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 maxima with Kirkwood function{ε, 1/ε and f(ε) }

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

Introduction

The 2,3-diaza analogues of 1,3-butadiene known as azines (C=N-N=C) are also occasionally referred to as N—N connected di imines[1]. Conventionally, these compounds are created by condensation of hydrazine with aldehydes or ketones[2]. Other techniques for manufacturing azines have also been reported in light of recent advances in chemistry [3]. Azines may also possess biological features as antifungal, antibacterial, antihypertensive and anticancer activities[4–9]. It has been demonstrated that a variety of heterocyclic compounds exhibit pharmacological properties [10–11]. They make good drug development candidates for the pharmacology sector. It is widely known that azines, which are polydentate ligands generated from 2-pyridinecarboxaldehyde, can form extremely stable complexes with various cations [8]. Azines have grown to be very important in chemical synthesis [12–15]. The synthesis of new organometallic compounds has frequently utilised azines as ligands [16–18]. Azines exhibit good electrical, linear and non-linear optical characteristics despite these synthetic uses [19–22]. For the separation, purification, and characterisation of carbonyl compounds, azines are helpful [23]. Recently, using theoretical techniques and spectral analyses, we were able to synthesis several 4-biphenylcarboxaldehydes and establish their conformations [24&25]. No major research has been done in this regard for symmetrical azine, despite the fact that the UV absorption spectra of simple chalcone have received significantly greater attention for study and interpretation.

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 methods

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.

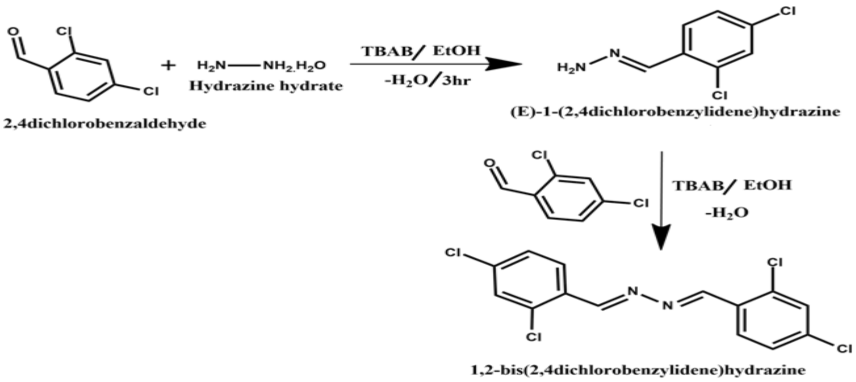


Image 1: Study experiment

Results and Discussion

We are aware that there are cis and trans versions of molecules with the -C=N-N-N-C=N- group. The spectra of the s-cis and s-trans forms plainly show major differences, according to Black and Lutz.

It is believed that these forms are made up of the azine and azo groups, two distinct and independently non-conjugated chromophoric systems. As a result, one may anticipate that these chromophores in azine will have two distinct distinctive bands.

Only transition is the main absorber in each spectrum and it exhibits itself as two peaks at 350 and 220-250 nm. In every instance, the latter shift is less noticeable. None of the cases show any sign of a лп* transition. Table 1 lists the major absorption maxima in ethanol and hexane.

Effect of solvents on the ultraviolet absorption spectra

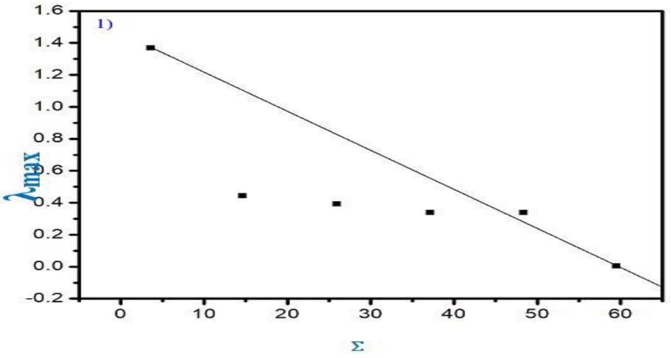
It is common knowledge that raising the solvent's polarity causes the absorption to shift to a longer wavelength when an excited state has a significant charge separation from its ground state. Given that one of the electronic transitions in the symmetrical azine is л →л*, this transition is predicted to cause the solvent's polarity to increase, shifting the maximum absorption wavelength to a longer wavelength. As a result, the compound's UV absorption spectra were captured in mixes of ethanol and water with various dielectric constants and hexane. The electronic transition from a non-solvated ground state to a non-solvated excited state is thought to be the cause of the absorption maximum in hexane.The difference in absorption maxima between alcohol-water mixtures and hexane is a direct indicator of the investigated compound's excited state stabilisation energy at various alcohol-water mixture concentrations. The values of max = [max (ethanol-water) - max (hexane)] and the solvent mixture's dielectric characteristics are provided in Tables 1 and 2.

Table 1. Absorption maxima of symmetrical azine

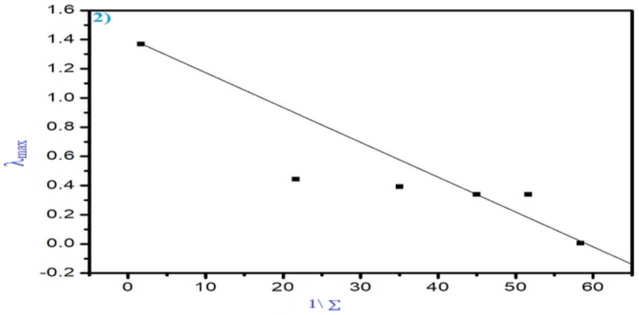
Ethanol(%)in ethanol-water	**λmax (nm)**	**Δλmax (nm)**
100	316	93
90	280	57
80	278	55
70	276	53
60	276	53
50	263	40

Hexane = 223nm
The plots of $\Delta\lambda_{max}$ *versus* ε, 1/ε and f(ε) =ε −1/2ε+1, Kirkwood function dielectric 2ε +1 constant are shown in **Fig. 1(a-c)**

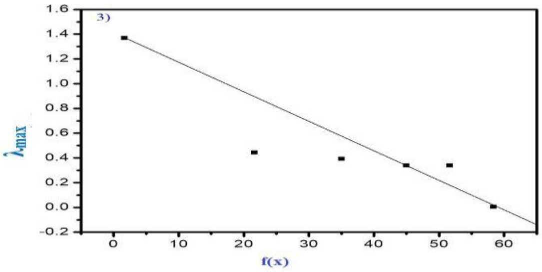
Fig 1(a-c): Kirkwood function



(a)



(b)



(c)

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 [26]

Ethanol (%) inethanol-water	**ε**	**1/ε**	**f(ε)=** $\frac{\varepsilon-1}{2\varepsilon+1}$
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

Since there is a perfect link between the stabilisation energy of the excited state and the medium's dielectric constant, it was thought to be of great interest to investigate whether there is a correlation between the two by adjusting the alcohols themselves.

As a result, the compound's ultraviolet absorption spectra were captured in hexane as well as in a number of alcohols with different dielectric constants, including 1-butanol, 2-propanol, methanol, ethanol and 1-propanol. As was already indicated, the difference between the absorption maxima in hexane and those in different alcohols is a direct indicator of the excited state stabilisation energy of the symmetrical azine being studied in those alcohols. Table 3 presents the absorption maxima λmax,Δλmax and log Δλmax in various solvents.

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$\Delta\lambda_{max}$ (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 −1/2ε+1

2 ε+1is 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

One may anticipate that raising the polarity of the alcohols will stabilise the excited state because the excited state in the azine involves charge separations. Therefore, an attempt was made to determine whether there was any correlation between log Δλmax versus ε, 1/ε and f(ε). The link was quite strong in each and every case.

The compound's UV absorption spectra were also captured in a variety of polar and nonpolar aprotic solvents, including benzene, ethyl acetate, hexane, acetone, DMF and DMSO. Table 4 lists the maximum values.

Red shifts are seen when the solvent's polarity changes from polar protic to polar aprotic, but hypsochromic shifts are seen when the solvent's polarity changes from polar to non-polar. 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 2,4-dichlorobenzaldehyde-derived symmetrical azine was recorded in a variety of solvents, including benzene, ethyl acetate, hexane, acetone, DMF and DMSO, as well as in various concentrations of alcohol water. As the solvent polarity rises, the absorption band experiences a hypsochromic shift (or blue shift), indicating that the ground state is more dipolar.

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