrogen atom of functional moiety i.e. azomethine linkage (—C═N—) of the aldimines is connected exclusively to either an aryl or an alkyl group [25]. In addition, the aldimines, **1a**, **1b** and **1e** have –OCH_3 group as the donor and —C═N— group as the acceptor promoting thereby the vectorial flow of electron from the substituent-OCH_3 to the —C═N— center (Fig. 3).

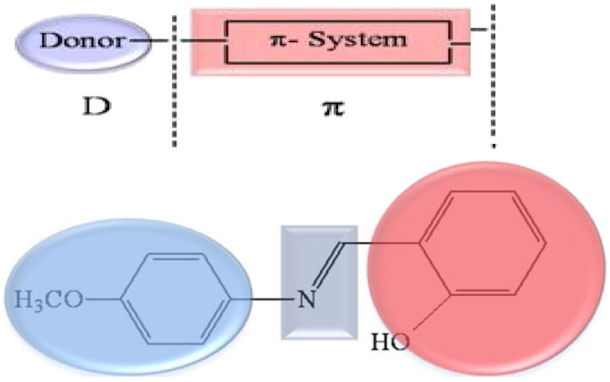


Fig. 3. Schematic representation of organic D-π- aldimine, where D is electron donor of the organic aldimine and π is conjugated system that acts as electron acceptor.

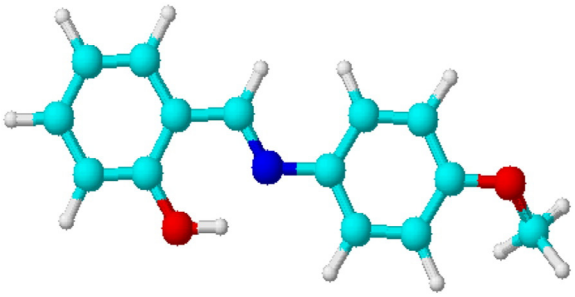


Fig. 4. O—H…. N intramolecular H-bonding in aldimine **1a.**

The aldimines, **1a** and **1c** (*o*-hydroxy substituted aldimines) are quite fascinating set of compounds for studying H-bond properties because of the possibility of intramolecular hydrogen bonding as a result of prominent π-electron coupling between their acid and base centers [Fig. 4, 19–22,26–27]

The electronic absorption spectra of the compounds were obtained in 13 different organic solvents. Some representative spectra of **1a** to **1f are** shown in Figs. 5–10. The spectra comprised of several absorption bands in the range 200 to 500 nm. The analyses of the electronic spectra of *o*-hydroxy substituted aldimines **1a** and **1c** envisaged four distinct

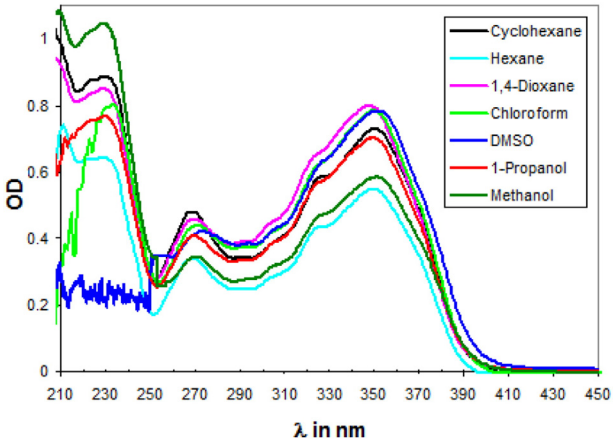


Fig. 5. Electronic absorption spectra of **1a** = [5×10^{-5} M] in different solvents.

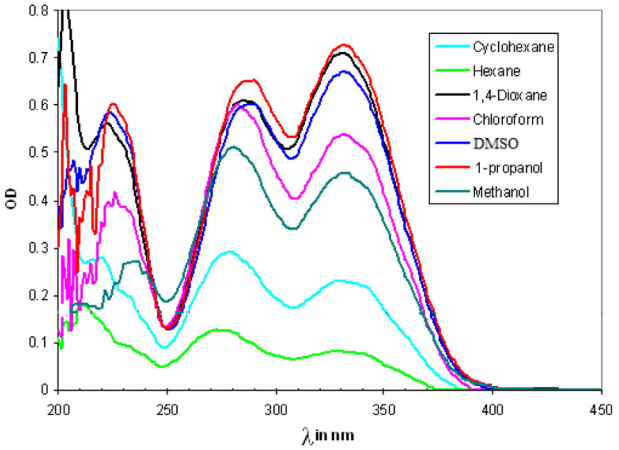


Fig. 6. Electronic absorption spectra of **1b** = [5×10^{-5} M] in different solvents.

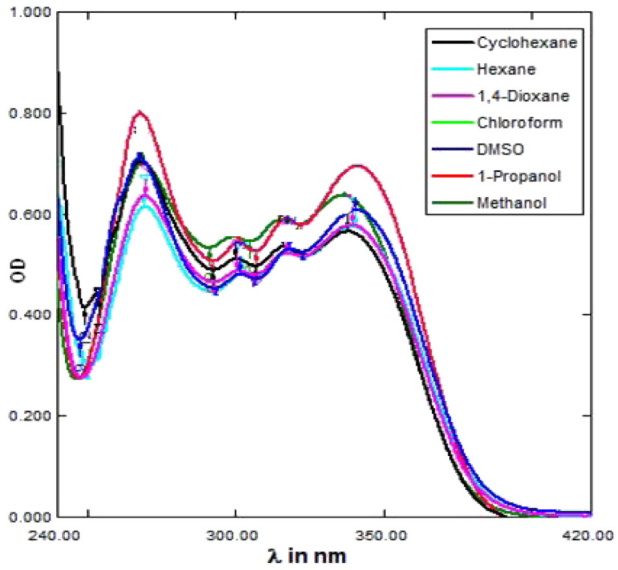


Fig. 7. Electronic absorption spectra of **1c** = [5×10^{-5} M] in different solvents.

bands whereas **1b**, **1d**, **1e**, **1f** exhibited only three bands in presence of all solvents (Table 1, Figs. 5–10). The peaks were however, not very distinct in some cases due to broadening phenomena. The exact bands in those cases were obtained by fitting Gaussian curve. The representative spectra for **1a** to **1f** in cyclohexane and its Gaussian fitting curve were provided in Figs. 11–12.

The distinct four bands in UV–visible absorption spectra of the *o*-hydroxy substituted aldimines (**1a** and **1c**) obtained in organic solvents were assigned as A, B, C, D [28–30] whereas the three bands in **1b** and **1d** were assigned as A, C, D. The 'B' band was not distinguished properly in some cases due to overlapping with 'A' band. The band 'A' located at 222–271 nm was attributed to the moderate energy π-π* transition of the aromatic ring [31] while the second band B at 275–295 nm in case of aldimine **1a** and **1c** was attributed to low energy π-π* transition of the aromatic ring [30]. These two bands were sensitive to the substitution on the aromatic rings but were slightly influenced by changing the

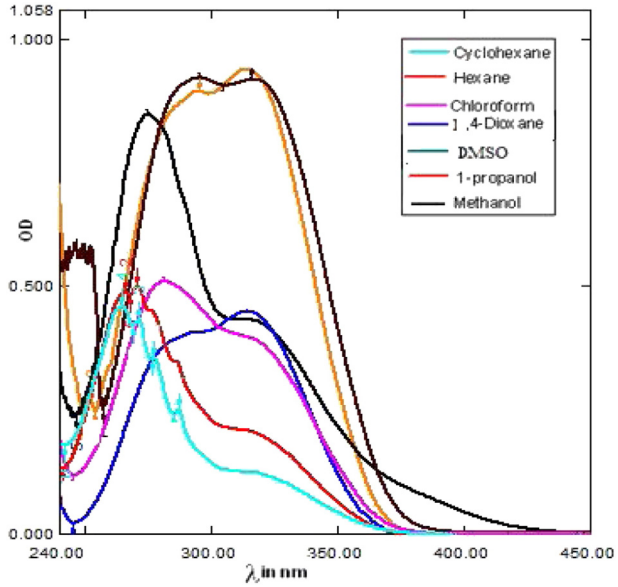


Fig. 8. Electronic absorption spectra of **1d** = [5×10^{-5} M] in different solvents.

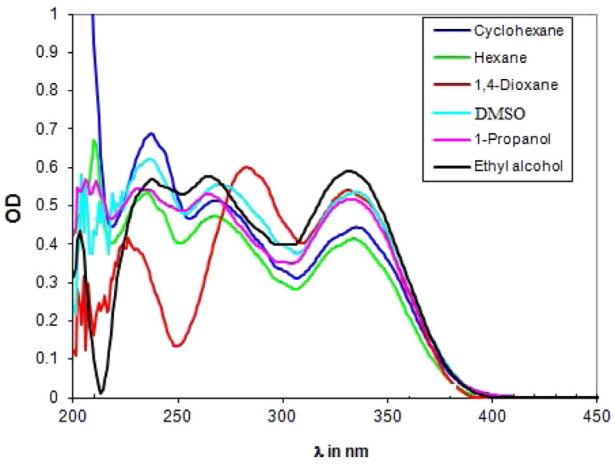


Fig. 9. Electronic absorption spectra of **1e** = [5×10^{-5} M] in different solvents.

solvent polarity [32]. The third band, 'C' band located at 266–328 nm was assigned to π-π* transition involving the π-electrons of the azomethine (—CH═N—) groups [28–30].

The broad band observed in the range 316–355 nm (D band) is due to the intramolecular charge transfer band (CT band) originating from the 4-methoxyaniline/aniline moiety as a source to the —C═N— as a sink [28–29]. This CT band is commonly observed in *o*-hydroxyl aldimines and is based on strong intramolecular H-bonding between the hydroxyl group of the salicylidene unit and the nitrogen atom of azomethine unit [33]. This peak, although was a well defined one, but appeared either as shoulders or as distinct splitted peaks. The distinct broadening of the intramolecular CT band was ascribed to the existence of enol-keto toutmeric equilibrium originating from the OH group in *o*-position to the C═N center [28] as shown in Scheme 1. The forbidden n-π* transition band due to the imino group had insignificant absorption in case of all aldimines [34].

The CT band was confirmed by calculating the energy of charge transfer band (E_{CT}) theoretically using Briegleb relation [Eq. (1) Ref 35].

$$E_{CT} = (IP - EA) + C\ldots \quad (1)$$

where IP is the ionization potential of the donor part (aniline and *p*-anisidine), EA is the electron affinity of the acceptor part (—C═N group) and 'C' term is the columbic force of attraction between the

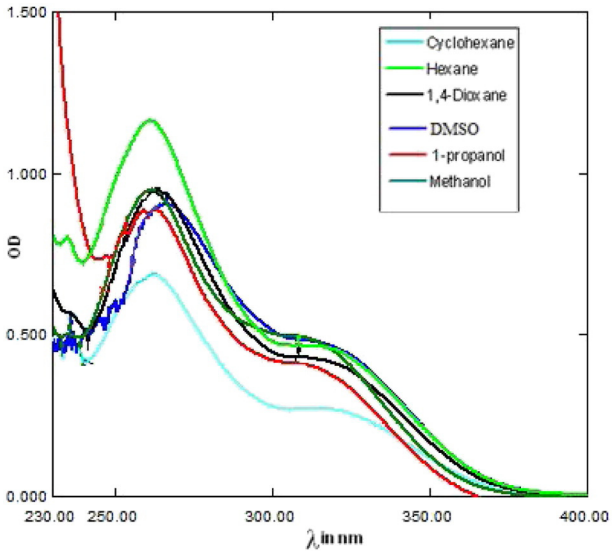


Fig. 10. Electronic absorption spectra of **1f** = [5×10^{-5} M] in different solvents.

Table 1
Data from UV–Vis spectra of Aldimines (λ_{max} in nm and ε_{max} in L mol^{-1} cm^{-1} × 10^{-4}).

Solvent	Compound	Band A (π-π* Ar)		Band B (π-π*Ar)		Band C (π-π*—C═N group)		Band D (CT)	
		λ_{max}	ε_{max}	λ_{max}	ε_{max}	λ_{max}	ε_{max}	λ_{max}	ε_{max}
Cyclohexane	**1a**	233.00	1.75	275.00	0.95	319.00	1.21	355.00	1.41
	1b	235.00	0.36	–	–	283.80	1.22	336.00	0.45
	1c	266.00	1.42	298.00	0.94	312.00	0.99	347.00	1.17
	1d	219.00	0.99	–	–	266.00	0.91	317.00	0.25
	1e	236.00	1.37	271.00	1.02	335.00	0.89	–	–
	1f	247.00	1.74	272.00	0.66	325.00	0.22	–	–
1,4-Dioxane	**1a**	231.00	1.69	285.00	0.77	319.00	1.21	351.00	1.58
	1b	222.00	1.12	–	–	283.80	1.22	330.00	1.42
	1c	271.00	1.27	300.00	0.97	315.00	1.03	343.00	1.03
	1d	219.00	1.04	–	–	277.00	0.99	316.00	0.79
	1e	226.00	0.83	280.00	1.18	334.00	1.07	–	–
	1f	215.00	1.70	262.00	1.90	314.00	0.85	–	–
Methanol	**1a**	231.00	0.76	290.00	0.55	321.00	0.87	351.00	1.17
	1b	236.00	0.54	–	–	284.00	1.01	335.00	1.09
	1c	270.00	1.34	295.00	1.05	311.00	1.12	340.00	1.21
	1d	223.00	0.75	–	–	279.00	0.73	316.00	0.89
	1e	238.00	0.90	264.00	0.93	337.00	0.85	–	–
	1f	215.00	1.67	260.00	1.89	307.00	0.992	–	–

electron transferred and the positive hole left behind. The IP values for para anisidene and aniline are taken as 7.82 and 7.70, respectively [36]). The EA is taken as −1.3 eV, [Ref 35] and 'C' term is taken as either 5.2 or 5.6 eV [Ref 35].

The E_{CT} values was also calculated experimentally from Eq. (2) [Ref 28].

$$E_{CT}\ (eV) = 1241.6/\lambda_{max}(nm)\ldots \quad (2)$$

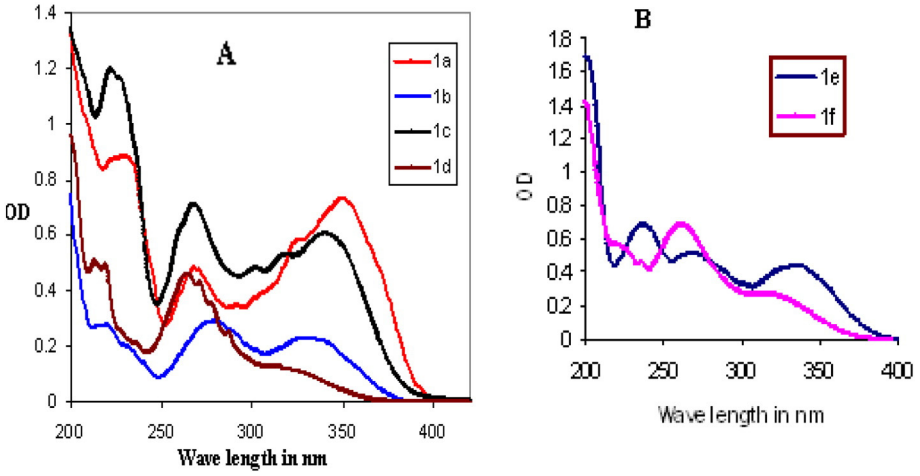


Fig. 11. Electronic spectra of **1a** to **1d** (A) and **1e** to **1f** (B) in cyclohexane.

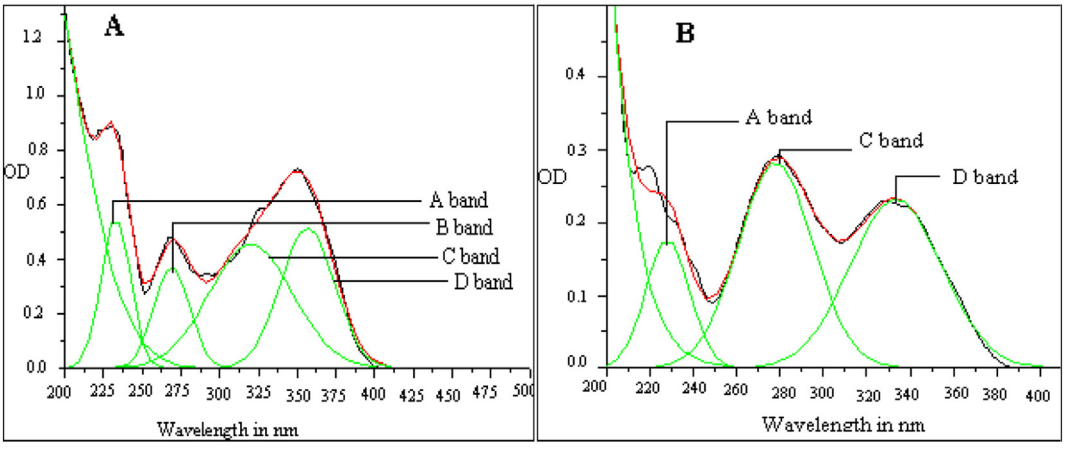
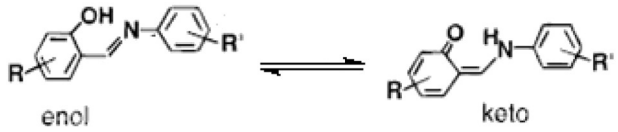


Fig. 12. Gaussian fitting curve for **1a** (A) and **1b** (B) in cyclohexane.



Scheme 1. Keto-enol tautomerism in *o*-hydroxy substituted aldimines.

where, λ_{max}(nm) were experimentally obtained wavelengths of the CT band. The E_{CT} values thus obtained were compared with E_{CT} values obtained theoretically from Eq. (1) using the two extreme values of C. The E_{CT} values obtained in both the ways compared very well with each other. A representative set of data for aldimine **1a** is provided in Table 2. The oscillator strength, "f" for the CT band was determined by applying the Eq. (3) [Ref 37].

$$f = 4.6 \times 10^{-9} \varepsilon_{max} \Delta\nu_{1/2} \ldots \quad (3)$$

where ε_{max} was molar extinction coefficient (L mol^{-1} cm^{-1}) and $\Delta\nu_{1/2}$ cm^{-1} was bandwidth at half value of the absorbance. The calculated values all of these parameters are given in Table 2. The electronic absorption spectral data of aldimines were also used to calculate the ionization potentials of the molecules using the general Eq. (4) (Ref-28)

$$IP = a + bE_{max} \ldots \quad (4)$$

where IP was the ionization potential of the molecule, *a* and *b* were constants having the values (i) 4.39 and 0.857 [Ref 38], or (ii) 5.15 and 0.778 [Ref 39] or (iii) 5.11 and 0.701 [Ref. 40], and E_{max} was the energy of the lowest electronic transition. The IP values calculated using the different values for *a* and *b* were in good agreement with each other (Table 2). The mean values for IP were also determined.

3.2. Study of keto-enol tautomerism

Usually the keto tautomer (NH-form, Scheme 1) for aldimines, **1a, 1b, 1c, 1d** appears at longer wave length (around 400 nm or beyond) and the enol tautomer (OH-form, Scheme 1) appeared at shorter wave length (<400 nm)[8–11,15–16]. The absence of NH absorption band in the spectra (Figs. 5–10) indicated that the compound **1a** existed mainly in the OH form and therefore, the charge transfer band 'D' was assigned to the OH band. Intramolecular proton transfer occurred, but the equilibrium shifted strongly towards the enol form (OH— form) which was also evident from the IR data. (Supplementary Table S1).

The absence of splitting peaks or shoulders at longer wave length (>400 nm) suggested the shifting of keto-enol tutomerism to enol form and the band was ascribed as OH-band exclusively for **1a** and **1c**. The probable formation of keto-enol tautomerism was explored in acidic and basic environments by adding HCl and NaOH to the organic solvents (Table 3).

Table 2
UV-Vis data of the aldimine **1a.**

Solvent	E_{CT}(eV) from Eq. (2)	IP_1(eV)	IP_2(eV)	IP_3(eV)	Mean IP(eV)	f L mol^{-1} cm^{-2}	E_{CT}(eV) from Eq. (1) when [C = 5.6 ev]
Cylohexane	3.497	7.660	8.120	7.790	7.860	0.207	3.520
Hexane	3.497	7.670	8.130	7.790	7.870	0.162	3.520
Tolune	3.478	7.650	8.110	7.780	7.850	0.225	3.520
Dioxane	3.537	7.720	8.180	7.840	7.910	0.286	3.520
THF	3.532	7.700	8.160	7.820	7.890	0.244	3.520
$CHCl_3$	3.527	7.700	8.160	7.820	7.890	0.261	3.520
DMF	3.512	7.690	8.150	7.810	7.880	0.269	3.520
DMSO	3.507	7.680	8.140	7.800	7.870	0.265	3.520
2-Propanol	3.507	7.710	8.170	7.830	7.900	0.232	3.520
1-Butanol	3.517	7.700	8.160	7.820	7.890	0.201	3.520
1-Propanol	3.522	7.710	8.170	7.830	7.900	0.227	3.520
Ethanol	3.527	7.670	8.130	7.790	7.870	0.248	3.520
Methanol	3.537	7.700	8.160	7.820	7.890	0.192	3.520

E_{CT}(eV) from Eq. (1) when [C = 5.2 ev] = 3.920.

Table 3
Individual spectral characteristics of both enol and keto tautomers in different solvents (λ_{max} in nm and ε_{max} in L mol^{-1} cm^{-1} × 10^{-4}).

		Acidic [HCl] = 0.002 M		Basic [NaOH] = 0.002 M	
Aldimine	Solvent	$\lambda_{max}/\varepsilon_{max}$ Enol form	$\lambda_{max}/\varepsilon_{max}$ Keto form	$\lambda_{max}/\varepsilon_{max}$ Enol form	$\lambda_{max}/\varepsilon_{max}$ Keto form
1a	1,4-Dioxane	349.00/1.94	–	350.00/2.14	–
	$CHCl_3$	351.00/2.56	–	351.00/2.69	–
	DMSO	352.00/1.55	–	305.00/0.588	428.00/1.26
	Methanol	348.00/1.48	405.00/1.24	349.00/1.78	
1b	1,4-Dioxane	273.00/2.94	–	330.00/2.26	–
	$CHCl_3$	332.00/1.08	–	332.00/1.06	–
	DMSO	353.00/0.55	391.00/0.654	364.00/3.20	389.00/4.48
	Methanol	349.00/0.71	385.00/1.34	331.00/2.32	–
1c	1,4-Dioxane	322.00/0.61	–	344.00/0.746	389.00/0.600
	$CHCl_3$	340.00/1.27	–	340.00/1.19	–
	DMSO	273.00/1.05	427.00/1.05	272.00/0.96	428.00/1.49
	Methanol	324.00/0.274	–	339.00/0.894	385.00/0.392
1d	1,4-Dioxane	271.00/2.24	–	300/.001.02	352.00/3.35
	$CHCl_3$	272.00/2.00	–	279.00/0.0.78	322.00/0.75
	DMSO	287.80/1.75	–	312.00/0.788	387.00/3.84
	Methanol	285.00/1.10	–	294.00/0.700	349.00/3.09

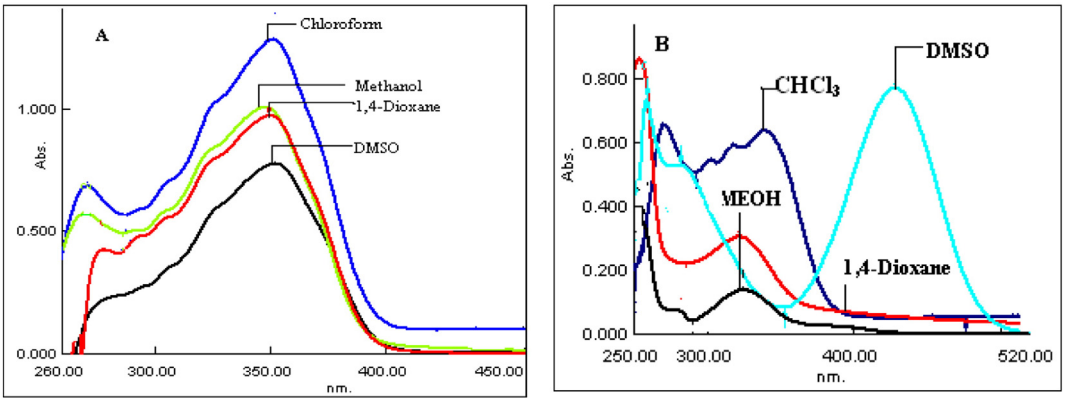
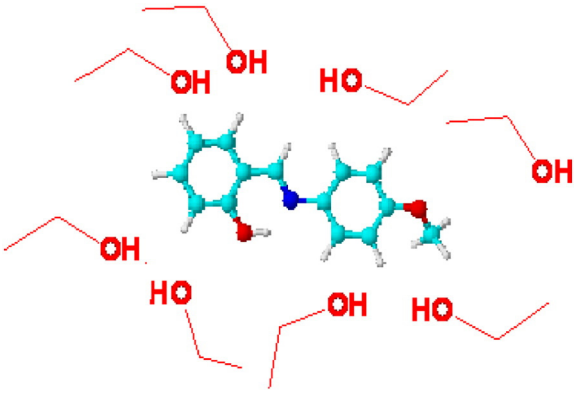


Fig. 13. Acid effect on aldimine **1a** (A) and **1c** (B) in different solvent ([HCl] = 0.002 M).



Scheme 2. Localization of *o*-hydroxybenzylidene-4-methoxyaniline in ethanol.

*3.2.1. Tautomerization in case of ortho-hydroxy substituted aldimines, **1a** and **1c***

Generally, tautomerization in aldimine depends upon the specific solute–solvent interactions, e.g. hydrogen bonding, and nonspecific bulk interactions with the solvent [41]. In polar solvents the equilibrium shifts towards the keto form [41]. In presence of methanol and to some extent in $CHCl_3$, the substiuents in donor and acceptor stabilize keto and enol tautomers. [41]. The dominating tautomer-H…OH-solvent interaction (via movable proton of the aldimines, **1a** and **1c** and oxygen of the solvent methanol) would require breaking of the intramolecular hydrogen bond. For these molecules a tautomer- O.... H– solvent interaction with alcohols as well as $CHCl_3$ should be energetically more favorable [41]. Thus, the keto tautomer might be predominated in polar solvent in **1a** and **1c.**

But in the present investigation for **1a** and **1c** the enol tautomer predominated in all polar neat solvents as well as in acidic conditions of the solvent ([HCl] = 10^{-4} M to 2×10^{-3} M). On the other hand in acidic DMSO having [HCl] = 0.002 M, keto form of **1c** outweighed**.** The electronic absorption spectra of **1a** and **1c** in different acidic solvents are shown in Fig. 13(A and B**)**.

In presence of all polar solvents in acidic conditions, hydrogen bonding between aldimine (**1a**/**1c**) and the solvent (tautomer-H…OH) did not occur indicating the solvation to be due to nonspecific dispersive interaction [41]. Due to the presence of strong electron releasing —OCH_3 group in para position of the aldimine **1a,** the strength of intramolecular hydrogen bond increased [42] making the solute-solvent interaction via moveable proton and the oxygen of the solvent to be unfavourable. As a result, the aldimine **1a** was preferably present in enol form in the solvent cage as shown in Scheme 2.

DMSO has greater basic character compared to $CHCl_3$, 1,4-dioxane, methanol etc. and therefore, it has excellent solvation power and capacity to promote hydrogen bonding [43]. The H^+ ion released from the phenolic —OH of the aldimine **1a** and **1c** could be easily stabilized by DMSO. Consequently, keto form of both the aldimine **1a** and **1c** predominated in basic DMSO (Fig. 14A).

In case of aldimine **1c**, since the intramolecular hydrogen bonding is weak in compared to **1a** and its keto form exists with lower extinction coefficient in polar solvents like basic methanol and basic 1,4-dioxane [Fig. 14B].

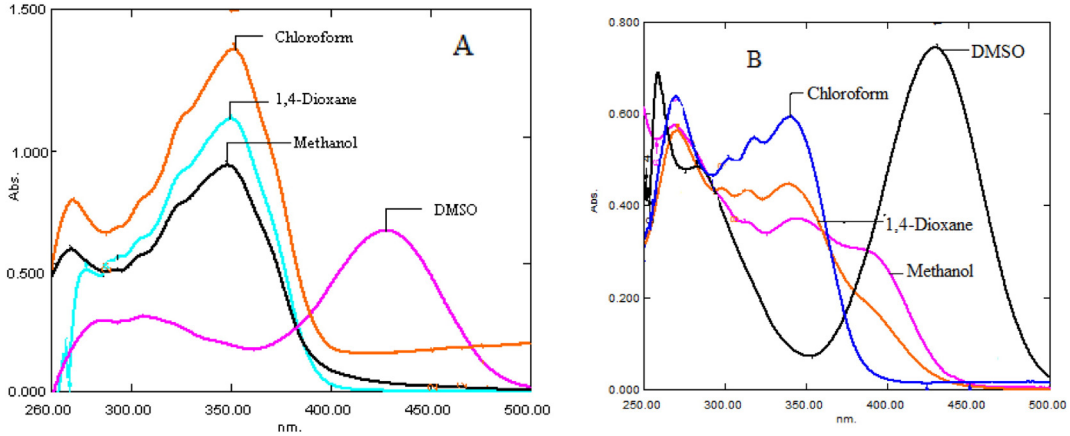


Fig. 14. Base effect on aldimine **1a** (A) and **1c** = (B) in different solvents ([NaOH] = 0.002 M).

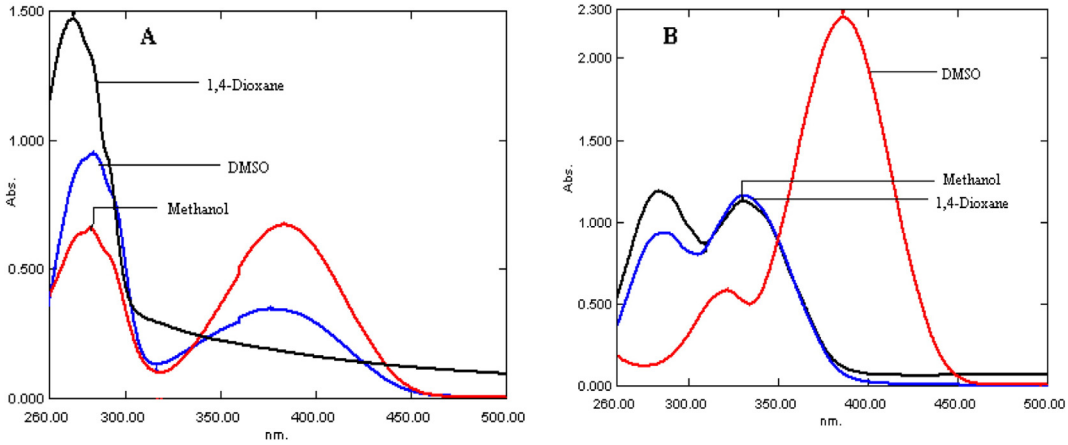


Fig. 15. Acid effect on aldimine **1b** in different solvents (A) ([HCl] = 0.002 M) Base effect on aldimine **1b** in different solvents (B) ([NaOH] = 0.002 M).

3.2.2. Tautomerization in *1b* and *1d*

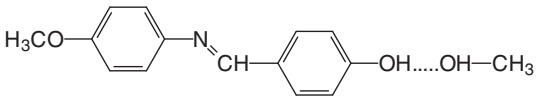
The keto form of aldimine **1b** predominated over its enol form in acidic DMSO and methanol [Fig. 15(A)]. On the other hand the keto form existed predominently in basic DMSO [Fig. 15(B)]. The existence of keto form in acidic methanol and DMSO was attributed to the free —OH group of **1b** which interacted strongly with the solvent (Schemes 3 and 4). The keto form of aldimine **1d** generally predominated in basic DMSO (Fig. 16) and enol form was stable in acidic solvent.

3.2.3. Description of tautomeric constant, K_T

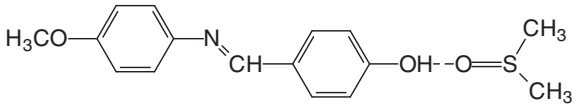
The tautomerization constants $K_{T's}$ (Hydrazo/Azo ratio of the pure tautomeric forms) are provided in Table 4. Analyses of the data suggested that although there was a trend towards an increase of K_T with increasing relative permittivity of solvent, the parameter in general could not be correlated with the tautomerization constants of the ortho substituted aldimines possibly due to the absence of any specific interactions with the solvent. The plot of relative permittivity of the solvents vs. the tautomerization constants of the aldimines, **1c** and **1d** (Fig. 17) yielded a good correlation with $R^2 = 0.998$ for the aldimine, **1d**. But in case of ortho substituted aldimine, **1c** scattered distribution was observed (Fig. 17).

3.2.4. Percentage calculation of enol and keto form

The % of enol and keto forms was calculated in basic DMSO. The highest % of keto form was for **1d** as given in Table 5.



Scheme 3. Hydrogen bonded structure of **1b** with methanol.



Scheme 4. Hydrogen bonded structure of **1b** in DMSO.

3.3. Conclusion

The tautomerization in salicylideneaniline and its analogues is of particular interest due to its close resemblance with thermochromism. Generally, tautomerization in aldimine depends upon the specific solute–solvent interaction e.g. hydrogen bonding, and nonspecific bulk interactions with the solvent. The enol form of aldimines was found to be more stable in neat solvents in contrast to the keto form which was stable in acidic or basic solvent system. Rapid enol to keto conversion has been noted in polar DMSO with the change of pH of the medium. A maximum 84% conversion of keto form of *p*-hydroxybenzyledeneaniline can find support from the tautomerization constant data. But in case of *o*-hydroxybenzyledeneaniline only 61% of the keto form was observed to be converted. The energy of the intramolecular charge transfer band

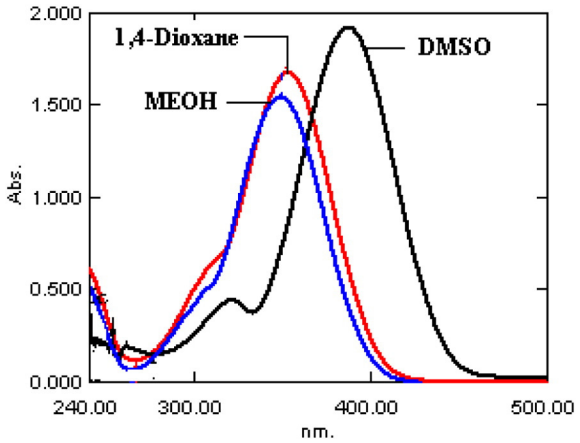


Fig. 16. Base effect on aldimine **1d** in different solvent ([NaOH] = 0.002 M).

Table 4
Measurement of K_T of **1c** and **1d** in different solvents [NaOH] = 0.002 M.

Aldimine	Relative permittivities	Solvents	K_T
1c	2.25	1,4-dioxane	0.804
	32.6	Methanol	0.44
	46.7	DMSO	1.55
1d	2.25	1,4-dioxane	3.29
	32.6	Methanol	4.42
	46.7	DMSO	4.87

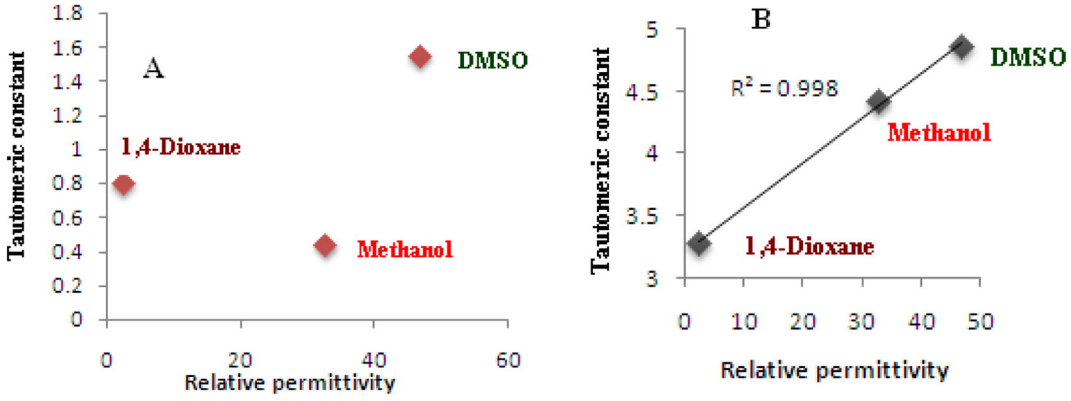


Fig. 17. A plot of the relative permittivities of the solvents vs. the tautomerization constants of **1c** (A) and **1d** (B).

Table 5
% of enol and keto form of **1a** to **1d** in basic DMSO.

Aldimine	Enol	Keto
1a	31%	69%
1b	41%	59%
1c	40%	61%
1d	16%	84%

(CT band) of *o*-hydroxy substituted aldimine originating from the 4-methoxyaniline/aniline moiety as a source to the —C═N— as a sink calculated from experimentally obtained wavelength compared very well with the theoretical by using the Briegleb relation.

Acknowledgements

The authors express their sincere thanks to CSIR (File No. 09/153(0067)/2011-EMR-I) for award of Research Associate fellowship to one of the authors (SP). Support of the UGC (DRS) and the FIST (DST) to the School of Chemistry, Sambalpur University are also gratefully acknowledged.

Appendix A. Supplementary data

Supplementary data to this article can be found online at http://dx.doi.org/10.1016/j.molliq.2016.09.036.

References

[1] Z. Cimerman, S. Miljanic, N. Galic, Croat. Chem. Acta 73 (2000) 81–95.
[2] P.A.N. Reddy, B.K. Santra, M. Nethaji, A.R. Chakravarty, J. Inorg. Biochem. 98 (2004) 377–386.
[3] A. Golcu, M. Tumer, H. Demirelli, R.A. Wheatley, Inorg. Chim. Acta 358 (2005) 1785–1797.
[4] M. Kabak, A. Elmali, Y. Elerman, J. Mol. Struct. 477 (1999) 151–158.
[5] K. Oyaizu, E. Tsuchida, Inorg. Chim. Acta 355 (2003) 414–419.
[6] S. Patai (Ed.), The Chemistry of the Carbon-Nitrogen Double Bond, J. Wiley and Sons, London, 1970.
[7] E. Jungreis, S. Thabet, Analytical Applications of Schiff Bases, Marcell Dekker, New York, 1969.
[8] M. Yildiz, Z. Kilic, T. Hokelek, J. Mol. Struct. 441 (1998) 1–10.
[9] H. Nazir, M. Yildiz, H. Yilmaz, M.N. Tahir, D. Ulku, J. Mol. Struct. 524 (2000) 241–250.
[10] H. Unver, Spectrosc. Lett. 34 (2001) 783–791.
[11] M. Yildiz, Spectrosc. Lett. 37 (2004) 367–381.
[12] E. Hadjoudis, Mol. Eng. 5 (1995) 301–337.
[13] J. Harada, H. Uekusa, Y. Ohashi, J. Am. Chem. Soc. 121 (1999) 5809–5810.
[14] M. Yildiz, H. Unver, B. Dulger, D. Erdener, N. Ocak, A. Erdonmez, T. Nuri Durlu, J. Mol. Struct. 738 (2005) 253–260.
[15] H. Unver, M. Yildiz, D.M. Zengin, S. Ozbey, E. Kendi, J. Chem. Crystallogr. 31 (2001) 211–216.
[16] M. Gavranic, B. Kaitner, E. Mestrovic, J. Chem. Crystallogr. 26 (1996) 23–28.
[17] K. Bernado, S. Leppard, A. Robert, G. Commenges, F. Dahan, B. Munier, Inorg. Chem. 35 (1996) 387–396.
[18] A.M. Daly, T.C. Dalton, M.F. Renehan, D.G. Gilheany, Tetrahedron Lett. 40 (1996) 3617–3620.
[19] P.K. Misra, B.K. Mishra, Ind. J. Chem. A 27 (1988) 889–892.
[20] S. Panigrahi, M. Chakroborty, P.K. Misra, J. Colloid Interface Sci. 306 (2007) 137–142.
[21] S. Panigrahi, P. Suna, P.K. Misra, Colloids Surf. A 415 (2012) 349–357.
[22] P. Suna, A.K. Naik, S. Panigrahi, P.K. Misra, Int. J. Adv. Chem. Sci. Appl. 1 (2013) 32–35.
[23] V. Guner, S. Bayari, Spectrosc. Lett. 35 (2002) 83–98.
[24] M. Nakamura, K. Kornatsu, Y. Gondo, K. Ohta, Y. Ueda, Chem. Pharm. Bull. 15 (1967) 585–592.
[25] From Wikipedia, the free encyclopedia, http://en.wikipedia.org/wiki/Schiff base.
[26] W. Schilf, J. Mol. Struct. 689 (2004) 245–249.
[27] A. Filarowski, A. Koll, A. Karpfen, P. Wolschann, Chem. Phys. 297 (2004) 323–332.
[28] R.M. Issa, A.A. Hassanein, I.M. El-Mehasseb, R.I.A. El-Wadoud, Spectrochim. Acta A 65 (2006) 206–214.
[29] R.M. Issa, A.M. Khedr, H.F. Rizk, Spectrochim. Acta A 62 (2005) 621–629.
[30] R.M. Issa, A.M. Khedr, H. Rizk, J. Chin. Chem. Soc. 55 (2008) 875–884.
[31] H.A. Dessouki, M. Gaber, A.L. El-Ansary, Egypt. J. Chem. 32 (1989) 639–650.
[32] A.M. Khedr, M. Gaber, R.M. Issa, H. Erten, Dyes Pigments 67 (2005) 117–126.
[33] M. Yildiz, H. Unver, D. Erdener, N. Ocak, A. Erdonmez, T.N. Durlu, Cryst. Res. Technol. 41 (2006) 600–606.
[34] H.H. Jaffe, S. Yeh, R.W. Gardner, J. Mol. Spectrosc. 2 (1958) 120–136.
[35] G. Breigleb, H.Z. Delle, Electrochem. (Ber. Bausengesell. Phys. Chem.) 64 (1960) 347; Z. Phys. Chem. (Frankfurt) 24 (1960) 359.
[36] CRC handbook of chemistry and physics NIOSH pocket guide to chemical hazards HYPERLINK, http://webbook.nist.gov (www.indsci.com/docs/manuals/VX500_IP.pdf).
[37] A. Reisey, L.J. Leyshon, D. Saundevs, M.V. Mijavic, A. Bright, J. Bogie, J. Am. Chem. Soc. 94 (1972) 2414–2421.
[38] F.A. Masten, J. Chem. Phys. 24 (1956) 602–606, http://dx.doi.org/10.1063/1.1742553.
[39] (a) R.S. Becker, W.F. Wentworth, J. Am. Chem. Soc. 84 (1962) 4263–4266; (b) R.S. Becker, W.F. Wentworth, J. Am. Chem. Soc. 85 (1963) 2210–2214.
[40] C.D. Wheast, Hand Book of Chemistry and Physics, 50th ed. The Chemical Rubber Company, Ohio, USA, 1969.
[41] L. Antonov, W.F. Fabian, D. Nedeltcheva, F.S. Kamounah, J. Chem. Soc. Perkin Trans. 2 (2000) 1173–1179.
[42] A. Filarowskia, T. Głowiakaa, A. Kolla, J. Mol. Struct. 484 (1999) 75–89.
[43] Concept of acids and bases www.google.com