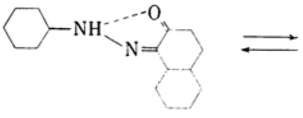
*Studies of Absorption Spectra of Azo Dyes and Their Metal-complexes. VI. The Tautomerism of Phenolazo-β-naphthols and of Phenolazo-α-naphthols**

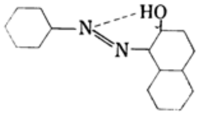
By Yoshiharu Yagi

(Received July 15, 1963)

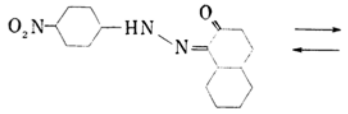
It had long been recognized[1] that phenylazo-β-naphthol (I) and phenylazo-α-naphthol (XI) are in a tautomeric equilibrium between the azo and the quinonehydrazone forms. This study was undertaken in order to obtain more information about this tautomerism.



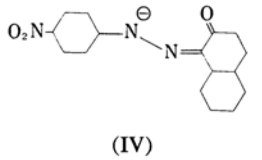
(I)



(II)



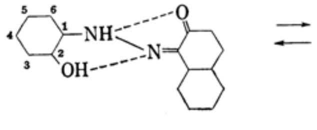
(III)



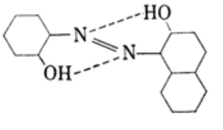
(IV)

In an aqueous methanol containing sodium hydroxide, the hydrazone band[2] of I near 500 mμ markedly decreases in intensity, while the absorption intensity of the azo band increases near 445 mμ. If I turns into a sodium salt by an addition of alkali metal hydroxide, thus forming an anionic species, there should be an appreciable bathochromic displacement of the bands according to the polarity increase of the absorbing system. Compound I, therefore, is not considered to from a salt under such conditions. However, azo compound III, known as pigment Para Red, is an exceptional case. This exists almost exclusively in the phenylhydrazone form (488.6 mμ in 95% methanol) as a result of the strong electron-withdrawing property of a nitro group. The addition of sodium hydroxide to this system, however, causes the appearance of a new band near 550 mμ, and the hydrazone band disappears with an increase in the concentration of alkali metal hydroxide. It is evident that III forms an anion IV in such circumstances, since no band corresponding to the azo form has been observed.

In the equilibrium of phenolazo-β-naphthol (V) in various organic solvents, the hydrazone form is generally more dominant than azo compound I. The phenolic hydroxyl group of V or XII is, in any solvent, in an undissociated state, whereas those of phenolazoacetoacetamides in Part II[3] have been found to be strongly acidic, and thus their dissociation occured in aqueous alcohol.



(V)



(VI)

It had previously[4] been known that such *o, o'*-dihydroxyazo compounds as V undergo marked color changes according to the pH ranges of the media, neutral (weakly acidic), weakly alkaline or strongly alkaline. However, no exact explanation of this has yet been made. Compound V in aqueous 50% methanol shows the hydrazone and the azo bands at 508 mμ

---

* Parts I—V, This Bulletin, **36**, 487, 492, 500, 506, 512 (1963).

[1] K. Auwers et. al. *Ann.*, **378**, 210 (1911); **487**, 79 (1931); A. Burawoy et al. ibid., **503**, 180 (1933); **504**, 71 (1933); **509**, 60 (1934); R. Kuhn and F. Bär, ibid., **516**, 143.

[2] A. Burawoy, *J. Chem. Soc.*, **1952**, 4793.

[3] Y. Yagi, This Bulletin, **36**, 492 (1963).

[4] H. Shingu et al., *J. Chem. Soc. Japan* (*Nippon Kwagaku Kwaishi*), **60**, 542, 595 (1939); J. B. Müller et al., *Helv. Chim. Acta*, **35**, 2579 (1952).

TABLE I. ELECTRONIC ABSORPTION SPECTRA OF PHENOLAZO-β-NAPHTHOLS

Compound	Solvent	Absorption band λ_{max}, mμ ($\varepsilon_{max}\times 10^{-4}$)				
V	50% MeOH	538.5*(1.81) 508.0 (2.12) 422.1 (0.72)		314.8(0.65)	261.5 (1.08)	230.8(2.99)
V	Same as above but containing 0.01 N NaOH	576.1 (2.06)	387.0(0.52)	327.8(0.50)	283.0*(0.84) 267.0*(1.20)	222.3(3.10)
V	Same as above but containing 0.1 N NaOH	573.8 (1.86)	389.8(0.51)	328.3(0.48)	283.3*(0.85) 266.5*(1.24)	227.7(2.82)
V	Same as above but containing 0.5 N KOH	608.5*(0.60) 526.7 (1.23) 446.1*(0.84)		336.0(0.48)	268.0*(1.57)	235.8(2.61)
5-NO_2 Derivative	95% MeOH	590.0*(0.73) 517.5 (1.82) 392.0*(0.92)		309.5(1.16)	261.0*(1.38)	228.9(3.33)
5-NO_2 Derivative	Same as above but containing 0.01 N NaOH	561.5 (2.27) 401.9 (1.16)		329.0(1.00)	268.1*(1.28)	230.6(2.89)
5-NO_2 Derivative	Same as above but containing 0.5 N KOH	550.3 (1.70) 440.0 (1.23)		363.0(1.12)	275.4*(1.34)	235.2(2.72)
4-NO_2 Derivative	95% MeOH	612.4*(0.89) 529.7 (2.32) 405.0*(0.69)		325.0(0.70) 306.*5(0.62)	263.5*(0.97)	227.4(3.35)
4-NO_2 Derivative	Same as above but containing 0.01 N NaOH	584.5 (2.64) 395.3 (0.73)		323.2(0.80)	269.3*(1.33)	231.5(3.31)
4-NO_2 Derivative	Same as above but containing 0.5 N KOH	588.7 (2.28) 400.6 (0.67)		323.3(0.77)	268.3*(1.48)	233.2(3.19)

A group of bands is shown in the same column. Visible absorption bands are shown in the same column.

* Inflection.

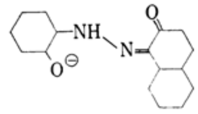
TABLE II. ELECTRONIC ABSORPTION SPECTRA OF PHENYL- AND PHENOLAZO-α-NAPHTHOL

Compound	Solvent	Absorption band λ_{max}, mμ ($\varepsilon_{max}\times 10^{-4}$)				
I	*n*-Hexane	492.5 (1.48) 424.0*(0.70)	352.5 (1.05)	297.7 (1.64) 289.8 (1.65) 265.9*(0.84)	240.7*(1.24) 224.2 (1.77)	
II	*n*-Hexane	559.2*(0.08)	467.8 (1.53)	346.8 (1.16)	302.3 (1.49) 292.3*(1.38)	266.8*(0.65) 258.0*(0.76) 225.9 (2.14)
	Chloroform	562.9*(0.26)	477.2 (1.54)	349.9 (1.19)	303.8 (1.58) 295.3*(1.48)	—
	Acetic acid	552.5*(0.81)	486.3 (1.41)	349.0 (0.95)	300.8 (1.52) 292.0*(1.42)	—
	Methanol**-chloroform		560.5*(1.05) 512.3 (1.49) 486.0*(1.40)	349.0 (0.80)	303.5 (1.41) 294.3*(1.30)	—

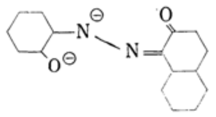
** A chloroformic solution containing 30 g. of methanol per 100 ml.

and 422.1 mμ respectively. When measured in the medium roughly the same but containing sodium hydroxide, the hydrazone band undergoes a remarkable shift toward a longer wavelength in the alkali concentration near about 0.01~0.1 N. The molecular structure at this state corresponds to structure VII.

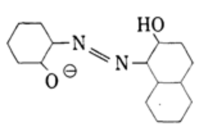
In the neighborhood of the concentration about 0.5~1.0 N, it is noteworthy that the relative intensity of the azo band markedly increases at about 450 mμ. If a two-step dissociation, VII→VIII or IX→X, occurs upon the concentration increase of sodium hydroxide, the increased polarity of the absorbing system



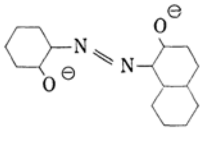
(VII)



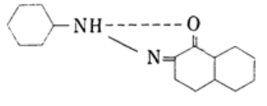
(VIII)



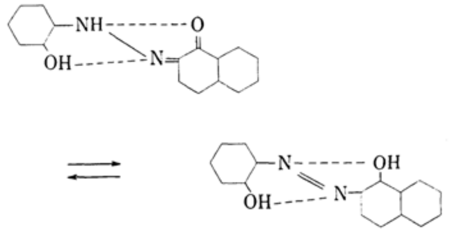
(IX)



(X)



(XI)



(XII)

would cause a displacement of the spectrum toward a longer wavelength as compared with the absorption maximum of the ionized hydrazone form corresponding to VII. Such spectral change, therefore, may be attributed to the fact that the tautomeric equilibrium is inclined to the azo form, presumably because of (i) an increase in the basic nature of the solvent system, and (ii) an elevation of the electron-donating power of the hydroxyl upon dissociation.

The spectra of the derivatives of V supported the above explanation: the 5-NO_2 derivative in neutral 95% methanol has an absorption corresponding to structure VII as a shoulder (560 mμ) of the main hydrazone band (517 mμ). By the addition of alkali metal hydroxide, the main hydrazone band is turned into this new band. In spite of the concentration increase of alkali metal hydroxide, the location of this band does not change. The azo band, however, undergoes a slight bathochromic and hyperchromic displacement. In the case of the 4-NO_2 derivative, however, the hydrazone structure is exclusively dominant because the electronegative nitro group is para to the hydrazone group. The weak azo band shows no change in location and in intensity in spite of the concentration increase of alkali metal hydroxide. It follows that it is harder for a dissociation VI→IX to proceed than for a dissociation V→VII.

The tautomerism of phenylazo-α-naphthol (XI) is somewhat different from that of I. In *n*-hexane, the weak inflection at 424 mμ proves the slight existence of the azo form of XI, as is shown in Table II. However, the hydrazone band of XI (λ_{max} 507.5 mμ; ε_{max} 1.68×10^4) in 50% aqueous methanol undergoes almost no change in intensity and in location, in spite of the basicity increase of the solvent upon the addition of sodium hydroxide to this system. These facts show that the azo $\rightleftarrows$ quinonehydrazone tautomeric equilibria of the compounds of type XI are biased toward the hydrazone tautomer in any solvent.

With regard to phenolazo-α-naphthol (XII) the tautomeric eqilibrium is biased to the azo form as a result of the electropositive character of the phenolic hydroxyl group.[5] In the visible absorption region, there is a weak inflection at a longer wavelength side (about 500 mμ) of the main aborption band. This absorption has a relatively high intensity in an acetic acid medium whereas the intensity of the main absorption band at 486.3 mμ is relatively low. In a polar solvent such as methanol, XII also shows a sharply absorbing band at 528.5 mμ, and there is no absorption on a longer wavelength side. Moreover, the visible absorption maximum of XII in *n*-hexane is located at a shorter wavelength position than that of XI, notwithstanding the introduction of the hydroxyl group, with its effectively auxochromic nature.

The azo $\rightleftarrows$ quinonehydrazone tautomerism of XII, therefore, is concluded to be as follows; XII in non-polar solvents exists exclusively as the azo form, resulting in the merely slight appearance of the hydrazone form as the inflection. This equilibrium, however, is susceptible to any increase in the polarity in the solvent system.

The spectral behavior in a mixed solvent system, as is shown in the table, confirms the above view; the addition of methanol to the chloroformic solution of XII converts the visible bands into what appears to be a single absorption band. Such spectra suggest nearly equal contributions of the azo and the hydrazone forms to the tautomeric equilibrium; i. e., the former appears as an inflection at 486.0 mμ, and the latter, at 560.5 mμ.

The author wishes to express his deep gratitude to the late Professor Ryutaro Tsuchida for his kindness in participating in discussions

---

[5] A. Burawoy and A. R. Thompson, *J. Chem. Soc.*, **1953**, 1443.

throughout this work. The author is also indebted to the Sumitomo Chemical Co., Ltd., for its permission to publish this work and to Mr. Kikuo Kimura for his assistance in this study.

Osaka Works
Sumitomo Chemical Co., Ltd.
Konohana-ku, Osaka