

Some Studies on Azo Dyes. II

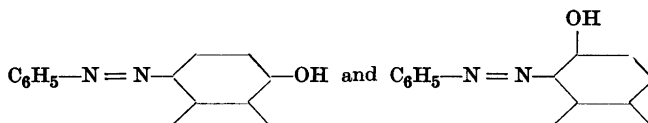
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In a previous publication¹ the author discussed the effect of an *o*-methyl group, *o*- and *m*-carboxyl groups, and combinations of the two on the absorption spectra of 4-phenylazo-phenol and 1-phenylazo-naphthol-(2). It was found that hydrogen bond formation in dyes containing an *o*-carboxyl group stabilized the hydrazone form and caused a displacement of the azo-hydrazone equilibrium toward the right. Some quantitative values for the relative amount of hydrazone form in the β -naphthol dyes were given.

The purpose of the present paper was to examine the effect of linearly annulated benzene nuclei on the absorption spectra of *o*- and *p*-hydroxy azo dyes.

For this purpose, the two isomeric series of dyes



with the auxochrome contained in a benzene, naphthalene, and anthracene nucleus, were synthesized and examined. The six corresponding O—CH₃ derivatives were also prepared.

THE ABSORPTION CURVES OF THE DYES

Fig. 1 shows the absorption curves of 2-phenylazo-phenol and its *O*-methyl ether. It can be seen that the hydroxy compound shows a double maximum (325 and 373 $m\mu$). The methoxy compound, however, shows only a single maximum at 322 $m\mu$.

Fig. 2 shows the curves of 1-phenylazo-naphthol-(2) and its *O*-methyl ether. In the visible region this hydroxy compound also shows a double

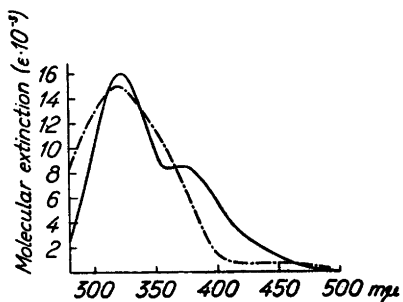


Fig. 1. Absorption curves of *o*-phenol dyes.

— 2-phenylazo-phenol
 - - - 2-phenylazo-phenol, methyl ether

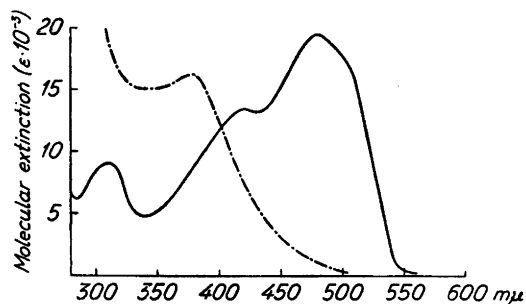


Fig. 2. Absorption curves of β -naphthol dyes.

— 1-phenylazo-naphthol-(2)
 - - - 1-phenylazo-naphthol-(2), methyl ether

maximum (422 and 480 $m\mu$). The methoxy compound shows only a single maximum at 380 $m\mu$.

Fig. 3 shows the curve of 1-phenylazo-anthrol-(2). The hydroxy compound, in this case, shows only a single, almost symmetrical maximum (511 $m\mu$), in the visible region. The $O-CH_3$ derivative could not be obtained in a pure crystalline state, but spectrophotometric studies on the methylation product indicated that this derivative shows an absorption band at approximately 435 $m\mu$. (As indicated in the figure.)

Fig. 4 shows the absorption curves of 4-phenylazo-phenol and its *O*-methyl ether. It can be seen that both of these show only a single, almost symmetrical maximum (349 and 343 $m\mu$ respectively) in the region examined.

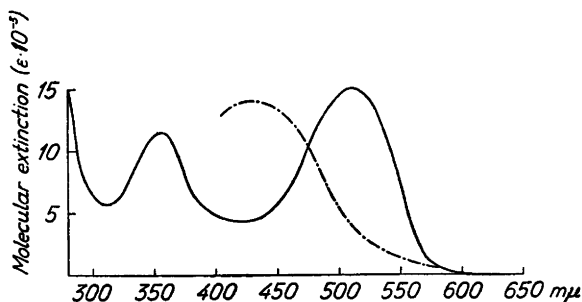


Fig. 3. Absorption curves of β -anthrol dyes.

— 1-phenylazo-anthrol-(2)
 - - - approximate absorption band of 1-phenylazo-anthrol-(2), methyl ether

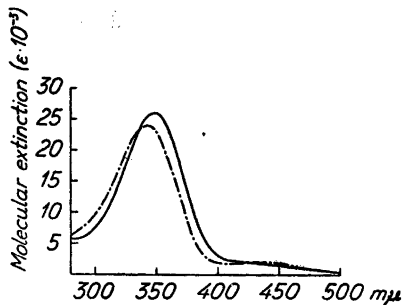


Fig. 4. Absorption curves of *p*-phenol dyes.

— 4-phenylazo-phenol
 - - - 4-phenylazo-phenol, methyl ether

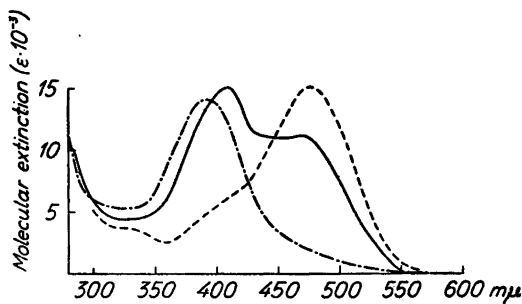


Fig. 5. Absorption curves of α -naphthol dyes.

— 4-phenylazo-naphthol-(1)
 - - - 4-phenylazo-naphthol-(1), methyl ether
 - · - 4-phenylazo-naphthol-(1) in acetic acid

Fig. 5 shows the curves of 4-phenylazo-naphthol-(1) in alcohol and glacial acetic acid and its O-methyl ether in alcohol. The hydroxy compound (in alcohol) shows a double maximum (410 and 470 $m\mu$), while in acetic acid it shows only a single maximum (475 $m\mu$). The O-methyl derivative shows only a single maximum at 392 $m\mu$.

Fig. 6 shows the curves of 4-phenylazo-anthrol-(1) and its O-methyl ether. In the visible range both of these dyes show only a single, almost symmetrical maximum at 506 and 445 $m\mu$, respectively.

All of the measurements were made in 96 % alcohol, except as noted. The extinction values of the O—CH₃ derivatives have been computed so as to best show their relationship to the corresponding dye.

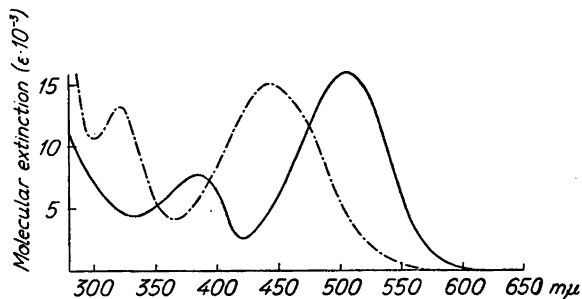


Fig. 6. Absorption curves of α -anthrol dyes.

— 4-phenylazo-anthrol-(1)
 - - - 4-phenylazo-anthrol-(1), methyl ether

The location of the absorption maxima are summarized in Table 1.

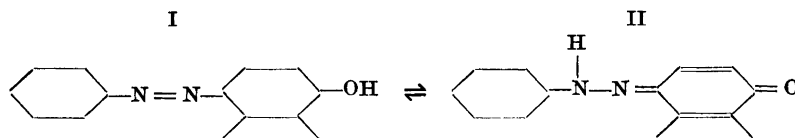
Table 1. The location of the absorption maxima.

Dye	Max. (m μ)
4-Phenylazo-phenol	349
4-Phenylazo-phenol, methyl ether	343
2-Phenylazo-phenol	{ 325
2-Phenylazo-phenol, methyl ether	{ 373
	322
4-Phenylazo-naphthol-(1)	{ 410
4-Phenylazo-naphthol-(1) (HOAc sol.)	{ 470
4-Phenylazo-naphthol-(1), methyl ether	475
α -Naphthoquinone-methylphenyl-hydrazone *	392
	466
1-Phenylazo-naphthol-(2)	{ 422
1-Phenylazo-naphthol-(2), methyl ether	{ 480
	380
4-Phenylazo-anthrol-(1)	506
4-Phenylazo-anthrol-(1), methyl ether	442
1-Phenylazo-anthrol-(2)	511
1-Phenylazo-anthrol-(2), methyl ether	435

* in benzene sol., Kuhn and Bär²

AZO AND HYDRAZONE BANDS

The azo-hydrazone tautomerism is a form of prototropy, where a proton migrates between an azo N atom and a phenolic O atom.



If this mobile proton is replaced by a methyl group attached to either the O or N atoms, the resultant methyl derivative cannot exhibit tautomerism and should indicate the approximate location of the absorption band of the corresponding form of the actual dye. That is to say, the O—CH₃ derivatives should indicate the absorption band of the azo form (I) and the N—CH₃ derivative that of the hydrazone form (II).

Kuhn and Bär², in their studies on this tautomerism, made use of this fact and studied the *o*- and *p*-phenol and naphthol dyes and some of their O and N derivatives. The present author has synthesized and examined the remaining O—CH₃ derivatives of these dyes and also the *o* and *p*-anthrol dyes and their O—CH₃ derivatives. The results tend to confirm Kuhn and Bär's theory.

4-Phenylazo-phenol shows only a single maximum which agrees very closely with that of its O—CH₃ derivative. For this reason it is assumed to exist almost completely in the azo form. The *ortho* isomer (2-phenylazo-phenol), however, shows a double maximum. The band which is similar to the O—CH₃ derivative is assumed to be due to the azo form while the band at longer wave length is assumed to be due to the hydrazone form.

Both of the naphthol dyes show a double maximum. The maxima at shorter wave lengths agree fairly well with the O—CH₃ derivatives, and are therefore assumed to be due to the azo form. The maximum at the longer wave length, in the case of the α -naphthol dye, agrees fairly well with both the N—CH₃ derivative and with the curve of the dye in acetic acid (in which Kuhn and Bär² state that the dye exists mainly in the hydrazone form). For this reason these maxima are assumed to be due to the hydrazone form.

The two anthrol dyes show only a single maximum in the visible range which differs widely from that of their O—CH₃ derivatives. For this reason

Table 2. The location of the azo and hydrazone bands.

Dye	Azo band (m μ)	Hydrazone band (m μ)
<i>p</i> -Series		
4-Phenylazo-phenol	343	...
4-Phenylazo-naphthol-(1)	392	475
4-Phenylazo-anthrol-(1)	442	506
<i>o</i> -Series		
2-Phenylazo-phenol	322	385
1-Phenylazo-naphthol-(2)	380	480
1-Phenylazo-anthrol-(2)	435	511

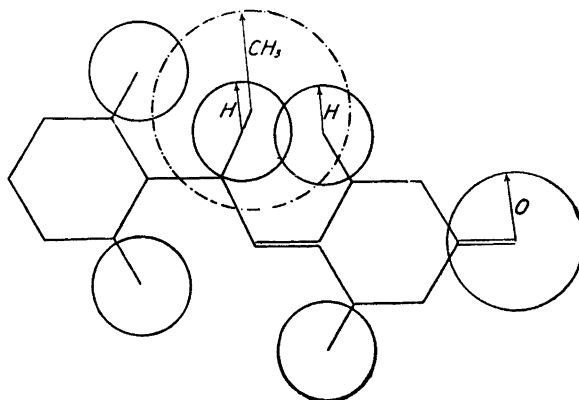


Fig. 7. Schematic diagram of hydrazone form of *p*-hydroxy azo dye, drawn to scale. The circles are the van der Waal radii of the atoms concerned.

the dyes are assumed to exist almost completely in the hydrazone form absorbing at the longer wave length.

On this basis, the following approximate values can be assigned for the absorption bands of the azo and hydrazone forms of the dyes.

THE CONFIGURATION OF THE N- AND O-METHYL DERIVATIVES OF THE DYES

In the foregoing it was stated that the N—CH₃ and O—CH₃ derivatives of the dyes should indicate the approximate positions of the hydrazone and azo bands of the corresponding dye. The validity of the use of these derivatives, however, should be further discussed.

The general similarity between the absorption curves of hydroxy and methoxy compounds, due to the "cushioning" effect of the oxygen atom, is well established³. Less is known regarding the use of N-methyl derivatives. It would be expected, however, that the replacement of an N—H group by a N—CH₃ group would not cause any appreciable shift in the location of the absorption band.

The question also arises, however, whether or not there would be any steric effect caused by the replacement of a relatively small hydrogen atom by a twice as large methyl group.

Resonance in the azo dyes, giving all of the bonds partial double bond character, tends to make the entire molecule coplanar⁴. In *cis* azo benzene, however, steric effects cause the phenyl groups to be rotated by approximately 50°⁵. This steric effect can be predicted by drawing the *cis* azo benzene

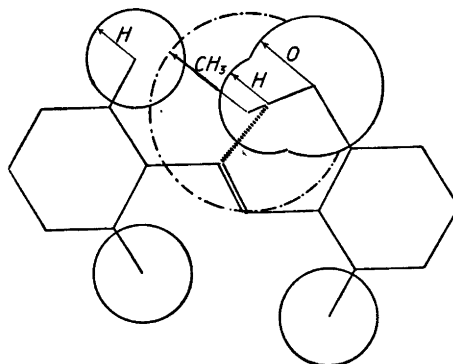


Fig. 8. Schematic diagram of azo form of *o*-hydroxy azo dye, drawn to scale.

molecule to scale with the use of 1.0 Å for the van der Waals radius for hydrogen ⁴.

In the *p*-hydroxy dye series, the replacement of the hydroxyl group by a methoxy group would obviously not cause any steric interference on the configuration of the molecule.

If the above-mentioned technique is applied to the hydrazone form of the *p*-hydroxy dye (using a van der Waal radius of 1.0 Å for hydrogen, 1.4 Å for oxygen, and 2.0 Å for the methyl group), Fig. 7 is obtained. It can be seen from this figure that the H attached to the hydrazone grouping overlaps only slightly the adjacent H atom. That is to say, there would be little or no steric interference towards the coplanarity of the molecule. If this H is replaced by a CH₃ group (dot-dash circle), however, it can be seen that the overlapping is nearly complete. This means that the N—CH₃ group would tend to prevent the coplanar configuration of the N—H form.

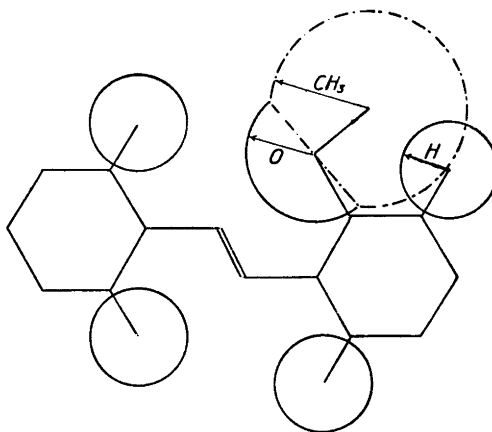


Fig. 9. Schematic diagram of alternative azo form of *o*-hydroxy azo dye, drawn to scale.

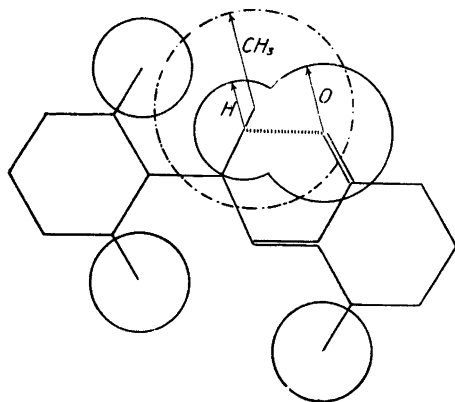


Fig. 10. Schematic diagram of hydrazone form of *o*-hydroxy azo dye, drawn to scale.

A similar drawing for the azo form of the *o*-hydroxy dye, containing an O—H . . . N hydrogen bond, is shown in Fig. 8. It can be seen that the OH group causes no steric interference and the molecule would be coplanar. If this H atom is replaced by a CH₃ group (dot-dash curve), it overlaps the center of the N atom, to which it is not bound, and thereby tends to prevent coplanarity. In this case, however, there is free rotation about the C—OH bond and the strain could be relieved by such a rotation rather than by a rotation of the phenyl groups. If the C—OCH₃ rotates by 180°, the configuration shown in Fig. 9 is obtained. Here also the CH₃ group overlaps considerably the *o*-hydrogen atom. It will be noticed, however, that a rotation of 90° removes all steric interference and allows the phenyl groups to remain coplanar for both the OH and OCH₃ forms.

A similar drawing for the hydrazone form of the *o*-hydroxy dye, containing an N—H . . . O hydrogen bond, is shown in Fig. 10. Here also, as in the case of the hydrazone form of the *p*-hydroxy dye, the replacement of the N—H by a N—CH₃ group causes strong steric interference and would tend to prevent the coplanar configuration of the N—H form.

Thus it would appear as if the OCH₃ derivative of the *p*-hydroxy dyes can maintain the same configuration as the OH form, while the OCH₃ derivative of the *o*-hydroxy dyes would be rotated by 90° around the C—OCH₃ bond. It would also appear as if the N—CH₃ derivatives of both *o*- and *p*-hydroxy dyes cannot achieve the coplanar configuration of the N—H form.

How much effect these changes would have on the visible absorption spectrum is not known. The close similarity between the OH and OCH₃ curves for the *o*- and *p*-phenol dyes tends to indicate that the effect is slight. In the only case where the N—CH₃ derivative can be compared (*α*-naphtho-

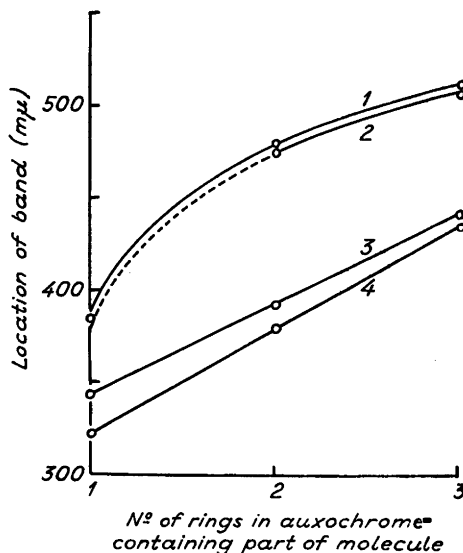


Fig. 11. Effect of linearly annulated benzene nuclei on the location of the azo and hydrazone bands.

Curve 1. hydrazone band of *o*-hydroxy dye
 Curve 2. hydrazone band of *p*-hydroxy dye
 Curve 3. azo band of *p*-hydroxy dye
 Curve 4. azo band of *o*-hydroxy dye

quinone-methylphenyl-hydrazone), it agrees fairly well with the value for the hydrazone form (see Tables 1 and 2) and thereby indicates that, in this case also, the effect of the change in configuration has little effect on the visible spectrum.

THE EFFECT OF LINEARLY ANNULATED BENZENE NUCLEI ON THE AZO AND HYDRAZONE BANDS

If the values for the location of the azo and hydrazone bands, shown in Table 2, are plotted against the number of rings in the auxochrome-containing part of the molecule, the curves shown in Fig. 11 are obtained.

In this Fig., curves 1 and 2 show the effect of linearly annulated benzene nuclei on the location of the hydrazone band of *o* and *p*-hydroxy azo dyes, respectively. It can be seen that the hydrazone band of the *o*-hydroxy dye is located at slightly longer wave lengths than that of its isomer; however, the difference is very small. This fact can be verified by comparing the curves of the two anthrol dyes (Figs. 3 and 6) as well as the β -naphthol dye in alcohol (Fig. 2) and the α -naphthol dye in acetic acid (Fig. 5), in both of which the hydrazone form predominates. No value for the hydrazone band of the 4-phenylazophenol dye could be obtained. An extrapolation of curve 2 (as shown by the dotted line) would, however, tend to indicate that the hydrazone band of this dye should be located at approx. 375 $m\mu$.

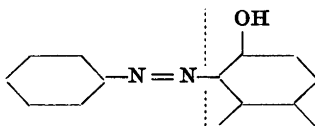
Curves 3 and 4 show the effect of linearly annulated benzene nuclei on the azo bands of *p*- and *o*-hydroxy azo dyes, respectively. It will be noticed that in this case, in contrast to the hydrazone bands, the azo bands of the *p*-hydroxy dyes are located at longer wave lengths than the *ortho* isomers. This difference between the location of the azo bands of the isomeric dyes seems to decrease as the number of annulated rings increases.

The similarity between curves 1 and 2 indicates that the annulation of benzene nuclei to the hydrazone form of the dye has approx. the same effect on both the *ortho* and *para* isomers. In the same way, the similarity between curves 3 and 4 indicates that the azo bands of both isomers are similarly affected by linear annulation. On the other hand, linear annulation does not have the same effect on the azo and hydrazone bands of dyes in the same series. This is shown by the dissimilarity in the curves 1 & 4 and 2 & 3. That is to say, the annulation of one benzene nucleus to the *ortho* phenol dye causes a much greater bathochromic effect on the hydrazone band than on the azo band. The same is true in the *para* series.

The linearity of the bathochromic effect on the azo bands (curves 3 and 4) is striking. Lewis and Calvin⁶ have found a similar linear relationship between the absorption max. and the number of conjugated double bonds between chromophors in a series of carbocyanines. This they explained on the basis of resonance in the conjugated chain.

In the case of the azo dyes, the auxochrome and chromophor are also separated by a resonating group, *i. e.*, a benzene, naphthalene, or anthracene group. It is very possible that these act in a similar manner as the resonating chain in the carbocyanines. It is the author's purpose to discuss qualitatively the influence of linearly annulated benzene nuclei on the hydrazone and azo bands of azo dyes in terms of enhanced resonance possibilities.

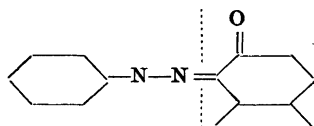
The linear relationship in curves 3 and 4 may be explained in the following way:



The resonance in the left-hand portion of all the dyes (in the azo form) may be considered to be approximately constant, and therefore only the resonance in the auxochromic part need be discussed. The resonance energies of benzene, naphthalene, and anthracene are shown in Table 3. It can be seen that there is an approximately linear relationship between the resonance energies of these three structures, within the fairly large limit of accuracy of

the energy values. The addition of the approximately constant resonance energies of the phenylazo and hydroxyl groups would not affect the linearity of the resonance energies. Thus it can be seen that both the location of the azo band and the resonance energies are linear functions of the number of annulated benzene nuclei.

The hydrazone bands, as can be seen from curves 1 and 2, (Fig. 11) are not linear functions of the number of linearly annulated rings. This non-linearity can, however, be explained in exactly the same manner as was used for the azo bands.



As before, the resonance in the left-hand part of the molecule may be considered constant. An approximate value of the relative resonance energies of the quinoid structures (right-hand part) can be obtained by comparing the 1,2-benzo-, naphtho-, and anthraquinones. The resonance energies of these substances are shown in Table 3. It must be noted that the accuracy of these values is undoubtedly not too great. Their general relationship is, however, supported by other facts. The very low resonance in the benzoquinone structure, for example, is shown by the interatomic distances. The C—C value for this substance is 1.50 Å⁷, which corresponds to 92 % single bond character⁴, and the C=C value is 1.32 Å⁷, which corresponds to 100 % double bond character⁴, showing that the resonance is slight. The increase in resonance energy is also manifested in the reduction in redox-potential (see Table 4).

It can be seen from Table 3 that the linear annulation of a benzene nucleus to 1,2-benzoquinone causes a relatively large increase in resonance energy (approx. 50 kcal/mole) whereas the annulation of another nucleus has a much smaller effect (approx. 30 kcal/mole). This non-linear increase in resonance energy is similar to the increase in the hydrazone band (curves 1 and 2, Fig. 11), in which a large bathochromic effect is noted on the annulation of one benzene nucleus and a much smaller bathochromic effect on the annulation of an additional nucleus.

Thus, once again, a parallel relationship is found to exist between the increase in resonance energy and the shift in the location of the hydrazone band.

Although the above discussion was based on the *o*-hydroxy dyes, the same results are obtained using the *p*-hydroxy dyes (*cf.* resonance energies of the 1,4-quinones, Table 3).

Table 3. The resonance energies of the benzoid and quinoid structures.

Substance	Resonance energy kcal/mole	Diff.
Benzene	41 ¹	
Naphthalene	75 ²	34
Anthracene	105 ²	30
1,2-Benzoquinone	10 ³	
1,2-Naphthoquinone	60 ³	50
1,2-Anthraquinone	90 ³	30
1,4-Benzoquinone	15 ³	
1,4-Naphthoquinone	62 ³	47
1,4-Anthraquinone	95 ³	33

1. Dewar, M. J. S. *The electronic theory of organic chemistry*, Oxford (1949).
2. Pauling, L. *The nature of the chemical bond*, Ithaca, N. Y. (1948).
3. Calculated from data given by Berliner, E. *J. Am. Chem. Soc.* **68** (1946) 49.

(The values for the anthraquinones were obtained by using the redox-potentials, see Table 4, and the curve given by Berliner.)

AZO-HYDRAZONE EQUILIBRIUM

The author has previously discussed ¹ the effect of hydrogen bond formation on the azo-hydrazone equilibrium in azo dyes. The effect of linearly annulated benzene nuclei on this equilibrium has now been examined.

It was found that as the number of linearly annulated rings, in the auxochrome-containing part of the molecule, increased, the relative amount of hydrazone form increased, until in the anthrol dyes the equilibrium was apparently completely displaced in favor of the hydrazone form.

In the above-mentioned paper ¹, the author discussed the breakdown of the absorption spectrum of 1-phenylazo-naphthol-(2) and various derivatives into the component azo and hydrazone bands. The use of the value $\frac{\epsilon_H}{\epsilon_A + \epsilon_H}$ as indicative of the relative amount of hydrazone form was also discussed.

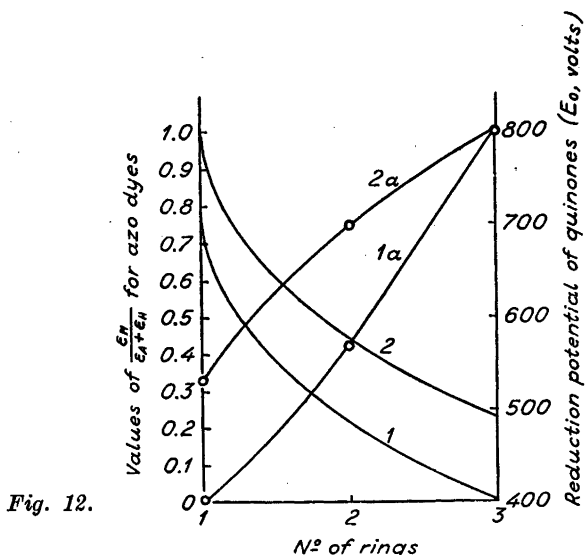


Fig. 12.

Using the values given in Table 2 as indicative of the approximate location of the hydrazone and azo bands, the double maxima curves of 2-phenylazo-phenol and 4-phenylazo-naphthol-(1) can also be broken down into their component azo and hydrazone bands and the values of $\frac{\epsilon_H}{\epsilon_A + \epsilon_H}$ calculated. It was found that 2-phenylazo-phenol gave a value of approx. 0.32 for $\frac{\epsilon_H}{\epsilon_A + \epsilon_H}$ and 4-phenylazo-naphthol-(1) a value of approx. 0.42. The value for 1-phenylazo-naphthol-(2), previously found, is approx. 0.75. As previously discussed¹, if the extinction values for the pure azo and hydrazone forms are similar, then the above values times one hundred are the approximate percent hydrazone form.

The nearly perfect symmetry of the 4-phenylazo-phenol curve and its close similarity to the curve of its O—CH₃ derivative (see Table 1 and Fig. 4) tend to indicate that this dye exists completely in the azo form, *i. e.*,

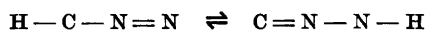
$$\frac{\epsilon_H}{\epsilon_A + \epsilon_H} \approx 0.$$

The maxima in the visible spectrum for both 4-phenylazo-anthrol-(1) and 1-phenylazo-anthrol-(2) are also almost perfectly symmetrical but differ widely from those of their O—CH₃ derivatives. For these reasons, it appears as if these dyes exist almost completely in the hydrazone form, *i. e.*,

$$\frac{\epsilon_H}{\epsilon_A + \epsilon_H} \approx 1.$$

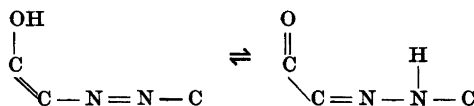
If these values of $\frac{\epsilon_H}{\epsilon_A + \epsilon_H}$ are plotted against the number of rings in the auxochrome-containing part of the molecule, *i. e.*, in the phenolic component, the curves 1 a and 2 a in Fig. 12 are obtained. This shows that as the number of rings in the phenolic component of *p*-hydroxy azo dyes increases from 1 to 3 the relative amount of hydrazone form increases from 0 to 1.0. In the *o*-hydroxy dyes, the same increase in the number of rings causes the amount of hydrazone form to increase from approx. 0.3 to 1.0.

One cause of this shift in the azo-hydrazone equilibrium would be expected to be a change in the relative stability of the two forms. Branch and Calvin⁸ have calculated that the hydrazone form of the triad system:



is more stable by approximately 9 kcal./mole.

A system such as:



which occurs in *o*-hydroxy dyes, gives a value of 432 kcal./mole for the summation of bond energies for the azo form and 456 kcal./mole for the hydrazone form. That is, the hydrazone form, neglecting resonance effects, is more stable by approx. 24 kcal./mole. Thus it can be seen that the hydrazone grouping is, in general, more stable than the azo grouping.

Also the stability of the resulting quinoid structure in the hydrazone form would be expected to be of importance. Table 4 shows the reduction potentials of the 1,2- and 1,4- quinones. Curves 1 and 2 in Fig. 12 show the plot of these values. It can be seen that as the stability of the quinoid structure increases (*i. e.*, as the reduction potential decreases) the relative amount of the hydrazone form of the dye (which contains the quinoid structure) increases.

On this basis, the curves 1 a and 2 a in Fig. 12 could be explained in the following way. Although the hydrazone grouping is, in itself, always more stable than the azo grouping, the relative instability of the quinoid structure in the phenol dyes counteracts this effect and causes an equilibrium to be established which favors the azo form. In the naphthol dyes, which contain the relatively more stable 1,2- or 1,4-naphthoquinone structures, the equilibrium is displaced further toward the hydrazone form. In the anthrol dyes, the anthraquinone structures are so stable that the equilibrium is displaced completely in favor of the hydrazone form.

Table 4. Reduction potentials of quinones (25°).

Quinone	E_0 volts	
	Aq. sol.	Alc. sol.
1,4-Benzoquinone	0.699	0.715 ¹
1,2 »	0.794 ²
1,4-Naphthoquinone	0.470 ³	0.484 ⁴
1,2 »	0.555 ⁴	0.576 ²
1,4-Anthraquinone	0.401 ⁵
1,2 »	0.490 ⁶

¹ Fieser, L. F. *J. Am. Chem. Soc.* **52** (1930) 4915.

² Fieser, L. F., and Peters, M. A. *Ibid.* **53** (1931) 793.

³ La Mer, V. K., and Baker, L. E. *Ibid.* **44** (1922) 1954.

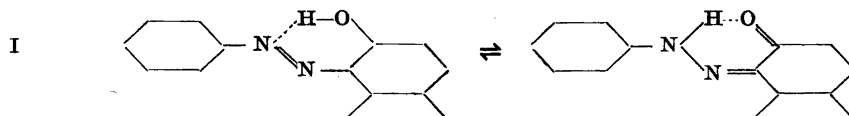
⁴ Fieser, L. F., and Fieser, M. *Ibid.* **56** (1934) 1565.

⁵ Fieser, L. F. *Ibid.* **50** (1928) 465.

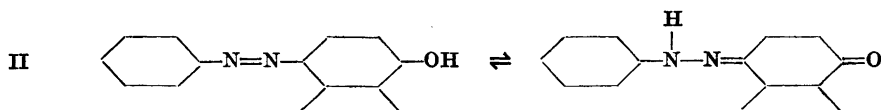
⁶ Conant, J. B., and Fieser, L. F. *Ibid.* **46** (1924) 1858.

It will be noticed, that the 1,4-quinone structure is always more stable than the isomeric 1,2-quinone (Table 4). On the basis of the above reasoning, one would expect that the *p*-hydroxy dyes would therefore show a larger amount of hydrazone form than the corresponding *o*-hydroxy dyes. This, however, is not the case. The *o*-phenol and β -naphthol dyes both show a larger $\frac{\epsilon_H}{\epsilon_A + \epsilon_H}$ value than the isomeric *p*-phenol and α -naphthol dyes (Fig. 12). This fact would tend to indicate that there is another factor which influences the position of the azo-hydrazone equilibrium.

In the *o*-hydroxy dyes the tautomeric equilibrium is between the following two structures:



whereas that in the *p*-hydroxy dyes is between the structures:



In I, the change between the azo and hydrazone form is very easily accomplished by a slight displacement of the proton and a simultaneous rearrangement of the electrons. This undoubtedly intramolecular mechanism should allow for a very mobile tautomerism ⁹.

The equilibrium II, which is accompanied by a relatively large displacement of the proton, must proceed by some other mechanism and would not be expected to be as mobile as I. It is possible that II involves an intermolecular mechanism since it shows a great dependence on solvent, whereas I is almost independent of solvent ².

Thus the relatively greater amount of hydrazone form in the *o*-hydroxy dyes, in spite of the lower stability of its 1,2-quinoid structure, can be ascribed to some factor dependent on the mechanism or mobility of the tautomerism. This point will be further discussed in a later publication.

EXPERIMENTAL

β-Anthrol. Sodium anthraquinone-(2)-sulfonate was reduced according to Liebermann ¹⁰. Recrystallization from boiling water yielded almost colorless crystals, which were dried at 165° to remove all water of crystallization. Yield approx. 65 %.

$C_{14}H_9SO_3Na$ (280.27)	Calc.	S	11.44
	Found	»	11.55

The resultant sodium anthracene-(2)-sulfonate was fused with KOH according to Lagodzinski ¹¹. Recrystallization from benzene yielded light yellow-tan crystals. The yield of crude *β*-anthrol was approx. quantitative. M. p. 253–254° (lit. 255°).

$C_{14}H_{10}O$ (194.22)	Calc.	C	86.57	H	5.19
	Found	»	86.43	»	5.06

α-Anthrol. Sodium anthraquinone-(1)-sulfonate was reduced according to Schmidt ¹² and the resulting sodium anthracene-(1)-sulfonate was fused with KOH according to Dienel ¹³.

Recrystallization from aqueous alcohol yielded yellow-tan crystals. M. p. 150–151° (lit. 150–153°).

$C_{14}H_{10}O$ (194.22)	Calc.	C	86.57	H	5.19
	Found	»	86.48	»	5.08

4-Phenylazo-phenol. The preparation of this dye was given in detail in a previous publication ¹.

It was obtained as yellow-brown crystals from aqueous alcohol. M. p. 151–152° (lit. 152, 154°).

$C_{12}H_{10}N_2O$ (198.22)	Calc.	N	14.13
	Found	»	13.97

4-Phenylazo-phenol, methyl ether. This was prepared from the above with diazomethane according to Smith¹⁴. Two recrystallizations from petroleum ether yielded orange-red plates. M. p. 52–53° (lit. 53°).

4-Phenylazo-naphthol-(1). This was prepared in the usual manner¹ from α -naphthol and benzene diazonium chloride.

Two recrystallizations from benzene yielded dark-violet crystals. M. p. 205–206° (lit. 206°).

$C_{16}H_{12}N_2O$ (248.27)	Calc.	N	11.31
	Found	»	11.34

4-Phenylazo-naphthol-(1), methyl ether. This was prepared from the above by means of dimethyl sulfate according to Charrier¹⁵.

Recrystallization from aqueous alcohol yielded red-orange crystals. M. p. 82–83° (lit. 83°).

4-Phenylazo-anthrol-(1). This was prepared according to Sircar¹⁶. However, it could not be obtained in a crystalline form, as claimed by the above author, but precipitated from benzene as a dark-violet powder.

$C_{20}H_{14}N_2O$ (298.33)	Calc.	N	9.40
	Found	»	9.60

4-Phenylazo-anthrol-(1), methyl ether. 1 g of 4-phenylazo-anthrol-(1) was added to 100 ml of aqueous NaOH (5 g NaOH per 100 ml water). 5 ml of dimethyl sulfate were added and the mixture was refluxed on a water bath for several hours. It was then poured into a large excess of water and extracted several times with large amounts of ether. The ether was dried over Na_2SO_4 and evaporated. The resultant red powder was recrystallized first from 96 % alcohol and then from benzene yielding fine red crystals. M. p. 140–141°.

$C_{21}H_{16}N_2O$ (312.36)	Calc.	OCH ₃	9.93
	Found	»	9.98

This compound is not previously reported in the literature.

2-Phenylazo-phenol. This was prepared according to Bamberger¹⁷. Recrystallization from ether and alcohol-water yielded fine orange needles. M. p. 81–82° (lit. 82.5–83°).

2-Phenylazo-phenol, methyl ether. This was also prepared according to Bamberger¹⁸ from *o*-anisidine and nitrosobenzene. The orange oil obtained, however, did not crystallize even after standing several months *in vacuo* at 0°. A methoxyl determination on the orange oil, however, showed the substance to be quite pure.

Calc.	OCH ₃	14.62
Found	»	14.89

1-Phenylazo-naphthol-(2). The preparation of this dye was given in detail in a previous publication¹.

It was obtained as red-orange needles from ether. M. p. 131–132° (lit. 128.5°).

$C_{16}H_{12}N_2O$ (248.27)	Calc.	N	11.31
	Found	»	11.28

1-Phenylazo-naphthol-(2), methyl ether. The above dye was methylated according to Charrier¹⁵ with dimethyl sulfate.

Recrystallization from aqueous alcohol yielded beautiful red plates. M. p. 61–62° (lit. 62°).

1-Phenylazo-anthrol-(2). This dye was prepared in the same manner as the isomeric α -anthrol dye.

Two recrystallizations from 96 % alcohol yielded fine red-orange needles. M. p. 199° (decomposition).

$C_{20}H_{14}N_2O$ (298.33)	Calc.	N	9.40
	Found	»	9.61

The isolation of this dye has not previously been reported.

1-Phenylazo-anthrol-(2), methyl ether. Attempts were made to methylate the above dye with dimethyl sulfate in aqueous KOH and with methyl iodide and silver oxide. In neither case could the absolutely pure crystalline substance be obtained.

SUMMARY

The effect of linearly annulated benzene nuclei on the isomeric *o*- and *p*-hydroxy azo dyes has been examined. The absorption curves of the phenolic dyes and their methyl ethers are given. The location of the azo and hydrazone bands of each of the dyes is discussed, as well as the configuration of the O—CH₃ and N—CH₃ derivatives.

The shift in the location of the azo and hydrazone bands caused by linear annulation is explained on the basis of resonance. It was found that the azo band showed a linear increase while the hydrazone band did not.

The location of the azo-hydrazone equilibrium is explained on the basis of three factors:

1. The relatively greater stability of the hydrazone grouping.
2. The relative stability of the quinoid structure in the hydrazone form.
3. A factor depending on the mechanism or mobility of the tautomerism.

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