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SPECTRAL CHARACTERISTICS OF SOME ARYLAZOPYRAZOLONES

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Electronic, IR and ^{1}H NMR spectroscopy were made to investigate the role of the molecular structure and of the solvent polarity on the spectral properties of some arylazopyrazoline-5-ones. Based on the spectral shifts in pure organic solvents and buffer solutions, the absorption bands observed in the UV and visible spectra of the studied compounds have been assigned. The IR and ^{1}H NMR spectra confirmed that the compounds exist as hydrazo-keto structure. Further, the pk_a values were determined using spectrophotometric and potentiometric methods.

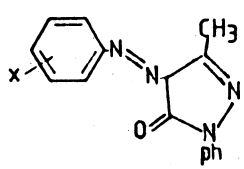
INTRODUCTION

The tautomeric structure of 4-arylazopyrazoline-5-ones has been extensively investigated. Various conclusions have been published concerning the structure of this class of compounds. Some authors have shown that these compounds exist mainly in the solid state and in solution as hydrazo-keto structure [1–3]. Others have proposed that the azo-keto structure was the predominant one[4]. Since little is reported about the spectral properties of the azopyrazolones in their solution state, it seems to be interesting to draw some general conclusions concerning the interaction of these compounds with organic solvents of different polarities or in buffer solutions of varying pH's.

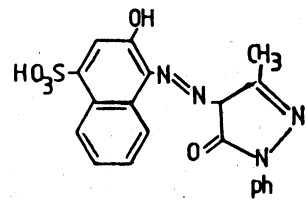
In the present investigation, the electronic, IR and ^{1}H NMR spectra of some arylazopyrazoline-5-ones containing simple or condensed ring systems were studied. This work has been made with the intention to assign the absorption bands to the possible electronic transitions as well as to collect more information concerning the structure of these compounds. Moreover, the acidity constants were determined and discussed.

EXPERIMENTAL

Arylazopyrazoline-5-ones under study were prepared from pure grade chemicals as previously described[5]. The structure of each compound was checked by elemental analysis. The prepared compounds have the structures:



Compound I-V



Compound VI

x = *o*-OH(I); *m*-OH, *p*-COOH(II); *o*-COOH(III); *p*-SO_3H(IV): *o*-CH_3(V)

The solvents used (EtOH, $CHCl_3$, CCl_4, DMF, cyclohexane) were spectral grade (BDH or E. Merck) products. The buffer solutions used for pH control were members of the modified universal series of Briton[6]. The pH values were checked by a Digital MV pH-meter accurate to ±0.05 units. The electronic spectra were recorded on a Shimadzo recording 240 spectrophotometer at 25°C using 1 cm matched silica cells. Infrared spectra in 4000-200 cm^{-1} region were obtained on a perkin-Elmer 599B i.r. spectrophotometer using KBr pellets of the sample. ^1H NMR spectra were determined on a EM 390-90 MHZ spectrometer using DMSO as solvent. Chemical shifts values are reported as (δ) ppm relative to TMS as an internal standard.

RESULTS AND DISCUSSION

Electronic spectra in pure organic solvents

The band maxima and the molar extinction coefficients obtained in the spectra of the compounds I-VI in organic solvents of varying polarities are given in Table 1 (Figs 1, 2). The recorded absorption spectra in ethanol exhibit mainly three bands. In the light of the spectra of azo-compounds reported before [7-9], it is possible to assign the shorter wavelength band (*ca.* 205 mm) to a π-π* transition of the pyrazolone ring system corresponding to the $1\,L_a \leftarrow 1\,A$ state, since its

TABLE 1
ELECTRONIC SPECTRAL CHARACTERISTICS* OF THE ARYLAZO-5-PYRAZOLONES I–VI IN ORGANIC SOLVENTS AT 25°C

Compound	EtOH		$CHCl_3$		CCl_4		Cyclohexane		DMF	
	λ_{max}	ε_{max}	λ_{max}	ε_{max}	λ_{max}	ε_{max}	λ_{max}	ε_{max}	λ_{max}	ε_{max}
I (*o*-OH)	204	23.7	—	—	—	—	—	—	—	—
	256	24.6	256	23.9	260	17.3	246	24.9	268	19.2
	428	08.2	422	08.7	420	08.9	408	08.4	438	09.8
II (*m*-OH, *p*-COOH)	266	23.1	256	19.5	248	25.2	246	24.9	264	16.7
	284	12.0	278	13.2	278	10.8	276	12.5	288	10.8
	404	22.0	398	26.6	396	23.4	394	26.0	412	18.6
III (*o*-COOH)	204	20.5	—	—	—	—	—	—	—	—
	258	18.2	258	16.0	256	16.2	250	16.7	268	11.5
	394	18.7	395	21.6	392	21.5	388	20.0	408	20.5
IV (*p*-SO_3H)	205	19.0	—	—	—	—	—	—	—	—
	250	19.5	248	12.0	250	08.2	230	21.7	265	12.0
	395	22.5	394	14.6	392	09.5	380	04.2	405	21.2
V (*o*-CH_3)	206	24.2	—	—	—	—	—	—	—	—
	257	25.0	256	20.0	260	16.5	250	25.5	264	26.0
	408	24.9	405	21.8	400	22.0	395	21.9	410	22.2
VI (*o*-OH, *p*-SO_3H)	248	23.7	250	15.5	260	15.0	242	24.0	270	15.1
	330 sh	07.7	324	06.5	320	05.8	310	06.5	342	07.2
	478	07.4	470	06.6	460	06.0	450	06.8	500	08.8

*λ_{max}, nm; ε_{max}, $gm.mole^{-1}\,cm^2$

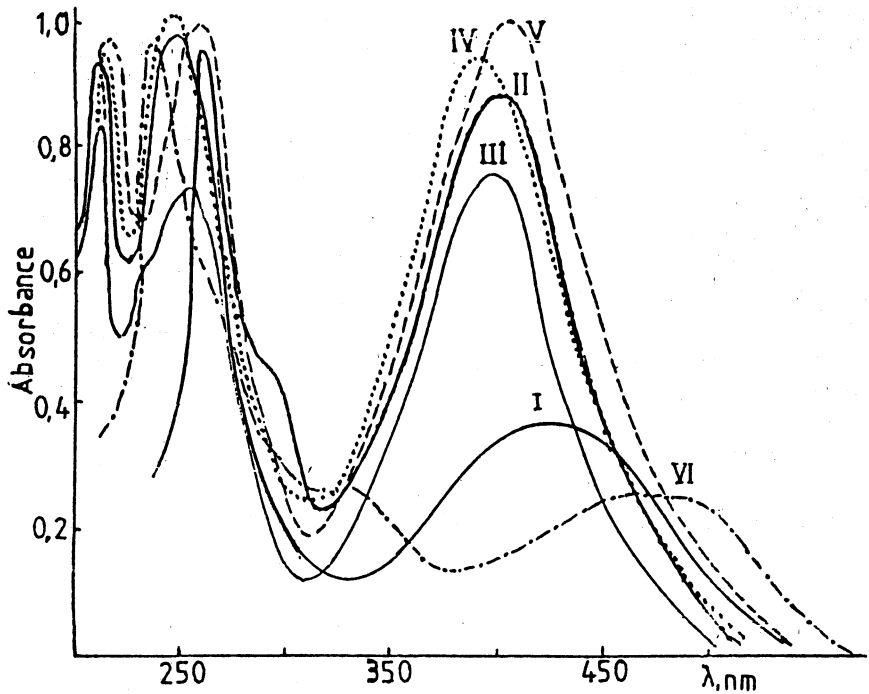


Fig. 1 Spectra of 4.0×10^{5} M of compounds I-VI in ethanol at 25°C

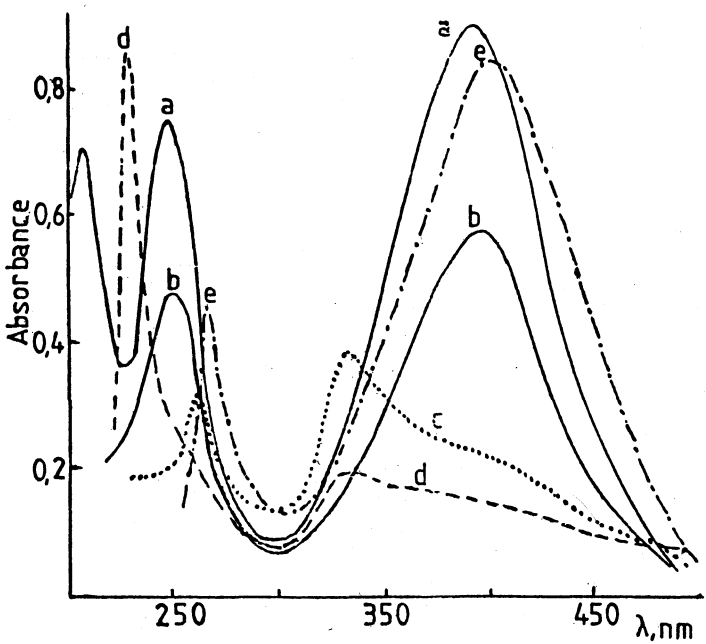
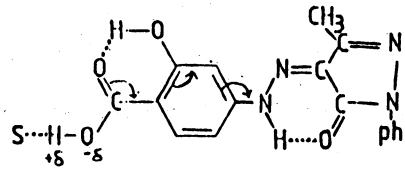


Fig. 2. Spectra of 4.0×10^{-5} M of compound IV in a—EtOH; b—$CHCl_3$; c—CCl_4; d—Cyclohexane; e—DMF.

position is slightly affected by the nature of substituent (X). The absence of this band in the spectra of compounds II and VI can be presumably attributed to its overlap with the second π-π^* band. The second band located within the range 248-266 nm is sensitive to substituent (X) and shows a slight red shift with increasing solvent polarity. Thus, it may be due to the low energy π-π^* transition ($1L_b \leftarrow 1A$ state) of the benzene ring. These two UV bands are characterized by high molar extinction coefficients. This is in agreement with the general properties of π-π^* transitions.

The shoulder observed within the range 276–288 nm, in the spectra of compound II in all solvents, can be ascribed to an intramolecular CT interaction within the possible intramolecular interaction between the *o*-COOH and *m*-OH groups of this compound[10]. The red shift observed for this band in proton acceptor solvents (DMF;EtOH), supports this assignment as it can be presumably attributed to the intermolecular H-bond formed between the solvent molecules(S) and the proton of the COOH group, as seen in the below scheme. This interaction leaves a residual negative charge on the oxygen of the carboxyl OH group, which increases its polarization, and thus, its donor character. Accordingly, the CT is enhanced and undergoes a red shift in proton acceptor solvents.



Moreover, an extra shoulder is observed in the spectrum of compound VI (X = *o*-OH, *p*-SO_3H) at 330 nm. Since this shoulder is highly sensitive to changing solvent polarity, it can be attributed to CT originated from the π electrons of the aryl moiety to the *p*-SO_3H group under the acceptor character of this group. This assignment is confirmed by the linear variation of the absorbance of this shoulder with the solute concentration. On the other hand, this type of CT will lead to decrease the charge density on the aromatic ring, which in turn enhances a second CT from *o*-OH group of the same compound to C=O group[11]. This is in line with the location of a second CT band for compound VI at longer wavelength (478 nm) than that for the other compounds.

The high molar absorptivity band observed in the region 404-478 nm can be attributed to an intramolecular CT transition within the whole molecule. This CT seems to originate from the X-phenyl moiety as electron donor center to the pyrazolone C=O group which acts as an electron acceptor. The position of this CT band is quite sensitive to the nature and position of the substituent (X). Generally, it has low excitation energy in compounds having an electron releasing substituents in *o*-position, since the latter acts as a donor center. On the other hand, in compounds having an electron accpting substituents (X) (II–IV), the CT band is located at lower wavelength than that in other compounds. This can be interpreted on the base that the compounds under study exist in solution as a chelated hydrazo-keto structure. Thus, one should expect that the λ_{max} of CT band for compounds having electron accepting substituents is blue shifted relative

to that having electron donating character as a result of decreasing the strength of the intramolecular H-bond existing between the hydrazo hydrogen and the carbonyl oxygen.

The results of solvent effect (Table 1) reveal that the CT band is characterized by high molar extinction coefficient in all solvents used. This can be considered as a convincing evidence for the possible existence of a chelated hydrazo-keto structure of the arylazopyrazolones studied, since the azo structure is characterized by low extinction coefficient π–π^* band[7,12]. Furthermore, the red shift observed in the position of the CT band as the solvent polarity increases support its assignment and can be ascribed to the stabilization of the polar excited state $-\bar{N}-H\ldots\overset{+}{O}$ by polar solvent molecules.

The data also show that, though DMF and EtOH have nearly the same basicity $\{pk_s=18.0$ and 18.9 $(\text{mol-dm}^{-3})^2$ respectively[13]$\}$, the CT band exhibits slight red shift in DMF relative to that in EtOH. This behaviour suggests that specific solute-solvent interaction rather than electrostatic ones, play important role on the electronic spectral behaviour of the investigated compounds. Thus the high possibility of the H-bonding formation with DMF rather than with EtOH, can be mainly attributed to the low ionisation potential of DMF (9.12 ev) relative to that of EtOH (10.49 ev)[14]. This reflects itself in an easier electron transfer from DMF oxygen atom to the antibonding molecular orbital of the hydrazo NH bond. On the other hand, the location of the CT band in DMF with its high molar absorptivity character, can be considered as an evidence for the hydrazo structure since the N–H ... O is the only possible solute-DMF interaction.

Electronic spectra in aqueous buffer solutions

Convincing evidence for the CT nature of the longer wavelength band, can be provided by studying the spectral behaviour of the compounds I–IV and VI

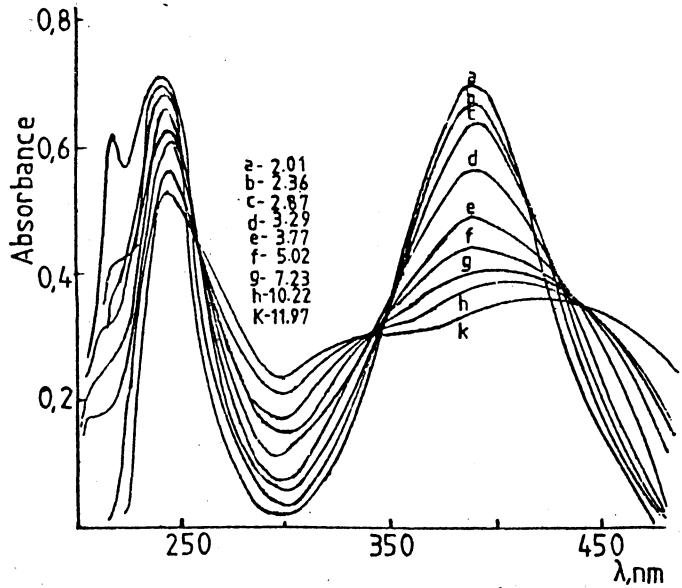


Fig. 3 Spectra of compound IV in aqueous universal buffer solution.

in aqueous buffer solutions of varying pH's (Fig. 3 as representative). Generally, the spectra are characterized by one main visible band. As the pH of medium increases, the extinction coefficient of this band decreases (compounds III and IV) or increases (compounds I, II and VI). Since the excitation responsible for this band is suggested to be CT interaction within the chelated hydrazone form, this behaviour can be explained on the base that CT interaction is difficult to occur in compounds containing electron accepting substituent (III, IV), while in case of I, II and VI, the CT interaction is facilitated as a result of high mesomeric interaction of the ionized OH group with the rest of the molecule. Moreover, as the pH is further increased above pH 10.22, the intensity of the band is decreased with slightly blue shift and then it is broadened. This may be due to the destruction of the intramolecular H- bond existing in these compounds.

The variation of absorbance of CT band with pH is utilized for determination of the pk_α values of the studied compounds applying different spectrophotometric methods[15]. It is worth mentioning that the ionisation of *p*-COOH (II) and *p*-SO_3H (VI) groups are not considered spectrophotometrically, since they do not cause any spectral changes in solutions of pH's ≤ 4.42. Similar behaviour has been observed before and attributed to the non-coplanar of COOH group[16] and non-conjugation of SO_3H group[17] with the rest of molecule. The pk_α values for COOH and SO_3H groups belonging to compounds II and VI are determined by potentiometric method. Also, the deprotonation of hydrazo moiety may be occurs at higher pH's, and thus, it is not possible to determine its value under the present experimental conditions.

The limit accuracy of the determined pk_α values are checked by making use of the least-squares method. The results are collected in Table 2 indicate that the pk_α value of *o*-OH group of compound I is higher than that of compound VI. Also, the pk_α value of SO_3H in case of compound IV is higher than that for compound VI. This is due to increase in the resonance interaction of naphthalene moiety, which leads to increase in the ionisation of the OH and SO_3H group of compound VI. Moreover, the pk_α value of *p*-COOH group for compound II is in the same range as *o*-COOH group for compound III. This can be attributed to the possible intramolecular H-bond formation between the OH and COOH (II) or between the COOH hydroxyl group and hydrazo hydrogen(III)

TABLE 2
MEAN pK_α VALUES OBTAINED FOR COMPOUNDS I–IV AND VI AT 25°C.

Compound	$pK_{\alpha1}$	$pK_{\alpha2}$
I	8.52 ± 0.03	
II	5.28 ± 0.05	8.07 ± 0.01
III	5.26 ± 0.04	
IV	3.56 ± 0.06	
VI	3.13 ± 0.02	8.12 ± 0.02

I.R. and 1H NMR spectra

The important IR and proton NMR spectral data of the major bands observed in the present work are listed in Table 3. The IR spectra of the solid compounds exhibit a band in the region 3420-2980 cm^{-1} which can be assigned to the intramolecular H-bonding NH or OH stretching vibration, since it is not easy to distinguish the two H-bonded forms. The very broad and weak nature of this band (undetectable in compound VI), makes the assignment to ν_{NH} mode more probable. The presence of this band in the spectra of IV and V (not contain OH group), can be considered as a further evidence for the ν_{NH} assignment. The strong band appears at 1658–1644 cm^{-1} rang, can be assigned to the pyrazolone $\nu_{C=O}$ mode in agreement with previous work[4,18] . The lower frequency shift of this band than that for simple 5-pyrazolones (*ca.*1710 cm^{-1}) suggests that C=O group is involved in intramolecular H-bonding. This lowering is increased in compounds containing electron donor substituents.

TABLE 3
IMPORTANT IR (cm^{-1}) AND ^1H NMR (ppm) DATA OF AZOPYRAZOLONES I–VI

Compound						Assignment
I	II	III	IV	V	VI	
(a) i.r. frequencies						
3080w	2980b	3000b	3420w	3400w	—	ν_{NH} strething
1650m	1650	1654s	1645m	1646s	1644w	$\nu_{C=O}$ stretching
1594s	1580	1577	1580s	1578	1590	$\nu_{C=N}$ stretching
1240s	1235s	1265s	1260s	1250s	1230	δ_{NH} deformation
(b) ^1H NMR signals						
2.3	2.3	2.4	2.2	2.1	2.4	δ_{CH_3} protons
—	—	5.2	4.8	—	—	δ_{NH} protons
7.1–7.8	7.1–7.9	7.2–8.0	7.1–8.2	7.2–7.9	7.1–8.3	δ ring protons
14.1	13.9	—	—	13.9	14.0	δ_{NH} protons

s, strong; b, broad; w, weak

The second strong band in the region 1594–1587 cm^{-1} may be unequivocally attributed to the stretching vibration of the C=N group since the aromatic ring vibrations appear in this region. Some authors assigned the band near 1570 cm^{-1} to the bending vibration of NH group (δ_{NH})[19]. Moreover the very strong band observed in the spectra of all compounds studied in the region 1230–1265 cm^{-1} is due to the deformation vibration of NH.

In view of the above IR observations, it is concluded that the studied compounds exist mainly in the solid state as hydrazo-keto structure. This point of view is confirmed by the ^1H NMR results (Table 3). Generally, the NMR spectra of the compounds show no signal in the 6.4 ppm region corresponding to the C_4 proton of pyrazolone moiety[20]. Except in case of compounds III and IV the low field signal observed, around 14.0 ppm can be assigned to the H-bonded hydrazone NH protons since the OH of azo-hydroxy form absorb at

around 9.2 ppm[1]. The large width and broad shape of this signal confirm its assignment. However, this signal is absent in the spectra of III and IV. This can be ascribed on the base that the hydrazone NH hydrogen of these compounds might not be involved in H-bond. This is reinforced by the appearance of a weak signal at 5.2 and 4.8 ppm in the spectra of III and IV respectively, which is attributed to the free hydrazone NH proton. Accordingly, it is suggested that the electron donating substituents enhance the stability of the chelated hydrazo-keto structure of the studied compounds.

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