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On Absorption Spectra of *o*- and *p*-Hydroxyazo-dyes Derived from 1-Phenylazonaphthalene

by

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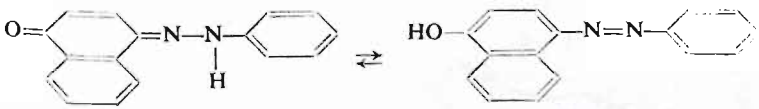
The structure of hydroxyazo-dyes having the OH group in positions conjugated with the azo group (*ortho* and *para*) has since long been a point of interest to organic chemists, dyers and colourists. Either azo, or quinone hydrazone structures were attributed [1]—[3] to them, the zwitterionic betaine structure also being proposed [4], [5]. That these dyes exhibit tautomerism is generally accepted by now. The shifts of tautomeric equilibrium between hydroxyazo ("azo") and quinone hydrazone ("hydrazone") tautomers in several solvents are best observed from electronic absorption spectra of the dyes under discussion.

Kuhn and Bär [6] were the first to point out that in solutions of 4-phenylazo-1-naphthol solvent-dependent equilibria exist:



(hydrazone form) (azo form)

Their results were confirmed and developed by several authors [7]—[12]. It is known, that the tautomeric equilibria in question vary considerably with the nature and the position of substituents in the phenyl group [7], [11]: for example the electron-attracting substituents (e.g. NO_2 group) strongly shift the equilibrium towards the hydrazone form. It has been pointed out recently [12], that, on cooling the solution of 4-phenylazo-1-naphthol in methylcyclohexane, this equilibrium strongly shifts towards the hydrazone form. The alcoholic solution at —140° on the contrary contains practically only the azo form (cf. also Fig. 5).

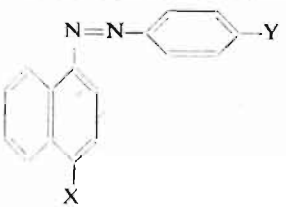
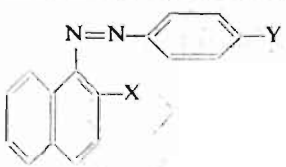
In our previous papers [13], [14] the spectra of several *o*- and *p*-acetoxy-, *o*- and *p*-methoxy-, and *p*-acetylaminomonoazo-dyes derived from 1-phenylazonaphthalene (PAN) have been examined. The spectra of the dyes mentioned above generally resemble the spectrum of PAN (cf. Figs. 1—3 and 6—8), what confirms their azo structure. In our opinion, the differences observed in these spectra (most

pronounced for methoxyazo-dyes because the CH_3O group exhibits the strongest auxochromic properties) are only due to the influence of substituents (conjugation) upon the chromophoric system of PAN. However we know that in solutions of *o*- and *p*-hydroxyazo-dyes there exist solvent- and temperature-dependent equilibria of two tautomeric forms. Each tautomer has its own characteristic absorption spectrum. Thus the structure of spectra of hydroxyazo-dyes is more complex, because they contain absorption bands of both tautomeric forms. It has been already pointed out [6]—[12] that the two bands found near 420 and 460—480 mμ in the spectra of phenylazonaphthols can be ascribed to the azo- and phenylhydrazone tautomers, respectively. Their relative intensities can approximately indicate the amounts of tautomeric forms present in the solution. The aim of our present work is to explain the origin of the other bands found in the spectra of hydroxyazo-dyes derived from PAN.

Absorption spectra (in 95% ethanol, *cyclo*hexane or benzene at room temp., from 210 to 550 mμ) of four *o*- and *p*-hydroxyazo-dyes (formulae and abbreviations of the discussed dyes are to be found in Table I), derived from 1-phenylazonaphthalene (PAN) are given in our paper. For comparison several spectra of their *O*-acetyl- and *O*-methyl derivatives are also discussed. Our own results are given in Figs. 1—3, 6—8. Two graphs (Figs. 4, 5) redrawn from the literature [9], [12] are also included and discussed.

TABLE I

Abbreviations for dyes used in the text

X	Y	 (I)	 (II)
CH_3COO	H	Ia	IIa
CH_3O	H	Ib	IIb
HO	H	Ic	IIc
CH_3COO	NO_2	Id	IId
HO	NO_2	Ie	IIe

The absorption spectrum of the dye (Ic) in ethanol at room temperature is composed of four bands (Figs. 2 and 5). The greater intensity of the band found at 408 mμ indicates that the azo-form occurs in a somewhat greater amount in ethanolic than in a benzene solution (in spite of polarity of ethanol). Very likely the hydroxyazo-form in ethanol is stabilized through intermolecular hydrogen bonds between the solute and solvent molecules.

The spectra of (Ic) and (Ib) are very similar in the ultraviolet region (Figs. 1 and 2). The intensity of both shortwave bands increases on cooling the alcoholic solution of (Ic), and diminishes in methyl*cyclo*hexane (Fig. 5). This provides ex-

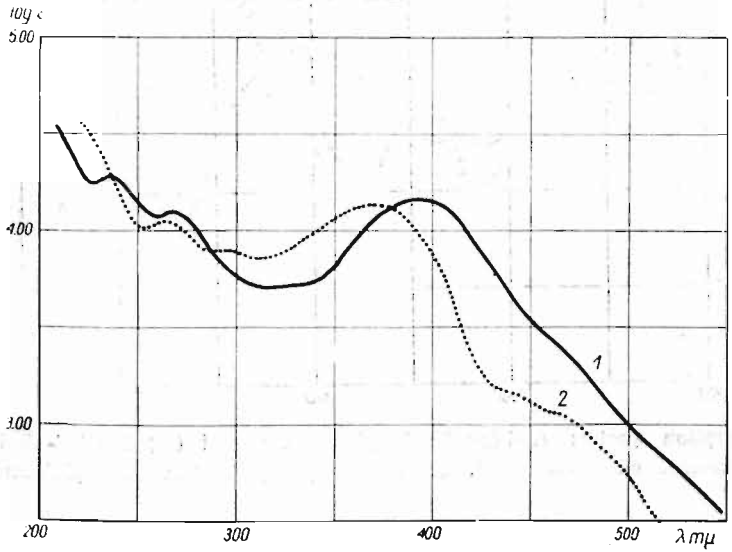


Fig. 1. Absorption spectra in ethyl alcohol: *1*. 4-phenylazo-1-methoxynaphthalene (Ib), *2*. 4-phenylazo-1-acetoxynaphthalene (Ia)

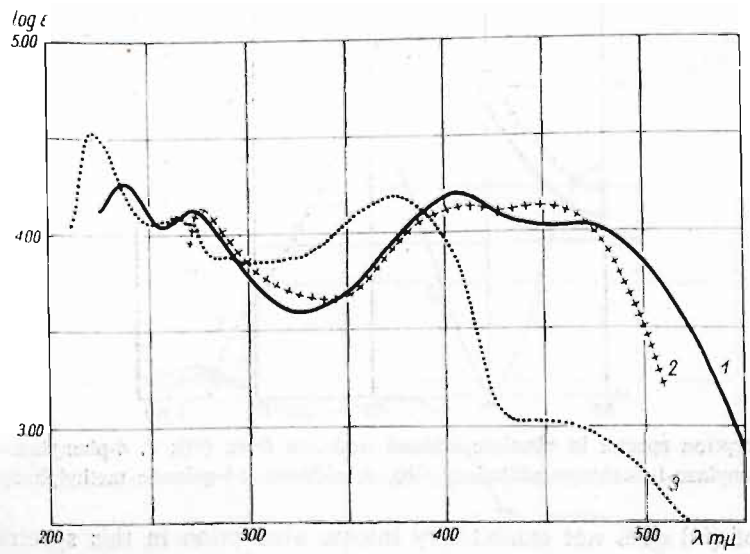


Fig. 2. Absorption spectra: *1*. 4-phenylazo-1-naphthol (Ic) in ethyl alcohol, *2*. (Ic) in benzene, *3*. 4-phenylazo-1-acetoxynaphthalene (Ia) in *cyclo*hexane

perimental evidence that these bands belong mainly to the azo tautomer and correspond to "naphthalenic" bands I and II, present in the spectra of PAN (Ia), (Ib), (IIa), (IIb), etc. [13], [14]. It is believed that the spectrum of the phenylhydrazone

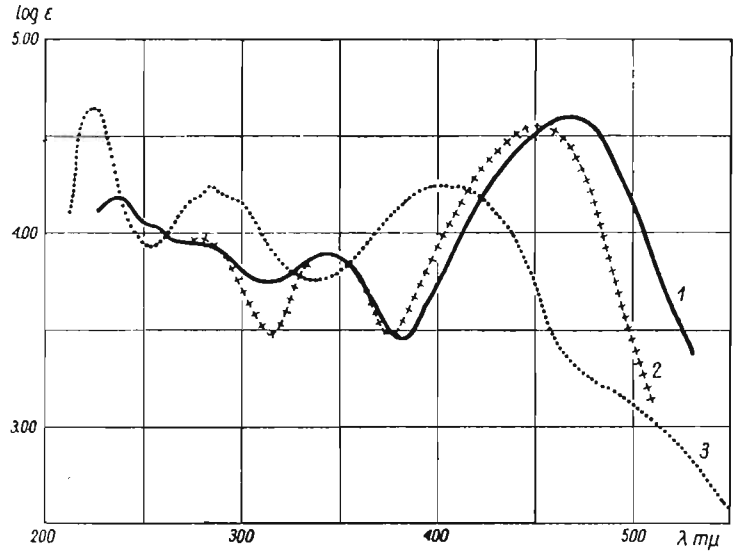


Fig. 3. Absorption spectra: *1.* 4-(*p*-nitrophenylazo)-1-naphthol (Ie) in ethyl alcohol, *2.* (Ie) in benzene (concn. not established), *3.* 4-(*p*-nitrophenylazo)-1-acetoxynaphthalene (Id) in *cyclo*hexane

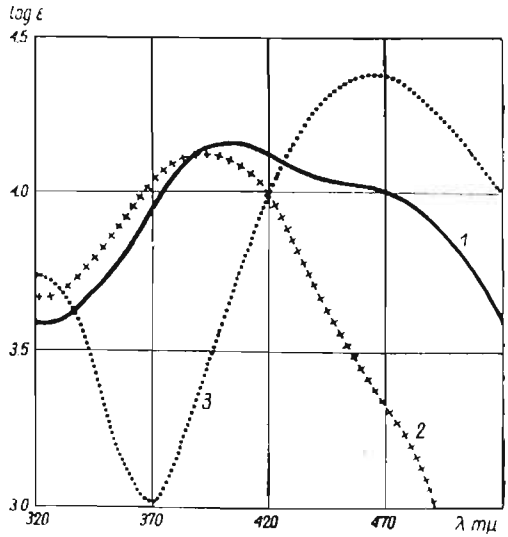


Fig. 4. Absorption spectra in absolute ethanol (redrawn from [9]): *1.* 4-phenylazo-1-naphthol (Ic), *2.* 4-phenylazo-1-methoxynaphthalene (Ib), *3.* naphtha-1:4-quinone methylphenylhydrazone

tautomer of (Ic) does not exhibit very intense absorption in this spectral region, but further experimental evidence should be given to support this interpretation (cf. Fig. 9).

The spectrum of (Ic) in the visual and the near ultraviolet range is different from that of (Ic), because the NO_2 group in *para* position to the benzene ring strongly shifts tautomeric equilibrium towards the quinoid hydrazone form [7]. It gives rise to a new absorption band in the 346 mμ region. This band is believed to derive

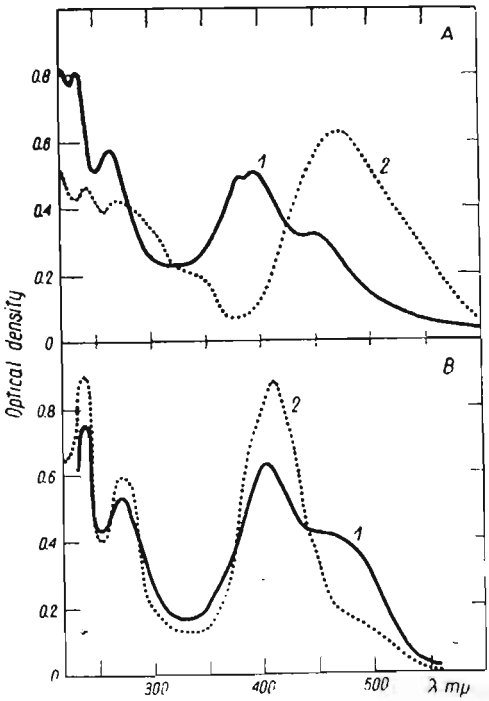


Fig. 5. Absorption spectra of 4-phenylazo-1-naphthol (Ic) (redrawn from [12]): (*A*) *1.* solution of (Ic) at room temperature in methyl*cyclo*hexane, *2.* as above, cooled to —90°, (*B*) *1.* solution of (Ic) in ethanol-methanol (7:3) at +20°, *2.* as above, cooled to —120°

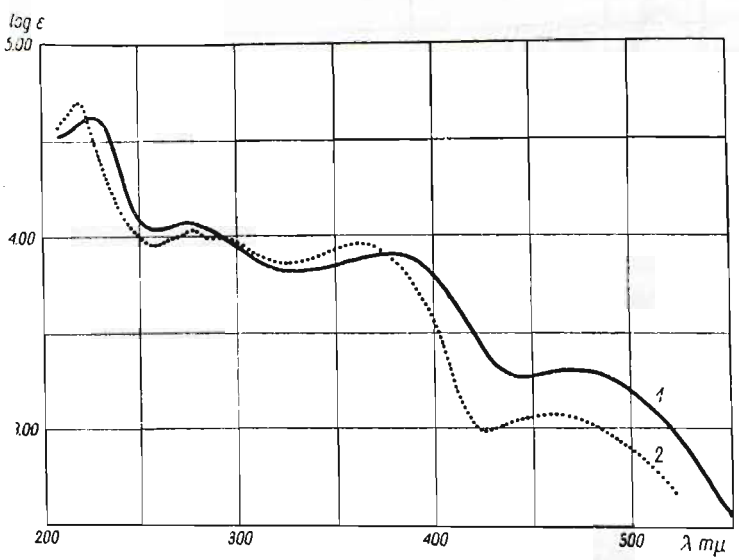


Fig. 6. Absorption spectra in ethyl alcohol: *1.* 1-phenylazo-2-methoxynaphthalene (IIb), *2.* 1-phenylazo-2-acetoxynaphthalene (IIa)

from the hydrazone tautomer. We suppose that this band is fully submerged in the spectra of (Ic) at room temperature, and gives a shoulder near 330 mμ when (Ic) is cooled in methyl*cyclo*hexane (Fig. 5). Further experimental evidence of the

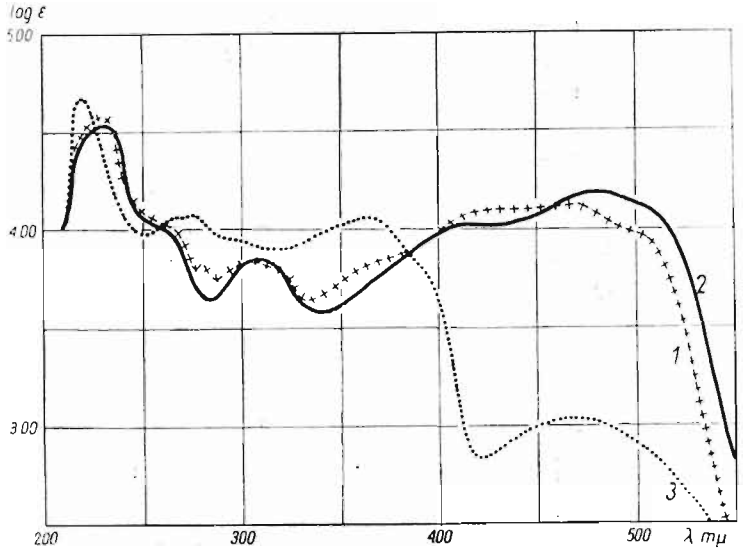


Fig. 7. Absorption spectra: *1*. 1-phenylazo-2-naphthol (IIc) in *cyclo*hexane, *2*. (IIc) in ethyl alcohol, *3*. 1-phenylazo-2-acetoxynaphthalene (IIa) in *cyclo*hexane

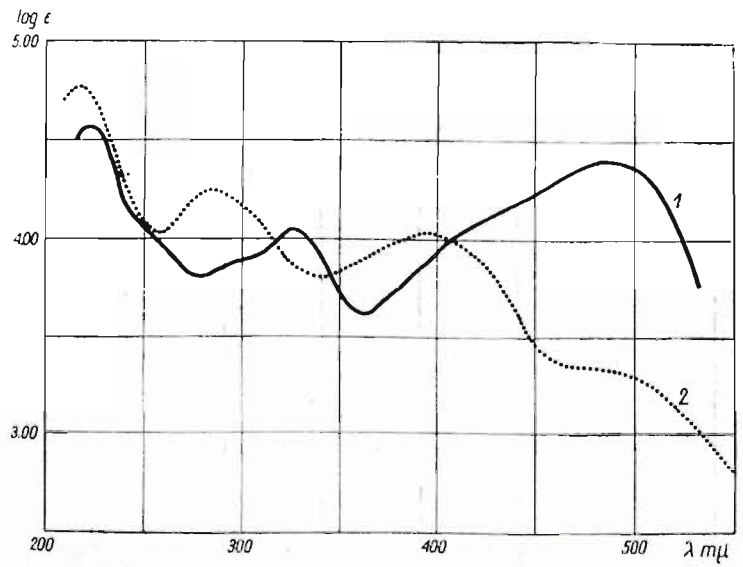


Fig. 8. Absorption spectra in ethyl alcohol: *1*. 1-(*p*-nitrophenylazo)-2-naphthol (IIe), *2*. 1-(*p*-nitrophenylazo)-2-acetoxynaphthalene (IId)

"hydrazone" origin of this band is obtained from the spectra of (Ia), (Ib), (Id) which possess a well-established azo structure [3], [6], [13]—[16] (Figs. 1—4), and of naphtha-1:4-quinone methylphenylhydrazone — a model of the phenylhydrazone

tautomer (Figs. 4 and 9). The former compounds have minima, the latter has a band in the spectral range 300—340 mμ.

The absorption spectrum of (IIc) is composed of five bands (Fig. 7). Two of these within the visible range (λ_{max} = 415 and 480 mμ in alcohol) — belong, to azo and phenylhydrazone tautomers, respectively [6], [11]. The greater intensity of the latter band indicates that this dye exists in ethanolic solution predominantly in the hydrazone form, in contrast to (Ic). In this case it seems that the intramolecular hydrogen bonding, present in the molecules of *o*-hydroxyazo-dyes [17]—[23] causes the position of tautomeric equilibrium to be mainly determined by solvent polarity.

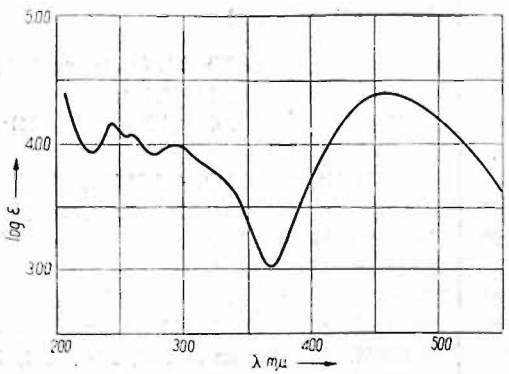


Fig. 9. (*received November 28, 1960*) Absorption spectrum of naphtha-1:4-quinone methylphenylhydrazone in 95% ethanol [λ_{max} mμ (log ε_{max}): 244 (4.16), 259 (4.08), 292 (3.98), 460 (4.39)]

The spectrum of (IIc) within the ultraviolet range is composed of three bands. It should be noted, that the "naphthalenic" band I in the spectrum of (IIb) exhibits far greater intensity and is found at shorter wavelengths than the corresponding band in the spectrum of (Ib) (Figs. 1 and 6). Similarly the corresponding shortwave band in the spectra of *o*-hydroxyazo-dyes is more intense and is found at shorter wavelengths than in the spectra of *p*-hydroxyazo-dyes (compare Figs. 2 and 7, 3 and 8).

It has been claimed [8] that the band present in the spectra of *o*-hydroxyazo-dyes derived from PAN at 310—320 mμ correspond to the peak in the naphthalene spectrum at 311 mμ. We suppose, however, that this band should also be ascribed to quinone hydrazone tautomers*). It appears that the discussed band is absent in the spectra of (IIa), (IIb), (IId) (Figs. 6—8) and is present in those of *o*-hydroxyazo-dyes derived from PAN (Figs. 7 and 8, see also the spectra of other arylazo-2-naphthols given in [6], [8], [11], [24]—[26]). Introduction of NO_2 into the *para* position of the phenyl ring of the dye (IIc) exerts little effect upon the structure of the spectrum,

*) Recently we have established [27], that the corresponding arylazo-2-naphthylamines exhibit a fairly similar structure of their spectra in the UV range, thus indicating a similar structure of their molecules. On the contrary spectra of 4-arylazo-1-naphthylamines seem to confirm the azo structure. This subject will be dealt with in a future paper.

because tautomeric equilibrium in an alcoholic solution of (IIc) is already strongly shifted in favour of the phenylhydrazone tautomer (Figs. 7 and 8). The spectrum of (IIe) in benzene solution is given in [20].

Data on absorption spectra for the discussed dyes (at room temp.) are given as follows.

Compd.	m.p.	$\lambda_{max.}$ $m\mu$ (log $\varepsilon_{max.}$)
		a) in 95% ethanol
(Ia)	126°	*ca* 220 (4.56), 263 (4.05), 371 (4.14), *ca* 440 (3.17);
(Ib)	80—81°	236 (4.29), 271 (4.10), 396 (4.17);
(Ic)	201—202° *decomp.*	237 (4.27), 272 (4.13), 408 (4.21), 466 (4.04);
(Id)	167—168°	*ca* 225 (4.54), 286 (4.16), 404 (4.18);
(Ie)	278—279°	237 (4.19), *ca* 278 (3.94), 346 (3.90), 468 (4.61);
(IIa)	119—120°	219 (4.71), 277 (4.04), *ca* 287 (3.99), 364 (3.95), 460 (3.07);
(IIb)	60—62°	226 (4.61), 276 (4.06), 380 (3.91), 470 (3.31);
(IIc)	132—133°	229 (4.55), inflexion *ca* 260, 309 (3.86), 415 (4.04), 480 (4.19);
(IId)	193—195°	219 (4.77), 286 (4.25), 395 (4.03), *ca* 470 (3.37);
(IIe)	253°	*ca* 225 (4.55), inflexion *ca* 260, 327 (4.06), 486 (4.40);
		b) in *cyclo*hexane
(Ia)	—	222 (4.53), 264 (4.10), 272 (4.07), 374 (4.18), 448 (3.02);
(Id)	—	224 (4.65), 284 (4.24), 401 (4.24);
(IIa)	—	221 (4.69), 278 (4.09), 368 (4.07), 463 (3.05);
(IIc)	—	230 (4.59), *ca* 265 (4.02), 280 (3.82), 304 (3.84), *ca* 428 (4.10), 468 (4.12);
		c) in benzene
(Ic)	—	277 (4.14), 410 (4.14), 448 (4.13);
(Ic)	—	277 (—), 346 (—), 453 (—) conc. not established

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