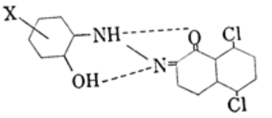
Studies of the Absorption Spectra of Azo Dyes and Their Metal-complexes. VIII. The Absorption Spectra of Azo Compounds Derived from 5,8-Dichloro-1-naphthol and Their Metal-complexes

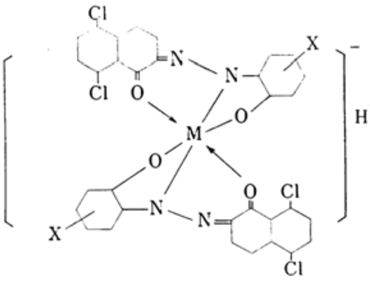
By Yoshiharu YAGI

(Received August 5, 1963)

In the field of dye chemistry, the 2 : 1-metal complex dyes (II) derived from 2-(2'-hydroxyarylazo)-5, 8-dichloro-1-naphthols (I) have been of much interest[1] because of their deeper and relatively clear dyeing shades on the proteinic fibers as compared with the series of complexes studied previously.[2,3] This paper has been undertaken to obtain fundamental information on these azo compounds and their metal complexes.



(I)



(II)
(X: Substituent)

Table I shows the electronic absorption spectra of compound I (X=H) and its methoxy analogue. The characteristic shape of each absorption band exhibits almost no change in spite of the polarity variation of the media. It is noteworthy that both compounds in Table I show splittings of the visible absorption bands and that such absorption maxima are located at markedly longer wavelengths than those of phenolazo-β-naphthols and phenolazo-α-naphthols.[3] If the azo and the quinonehydrazone form coexist[1,3,4,] the azo band should appear at about 450 mμ or at a longer wavelength than 450 mμ. No such absorption can, however, be observed at all in a variety of solvents. Compound I and/or its derivatives, therefore, are considered to have the hydrazone structure exclusively.

Table II shows the electronic absorption spectra of the 2 : 1-chromium(III)- and cobalt(III)- complexes (II) of ligands I, the phenolic nuclei of which are substituted by various kinds of groups in the 4- or 5-position. Marked band-shifts with the complex formation are observed over all the spectra, particularly in the visible region, resulting in appreciably bathochromic displacements and the broad deformation of the bands.

As to the spectra of ligands I, the λ_{max} values of the visible absorptions are in the region of 513~570 mμ and shift towards shorter wavelengths with the introduction of the electronegative substituent at the 5-position of the phenolic ring. There are characteristic inflections close to the main visible bands of the ligands and of their metal-complexes in Table II. In some ligands I (when X=H and

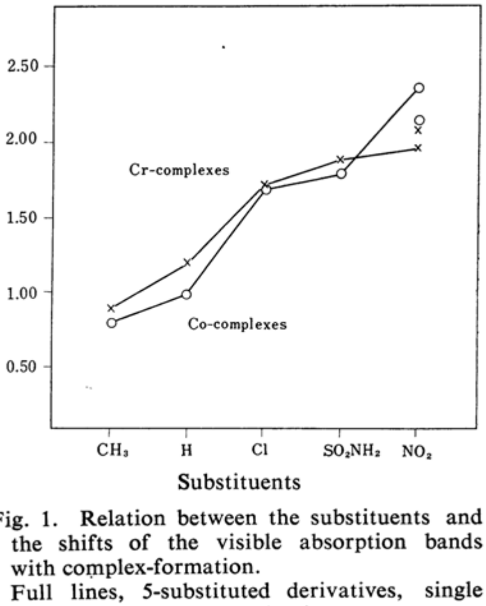


Fig. 1. Relation between the substituents and the shifts of the visible absorption bands with complex-formation.
Full lines, 5-substituted derivatives, single marks, 4-substituted derivatives

---

[1] CIBA Ltd., Brit. Pat. 724157; U. S. Pat. 2495244; Swiss Pat. 305634-5.

[2] Y. Yagi, Part I-V of this study, This Bulletin, **36**, 487, 492, 500, 506, 512 (1963).

[3] Y. Yagi, Part VI of this study, This Bulletin, **37**, 1875 (1964).

[4] 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).

TABLE I. ELECTRONIC ABSORPTION SPECTRA OF DERIVATIVES OF 2-PHENYLAZO-5,8-DICHLORO-1-NAPHTHOL IN VARIOUS SOLVENT

Compound	Solvent	Absorption bands, λ_{max}, mμ ($\varepsilon_{max} \times 10^{-4}$)						
2-(2′-Methoxy-phenylazo)-5,8-dichlor-1-naphthol	St. Solv.	550.0 (1.42)	525.0 (1.44)	(383.0*) (0.60)	(358.3*) (0.70)	319.0 (0.99)	305.7 (1.03)	246.5 (1.60)
	n-Hexane	543.8 (1.30)	512.6 (1.28)	(383.0*) (0.51)	(357.3*) (0.64)	319.2 (0.84)	302.5 (0.89)	247.0 (1.36)
2-(2′-Hydroxy-phenylazo)-5,8-dichlor-1-naphthol (I)	50% MeOH	558.4 (2.30)	531.4 (2.34)	(394.0*) (0.50)	355.0*) (0.82)	320.6 (1.50)	305.3* (1.34)	247.9 (1.57)
	Pyridine	569.7 (2.69)	535.3 (2.54)	(399.0*) (0.50)	362.0* (0.83)	325.7 (1.33)	309.7* (1.21)	—

St. Solv.: A standard solvent which denotes 95% aqueous methanol containing 0.1 g. of acetic acid per liter.

* Inflection.

Absorption bands in parentheses are indistinct bands.

TABLE II. VISIBLE ABSORPTION SPECTRA OF THE DERIVATIVES OF (I) AND THEIR METAL-COMPLEXES

Substituent	Absorption bands; λ_{max}, mμ ($\varepsilon_{max} \times 10^{-4}$)						
	Ligand Dyes		Chromium-complexes		Cobalt-complexes		
5-CH_3	570.0 (2.48)	536.9 (2.48)	(610.2*) (1.90)	561.4 (2.77)	564.2 (2.94)	522.9* (2.43)	
H	554.4 (2.43)	524.2 (2.47)	(611.2*) (1.58)	553.1 (2.96)	558.9 (2.92)	516.7* (2.39)	
5-Cl	558.4* (2.29)	521.2 (2.64)	(614.4*) (2.25)	571.7 (2.91)	571.9 (2.94)	530.0* (2.33)	
5-SO_2NH_2	553.0* (2.18)	516.0 (2.64)	642.9* (1.58)	568.8 (2.53)	571.4 (3.00)	528.5* (2.39)	
5-NO_2	549.0* (2.05)	513.5 (2.59)	644.0* (1.95)	584.2 (2.38)	570.6 (3.01)	527.3* (2.43)	486.8* (1.96)
4-NO_2	573.1* (2.66)	535.0 (3.21)	672.2* (2.45)	603.4 (2.94)	601.7 (3.51)	556.7* (2.75)	

The solvent used is 95% aqueous methanol containing 0.1 g. of acetic acid per liter (the standard solvent).

CH_3), the inflection forms an absorption band, and its intensity is just that, or almost equal to that, of the main band. Regarding the complex bands, the inflection is located on the shorter or the longer wavelength side of the main absorption band of the cobalt(III) or the chromium(III) complex respectively; generally the more electronegative the substituent in the phenolic nucleus, the more intensive the inflection.

The degree of the bathochromic shifts of the visible absorption bands of I and its derivatives with the complex formation, i. e., $\Delta\nu$ (in cm^{-1}) [(ν_{max} of a ligand-band) − (ν_{max} of the corresponding complex-band)] is shown in Fig. 1. Substituents at the abscissa are conveniently arranged in the order of the electronegativity at regular intervals.⁵⁾ In this graph, the absorption maxima of the shorter wavelength-side band have been taken as the location of the visible absorptions of the ligands (I, when X=CH_3 and H).

The magnitudes of $\Delta\nu$ in these systems are smaller than those of the phenolazo-β-naphthol series but nearly equal to those of the phenolazo-α-naphthol series discussed in the preceding paper.⁶⁾

As was described in part III of this study, such bathochromic displacements of the bands with the complex formation may be ascribed mainly to two factors; (i) the polarity of the M–O (M, tervalent central metal; O, phenolic oxygen) bond, and (ii) the formation of the resonance-stabilized system involving the aromatic nuclei and the chelate rings. It would be reasonable to apply the above consideration to the system of this study.

If factor ii predominates, the perturbation of the π-electron system by the dπ-pπ interaction between the hydrazone group and the central metal will be emphasized in a system that has a group with a resonance effect as the substituent X. For example, a CH_3 group would cause a larger $\Delta\nu$ value than that in the case of X=H.⁶⁾ However, Fig. 1 shows a tendency toward a linear increase in the $\Delta\nu$ value with the increase in the negativity of the substituent. This suggests the dominant character of factor i. Moreover, the actual gradient of the graph becomes markedly steeper, taking into account the fact that the ν_{max} of the ligands (X=H and CH_3) have been taken from the shorter wavelength side bands. Although various factors are conceivable in accounting for such band shifts, the following explanation is considered to be the most reasonable: in the 2:1-metal complexes of formula II, there is a steric repulsion between

---

5) L. P. Hammett, *Chem. Revs.*, **17**, 125 (1935); H. H. Jaffé, ibid., 53, 191 (1953); H. C. Brown et al., *J. Am. Chem. Soc.*, **80**, 4979 (1958).

6) Y. Yagi, Part. VII of this study, This Bulletin, 37, 1878 (1964).

the chlorine atom and the quinone oxygen atom, so that the coplanarity of the chelate ring involving the metal atom and the quinone oxygen is much reduced (i. e., factor ii is not effectively operative). Thus, an electron-withdrawing group such as an -NO_2 polarizes the M–O bond and increases the polarizability of the absorbing system, resulting in the bathochromic displacements of the visible absorption bands. Such polarization can probably be attributed to both the resonance and the inductive effects, since the $\Delta\nu$ values of the 4-NO_2 derivatives are also appreciably large.

In the metal-complex systems of the previous papers, the wavelength locations of the visible absorption bands have been in the order, Cr > Co. However, this order is reversed in the greater part of Fig. 1. This is presumably because the M–O bond is more ionic in the cobalt(III)-complexes than in the chromium(III)-complexes.

The author wishes to express hearty thanks to the late Professor Ryutaro Tsuchida of Osaka University for his valuable discussions and encouragement. Thanks are also to be accorded to the Sumitomo Chemical Co., Ltd., for permission to publish this work and to Mr. Kikuo Kimura and Mr. Masao Kitajima for their assistance throughout this study.

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