

Spectrophotometric studies on some nitrosonaphthols

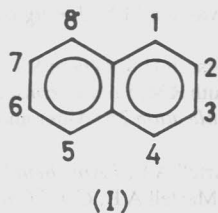
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Received 15 June 1988; revised 9 December 1988;
accepted 12 March 1989

The UV and visible absorption spectra of some nitroso naphthol derivatives have been studied in organic solvents of varying polarities. The dependence of the band shift on the nature of substituent, dielectric effect and specific solvation has been studied. The absorption spectra have also been studied in buffer solutions of varying pH values and the acid dissociation constants of the different ionisable groups have been determined using the half-height and the modified limiting absorbance methods. It is found that the nitroso substituent leads to a decrease in ionisation constants of the naphthalenic OH group.

Nitroso naphthols are widely used as analytical reagents¹⁻⁵. The electronic absorption spectra of some nitroso naphthols were studied⁶ in organic solvents. The present investigation deals with the UV and visible spectra of some nitroso naphthols in organic solvents of varying polarities and buffer solutions of different pH values. The aim of the present work was to study the dependence of band shift on the nature of substituent, dielectric effect and specific solvation.

The compounds under investigation have the general formula (I)



- (A) 1-OH, 2-NO, 4-SO₃Na (Nitroso Neville Winther's acid) (NNWA)
- (B) 1-NO, 2-OH, 6-SO₃Na (Nitroso Schaffer's acid) (NSA)
- (C) 1-NO, 2-OH, 3,6-SO₃Na (Nitroso-R salt) (NRS)
- (D) 1-OH, 2-COOH, 4-NO (Nitroso-1-hydroxy-2-naphthoic acid) (N1HNA)

- (E) 2-COOH, 3-OH, 4-NO (Nitroso-3-hydroxy-2-naphthoic acid) (N3HNA).

Experimental

Water used for preparing solutions was always twice distilled from an all glass equipment. All the chemicals were of CP grade. The nitroso naphthol derivatives were prepared and recrystallized by recommended methods^{4,7,8}. The solutions of nitroso compounds (10^{-3} M) were prepared by dissolving accurately weighed amounts in the required solvents. A series of buffer solutions covering the pH range 2.0-12.0 was prepared as recommended by Britton⁹. Measurements of pH values of partially aqueous solvents were carried out according to the method of Bate¹⁰. The spectra of the resulting solutions in the UV and visible regions were obtained at room temperature using a PYE UNICAM SP 1750 recording spectrophotometer. The solvents used, methanol, ethanol, isopropanol, cyclohexane, *n*-hexane and dioxan, were either of spectroscopic pure grade (spectrosol) from BDH or were purified using recommended methods¹¹.

Results and discussion

The electronic absorption spectra of the nitroso naphthols under investigation were recorded in organic solvents of different polarities such as methanol, ethanol, isopropanol, cyclohexane, *n*-hexane and dioxane.

The λ_{\max} values, the corresponding molar absorptivities (ϵ_{\max}) and oscillator strengths (f)¹² are listed in Table 1.

All the spectra exhibit a similar pattern showing mainly three transitions. The first band lying in the range 212-252 nm may be assigned to the medium energy π - π^* transition ($^1A \rightarrow ^1B_b$) within the naphthalene nucleus. The second band appearing in the range 254-290 nm may be attributed to the low energy electronic transition ($^1A \rightarrow ^1L_a$) within the naphthalene nucleus¹³. The band observed in the range 344-392 nm may be assigned to the transition ($^1A \rightarrow ^1L_b$), influenced by intramolecular charge transfer (Table 1).

One of the properties of the solvent, which shows a reasonable degree of correlation with the transition energy, is the static dielectric constant (D) or more precisely a function $f(D)$ or $\phi(D)$ ¹⁴ which leads to a linear relation if the dielectric constant is the only parameter governing the solvent shift.

Table 1—Electronic spectral data of (A-E) in different solvents

Compound	Solvent	${}^1A \rightarrow {}^1B_b$			${}^1A \rightarrow {}^1L_a$			${}^1A \rightarrow {}^1L_b$		
		λ_{\max} (nm)	$\epsilon \times 10^{-4}$	f	λ_{\max} (nm)	$\epsilon \times 10^{-4}$	f	λ_{\max} (nm)	$\epsilon \times 10^{-4}$	f
A	Ethanol	224	1.07	0.27	264	2.20	0.41	390	0.37	0.07
	Methanol	212	1.10	0.25	264	2.11	0.42	390	0.35	0.07
	Isopropanol	212	1.50	0.51	264	3.07	0.62	392	0.38	0.12
	Dioxan	—	—	—	264	2.03	0.41	392	0.53	0.11
B	Ethanol	222	2.20	0.46	268	1.87	0.48	370	0.38	0.12
	Methanol	228	1.90	0.52	268	1.90	0.54	370	0.43	0.13
	Dioxan	—	—	—	276	1.40	0.48	370	0.47	0.14
C	<i>n</i> -hexane	—	—	—	268	1.43	0.57	372	0.45	0.15
	Ethanol	226	2.70	1.14	272	1.82	0.57	376	0.60	0.17
	Methanol	228	2.47	0.58	274	1.88	0.61	372	0.62	0.17
	Isopropanol	224	2.20	0.78	270	1.47	0.49	372	0.50	0.17
	Dioxan	224	1.93	0.51	264	1.15	0.53	372	0.40	0.19
D	Ethanol	218	4.33	1.79	254	4.67	1.07	344	0.53	0.11
	Methanol	220	3.40	0.98	254	4.67	1.24	344	0.53	0.11
	Isopropanol	226	3.67	1.63	254	4.67	1.24	344	0.53	0.11
	Cyclohexane	224	3.13	1.14	256	4.77	0.87	364	0.52	0.11
E	Dioxan	—	—	—	256	4.40	0.52	364	0.53	0.11
	Ethanol	240	8.50	1.93	288	1.00	0.20	356	0.30	0.06
	Methanol	240	8.25	1.99	288	1.00	0.20	356	0.30	0.06
	Isopropanol	240	8.05	1.83	288	1.00	0.20	364	0.30	0.06
	Dioxan	252	5.80	0.87	290	1.10	0.22	372	0.30	0.06
	Cyclohexane	240	7.85	1.75	286	1.10	0.22	368	0.35	0.07
	<i>n</i> -hexane	242	5.05	1.13	288	0.55	0.11	368	0.10	0.02

$$f(D) = \frac{2(D-1)}{2D+1}$$

$$\phi(D) = \frac{D-1}{D+1}$$

The plots of $f(D)$ and $\phi(D)$ against the wave number ($\bar{\nu}_{\max}$ in cm^{-1}) are not strictly linear (Fig. 1) which indicates that the spectral shifts are not governed solely by the dielectric effect of the solvents. Other factors such as hydrogen bonding¹⁵ and complex formation between the solute and solvent molecules may influence the spectral shifts leading to increased solvolysis of the molecule. The observed shift is the net result of these different factors.

Effect of substituent

Compounds (I) A, B and C show more or less the same spectral behaviour (Table 1) except that the C.T. band (370-376 nm) is red shifted in the case of A, which may be attributed to the antagonising effect of the sulphonic group in position 4 of the naphthalene moiety on C.T. band (in positions 3 and 6 in the case of B and C).

The introduction of COOH group leads to variations in the previously mentioned three bands. The C.T. band is blue shifted, which may reflect the retarding effect of the COOH group on π -system of the molecule. This is supported by the shift of both ${}^1A \rightarrow {}^1B_b$ and ${}^1A \rightarrow {}^1L_a$ bands in two different directions depending on the position of nitroso group with respect to OH and COOH groups. These two bands were observed at longer wavelengths in the case of (I) E. This may be due to the variation of symmetry of the molecules as a result of variation of the positions of OH and COOH groups with respect to the NO group, i.e., electron density redistribution over the whole molecule. For (I) D, the red shift may be due to the increase in conjugation in the molecule and formation of H-bonding between OH group in position 2 and NO in position 1.

Absorption spectra in buffer solutions

The absorption spectra of the nitrosophthols in buffer solutions of varying pH values were recorded to investigate the spectral properties of the species liable to exist in such media and to determine the ionisation constant (pK) values of the OH groups.

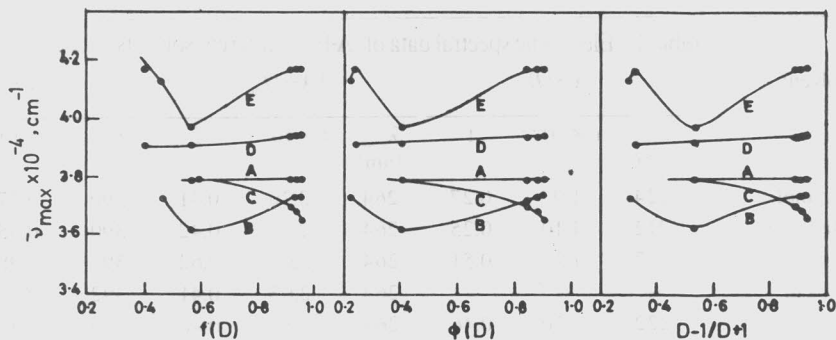


Fig. 1—Relation between $\bar{\nu}_{\max}$ of (A-E) and $D - 1/D + 1 f(D)$ and $\phi(D)$ of solvents of different polarities (methanol, ethanol, isopropanol, cyclohexane and *n*-hexane)

The absorption spectra of the investigated ligands in the pH range 2.0-6.0 are characterized by a strong band in the range 328-388 nm. This band is due to absorption of the nonionized form liable to exist in such solutions and may be assigned to $\pi-\pi^*$ electronic transition within the aromatic ring influenced by intramolecular charge transfer¹⁶. The spectra in alkaline solutions are characterized by the presence of two bands in the range 328-388 and 410-440 nm. The absorbance of the first band increases gradually with increase in pH attaining a maximum value in the pH range 8.0-12.0 for (I) A and B while it decreases gradually with increase in pH for the compound C.

The absorbance of the second band at longer wavelength increases gradually with increase in pH attaining a limiting value at pH 8.0-12.0 indicating that most of the acid form is transformed to its conjugate base.

The absorbance-pH curves (Fig. 2) are almost S-shaped with a sharp variation in absorbance within the pH range around the pK_a value of the ligand. The absorbance attains a limiting value at the extreme pH values in highly acidic or alkaline solutions indicating the existence of only one ionisation step which is ionisation of the naphthalenic hydroxyl group.

The variation of absorbance with pH was used to calculate the ionisation constants of the investigated ligands using (a) the half-height method¹⁷ and (b) the modified limiting absorbance method¹⁷. The values are given in Table 2.

The results obtained for NNWA, NSA and NRS are of the same order as those obtained potentiometrically¹⁸. The absorption spectra of N1HNA were measured in ethanolic (40% v/v) buffer solutions.

The ionisation of the strongly acidic carboxylic group or sulphonic acid group occurred at lower pH values due to the high stabilization of the corresponding anion by resonance. These substituents do



Fig. 2—Absorbance-pH curves of the ligand (A)

Table 2—Collective data of pK values for the investigated ligands from the spectrophotometric measurements

Compound	λ_{\max} (nm)	pK		Mean pK
		1st method	2nd method	
A	408	6.14	6.14	6.06
	428	6.10	6.08	
	448	5.80	6.12	
B	408	7.00	7.00	6.99
	428	7.00	6.97	
C	408	6.90	6.97	6.93
	428	6.90	6.93	
D	420	7.20	7.20	7.06, 4.06 (ref. 20)*
	440	7.10	7.04	
E	460	7.00	6.82	10.50, 3.95 (ref. 20)
	—	—	—	

*The ionization constant of the COOH group.

not produce any spectral changes¹⁹. The ionisation constants of such groups were previously determined potentiometrically²⁰.

In the ligands (A-C) the effect of the negative sulphate group on the ionisation of OH group may

be attributed to the electrostatic charge, the mesomeric, and the inductive effects. The electrostatic effect of the negative sulphonate group retards the ionisation of the OH group in ligands (A), while both mesomeric and inductive effects increase the acid strength. The mesomeric effect is predominant especially when the sulphonate group is located in *para*-position to the hydroxyl group. Thus, ligand (A) is clearly characterized by the lowest pK_a value. Generally, the introduction of nitroso group in the investigated ligand led to a decrease in the ionisation constants in comparison with those of the non-nitroso ligands¹⁸.

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