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Spectral (u.v.–vis, i.r. and MS), electrochemical and metallochromic properties of 2-hydroxy-benzoylhydrazones of acetylpyridines

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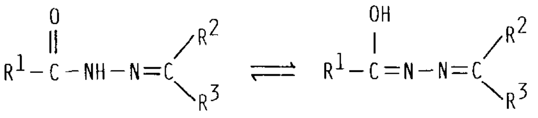
Abstract—The synthesis, electronic, infra-red and mass spectra of salicyloylhydrazones of 2-, 3-, and 4-acetylpyridine are reported. Ultraviolet absorption spectra have been applied to determine the dissociation constants which are ranged between 4.0–4.5 (pyridine nitrogen) and 6.2–6.3 (OH group). Infrared spectra show that strong intramolecular H-bonding exists in the solid compounds. Fragmentation of these compounds were found to undergo skeletal rearrangement in addition to either CO–N or N–N simple bond cleavage; pyridine nitrogen position contributes in the paths leading to ions. These aroylhydrazones exhibit polarograms that show several reduction waves, the positions of which change with the pH value. Of the three compounds, 3-pyridyl derivative was the most difficult to reduce. The chelating properties of the compounds towards metal ions were investigated. The 2-acetylpyridine derivative results to be the most adequate ligand, as well as a good preconcentrating agent for metal ions.

INTRODUCTION

Great attention is actually being devoted to the chemistry of aroylhydrazones because of their pharmacological, agricultural and analytical potential, as well as other uses. Furthermore, their coordination compounds have gained increasing interest [1]. Aroylhydrazones derived from pyridinic ketones have been employed, among other uses, as analytical reagents for determining metal ion traces [2–5]. The chelating behaviour towards metal ions of 2-benzoylpyridine [6, 7] and 2,6-diacetylpyridine [8–15] derivatives have been also investigated. These compounds are noteworthy for their remarkable versatility as chelating agents and for their tendency to produce stereochemistries of high coordination number [14].

The functional grouping causes these compounds to behave as bidentate ligands for metal ions and it may show tautomeric structures:



They form coordination compounds through the oxygen atom of either the carbonyl (8–14) or the enol group and through the imine nitrogen atom, a five-membered ring being produced. Neutral metal complexes can be formed. This type of hydrazone may behave as a terdentate chelating agent, provided the R^1 residue presents a donor atom in the adequate position, as it occurs in salicyloylhydrazide derivatives (although in these cases, the compounds act commonly as "ON" donor ligands if R^2 and R^3 do not show ligating tendency [16–18]), or in the 2-pyridylhydrazide derivatives ("NON" ligands [19, 20]). Terdentate ligands may also be obtained if R^2 and/or R^3 residues are groups such as *o*-hydroxyphenyl ("ONO" ligands [16, 21–24]), 2-pyridyl ("ONN" ligands [17, 18, 25]) or hydroxy imine ("ONN" ligands [26–29]). Chelating ligands with higher number of coordination positions may be prepared by convenient selection of the condensation products: aroylhydrazide (R^1–$CONHNH_2$) and di- or tri-ketones [8–15, 30].

In this work, salicyloylhydrazones (R^1 = *o*-(OH)Ph) of 2-, 3- and 4-acetylpyridine (R^2 = Me; R^3 = 2-py(2-APSH), 3-py(3-APSH) or 4-py(4-APSH) were prepared in order to compare their metallochromic properties, since they show several potential positions for bonding metal ions. The extraction colorimetric technique was applied to the metal complexes with the aim to evaluate and select the most suitable compounds for preconcentrating transition metal ions. The dissociation constants of these compounds are also reported and interpreted as a function of the *ortho* position of the OH group and of the position of the pyridine nitrogen atom. Infra-red and mass spectra were also recorded. The former shows that a strong intramolecular H-bond exists in the solid compounds. Mass fragmentation was found to undergo skeletal rearrangement in addition to CO–N and N–N simple bond cleavage. The electrochemical reduction of the three compounds was also investigated.

EXPERIMENTAL

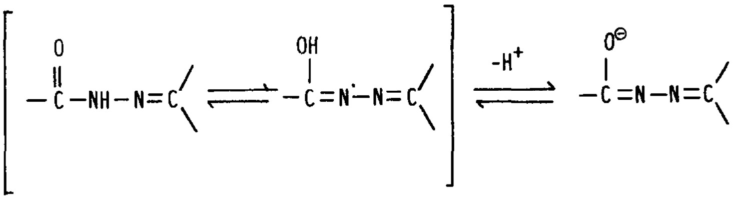
Infra-red spectra (4000–600 cm^{-1}) for KBr discs and electronic spectra (40,000–12,500 cm^{-1}) for organic and aqueous solutions were recorded on Perkin–Elmer 257 and 575 spectrophotometers, respectively. Mass spectra were determined with an A.E.I. MS-30 spectrometer operated at 70 eV; samples were introduced on the direct insertion probe with ion chamber temperature of *ca* 200°C. Polarograms were recorded on a Metrohm E-506 Polarecord, employing Pt wire and Ag/AgCl/3M KCl as auxiliary and reference electrodes, respectively. Potentiometric (Metrohm 645 pH-meter) and conductimetric (Philips PW 9505) measurements were also carried out. A Uvatom electrophoresis system was also used.

The three ligands were prepared according to the procedure described elsewhere [1]. In all cases, the solid Schiff's bases were collected by filtration and recrystallized from ethanol. The salicyloylhydrazide derivatives have a solubility in dimethylformamide greater than 20 g·l^{-1}, but in ethanol, methanol, water, chloroform or benzene, the solubility is less than 1 g·l^{-1}. Elemental analysis: found, C, 65.85, 65.70 and 65.92; H, 5.15, 5.30 and 5.07; N, 16.70, 16.76 and 16.51, for 2-APSH, 3-APSH and 4-APSH, respectively. $C_{14}H_{13}N_3O_2$ requires C, 65.87; H, 5.13 and N, 16.46%. Melting points were 230-4, 206-8 and 200-1°C for 2-APSH, 3-APSH and 4-APSH, respectively.

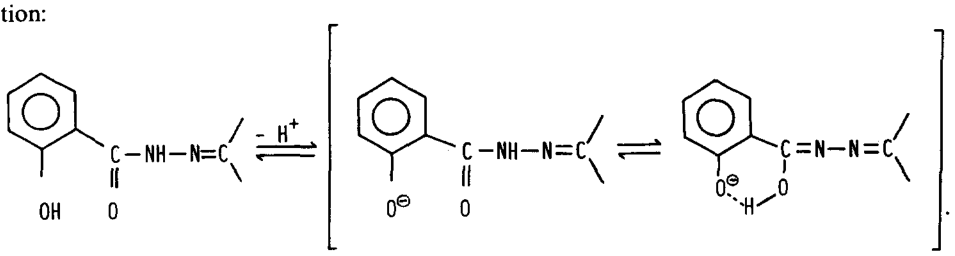
RESULTS AND DISCUSSION

Electronic spectra

Absorption spectra of the compounds were recorded in ethanol, chloroform and benzene and show two absorption maxima in the 35,600–33,000 cm^{-1} and 32,500–31,000 cm^{-1} that may be due to imine and salicyloyl chromophores, respectively [21]. Both absorption maxima suffer a blue shift with increasing solvent polarity. The electronic bands of the compounds show bathochromic shifts in acidic and basic media (Fig. 1). The absorption band (28,736–28,249 cm^{-1}) that appears in alkaline medium may be attributed to the wide chromophore system formed by splitting off of the H atom of the CONH group giving rise to an azine group [20], according to the reaction:



The compounds show several ionization steps, two of which were determined from the variation of absorbance vs pH by the STENSTRÖM and GOLDSMITH [31] and SOMMER [32] methods. The mean values found were 4.0 and 6.2 for 2-APSH, 4.3 and 6.2 for 3-APSH and 4.5 and 6.3 for 4-APSH. The first pK value may be caused by protonation of the pyridine nitrogen atom. It can be seen that p-derivative gives a greater pK value. This may be attributed to inductive effect of the hydrazidic chain. The second pK value is caused by deprotonation of the hydroxyl group, as deduced from potentiometric titration with NaOH solution. This fact causes the hydrogen atom of the NH group to split off to carbonyl group, giving rise to a strong intramolecular H-bond, according to the reaction:



This could explain the fact that deprotonation of the CONH group in salicyloylhydrazones does not occur in moderately basic medium, as it does in other related benzoylhydrazones [33].

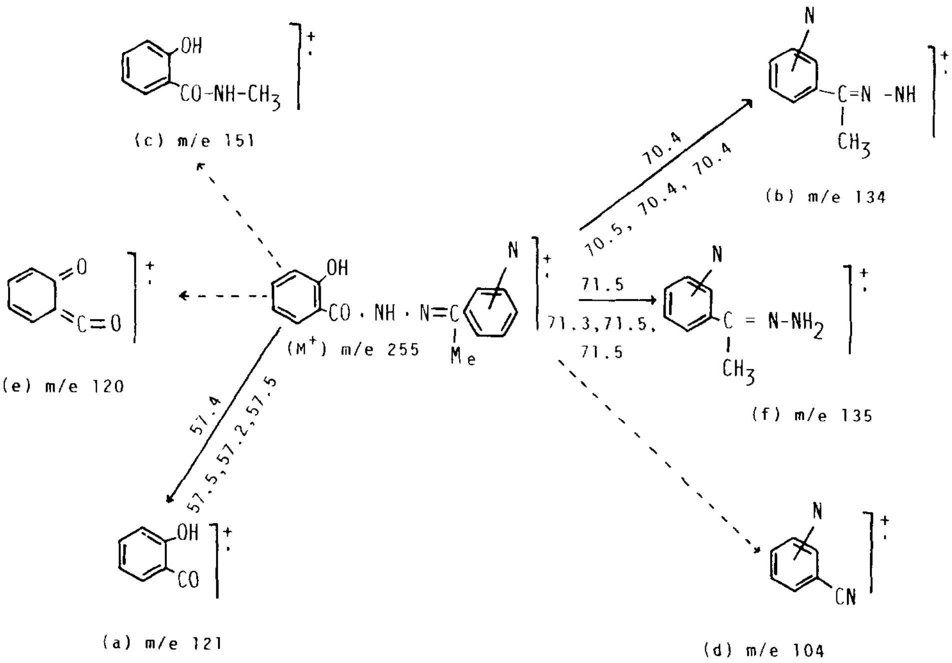
Infrared spectra

Examination of the spectra of the individual compounds shows that absorption bands are located in the same region. This fact may be anticipated owing to the expected similarity of the compounds. The bands assigned to the characterized vibrations are shown in Table 1, where 2-acetylpyridine benzoylhydrazone (2-APBH) is included for comparison. The well defined band at 3290–5 cm^{-1} in the salicyloylhydrazones may be assigned to bonded NH absorptions, probably in the *trans* form [34]. The position of the OH stretching vibration is observed in the 2800–2500 cm^{-1} region (absent in 2-APBH) indicating a strong intramolecular H-bond [14, 18]. This makes the salicyloylhydrazide derivatives less soluble compounds than the corresponding benzoylhydrazide derivatives [3, 35]. The presence of amide bands suggests that the compounds are in the *keto*-form in the solid state [21–24].

Mass spectra

The salicyloylhydrazones of acetylpyridines, (OH)PhCONH=NMePy, behave like other related aroylhydrazones when fragmentation pattern is examined [36]. They are cleaved either at the CO–N bond to yield two charged species of composition (a) (OH)PhCO and (b) PyMeC=NNH or at the N–N bond with simultaneous skeletal arrangement to yield the charged species of composition (c) (OH)PhCONHMe and (d) PyCN. Ion (a) is generally the base peak; (c) and (d) ions are not indeed of significant intensity. Complete mass spectra are shown in Table 2.

The molecular ions of the three pyridine derivatives yield major fragment ions at *m/e* 121 and 134, as shown



Scheme 1. Fragmentation pathways of the compounds. Metastable-confirmed transitions are indicated by solid arrows: numbers above solid arrows correspond to the calculated values of *m/e* and those below correspond to the measured values for 2-APSH, 3-APSH and 4-APSH, respectively.

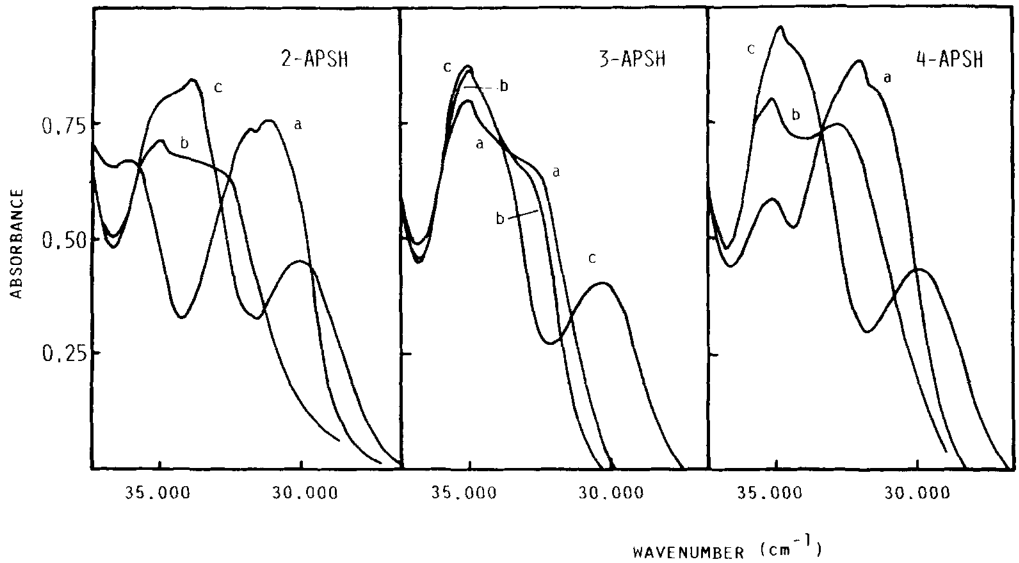


Fig. 1. Electronic spectra of 2-APSH, 3-APSH and 4-APSH (5×10^{-5} M) in aqueous medium at three pH values: (a) 2.7; (b) 4.7, and (c) 9.7.

in the fragmentation pattern scheme of the three aroylhydrazones. The occurrence of this cleavage is suggested from the observation of the corresponding metastable ions. Probably, the intensity of the peak at *m/e* 134 is related with the position of the pyridinic nitrogen, since in *ortho* derivative this is the base peak while in *meta* or *para* derivatives the base peak is the fragment at *m/e* 121. The cleavage of the CO–N bond with migration of the phenolic hydrogen atom may also occur yielding two charged species (e) and (f) at *m/e* 120 and 135, respectively. The occurrence of this cleavage is suggested by observation of the appropriate metastable transitions in the three compounds. Peaks at *m/e* 106 are also observed in the fragmentation process of the compounds. Metastable transitions corresponding to cleavage of 134 → 106 (*m/e* calculated, 83.8) are observed in the three compounds at *m/e* 84.0; this suggests that ion at *m/e* 106 may be originated

Table 1. Selected infra-red bands (cm^{-1}) of acetylpyridine derivatives

Assignment	2-APBH	2-APSH	3-APSH	4-APSH
$^{\nu}$NH	3210 sh 3185 m	3290 m	3290 m	3295 m
$^{\nu}$CH	3030 br, w	3050 br, w	3050 br, w	3050 br, w
$^{\nu}$as(CH$_3$)	2980 sh	2950	2950 w	2950 sh
$^{\nu}$s(CH$_3$)	2870 w	2860	2860 w	2860 w
$^{\nu}$OH	—	2730, 2590 w	2720, 2590 w	2700 br, w, 2580 w
Amide I	1665 sh 1650 vs	1660 sh 1640 vs	1670 sh 1660 vs	1670 sh 1660 vs
Ph and Py rings	1605–1440	1605–1435	1605–1430	1605–1410
Amide II	1540 s	1545 s	1545 s	1545 s
$^{\delta}$s(CH$_3$)	1375 w	1375 w	1380 w	1370 w
$^{\delta}$(CH)Py	785 s	795 s	810 w	820 s
$^{\delta}$(CH)Ph	750 m	755 m	755 m	755 s
$^{\delta}$(CH)Py		700 m		
$^{\delta}$(CH)Ph	700 s			

Table 2. Complete mass spectra of the reagents*

	R.I. (%)		
m/e	2-APSH	3-APSH	4-APSH
256	5	3	3
255	30	19	20
177	4	—	—
135	30	21	21
134	100	67	22
122	7	9	8
121	93	100	100
120	8	11	6
119	4	—	3
107	12	—	3
106	100	5	11
105	10	3	—
104	11	4	—
94	3	3	3
93	20	14	14
92	3	—	—
80	3	—	—
79	17	—	—
78	45	9	6
77	—	3	—
66	3	—	—
65	40	18	18
64	4	—	—
63	6	3	3
57	5	—	—
53	6	—	—
52	11	5	4
51	18	10	8

*All ions equal or greater than 3% of the base peak (arbitrarily 100%) and above *m/e* 50 have been summarized.

by skeletal arrangement and loss of two N in the ion of *m/e* 134. In the case of 2-APSH, the ion at *m/e* 106 shows high intensity, practically the same as the base peak, and it is possible that the position of the pyridinic nitrogen has a decisive influence owing to the possibility of intramolecular H-bond between iminic hydrogen and pyridinic nitrogen atoms. In conclusion, the results show that salicyloylhydrazones of acetylpyridines fragment by simple, predictable cleavages, as it occurs in other related aroylhydrazones [36], and, although skeletal arrangements take place, it does not impede the structural elucidation of these compounds by mass spectrometry.

Metallochromic properties of the compounds

The metal complex compounds are readily formed in buffered aqueous–ethanolic solutions. Table 3 shows some colorimetric characteristics of the soluble metal chelates. The electronic spectra of the aroylhydrazone solutions are different from those of their mixtures with metal ions, the two absorption bands of the reagents suffering a large red-shift on complexation, mainly in the case of 2-APSH. In order to compare possible coordination positions of the aroylhydrazones, the oxidation state of the iron chelates was tested. It was concluded that the compounds react with iron in both bivalent and trivalent state. The stoichiometric ratio for the iron(II) complexes was 1:3 in all instances. However, 2-APSH shows a remarkable behaviour in its reaction with iron(II), yielding a green complex which can be easily extracted into chloroform (the use of this reagent as a preconcentrating agent appears possible), since one proton per each two iron(II) ions was released on complexation as deduced from potentiometric titration and conductivity measurements. Besides, both electrical conductance and electrophoretical measurements in dimethylsulfoxide were consistent with the non-electrolyte nature of Fe(II)–2-APSH complex. In the formation of this complex, the appropriate chelation position of the pyridine N atom could explain the different reactivity of the *o*-derivative in relation to the *para* and *meta* compounds.

Preliminary polarographic study

The use of polarography to investigate the properties of organic compounds is of interest since they can furnish valuable information about reaction mechanisms and structure of a large number of organic compounds. Besides, these studies have shown to offer

Table 3. Some spectrophotometric characteristics of soluble metal complexes of the acetylpyridines derivatives

Ion	Aqueous medium (acetate buffer)						Chloroformic medium*	
	2-APSH		3-APSH		4-APSH		(2-APSH)	
	cm^{-1}	ε†	cm^{-1}	ε†	cm^{-1}	ε†	cm^{-1}	ε†
V(V)	25,907	17.5	<28,570‡	—	<28,570	—	23,923	4.2
Fe(II)	§	—	<28,570	—	<28,570	—	22,727 15,949	1.6 3.4
Fe(III)	28,570	26.5	28,570	2.7	28,570	2.5	23,529 15,949	4.1 6.0
Pd(II)	25,640	7.3	§		<28,570	—	23,810 22,727	4.4 3.8
Ga(III)	25,000	8.3	<28,570	—	—	—	23,697	3.5
Pb(II)	27,778	8.3	<28,570	—	—	—	24,096	2.1
Bi(III)	26,455	13.8	§	—	—	—	24,155	10.0

*Metal complexes were extracted into chloroform from acetate buffer solutions; Ni(II), Co(II), Cu(II) and Cd(II) gave coloured complexes at 24,175, 23,810, 24,096 and 24,155 cm^{-1}, respectively.

†Molar absorptivity ($\times 10^3$ $l\,mol^{-1}\,cm^{-1}$).

‡Molar absorptivities of bands lower than 28,570 cm^{-1} were not calculated.

§A precipitate is formed.

great potentialities and advantages in the organic analysis.

The polarograms of the compounds were performed on KH_2PO_4-Na_2HPO_4 buffer solutions in 5% v/v dioxane-water media. The aroylhydrazones studied showed several reduction waves up to a maximum of four, the positions of which change with the pH value, thus indicating that protons are involved in the reduction process (Fig. 2). The compounds behave in a similar way as other related compounds [37–40]. The wave presented by 2-APSH at −0.17 V is probably related with the *ortho* position of the pyridine N atom and could be used to characterize and/or determine selectively this compound in the presence of other related compounds. A preliminary study of the number of electrons involved in each reduction process indicates that the *ortho* derivative shows a reduction behaviour different from that of *meta*- and *para*-derivatives. The d.c. logarithmic analysis of the reduction process of the compounds appears to be a quasi-reversible d.c. electrode process. The interchanged electron numbers corresponding to the first (−0.17), second (−0.7 V) and third (−1.30 V) wave of 2-APSH is *ca* 2, 1 and 1, respectively; the first wave of 3-APSH (−0.6 V) and 4-APSH (−0.9 V) corresponds to an interchange of *ca* 2 electrons. In conclusion, the polarographic behaviour of acetylpyridine salicyloylhydrazones yields well defined waves suitable for analytical purposes.

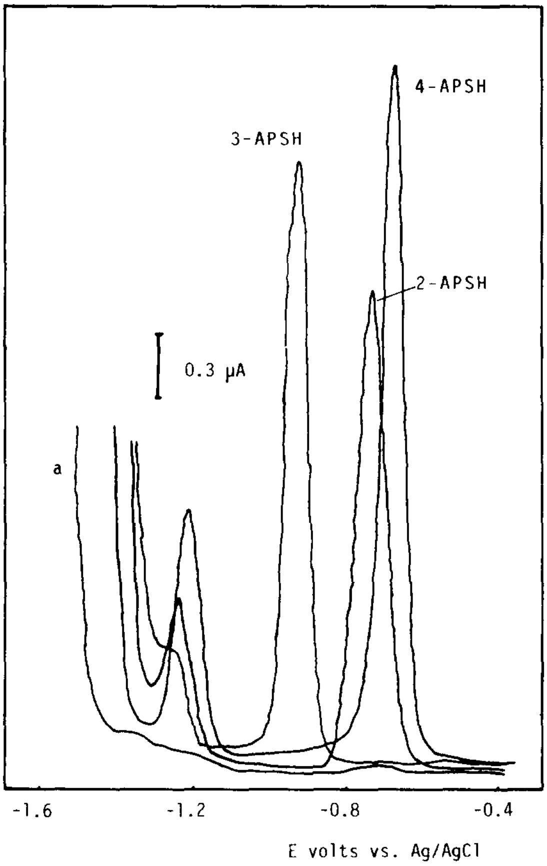


Fig. 2. Polarographic behaviour of 4×10^{-4} M salicyloylhydrazones of acetylpyridines in pH 6.1 buffer using the ddp technique. The peak at −0.17 V for 2-APSH is not shown in the figure. Each of the three compounds exhibit also a wave between −1.65 and −1.7 V. a: background electrolyte.

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