

## Some Studies on Azo Dyes. I

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The purpose of the present investigation was to examine the effect of amino-*p*-toluic and aminoterephthalic acid structures on the properties of the related azo dyes. These two amino acids have been prepared from *p*-cymene<sup>8,11</sup> a by-product of the sulfite pulping industry.

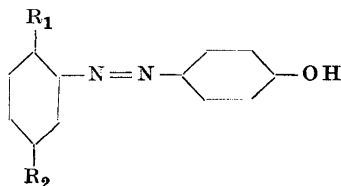
Two series of dyes were synthesized. One utilized phenol and the other  $\beta$ -naphthol as the phenolic component. The reason for this choice was two-fold: firstly they are the most common commercially used and secondly, they represent, in solution, the two different forms of azo compounds. That is to say, phenol dyes exist mainly in the azo form, whereas  $\beta$ -naphthol dyes exist mainly in the hydrazone form<sup>1</sup>.

The following substances were used as the amine component:

aniline  
*o*-toluidine  
*m*-amino-benzoic acid  
*o*-amino-benzoic acid  
 3-amino-*p*-toluic acid  
 aminoterephthalic acid

In this manner the effect of an *o*-methyl group, *o*- and *m*-carboxyl groups, and combinations of the two could be determined.

The nomenclature and formulae of the *p*-phenol dyes are shown below:



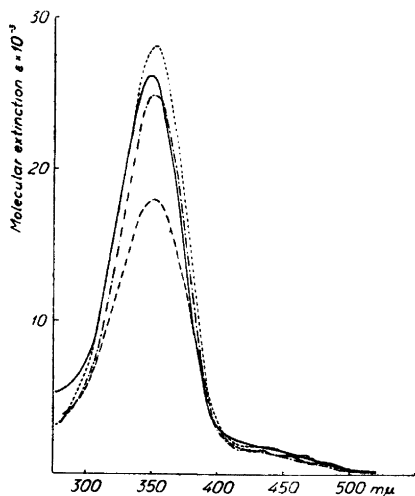


Fig. 1. Absorption curves of Phenol I, II, III, and V.

————— Phenol I  
 - - - - - Phenol II  
 - · - · - Phenol III  
 - - - - - Phenol V

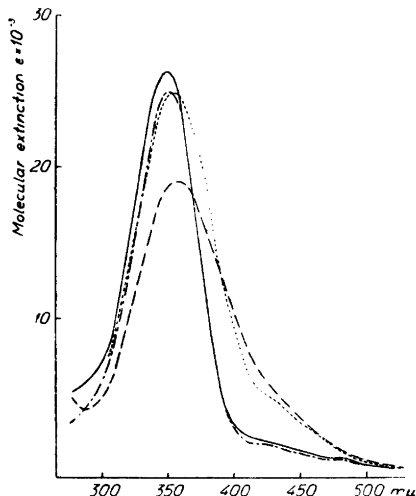


Fig. 2. Absorption curves of Phenol I, III, IV, and VI.

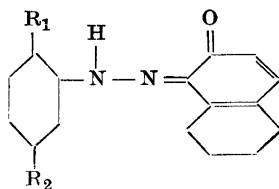
————— Phenol I  
 - · - · - Phenol III  
 - - - - - Phenol IV  
 - - - - - Phenol VI

Phenol I	$R_1 = H$	$R_2 = H$
Phenol II	$R_1 = CH_3$	$R_2 = H$
Phenol III	$R_1 = H$	$R_2 = COOH$
Phenol IV	$R_1 = COOH$	$R_2 = H$
Phenol V	$R_1 = CH_3$	$R_2 = COOH$
Phenol VI	$R_1 = COOH$	$R_2 = COOH$

Fig. 1 shows the absorption curves of Phenol I, II, III, and V in 96% alcohol. All of these dyes show a single, well-defined, almost symmetrical maximum at approximately 350  $m\mu$ , and are, in all respects, very similar.

Fig. 2 shows the absorption curves of Phenol I, III, IV, and VI. It can be seen that the both dyes containing an *o*-carboxyl group (IV and VI) show a maximum at slightly longer wave lengths than the other two, and show a strongly increased absorption in the region from 370 to 500  $m\mu$ .

The nomenclature and formulae of the dyes of the  $\beta$ -naphthol series are shown below:



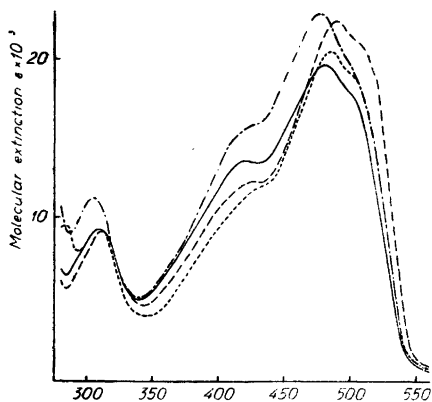


Fig. 3. Absorption curves of  $\beta$ -Naphthol I, II, III, and V.

—————	$\beta$ -Naphthol I
-----	$\beta$ -Naphthol II
- · - · - · -	$\beta$ -Naphthol III
-----	$\beta$ -Naphthol V

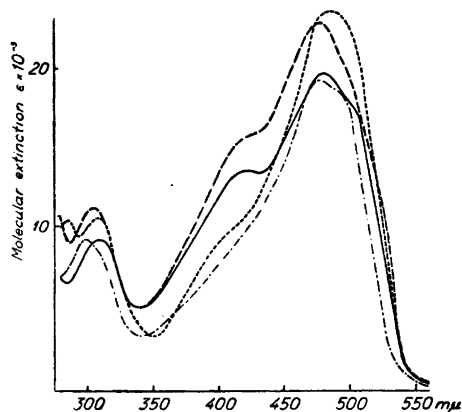


Fig. 4. Absorption curves of  $\beta$ -Naphthol I, III, IV, and VI.

—————	$\beta$ -Naphthol I
-----	$\beta$ -Naphthol III
- · - · - · -	$\beta$ -Naphthol IV
-----	$\beta$ -Naphthol VI

$\beta$ -Naphthol I	$R_1 = H$	$R_2 = H$
$\beta$ -Naphthol II	$R_1 = CH_3$	$R_2 = H$
$\beta$ -Naphthol III	$R_1 = H$	$R_2 = COOH$
$\beta$ -Naphthol IV	$R_1 = COOH$	$R_2 = H$
$\beta$ -Naphthol V	$R_1 = CH_3$	$R_2 = COOH$
$\beta$ -Naphthol VI	$R_1 = COOH$	$R_2 = COOH$

Fig. 3 shows the absorption curves of  $\beta$ -Naphthol I, II, III, and V, in 96 % alcohol. It can be seen that all the dyes show a maximum at approximately 310  $m\mu$ , which corresponds very closely to the position of absorption of the naphthalene nucleus (311  $m\mu$ )<sup>2</sup>. In addition, V shows a very small maximum at 284  $m\mu$ . In the visible range, all of the dyes show either a small maximum or an inflection at approximately 425  $m\mu$ , and a large maximum at approximately 480  $m\mu$ .

Fig. 4 shows the absorption spectrum of  $\beta$ -Naphthol I, III, IV, and VI. The max. at approximately 310  $m\mu$  is obvious in this series also. It can be seen that the inflection points, in the region around 425  $m\mu$ , so obvious in the dyes in Fig. 3, are almost completely missing in the dyes containing an *o*-carboxyl group (IV and VI). The characteristic maximum at approximately 480  $m\mu$  is common to all the dyes.

Table 1 summarizes the positions of the absorption maxima in both series.

Table 1. The location of the absorption maxima.

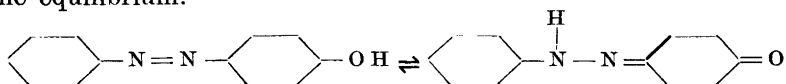
Dye		Location of max. in $m\mu$			
$\beta$ -Naphthol	I	—	312	421	480
»	II	—	312	427	488
»	III	—	305	425 *	478
»	IV	285	310	—	486
»	V	284	309	428	484
»	VI	—	298	—	478
Phenol	I	—	349	—	—
»	II	—	352	—	—
»	III	—	350	—	—
»	IV	—	358	—	—
»	V	—	351	—	—
»	VI	—	355	—	—

\* Inflection point

## DISCUSSION

As can be seen from Table 1, the effects of the various substituents on the location of the strongest absorption maximum are rather slight. A non-auxochromic *o*-methyl group causes a slight bathochromic effect, considerably stronger in the  $\beta$ -naphthol dye. An auxochromic *m*-carboxyl group has little effect, while an *o*-carboxyl group causes a relatively strong bathochromic effect in both series. The *o*-methyl and *m*-carboxyl groups together cause a deepening of the color which is intermediate between the effects of the two constituents alone. The effect of both an *o*- and *m*-carboxyl group differs in the two series. In the phenol dyes they cause a bathochromic effect, whereas in the  $\beta$ -naphthol dye they have little effect, if any a slight hypsochromic effect.

As mentioned previously, all of the phenol dyes are approximately symmetrical about 350  $m\mu$  except the two containing *o*-carboxyl groups. Kuhn and Bär<sup>1</sup> have determined that *p*-hydroxy-azo-benzene exists almost completely in the azo form, which shows a maximum at 350  $m\mu$ . The present author has shown<sup>3</sup> that the hydrazone form of this dye absorbs at approximately 375  $m\mu$ . The closeness of these two positions of maximum absorption would be expected to preclude the occurrence of a double maximum when the relative amount of the hydrazone form is small. The stronger absorption of Phenol IV and VI in the region above 370  $m\mu$ , however, would tend to indicate that the equilibrium:



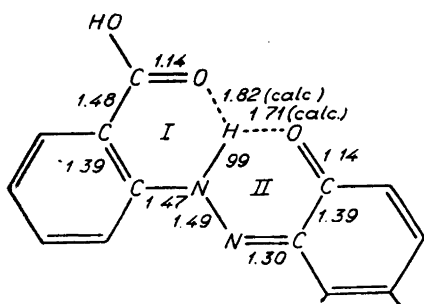


Fig. 5. Configuration of hydrazone form of *o*-carboxy dye

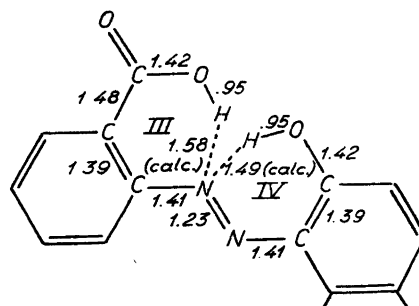


Fig. 6. Configuration of azo form of *o*-carboxy dye

is, in these cases, displaced to the right and that this, in turn, causes the increased absorption at the longer wave lengths. The symmetry of the other phenol dyes would tend to indicate that no such shift in the equilibrium has occurred.

Figs. 5 and 6 show the interatomic distances in the hydrazone and azo forms of azo dyes, respectively. In the hydrazone form of phenol dyes containing an *o*-carboxyl group, structure I would be expected to occur. That is to say, a hydrogen bond would be expected to occur between the *o*-carboxyl group and the  $>N-H$  of the hydrazone group. The calculated  $O \cdots H-N$  distance for this bond is approximately 2.81 Å. In the azo form of the same dyes, a similar hydrogen bond would be expected between the *o*-carboxyl group and the  $-N <$  of the azo group, as shown in structure III, Fig. 6. The interatomic  $O-H \cdots N$  distance for this bond is approximately 2.53 Å. No such hydrogen bonds are possible in any of the other phenol dyes. Each of these hydrogen bonds would be expected to exert a stabilizing influence on the corresponding form of the azo dye. The chelate ring in the hydrazone form, however, contains two conjugated double bonds. Thus it would be expected that the hydrogen bond in the hydrazone form would be more stable<sup>4</sup>, in spite of its slightly longer  $O \cdots H-N$  distance, than that in the azo form. The resultant increased stability of the hydrazone form would thus displace the equilibrium to the right. The value of 2.8 Å for this bond corresponds well with that for the strong hydrogen bond in diketopiperazine (2.85 Å) and is considerably less than that in urea (2.98 Å)<sup>5</sup>. The symmetry in the curves of the other phenol dyes, including that containing a *m*-carboxyl group, would tend to indicate that only in those forms where hydrogen bonds are possible is there any shift in the equilibrium toward the hydrazone form.

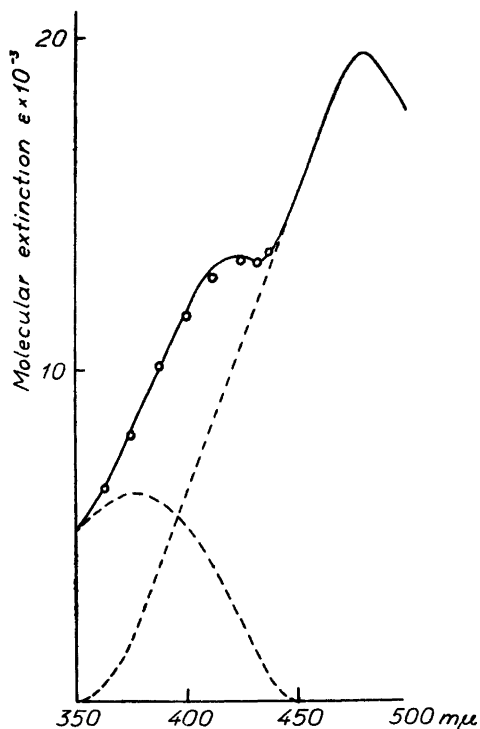


Fig. 7. Breakdown of  $\beta$ -Naphthol I absorption curve into Component azo and hydrazone bands.

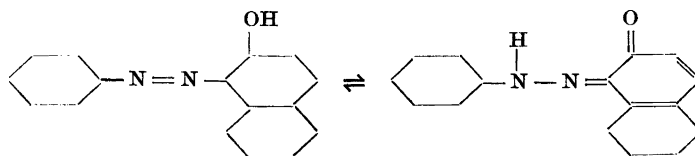
Solid curve: Actual  $\beta$ -Naphthol I absorption curve.

Dotted curves: Component azo and hydrazone bands.

Circles: Addition of azo and hydrazone bands.

However, since there is no double maximum or inflection point in these curves, it is not possible to break them down into components and to calculate quantitatively the relative amounts of the two forms.

In the  $\beta$ -naphthol series, all of the dyes, except those containing an *o*-carboxyl group, show either a slight maximum or an inflection point at approximately  $425\text{ m}\mu$ . The results of Kuhn and Bär's studies<sup>1</sup> on the O acetate and O benzoate derivatives of benzene-1-azo- $\beta$ -naphthol indicate that this dye exists mainly in the hydrazone form, which absorbs at  $480\text{ m}\mu$ , and that the azo form shows an absorption maximum at approximately  $390\text{ m}\mu$ . It would thus appear that the inflection at  $425\text{ m}\mu$  is due to a small amount of the dye, in the azo form, absorbing at  $390\text{ m}\mu$ . The two dyes containing an *o*-carboxyl group, however, do not show these inflection points and hence it would appear as if the equilibrium:



for these dyes has again been displaced to the right and that the amount of the azo form has been reduced to the point where it no longer manifests itself as an inflection or a maximum.

Fig. 7 shows the breakdown of benzene-1-azo- $\beta$ -naphthol into its two component curves. By applying this method of breakdown to all the curves and calculating the values of  $\frac{\epsilon_H}{\epsilon_A + \epsilon_H}$ , the figures in Table 2 were obtained.

Table 2. Relative amount of hydrazone form.

Dye	$\frac{\epsilon_H}{\epsilon_A + \epsilon_H}$ *	
$\beta$ -Naphthol I		.74
» II		.75
» III		.76
» IV		.81
» V		.75
» VI		.80

\*  $\epsilon_H$  = extinction of hydrazone form

$\epsilon_A$  = « » azo form

The values of the molecular extinction of the pure azo and hydrazone forms are not known. If they are similar, then  $\frac{\epsilon_H}{\epsilon_A + \epsilon_H} \cdot 100$  approaches the percent hydrazone form present. If not, the value is nevertheless a quantitative measure of the relative amount of hydrazone form.

It can be seen from Table 2 that all the dyes, except IV and VI, show approximately the same value for  $\frac{\epsilon_H}{\epsilon_A + \epsilon_H}$ . The values for IV and VI are higher showing that the relative amount of hydrazone form has increased.

$\beta$ -Naphthol IV and VI, which contain both an *o*-carboxyl and an *o'*-hydroxyl can have either structure I or II in Fig. 5 in the hydrazone form, and either III or IV in Fig. 6 in the azo form. Both possible chelate rings in the hydrazone form contain two conjugated double bonds. The O...H—N distance in structure I has been calculated to be approximately 2.81 Å, while that in structure II is 2.70 Å. Thus it would be expected that structure II would predominate, *i. e.* the hydrogen bond would exist mainly between the hydrazone H and the quinoid O of the naphthol.

In the azo form, the interatomic O—H...N distance for structure III has been calculated to be approximately 2.53 Å and for IV, 2.44 Å. More-

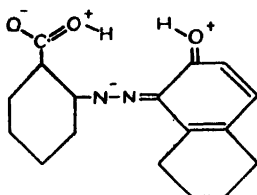


Fig. 8. Resonance structure of azo form of *o*-carboxy dye.

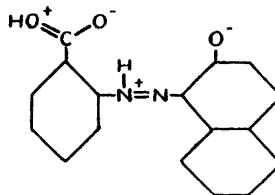


Fig. 9. Resonance structure of hydrazone form of *o*-carboxy dye.

over, structure IV contains two conjugated double bonds, whereas III contains only one. It would thus appear that structure IV would predominate, *i. e.* the hydrogen bond in the azo form is also between the hydroxyl group of the naphthol and the azo grouping.

Once again, these hydrogen bonds would be expected to stabilize their respective forms of the dye. The cause of the increased stabilization of the hydrazone form and the subsequent shift in the equilibrium is not as obvious, in this case, as in the phenol dyes.

Resonance in the dyes, to structures such as shown in Figs. 8 and 9, should be about equally effective in strengthening the hydrogen bonds in both forms, due to the increase in the electronegativity of one of the atoms concerned <sup>6</sup>. Thus one would expect no additional stabilizing effect on the hydrazone form from this cause alone.

Also, since it is assumed that the effective hydrogen bond formation is between the azo or hydrazone N and the phenolic O of the naphthol, the occurrence of only one conjugated double bond in structure III (Fig. 6) is of little importance, as this ring is not directly involved in hydrogen bond formation.

If structure IV (Fig. 6) is assumed to occur in the azo form, then the carboxyl group could not maintain the configuration shown, due to the close

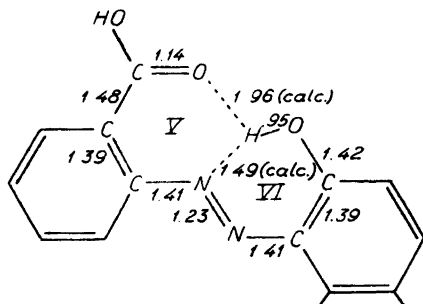


Fig. 10. Alternative configuration of azo form of *o*-carboxy, *o'*-hydroxy dye.



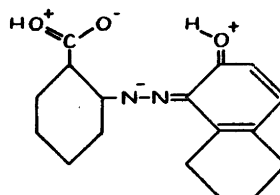


Fig. 11. Resonance structure of azo form of *o*-carboxy dye.

proximity of the hydrogen atoms. Resonance in the carboxyl group would probably cause it to rotate through  $180^\circ$  and assume the configuration shown in Fig. 10.

In this way the residual negative character of the carbonyl group would be closest to the residual positive charge of the hydrogen atom. This configuration is similar to that shown in Fig. 5 for the hydrazone form, and could resonate with structures such as shown in Fig. 11.

The calculated O—H...O distance, in Fig. 10, is approximately 2.91 Å.

It can be seen from Figs. 5 and 10 that in both the azo and hydrazone forms, one hydrogen atom can be attracted by two electronegative atoms. In the azo form the O—H...O distance (Fig. 10) is so much larger than the O—H...N distance that the carbonyl group would not be expected to exert much influence on the phenolic hydrogen atom, even though resonance affects the electronegativity of the two oxygen atoms (Fig. 11).

In the hydrazone form, however, the two interatomic distances are 2.70 and 2.81 Å, both of which are within the limits for strong hydrogen bonds. Resonance in this case would also tend to strengthen the bonds (Fig. 9). The difference in interatomic distances would also tend to be counteracted by the greater resonance in the carboxyl group (resonance energy 28 kcal/mole for carboxyl group and 7 kcal/mole for phenolic hydroxyl). It is thus possible that a bifurcated hydrogen bond exists between the hydrazone H and the two oxygen atoms, similar to that reported for glycine<sup>7</sup>. Even if an actual bifurcated bond is not formed, the carbonyl group, which is in such close proximity, undoubtedly exerts an influence on the hydrogen atom and thus stabilizes this form slightly in preference to the azo form. Thus, the equilibrium is displaced to a slight extent toward the hydrazone form.

## EXPERIMENTAL

### Aminoterephthalic acid

Terephthalic acid was prepared according to a previous publication by the author<sup>8</sup>, subsequently nitrated by a modification of de la Rue and Müller's method<sup>9</sup>, and the nitro acid reduced according to Kloeppel<sup>10</sup>.

30 ml of pure *p*-cymene were dissolved in 100 ml of acetic acid and this solution was slowly dropped into a heated (100°) solution of 450 g CrO<sub>3</sub> in 600 ml H<sub>2</sub>O, 750 ml of conc. H<sub>2</sub>SO<sub>4</sub>, and 2 l acetic acid. After the addition of all the cymene solution, the excess CrO<sub>3</sub> was destroyed with sulfurous acid and the mixture extracted with ether, in which terephthalic acid is insoluble, to remove by-products. The terephthalic acid was then removed by filtration and washed with boiling water. It was obtained as an almost white, amorphous powder. Yield approx. 70 %.

C <sub>8</sub> H <sub>6</sub> O <sub>4</sub> (166.13)	Titration eq. (calc.)	83.0
	»	» (found) 83.1

9 g of terephthalic acid were added to a solution of 53 ml fuming (20 % SO<sub>3</sub>) H<sub>2</sub>SO<sub>4</sub> and 50 ml of fuming HNO<sub>3</sub> (d. 1.52). The mixture was heated by a direct flame to the beginning of the reaction and then on a water bath for 1 ½ hours. After this it was heated on an electric plate just to the boiling point. It was then cooled, poured on ice, and allowed to stand for 24 hours at 5°. The precipitate was removed and recrystallized from boiling water. Yield approx. 75 %.

C <sub>8</sub> H <sub>5</sub> NO <sub>6</sub> (211.13)	Titration eq. (calc.)	105.6	M.P. (lit.)	270° (263°)
	»	» (found 106.2	M.P. (found)	269—270°

8 g of nitroterephthalic acid were added to a hot solution of 30 g SnCl<sub>2</sub> in 100 ml conc. HCl, and heated, with stirring, on a water bath for 1 hour. The solution was then cooled, filtered, and the precipitate washed with conc. HCl. The white crystals obtained were undoubtedly the HCl salt.

Upon recrystallization from hot water, the salt was destroyed and the free amino acid crystallized as lemon-yellow needles. Yield was approximately quantitative.

C <sub>8</sub> H <sub>7</sub> NO <sub>4</sub> (181.14)	N (calc.)	7.73 %
	N (found)	7.88 »

### 3-Amino-*p*-toluic acid

*p*-Cymene was oxidized and nitrated according to a previous publication<sup>11</sup> and then reduced<sup>10</sup>.

30 ml of *p*-cymene and 17 g of MnO<sub>2</sub> were added to 1 500 ml of conc. HNO<sub>3</sub> (d. 1.40). This mixture was refluxed for one hour. The resulting clear yellow solution deposited pale yellow crystals on cooling. These were removed and washed with a little cold water. The precipitate was then dissolved in aqueous ammonia, filtered, and acidified with HCl. The resulting precipitate was removed and recrystallized from boiling water. yield 55 %.

C <sub>8</sub> H <sub>7</sub> NO <sub>4</sub> (181.14)	N (calc.)	7.73 %	M.P. (lit.)	189°
	N (found)	7.70 »	M.P. (found)	188—189°

7 g of 3-nitro-*p*-toluic acid were added to a hot solution of 30 g SnCl<sub>2</sub> in 100 ml conc. HCl (37 %), and treated as with nitroterephthalic acid. The HCl salt was obtained in the form of yellow crystals upon recrystallization from water.

C<sub>8</sub>H<sub>9</sub>NO<sub>2</sub> · HCl (187.70) N (calc.) 7.46 % Titration eq. (calc.) 93.8  
N (found) 7.54 » » » (found) 93.3

The free amine melted at 166° (lit. 164—165°).

#### *m*-Aminobenzoic acid

Since no *m*-aminobenzoic acid was available, *m*-nitrobenzoic acid was reduced in the manner previously described.

C<sub>7</sub>H<sub>7</sub>NO<sub>2</sub> · HCl (173.7) N (calc.) 8.06 %  
N (found) 8.13 »

The free amine melted at 173—174° (lit. 174°).

#### Phenol I. 4-Phenylazophenol

Since all the dyes were prepared in a similar manner<sup>12</sup>, only the preparation of this dye will be given in detail.

1 g of aniline was placed in a beaker with 5 ml conc. HCl and a little ice. This mixture was cooled to 0 to 5° in an ice bath, and diazotized by the addition of an aqueous solution of .74 g NaNO<sub>2</sub> in 10 ml water. The temperature, during the addition of the NaNO<sub>2</sub>, was not allowed to exceed 5°. When the diazotization was complete, the solution was poured into an alkaline solution of 1 g phenol. The red solution obtained was allowed to stand for several hours, after which it was acidified with HCl.

The precipitate was removed and dried at 105°. Recrystallization from aqueous alcohol yielded light brown crystals.

C<sub>12</sub>H<sub>10</sub>N<sub>2</sub>O (198.22) N (calc.) 14.13 %  
N (found) 13.97 »

#### Phenol II. 4-(*o*-Tolylazo)-phenol

1 g of *o*-toluidine was diazotized and coupled as above. A dark oil was obtained. The solution was extracted with ether (3 × 250 ml), the ether dried over Na<sub>2</sub>SO<sub>4</sub>, and the solvent evaporated. The dark oil that was obtained did not crystallize even after standing at 5° for several months.

Finally, it was dissolved in the smallest possible amount of glacial acetic acid and shaken with a large excess of water. This deposited small brown needles after a week at 5°. Recrystallized from alcohol.

C<sub>13</sub>H<sub>12</sub>N<sub>2</sub>O (212.24) N (calc.) 13.20 %  
N (found) 12.98 »

## Phenol III. 4-(3-Carboxyphenylazo)-phenol

1 g of HCl salt of *m*-aminobenzoic acid was diazotized and coupled with phenol. Recrystallization from methanol yielded dark brown-violet crystals.

$C_{13}H_{10}N_2O_3$  (242.23) N (calc.) 11.11 %  
N (found) 11.20 »

## Phenol IV. 4-(2-Carboxyphenylazo)-phenol

1 g anthranilic acid was diazotized and coupled in the usual way. Recrystallization from methanol yielded light yellow-tan needles.

$C_{13}H_{10}N_2O_3$  (242.23) N (calc.) 11.11 %  
N (found) 11.22 »

## Phenol V. 4-(2-Methyl-5-carboxyphenylazo)-phenol

1 g of HCl salt of 3-amino-*p*-toluic acid was diazotized and coupled with phenol. Recrystallization from methanol yielded dark violet-brown crystals.

$C_{14}H_{12}N_2O_3$  (256.26) N (calc.) 10.93 %  
N (found) 10.62 »

## Phenol VI. 4-(2,5-Dicarboxyphenylazo)-phenol

1 g of aminoterephthalic acid was diazotized and coupled in the usual manner. Recrystallization from hot water and from ethanol yielded fine orange needles.

$C_{14}H_{10}N_2O_5$  (286.24) N (calc.) 9.80 %  
N (found) 9.96 »

 $\beta$ -Naphthol I. 1-Phenylazo-2-hydroxynaphthalene

1 g of aniline was diazotized and coupled, as above, with  $\beta$ -naphthol. Recrystallization from alcohol yielded orange-red needles.

$C_{16}H_{12}N_2O$  (248.27) N (calc.) 11.31 %  
N (found) 11.28 »

 $\beta$ -Naphthol II. 1-(*o*-Tolylazo)-2-hydroxynaphthalene

1 g *o*-toluidine was diazotized, as above, and coupled with  $\beta$ -naphthol. Recrystallization from ether yielded dark red crystals.

$C_{17}H_{14}N_2O$  (262.30) N (calc.) 10.68 %  
N (found) 10.43 »

 $\beta$ -Naphthol III. 1-(3-Carboxyphenylazo)-2-hydroxynaphthalene

1 g of HCl salt of *m*-aminobenzoic acid was diazotized and coupled with  $\beta$ -naphthol. Recrystallization from methanol yielded dark red crystals.

$C_{17}H_{12}N_2O_3$  (292.28) N (calc.) 9.60 %  
N (found) 9.50 »

**$\beta$ -Naphthol IV. 1-(2-Carboxyphenylazo)-2-hydroxynaphthalene**

1 g anthranilic acid was diazotized and coupled as above.

Recrystallization from glacial acetic acid yielded fine red needles.

$C_{17}H_{12}N_2O_3$  (292.28) N (calc.) 9.60 %  
N (found) 9.64 »

 **$\beta$ -Naphthol V. 1-(2-Methyl-5-carboxyphenylazo)-2-hydroxynaphthalene**

1 g of HCl salt of 3-amino-*p*-toluic acid was diazotized and coupled with  $\beta$ -naphthol.

Recrystallization from alcohol yielded dark red crystals.

$C_{18}H_{14}N_2O_3$  (306.31) N (calc.) 9.16 %  
N (found) 9.24 »

This dye showed an interesting phenomena, which was later found to be common to many of the azo dyes. Different conditions of recrystallization (solvent, temp., etc.) seemed to yield different crystal modifications. In this particular dye, recrystallization from methanol yielded a red product, whereas recrystallization from ether yielded an orange product. The later showed strong orange fluorescence in ultra-violet light, while the red form showed no tendency to fluorescence. Heating the two forms at 200° for many hours seemed to produce an intermediate form, *i. e.* the fluorescence of the orange form decreased while that of the red form increased. The visible color also changed to an intermediate orange-red. A spectroscopic comparison of the two forms (in ethanol) gave, however, identical curves.

A chemical analysis of the two forms showed almost identical nitrogen contents. This result would eliminate the possibility of any alcohol or ether of crystallization.

The two forms were completely interchangeable by recrystallization from the corresponding solvent.

For these reasons, this phenomena, and others of similar type, was considered to be due to polymorphism.

 **$\beta$ -Naphthol VI. 1-(2,5-Dicarboxyphenylazo)-2-hydroxynaphthalene**

1 g of aminoterephthalic acid was diazotized and coupled, in usual way, with  $\beta$ -naphthol.

Recrystallization from glacial acetic acid yielded red-orange needles.

$C_{18}H_{12}N_2O_5$  (336.30) N (calc.) 8.33 %  
N (found) 8.26 »

## SUMMARY

The effect of an *o*-methyl group, *o*- and *m*-carboxyl groups, and combinations of the two on the absorption spectra of phenylazo-phenol and phenylazo- $\beta$ -naphthol has been examined and the absorption curves of the dyes in 96 % alcohol are given.

The effect of these groups on the azo-hydrazone tautomerism is also discussed. The increase in the hydrazone form for dyes containing an *o*-carboxyl group is explained in terms of hydrogen bond formation. The possibility of a bifurcated hydrogen bond in the  $\beta$ -naphthol dye is discussed.

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