BULLETIN DE L'ACADÉMIE
POLONAISE DES SCIENCES
Série des sciences chimiques
Volume VIII, No. 10, 1960

ORGANIC CHEMISTRY

On Absorption Spectra of Monoazo-dyes Derived from 1-Phenylazonaphthalene and 1-Phenylazoanthracene

by

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Presented by T. URBAŃSKI on August 13, 1960

The ultraviolet and visible absorption spectrum of 1-phenylazonaphthalene (PAN) is composed of four bands [1]—[3]: a weak *R*-band and an intense *K*-band are present at 463 mμ and 372 mμ, respectively. Two other bands are to be found in the shortwave part of the spectrum. The band at 219 mμ (we term it band I) is very intense, the second band (we term it band II) with a marked structure ($\lambda_{\max} = 266,273,290$ mμ) has a moderate intensity. Badger and Buttery [1] found, that the spectra of all phenylazonaphthalenes, azonaphthalenes, and their azoxy-derivatives have a similar structure in the ultraviolet region. They stated, that bands I and II arise from naphthalenic ring systems: band I apparently corresponds to a similar single peak at 221 mμ, peaks of band II apparently correspond to the other three peaks in the spectrum of naphthalene at 266, 275, and 285 mμ. Perekalin and Savost'yanova [4] have also reported that the ultraviolet spectra of several intermediates and azo-dyes derived from naphthalene contain bands characteristic for the naphthalene ring. In their opinion band I is connected only with electronic transitions in the naphthalene ring system, band II is mainly connected with changes of electronic states of the naphthalene ring, modified by substituents. In the visible region of the spectra of azo-dyes the characteristic bands which may be ascribed to the conjugation between the azo-group, the naphthalene ring system, and substituents, are present. Boguslavskaya, Bogoslovskii and Javorskii [5] have recently determined the absorption spectra of several monoazo-dyes derived from 1,1'-azonaphthalene (obtained by coupling diazotized 1-naphthylaminesulphonic acids with naphthols and naphthylamines). They also concluded that in the ultraviolet range of the discussed spectra bands characteristic for intermediates, and — in the visible range — for azo-dyes are present.

The origin of *K*- and *R*-bands has already been discussed in the literature [1], [3], [7] (cf. also our work [6]). In the present paper we mainly tried to elucidate the origin of two shortwave bands present in spectra of PAN and its derivatives*).

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*) It is known [2], [8]—[12] that several derivatives of PAN (for example *o*- and *p*-hydroxyazo-compounds) exhibit tautomerism: the solutions are shown to contain solvent- and temperature-

Spectral data of Badger and Buttery [1] (in alcohol) indicate the "naphthalenic" origin of bands I and II found in the spectra of phenylazonaphthalenes and azonaphthalenes:

Compound	Band I	Band II	K-band
	λ_{max} mμ (log ε_{max}).		
1-phenylazonaphthalene	219 (4.58)	266 (4.03), 273 (4.03), 290 (3.94)	372 (4.10)
2-phenylazonaphthalene	219 (4.48)	265 (4.13), 277 (4.13), 287 (4.13)	328 (4.28)
1,1′-azonaphthalene	214 (4.87)	266 (4.26)	400 (4.21)
2,2′-azonaphthalene	214 (4.57)	262 (4.39), 278 (4.28), 290 (4.18)	335 (4.37)

The short wavelength bands are far more intense in the azonaphthalene spectra than in those of phenylazonaphthalenes but their positions are practically unchanged (in contrast to K-bands). This confirms their "naphthalenic" origin.

The PAN molecule is, however, composed of two ring systems (naphthalenic and benzenoid) interconnected by the —N=N— group. Each of these systems is undoubtedly capable of playing the part of a partial chromophore. It may thus be expected that the intense band I in the spectra of PAN and its derivatives arises from the weak benzenoid partial chromophore band (found in the spectrum of azobenzene at 228 mμ [6]) fully overlapped by the intense naphthalenic partial chromophore band (at 214 mμ in the spectra of azonaphthalenes). We suggest that it is the naphthalenic system which mainly determines the intensity and the position of band I.

Comparison of absorption spectra of naphthalene and anthracene (Fig. 1) indicates that the intense band found in the spectrum of naphthalene at 220 mμ,

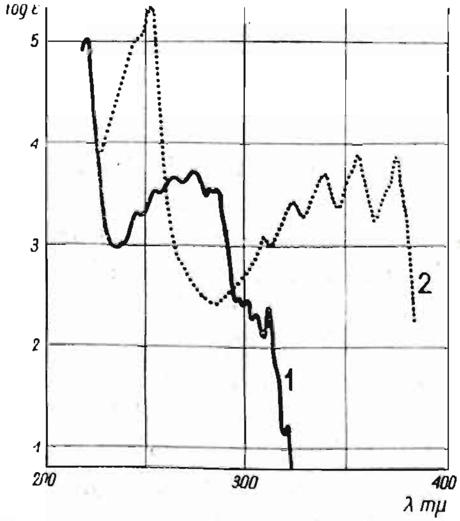

Fig. 1. Absorption spectra in ethyl alcohol (redrawn from [16]): 1. naphthalene, 2. anthracene

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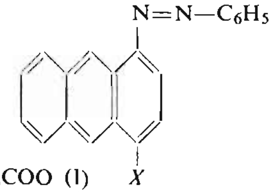
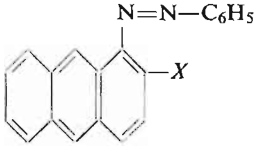
dependent equilibria of the phenylhydrazone and azo-tautomers. The effects of substituents and of the position of the OH group on these equilibria are also widely known. Absorption spectra of these dyes are thus much more complex, because each of the tautomers has its own characteristic absorption spectrum. Only the azo-tautomer bands may arise from the chromophore system of PAN. This will be dealt with in another paper [20].

is strongly shifted to longer wavelengths and its intensity in the spectrum of anthracene is far greater. We expect similar effects to be found, when the spectra of dyes derived from PAN and 1-phenylazoanthracene (PAA) are compared. In our opinion this would indirectly confirm formerly expressed suggestions that band I in the spectra of PAN and its derivatives is mainly of "naphthalenic" origin. We also expected that a weak benzenoid partial chromophore band is likely to be fully submerged in the spectra of PAN and its derivatives might be seen in the spectra of PAA derivatives.

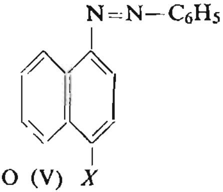
Thus we compared absorption spectra of several monoazo-dyes derived from PAA and PAN (Figs. 2—5), respectively:



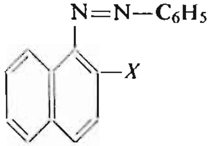
X=CH_3COO (I)
X=OH (II)



X=CH_3CONH (III)
X=NH_2 (IV)



X=CH_3COO (V)
X=OH (VI)



X=CH_3CONH (VII)
X=NH_2 (VIII)

Absorption spectra of the discussed dyes indicate that our suggestions may very likely be correct. Comparison of spectra of (I) and (V) (Fig. 2) (the spectra

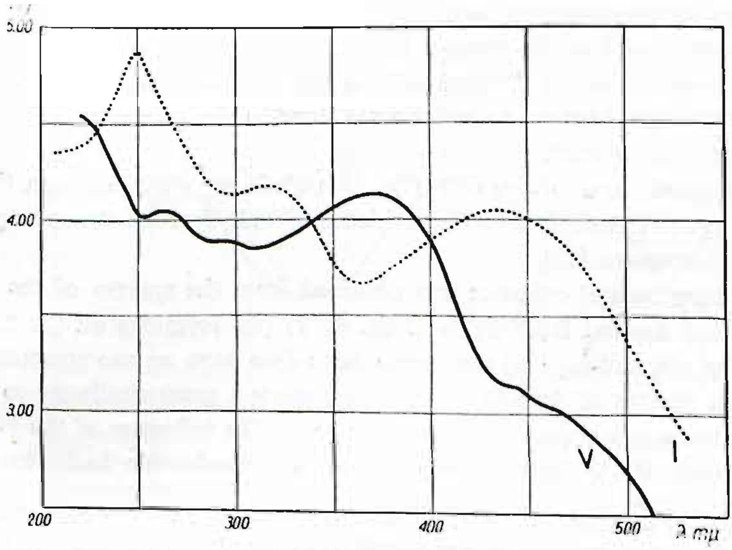


Fig. 2. Absorption spectra in ethyl alcohol (numbering of curves on Figs. 2—7 corresponds to the numbers of compounds used in the text)

also confirm the azo structure of these dyes and differ little from those of PAA and PAN, because the CH_3COO group has very weak auxochromic properties) indicates that band I in the spectrum of (I) exhibits a considerable bathochromic shift with a marked hyperchromic effect. We have not been able, however, to find the postulated "benzenoid" band in the spectrum of (I) (probably on account of its being entirely overlapped by the intense band I), in spite of the existence of a weak band near 235 mμ in the spectra of (III) and (IV)*) (Figs. 3, 4). It should be noted, however, that the intense band I in the spectra of dyes (III) and (IV) is additionally shifted to the red (because NH_2 and $NHCOCH_3$ groups have stronger auxochromic properties than the CH_3COO group): thus a weak band may exist at 235 mμ. The suggestion, however of the "benzenoid" origin of the mentioned band requires further confirmation, because a similar weak band in the spectrum of 2-anthramine is also found [19] to exist.

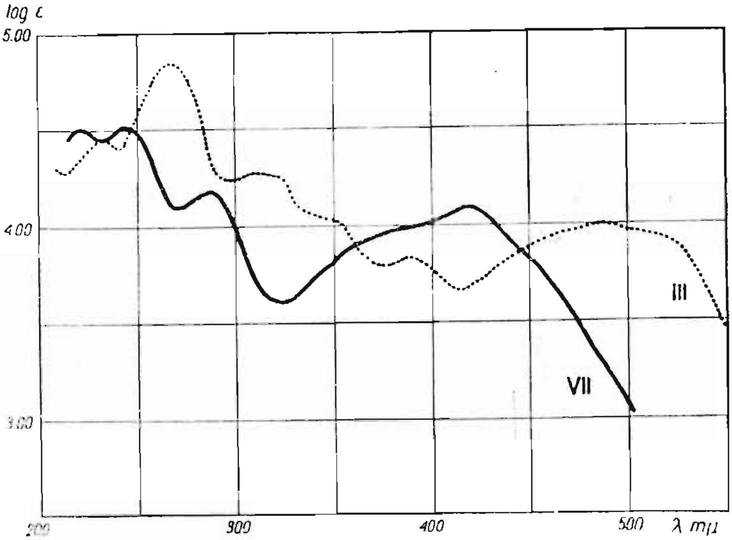


Fig. 3, Absorption spectra in ethyl alcohol

The absorption curve of dye (II) (Fig. 5) is distinctly different from the spectra of (I)—(III) and (VI) and gives further evidence of its hydrazone structure postulated formerly by Ospenson [12].

Further experimental evidence was obtained from the spectra of the following acetoxyazo-dyes derived from PAN (Figs. 6, 7) (cf. formulas on the next page).

It has been claimed [2] [14] that acetoxyazo-dyes have an azo structure. Indeed all absorption spectra of dyes (V), (IX)—(XI) show a great similarity to the PAN spectrum in the whole region under examination. The influence of the NO_2 group in *para* position of the benzene ring induces a considerable bathochromic shift

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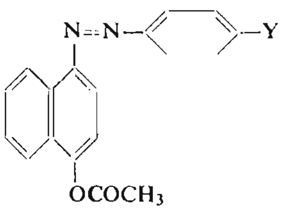
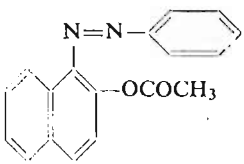
*) It is generally accepted [8], [9], [11], [12] that tautomeric equilibria exist in solutions of dye (VI). Very likely such equilibria are also present in the solutions of dyes (III), (IV), (VII), (VIII). It is postulated, moreover, [17], [18] that internal hydrogen bonds are present in *o*-amino- and *o*-acetylaminoazo-dyes.



Y=H (V)
Y=NO_2 (IX)



Y=H (X)
Y=NO_2 (XI)

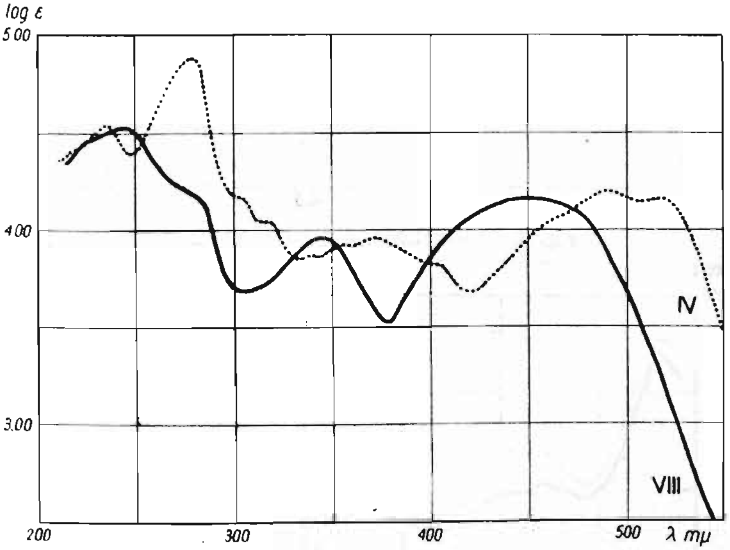


Fig. 4 Absorption spectra in ethyl alcohol

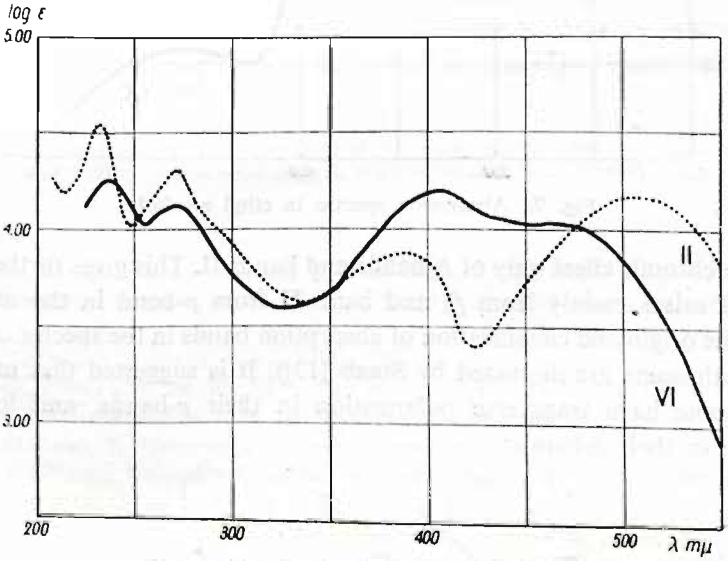


Fig. 5. Absorption spectra in ethyl alcohol

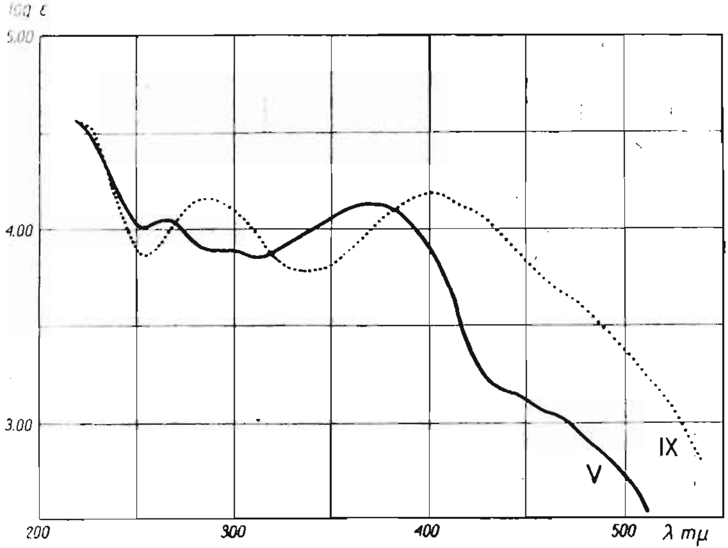


Fig. 6. Absorption spectra in ethyl alcohol

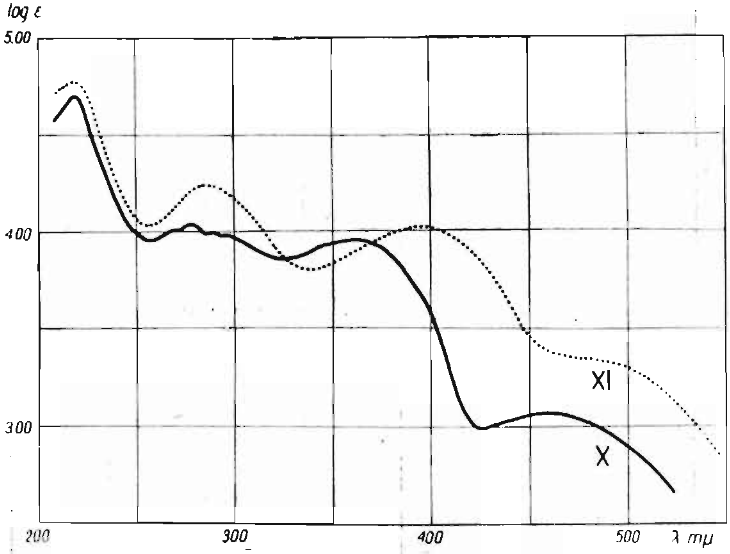
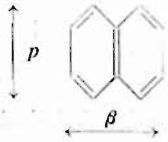
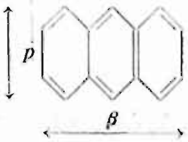


Fig. 7. Absorption spectra in ethyl alcohol

with a hyperchromic effect only of *K*-bands and bands II. This gives further evidence that band I arises mainly from β, and band II from *p*-band in the naphthalene spectrum (the origin and classification of absorption bands in the spectra of naphthalene and anthracene are discussed by Staab [13]). It is suggested that naphthalene and anthracene have transverse polarization in their *p*-bands, and longitudinal polarization in their β-bands:





The electron-accepting NO_2 group exhibits displacement of π-electrons in molecules of the discussed dyes (in the ground state), generally in the same direction as in the case of electronic transition connected with band II. The effect of the NO_2 group should exhibit a marked bathochromic shift rather of band II than of I.

Experimental details of the method of preparation of the known compounds (II)—(XI) will be reported elsewhere [15]. Dye (I) in the form of orange red needles (m.p. 163—165° from dil. alcohol) is new to literature and was obtained by refluxing the known dye (II) [12] with acetic anhydride and sodium acetate or pyridine during several hours.

Data on absorption spectra (in 95% ethanol at room temp.) for the discussed dyes are given as follows.

Compd.	m.p.	$\lambda_{max.}$ mμ (log $\varepsilon_{max.}$)
(I)	163—165°	250 (4.87), 317 (4.18), 438 (4.04);
(II)	234—235°	232 (4.56), 271 (4.32), 384 (3.89), 505 (4.18)
(III)	217—218°	234 (4.45), 267 (4.83), 312 (4.27), 390 (3.83), 490 (4.00);
(IV)	159°	236 (4.54), 280 (4.88), 316 (4.05), 372 (3.95), 405 (3.82), 490 (4.20), 515 (4.18);
(V)	126°	<220 (4,56), 263 (4,05), 371 (4.14), *ca* 440 (3.17);
(VI)	201—202° *decomp.*,	237 (4.27), 272 (4.13), 408 (4.21), 466 (4.04);
(VII)	150—152°	223 (4.50), 246 (4.52), 286 (4.19), 418 (4.09);
(VIII)	101—103°	243 (4.53), 345 (3.97), 446 (4.15);
(IX)	167—168°	*ca* 225 (4.54), 286 (4.16), 404 (4.18);
(X)	119—120°	219 (4.71), 277 (4.04), *ca* 287 (3.99), 364 (3.95), 460 (3.07);
(XI)	193—195°	219 (4.77), 286 (4.25), 395 (4.03), *ca* 470 (3.37).

The authors are much indebted to Professor W. Szymanowski, Physical Laboratory A, Technical University, Warsaw, for making available to them his spectrophotometers and to Miss S. Kwiatkowska, Institute of Organic Synthesis, Polish Academy of Sciences, for carrying out some of the experiments on absorption spectra.

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