SYNTHESIS AND SOLVATOCHROMIC STUDIES ON THE UV-ABSORPTION SPECTRA OF SYMMETRICAL AZINE DERIVED FROM 2,4-DICHLOROBENZALDEHYDE

ABSTRACT

Absorption spectra of symmetrical azine derived from 2,4-dichlorobenzaldehyde have been recorded in various solvents in the range 200–400nm. The effects of solvents on the absorption spectra of investigated compound is interpreted by correlation of absorption frequencies with Kirkwood function {ε, 1/ε and f(ε) }

Key word:, *symmetrical azines* ,Kirkwood function, absorption maxima,stabilization energy *antibacterial activity*

Introduction

Azines are 2,3-diaza analogues of 1,3-butadiene and are sometimes also referred as N—N linked diimines (C=N–N=C)[1]. These compounds are conventionally synthesised by the condensation of hydrazine with aldehydes/ketones[2]. With the latest developments in chemistry, several other methods of synthesizing azines have also been reported [3]. In addition, azines have potential biological properties, such as antibacterial, antihypertensive, antifungal, antibacterial and anticancer activities[4-9]. A number of heterocyclic compounds have been shown to possess pharmacological activities [10-11].They are useful candidates for drug development in the pharmacology industry. The ability of azines derived from 2-pyridinecarboxaldehyde as polydentate ligand to form very stable complexes with different cations is well known [8]. Azines, have achieved great significance in organic synthesis [12–15]. Azines have been used extensively as ligands for the synthesis of novel organometallic compounds [16–18]. Inspite of these synthetic utility, azines have good electronic, linear and non-linear optical properties [19-22]. Azines are useful for the isolation, purification and characterization of carbonyl compounds [23]. Recently we have synthesized and determined the conformations of some 4-biphenylcarboxaldehydes by theoretical methods and spectral studies [24&25]. Although, far more attention has been paid to study and interpret the ultraviolet absorption spectra of simple chalcone, no significant work has been carried out in this direction symmetrical azine.

Therefore the present work summarises the result of a detailed research carried out on solvatochromic effect on the ultraviolet absorption spectra of symmetrical azine derived from 2,4-dichlorobenzaldehyde.

Experimental details

The ethanolic solution of 2,4-dichlorobenzaldehyde (0.7g) and hydrazine hydrate (0.2002g) is stirred with small quantity of TBAB as a catalyst for 6 hours to form these (E)-1-(2,4-dichlorobenzylidene)hydrazine. Further,(E)1-(2,dichlorobenzylidene)hydrazine(0.3780g) react with 2,4-dichlorobenzaldehyde (0.1001)g to form a 1,2- bis(3,4-dimethoxybenzylidene)hydrazine.

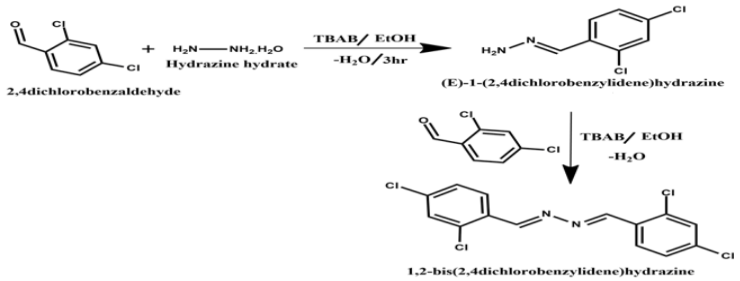


Image 1: Study experiment

Results and Discussion

We know that compounds with -C=N-N-N-C=N- group exist in *cis* and *trans* forms. Black and Lutz have clearly indicated that significant difference exists in the spectra of *s-cis* and *s-trans* forms.

These forms are thought to consist of two different independently non-conjugated chromophoric systems, namely azine and azo groups. Hence one might expect two independent characteristic bands for these chromophores in azine.

In all the spectra the principal absorption is only л→ л*transition and that it occurs as two peaks around 350 and 220-250 nm. The latter transition is less prominent in all the cases. There is no indication of л→n* transition in any of the cases. The prominent absorption maxima in ethanol and in hexane are presented in **Table 1**

Effect of solvents on the ultraviolet absorption spectra

It is well known that when an excited state has considerable charge separation relative to its ground state, the absorption is shifted to longer wavelength by increasing the polarity of the solvent. As one of the electronic transitions in the symmetrical azine is л → л*, this transition is expected to shift its wavelength of maximum absorption to longer wavelength by increasing the polarity of the solvent. Hence the ultraviolet absorption spectra of the compound was recorded in hexane and in ethanol-water mixtures of varying dielectric constant. The absorption maximum in hexane is considered that due to electronic transition from a non-solvated ground state to a non-solvated excited state. The difference in absorption maxima between those in alcohol-water mixtures and those in hexane is a direct measure of the excited state stabilization energy of the compound under investigation in various percentage of alcohol-water mixture. The $\Delta\lambda_{max}$ = [λ_{max} (ethanol-water) - λ_{max} (hexane)] values and the dielectric parameters of the solvent mixture are given in **Table 1&2**

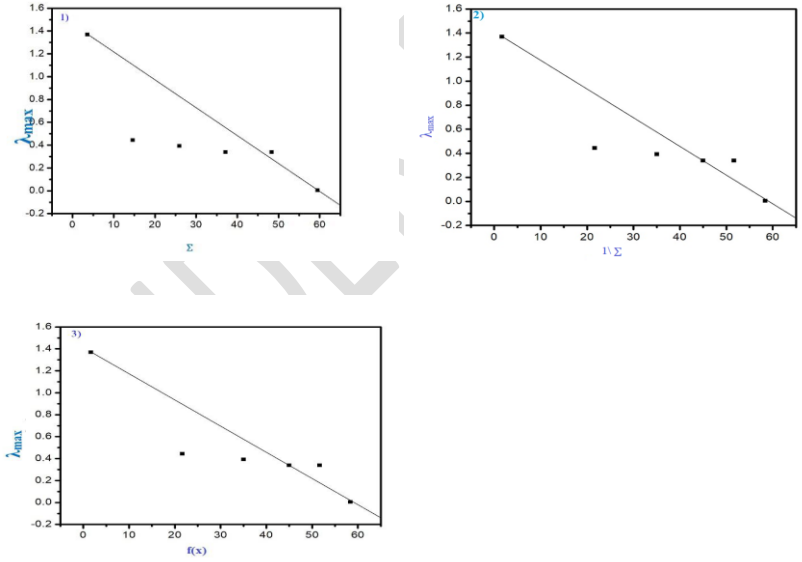
Table 1. Absorption maxima of symmetrical azine

Ethanol(%)in ethanol-water	λmax (nm)	Δλmax (nm)
100	316	93
90	280	57
80	278	55
70	276	53
60	276	53
50	263	40

Hexane = 223nm

The plots of $\Delta\lambda_{max}$ *versus* ε, 1/ε and f(ε) = ε −1/2 ε+1, Kirkwood function dielectric 2 ε +1 constant are shown in **Fig. 1-3**

Fig 1-3: Kirkwood function



In all the plots there is a perfect linearity between the stabilization energy and the dielectric constants of the alcohol-water mixtures establishing the fact that the stabilization energy is increased by solvation of the excited state.

Table -2

Dielectric constant of various percentage of ethanol-water mixtures

Ethanol (%) inethanol-water	**ε**	**1/ε**	**$f(\varepsilon)=\frac{\varepsilon-1}{2\varepsilon+1}$**
100	24.30	0.041	0.469
90	29.80	0.033	0.475
80	35.48	0.028	0.479
70	41.07	0.024	0.482
60	46.66	0.021	0.484
50	52.25	0.019	0.486
40	57.84	0.017	0.488

As there is perfect correlation between the stabilization energy the excited state and dielectric constant of the medium, it was thought of great interest to see if any correlation exists between stabilization energy of the excited state and dielectric constant of the medium by varying the alcohols themselves.

Hence the ultraviolet absorption spectra of the compound was recorded in hexane and in various alcohols of varying dielectric constants such as 1-butanol, 2- propanol, methanol, ethanol and 1-propanol. As mentioned earlier the difference in absorption maxima between those in hexane and those in various alcohols is a direct measure of excited state stabilization energy of symmetrical azine under investigation in various alcohols. The absorption maxima λ_{max},$\Delta\lambda_{max}$ and log $\Delta\lambda_{max}$ in various solvents are presented in **Table 3**

Table -3 λ_{max} **,** $\Delta\lambda_{max}$ **and log** $\Delta\lambda_{max}$ **of Azine in various alcohols**

S.No.	Solvent	λ_{max}(nm)	$\Delta\lambda_{max}$ (nm)	log$\lambda\Delta\lambda_{max}$ (nm)
1.	1-Propanol	318.5	95.5	1.9800
2.	1-Butanol	316.5	93.5	1.9708
3.	Ethanol	316	93	1.9684
4.	Methanol	314	91	1.9590
5.	2-Propanol	302.5	79.5	1.9003

(n-Hexane = 223 nm
$\Delta\lambda_{max}$ = (λ_{max} ethanol - λ_{max} hexane)
The solvent effect is best interpreted in terms of the following properties:

(a) the dielectric behaviour

(b) the ability of the medium to solvate

(c) the ability of protic solvent to form hydrogen bond with negative end of the dipole.

The Kirkwood function of the dielectric constant f(ε) = ε −1/2 ε+1

2 ε+1 is a suitable measure of (a) while (b) and (c) together are governed mainly by the polar effect of the alkyl group of the alcohol, suitably measured by the Taft polar substituent constants л* the solvent parameter employed are compiled in **Table 4**.

`TABLE-4

Polar effect of the alkyl group of the alcohol

SOLVENT	λmax(nm)
Ethanol	316
Ethyl acetate	315
Acetone	333
DMSO	321
DMF	318
Hexane	317.5
Benzene	322
Chloroform	283
Diethylether	320

Since the excited state in the azine involves charge separations, one might expect that the excited state will be stabilized by increasing the polarity of the alcohols. Hence it was attempted to see if any correlation existed between log $\Delta\lambda_{max}$ versus ε, 1/ε and f(ε). In all the cases the correlation were extremely good.
The UV absorption spectra of compound was also recorded in various polar aprotic and nonpolar aprotic solvents like Benzene, Ethyl acetate, Hexane, Acetone, DMF, DMSO and the λmax values are given in Table-**4**

When the solvent is changed from polar protic to polar aprotic then observed a red shift but when the polarity of the solvent is changed from (polar >non polar) there occurs a hypsochromic shift. Also there observed a bathochromic shift of the solvent polarity changes from nonpolar to polar aprotic solvent
Nonpolar => polar aprotic => polar protic.

Conclusion

The UV spectrum of the symmetrical azine derived from 2,4-dichlorobenzaldehyde was recorded in various solvent and the absorption band undergoes a hypsochromic shift (or) blue shift as the solvent polarity increases showing that the ground state is more dipolar.

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