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THERMAL AND TEMPERATURE DEPENDENCE OF ELECTRICAL CONDUCTIVITY STUDIES ON PHENYLHYDRAZO AND BENZENEAZO BENZOYLACETONES AND THEIR ISONICOTINOYL HYDRAZONES

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ABSTRACT

Coupling of benzenediazonium chloride with benzoylacetone at two different pH values in a 1:1 molar ratio gave two different tautomers PHB and BAB. The condensation of these dyes with isonicotinic acid hydrazide (INH) gave two different hydrazones PHBH and BABH. Thermal studies (DTA and TG) showed that azo compounds are thermally more stable than their corresponding hydrazo compounds and spectral analyses (IR and electronic) gave more information about the structure of PHBH which shows thermochromic behaviour below its melting. DC electrical conductivity for these compounds were measured in the temperature range 25 - 70 °C giving semiconducting behaviour, and the activation energies for conduction were calculated. Valuable results were obtained from the comparison between ΔE of the azo and hydrazo tautomers and of the dye and its hydrazone. A graphical method was suggested to make simple comparison between values of electrical conductivity exponent.

INTRODUCTION

Isonicotinoyl hydrazones derived from carbonyl, dicarbonyl compounds and also 2 - hydroxy aromatic aldehydes and ketones and some complexes of these hydrazones are known for their biological and antitubercular activities [1 - 3]. In analytical chemistry, hydrazones are extensively used in the detection, determination and isolation of compounds containing carbonyl groups.

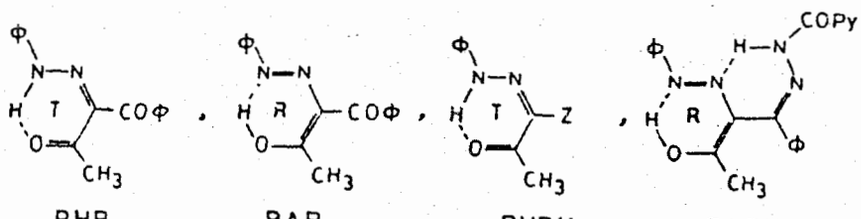
In continuation with our earlier studies on the thermo- conductimetric properties of solid hydrazones of isonicotinic acid hydrazide and their complexes

[4,5], in the present work, the DC electrical conductivity and thermal analyses were carried out to ascertain the thermal stability and to obtain information about the electrical conductivity of benzeneazo benzoylacetone (BAB) and its phenylhydrazo benzoylacetone (PHB) and also their isonicotinoyl hydrazones (BABH) and (PHBH) . Their activation energies for conduction have been calculated and some conclusions were extracted. PHBH exhibits an irreversible thermochromic behaviour.

EXPERIMENTAL

The chelating agents PHB and BAB were prepared according to Vogel [6], the former , in the presence of sodium acetate [7] and the latter, in 20% sodium hydroxide [8]. Phenylhydrazo benzoylacetone isonicotinoylhydrazone (PHBH) was prepared as described by Sacconi [9] while benzene azo benzoylacetone isonicotinoylhydrazone (BABH) was prepared by the solid state reaction technique [10] , by heating a mixture of equimolecular amounts of BAB and INH for an hour at 160°C in an oven. The purity of the products was checked by constant melting point, elemental analysis, ^{1}H NMR and TLC . Their structures were characterised as given in our earlier work [10].

The compounds have the structural formulae



where Z : $-C(\varnothing) = N.NHCOPy$, Z′ : $-C(CH_3) = N.NHCOPy$ and $\varnothing : C_6H_5-$

Colour	orange	violet	pale yellow	deep red
M.P.°C	95	140	160	125

where , the INH moiety in PHBH is present in the imidol form while in BABH in the imide form ; where the OH group is in the free or H-bonded form.

$$= N-NH-CO-Py \rightleftharpoons = N-N = C\begin{matrix}\diagup OH \\ \diagdown Py\end{matrix} \quad \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots (I)$$

where Py : pyridyl group.

Spectral studies were made using Perkin Elmer 598 IR and 550 S UV VIS spectrophotometers. The thermal analyses were carried out using a Schimadzu DT-30 thermal analyzer, by heating at $10^{\circ}C.min^{-1}$ from ambient temperature to $500^{\circ}C$ in air. The DC electrical conductivity in the exponential form ($p\sigma$) was measured as a function of temperature (1000 /T) from 25 to $70^{\circ}C$ using a spring- loaded sample holder in a wire-wound cylindrical furnace. In this study, the current was measured by means of a Keithley electrometer model 616, with a smoothing adjustable power supply (0 – 1 KV). A fixed voltage of 300 V was applied. The temperature of the specimen was measured using a chromel-alumel thermocouple.

RESULTS AND DISCUSSION

a) Thermal study

The DTA and TG data of the investigated compounds summarized in Table 1. These compounds are thermally stable up to $80^{\circ}C$ and can be dried safely below $80^{\circ}C$ and show medium endothermic peaks at their melting. The weak broad exothermic peaks appearing before melting are due to fission of the hydrogen

TABLE 1: Thermal analyses data for PHB, BAB and their hydrazones PHBH and BABH

Compound	Temp.°C	DTA	Assignment
PHB	95	endo (m)	(no weight loss) due to melting
	143 - 265	—	100% weight loss.
BAB	70 - 90	endo (w)	due to fission of H-bond and rearrangement
	140	endo (m)	(no weight loss) due to melting
	150- 265	exo (s)	56 % weight loss
PHBH	80 - 125	endo (br)	may be due to fission and rearrangement
	160	endo (m)	(no weight loss) due to melting
	160 - 292	—	100% weight loss
BABH	125	endo (m)	(no weight loss) due to melting
	170 - 230	exo (s)	56% weight loss

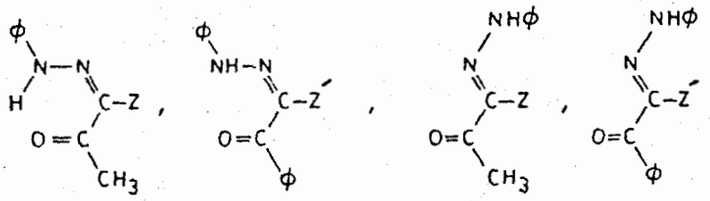
(br) : broad , (vs) : very strong , (s) : strong, (m) : medium and (w) : weak

bond followed by rearrange ment. DTA curves of the azo compounds after melting show broad exothermic peaks with 56% weight loss, and further partial decompositions occur at higher temperatures than 500°C. On the other hand, hydrazo compounds after melting decompose completely in one step with 100% weight loss before 300°C.i.e. azo compounds are thermally more stable than their corresponding hydrazo conformers.

b) Thermochromism of PHBH

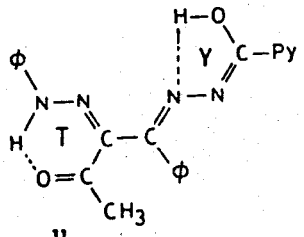
Among the compounds investigated, only PHBH shows thermochromic behaviour when heated for half an hour at 90°C in an oven, its colour changed from yellow (P_0) to pale red ($P_{0.5}$) without weight loss. When the time is increased to 2 hrs. where the substance is still in the oven, the colour changed again to pale yellow (P_2) with no weight loss.

The classical spatial arrangement of PHBH molecule allows the existence of four possible structures due to geometrical isomerism. These may be depicted diagrammatically as shown below (I_a–I_d).

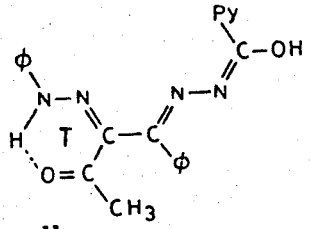


Ia Ib Ic Id

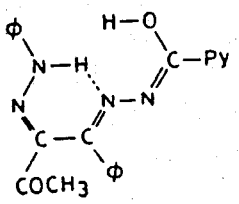
Taking into account chelate structure involving hydrogen bonding, the syn configuration must be depicted as $II_{a,b}$, while the anti must depicted as $II_{c,d}$.



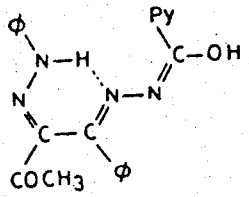
IIa



IIb



IIc



IId

The syn structure is consistent with hydrogen bonding because of the non-planar arrangement of the molecule. In the anti forms, on the other hand, hydrogen bonding does not appear to be spatially possible.

Comparing the IR bands diagnostic of P_0 and $P_{0.5}$ (Table 2), along with tentative assignment, it was found that, the IR spectra of P_0 and $P_{0.5}$ are nearly identical except that new three bands at 1570 ($\upsilon_{N=N}$) [11], 1550 (υ_{NCO}) [12] and 1275 cm^{-1} ($\upsilon_{C\text{-}OH}$) [10] appeared due to heating. On the other hand, the spectrum of P_2 reveals much changes. The disappearance of the imidol (INH) bands at 3400 (υ_{OH}) and 1630 cm^{-1} ($\upsilon_{C=N}$) [12,13] and the appearance of imide bands at 1690 (υ_{CO}), 3145 cm^{-1} (υ_{NH}) free, 1550 and 1245 cm^{-1} [14] this can be explained as thermal imidol → imide tautomerism. Moreover, the appearance of new bands in the spectrum of P_2 at 2963($\upsilon_{=C\text{-}H}$) [12], 1650 ($\upsilon_{C=O}$) and 1570 and 1420 cm^{-1} of the cis and trans azo group ($\upsilon_{N=N}$) and 805 cm^{-1} ($\delta_{=C\text{-}H}$) can be illustrated in terms of thermal enol-keto tautomerism.

TABLE 2: Effect of heating at 90°C for half hr. and two hr. on IR spectral bands of PHBH.

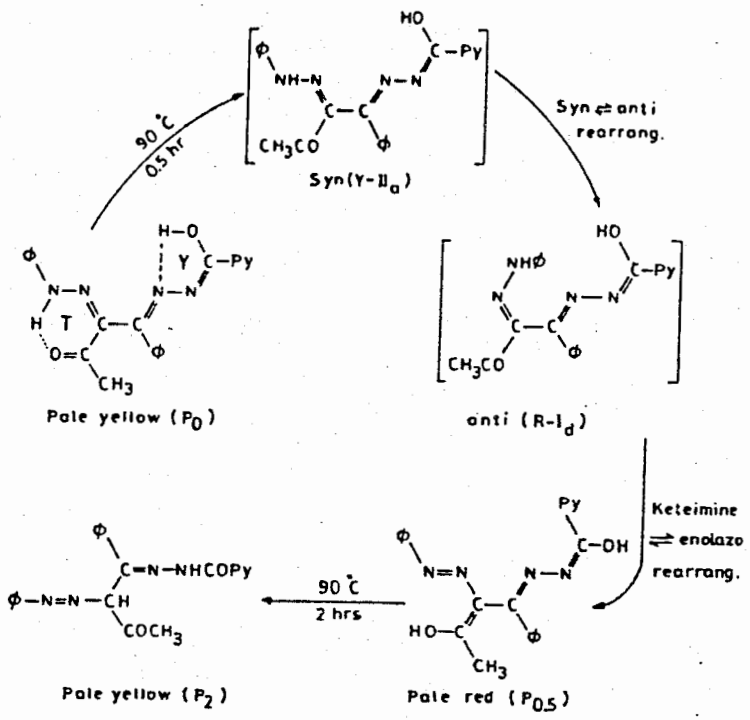
	original (P_0)	$P^{a}_{0.5}$	P^{b}_{2}
OH (free) INH	υ 3400	υ 3400	—
	δ 1050 (m)	δ 1050 (m)	—
$\upsilon_{NH...O}$ ···· (ring)	3200 (br)	3200 (br.)	—
υ_{NH} (free)···(INH)	—	—	3146
υ_{C-H} ····· (β .D.)[c]	—	—	2963
$\upsilon_{C=O}$ ····· (INH)	—	—	1690 (vs)
$\upsilon_{C=O}$ ····· (β .D.)	—	—	1650
$\upsilon_{C=N}$ ····· (ring)	1630	1630	
$\upsilon_{N=N}$	—	1570	1570 - 1420
$\upsilon_{imide-II}$	—	—	1550
$\upsilon_{imide-III}$	—	—	1275

a : the product obtained after heating in an oven at 90°C for half an hour, a mixture of P_o and $P_{0.5}$

b: the product obtained after heating in an oven at 90°C for two hours .

c: β -diketonate.

The previous IR results are supported by the electronic spectra in the solid state (in paraffin oil). The spectrum of P_0 is characterized by a band at 372 nm assigned to $n-\pi^*$ transition of the C=N of the ring T [10, 15]. This band disappeared in the spectra of $P_{0.5}$ and P_2 , and instead a new band appeared at 327 nm assigned to $\pi-\pi^*$ transition of the imidol moiety [16], while the spectrum of P_2 manifests a new band at 390 nm assigned to $n-\pi^*$ transition of the free N=N group [17]. Based on the forementioned discussion we can assign the stable yellow form II_a to the syn form and the unstable red form $R\text{-}I_c$ to the anti form. Thus, the first change on heating involves a change of configuration from syn to anti by rupturing the H-bonds in rings T and Y, followed by ketoimine → enolazo rearrangement.



Scheme-I

c) Electrical conductivity:

Figure 1 shows the variation of the electrical conductivity exponent of PHB, BAB and their hydrazones PHBH and BABH as a function of the reciprocal absolute temperature. The results obtained fit the Arrhenius relation.

$$\sigma = \sigma_0 \exp(-\Delta E / 2kT) \quad \ldots\ldots (2)$$

where σ is the conductivity , σ_0 preexponential factor.

From this relation, the activation energy for conduction $\Delta E(eV)$ was calculated as :

Compound	$\Delta E(eV)$
PHB	0.10
BAB	0.08
PHBH	0.16
BABH	0.14

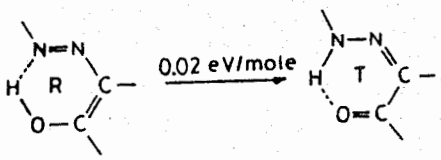
These values are lower than that obtained for isatin isonicotinoyl hydrazone ($\Delta E = 0.28$ eV) which is thermally stable up to Ca 300°C [5].

From (Table 3) , it is clearly noticed that the conductivity increases with rising the temperature indicating semiconducting behaviour [4], where pure extrinsic conduction mechanism is predominant due to the enhanced delocalization of π–electrons which are characterized by low activation energy ($\Delta E = 0.08$–0.16 eV). From this studyone can conclude that:

i) The azo compounds BAB and BABH have lower values of ΔE than the corresponding hydrazo compounds PHB and PHBH by 0.02 eV/mole, this may be attributed to the relatively higher stability of the hydrazo compounds than the azo compounds, i.e. the energy required to transform the azo compound to its corresponding hydrazo compound or the energy required to transform ring T to ring R.

TABLE 3. Variation of $p\sigma$ ($S.cm^{-1}$) with 1000/T (K^{-1}) for the investigated compounds.

t (°C)	T (K)	1000 / T	pσ					
			PHB	BAB	PHBH	BABH	(Δpσ) Dye	(Δ pσ) Hydrazone
25	298	3.36	8.65	7.47	5.19	5.59	1.18	- 0.40
30	303	3.30	8.58	7.46	5.16	5.56	1.12	- 0.40
35	308	3.25	8.56	7.43	5.00	5.47	1.13	- 0.47
40	313	3.19	8.55	7.43	4.98	5.41	1.12	- 0.57
45	318	3.14	8.52	7.40	4.94	5.39	1.12	- 0.45
50	323	3.10	8.49	7.36	4.91	5.35	1.13	- 0.44
55	328	3.05	8.47	7.34	4.87	5.33	1.13	- 0.46
60	333	3.00	8.43	7.32	4.87	5.31	1.11	- 0.44
65	338	2.96	8.43	7.31	4.85	5.29	1.12	- 0.44
70	343	2.92	8.42	7.30	4.85	5.28	1.12	- 0.43



(3)

ii) On the other hand, ΔE of the dyes PHB or BAB is lower than that of its corresponding isonicotinoyl hydrazone by 0.06 eV/mole, which may be the energy required to activate the isonicotinoyl moiety.

iii) Although the observed higher conductivity exponent (pσ) values of the azo compound BAB (Table 3) than those of the hydrazo compound PHB by ca. 1.12 $S.cm^{-1}$ may be explained as the O–H group in ring R is more conductive than the N–H group in ring T, this observation is reversed for hydrazones, as PHBH has higher pσ values than those of BABH by only ca. 0.43 $S.cm^{-1}$ that may be explained as the free OH group of isonicotinoyl moiety in PHBH is more conductive than the H–bonded O–H group of BABH.

iv) In general the hydrazones PHBH and BABH have higher conductivity values than the corresponding hydrazo PHB and azo compound BAB.

In order to make simple the comparison between values of electrical conductivity exponent, of two compounds(1) and (2) like graphical representation a trial is made by taking the rate of change of pσ every 5 °C , then plotting R versus, t °C where

$$R = \Delta p\sigma \times 100 \quad \text{.....} \quad (4)$$

The results are given in (Table 4) and represented in Fig. 2. From this Figure, it becomes clear that above 35 °C compounds investigated have R–values between 0 and 4 $S.cm^{-1}$ and the hydrazones PHBH and BABH are more conductors and have values 16 and 9 $S.cm^{-1}$ in the temperature range 30–35 °C.

TABLE 4. Rate of change of the exponential value (R) electrical conductivity ($S.cm^{-1}$) versus t °C for the investigated compounds.

t °C	$R = (\Delta p\sigma) \times 100$			
	PHB	BAB	PHBH	BABH
25	7	1	3	3
30	2	3	16	9
35	1	0	2	6
40	3	3	4	2
45	3	4	3	4
50	2	2	4	2
55	4	2	0	2
60	0	1	2	2
65	1	1	0	1
70				

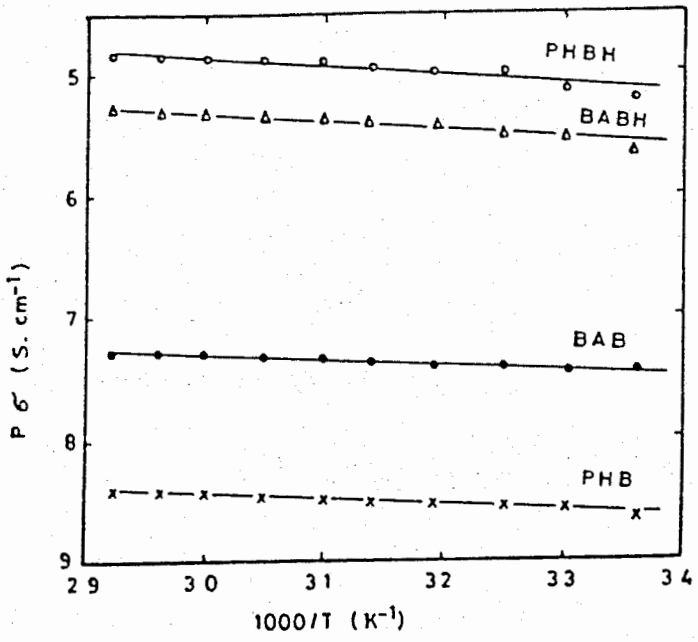


Fig. 1. Pσ vs. 1000/T (K^{-1}) for the dyes PHB and BAB and their hydrazones PHBH and BABH.

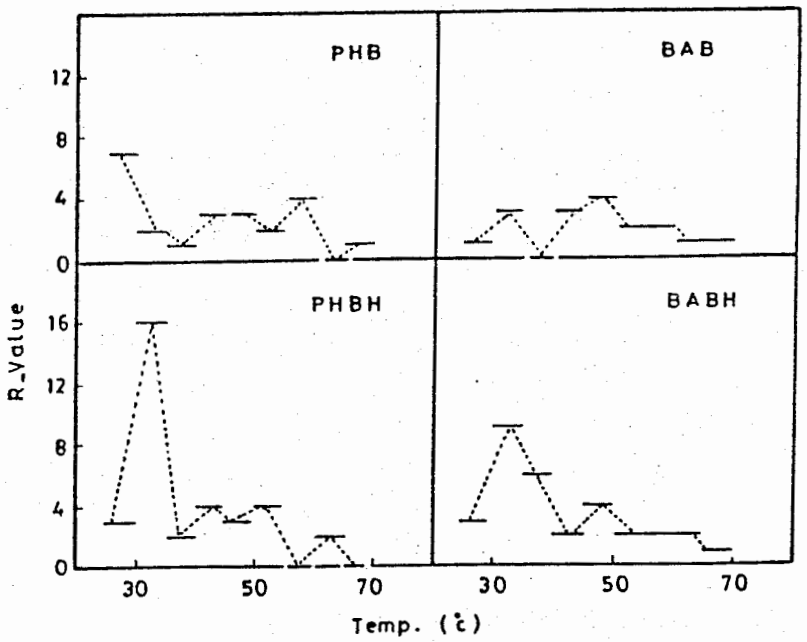


Fig. 2. R-Value vs. t (°c) for the dyes PHB and BAB and their hydrazones PHBH and BABH.

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