Aspects of acyclic azine chemistry—I. The effect of structure and solvents on the electronic absorption spectra of benzaldazine, o-, m- and phydroxybenzaldazines

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Abstract—The electronic absorption spectra of benzaldazine, *o*-, *m*-, and *p*-hydroxybenzaldazines have been separately examined in various solvents (20 solvents and solvent mixtures) The observed three groups of bands designated as α (200–225 nm), β (289–307 nm) and γ (352–375 nm) are attributed to $\pi^* \leftarrow \pi$ transitions although experimental evidence based on spectra obtained in concentrated sulphuric acid reveals that $\pi^* \leftarrow \sigma(n)$ transitions constitute part of the γ -band On the basis of group theoretic analysis, in the singlet manifold, all $\pi^* \leftarrow \sigma(n)$ transitions (i.e. ${}^{1}A_u \leftarrow 1{}^{1}A_g$) are out-of-plane (z) polarized while all $\pi^* \leftarrow \pi$ transitions (i.e. ${}^{1}B_u \leftarrow 1{}^{1}A_g$) are in-plane (x, y) polarized In the rationalization of data, the theory of resonance has been employed where deemed useful The shifts of bands with solvents have been traced

INTRODUCTION

The electronic absorption spectra of benzaldehyde, o-, m- and p-hydroxy substituted benzaldehydes have been studied by DOUB and VANDENBELT [1], while SANTAVY and co-workers [2] have carried out extensive studies on the influence of various solvents on the uv spectra of these aldehydes ALEXANDER and co-workers [3] have studied the effects of solvent on the u v absorption spectra of o-, m-, and p-hydroxybenzylideneimines, all of which are Schiff bases derived from the corresponding hydroxybenzaldehydes and monoamines Only recently, detailed u v spectroscopic studies including quantum chemical calculations of salicylaldehydes and N-ethylsalicylaldimines have been reported by SELISKAR [4] But no electronic absorption spectroscopic studies of the Schiff bases derived from the above hydroxybenzaldehydes and diamines (e g hydrazine) have been reported

In this communication, the results of measurements of the electronic absorption spectra of unsubstituted and o-, m-, p-hydroxybenzaldazines



 $\mathbf{R} = \mathbf{H} \text{ or } \mathbf{O}\mathbf{H}$

with the general structure, in various solvents are reported and the effects of structure and solvent discussed

EXPERIMENTAL

Preparation of the azines The aldehyde $(0 \ 1 \ mol)$ was dissolved in 95% ethanol $(60 \ ml)$ Hydrazine hydrate $(0 \ 05 \ mol)$ was also dissolved in 95% ethanol $(25 \ ml)$ and added slowly with constant stirring to the aldehyde solu-

tion The reaction was usually exothermic and was driven to completion by refluxing the reaction mixture for about 1 h Cooling to room temperature led to the deposition of crystals which were filtered off under suction and recrystallized from ethanol/water (1 1) and then air dried The following results were obtained for the products Benzaldazine

colour of Crystals yellow,

mp 91–93°C.

microanalysis Calculated for $\dot{C}_{14}H_{10}N_2,\,C,\,81$ 54, H, 4 89, N, 13 58% , found C, 81 38, H, 4 70, N, 13 62%

Salicylaldazine colour of crystals bright yellow,

m p 223°C, microanalysis Calculated for $C_{14}H_{12}O_2N_2$, C, 70 00,

H, 5 04, N, 11 66%, found C, 70 08, H, 4 99, N, 11 53%

m-hydroxybenzaldazine

colour of crystals dark brown,

m p 207–209°C,

microanalysis Calculated for C₁₄H₁₂O₂N₂, C, 70 00,

H, 5 04, N, 11 66%, found C, 69 95, H, 5 00, N, 11 42%

p-hydroxybenzaldazine

colour of crystals yellowish brown,

mp 270°C,

microanalysis Calculated for $C_{14}H_{12}O_2N_2$, C, 70 00,

H, 50 4, N, 11 66%, found C, 70 10, N, 4 85, N, 11 80%

Spectra The solvents for spectral measurements were supplied by Merck as special grades for spectroscopy and were used without further purification

Electronic absorption spectral measurements were made with Pye-Unicam SP 8000 and SP 500, and proton magnetic resonance measurements were carried out on a Varian Associates T-60 spectrometer with tetramethylsilane (TMS) as internal standard

RESULTS AND DISCUSSION

An examination of the electronic absorption spectral data for the acyclic azines under study in the various solvents (Table 1) reveals that three band systems appearing at 200–225 nm, 289– 307 nm and 352–375 nm can be identified Which band or combination of bands that appear for a particular azine in a specific solvent depends on

 Table 1 Electronic absorption spectral data for benzaldazine, salicylaldazine, M-hydroxybenzaldazine, and p-hydroxybenzaldazine in varous solvents

Solvent	Benzaldazıne		Salıcylaldazıne		m-hydroxyben- zaldazme		p-hydroxyben- zaldazine	
	λmax(nm)	€	λmax(nm)	£	λmax(nm)	e	λmax(nm)	ε
Methanol	207 300 310 sh	24,025 44,206 39,882	215 295	26,428 26,428	215 297(br)	31,233 31,233	227 332	20,902 51,894
	_		360	32,584				
Ethanol	_		220	28,350	213 245 sh	24,986 11,052	235	7,208
	300 310 sh	44,687 39,401	295 	29,311	300 325 sh	41,323 31,713	332	54,056 —
1-propanol	301 310 sh	31,233 27,869	240 297 364	14,896 25,947 23,345	213 br 300 325 sh	27,869 31,713 24,986	240 335	5,766 37,479
1-butanol	301 310 sh	40,362 36,038	225 297 363	22,584 27,389 24,506	215 300 325 sh	32,674 36,038 28,350	230 335 	14,415 42,524
Dioxane	259 267 sh	17,298	220(br)	25,947	217	36,518	225	20,181
	301 5 313 sh	42,284 36,999	289	27,389	300	36,518	325	44,687
	321 sh	18,259	360	22,584	325 sh	30,272		
Ethanol/ water (1 1)	222 300	11,532 41 804	225 297 352	14,415 15,376 13,454	214 302	28,830 31,713	227 332	15,138 38,200
Ethanol/ water (3 1)	223 300	13,935 47,089 —	220 295 356	18,259 22,103 19,701	215 300	25,947 29,311	229 332	15,138 46,849 —
Dioxane/ water (1 1)	220 303	12,013 40,362 —	(249) (255) (260 5)	15,376 19,220 18,740	216 302	25,467 28,830 	227 332	13,694 34,596
DMSO	305 315 sh	34,116 30,272	297	24,506	220 305 325 sh	37,960 23,545 21,142	333	41,804
Acetone	328 5	13 454		27,809	223 330	33,635 24,506	330	45 407
Ethyl acetate	300 311 sh	36,999 32,674	295 360	29,791 25,467	210 299 325 sh	37,479 33,155 26 428	325	49 732
Acetic acid	207 210 sh 300	24,025 39,882 44,206 —	 295 358	 19,220 15,376	219 239 5 297	32,474 28,830 35,557	325(br)	 25 947
Acetonitrile	298 310 sh	22 103 10 220	222 5 294	25,947 30,752	215 298	36,038 32,674	229	20,181
	325 sh	8,649 —	355	 25,467	325 sh	25,947	325	43,245
Chloroform	303	32,674	295	29,311				_
	313 sh	28,830	362	25,947		—		_

Table 1 (contd)

Solvent	Benzaldazıne		Salıcylaldazıne		m-hydroxyben- zaldazıne		p-hydroxyben- zaldazıne	
	λ max(nm)	E	λ max(nm)	e	λ max(nm)	E	λ max(nm)	E
Carbon								
tetrachloride	302 5	41,804	296	35,557	_	_		
	314 sh	36,999		—				
	_		363	32,194			_	
Carbon disulphide								
<i>I</i>		—	385	22,103	—			
Cyclohexane	217	14,415	225 br	30,272	—		_	
- ,	300	36,518	294	29,311	_		_	
	312 sh	32,194	300 sh	26,908		-		
	325 sh	14,896		—	_		_	—
	_	-	364	26,428		—	_	—
Benzene								
	304	32,674	296	22,103		—	_	
	315 sh	28,830		_		—	—	—
	_	_	360	20,662				
Concentrated	215	10,571	224	38,921	206	62,465	224	14,415
sulphuric	_	<u> </u>			255 br	61,054	—	
acid	297	38,440	284	22,584	297	37,479	—	
	375	16,337	363	5,766			418	52,855
Pyridine	_	_			222	41,804	—	_
,	307	29,791	306	20,700	305 br	29,752	335	43,245
	316 sh	26,908	_		_			—
	337 sh	13,935	360	24,025		—		

Sh, shoulder, br, broad

both the position of the hydroxyl substituent in the benzene ring and on the solvent, factors which also determine the precise band position Henceforth the three groups of bands will be designated as follows

> 200–225 nm α-band, 289–307 nm β-band, 352–375 nm γ -band

Tentative assignments of these bands based on group theoretic analysis will be made Group theoretic analyses reveal that the electronic states of the acyclic azines (transazines) may be described within the C_{2h} point group (Fig 1) In these studies, the benzaldazine skeleton is considered as the basic structural skeleton while the OH substituents are regarded as perturbations

The orbital symmetry of the bonding molecular orbitals is A_u while that of the non-bonding molecular orbitals is B_g The ground state is of orbital symmetry A_g , all monoexcited $\pi\pi^*$ states are of orbital symmetry B_u , while all $\sigma(n)\pi^*$ states are of specie A_u Beginning with ground electronic singlet state $(=1^1A_g)$ excited states are designated as follows $1^{13}B_u$, $2^{13}B_u$, $, 1^{13}A_u$, $2^{13}A_u$, In the singlet manifold all $\pi^* \leftarrow \sigma(n)$ transitions (i e ${}^1A_u \leftarrow 1{}^1A_g$) are out-of-plane (z) polarized while all $\pi^* \leftarrow \pi$ transitions (i e ${}^1B_u \leftarrow 1{}^1A_g$) are inplane (x, y) polarized



Fig 1

The observed three groups of bands- α , β and γ -bands are attributed to $\pi^* \leftarrow \pi$ transitions although $\pi^* \leftarrow \sigma(n)$ transitions are allowed Experimental evidence based on spectra in concentrated sulphuric acid reveals that the $\pi^* \leftarrow \sigma(n)$ transitions constitute part of the γ -band (352–375 nm)

In terms of valence bond theory and illustrating with benzaldazine, this molecule may be considered as a resonance hybrid of the following forms



Fig 2

The ground state may have some contributions from the polar resonance forms such as (b), (c) and (d), whereas the excited states may have extensive contribution of these polar forms For the systems under consideration the influence of solvent will be appreciable since the polar structures with separated charges are stabilized by polar solvents. In other words, the contribution of the polar forms would be expected to increase with increasing solvent polarity

Electronic spectra of benzaldazine and salicylaldazine in cyclohexane

It is an established fact that the solution spectrum of a compound in a non-polar and nonhydrogen bonding solvent like cyclohexane, just like the vapour spectrum, does not have its vibrational structure obscured as would be the case in a hydroxylic solvent The electronic spectra of these acyclic azines in cyclohexane may therefore unveil some interesting features which may be obscured in some other solvents The cyclohexane solution of benzaldazine exhibits two intense absorption peaks at $\lambda > 190$ nm as shown in Table 1 The α -band appears at 217 nm ($\epsilon = 14,415$) while the β -band has its maximum absorption at 300 nm ($\epsilon = 36,518$) with shoulders at 312 ($\epsilon = 32,194$) and 325 nm ($\epsilon = 14,896$) The γ -band is absent With salicylaldazine in cyclohexane, three intense bands are obtained The α -band appears at 225 ($\epsilon = 30,272$), the β -band at 294 nm ($\epsilon = 29311$) while the γ band emerges at 364 nm ($\epsilon = 26,428$) The appearance of the γ -band in the case of salicylaldazine may be attributed to the presence of hydroxyl groups in positions ortho to the aldimino (-CH=N-) groups leading to chelation through O-H N hydrogen-bonding, a situation which increases the delocalisation of the π -electrons Unfortunately the spectra of m- and p-hydroxybenzaldazines could not be obtained in this solvent due to solubility problems

The spectral data for the four benzaldazines in methanol are shown in Table 1 The four benzaldazines possess the α -band in methanol benzaldazine (207 nm, $\epsilon = 24,025$), salicylaldazine (215 nm. $\epsilon = 26,428),$ m-hydroxybenzaldazine (215 nm, $\epsilon = 31,233$), and *p*-hydroxybenzaldazine (227 nm, $\epsilon = 20,902$) This short wavelength intense band may contain intensity from more than one $\pi^* \leftarrow \pi$ transition This band appears to be due to the basic nucleus of the system-the benzaldazine structural skeleton since it appears in the spectra of the four azines The observed red shift as we move from benzaldazine through o-hydroxybenzaldazine (salicylaldazine) to p-hydroxybenzaldazine is certainly due to the resonance effect of the hydroxyl substituent which is greater in the ortho and para positions as would be expected The β -band (medium wavelength band ~ 300 nm) appears in the spectra of benzaldazine, 0hydroxybenzaldazine and m-hydroxybenzaldazine (Table 1) but has suffered extensive shift to 332 nm $(\epsilon = 51,894)$ in p-hydroxybenzaldazine, having apparently merged with the γ -band of this compound, a hypothesis supported by the broadness and high intensity of this band centered at 332 nm. This is probably due to extended conjugation in the phydroxybenzaldazine leading to increased delocalization of the π -electrons and consequent lowering of the difference in energy levels. This band is due to $\pi^* \leftarrow \pi$ transition and may be assigned as $2^{1}B_{u} \leftarrow 1^{1}A_{g}$ The γ -band is exhibited very clearly by salicylaldazine (Fig 3) It is blue shifted in benzaldazine and *m*-hydroxybenzaldazine appearing as shoulders in both cases at 320 nm. In the case of p-hydroxybenzaldazine, as mentioned earher it has apparently merged with the β -band The γ -band has a high molar extinction coefficient ($\epsilon =$ 26,428 in salicylaldazine) which indicates that the intensity must be attributed to an electric-dipole allowed $\pi^* \leftarrow \pi$ transition in the singlet manifold Group theoretic analysis suggests that part of the intensity be assigned to the $1^{1}B_{u} \leftarrow 1^{1}A_{g}$ transition The intensity of this band is reduced in the case of salicylaldazine from $\epsilon = 32,584$ to $\epsilon = 5,766$ in concentrated sulphuric acid, a fact suggesting that another transition, i.e. $\pi^* \leftarrow \sigma(n)$ constitutes part of this band

It is relevant to mention that an important factor that would influence the electronic absorption spec-



Fig 3 The electronic absorption spectra of benzaldazine (I), salicylaldazine (II), m-hydroxybenzaldazine (III), and p-hydroxybenzaldazine (IV), in methanol (Molarity 2.08×10^{-5} gmol)

tral behaviour of the azines include the possibility of intramolecular hydrogen-bonding In the case of o-hydroxybenzaldazine (salicylaldazine), intramolecular hydrogen-bonding leading to chelation would make this molecule planar There would be increased delocalization of electrons leading to an overall lowering of the energy differences between the eigenstates Bathochromic shifts in the positions of the electronic absorption bands would be expected and this might lead to emergence of new bands (rather than shoulders) relative to the unsubstituted and m- and p-hydroxybenzaldazines in the same solvent

Solvent effects

The absence of influence of tautomerism The role of solvent on the emergence and disappearance of certain bands have not been discussed in terms of tautomeric species present in solution as is sometimes done [5, 6] since a combination of electronic absorption and proton magnetic resonance spectral data reveals that such a conclusion could be in error For example, salicylaldazine possesses identical PMR spectra in both carbon tetrachloride and carbon disulphide (Table 2), a fact which demonstrates clearly that the molecule exists in the same form in both solvents but exhibits different electronic absorption spectral patterns in the two solvents having two absorption bands in CCl₄ and only one absorption band in CS_2 (Table 1) The above evidence reveals that although absorption band positions may be altered by the emergence of new tautomeric species in solution that also band positions may be influenced by other factors affecting

Table 2 PMR spectral data for salicylaldazine with proton assignments (chemical shifts, δ, in ppm)

Solvent	Phenyl multiplet	Hydroxyl proton	Aldımıno Proton H-C = N-
CCl₄	6 65-7 40	10 95	8 67
CS ₂	6 75–7 50	11 20	8 83

the relative stabilization of the ground and excited states such as the dielectric constant of the solvent and specific solvent effects such as hydrogenbonding

Solvent effects on benzaldazine The short wavelength band, α -band (200–220 nm) is heavily solvent dependent This band is present only in spectra taken in such hydrogen-bonding solvents with fairly high dielectric constants as methanol ($\epsilon_{25^{\circ}C} = 32\ 70$), ethanol/water (1 1), ethanol/water (3 1), dioxane/water (1 1), and concentrated sulphuric acid (Table 1) It is absent in all other solvents except acetic acid and cyclohexane

It is interesting to note that this α -band is absent in spectra taken in such polar but non-hydrogenbonding solvents as DMSO ($\epsilon_{25^{\circ}C} = 46.68$), acetonitrile ($\epsilon_{20^{\circ}C} = 37.5$), and acetone ($\epsilon_{25^{\circ}C} =$ 20.70) It is also absent in such hydrogen-bonding solvents as ethanol ($\epsilon_{25^{\circ}C} = 24.55$), 1-propanol ($\epsilon_{25^{\circ}C} = 20.33$), and 1-butanol ($\epsilon_{25^{\circ}C} = 17.51$) The emergence of this band only in hydrogen-bonding solvents with fairly high dielectric constant (except in the case of acetic acid and cyclohexane) may be due to the following factors which influence the excitation energy

(1) hydrogen-bonding will lower the energy of the ground state (the azine molecule contains two nitrogen atoms which are centres for hydrogen-bonding) However hydrogen-bonding will be less important in the excited state because of the positive charge on nitrogen [Fig 2(d)] Hence, hydrogen-bonding will lower the energy of the ground state more than that of the excited state, with a consequent increase in a excitation energy and a blue shift

(1) High dielectric constant will favour production of such polar structures as are illustrated in Fig 2(b-d) The dipolar excited state will be stabilized by an increase in the dielectric constant more than the non-polar ground state [7] Therefore, a solvent possessing the two properties of being hydrogen-bonding and having a high dielectric constant will combine the two effects This will consequently lead to a higher transition energy than would have been otherwise in a solvent not combining these two properties, and the emergence of a short wavelength band would be expected

The medium wavelength band-the β -band $(\sim 300 \text{ nm})$ appears not to be as much solvent dependent as the α -band (Table 1) but there is a red shift as we move from hydrogen-bonding solvents such as the alcohols (~ 300 nm) to the nonhydrogen-bonding dipolar solvents. DMSO (305 nm) and acetone (328 5 nm) In these latter non-hydrogen-bonding solvents the dielectric constant factor appears to have played a major role resulting in a reduction in excitation energy and a consequent red shift

The γ -band is absent in all the other solvents except in concentrated sulphuric acid in which it appears at 375 nm

Solvent effects on salicylaldazine The spectra of this compound in polar hydrogen-bonding solvents, dioxane, acetonitrile and cyclohexane show three discrete bands, the α -band (215–225 nm), the β band (289–297 nm), and the γ -band (352–364 nm) The α -band is absent in the aprotic solvents-DMSO, acetone, ethyl acetate, carbon tetrachloride, carbon disulphide, benzene and pyridine, although it is also absent in chloroform and acetic acid, two solvents which possess relatively easily ionisable protons This trend is similar to what was observed in the case of benzaldazine where the α -band appeared only in hydrogen-bonding solvents with fairly high dielectric constant. In acetone and carbon disulphide only the γ -band was observed at 360 and 385 nm respectively Table 1 shows the details of the spectral data

Solvent effects on m-hydroxybenzaldazine The spectra of this compound show only two discrete bands in all the solvents (Table 1),-the α (213-223 nm) and β (297-305 nm)-bands The γ -band $(\sim 360 \text{ nm})$ is absent. This result is similar to what was obtained in the case of unsubstituted benzaldazine This is hardly surprising since the hydroxyl substituent being in the meta position displays no appreciable resonance effect on the benzene ring

The α -band suffers a red shift as we move from polar protic solvents (e g methanol) to polar aprotic solvents with fairly high dielectric constant (e g DMSO) This is probably because the dipolar excited state will be stabilized by an increase in dielectric constant more than the non-dipolar ground state Thus as the dielectric constant of the solvent increases, the excitation energy gets reduced leading to a red shift On the other hand, in a hydrogen-bonding solvent, the energy of the ground state will be lowered more than that of the excited state (hydrogen-bonding is less important in the excited state partly because of the positive charge on nitrogen) with a consequent increase in excitation energy and a blue shift Consequently, as we move from polar protic to polar aprotic solvents a red shift will be observed The dielectric constant factor and the hydrogen-bonding factor are complementary in this case and lead to a red shift as observed

Unfortunately because of solubility problems, the spectra of this compound could not be obtained in chloroform, carbon tetrachloride, carbon disulphide, cyclohexane and benzene

Solvent effects on p-hydroxybenzaldazine This compound exhibits two types of spectra The spectra of this compound show only two discrete bands, the α -band (225-240 nm) and β -band (325-335 nm) in the alcohols, dioxane, alcohol/water, and dioxane/water, whereas in the polar aprotic solvents-DMSO, acetone, ethyl acetate, pyridine, and the ionizable acetic acid only the β -band (325-333 nm) is obtained. The α and β -bands of this compound are red shifted relative to those of mhydroxybenzaldehydeazine as would be expected from the para position of the hydroxyl substituent

The spectra of this compound could not be obtained in chloroform, carbon tetrachloride, carbon disulphide, cyclohexane, and benzene because of solubility problems

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REFERENCES

- [1] L DOUB and J M VANDENBELT, J Am Chem Soc
- **71,** 2414 (1949), **77,** 4535 (1955) [2] F SANTARY, D WALTEROVA, and L HRUBAN, Collection Czechoslov Chem Commun 37, 1825 (1972)
- [3] P W ALEXANDER and R J SLECT, Aust J Chem, 23, 1183 (1970)
- [4] C J SELISKAR, J Mol Spectrosc 53, 140 (1974), J Phys Chem 81, 1331 (1977)
- [5] D HEINERT and A E MARTELL, J Am Chem Soc 84. 3257 (1962)
- [6] S MATSUMATO and J MATSUSHIMA, J Am Chem Soc 96, 5228 (1974)
- [7] N S BAYLISS and E G MCRAE, J Phys Chem 58, 1002 (1954)