

## SPECTRAL STUDIES ON BENZENEAZO AND PHENYLHYDRAZO BENZOYLACETONE ISONICOTINOYLHYDRAZONES

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### ABSTRACT

*Coupling of benzenediazonium chloride with benzoylacetone at two different pH values in 1:1 molar ratio gave two different tautomers ; orange (PHB) and violet (BAB) . Their condensation with Isonicotinic acid hydrazide (INH) gave with the former the yellow hydrazone (PHBH) from ethanol , and with the latter the deep red crystals (BABH) as a result of fusion. Analytical, conductivity, pH, IR, electronic and NMR spectra and optical activity measurements showed that PHB and PHBH are the ketoimine tautomers while BAB and BABH the enolazo tautomers. Isonicotinoyl hydrazone moiety in PHBH and in BABH is present in the imidol and imide forms respectively.*

### INTRODUCTION

Hydrazones derived from isonicotinic acid hydrazide (INH) are well known for their specific antitubercular, antibacterial and antitumor activities (1,2) . Also some complexes derived from these hydrazones have remarkable antibacterial activity (3) . Hydrazones of INH have been used as analytical reagents (4) , and those of  $\beta$ - diketones have been synthesised and characterised (5).

The purpose of the present investigation was undertaken to identify the product of coupling of benzenediazonium chloride with benzoylacetone at

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different pH-values using either sodium acetate or sodium hydroxide. Azo and hydrazo compounds obtained were identified in the solid state and in solution using different techniques. This study was extended to include the preparation and investigation of their INH hydrazones.

## EXPERIMENTAL

### a) Preparation of the dyestuffs(I) and (II) :

The dyestuffs were prepared according to the general method by coupling benzenediazonium chloride with benzoylacetone in (1:1) molar ratio, below 5°C in the presence of sodium acetate (in the first case) or 20% sodium hydroxide (in the second case). The resulting solutions were acidified with (1:1) HCl until pH 3, orange (I) and violet (II) compounds were separated out from sodium acetate and NaOH media respectively. These were recrystallized from ethanol in case of (I) and from toluene in case of (II) till constant melting point.

### b) Preparation of Isonicotinoylhydrazones of (I) and (II) :

Attempts were made to prepare these hydrazones from the parent dyestuffs and INH by the method described by Ojha (5) but, no products could be obtained. Trials were made by mixing equimolecular amounts of the dyestuffs and INH in ethanol with stirring in case of (I), pale yellow product (III) was separated out. In case of (II) very low yield was obtained. This hydrazone was prepared using solid state reaction technique (6), by mixing equimolecular amounts of (II) and INH and the mixture was heated for an hour at 160°C in a

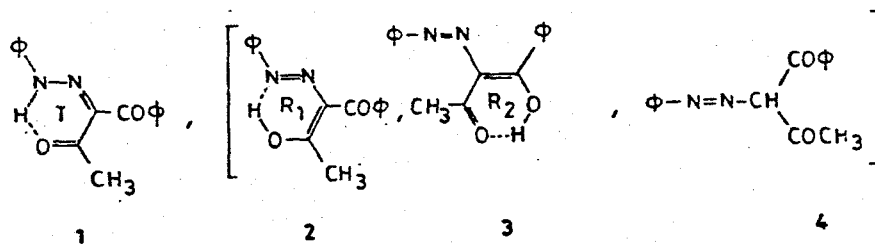
drying oven whereupon, deep red compound (IV) was obtained. Both hydrazones (III) and (IV) were purified by washing with petroleum ether to get ride of unreacted dyestuffs then crystallized from benzene to get ride of unreacted INH. The purity was confirmed by elemental analysis,  $^1\text{H}$  NMR spectra and TLC. All the investigated compounds (I – IV) are soluble in MeOH, EtOH,  $\text{Me}_2\text{CO}$ ,  $\text{C}_6\text{H}_6$ ,  $\text{CHCl}_3$ ,  $\text{CCl}_4$ , cyclo and n-hexanes. Dyestuffs are also soluble in petroleum ether but the hydrazones are insoluble in it.

A Chemtrix 62 digital pH-meter and Bibby conductimeter MC 1 were used for pH and conductance measurements. Spectral studies were made using Perkin Elmer 598 IR and 550 S UV-VIS spectrophotometers and a Bruker AC 250 FT NMR spectrometer with TMS as an internal standard and DMSO as solvent. Optical activity measurements were performed using Porex Atago polarimeter..

## RESULTS AND DISCUSSION

The elemental analysis and other physical properties of the compounds under investigation are summarized in Table 1.

The classical spatial arrangement of the dyestuffs I and II allows the existence of four possible structures that depicted below:



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Table 1. Physical properties of the dyestuffs and their INH hydrazones.

Properties	I	II	III	IV
Colour	Orange	Violet	Pale yellow	Deep red
Melting point °C	95 <sup>(a)</sup>	140	160	125
$\Lambda_m$ (S.cm <sup>2</sup> .mol <sup>-1</sup> )	2.35 <sup>(b)</sup>	4.15 <sup>(b)</sup>	3.80 <sup>(b)</sup> $\mu$ s 9.30 <sup>(c)</sup> ms 4.95 <sup>(d)</sup> ms	13.30 <sup>(b)</sup> $\mu$ s 12.13 <sup>(c)</sup> ms 5.16 <sup>(d)</sup> ms
Anal-data % <sup>(e)</sup>				
C	72.2 (71.3)	72.2 (71.9)	68.6 (69.4)	68.6 (68.2)
H	5.3 (5.5)	5.3 (5.7)	4.9 (5.3)	4.9 (5.0)
N	10.5 (10.2)	10.5 (10.4)	18.2 (18.1)	18.2 (18.1)

(a) : A value given in ref.(5) is 98-99°C

(b) : Conductance of 10<sup>-3</sup> M solution (50% EtOH/H<sub>2</sub>O)

(c) : Conductance of 10<sup>-3</sup> M solution in 0.2 M HCl.

(d) : Conductance of 10<sup>-3</sup> M solution in 0.2 M NaOH.

(e) : Values in paranthesis denote % found.

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The authenticity of the isolated compounds was established by means of their analytical and physical properties.

### I. Optical activity measurements :

The results showed that the prepared dyestuffs are optically inactive, so structure 4 is excluded.

### II. Calculation of bond dissociation energy (Ed) :

The bond dissociation energies was calculated <sup>(7)</sup> for the dyes prepared. It was found that  $E_d$  for structures 4 is 1882.5 but for other structures is 1928.9 k.cal/gram bond, confirming that structure 4 is less stable and excluded.

### III. Solution conductance:

Molar conductance values Table 1 ( $\Lambda_m$ ) in 50% EtOH/H<sub>2</sub>O lie in the (2.35 – 13.30  $\mu\text{s.cm}^2.\text{mol}^{-1}$ ) range indicating their nonelectrolytic nature. The relative higher  $\Lambda_m$  values may be assigned to the enolazo compounds while the lower  $\Lambda_m$  values to those of the hydrazo compounds. Also in acidic and basic solutions the hydrazone (IV) has higher conductivity value than that of (III). This may be due to the higher polarity of ring R than ring T.

### IV. Infrared and <sup>1</sup>H NMR spectra :

#### a) Compounds I and III:

The IR spectra of these compounds (Fig.1) exhibit strong bands, at 1630  $\text{cm}^{-1}$  ( $\nu_{\text{C=O}}$ ) of the acetyl group and 1600  $\text{cm}^{-1}$  azomethine ( $\nu_{\text{C=N}}$ ), medium

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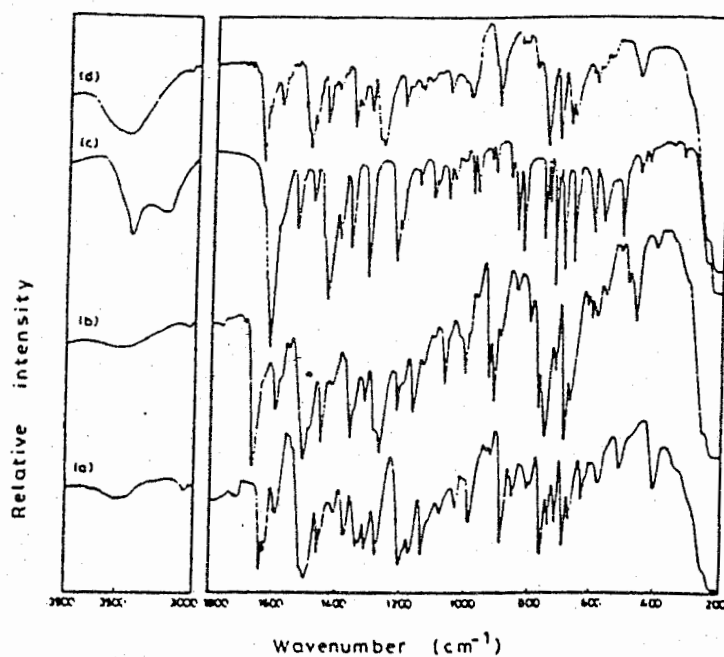


Fig. 1. IR spectra of (a) PHB, (b) BAB, (c) PHBH and (d) BABH.

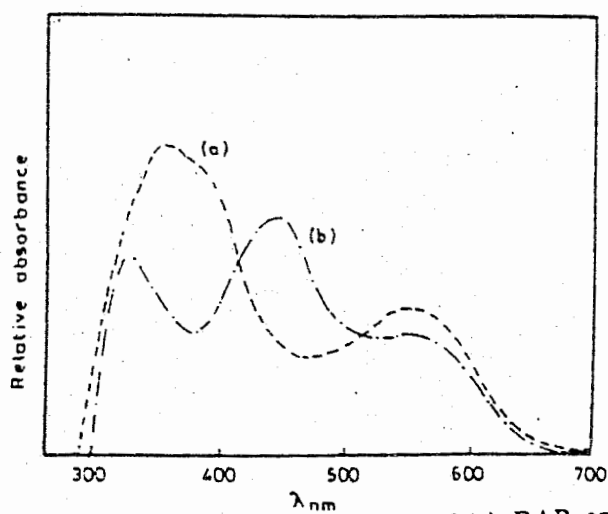
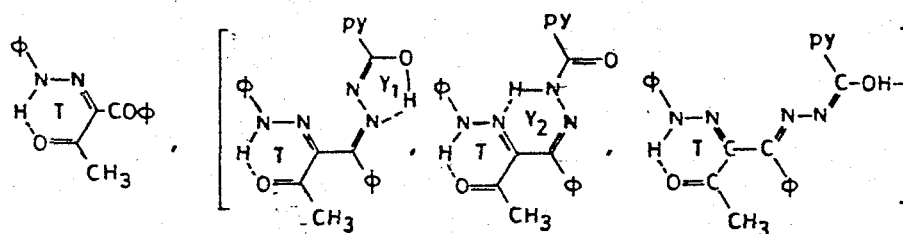


Fig. 3. Electronic spectral curves of (a) BAB and (b) its hydrazone (BABH) dyes in conc. HCl.

bands at  $810-800\text{ cm}^{-1}$  ( $\delta_{\text{NH OOP}}$ ) and  $860-850\text{ cm}^{-1}$  ( $\nu_{\text{N-NH}}$ ) showing that such compounds are the hydrazo tautomer that exists exclusively in an intramolecular (NH...O) keto imine tautomeric form (7) in the six membered chelate ring T. In the spectrum of (I), the presence of a strong band at  $1650\text{ cm}^{-1}$  is assigned to  $\nu_{\text{C=O}}$  of the side chain free benzoyl group rather than acetyl group (8). In the spectrum of (III) the disappearance of this band, and the appearance of sharp distinguished bands (Fig.1) at  $3400$  ( $\nu_{\text{OH free}}$ ),  $3160$  ( $\nu_{\text{OH...N}}$ ),  $1630$  ( $\nu_{\text{C=N}}$ ),  $1540$  ( $\nu_{\text{NCO}}$ ) and  $915\text{ cm}^{-1}$  ( $\nu_{\text{N-N}}$ ) is a good evidence that the INH moiety in (III) is present in the imidol form.

The  $^1\text{H NMR}$  spectra of such hydrazo compounds in DMSO and  $\text{D}_2\text{O}$  (Table 2) provide further evidence for the proposed structures. The spectra show broad singlets at  $12.45\text{ ppm}$  and disappeared in  $\text{D}_2\text{O}$ , assigned to (NH...O)(9). On the other hand, the spectrum of (III) shows three peaks at  $12.20$ ,  $11.07$  and  $6.05\text{ ppm}$  that may be assigned to inter and intramolecularly bonded (OH...N), and (NH...N) and the latter due to free OH of the INH moiety (10).



(I): PHB

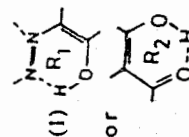
(III): PHBH

phenylhydrazo  
benzoylacetone

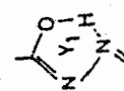
phenylhydrazobenzoylacetone  
isonicotinoylhydrazone

Table 2: I.R. and <sup>1</sup>H NMR spectra of the investigated compounds.

Compound	IR bands (cm <sup>-1</sup> )		INH bands	<sup>1</sup> H NMR bands (in DMSO and disappeared in D <sub>2</sub> O)	
	H-Chelate rings R(1) and T(2)	Side chain C=O or C=N(3)		OH δ, (ppm)	NH δ, (ppm)
IV	Ring-R ν <sub>OH</sub> ... (HB) ..... 3450 ν <sub>N=N</sub> ..... [ 1570 1420 ] β DK <sup>(5)</sup> ..... 1590 δ OH ..... 1070	ν <sub>C=N</sub> 1625	ν <sub>N-N</sub> ..... 915 ν <sub>C=O</sub> ..... 1650	14.1 (1H,s) br. (OH...N) Ring-R <sub>1</sub> 11.3 (1H,s) br. (OH...N) Ring-R <sub>4</sub>	12.8 (1H,s) ..... (NH...N) 3.8 (1H,s) ..... NH free
III	Ring-T ν <sub>NH</sub> (HB) ..... 3180 ν <sub>C=O</sub> ..... 1630 ν <sub>C=N</sub> (azine) ... 1600 ν <sub>N-NH</sub> ..... 850	ν <sub>C=N</sub> 1630	ν <sub>N-N</sub> ..... 915 ν <sub>NCO</sub> (Ring Y) 1540 ν <sub>OH</sub> (free) ..... 3400 ν <sub>OH...N</sub> ..... } ν <sub>NH...O</sub> ..... } 3180	12.20 (1H,s) br. (OH...N) Ring-Y <sub>1</sub> 6.05 (1H,s) br. .... OH free	12.45(1H,s)(NH...O) Ring-T 11.07 (1H,s) br.(NH...N)Ring-Y <sub>2</sub>
II	Ring-R ν <sub>OH</sub> ... (HB) 3450 ν <sub>N=N</sub> ..... [ 1570 1420 ] β DK <sup>(5)</sup> ..... 1590 δ OH ..... 1070	ν <sub>C=O</sub> 1665	---	14.0 (1H,s) br... (OH...O) Ring R <sub>2</sub> 11.3 (1H,s) br. (OH...N) Ring-R <sub>1</sub>	
I	Ring-T ν <sub>C=O</sub> ..... 1630 ν <sub>C=N</sub> (azine) ... 1600 ν <sub>N-NH</sub> ..... 860	ν <sub>C=O</sub> 1650	---		12.45(1H,s)(NH...O) Ring-T



(3) C=N of the hydrazone



(5) β -diketonate

s : singlet  
br : broad



b) Compounds II and IV:

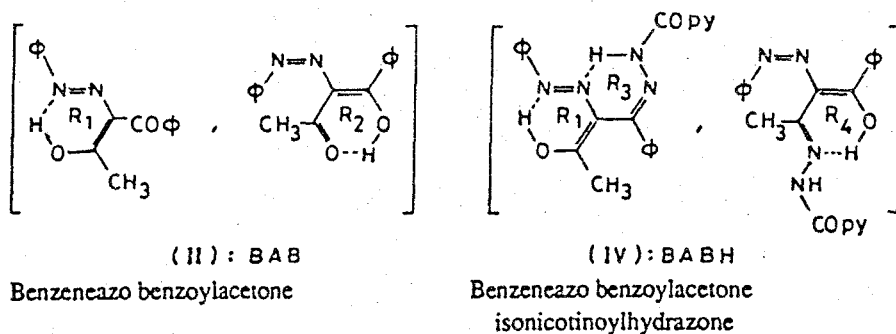
In their IR spectra, the presence of weak bands at  $1570\text{ cm}^{-1}$  and medium bands at  $1420\text{ cm}^{-1}$  which are not present in the spectra of the hydrazo compounds indicates that these two bands are assigned to  $(\nu_{\text{N}=\text{N}})$  of the azo group (11) in the free cis and trans H-bonded forms. The broad bands centered at  $3450\text{ cm}^{-1}$  ( $\nu_{\text{OH}\cdots\text{HB}}$ ), medium bands at  $1070\text{ cm}^{-1}$  ( $\delta_{\text{OH}}$ ) and at  $1590\text{ cm}^{-1}$  (enolize  $\beta$ -diketone moiety) (12) are characteristic bands of the H-chelate ring R. The spectrum of (II) exhibits a strong band at  $1665\text{ cm}^{-1}$  ( $\nu_{\text{C}=\text{O}}$ ) which is absent in the spectrum of (IV), this band is assigned to the conjugated side chain benzoyl group. In the spectrum of (IV), the appearance of new bands at  $1625\text{ cm}^{-1}$  ( $\nu_{\text{C}=\text{N}}$ ),  $1650\text{ cm}^{-1}$  ( $\nu_{\text{C}=\text{O}}$ ) and  $915\text{ cm}^{-1}$  ( $\nu_{\text{N}-\text{N}}$ ) as that present in the spectrum of the hydrazone (III) indicates that the INH moiety is present in the imide form ( $-\text{HN}-\text{CO}-$ ) (13,14).

The  $^1\text{H}$  NMR spectrum of such azo compound (II) reveals two broad singlets at 14.0 and 11.3 ppm that disappeared in  $\text{D}_2\text{O}$  and may be assigned to intramolecular H-bonded ( $\text{OH}\cdots\text{O}$ ) and ( $\text{OH}\cdots\text{N}$ ) of the rings  $\text{R}_2$  and  $\text{R}_4$ . The hydrazone (IV) reveals two singlets at 14.1 and 11.3 ppm assigned to H-bonded ( $\text{OH}\cdots\text{N}$ ) of rings  $\text{R}_1$  and  $\text{R}_4$  and two more bands at 3.8 and 12.8 ppm, due to NH free and ( $\text{NH}\cdots\text{N}$ ) of the imide group in a 6-membered chelate ring  $\text{R}_3$ .

Finally, the IR bands of the pyridyl moiety appear, in both hydrazones at  $1480, 1410, 990$  and  $660\text{ cm}^{-1}$  (10) and their  $^1\text{H}$  NMR spectra reveal multiplet

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signals at 6.9 – 9.0 ppm and singlets at 2.2 – 2.6 ppm, the former is assigned to aromatic and /or pyridyl, and the latter is assigned to acetyl group. These assignments suggest that, compounds (I) and (III) are present in the hydrazo form while (II) and (IV) are in the azoform in which N=N group is present in the free or H-bonded forms.



### V. Electronic spectra:

The absorption spectra of the compounds under investigation in the solid state and in neutral basic and acidic solutions were recorded. Values of  $\lambda_{\max}$  (nm) of the bands are recorded in Tables (3 and 4).

#### a) In the solid state:

The spectra of the compounds in Nujol mull are characterized by three intense bands above 300 nm. Band-A (400– 443 nm) assigned to  $n - \pi^*$  transition of N=N or C=N influenced by the intramolecular charge transfer (CT) transition within the whole molecule and through the 6-membered H-chelate

Table 3: The electronic spectral bands ( $\lambda_{\text{max}}$ , nm) of PHB, BAB and their hydrazones PHBH and BABH in the solid state.

PHB	BAB	PHBH	BABH	Band	Assignment
405	401	410	442	A	Intramolecular CT transition within the whole molecule with $n-\pi^*$ transition of N=N or C=N groups
372 356 <sup>a</sup>	368	371 356 <sup>a</sup>	372	B <sub>1</sub> B <sub>2</sub>	$n-\pi^*$ transition of aromatic C=O or C=N (hydrazone) in conjugation with rings R or T.
—	—	337	—	C	$\pi-\pi^*$ transition of the imidol moiety of (INH)
284 249 <sup>a</sup>	283	284	286	D <sub>1</sub> D <sub>2</sub>	$\pi-\pi^*$ transition of aromatic C=O or C=N in conjugation with rings R or T.
—	259	—	257	E	$\pi-\pi^*$ transition of N=N in conjugation within enolazo ring-R
—	—	—	253	F	$\pi-\pi^*$ transition of C=O (imide) of the INH moiety.
—	242	—	—	G	CT transition of the enolazo form of the $\beta$ -diketonate.

<sup>a</sup> assigned to H-bonded acetyl group of ring T.

Table 4: The electronic spectral bands ( $\lambda_{\text{max}}$ , nm) of the hydrazo and azo compounds in solution

PHB	PHBH		BAB		BABH		Band
	ErOH Yellow	dil-NaOH Orange	ErOH Red	dil-NaOH Orange	ErOH Red	dil-NaOH Orange	
380	422	430	382	380	430	440	A
367	—	—	—	368,361	343	344	B
—	343	325	—	—	—	—	C
278	277	278	269	—	265	330	D
—	—	—	—	—	260	—	F
—	—	—	245	242	245	246	G

(1) In conc. HCl, the bands are 554 and 364 nm. (2) In conc. HCl, the bands are 547, 443 nm.

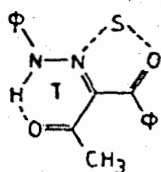
rings R or T (15,16). Band-B<sub>1</sub> (368 – 372 nm) and band-D<sub>1</sub> (282 – 287 nm) assigned to  $n-\pi^*$  and  $\pi-\pi^*$ -transitions of the free C=O in conjugation with and in the side chain of rings R or T (compounds I and II) or of the C=N of the hydrazone produced by its condensation with INH (17).

Hydrazo compounds (I and III) show two more bands B<sub>2</sub> and D<sub>2</sub> at 249, 356 nm, assigned to H-bonded acetyl group of ring T. The spectrum of the hydrazone (III) is characterized by an extra band (C) at 337 nm which is absent in the spectrum of the other hydrazone (IV), this band is assigned to CT transition within the imidol moiety (18).

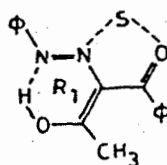
The spectra of the azo compounds show two more bands, band-E at (257– 259 nm) and band-G at 242 nm that may be assigned to  $\pi-\pi^*$ -transitions of the N=N and CT transition of the enol-azo form of  $\beta$ -diketonate moiety (19). On the other hand, the spectrum of (IV) displays more four bands at 272 , 270, 265 and 253 (band-F) nm, , these bands are not present in the spectrum of its parent dye (II), so they may be assigned to the imide group of the INH.

Based on physical, analytical and spectral results we can suggest that the solid dye prepared in sodium acetate (I) and its hydrazone (III) are the ketoimine hydrazo tautomeric forms but the dye prepared in NaOH (II) and its hydrazone (IV) are the enolazo tautomeric forms as given before.

b) In aqueous ethanolic solution:

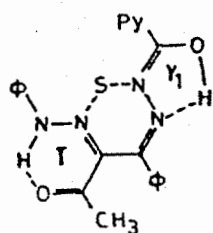


(I) A

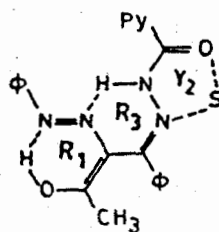


(II) A

The spectra of aqueous ethanolic solutions of PHB and BAB compared with those made in Nujol mull show blue shifts in band-A that may be due to intermolecular H-bond (N...S...O) formed with the solvent (S) in a 5-membered chelate ring (18,19).



(III) A

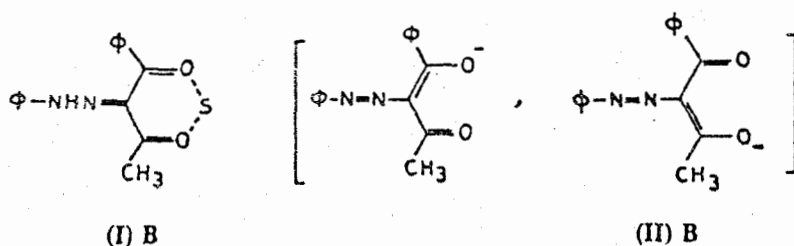


(IV) A

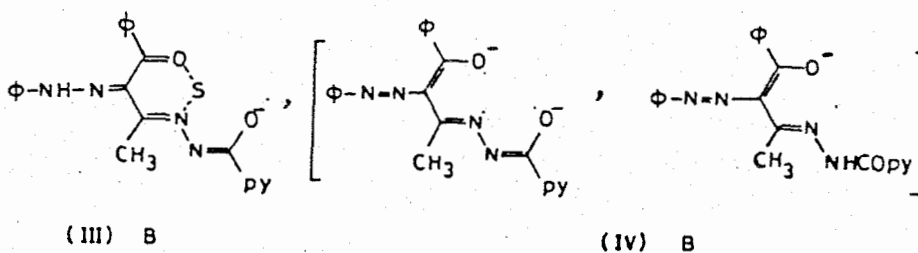
The red shift observed in this band of PHBH, can be assigned to intermolecular H-bonded nitrogen atoms of INH and of ring-T with the solvent (N...S...N) through a 6-membered chelate ring and intramolecular H-bonded (O-H...N) in a 5-membered chelate ring (Y<sub>1</sub>) through the enol form of INH moiety (19). In contrary to PHBH, the hydrazone BABH manifests blue shift in bands -A and -B, that may be explained as due to intermolecular H-bond with the solvent in a 5-membered chelate ring (Y<sub>2</sub>) through the keto form of INH moiety. The presence of band-B at 343 nm and band -F at 260 nm in

the spectrum of BABH (absent in PHBH) is assigned to  $n-\pi^*$  and  $\pi-\pi^*$  transitions of the solvated C=O group of the INH in ring (Y<sub>2</sub>)<sup>(16)</sup>. Based on the previous discussion, the investigated compounds, in aqueous ethanolic solution can be represented as (I)A–(IV)A.

c) Effect of dilute NaOH:



On adding dilute solution of NaOH to ethanolic solutions of the investigated compounds, the colour is turned orange. The spectrum of the resulting solution Fig.(2) of BAB shows bands-A, B and G, also a new band appeared at 361 nm which may be assigned to  $n-\pi^*$ -transition of another C=O group arised from the resonance in  $\beta$ -diketone chelate ring R<sub>2</sub>. On the other hand, the spectral curve of PHB shows bands-B at 366 and 358 nm assigned to  $n-\pi^*$  transition of two H-bonded C=O groups. The spectrum shows also disappearance of band-A indicating the absence of ring -T, so structures (I)B and (II)B may be suggested to PHB and BAB in alkaline medium.



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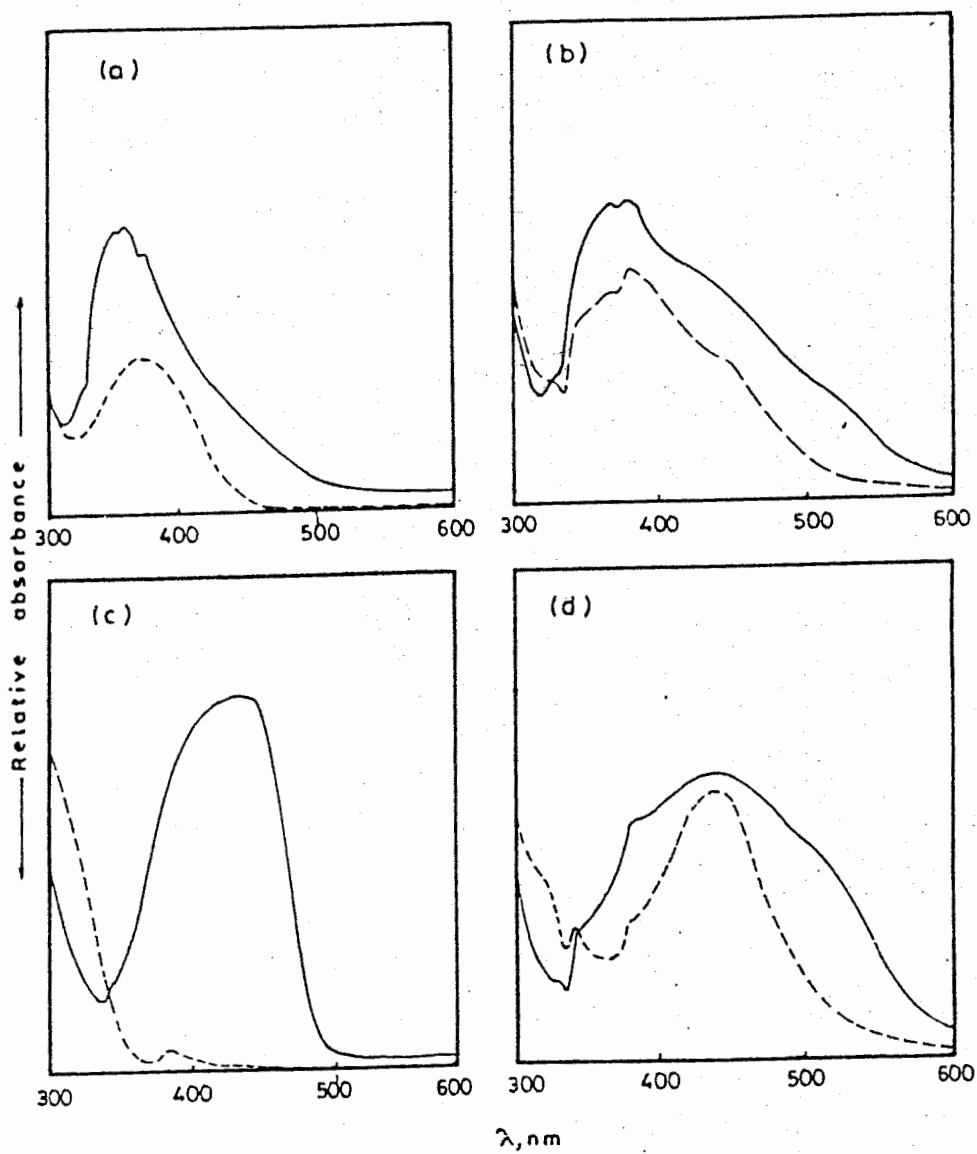


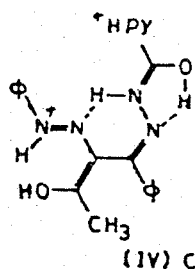
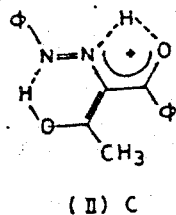
Fig.2. Electronic spectra of acidic (---) and basic (—) ethanolic solutions of (a) PHB, (b) BAB, (c) PHBH and (d) BABH.



In the spectrum of BABH the red shift observed in band -A indicates the presence of free unsolvated azo group. As the pH of BABH solution increases above pH 7, the absorbance of band -F (py-CO-) decreases and band-C at 330 nm (-C(OH) = N) increases, this observation makes us to suggest structures (IV)B for BABH where the INH moiety is present in the enol and keto forms. On the other hand, Band -A of PHBH shows bathochromic shift from 422 to 430 nm which may be due to desolvation, also the appearance of band-C at 325 nm, indicates that the INH moiety is present in the free enol form so, structures (III)B are suggested for PHBH in basic solution.

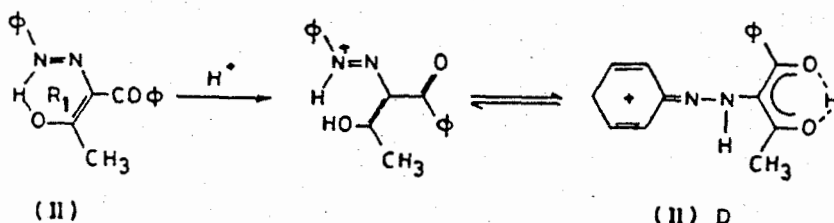
d) Effect of acidity:

The addition of dilute HCl to solutions of the azo compounds changes the colour from red to yellow. Band -A of BAB shows no change in its  $\lambda_{max}$  but of BABH is bathochromically shifted to 442 nm due, as given before, to cleavage of (N-H...N) H-bond. The disappearance of band -F in BABH indicates that protonation occurs through the INH moiety. The disappearance of bands -B and D in BAB may be due to the absence of C=O group, this may be explained by the resonance of the proton between the azo N and the carbonyl O. So, structures (II)C and (IV)C are suggested for BAB and BABH in dil.HCl solutions.

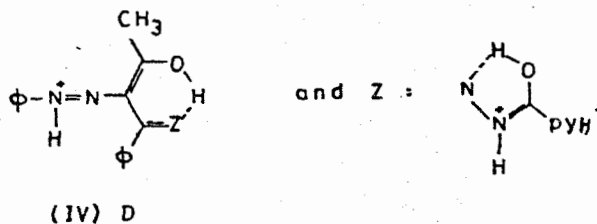


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Furthermore solutions of the azo compounds when treated with conc. HCl (pH < 1) violet colour appears, the spectral curves of BAB and BABH Fig.(3) manifest new bands at Ca. 550 nm assigned to CT transitions of the ionic diazo groups in which protonation occurs through N atom adjacent to aromatic group (20). In the spectrum of BAB, the disappearance of band-A may be due to the absence of N=N group, and the appearance of a new band at 364 nm may be assigned to C=N group oxo to quinonoid benzene ring as illustrated in the following equation:



The spectrum of BABH manifests also band -A at 443 nm and band -C at 328 nm (imidol) suggesting structure (IV)D for BABH in conc. acid.

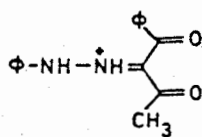


On the other hand, the spectrum of PHB in dil. HCl shows no colour changes, however the absence of band-A and the presence of bands-B and D red-shifted assigning to the terminal free C=O group, indicates cleavage of ring-T and formula (I)C may be suggested for PHB in acidic solution. On the other hand, when dil.HCl solution is added to the solution of PHBH, the yellow

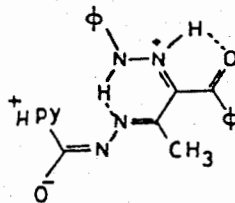
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colour disappeared and colourless solution is obtained. In the spectral curve, band-A at 422 nm disappeared and the presence of two bands at 384 and 325 nm (free imidol moiety) suggest formula (III)C for PHBH in acidic medium.



(I) C



(III) C

### CONCLUSION:

Based on the forementioned results, we can say that, the dyes prepared in sodium acetate medium is the keto-imine and the dyes prepared in sodium hydroxide is the enolazo tautomer. Although in the solid state, the compound may be a single product, in solution a mixture of compounds may be present depending on the solvent and pH of the medium.

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