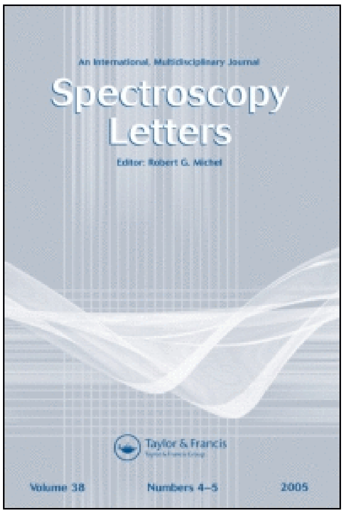

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Electronic Spectral Studies on Compounds Containing Nitroso Group

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ELECTRONIC SPECTRAL STUDIES ON COMPOUNDS CONTAINING NITROSO GROUP

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Abstract- The electronic spectral properties of several compounds containing nitroso group (4-bromo-2-nitrosophenol,4-aldehydo-2-nitroso phenol,4-acetyl-2-nitrosophenol,4-carboxy-2-nitrosophenol,nitroso-pyrogallol,nitoso salicylic acid and nitroso gallic acid) were investigated in presence of different solvents and different pH's. The pK's values were determined and related with the molecular structure of the compounds. The electronic transitions and the nature of the hydrogen bond were assigned . The phenomena of tautomerism was explained.

INTRODUCTION

One of the most outstanding aspects of recent chemistry is the investigation on model compounds which for their electronic configuration and coordination geometry exhibit reactivity pattern. In our laboratory, Masoud etal(1-12) made a considerable interest on the chemistry of the potential ligands containing the "hard" atoms nitrogen and oxygen in nitroso compounds.

In a sequel of continuation of studies , it is felt to study the electronic spectra of several compounds containing nitroso group in presence of different solvents and different pH's . The major objective of such work lies in the following: i) evaluation of the pK's values and relating with the molecular structure of the compounds, ii) assigning of the electronic transitions, iii) explaining the

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** Abstracted from her M.Sc.thesis .

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phenomena of tautomerism, iv) illustrating the type of hydrogen bonding exists.

EXPERIMENTAL

Synthesis of ligands

They were prepared by direct nitrosation(13) of the parent phenols(4-X-phenols, X= $-CHO,-Br,-COOH,-COCH_3$;pyrogallol;salicylic acid and gallic acid).

Preparation of stock solutions of the ligands

10^{-3}M-stock solutions were prepared by dissolving the required weight of each compound in the proper solvent.

Buffer solutions

Universal buffer solution of pH range 2-12 was prepared as usual(14).

Purification of solvents

Ethanol and Dioxane were purified as reported(15,16) ,while DMSO and DMF were of a spectroscopic grade(BDH).

Instruments

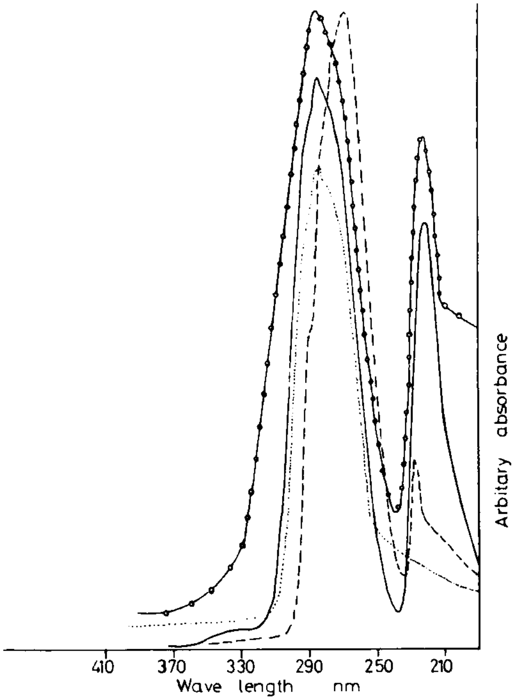
Pye Unicam pH meter model 291 MK 2 type was used for pH-measurements. The electronic spectra were recorded using Pye Unicam SP 1750 spectrophotometer. The nmr spectra were recorded using a EM-390 90 MHz NMR spectrometer in presence of deuterated acetone as a solvent.

RESULTS and DISCUSSION

Effect of pH on the electronic spectra of the free ligands:

In all the ligands under investigation,the spectra indicate that the intensity and the band position and their numbers are pH dependent.

The electronic spectra of 1.2×10^{-4}M-4-bromo-2-nitroso phenol in pH range (2.04-9.22) gave two characteristic bands at 224, and 260 nm. At pH$>$9.22, a clear red shift occurs with the formation of two intense bands at 244 and 294 nm. Two isobestic points were found at 230 and 280 nm. The first one is due to the equilibrium



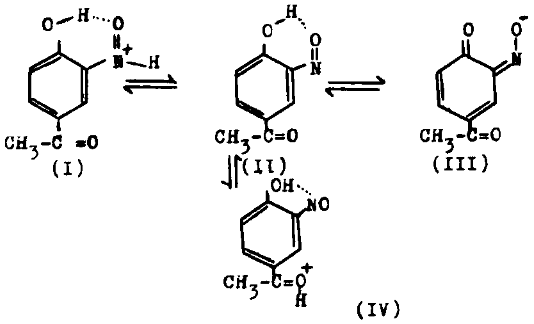
Figure(1). Effect of solvents on the electronic spectra of 4-aldehydo-2-nitroso phenol

—— Ethanol ·········DMSO

--- Dioxane -o-o- H_2O

between the protonized species and the neutral skeleton, while the second one is due to the equilibrium between the neutral and the oximate structure.

However the effect of pH range 2.10-6.70 on the electronic spectra of $1.636X10^{-3}M$-4-acetyl-2-nitrosophenol gave two bands at 270 and 480 nm. At pH$>$7.76, the 270 nm band is steadily decreased with clear red shift and formation of two bands at 330 and 540 nm. Four isobestic points are existing at 244,290,400 and 510 nm. Such observations give the idea for the existence of the following equilibria:

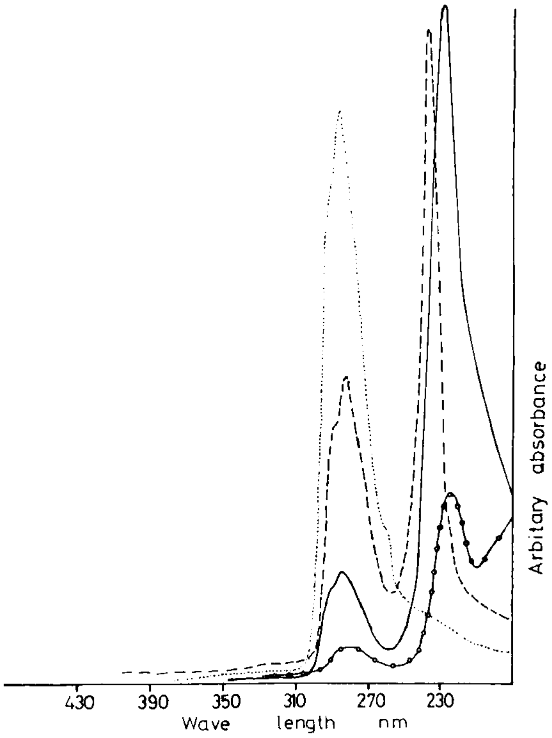


In 4-aldehydo and 4-acetyl-compounds, general trends are observed in both cases .Three isobestic points are appeared at 230,250 and 300 nm . Such isobestic points proved the existence of complicated equilibria .

The electronic spectra of $6X10^{-5}$M-2-nitroso-m-cresol in the pH range 2.02-5.10 gave only one spectral band at 300 nm .In the pH range 6-8,two bands are observed at 300,and 394 nm,denoting the existence of both tautomers (nitroso $\rightleftharpoons$ ketooxime) . The increase of pH showed that the 300 nm band is steadily decreased , while the 394 nm band becomes more intense due to the formation of the oximate structure .Two isobestic points are appeared,at 260 and 340 nm. The data indicate the nitrosophenol structure occurs at low acidities, and the ketooxime skeleton is built at higher alkalinities.

The electronic spectra of $6X10^{-5}$M-4-carboxy-2-nitrosophenol in the pH range (2.00-5.00) gave three bands at 238,278,and 342 nm. On increasing the pH above 5, the 238 nm band disappears, while the 278 nm becomes more intense. Three isobestic points are appeared proving the equilibria between the protonated,neutral and the oximate skeleton.

The electronic spectra of nitroso pyrogallol and nitroso gallic acid compounds are of complicated equilibria, due to their relative slight bulkness .The lower wavelength region can be ascribed to $\pi-\pi^*$ transition while that at longer wavelength side can be related to the anionic forms. This change can be ascribed to easier excitation of π-electron system leading to a higher delocalization of the electron clouds on the rings. The nature of electronic transitions in hydrogen bond of different phenolic compounds were deeply

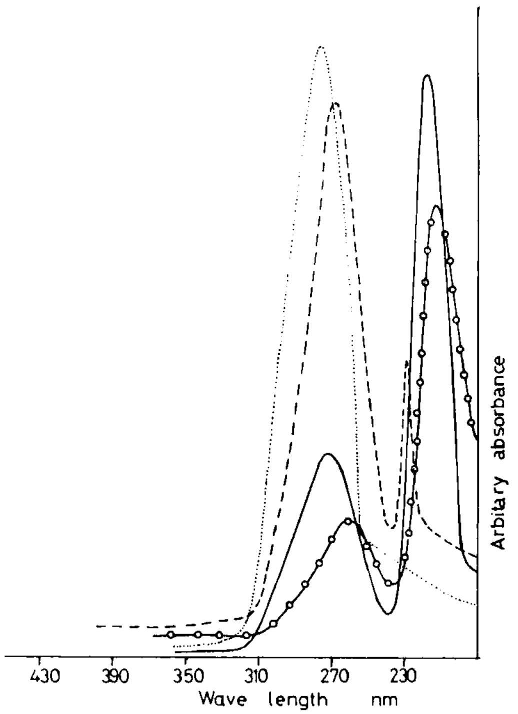


Figure(2). Effect of solvents on the electronic spectra of 4-Bromo-2-nitroso phenol

—— Ethanol ·········DMSO

– – – Dioxane —o—o— H_2O

investigated and the hydrogen bond energies for ground and excited states and the factors responsible for hydrogen bond effects were discussed in detail(17). The electronic spectra of 8 X 10^{-5}M-nitroso pyrogallol in the pH range 2-5, two bands are appeared at 278 and 322 nm in a weak and strong features respectively. In solution of pH range 5-8, a new band is apparent with λ_{max} 330 nm. The intensity of such band increases with increasing pH. At pH 9, two bands are formed at 330 nm, with the reformation of the 322 nm band. The intensity decreases with further increase of pH up to pH 12.8 .In strong alkaline solutions (pH 12.8), a noticeable band is apparent

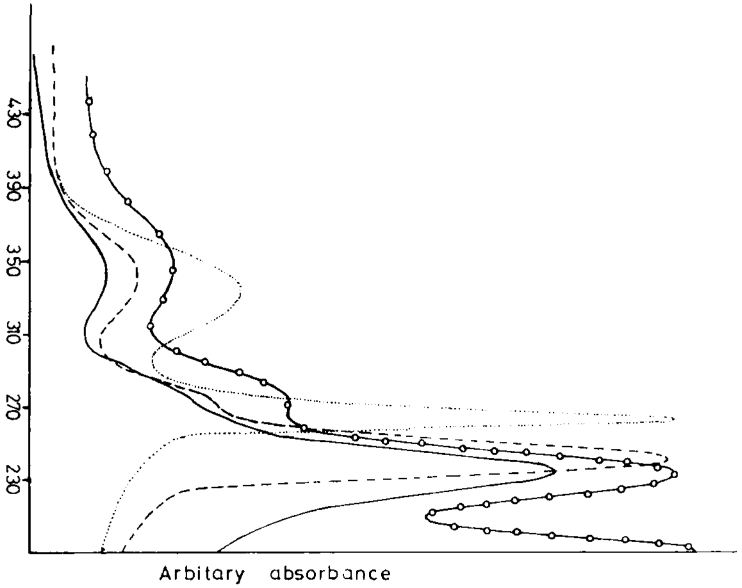


Figure(3). Effect of solvents on the electronic spectra of nitroso-Gallic acid

—— Ethanol .... DMSO
- - - -Dioxane —o—o— H_2O

at 442 nm. The non-existence of clear isobestic points interprett the overlapping of the absorption of the different species exist. Such data explain the acid-base properties of the compound.

The electronic spectra of 8 X 10^{-5}M-nitroso-gallic acid in the pH range (2.10-7.80) gave two characteristic bands at 220 nm,and the other in the wavelength range 260-274 nm.The first is sharp and the second is broad .On increasing the pH from 2.10 to 7.80, the former band becomes more intense, while the later one undergoes a regular bathochromic shift on increasing the pH. Above pH 7.8, both bands become less intense. Three isobestic points are appeared at 232,264,and292 nm.



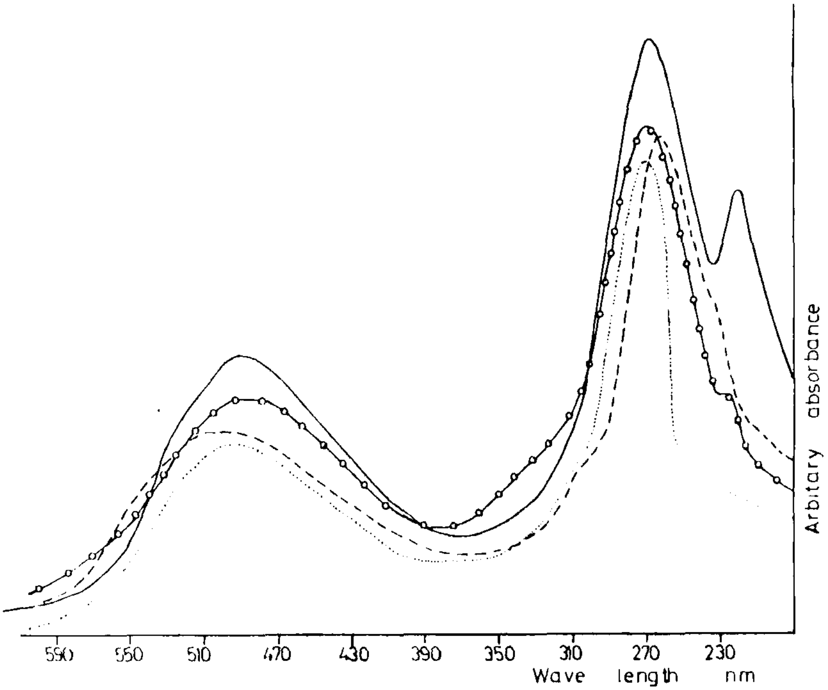
Figure(4) Effect of solvents on the electronic spectra of 4-Carboxy-2-nitroso phenol

— Ethanol ·····DMSO
--- Dioxane -o—o- H_2O

In all these compounds ,it is apparent that regular bathochromic shift occurs with pH. The obtained spectral bands at lower wavelength are assigned to the nitroso absorption while that at longer wavelength is due to the oximate skeleton . The later occurs in alkaline solution . The site of protonation calls for comments. Two atoms are available for H^+, namely oxygen and nitrogen. However, the oxygen-nitroso is in hydrogen bonding structure, so the nitrogen atom is ready for H^+ to give the protonised species.

Evaluation for the dissociation constants spectrophotometrically:

Different methods are used for such purpose depends on the studies based on the effect of pH on the electronic spectra. These methods are: half-height(18), limiting absorption(19), and



Figure(5) Effect of solvents on the electronic spectra of 4-Acetyl-2-nitroso phenol

— Ethanol ·······DMSO
---Dioxane —o—o— H_2O

Colleter(20). The data are collected in Table (1). The obtained pK's values are related with the molecular structure, where :

1. The average pK value for nitroso-m-cresol is found to be 7.14 This value is smaller than that of the parent m-cresol which is of the phenol family. The phenols(21), in general, are of pK$\sim$10. The decrease in pK's could be attributed to the electron attracting property of the nitroso group.

2. The decrease in the pK value for the 4-bromo-2-nitroso phenol (9.54) to that of the parent phenol(10), is highly related to the electronegativity of the bromine atom.

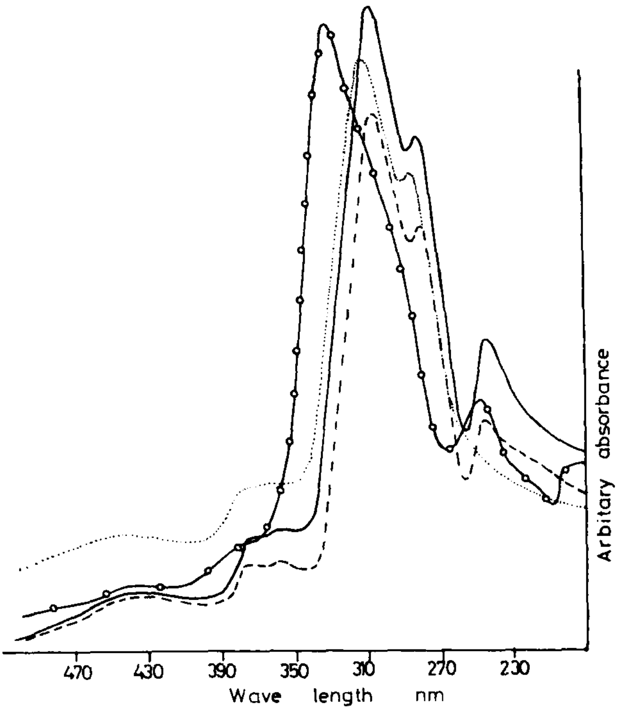
3. Similarly, the electron attracting property of the C=O group leads to lower the pK value of the parent phenol (10), to be 7.39

Table 1: Summary for the obtained pK's values spectrophotometrically

Ligand	Half height	Limiting absorbance	Colleter	Average pK
Nitroso-m-cresol	7.10	6.97	7.16,7.30,7.17	7.14±0.1
4-acetyl-2-nitroso phenol	3.65		7.60,7.10,7.56	7.61±0.33
	7.90	7.90		
4-bromo-2-nitroso phenol	9.60	9.50	9.31,9.80,9.49	9.54±0.18
Nitroso-pyrogallol	5.60	5.40	5.16,5.80,5.66	5.52 ±0.25
	9.80	9.80	9.40,9.32,9.90	9.64±0.26
Nitroso-gallic acid	4.05	4.05	3.38,4.20,4.14	4.06±0.30
	6.90	6.90	6.50,7.18,6.48	6.80±0.30
	10.50	10.45	10.9,10.09,10.40	10.47±0.29
4-carboxy-2-nitroso phenol	3.65	3.65	4.00,3.45,3.36	3.62±0.25
	6.40	6.40	6.08,6.16,6.33	6.27±0.15
4-aldehydo-2-nitroso phenol	7.40	7.40	7.34,7.30,7.55	7.34±0.10

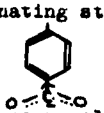
and 7.61 in case of the synthesized 4-aldehydo-2-nitrosophenol and 4-acetyl-2-nitrosophenol compounds, respectively.

4. In case of pyrogallol system: pyrogallol is controlled by -I and +M effects in the ground state. On reaction in the nitroso compound , +M and +E are strongly coupled to give two pK's values: 5.52 and 9.64. The -OH group is an electron donor by +M and -I leading to that the third proton cannot be ionized easily due to the presence of strong intramolecular hydrogen bond. In the same time the -OH group facilitates the proton removal from one of the adjacent -OH groups. The introduction of a -COOH group to give the corresponding gallic acid system leads to give three pK's values for the nitroso gallic acid compound : 4.06, 6.80 and 10.47, compared to that the gallic acid itself with a pK value of 4.41. The well known chemistry of the -COOH group is that it

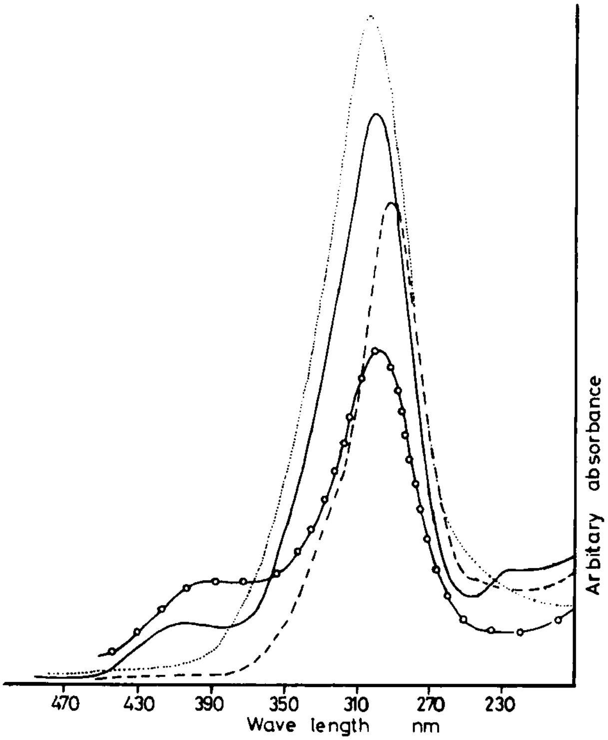


Figure(6). Effect of solvents on the electronic spectra of nitroso-pyrogallol

possess electron attracting properties to decrease the pK of -OH i.e. the intramolecular hydrogen bond(22). Looking for the obtained data for nitroso gallic acid, the following is deduced: the pK value amounting to 6.8 is assigned to the ionization of the carboxy group. The unexpected pK value of the -OH group suggests that the -COOH group assisted the formation of strong intramolecular hydrogen bond ,i.e.the carboxy group probably behaves as an electron donor since it ionized through its resonating strucure:



5. In case of 4-carboxy-2-nitrosophenol compound,two pK's values are found to be 3.62 and 6.27,compared to 4.84 and 9.32 in case of



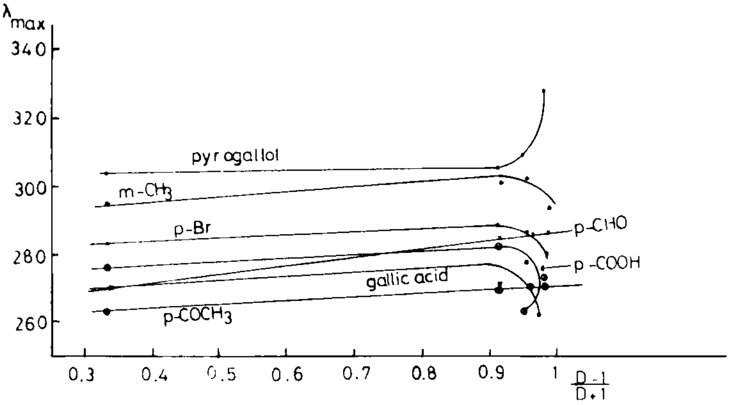
Figure(7). Effect of solvents on the electronic specta of nitroso-m-Cresol

— Ethanol ·······DMSO
---Dioxane -o—o-H_2O

4-hydroxy benzoic acid,and 4.21 in the parent benzoic acid. The Lower pK's values of the 4-carboxy-2-nitrosophenol compound is related to the electron attracting property of the nitroso group. The absence of a value corresponding to -OH,pinpoints to the existence of the oxime tautomer.

Effect of Solvents on the Electronic Spectra:

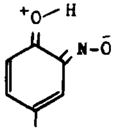
The absorption spectra of the parent phenolic compounds in the UV region are composed of two bands lying within the range 215-225nm and 270-300nm,that may be due to the local excitation of the π -system mainly of the aromatic rings giving π -π^*transition(L_a-A , and



Figure(8) λmax-D-1/D+1 relationship for free nitroso ligands

L_b-A respectively)(23). The ability of 2-nitrosophenols to form stable complex salts indicates that they contain an internal hydrogen bond to displace the B- and the K-bands of phenols to longer wavelengths. This is related to that the polarity in the absorbing system in the ground state is increased by polarization.The effect of an internal H bond on R-bands is in contrast to the B- and K-bands(24). In all solvents, 2-nitrosophenols exhibit the characteristic R-band of the nitroso group(673-715nm),i.e.they exist as the true nitrosophenol tautomer with the presence of small amounts of the oxime tautomer(25). The spectra of 1-nitroso-2-naphthol gave two bands of high and low intensities assigned as K- and B-bands,respectively(26). The C-nitroso group may be expected to show a weak band around 700nm due to $\sigma \rightarrow \pi^*$ transition(27). In all our ligands under investigation no any spectral bands could be located for such transition i.e. the electronic spectra data exclude $\sigma \rightarrow \pi^*$ transition. It is reported that the UV spectra of p-hydroxybenzaldehyde in ethanol gave two strong bands located at 230 and 300 nm(28). On comparing the electronic spectra for the latter compound to that of 4-aldehydo-2-nitrosophenol, in ethanol, remarkable features are noticed. These two bands 230 and 300 nm are blue shifted to be at 221 and 285 nm. Beside this a new band is formed at 338 nm, which is not existing in the parent phenol. This could be explained on the premise of the existing of the compound in the nitrosophenol form with the prediction of the existence of the oxime tautomer. However, the 338 nm band is absent in the other solvents.

The absorption spectra of 4-bromo-2-nitrosophenol, and nitroso gallic acid, in dioxane, ethanol, DMSO and H_2O, exhibit two bands lying within the range 221-236 nm, and 261-289 nm. The data are due to the local excitation of the π-system mainly of the aromatic rings giving π-π^* transition. In general the electronic spectra show that the latter nitroso ligands exist in solutions as the true nitrosophenol tautomer. The first band (221-236 nm) in both ligands is subjected to blue shifts on going from dioxane, ethanol, DMSO to H_2O respectively, indicating the existence of an internal hydrogen bond. This cannot be interpreted as a non-localized bond,i.e. a resonance hybrid is assumed to exist.The second band(261-289nm) is subjected to red shifts.In presence of hydrogen bonding solvents,a very small red shifted is apparent.This can be attributed to the predominant contribution of polar structures stabilized by solvent polarity,resulting in a bathochromic shift of the bands concerned.The solvation is a major factor to cause the appearance of new bands usually at higher wavelengths with a continuous shift to the red of the initial bands with increasing solvent polarity and hydrogen-bonding properties.



4-carboxy-2-nitrosophenol gave three electronic spectral bands in the wavelength range 234-242,264-282 and 335-347nm. The first band is absent in presence of DMSO. The former band may be due to the local excitation of the π -system mainly of the aromatic rings giving π -π^* transition. In all solvents,this compound exhibits the characteristic B- and K- bands(24).Also,the presence of an internal hydrogen bond is supported by the characteristic blue shift of its maximum in ethanol and water,respectively(24). The presence of the oxime tautomer is confirmed by the appearance,in all solvents,the expected K-band in the region 335-347nm. Similarly, 4-acetyl-2-nitrosophenol gave electronic spectral bands assigned to $\pi-\pi^*$ transition with the tracing of B- and K- bands.The assigned band for the nitroso tautomer is much stronger than that of the oxime to verify that this ligand predominates in the nitroso rather than the oxime.An internal hydrogen bond is indicated by the appreciable red shift of the electronic spectra in presence of non-hydroxylic solvents as compared with ethanol and water. This let to assume that the accumulation of the charge density on the nitroso functional group destructs the intramolecular hydrogen bond,to depict the

Table 2: λ_{max} for the nitroso ligands in different solvents

Ligand	Solvents			
	Dioxane	Ethanol	DMSO	H_2O
4-aldehydo-2-nitroso-phenol	226(s)	221(s)		222(s)
	270(s)	285(s)	286(s)	286(s)
		338(b)		
4-bromo-2-nitroso-phenol	236(s)	229(s)		224(m)
	283(s)	289(s)	286(s)	284(b)
4-carboxy-2-nitroso-phenol	242(s)	236(s)		234(s)
	276(sh)	282(w)	264(s)	276(sh)
	344(b)	347(b)	335(s)	344(m)
4-acetyl-2-nitroso-phenol		222(m)		226(w)
	264(s)	270(s)	270(s)	270(s)
	310(sh)		310(sh)	
	503(b)	492(b)	494(s)	486(b)
nitroso-m-cresol		230(w)		
	294(s)	302(s)	304(s)	300(s)
		411(b)		394(sh)
nitroso-pyrogallol	246(m)	245(m)		246(m)
	280(w)	280(w)	285(w)	
	304(s)	306(s)	310(s)	330(s)
	358(w)	360(w)	364(w)	
	378(sh)	378(sh)	380(sh)	378(sh)
	438(sh)	441(sh)	445(b)	438(b)
nitroso-gallic acid	230(s)	218(s)		214(s)
	270(s)	272(s)	278(s)	261(m)

sh = shoulder m = medium b = broad
s = strong w = weak

existence of the oxime tautomer. Nitroso pyrogallol gave bands lying within the range 245-246,280-285,304-330,358-364,378-380 and 438-445nm. The first region is subjected to slight blue shift,where the other regions are red shifted on going from dioxane,ethanol and DMSO, respectively. The first two regions may be due to the local excitation of the π -system mainly of the aromatic rings giving $\pi - \pi^*$transition. The 304-330nm express the nitroso tautomer,and the last three regions express the oxime tautomer. The second and the third regions should be comparible with the B- and K- bands,respectively. The hypsochromic displacement of the B- and K- bands containing an internal hydrogen bond in solvents from water to ethanol(24)might be due to a partial replacement of this bond by an external hydrogen bond of the solvent(24).Similar situation is apparent on discussing the electronic spectra of 2-nitroso-m-cresol.An internal hydrogen bond is probably present and this compound exists mainly in the nitrosophenol tautomer with the possible existence of the oxime skeleton in presence of ethanol.

The only property of the solvent which shows a reasonable degree of correlation with the transition energy is the dielectric constant. The plot of λ_{max} versus D-1/D+1(D is the dielectric constant of the solvent-H_2O,dioxan,dimethylsulphoxide and ethanol) gives linear relations in case of 4-aldehydo and 4-acetyl-2-nitrosophenols,where the dielectric force is predominant. Deviation occurs in presence of 3-methyl,4-bromo,4-carboxy-2-nitrosophenols,nitroso gallic acid and nitroso pyrogallol. This is an evidence to that a specific association occurs(24).

The results are collected in Table(2).

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