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Studies on Diazo Type Process. VII. Electronic Spectra of 2-(Substituted phenylazo)-1-naphthol-4-sulfonic Acid

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The absorption of 2-(substituted phenylazo)-1-naphthol-4-sulfonic acid has been studied in neutral, acidic, and alkaline aqueous solutions as well as in solid state. Assignment of band positions to azo and hydrazone tautomers has been made by calculations using the SCF-CI-MO method. Introduction of electron-donating (or electron-withdrawing) substituent in the diazo part showed bathochromic (or hypsochromic) shift of the absorption band, which was elucidated by the charge migration and the character of the substituents taking into account azo-hydrazone tautomerism. In case of compounds containing electron-donating substituents, aggregation seems to take place in the solid state.

This paper deals with a study of the physicochemical properties of azo dyes formed in 'diazo-printing' process. Substituted benzenediazonium salt and 1-naphthol-4-sulfonic acid (NW acid) are sometimes used as the photosensitive 'diazo' and 'coupler' components, respectively.[1] Coloration of the dyes formed by the reaction between the above compounds is important.

Attempts have been made to correlate the color of azo dyes with the electronic configuration. Griffiths observed a linear relationship between the absorption maxima in the visible region and the electron-withdrawing power (σ-value) of the substituents on 4-substituted phenylazo-1-naphthols in a certain range of σ value ($\sigma > -0.16$).[2,3] His explanation is not applicable to the phenylazo-1-naphthols with strongly electron-donating substituents which are widely used for imaging processes.

The electronic spectra were measured in the visible region for 2-(substituted phenylazo)-1-naphthol-4-sulfonic acids with various electron-donating or electron-withdrawing substituents, including the dye actually used for diazo-printing process. The absorption maxima of some compounds could not be explained by Griffith's relationship. The band assignment and band shift caused by the substituents are interpreted by the SCF-CI-MO method with PPP approximation.

Experimental

Materials. Substituted benzenediazonium salts were prepared from the corresponding amines (analytical grade), precipitated as tetrafluoroborates and then coupled with NW acid. The resulting dyes were purified by repeated recrystallization from water or ethanol and stores in the dark. The other materials used were of analytical grade.

Methods. Absorption spectra in aqueous solutions were measured with Shimadzu (model UV-180) and Carl-Zeiss-Jena 'Specord UV-Vis' spectrophotometers. For solid state absorption stectra the 'Opal glass method' developed by Shibata[4] was used. A small amount of solid compound was rubbed between two sheets of transparent paper (medical wrapper, Tokyo Ikarika Kikai shoji Co.) and the resulting translucent paper was used for recording the spectrum with a Shimadzu spectrophotometer, type DPS-50L. The reflection spectra were also measured with a Shimadzu Spectrophotometer QV-50, but no distinct difference was observed.

Results and Discussion

Analysis of the Absorption Spectra. In general, azo dyes exist as an azo-hydrazone tautomer (Fig. 1). The spectra of the compounds have been determined in neutral, alkaline (0.1 mol dm^{-3} NaOH), and acidic (0.1 mol dm^{-3} HClO$_4$) aqueous solutions as well as

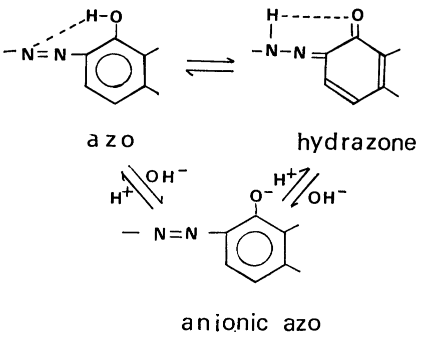

Fig. 1. Azo-hydrazone tautomerism and anionic azo form.

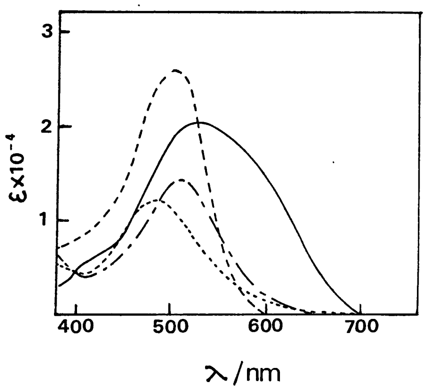

Fig. 2. Absorption spectra of 2-(*p*-dimethylaminophenylazo)-1-naphthol-4-sulfonic acid in acidic, neutral, and alkaline aqueous solutions.
······: Below pH 4.2, —·—: at pH 4.8—5.2, ——: at pH 5.5—8.0, ----: above pH 9.0.

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in the solid state. As an example, Fig. 2 shows the spectra in neutral, acidic, and alkaline solutions of (*p*-dimethylamino phenylazo)-1-naphthol-4-sulfonic acid. The positions of the main absorption maxima in the visible range are summarized in Table 1.

The main visible absorption maximum lies in the range 490—520 nm in neutral aqueous medium. This can be assigned to hydrazone tautomer of the equilibrium,[5] since hydrazone tautomer usually absorbs in a visible region greater than 460 nm, and the azo tautomer in a shorter wavelength region 400—460 nm.[6–14] In our compounds no band is seen which can be ascribed to azo tautomer, except for a very weak shoulder in a few cases. This indicates the predominance of hydrazone tautomer in neutral aqueous solutions, in line with the conclusions of Gabor *et al.*[9] and Yagi[10] on 2-phenylazo-1-naphthol in non-aqueous solvents. NMR studies also support this view.[9,15] Furthermore, the band is assigned to a π-π^* transition from the bathochromic shift caused by polar solvent.[12]

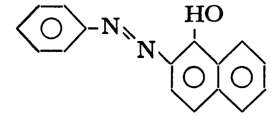
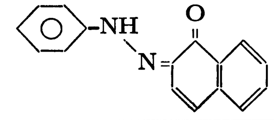
In order to confirm our assignment, quantum mechanical calculations were made by the SCF-CI-MO method with PPP approximation for both azo and hydrazone forms of the parent compound, 2-phenylazo-1-naphthol. Details of the method have been reported by one of us (S.S).[16] The values of the calculated transition energies (ΔE) and oscillator strengths (f) are given in Table 2. The calculated transition energies for the hydrazone agree with experimental data.

TABLE 1. VISIBLE ABSORPTION MAXIMA OF 2-(SUBSTITUTED PHENYLAZO)-1-NAPHTHOL-4-SULFONIC ACID

Serial No.	Substituent	σ[a)]	Frequency 10^{-4}/cm^{-1} (Wavelength/nm in parentheses) Neutral aqueous	Acidic aqueous	Alkaline aqueous	Solid
1	*p*-NO_2	+0.78	2.02 (495)	2.05 (489)	1.88 (531)	2.02 (495)
2	*p*-CN	+0.69	2.04 (491)	2.04 (491)	1.97 (507)	2.04 (490)
3	*p*-Br	+0.23	2.02 (496)	2.02 (496)	2.05 (487)	2.01 (497)
4	*p*-Cl	+0.22	2.02 (494)	2.02 (494)	2.06 (485)	2.04 (488)
5	*p*-F	+0.06	2.03 (492)	2.03 (492)	2.10 (476)	1.99 (502)
6	H	0	2.03 (492)	2.03 (492)	2.09 (479)	2.00 (500)
7	*p*-CH_3	−0.17	2.00 (499)	2.00 (499)	2.08 (481)	2.00 (503)
8	*p*-OCH_3	−0.27	1.98 (505)	1.98 (505)	2.08 (480)	2.00 (500)
9	*p*-$N(C_2H_5)_2$	−0.81[b)] +0.78[c)]	1.93 (517)	2.07 (483)	1.99 (505)	2.05 (488)
10	*p*-$N(CH_3)_2$	−0.83 +0.80[c)]	1.92 (520)	2.06 (485)	2.01 (498)	2.06 (485)

a) Values taken from Ref. 20. b) For neutral and alkaline conditions: σ value of *p*-diethylamino substituent is not taken from the reference. Comparing *p*-ethyl substituent ($\sigma = -0.15$) with *p*-methyl one ($\sigma = -0.17$), the value of *p*-diethylamino substituent is estimated to be −0.18. c) For acidic condition: Hammett σ value is not taken from the reference. The value is estimated by comparing the Taft σ value[21] of protonated dimethylamino group with that of unprotonated one.

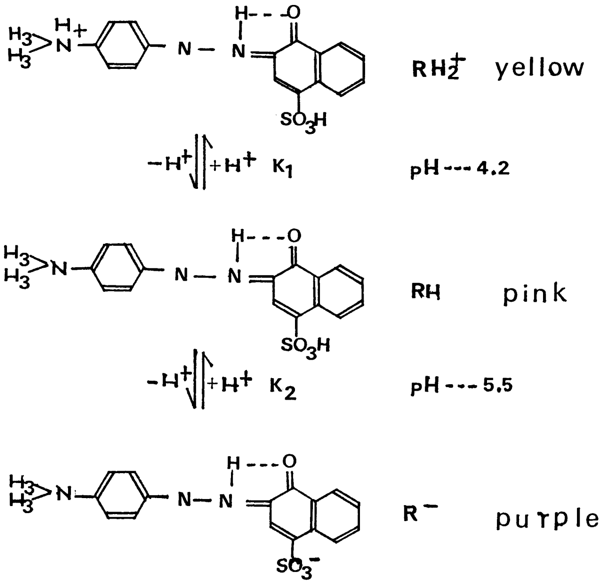
TABLE 2. DIFFERENT PARAMETERS OBTAINED BY SCF-CI-MO CALCULATION

Compound	Structure	ΔE(calcd)[a)]/eV	f(calcd)	ΔE(expt)[a)]/eV
	azo	2.90(427) 3.93(315) 4.13(300)	0.65 0.14 0.63	
	hydrazone	2.60(477) 3.75(331) 4.48(277)	1.11 0.31 0.37	2.52(492) 3.54(350) 4.25(291)

a) Values in the parentheses give the wavelengths(nm) of the corresponding absorption bands.

In highly alkaline solutions where the phenolic group is completely dissociated, the compounds have predominantly azo character and seem to exist in anionic azo form[3] (Fig. 1).

In highly acidic medium the visible spectrum does not change markedly from that in neutral aqueous medium except in the case of (a) *p*-dimethylamino and (b) *p*-diethylamino derivatives. Figure 2 shows this for (a). When the solution of (a) is acidified from neutral condition, the color turns from purple to pink at pH 5.2, and from pink to yellow around pH 4.2. The spectrum in highly acidic medium below pH 4.2, which shows an absorption maximum at 485 nm, differs from that around pH 5.0 (maximum at 510 nm), and from that in the neutral medium (maximum at 520 nm). The results suggest the following acid-base equilibria:



Formulae dissociation equilibria of 2-(*p*-dimethylaminophenylazo)-1-naphthol-4-sulfonic acid.

The markedly different spectrum in the acidic medium in the case of dialkylamino derivatives is ascribed to the protonation of the dialkylamino group. The protonated group behaves as an electron-withdrawing one (Table 1), the absorption peak shifting to the shorter wavelength region. A slight change is also observed in the *p*-nitro derivative [λ_{max}(neutral)= 495 nm and λ_{max} (acidic)=489 nm]. This might be due to the slight dissociation of the phenolic group even in the neutral medium since some nitro phenols are reported to be strong acids.[17]

Spectra in the solid state have been taken because of their industrial importance (Fig. 6). In the solid state spectra of these compounds, there is no clear band or shoulder which can be ascribed to the azo tautomer. Thus, in the solid state also the present compounds exist predominantly as hydrazone tautomer, in agreement with the results of NMR studies.[10,15]

Dependence of Absorption Maxima on Substituent Constants. According to the theoretical calculation[6,18] on 2-phenylazo-1-naphthol during the course of the lowest π-π^* transition ($S_0 \rightarrow S_1$), there is a charge migration from the naphthalene ring towards the azo link and, to some extent, to the benzene ring in the case of azo structure. The charge migration is in the opposite direction in the hydrazone structure, from the benzene ring and N_α atom to the N_β atom and the naphthalene ring. The approximate direction of the migration moment (movement of charge) is shown in Fig. 3.

In order to elucidate the influence of the substituents on the charge migration of 2-(*p*-substituted phenylazo)-1-naphthol, Hammett's constants were employed to estimate the character of substituents. Figure 4 shows the plots of ν_{max} in the visible region *vs.* σ values of the substituents. The plots seem scattered, but two approximate straight lines are drawn with different slopes in positive and negative ranges of σ values. This is in contrast with the linear relationship between ν_{max} and σ observed on 4-phenylazo-1-naphthol derivatives by Griffiths.[3] The present set of compounds being predominantly in hydrazone structure in neutral medium, introduction of electron-donating substituents in the diazo part facilitates charge migration, resulting in bathochromic shift of the main visible band (Fig.

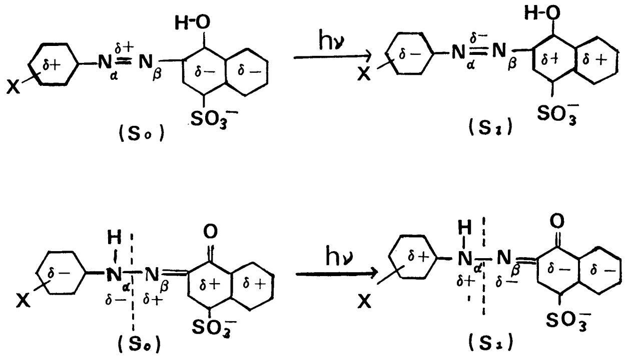


Fig. 3. Approximate scheme of charge migration during electronic transition.

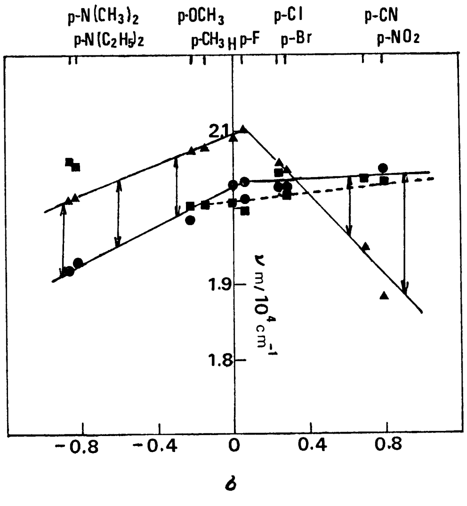


Fig. 4. Plots of ν_{max} of 2-(substituted phenylazo)-1-naphthol-4-sulfonic acid dyes agaist σ values of the substituents.

●: Neutral aqueous solution (ν_{max} of *p*-nitro derivative is in acidic solution, because the phenolic group is partly dissociated even in neutral solution), ▲: alkaline aqueous solution, ■: solid.

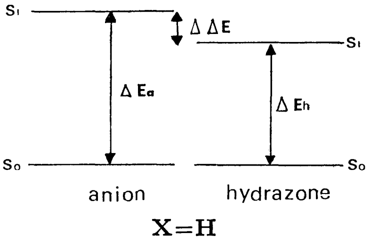


Fig. 5. Energy level diagram of the anionic azo and hydrazone forms of 2-(unsubstituted phenylazo)-1-naphthol-4-sulfonic acid.

4). The presence of electron-withdrawing substituents might cause a slight hypsochromic shift of the visible band, indicating opposition to the charge migration during the course of electronic transition. The influence of electron-withdrawing substituents in the diazo part on the visible band position is not as pronounced as that of electron-donating substituents (Fig. 4).

The dyes exist in anionic azo form in alkaline solutions (Fig. 1).[3] The unsubstituted compound (X=H) was found to show absorption at a shorter wavelength (higher ν) in alkaline solution than in neutral solution (Fig. 4 and Table 1). This is schematically explained in Fig. 5. From the foregoing discussions and Fig. 3, it is evident that electron-donating groups on hydrazone form decrease ΔE_h, while the groups on anionic azo form increase ΔE_a value. Consequently $\Delta\Delta E$ value ($\Delta E_a - \Delta E_h$) increases. Similarly ΔE_a is lowered more than ΔE_h by electron-withdrawing groups. This causes a decrease in $\Delta\Delta E$ and $\Delta\nu_{max}$ [ν_{max}(alkaline)$-\nu_{max}$(neutral)], which is proportional to $\Delta\Delta E$, with increasing σ-value (Fig. 4). The results are in line with the above discussion. Figure 4 shows that $\Delta\Delta E$ is positive for the compounds containing electron-donating and weak electron-withdrawing substituents and negative for highly electron-withdrawing substituents such as *p*-cyano and *p*-nitro groups. This is in line with the result obtained by Griffith.[2,3]

In the solid state, where the structure of the dyes is the same as in the neutral aqueous solutions as shown by the electronic spectra, the dependence of ν_{max} on σ is expected to be similar to that in neutral aqueous solution. The plot (ν_{max} *vs.* σ) in the case of compounds with electron-withdrawing substituents ($\sigma>0$) is as expected (Fig. 4). For compounds with strongly electron-donating substituents (*p*-methoxyl, *p*-dimethylamino, and *p*-diethylamino) the absorption peaks are at frequencies higher than those expected from the above consideration. The apparent anomalous behavior of these compounds is explained in the following. There is a greater scattering in the plot ν_{max} *vs.* σ in the solid state. The correlation in the solid spectra is not as good as desired. However qualitative conclusion can be drawn from it.

Aggregation in the Solid State. Distinct shoulders are present at the longer wavelength region (580—650 nm) of the main absorption bands in the solid spectra of *p*-methoxy, *p*-dimethylamino, and *p*-diethylamino derivatives. Figure 6 shows the solid absorption spectrum of *p*-dimethylamino derivative. This is not present in the other compounds. Thus the color of the above compounds is not red as expected from the position of the main absorption bands, but purple. This shoulder does not appear in the absorption spectra in aqueous solutions.

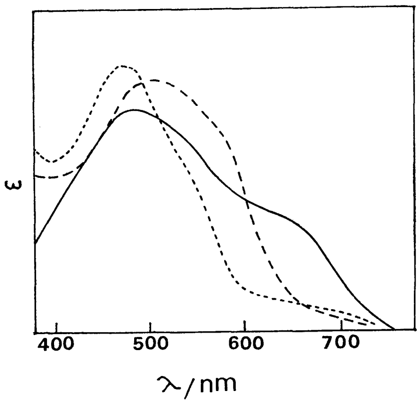


Fig. 6. Solid absorption spectra of 2-(*p*-dimethylaminophenylazo)-1-naphthol-4-sulfonic acid.
——: Untreated, ----: after treatment with alkali, ……: after treatment with acid. Molar absorptivity, arbitary.

Appearance of the additional bands might be due to the presence of aggregate species in the solid state of the compounds, as in the case of cyanine dyes used for sensitizing silver halides.[19] Only the *p*-methoxy, *p*-dimethylamino, and *p*-diethylamino derivatives of the present series of compounds form aggregate species in the solid state. The reason might be as follows. These compounds, like all other compounds, exist mainly in the hydrazone form in the solid state. There are strong donor and acceptor groups at the two ends of the molecules of these compounds. The donor groups are enhanced by the strongly electron-donating substituents. Such a situation can favor aggregation.

The aggregate band at the longer wavelength disappears in the spectrum of the *p*-dimethylamino or *p*-diethylamino derivative if a pinch of the solid compound is treated with a drop of strong acid or alkali and dried before the measurement, though no change in external appearance was observed. Figure 6 shows the solid state absorption spectra of the *p*-dimethylamino derivative before and after treatment with acid or alkali. Treatment with strong acid protonates the dialkylamino group and that with strong alkali converts the dye into anionic azo structure. In both cases, donor and acceptor groups are not simultaneously present in the molecule. The results might suport the cause of aggregation.

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