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Preparation and Characterization of Some New Azoxine S Azo Dyes

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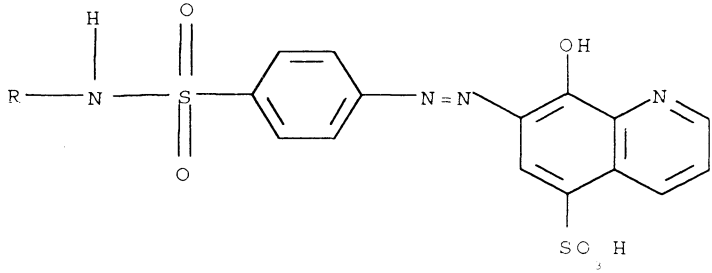
New azoxine S dyes were prepared by coupling some diazotized sulpha drugs with 8-hydroxyquinoline-5-sulphonic acid. Their structures were investigated using elemental analysis, IR and NMR absorption spectra and thermogravimetric analysis. The UV and visible absorption spectra of the prepared compounds were scanned in ethanol and the absorption bands were assigned to their electronic transitions. The UV and visible spectra were scanned also in different solvents of varying polarities and the relations between different solvent parameters and λ_{max} were plotted, but no linear relations were obtained; so there is no single parameter that affects spectral shifts. The ionization constants of the ionizable groups of the prepared azoxine S dyes were calculated spectrophotometrically using the half height and limiting absorbance methods.

INTRODUCTION

Though azo dyes were used extensively as analytical reagents either as chromophoric or metallochromic indicators, yet azo dyes containing 8-hydroxy quinoline-5-sulphonic acid (azoxine S) nucleus have paid little attention to analytical chemists. Phenylazo-8-hydroxyquinoline was first prepared[1] in 1988, after which much work on the preparation of these dyes has been carried out[2–4]. This includes the determination of their ionization constants potentiometrically[5,6] and photometrically[4,6,7]. Also, studies including the absorption spectra of these compounds were carried out[8].

The present work aims to prepared some new azoxine S dyes by coupling some diazotized sulfa drugs with 8-hydroxyquinoline-5-sulphonic acid, elucidate their structures applying various techniques, and determine their acid dissociation constants. The absorption spectra in different organic solvents were studied. The investigated azo compounds are represented as follows:



where R = 2-pyrimidyl (Ia), 4,6-dimethyl-5-pyrimidyl (Ib), 4-methyl-2-pyrimidyl (Ic), 5-methyl-3-isoxazolyl (Id), and amino imino methyl (Ie).

EXPERIMENTAL

The water used was always redistilled from all glass equipments. The chemicals used were always of the chemically pure grade. The azo dyes under investigation were prepared by coupling the diazotized sulfa drug with 8-hydroxyquinoline-5-sulphonic acid in sodium hydroxide medium[9]. The product was left in the refrigerator overnight and then acidified with dilute acetic acid. The resultant crude dyes were recrystallized from 50% (v/v) ethanol-water mixture three times. The purity of the prepared azo dyes was confirmed by elemental analysis. All compounds char at *ca.* 370°C.

The IR absorption spectra were obtained by applying the KBr disc technique using a Pye Unicam SP 3–300 infrared spectrophotometer. The nuclear magnetic resonance spectra (NMR) of the azo dyes were scanned using Bruker Wp 200 MHz NMR spectrophotometer. The thermogravimetric analysis (TG) was performed using Shimadzu thermal analyzer, where the weight losses of 5 mg sample were measured from room temperature up to 500°C at a rate of 10°C/min. The UV and visible absorption spectra were recorded with the aid of Perkin-Elmer Lambda 1 spectrophotometer.

The organic solvents used for spectral measurements were either spectroscopic pure (spectrosol) or purified by the recommended methods.[9]

RESULTS AND DISCUSSION

The following discussion is concerned with the investigation of the azoxine S sulfa azo dyes (Ia–Ie). The IR, UV and NMR spectra and thermogravimetric analysis (TG) of these dyes are investigated for the sake of identification of their structures. The electronic transitions of these dyes in some organic solvents of different polarities and the effect of solvent parameters are discussed. Also, the ionization constants of the dyes are determined spectrophotometrically.

Infrared studies

The IR spectra of the azoxine S sulfa azo dyes are scanned within the range 4000–400 cm^{-1}. The IR spectra of these dyes show a broad band at 3500–3460 cm^{-1} (Table-1) corresponding to the stretching frequency of the OH group (ν_{OH})[10]. The broad appearance may be due to its relatively low frequency and presence of a number of water molecules (as predicted from TG study). Another reason for the broad appearance of the OH-stretching frequency may be due to the existence of intramolecular hydrogen bonding; thus,

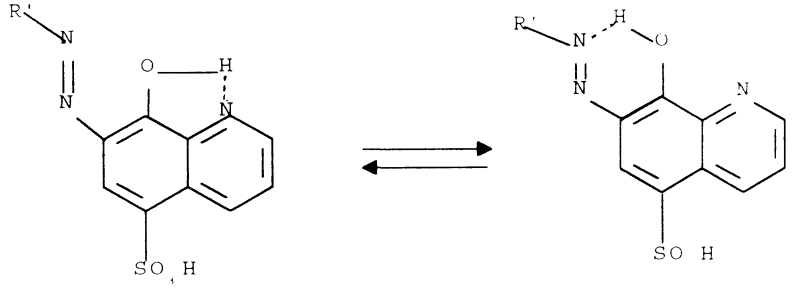


TABLE-1
BAND ASSIGNMENTS (cm^{-1}) OF IR SPECTRA OF SULPHA AZOXINE S AZO-DYES (Ia–e)

Band assignment	Ia	Ib	Ic	Id	Ie
ν(OH)	3500 vb	3500 vb	3480 vb	3460 vb	3460 vb
ν(NH)	3100 w	3100 w	3100 w	3100 w	3120 w
ν(C=C) skeleton vib.	1580 s	1590 s	1600 s	1590 s	1640 s
(overlapped with C=N)	1510 s	1510 s	1510 s	1515 s	1510 s
ν(N=N)	1450 w	1440 w	1400 w	1420 w	1400 w
ν(C—O)	—	—	1250 m	1250 w	1250 w
δ(OH)	1210 w	1210 w	1210 s	1210 w	1210 w
$\nu(SO_2)$	1150 s	1140 s	1135 s	1140 m	1135 s
ν(C—N)	1080 m	1070 s	1080 s	1090 s	1070 w
$\nu(SO_3H)$	1050 s	1050 s	1050 s	1050 s	1050 s
γ(CH)	800 s	850 s	775 s	825 w	825 w

vb: very broad, s: strong, m: medium, w: weak.

A weak band is shown in the range 3120–3100 cm^{-1} (Table-1), which may be assigned to the stretching of the NH group[10]. The shift to lower wave number and the weak nature of the band may be attributed to the formation of hydrogen bond with the neighbouring SO_2 group.

The two bands appearing at 1640–1580 cm^{-1} and 1510 cm^{-1} may be attributed to the overlapping of the bands due to C=C and C=N stretching vibration, which are so close that it is doubtful whether either can be regarded as retaining its individual character[11]. The band appearing at 1450–1400 cm^{-1} may be attributed to the N=N asymmetric stretching[10].

The compounds under investigation display, also, a band at 1150–1135 cm^{-1} attributed to stretching vibration of the sulphone group[12], a band at 1090–1070 cm^{-1} considered to be associated with ν(C—N)[10], and the band appearing at 1050 cm^{-1} may be attributed to the stretching vibration of the SO_3 group.

Nuclear Magnetic Resonance Spectra (^{1}H NMR)

The ^{1}H NMR spectrum of 8-hydroxyquinoline-5-sulphonic acid scanned using deuterated dimethyl sulphoxide as solvent and tetramethylsilane as internal standard comprises a group of signals at 9.0, 8.2, 9.8, 8.8 and 7.4 ppm (Table-2), which are assigned to H(2), H(3), H(4), H(6) and H(7), respectively, in addition to a broad signal at 4.4 ppm ascribed to the protons of quinolinic OH and sulphonic acid gorup.

The ^{1}H NMR spectra of the azoxine S azo dyes (Ia, Ib, Id and Ie) reveal the presence of a broad signal at 3.5–4 ppm which may be assigned to the protons

of the quinolinic OH, NH and sulphonic acid groups in addition to water molecules present in the dye molecule. The signal due to OH, NH and sulphonic acid groups disappear on deuteration, which confirms such assignment. The signal displayed at 7.0–9.0 ppm region may be assigned to the aromatic protons of sulfa and H(3) and H(8) of quinoline, while the signal at 8.9–9.8 ppm may be ascribed to H(2) and H(4) of the quinoline ring (Table-2).

TABLE-2
PROTON NMR SPECTRAL DATA OF THE INVESTIGATED SULPHA AZOXINE S AZO-DYES (Ia–e)

Dye	Chemical shift ppm	Assignment
Ia	3.5	SO_3H, OH groups and H_2O.
	7.0–8.6	Aromatic protons of sulpha moiety and $H_{(3)}$, $H_{(6)}$ of quinoline.
	8.9–9.2	$H_{(2)}$ and $H_{(4)}$ of quinoline.
	12	NH group.
Ib	3.5	NH, SO_3H, OH groups and H_2O.
	6.8	CH of the pyrimidine ring.
	7.7–8.3	Aromatic protons of sulpha moiety and $H_{(3)}$, $H_{(6)}$ of quinoline.
	8.9–9.1	$H_{(2)}$ and $H_{(4)}$ of quinoline.
Ic	4	NH, SO_3H, OH groups and H_2O.
	7.5–9.0	Aromatic protons of sulpha moiety and $H_{(3)}$, $H_{(6)}$ of quinoline.
	9.5–9.8	$H_{(2)}$ and $H_{(4)}$ of quinoline.
Id	3.5	SO_3H, OH groups and H_2O.
	6.2	CH of the five membered ring.
	7.7–8.2	Aromatic protons of sulpha moiety and $H_{(3)}$, $H_{(6)}$ of quinoline.
	8.9–9.1	$H_{(2)}$ and $H_{(4)}$ of quinoline.
	11.5	NH group.
Ie	3.5	NH, SO_3H, OH groups and H_2O.
	6.8	NH_2 group.
	7.7–8.4	Aromatic protons of sulpha moiety and $H_{(3)}$, $H_{(6)}$ of quinoline.
	8.9–9.1	$H_{(2)}$ and $H_{(4)}$ of quinoline.

The spectrum of Ib displays a signal at 6.8 ppm ascribed to the proton of the pyrimidine ring, whereas the spectrum of Id comprises a signal at 6.2 ppm ascribed to the hetero five membered ring of sulphamethoxazol. For Ie, the aliphatic amino group displays a signal at 6.8 ppm.

Thermogravimetric Analysis (TG)

It is of interest to mention that the results of elemental analyses were in agreement with the theoretical values only after assuming the existence of water molecules, a character which is mostly common to organic compounds containing sulphonic acid group[12]. Thus, thermogravimetric analysis (TG) is carried out to verify this assumption and to get information about the number of water molecules associated with the prepared dyes. The weight loss was measured from the ambient temperature up to 500°C applying a heating rate of 10°C/min. The results reveal the presence of three, five, two, five and six water molecules within the structure of the compounds Ia–Ie, respectively (Table-3).

TABLE-3
THERMOGRAVIMETRIC DATA OF THE INVESTIGATED SULPHA AZOXINE S AZO-DYES (Ia–e)

Dye	Weight loss %		Temperature range °C	No. of water molecules
	Calcd.	Found		
Ia	6.66	6.50	115	2
	3.30	3.00	140–220	1
Ib	5.95	5.70	100	2
	2.97	2.70	140–280	1
	5.95	6.00	280–300	2
Ic	6.39	7.00	100–210	2
Id	6.21	6.00	100	2
	3.10	3.00	140–190	1
	6.21	7.00	210–300	2
Ie	13.25	12.50	140	4
	6.22	6.50	270–300	2

The loss below 100°C is attributed to the moisture and hygroscopic water, since the azoxine S dyes are hygroscopic in nature. The number of these water molecules ranges from 2 to 4 per dye molecule as indicated by the per cent weight loss below 100° or 140°C.

Water molecules bonded to the sulphonic acid group are expelled in the temperature range of 150–300°C. For the dyes Ia, Ib and Id, one water molecule is expelled in the temperature range 140–280°C, while for dye Ie, two water molecules are removed at 280–300°C and 210–300°C for dyes Ib and Id, respectively. The results obtained are in good agreement with the results of elemental analysis.

The Electronic Absorption Spectra

Absorption Spectra in Ethanol: The electronic absorption spectra of the investigated azo compounds in ethanol display three bands (Table-4). The first band (band A) lying at 204–236 nm, may be assigned to the medium energy π-π^* transition within the phenyl ring (^1L–^1A)[13]. The location of such band at longer wavelength, in comparison with that for the benzene ring alone, is due to the increased delocalization of the π-system and hence the decrease of the energy gap between the two energy states. The second band (band B) observed within the wavelength 311–330 nm may be assigned to n-π^* transition within the quinoline moiety. This band is observed at 316 nm in case of 8-hydroxyquinoline-5-sulphonic acid which is taken as an evidence for the local nature of this band. A shoulder is observed within the range 400–415 nm, which may be assigned to n-π^* transition within the azo group. The third band (band C) lying at 481–500 nm may be assigned to π-π^* transition within the azo group influenced by charge-transfer interaction within the whole molecule.

Solvent Effect on Absorption Bands: Most investigations of the spectral properties of the molecules are performed in solutions. Consequently, the electronic spectra of azoxine S dye solutions are affected by the nature of the

TABLE-4
ABSORPTION BANDS OF SULPHA AZOXINE S AZO-DYES (Ia–e) IN ORGANIC SOLVENTS

Solvent	Ia			Ib			Ic			Id			Ie		
	A	B	C	A	B	C	A	B	C	A	B	C	A	B	C
Dioxane	—	311	485	—	311	485	—	318	484	—	315	485	—	311	490
Pyridine	—	321	484	—	322	494	—	320	481	—	320	490	—	321	492
			(8.8×10^3)			(9.6×10^3)			(1.06×10^4)			(1.1×10^4)			(2.0×10^4)
2-propanol	—	316	494	—	316	494	—	316	490	—	315	493	—	315	494
Acetone	—	328	491	—	329	493	—	329	491	—	330	491	—	325	498
Ethanol	204	316	492	204	315	492	221	316	493	205	319	493	205	316	492
DMF	—	317	494	—	319	496	—	320	500	—	317	488	—	319	494
Water	232	316	489	236	314	490	235	314	487	—	317	489	—	318	488
			(1.04×10^4)			(1.02×10^4)			(7.0×10^3)			(1.0×10^4)			(8.8×10^3)

*The values between brackets represent the molar absorptivities.

TABLE-5
IONIZATION CONSTANTS OF SULPHA AZOXINE S AZO-DYES (Ia–e)

Dye	λ_{nm}	pK_p			pK_{OH}			pK_{NH}		
		1st method	2nd method	Mean ±S	1st method	2nd method	Mean ±S	1st method	2nd method	Mean ±S
Ia	530	2.80	2.70	2.70	7.40	7.36	7.44	10.37	10.29	10.45
	500	2.55	2.70	±0.16	7.25	7.31	±0.19	10.40	10.34	±0.17
	320	2.92	3.00		7.75	7.61		10.59	10.74	
Ib	535	3.05	3.00	3.02	7.60	7.66	7.64	11.02	10.88	10.99
	505	3.10	3.10	±0.09	7.70	7.72	±0.06	11.02	10.94	±0.08
	347	2.90	2.95		7.55	7.61		11.12	10.97	
Ic	533	2.75	2.90	2.65	7.90	7.81	7.76	10.82	10.84	10.81
	504	2.80	2.65	±0.20	7.50	7.36	±0.27	10.65	10.69	±0.12
	334	2.35	2.50		8.10	7.90		11.00	10.87	
Id	530	2.40	2.50	2.40	7.55	7.61	7.67	10.85	10.94	10.93
	490	2.30	2.45	±0.09	7.75	7.66	±0.09	11.00	10.95	±0.05
	346	2.30	2.50		7.80	7.70		10.95	10.89	
Ie	533	2.55	2.70	2.72	7.10	7.20	7.08	11.97	10.78	11.84
	503	3.00	2.90	±0.18	7.15	7.01	±0.07	12.00	10.80	±0.11
	348	2.60	2.61		7.00	7.06		11.85	11.69	

Ist method : Limiting absorbance method.
2nd method : Half height method.
±S : Standard deviation.

solvent used. The solvent effect may lead to substantial changes in the optical properties and absorption maximum (λ_{max}). However, the absorption spectra in different solvents are influenced by the physical properties of the solvent (dipole moment, dielectric constant and refractive index), the difference in solvation energy from one solvent to another and the change in the polarity and dipole moment of the solute through excitation. Accordingly, the solvent effect is the sum of the different factors which may be additive or subtractive.

The absorption spectra of the azoxine S azo dyes under investigation were scanned in some organic solvents of different polarities such as dioxane, pyridine, 2-propanol, acetone, ethanol, DMF and water. The λ_{max} is plotted against the different solvent parameters as D[14], (D – 1)/(D + 1)[15], F(D), Φ(D)[16], π*[17], β[18] and Z[19]. All the plots are not strictly linear relations which may be taken as evidence that the spectral shifts are not governed solely by any of these parameters. Based on these results, the shift in band position would be attributed to combined effects of the dielectric constant, refractive index, change in the solvation energies of the ground and the excited states as, well as the probable formation of the solute-solvent molecular complexes. Another possible factor is the changes in the strength of the intermolecular hydrogen bonding governed by proton-donor acceptor interaction between solute and solvent molecules.

Spectrophotometeric determination of pK values

The ionization constants of the ionizable groups of the azoxine S dyes (Ia–Ie) are calculated spectrophotometrically using the half height and the limiting absorbance methods[20].

The absorbance-pH curves were plotted in three different regions at the selected wavelengths. The first one within the pH-range 1–6, which represents the deprotonation of the quinolinic nitrogen. The second, within the pH-range 6.0–9.5, which represents the ionization of the quinolinic OH group. The third, within the pH-range 10–12.77, represents the ionization of the NH group of sulfa moiety.

The results are treated statistically and the values are given in Table-5. From the table, it is shown that the values of the deprotonation constant of the quinolinic nitrogen (pK_p) ranges from 2.40 ± 0.09 for Id to 3.02 ± 0.09 for Ib. The ionization constant of the OH group (pK_{OH}) ranges from 7.08 ± 0.07 for Ie to 7.76 ± 0.27 for Ic. The ionization constant of the NH group (pK_{NH}) ranges from 10.45 ± 0.17 for Ia to 11.84 ± 0.11 for Ic.

REFERENCES

1. Matheus, *Ber.*, **21**, 1642 (1888).
2. D. Nardi, A. Tajana and E. Massarani, *Chem. Ber.*, **101**, 2285 (1968).
3. E. Gruszecka-Kowalik, R.D. Haugwitz and L.H. Zalkow, *Biochem. Biophys. Res. Commun.*, **187**, 1409 (1992).
4. H. Huang, F. Kai, M. Hirohata, M. Nakamura, S. Matsuzaki, K. Komori and Y. Tsunematsu, *J. Coord. Chem.*, **30**, 131 (1993).
5. A.L. El-Ansary, Y.M. Issa and I.M. Kenawi, *Microchem. J.*, **28**, 64 (1983).
6. H. Khalifa, Y.M. Issa, S.S. Badawy and I.M. Kenawi, *Egypt. J. Chem.*, **22**, 355 (1979).

7. Y.M. Issa, M.M. Khater, A.L. El-Ansary and S.S. Badawy, *Indian Text J.*, 95 (1983).
8. E. Uusitalo, *Suomen Kemistilechti*, **31B**, 264 (1958); *Chem. Abstr.*, **53**, 2778 (1959).
9. A.I. Vogel, Practical Organic Chemistry Including Quantitative Organic Analysis, 3rd Ed., Longmans, London (1989).
10. L.J. Bellamy, The Infra-red Spectra of Complex Molecules, Chapman and Hall, London, Chapter 6, p. 109 (1975).
11. J. Fabian, M. Legrand and P. Poirier, *Bull. Soc. Chim. Fr.*, 1499 (1956).
12. I.L. Finar, Organic Chemistry, Vol. 1, 6th Ed., Longman Group Ltd., London, pp. 405, 690 (1973).
13. G. Leandri, A. Mangini and R. Passerini, *J. Chem. Soc.*, 1386 (1957).
14. R.C. West, Hand Book of Chemistry and Physics, The Chemical Rubber Company, 60th Ed., Ohio, USA (1980).
15. L. Onsager, *J. Am. Chem. Soc.*, **58**, 1486 (1936).
16. P.J. Suppan, *J. Chem. Soc. (A)*, 3125 (1968).
17. M.J. Kamlet, J.L. Aboud and R.W. Taft, *J. Am. Chem. Soc.*, **99**, 6027 and 8325 (1977).
18. M.J. Kamlet and R.W. Taft, *J. Am. Chem. Soc.*, **98**, 377 (1976).
19. E.M. Kosower, *J. Am. Chem. Soc.*, **80**, 3253 (1958).
20. I.M. Issa, R.M. Issa, M.R. Mahmoud and Y.M. Temerk, *Z. Physik. Chem.*, **254**, 314 (1973).

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