

Spectroscopic Studies of Nicotinic Hydrazide and its Arylidene Derivatives

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Summary: The electronic absorption spectra, in different solvents as well as in buffer solutions, ir spectra and ^1H nmr spectra of nicotinic hydrazide and its arylidene derivatives are investigated. The important bands are assigned to the corresponding molecular vibrations and discussed in relation to molecular structure.

Introduction

In continuation of our studies on hydrazides of organic acids and their arylidene derivatives, the uv, ir and ^1H nmr spectra of nicotinic hydrazide and its condensation products with some aldehydes are investigated. Spectroscopic studies of hydrazides of organic acids became of special interest [1-3] since these function as antituberculous compounds [4], based on their ability to form more or less stable chelates with transition metal ions [5,6]. Hydrazides can behave as antimalarial agents [7] while their chelates with Cu(II) have fungicidal effect [8].

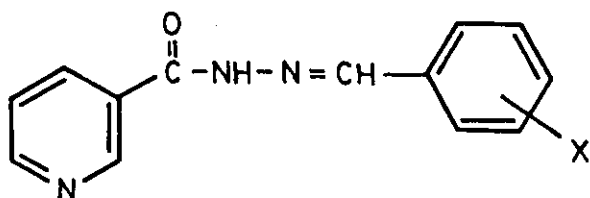
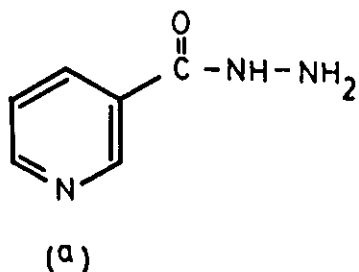
Experimental

All chemicals used in the present work were pure analytical grade BDH products. The nicotinic hydrazide was prepared by a method similar to that described by Struve [9], while the arylidene derivatives were prepared by condensation of the hydrazide with benzaldehyde derivatives in the usual manner used for the preparation of hydrazones [10]. The buffer solutions used for pH control were the components of the universal series of Britton and Robinson [11] containing 30% ethanol. The uv spectra were

recorded on a Unicam SP 8000 spectrophotometer using 1.0 cm matched silica cell. The ir spectra were obtained by the aid of the Unicam SP 1000 infrared spectrophotometer using the KBr Wafer technique. The ^1H nmr spectra were recorded in d_6 dimethyl sulphoxide (DMSO-d_6) on the varian 60 nmr spectrometer using tetramethyl silane as internal standard.

Results and Discussion

The compounds included in the present study have the general formula:



in which; X=p-NO₂(b), m-NO₂(c), o-NO₂(d), p-Cl(e), m-Cl(f), o-Cl(g), p-Br(h), H(i), m-CH₃(j), p-CH₃(k), o-OCH₃(l), p-OCH₃(m), o-OH(n), m-OH(n), m-OH(o) & p-OH(p).

I. The Electronic Absorption Spectra:

(a) Spectra in organic solvents:

The spectrum of nicotinic hydrazide exhibits, mainly two absorption bands located at 210 nm and 256 - 262 nm. The first one corresponds to the $\pi-\pi^*$ transition within the pyridine ring while the second band can be assigned to an intramolecular charge transfer involving the location of an electron from the hydrazine rest to the C=O group. This band lies at lower energies in case of isonicotinic hydrazide compared to nicotinic hydrazide. This can be ascribed to the much lower antagonising effect of the charge migration from the pyridine ring to the C=O group. Since the C=O group is in m-position to the nitrogen atom acting essentially as the donor centre on the pyridine ring.

The electronic absorption spectra of the arylidene derivatives (b-p) exhibit mainly three bands in ethanol and cyclohexane while in other solvents display only one or two bands from those at the longer wavelength side. The first band located at 210-224 nm can be assigned to the $\pi-\pi^*$ of the pyridine ring interacting with the medium energy transition of the phenyl group. The second band lying within the 232-290 nm range can be assigned to the low energy $\pi-\pi^*$ transition of the phenyl group. The last band at the longer wavelength side is observed within 290-325 nm

range. This band does not appear in the spectrum of nicotinic hydrazide and accordingly its appearance in the spectra of the arylidene derivatives is connected with the presence of the hydrazone part of the molecule, through the migration of the electron from α -nitrogen atom to the vacant π -orbital of the C=O group;



This band can be assigned to an intramolecular charge transfer (CT) involving the whole molecule [12]. The CT band shows a progressive red shift with increased polarity of the medium.

The spectra of the nitroderivatives (b-d) show an additional band within the 294-330 nm which corresponds to the $\theta \rightarrow \text{NO}_2$ interaction.

This band overlaps strongly with the CT band of (b) and (c). The spectra of compound (n) display a band at 332 nm corresponding to a $\pi-\pi^*$ transition within the chelate ring formed through intramolecular hydrogen bonding [13,14].

The application of the dielectric relations given by Gati and Szalay [15] or Suppan [16] did not give any linear relationship. This indicates that the dielectric constant of the medium is not the only factor influencing the band shift and so called specific solute - solvent interaction plays an important role in determining the band position. The change of the substituent on the arylidene ring causes an obvious shift of the CT band. The plot of the λ_{max} of the CT band as function of the σ_x^* Hammett constant or the $\sigma_{\theta x}^*$ are satisfactory linear

relations (Fig.1). The ρ -values are given in table I. The values are found to vary from one solvent to the other, denoting that the solution energy for the substituent groups contributes to solvent shift.

(E) Spectra in Buffer Solutions:

The absorption spectra of some of the arylidene nicotinic hydrazides in buffer solutions display some interesting changes with pH. Thus,

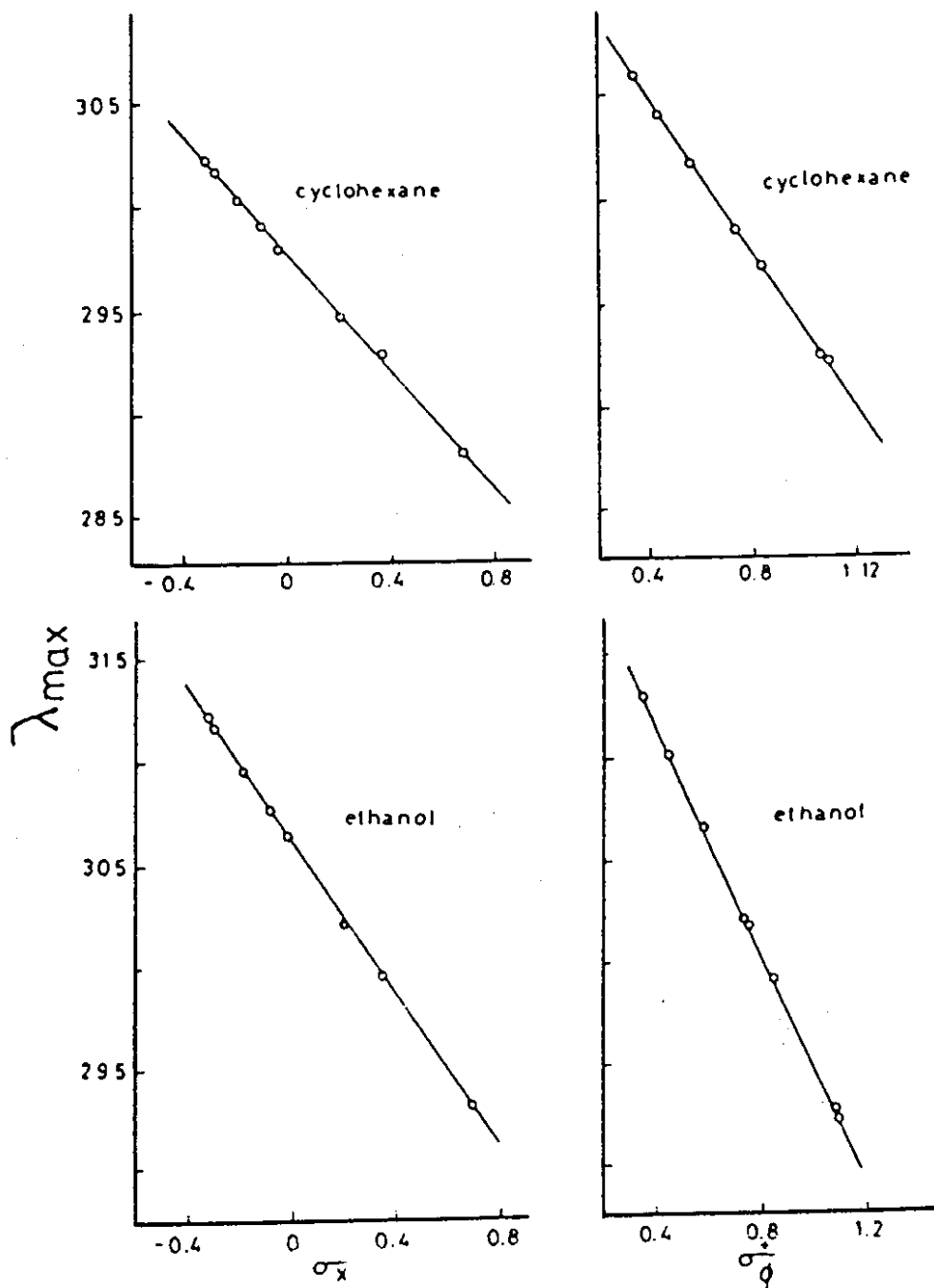


Fig. (1)

Table-1: The uv bands of nicotinic hydrazide and some of its arylidene derivatives in ethanol and cyclohexane.

Compound	Ethanol				Cyclohexane			
	A		B		A		B	
	λ	$\epsilon \times 10^{-3}$	λ	$\epsilon \times 10^{-3}$	λ	$\epsilon \times 10^{-3}$	λ	$\epsilon \times 10^{-3}$
I _a	210	13.00	262	6.8	-	-	256	-
I _b	224*	18.00	258	11.5	326	31.7	266	322
I _c	214	17.3	272	23.3	294	26.3	274	296
I _d	212*	21.5	272	19.3	290	19.7	266	290
I _e	222	21.7	-	-	306	32.8	-	298
I _f	224	19.7	-	-	298	23.3	-	292
I _g	218	20.0	286*	22.7	302	26.2	286*	294
I _h	222	18.00	-	-	306	29.3	-	298
I _i	218	21.3	290*	25.2	302	25.7	286*	298
I _j	222	17.7	-	-	300	23.7	-	294
I _k	222	21.0	-	-	306	30.0	-	296
I _l	212	22.0	290	15.5	302	15.7	290	318
I _m	224	19.5	258	8.7	316	30.5	-	310
I _n	214	23.2	232	16.7	288	14.7	232	288
I _o	216	26.7	-	-	298	14.2	-	296sh
I _p	224	19.5	260	8.7	332	15.7	-	332
					298	23.7	-	298
					318	30.3	262	320

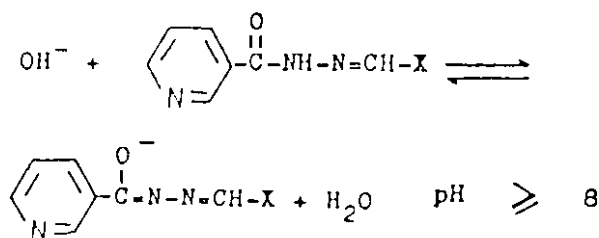
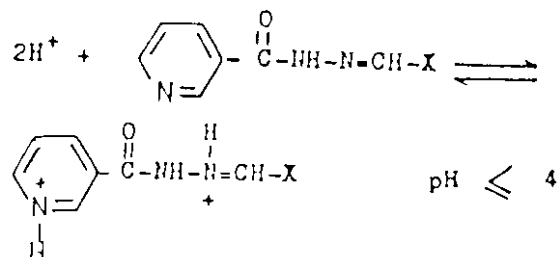
* shoulder p = -18.73 p' = -28.4 p = -14.08 p' = -19.2

some bands are shifted to longer wavelength and others appear by increasing pH of the medium. The spectra in buffer solutions, as shown in Fig.2 reveal one band, in most cases. At the same time, the intensity of absorbance decreases. For the compounds (b), (f) and (p) a more clear isosbestic point is observed at 350, 310 and 330 nm respectively, indicating an equilibrium within this pH range probably between the ionised and nonionised species.

The spectra of benzylidene nicotinic hydrazide solutions ($3 \times 10^{-5} M$) in a series of universal buffer solutions are shown in Fig.2. Within the pH range 3.75-10.36, the spectrum consists of only one band located at 298 nm. At pH = 10.62 this band appears to be slightly red shifted and a new band appears at 318 nm. The absorbance of the latter band increases with increasing pH value. The variation of absorbance with pH at some different wavelengths is given in Fig.2. The values of the dissociation constant of the compound as evaluated by different methods described before are recorded in Table-II.

Generally, for arylidene derivatives of acid hydrazides, two acid-base equilibria were traced over the pH range 2-12, corresponding to the protonation of the azomethine nitrogen and proton splitting from the amide linkage. This would also be the case for the compounds under investigation. Also, the protonation of the nitrogen atom of the pyridine ring would take place. As gathered from the pK_a values for the protonation of compounds containing these two centres, protonation of the pyridine and azomethine nitrogen would proceed simultaneously which makes it difficult to have a significant pK_a value. The

correct pK_a value would be for the dissociation of the amide proton. The pK_a values determined are given in Table-II. The acid-base equilibria set would be represented as follows:



The plot of pK_a as function of σ_x or σ_{θ}^* are satisfactory linear relations. This indicates that the pK_a value is directly affected by the nature of the substituent. Thus the Hammett linear free energy relationship is valid in the form:

$$pK_{a(x)} = pK_{a(H)} + \rho \sigma_x$$

The pK_a -values calculated from the least square method are given in Table-II.

II. The Infrared Spectra:

The assignment of the main bands in the infrared spectrum of nicotinic hydrazide as shown in Table-(III), was achieved by considering that given for acid hydrazides and their arylidenes as well as previous works on pyridine derivatives. In the spectra of the arylidene derivatives, the bands due to the various NH_2 -vibrations are no

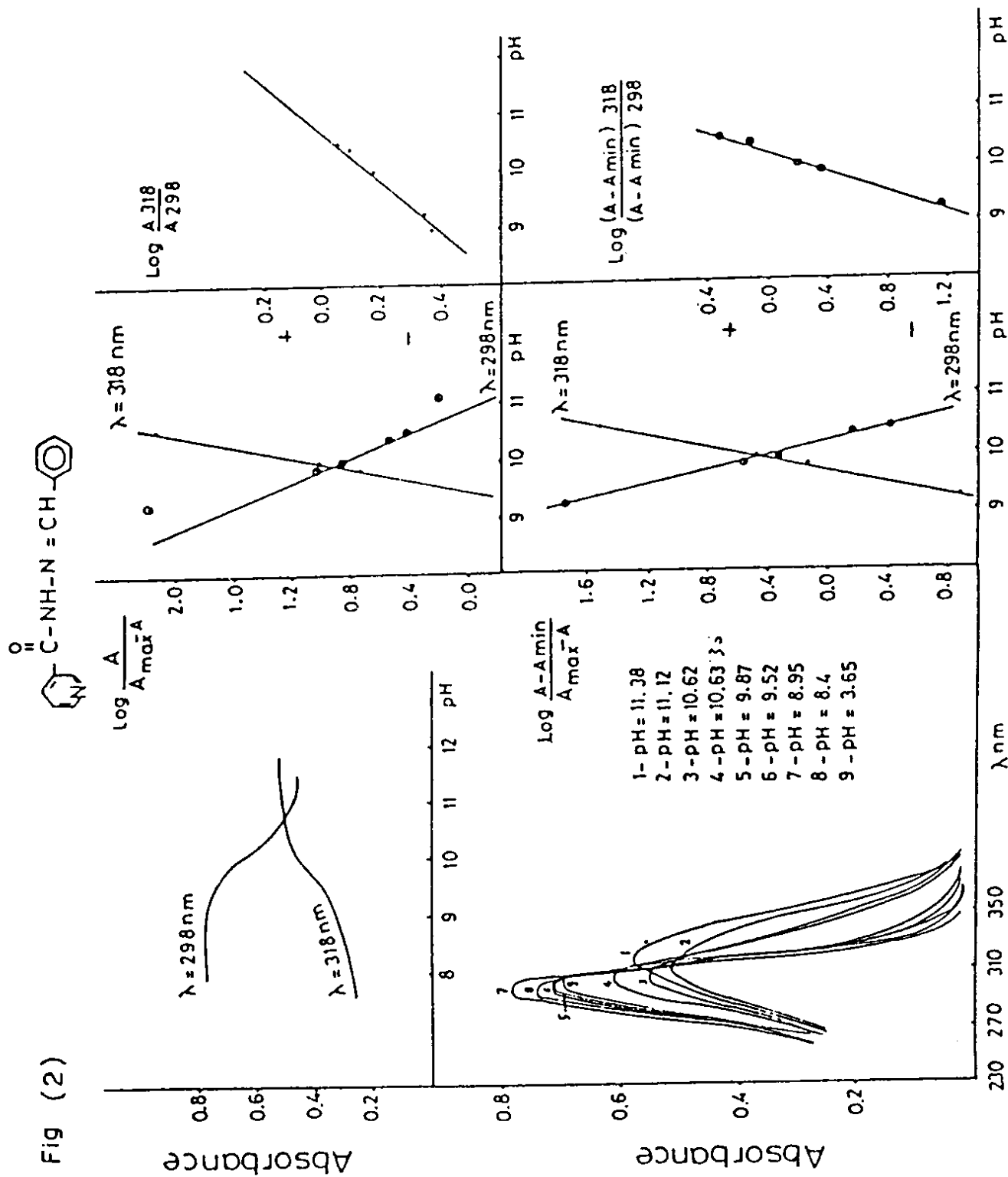


Table-II: The pK_a values of the arylidene derivatives of nicotinic hydrazone.

Comp.	Wave length		pK_a						Mean	G
	1 nm	2 nm	1	2	3	4	5	6	pK_a	K-Joule mole ⁻¹
I _b	324	376	9.90	9.96	10.00	9.75	10.15	9.70	9.91	2.999
I _d	272	350	9.78	9.77	9.80	9.80	11.05	9.95	10.025	3.034
I _e	304	338	10.25	10.15	10.45	10.20	10.90	10.05	10.33	3.127
I _f	294	320	9.99	10.13	10.05	9.80	10.55	9.85	10.06	3.045
I _g	298	350	10.70	10.95	10.95	10.55	11.40	10.45	10.75	3.252
I _h	307	350	11.28	11.18	12.30	10.30	12.05	11.30	11.40	3.450
I _i	298	318	10.00	10.07	9.90	9.95	10.70	10.20	10.14	3.067
I _j	300	347	11.00	10.45	10.45	10.80	11.50	10.65	10.88	3.292
I _k	304	330	10.20	10.33	10.40	10.30	10.85	10.25	10.39	3.144
I _m	312	358	10.35	10.21	10.65	10.25	11.70	10.40	10.593	3.2055
I _n	295	400	9.50	-	9.70	9.50	12.20	9.80	10.14	3.069
I _o	295	350	10.40	10.19	10.75	10.50	12.00	10.65	10.75	3.2524
I _p	315	350	9.10	9.28	9.30	9.05	9.30	8.85	9.146	2.788

1- Half height method. 2- Colleter method. 3- Limiting absorbance method.

4- Modified limiting absorbance method. 5- Isoabsorptive method. 6- Modified isoabsorptive method.

$$\rho(\sigma_x) = -0.45$$

$$\rho(\sigma_x^+) = -0.12$$

more observed being replaced by the C=N band and those for the arylidene ring. The bands due to the pyridine nucleus are but slightly influenced by changes of the substituent on the arylidene ring, while that of the arylidene ring show the common trends for changes of position and nature of the substituent (x). All the bands due to the (-C-NH-N=CH) part are influenced by the nature of the substituent on the arylidene ring. The

C=O and C=N bands shift to lower wavenumbers with increased donor character of the substituent, while those of the C-N and N-N display the counter shift.

The shift is actually governed by charge migration from the arylidene ring which affects the intramolecular charge transfer from the amide nitrogen to the C=O group.

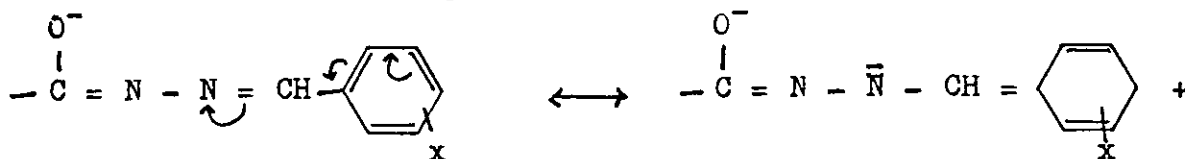


Table-III: Band Assignments of nicotinic hydrazide and some of its arylidene derivatives.

Compound	ν_{NH}	$\nu_{\text{C=O}}$	$\nu_{\text{C=N}}$	ν_{NH}	$\nu_{\text{C-N}}$	$\nu_{\text{N-N}}$	γ_{CH} (benzene)	γ_{CH} (pyridyl)
I _a	3220	1670	-	1545	1230sh	1190sh	-	888 835 710
I _b	3230	1640	1625	1540	1232	1150	-	805 835 750 705
I _c	3170	1645	1635	1560	1220	1150	890	805 730 710
I _d	3220	1650	1640	1545	1215	1150	-	795 750 845 - 710
I _e	3240	1660	1655	1560	1215	1165	-	845 820 915 - 710
I _f	3480	1660	1615	1560	1220	1150	890	825 - 704
I _g	3180	1650	1630	1565	1218	1155	-	895 730 850 762 710
I _h	3180	1640	1630	1545	1218	1140	-	845 820 915 - 708
I _i	3250	1645	1668	1545	1220	1190	-	755 690 915 735 705
I _j	3230	1650	1640	1560	1230	1170	895	795 780 945 735 700
I _k	3260	1655	1640	1545	1225	1170	-	850 815 915 732 715
I _l	3180	1635	1630	1560	1200	1150	-	825 735 845 770 705
I _m	3240	1670	1640	1545	1248	1170	-	830 810 920 770 710
I _n	3200+	1655	1635	1545	1195	1150	-	835 755 855 748 700
I _o	3100	1615	1605	1540	1240	1160	920	755 730 705
I _p	3200+	1640	1635	1570	1220	1165	-	860 820 910 - 705

p and p' values

sh = shoulder

p 14.1 16.7

p' 14.4 14.1

15.4

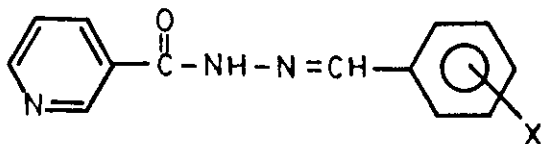
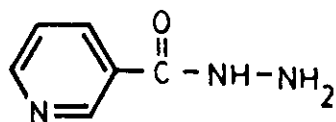
13.04

13.2

13.3

Table-IV

The ^1H nmr spectra of nicotinic hydrazide and some of its arylidene derivatives in DMSO.



Comp.	X	ppm					
		NH	OH	CH	other signals	Aromatic protons	
						benzene	pyridine
a	-	9.8	-	-	4.5 NH_2	-	9.1-7.4
b	<u>p</u> - NO_2	12.1	8.9	-	-	8.5-8.1	8.0-7.3
d	<u>o</u> - NO_2	12.1	8.9	8.6	-	8.3-7.9	7.8-7.2
e	<u>p</u> -Cl	11.8	8.8	8.6	-	8.4-7.9	7.8-7.2
f	<u>m</u> -Cl	11.9	8.9	8.6	-	8.4-7.8	7.7-7.2
g	<u>o</u> -Cl	12.1	9.0	8.7	-	8.3-7.5	7.4-7.1
h	<u>p</u> -Br	12.1	9.1	8.8	-	8.5-8.0	7.8-7.3
i	H	11.9	8.9	8.62	-	8.7-7.9	7.7-7.2
j	<u>m</u> - CH_3	11.9	9.0	8.7	2.3 CH_3	8.4-8.0	7.7-7.0
k	<u>p</u> - CH_3	11.8	8.9	8.6	2.1 CH_3	8.35-7.3	7.2-6.9
l	<u>o</u> - OCH_3	11.8	8.9	8.6	3.8 OCH_3	8.3-8.0	7.9-6.9
m	<u>p</u> - OCH_3	11.7	8.9	8.7	3.7 OCH_3	8.3-7.9	7.8-6.7
n	<u>o</u> -OH	12.0	8.9	8.6	11 OH**	8.35-7.4	7.3-6.6
o	<u>m</u> -OH	11.8	8.9	8.7	9.5 OH**	8.85-7.9	7.6-6.8
p	<u>p</u> -OH	11.7	9.0	8.6	9.8 OH**	8.4-7.9	7.7-6.6

* OH of carbinol imine form.

** Free OH group.

The plot of the wavenumbers for the different bands as a function of the σ -Hammett or $\sigma_{\theta, X}^*$ are linear relations with negative slopes for all bands. The ρ -values are given in Table-(III).

III. The ^1H nmr Spectra:

The proton nmr spectra of the compounds under investigation were

measured in d^6 -DMSO. The main signals of such compounds are collected in Table-(IV).

The spectrum of nicotinic hydrazide exhibits the multiplets for the pyridine nucleus within the δ 7.4-9.1 ppm range with integration corresponding to four protons. The NH-group leads to a broad singlet at δ 9.8 ppm with integration equivalent to one proton. This signal is shifted

to down field near δ 12 ppm, in the spectra of the arylidene derivatives. The NH_2 -group leads to the broad signal at δ 4.5 ppm with integration corresponding to two protons.

For the arylidene derivatives, the signal for the NH_2 -group is no more observed while that of the NH proton is shifted to the range δ 11.7-12.1 ppm as result of the lower shielding effect of the C=N group. The proton of the azomethine group shows a sharp (or broad in some cases) signal near δ 9 \pm 0.1 ppm which is not influenced by the addition of D_2O . The multiplets at δ 6.6 - 8.8 ppm are assigned of the aromatic protons of both arylidene and pyridine rings.

The ^1H nmr spectra of compounds (n), (o) and (p) show a sharp signal at δ 11.0, 9.5 and 9.8 ppm respectively which is assigned to the proton of the OH-group; this signal disappears on deuteration. The shift of the signal of (n) to down field is due to the contribution of the OH group in an intramolecular hydrogen bonding with the azomethine group.

The spectra of compounds (j) and (k) show sharp signals at δ 2.3 and 2.1 ppm respectively, which are characteristic of the protons of the CH_3 group while the OCH_3 groups of compounds (l) and (m) lead to sharp signals at δ 3.8 and δ 3.7 ppm respectively.

The position of the NH-signal is found to vary with the nature of the substituent on the arylidene ring. Generally, the signal is shifted to higher δ -value with increased acceptor character of the substituent (x) and decrease with donor one. This shift with changes of substituent (x)

reveals that the variation in the electron density on the arylidene ring is transferred to the amide group through the azomethine nitrogen.

The plot of the position of the NH and =CH signals as a function of the σ -Hammett or σ_{θ}^* constants are satisfactory linears with ρ -values amounting to 0.34 and 0.13, 0.35 or 0.1 for the two signals respectively.

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