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The thermal and temperature dependence of the electrical conductivity of phenylhydrazo and benzeneazo benzoylacetones and their isonicotinoyl hydrazones

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Abstract

The coupling of benzenediazonium chloride with benzoylacetone at two different pH values in 1:1 molar ratio gives two different tautomers, PHB and BAB, in that condensation of these dyes with isonicotinic acid hydrazide (INH) yields two different hydrazones PHBH and BABH. Thermal studies (DTA and TG) with spectral analyses (IR and electronic) have provided more information about the structure of PHBH which shows thermochromic behaviour. The d.c. electrical conductivities of these compounds were measured in the temperature range 25–70°C and were found to show semi-conducting behaviour. 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 in order to make a simple comparison between the values of the electrical conductivity exponent.

INTRODUCTION

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

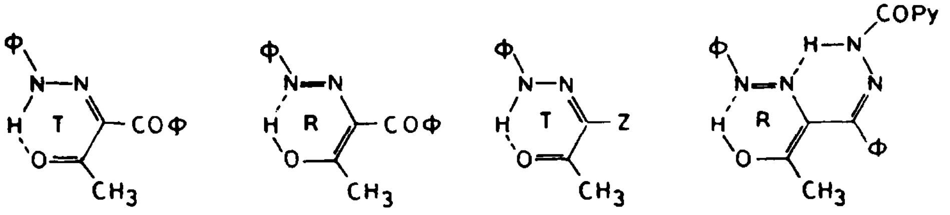
In a continuation of our earlier studies on the thermo-conductimetric properties of the solid hydrazones of isonicotinic acid hydrazide and their complexes [4, 5], the present work on the d.c. electrical conductivity and thermal analyses was carried out to ascertain the thermal stability and to obtain information about the electrical conductivity of benzene-azo-benzoylacetone (BAB), its phenylhydrazo-benzoylacetone (PHB) and also their isonicotinoyl hydrazones BABH and PHBH. Their activation energies for conduction have been calculated. 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 characterized by the methods of ref. 5.

Spectral studies were made using a Perkin-Elmer model 598 IR spectrophotometer and a Perkin-Elmer model 550 S UV/VIS spectrophotometer. Thermal analyses were carried out using a Shimadzu DT-30 thermal analyser, at a heating rate of 10°C of min^{-1} from ambient temperature to 500°C in air. The d.c. electrical conductivity (in the exponential form ($p\sigma$)) was measured as a function of temperature ($1000/T$) from 20 to 70°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 model 616 electrometer, 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.

The compounds have the structural formulae given in Exhibit 1, where Z is $-C(\phi){=}N \cdot NHCOPy$, Z′ is $-C(CH_3){=}N \cdot NHCOPy$, and ϕ is C_6H_5-. PHB is orange in colour and melts at 100°C; BAB is violet in colour and melts at 140°C; PHBH is pale yellow and melts at 160°C; BABH is deep red and melts at 125°C. The INH moiety in PHBH is present in the imidol form while in BABH it is in the imide form, and the OH group is in the free or H-bonded form, i.e.



PHB BAB PHBH BABH

Exhibit 1. Structural formulae.

$$=N{-}NH{-}CO{-}Py \rightleftharpoons =N{-}N{=}C{<}^{OH}_{Py} \qquad (1)$$

where Py is the pyridyl group.

RESULTS AND DISCUSSION

Thermal study

The DTA and TG diagrams of the investigated compounds are illustrated in Fig. 1 and their data are summarized in Table 1. These compounds are thermally stable up to 80°C and can safely be dried below 80°C. They show medium endothermic peaks on melting. The broad weak exothermic peaks which appear before melting are due to fission of the hydrogen bond

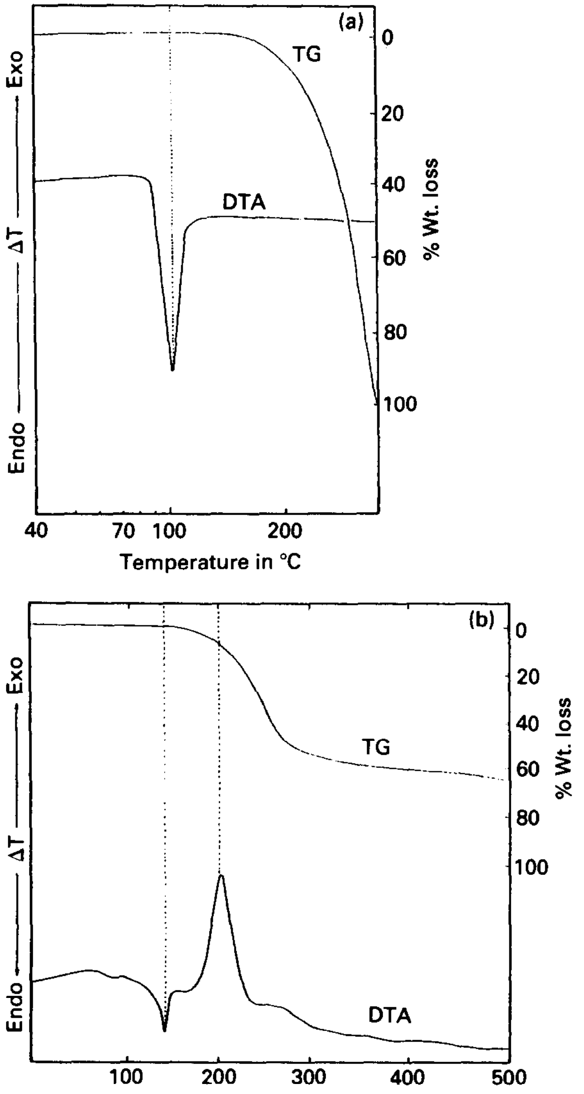


Fig. 1(a, b)

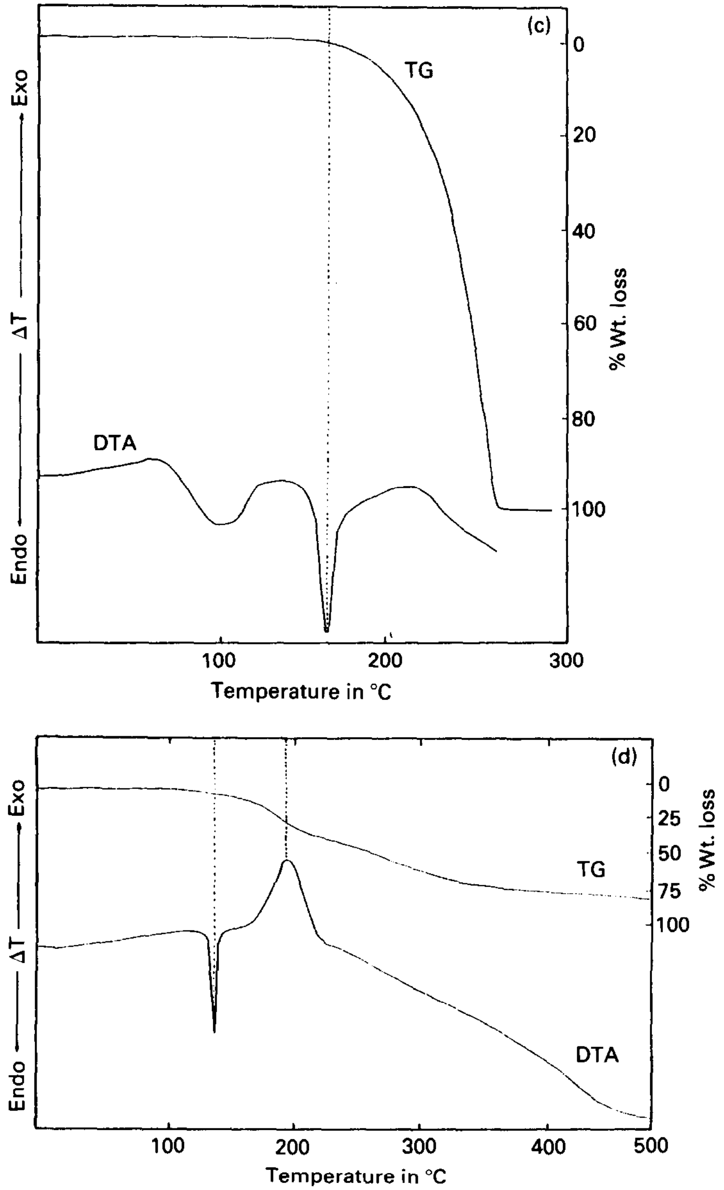


Fig. 1(c, d)

Fig. 1. DTA and TG curves for (a) PHB, (b) BAB, (c) PHBH and (d) BABH.

followed by rearrangement. DTA curves of the azo compounds after melting show broad exothermic peaks with 56% weight loss, and further partial decompositions occur at temperatures higher than 500°C. However, 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.

TABLE 1

Thermal analysis data for PHB, BAB and their hydrazones PHBH and BABH

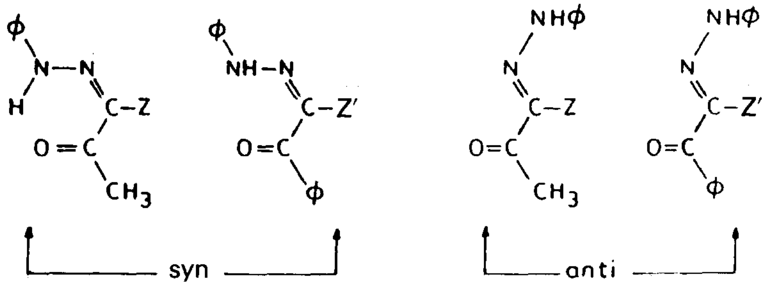
Compound	Temp./°C	DTA [a]	Assignment
PHB	30–80	Exo (w)	Due to fission of H bond and rearrangement
	100	Endo (m)	No weight loss; due to melting
	143–265	–	100% weight loss.
BAB	30–90	Exo (w)	Due to fission of H bond and rearrangement
	140	Endo (m)	No weight loss; due to melting
	150–265	Exo (s)	56% weight loss
PHBH	30–80	Exo (w)	Due to fission of H bond and rearrangement 1 [b]
	80–125	Endo (br)	May be due to rearrangement 2 [c]
	160	Endo (m)	No weight loss; due to melting
	160–292	–	100% weight loss
BABH	60–125	Exo (w)	Due to fission of H bond and rearrangement
	125	Endo (m)	No weight loss; due to melting
	170–230	Exo (s)	56% weight loss

[a] br, broad; vs, very strong; s, strong; m, medium; and w, weak. [b] *Syn*(Y–II_a) → *anti*(R–I_a).
[c] Ketoimine → enolazo.

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 at 90°C is increased to 2 h, the colour changes again to pale yellow (P_2) with no weight loss.

The classical spatial arrangement of the PHBH molecule allows for the existence of four possible structures due to geometrical isomerism. These may be depicted diagrammatically as (I_a–I_d) shown in Exhibit 2.



I_a I_b I_c I_d

Exhibit 2. Isomers of PHBH.

Taking into account the chelate structure involving hydrogen bonding, the syn-configuration must be depicted as $II_{a,b}$, while the anti-configuration must be depicted as $II_{c,d}$, as shown in Exhibit 3.

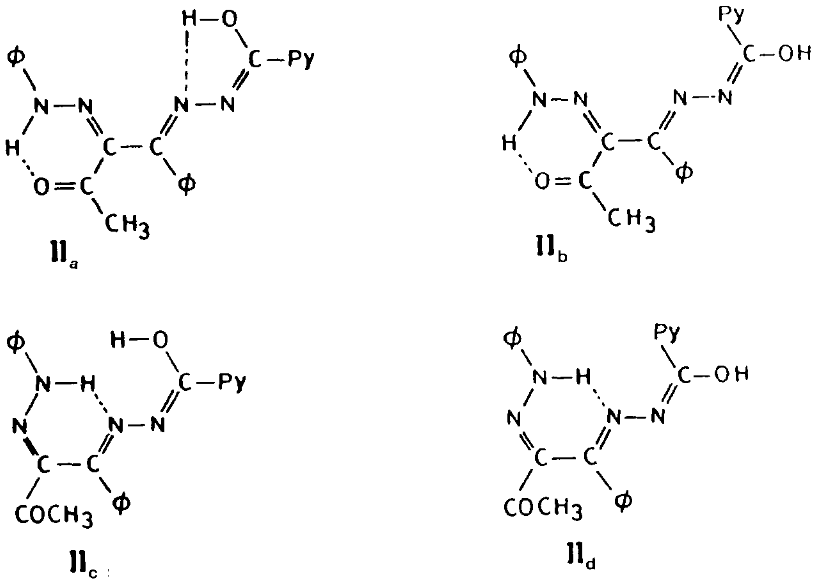


Exhibit 3. Chelates.

The syn structure is favourable for hydrogen bond formation because of the non-planar arrangement of the molecule. In the anti forms, however hydrogen bonding is not spatially possible.

Comparing the IR bands (Fig. 2) of P_0 and $P_{0.5}$ listed in Table 2 with their tentative assignments, it was found that the IR spectra of P_0 and $P_{0.5}$ are nearly identical except for three bands at 1570 (ν(N=N)), 1550 (ν(NCO)) and 1275 cm^{-1} (ν(C–OH)) which appear on heating. However, the spectrum of P_2 reveals considerable change. The imidol (INH) bands at 3400 (ν(OH)) and 1630 cm^{-1} (ν(C=N)) have disappeared and the imide bands appear at 1690 (very sharp) and a broad band at 3145 (ν(NH)) free, 1550 and 1245 cm^{-1}. This can be explained as the thermal imidol → imide tautomerism. Moreover, the appearance of new bands in the spectrum of P_2 at 2963 (ν(=C–H)), 1650 (ν(C=O)), 1570 and 1420 cm^{-1} of the *cis*- and *trans*-azo group (ν(N=N)), and at 805 cm^{-1} (δ(=C–H)) can be illustrated in terms of thermal enol–keto tautomerism.

The previous assignments to the IR spectra are supported by the changes in the electronic spectra (Fig. 3), measured in the solid state (in Nujol or paraffin oil). The spectrum of P_0 is characterized by a band at 372 nm

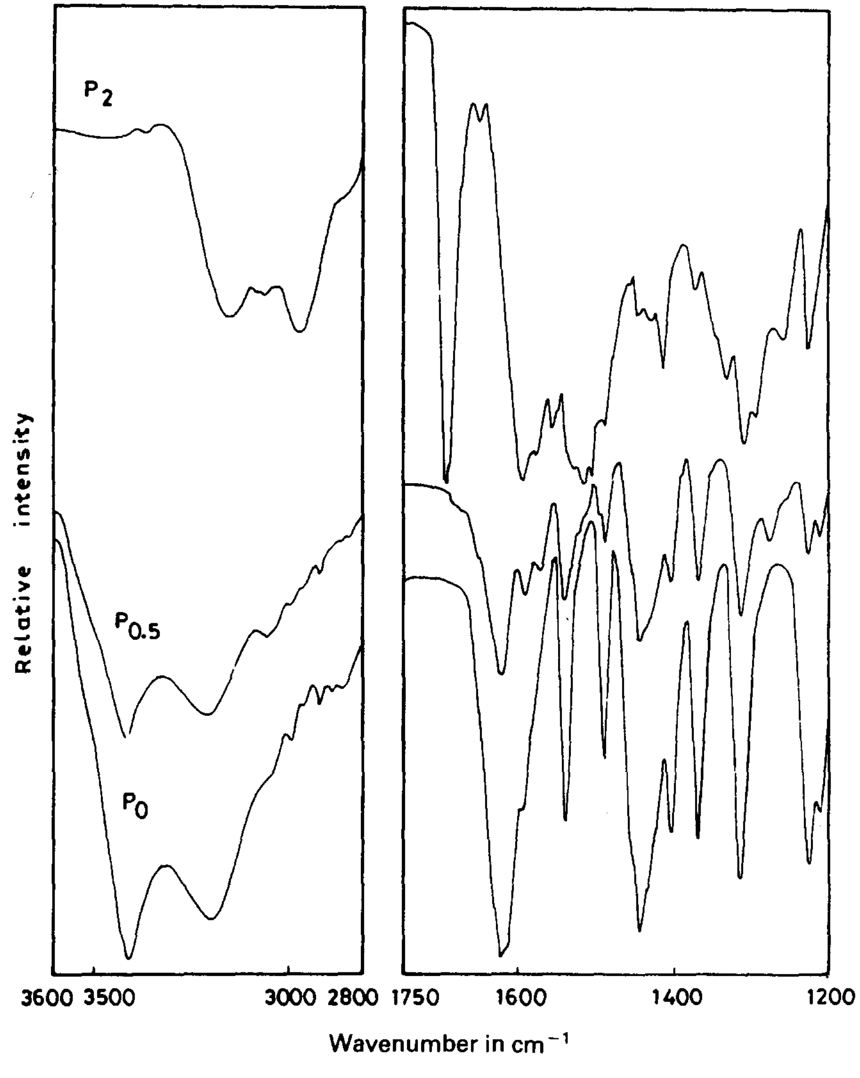


Fig. 2. IR spectral bands of the original PHBH (P_0), and the products ($P_{0.5}$) and (P_2) obtained after heating at 90°C for 0.5 and 2 h, respectively.

assigned to the n–π^* transition of the C=N group of the ring T. This band disappears in the spectra of $P_{0.5}$ and P_2, and instead a new band appears at 327 nm assigned to the π–π^* transition of the imidol moiety. The spectrum of P_2 manifests a new band at 390 nm assigned to the n–π^* transition of the free N=N group. Based on this we can assign the stable yellow form Y-II_a to the syn-form and the unstable red form R-I_c to the anti-form. Thus, the first change on heating involves a change in configuration from syn to anti by rupturing the H bonds in the rings T and Y, followed by ketoimine–enolazo tautomerism (see Exhibit 4).

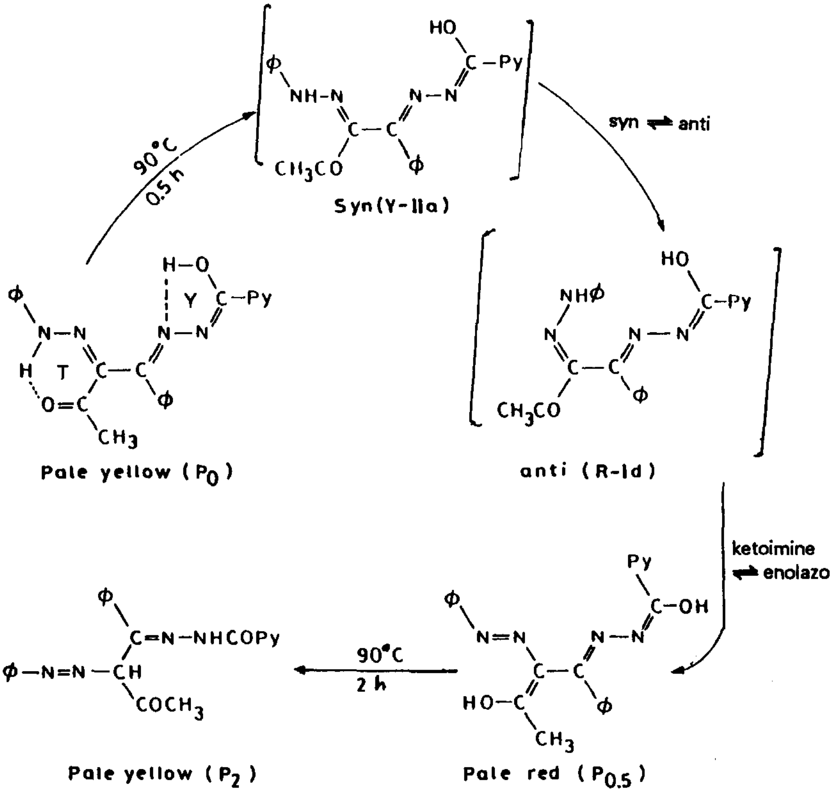


Exhibit 4. Tautomerism.

TABLE 2

Effect of heating at 90°C for 30 min and for 2 h on IR spectral bands of PHBH

	Original (P_0)	$P_{0.5}$ [a]	P_2 [b]
OH (free) INH	ν 3400	ν 3400	–
	δ 1050 (m)	δ 1050 (m)	–
ν(NH···O)····(ring)	3200 (br)	3200 (br)	–
ν(NH) (free)····(INH)	–	–	3146
ν(C–H)····(β-d) [c]	–	–	2963
ν((C=O)····(INH)	–	–	1690 (vs)
ν(C=O)····(β-d)	–	–	1650
ν(C=N)····(ring)	1630	1630	–
ν(N=N)	–	1570	1570–1420
ν(imide-II)	–	–	1550
ν(imide-III)	–	–	1275

[a] The product obtained after heating in an oven at 90°C for 30 min, a mixture of P_0 and $P_{0.5}$.
[b] The product obtained after heating in an oven at 90°C for 2 h. [c] β-Diketonate.

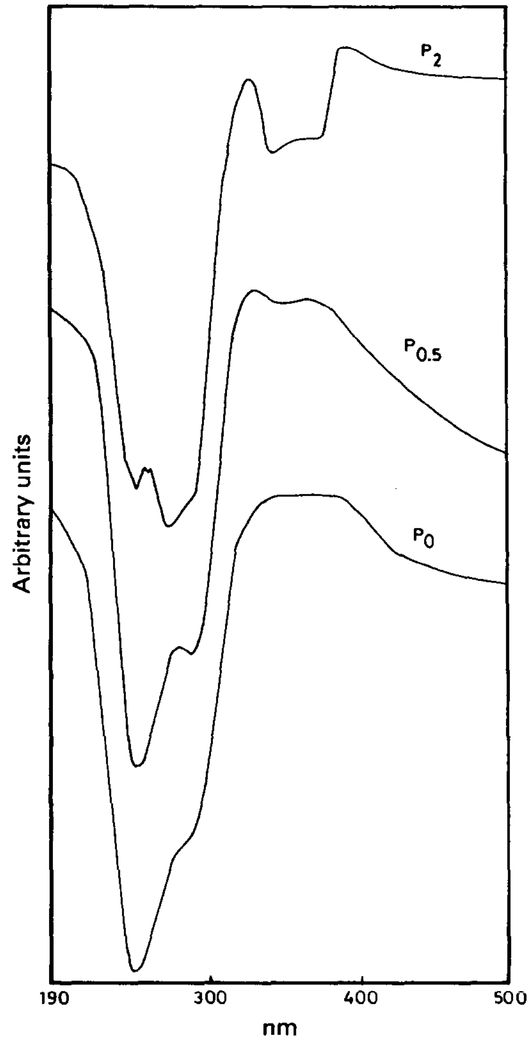


Fig. 3. The electronic spectra of the P_0, $P_{0.5}$ and P_2 forms of PHBH.

Electrical conductivity

Figure 4 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

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

where σ is the conductivity and σ_0 the pre-exponential factor.

From this relation, the activation energy for conduction ΔE/eV for each compound was calculated as: PHB, 0.10 eV; BAB, 0.08 eV; PHBH, 0.16 eV; and BABH, 0.14 eV.

From the results given in Table 3, it is clear that the conductivity increases with rising temperature, indicating semiconducting behaviour, in which a

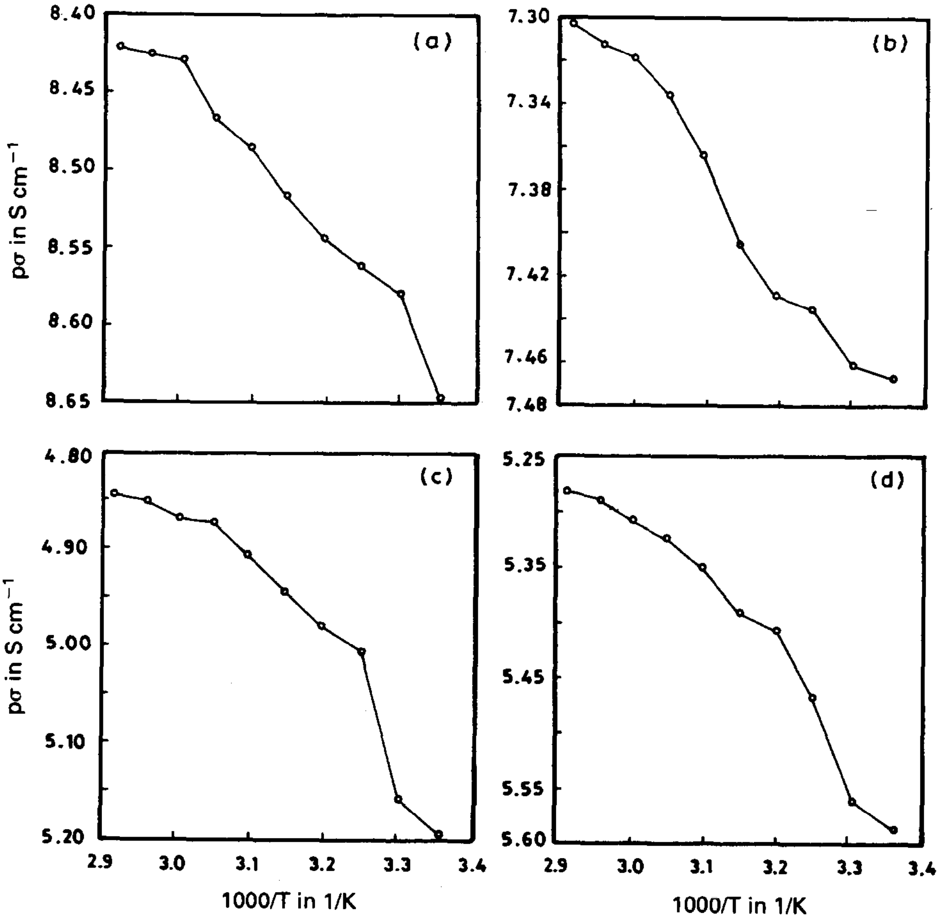
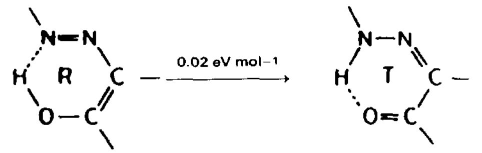


Fig. 4. Variation of conductivity exponent (S cm^{-1}) vs. $1000/T$ (K^{-1}) of (a) PHB, (b) BAB, (c) PHBH, and (d) BABH.

purely extrinsic conduction mechanism is predominant due to the enhanced delocalization of the π-electrons which are characterized by low activation energy ($\Delta E = 0.08-0.16$ eV). In summary:

(i) The azo compounds BAB and BABH have ΔE values lower by 0.02 eV mol^{-1}, than the corresponding hydrazo compounds PHB and PHBH (Fig. 5(i), (v)); this may be attributed to the relatively higher stability of the hydrazo over 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



(ii) However, the ΔE of the dyes PHB or BAB is lower by 0.06 eV mol^{-1} than that of the corresponding isonicotinoyl hydrazone (Fig. 5(ii), (iii)); this may represent the energy required to activate the isonicotinoyl moiety.

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

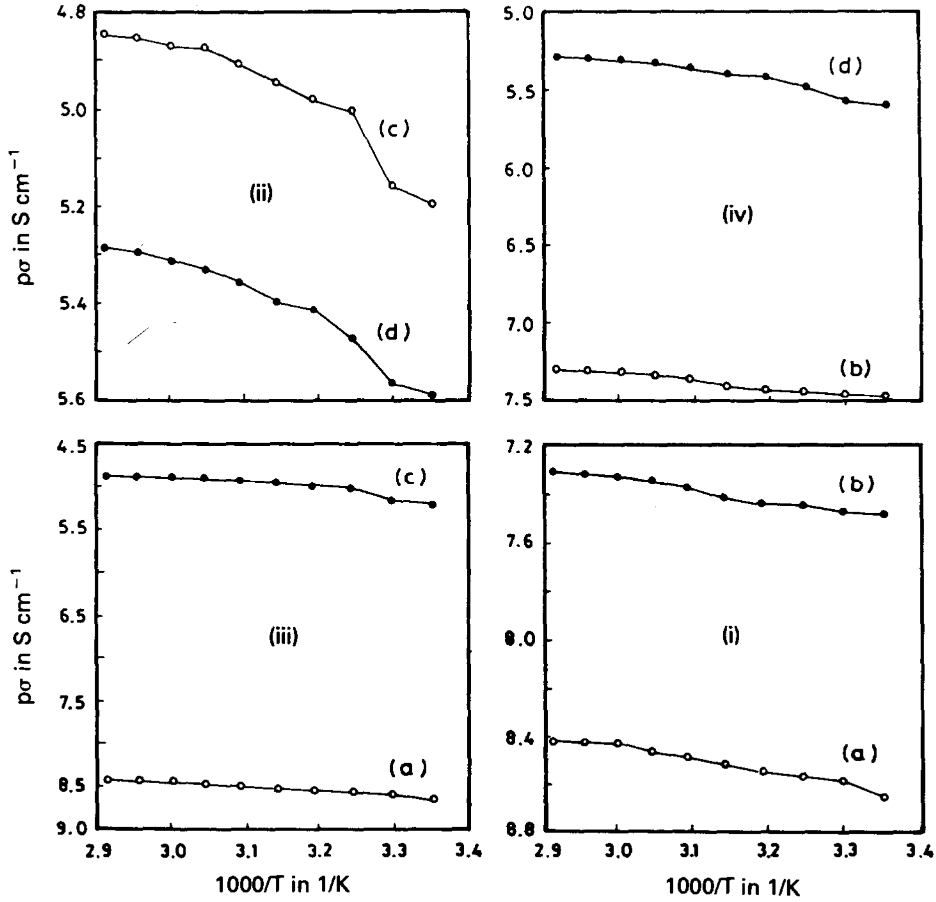


Fig. 5. Comparison of $p\sigma$ vs. $1000/T$ for (i) the dyes PHB (a) and BAB (b); (ii) the hydrazones PHBH (c) and BABH (d); (iii) the hydrazo PHB and its hydrazone PHBH; and (iv) the azo BAB and its hydrazone BABH.

TABLE 3

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

Temp./°C	T/K	$1000/T$	$p\sigma$					
			PHB	BAB	PHBH	BABH	($\Delta p\sigma$) Dye	($\Delta p\sigma$) 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

In order to simplify the comparison between values of the electrical conductivity exponent of two compounds (1) and (2) using a graphical representation, the rate of change of $p\sigma$ every 5°C was measured. Then R versus T (°C) was plotted, where

$$R = \Delta p\sigma \times 100 \tag{4}$$

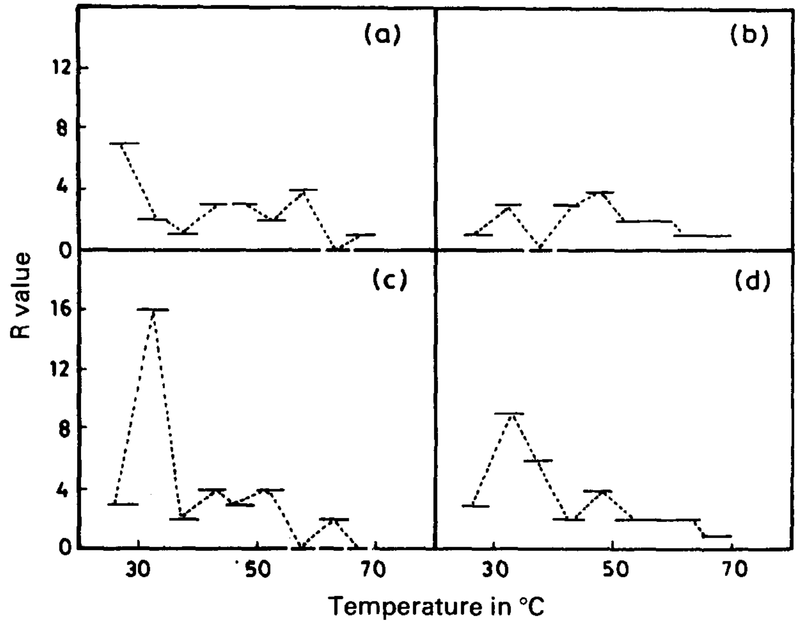


Fig. 6. R value of $\Delta p\sigma$ for (a) PHB, (b) BAB, (c) PHBH, and (d) BABH.

TABLE 4

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

Temp/°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				

The results are given in Table 4 and are represented in Fig. 6. From this figure, it is clear that above 35°C, the compounds investigated have R values between 0 and 4 S cm^{-1}, but the hydrazones PHBH and BABH are more conductive and have values between 16 and 9 S cm^{-1} in the temperature range 30–35°C.

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