

Notes

Electronic & IR Spectra of Some 4-Arylhydrazono-3-(3'-pyridyl)-2-pyrazolin-5-ones

M. A. KHATTAB*† & F. A. AMER

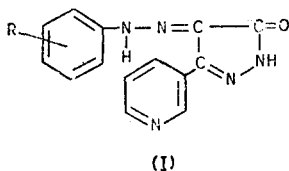
Chemistry Department, Faculty of Science, Mansoura University
A. R. Egypt

Received 16 April 1979; revised 22 November 1979; accepted
17 December 1979

The electronic absorption spectra of some 4-arylhydrazono-3-(3'-pyridyl)-2-pyrazolin-5-ones have been studied in organic solvents of varying polarities and in aqueous medium at different pH values. The spectral changes have been explained in terms of medium effect and molecular structure. The electronic shifts in buffer solutions are explained on the basis of an equilibrium between molecular and ionic species existing in solution. The dissociation constants have been determined from the variation of absorbance with pH.

IN an earlier publication¹ from our laboratories the results of studies on the electronic spectra of some hydrazones of 6-formyl-7-hydroxy-5-methoxy-2-methylchromone in organic solvent of different polarities were reported. The dissociation constants of these hydrazones in buffer solutions of varying pH values were also determined spectrophotometrically¹. Similar studies have now been extended to the title compounds.

The title compounds were prepared as follows: An ice-cold solution of 3-(3'-pyridyl)-2-pyrazolin-5-one (0.5 mol in 50 ml of pyridine) was treated with the cold diazonium chloride solution obtained from the appropriate amine (0.05 mol) and sodium nitrite solution (0.05 mol). The precipitated products (I_a-I_o) were crystallised from ethanol except those compounds derived from *o*- and *p*-nitroanilines which were crystallised from benzene-petroleum ether (40-60°C)



R=H(a), *p*-CH₃(b), *p*-OCH₃(c), *p*-NO₂(d), *p*-Cl(e),
p-Br(f), *p*-COOH(g), *o*-CH₃(h), *o*-OCH₃(i), *o*-NO₂(j),
o-Cl(k), *o*-COOH(l).

The solution for measurements were obtained by diluting 10⁻³M stock solutions in appropriate solvents (LR), purified by recommended methods². The buffer solutions were prepared as given by Britton³.

*Present address: Chemistry Department, Faculty of Science, Qatar University, Doha—Qatar P.O. Box 2713.

The electronic absorption spectra were recorded in ethanol, cyclohexane, ether, chloroform, carbon tetrachloride, dioxan and acetone on a Unicam SP 900 Spectrophotometer while the infrared spectra in KBr were recorded on a Unicam SP 2000 infrared spectrophotometer.

Electronic absorption spectra in ethanol comprise five absorption bands. The first band can be assigned to the $\pi-\pi^*$ transition within the aromatic rings corresponding to (¹L_a→A) level. In some compounds this band appears as a split band due to the resolution of the absorption bands of the two aromatic rings¹. The second and third bands appear as weak bands in the range 250-270 nm, only one band appears in compound IC, and represent absorption due to low energy $\pi-\pi^*$ transition of the aromatic rings (¹L_b→¹A). The band near 350 nm is a broad and composite one. It represents different types of transitions which may involve the $\pi-\pi^*$ transition of the carbonyl function and the $\pi-\pi^*$ transitions of the anil group influenced by charge transfer (CT) from the arylhydrazone system¹. The longer wavelength side, located in the range 390-440 nm is broad and solvent sensitive. It may correspond to a CT transition. The CT originates from the substituted phenyl ring to the carbonyl group by resonance and from the hetero ring by induction. The band is highly influenced by the nature and position of the substituent, the donor groups causing a red shift and acceptor ones a blue shift relative to the non-substituted compound (I_a). *o*-Substituted compounds show a blue shift which can be attributed to steric effects.

The spectra in different organic solvents indicate a weak solvent shift for the $\pi-\pi^*$ transition of aromatic ring, which is characteristic of electronic transitions within small parts of molecule. On the other hand, the CT band displays generally measurable shifts from polar to nonpolar solvents. The band is mostly shifted to lower energies with increased solvent polarity.

The IR spectra (ν_{max} in cm⁻¹) of the compounds exhibit ν_{NH} in the region 3150-3100 (±5) as a medium broad band. A strong band near 1670 can be assigned to $\nu_{\text{C=O}}$ (cyclic). The $\nu_{\text{C=N}}$ and $\nu_{\text{N=N}}$ are observed as shoulders near 1650 band 1640 respectively, with strong interactions with $\nu_{\text{C=O}}$. The band in the region 1605-1590 can be assigned to the benzene ring C=C skeletal vibration associated with the -NH-N= linkage in the 4-position on the pyrazolinone ring⁴. The band at about 1175 is very characteristic, and is slightly sensitive to the substituent (R). This band can be correlated with the heteroring-deformation vibration or the coupled vibration of the C-N and C-C linkages⁵. Strong or medium intensity bands are also observed in the range 1050-950. The position and intensity are relatively independent

of the nature of the substituent (R). The band can be tentatively assigned to the ring-breathing mode. A characteristic, strong or of medium intensity band at ~ 670 can be assigned to the ring deformation mode rather than for some fundamental modes of the other groups.

The spectra of the compounds in aqueous media show regular changes with pH of the medium, especially the CT band. The absorbance of the CT band decreases with increases in pH, meanwhile a new band develops at a shorter wavelength. Both the bands overlap to a large extent giving a very broad absorption band. At $pH \leq 8$ the original band vanishes and the new band only is observed. The spectra show a clear isosbestic point indicating the existence of an equilibrium between the non-charged molecules and ionized species. These equilibria correspond to proton elimination from the enol form. The plot of absorbance as a function of pH gives typical dissociation or association curve. These results are utilized for the determination of pK_a of the compounds employing (i) the half-height method⁶, (ii) the modified limiting absorbance method⁷, and (iii) the Colleter methods as modified for acid-base equilibria⁴. The mean pK_a values obtained are given in Table 1.

The position and extinction of the different absorption bands of the investigated compounds, are influenced by the nature of substituents. The observed λ_{max} changes in a more or less regular manner with the electron donor-acceptor character of the substituent (R). This fact finds support in the approximate linear correlation between λ_{max} and σ (the Hammett constant). Both λ_{max} and ϵ_{max} of the absorption bands seem to be readily influenced by the nature of the solvent used. The application of the Gati and Szalay⁹ equation reveals that the shift in band position is not essentially due to changes of the dielectric constant of the medium. Also, the dielectric functions given by Suppan¹⁰ are not valid

supporting that the role played by the dielectric constant of the medium is not the main factor responsible for the shift observed. The shift of the bands would thus be due to combined effect of several factors essentially the dielectric properties of the solvent and the specific solute-solvent interaction.

It is observed that $\nu_{C=O}$ (cyclic) shifts to lower frequency with increase in the value of Hammett's σ constant of substituent (R). Also, the plot of ν_{NH} versus σ (Hammett constant) is more or less linear. The relatively somewhat low values of the ν_{NH} may arise from possible intramolecular association through hydrogen bonding. Resonance through the molecule influences the bond order of C=N and N=N groups, consequently the frequency values of the two groups change in the same way.

The plot of pK_a as function of σ -constant is almost a linear relation, indicating the dependence of pK_a on the nature of the substituent. The values increase as the donor property of the substituent increases.

References

1. KHATTAB, M. A., ISSA, R. M. & KHALIFA, M. I., *Indian J. Chem.*, **15A** (1977), 962.
2. VOGEL, A. J., *Practical organic chemistry* (Longmans-Green, London), 1964.
3. BRITTON, H. T. S., *Hydrogen ions* Vol. I (Longmans-Green, London), 1952, 362.
4. YASUDA, H. & MIDORIKAWA, H., *J. org. Chem.*, **31** (1966), 1722.
5. KATRITSKY, A. R. & BOULTON, A. J., *Spectrochim. Acta*, **17** (1961), 238.
6. ISSA, R. M., *Egypt. J. Chem.*, **14** (1969), 17.
7. IBRAHIM, N. A., ISSA, R. M., ZAYAN, S. E. & EL-HEFNAWEY, G. B., *J. prakt. Chem.*, **314** (1973), 202.
8. COLLETER, C. R., *Anal. Acta*, **5** (1960), 415.
9. GATI, L. & SZALAY, L., *Acta phys. Chem. (Univ. Szegediensis)*, **5** (1957), 87.
10. SUPPAN, P., *J. chem. Soc.*, (1968), 3125.

A Study of [1,1] Padé Type Variational Function for Hydrogen as a Test System

K. V. SANE* & SUNIL SIKRI

Department of Chemistry, University of Delhi, Delhi 110 007

Received 28 January 1980; accepted 31 July 1980

A [1,1] Padé type variational function is shown to be superior to a linear variational function with the same number of parameters for 'strong perturbation' in the ground state of the hydrogen atom treated as a test system. Although considerably poorer than the [2,2] function studied earlier, the [1,1] function is nevertheless found to be sufficiently accurate to be useful—especially in view of its comparative simplicity—for such applications where high precision is not required.

THE summation¹ of the infinite order Brillouin-Wigner perturbation series subject of the "local energy gap" approximation has suggested the use of Padé type functions as trial functions for solving the Schrödinger equation by the variational method. Such functions have been employed so far with remarkable success on the hydrogen-like atoms treated² as a test system and on the ground state of the helium atom³. In the earlier study of the ground

TABLE 1 — DISSOCIATION CONSTANTS OF THE COMPOUNDS IN AQUEOUS SOLUTIONS

Compd.	$[\lambda_{max}$ in nm, ϵ_{max} in litre mol ⁻¹ cm ⁻¹ $\times 10^{-3}$]							
	Nonionic		Ionic		pK_a^*			
	λ_{max}	ϵ_{max}	λ_{max}	ϵ_{max}	(i)	(ii)	(iii)	Mean
I _a	425	7.3	380	3.4	7.85	7.60	7.95	7.8
I _b	440	8.2	385	7.6	8.40	8.40	8.45	8.4
I _c	456	6.5	390	3.2	8.70	8.70	8.90	8.8
I _d	430	—	390	—	5.40	5.30	5.50	5.4
I _e	420	9.7	370	8.4	6.50	6.20	6.20	6.3
I _f	430	—	390	—	6.85	6.70	6.85	6.8
I _g	450	—	360	—	6.60	6.55	6.65	6.6
I _h	436	7.6	384	5.6	8.35	8.35	8.45	8.4
I _i	452	2.1	384	7.4	8.50	8.40	8.65	8.5
I _j	430	—	390	—	6.80	6.80	6.80	6.8
I _k	415	10.2	380	8.1	6.20	6.25	6.45	6.3
I _l	425	—	384	—	6.15	6.10	6.05	6.1

* (i) Half-height method⁶

(ii) Limiting absorbance method⁷.

(iii) Colleter method⁸.