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Anomalous Behavior of Aminohydroxynaphthalenesulfonic Acids During Diazo Coupling†

Harold S. Freeman,‡ Wilson M. Whaley, Michelle K. Esancy and James F. Esancy

Department of Textile Chemistry, North Carolina State University,
Raleigh, North Carolina 27695, USA

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SUMMARY

The effect of pH on the diazo coupling reaction of some commonly used coupling components (J-acid, Gamma acid, H-acid and S-acid) with monosubstituted diazobenzenes has been investigated. The results demonstrate that, contrary to previous reports, selective diazo coupling ortho to an amino group of an aminohydroxynaphthalenesulfonic acid does not occur in weakly acidic (pH 5–6) media. In fact, such media were found to give nearly exclusive diazo coupling ortho or para to the hydroxyl group. The desired amine coupling reactions required a pH of 3·0–3·5 and occurred only with the more reactive diazonium salts. The structures of the dyes obtained were unambiguously determined with the aid of ^{1}H-NMR spectroscopy.

INTRODUCTION

It has been generally accepted[1–3] for many years that an aminohydroxynaphthalenesulfonic acid, such as H-acid (**1**; 4-amino-5-hydroxy-2,7-naphthalenedisulfonic acid), undergoes diazo coupling *ortho* to the

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‡ To whom correspondence should be addressed.

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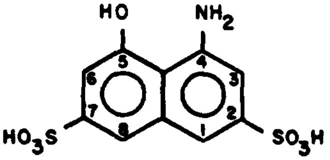

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amino group in weakly acidic (pH 5–6) media and *ortho* to the hydroxyl group at pH > 8. Numerous disazo dyes like CI Acid Black 1 (**2**) have been developed from this assumption. This particular dye (**2**) is reportedly prepared[4,5] in successive diazo couplings to H-acid; first with diazotized *para*-nitroaniline at pH 5–6, followed by coupling under alkaline conditions with benzenediazonium chloride (cf. Fig. 1). Attempts to repeat this synthesis in our laboratories normally afforded a reaction product which was more complex by TLC than expected.

In the 60 years which have passed since the early descriptions of the syntheses of dyes like **2**, only a few reports have appeared in the literature which deal with the effect of pH on the diazo coupling of aminohydroxynaphthalenesulfonic acids. Most of the papers[6–12] have appeared in the

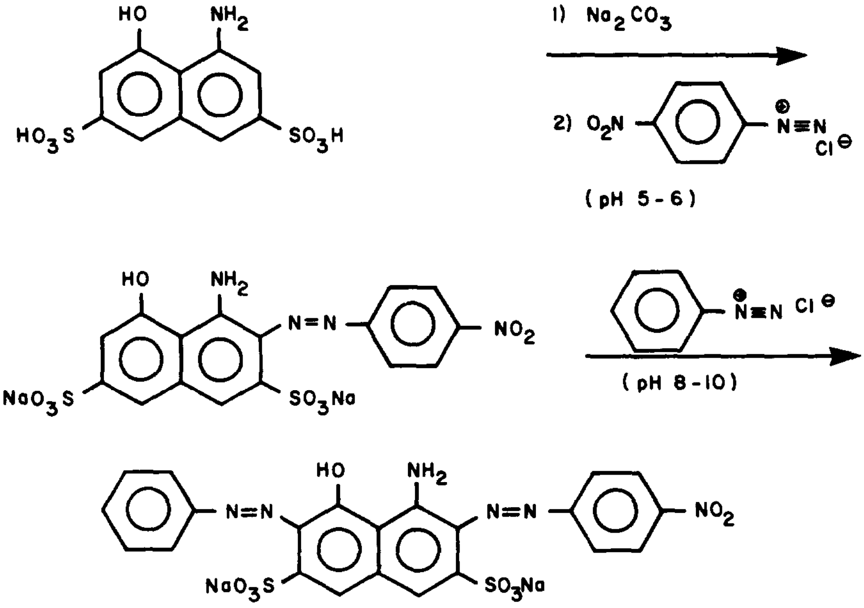

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Fig. 1. Synthesis of Acid Black 1 (**2**).

1 $R_1 = SO_3H$, $R_2 = 2\text{-}SO_3H$ (H-acid)

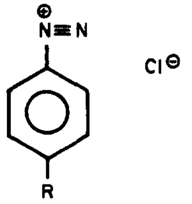
3 $R_1 = H$, $R_2 = 1\text{-}SO_3H$ (S-acid)

4a $6\text{-}NH_2$ (Gamma acid)

4b $7\text{-}NH_2$ (J-acid)

Fig. 2. Aminohydroxynaphthalenesulfonic acids studied.

patent literature and, in all but two of them,[11,12] no deviations from the historically used acid coupling conditions were employed when attempting to couple *ortho* to the amino group. In these latter two papers, it was shown that very little coupling of diazotized *para*-chloroaniline or *para*-nitroaniline to J-acid (**3**; 7-amino-4-hydroxy-2-naphthalenesulfonic acid) occurs at pH 5·5–7·8[11] and that for the diazo coupling of H-acid to itself, the ratio of coupling in the ring containing the hydroxyl group to the ring containing the amino group increases with increasing acidity of the reaction medium.[12] In addition to this surprising result, the workers reported that coupling occurs *para* to the hydroxyl group. Interestingly, the introduction of a second molecule of diazotized H-acid occurs by attack of the position *para* to the amino group of H-acid. In related work, it was shown[13] that the coupling rate, both *ortho* to the amino group and *ortho* to the hydroxyl group of H-acid, depends on the reactivity of the diazonium salt as well as the pH of the reaction medium.



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	R
a	H
b	OCH_3
c	$N(CH_3)_2$
d	CO_2H
e	NO_2

Fig. 3. Benzenediazonium salts used.

The paucity of papers in the dyestuffs literature which describe the selective diazo coupling of aminohydroxynaphthalenesulfonic acids by controlling pH, and the surprising complexity of the products derived from the use of traditional coupling conditions for preparing dyes like **2**, prompted us to report our experiences in this area.

This paper is concerned with the effect of pH on the diazo coupling reaction of the commonly used aminohydroxynaphthalenesulfonic acids listed in Fig. 2 with benzenediazonium salts of type **5** (cf. Fig. 3). An ^{1}H-NMR study made it possible to deduce the structures of the reaction products which were obtained during the course of this investigation.

RESULTS AND DISCUSSION

The aminohydroxynaphthalenesulfonic acid **4a** afforded selective diazo coupling *ortho* to the hydroxyl group at pH 9–10. Thus were obtained dyes of type **6** (Fig. 4) in good yields. Interestingly, the sulfonic acids **1**, **3** and **4b** underwent diazo coupling exclusively *para* to the hydroxyl group under alkaline conditions to give dyes **7**–**9**. These observations have not been previously reported as coupling reactions of these three sulfonic acids. Such results are consistent, however, with previous papers by Gatterman and Liberman[14] and Gatterman and Schulze[15] which indicate that the model compound 1,5-naphtholsulfonic acid (structurally similar to S-acid) couples *para* to the hydroxyl group under alkaline conditions. Those papers also describe the alkaline coupling of 1,3-naphtholsulfonic acid. That particular J-acid- and H-acid-like compound gave a mixture of *ortho* and *para* coupling. Zollinger[16] reported coupling *ortho* to the hydroxyl group of H-acid at pH > 8 and another group[17] reported *ortho* coupling to the hydroxyl group of Gamma acid at pH 7·8. This latter observation is consistent with our findings.

The NMR spectra of dyes **6**–**9** were characterized by a one-proton singlet (D_2O exchangeable) at very low field (15·5–16·1δ) which was attributed to the increased acidity of the aromatic hydroxyl proton *ortho* or *para* to the strongly electron-withdrawing azo moiety. Such peaks were not observed in the spectra of dyes formed on coupling *ortho* to the aromatic amino group. The products of the alkaline coupling reactions were purple to orange and usually exhibited higher R_f values on silica gel TLC plates than those formed at pH 3·0–3·5. Once the structures of the

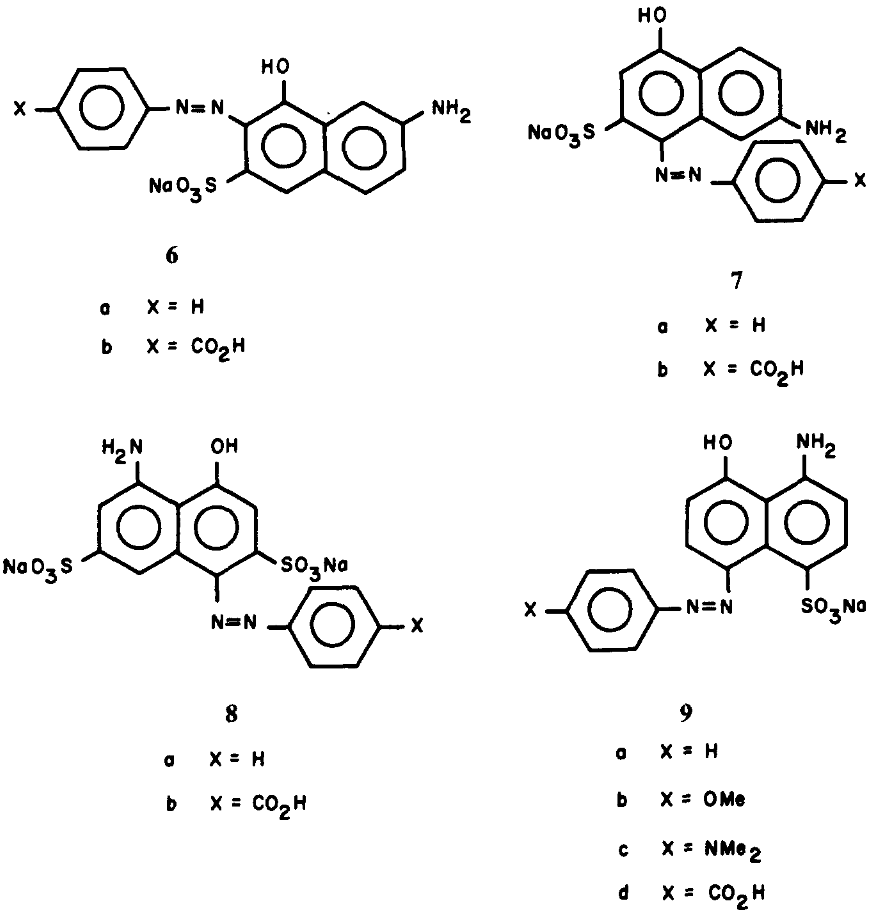


Fig. 4. Azo dyes formed at pH 9–10.

products of the reactions conducted at pH 9–10 were confirmed by ^{1}H-NMR, TLC was used to monitor the effect of pH on the selectivity of the coupling reaction. The pH was, therefore, lowered until TLC showed either the presence of a single new dye component or essentially no reaction taking place.

When diazo coupling was conducted at pH 5–6, little change in the TLC of the reaction products of either S-acid or H-acid was evident. NMR further confirmed that the monoazo dyes obtained at this lower pH were identical to those which formed at pH 9–10 (cf. Figs 5 and 6). H-acid also afforded selective coupling *para* to the hydroxyl group at a slightly

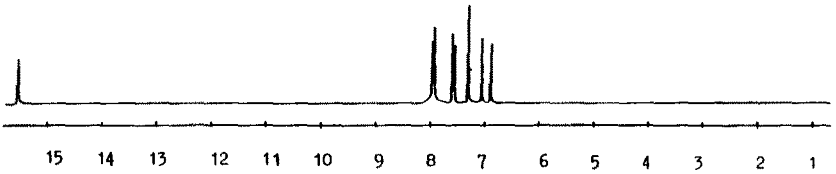


Fig. 5. ^{1}H-NMR spectrum of H-acid coupled with compound **5d** at pH 9–10.

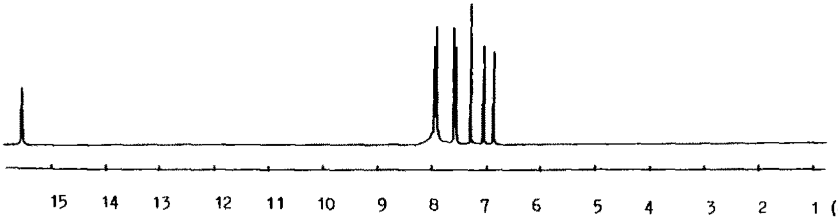
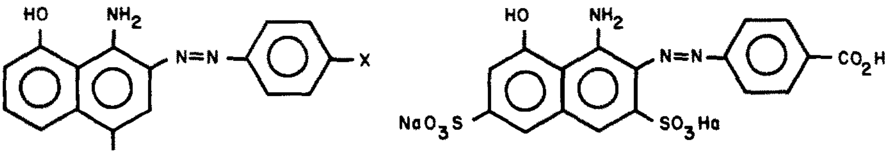


Fig. 6. ^{1}H-NMR spectrum of H-acid coupled with compound **5d** at pH 4·5

lower pH of 4·5. The other two aminohydroxynaphthalenesulfonic acids (**4a**,**b**) gave mixed coupling at pH 5–6. When the pH was lowered to 3·0–3·5, selective coupling *ortho* to the amino group was observed with S-acid when the diazo compounds **5d**,**e** were employed. When S-acid and **5a** were combined at pH 3·0–3·5, very little coupling occurred, even after two days. The small amount of dye which formed was identified as compound **9a**. Interestingly, the diazonium salts **5b**,**c** coupled to S-acid at pH 3·0–3·5 to give selective coupling *para* to the hydroxyl group, albeit in low yields. Thus it appears that electron-donating groups (e.g. OMe, NMe_2) prevent



10 **11**

	X
a	CO_2H
b	NO_2

Fig. 7. Azo dyes derived from S-acid and H-acid at pH 3·0–3·5.

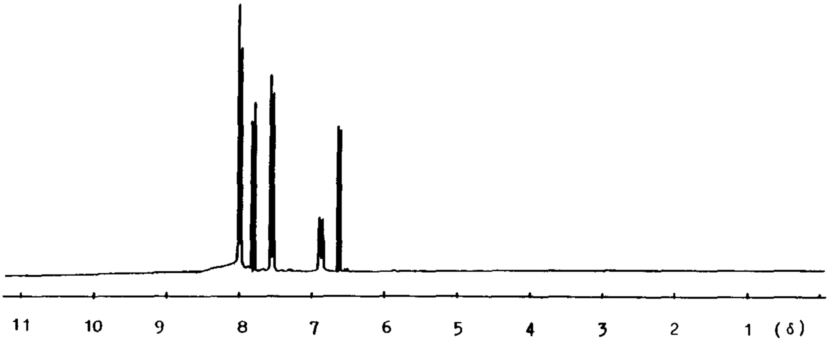


Fig. 8. ^{1}H-NMR spectrum of S-acid coupled with compound **5d** at pH 8–10 or pH 5–6.

diazo coupling in the amino-substituted ring of aminohydroxynaphthalenesulfonic acids, whereas electron-withdrawing groups (e.g. CO_2H, NO_2) facilitate the desired acid coupling reaction. These results are probably caused by the decreased reactivity of the ring containing the amino group due to protonation of the amino group in acid media. As the pH of the reaction medium is lowered, the concentration of free (unprotonated) amino groups decreases to the point where only the more reactive diazonium salts such as **5d,e** are sufficiently electrophilic to effect coupling. This latter point is consistent with the work of Zollinger,[16] who studied the effect of substituents on the reaction rates of diazonium ions.

At pH 3·0–3·5, J-acid (**4a**), Gamma acid (**4b**), and H-acid (**1**) were fairly unreactive when benzenediazonium chloride (**5a**) was used. However, each gave at least 70% coupling in the amino ring when the diazonium salt **5d** was used. Figure 7 shows the dyes obtained via selective coupling in the amino-substituted ring at pH 3·0–3·5. A comparison of the NMR spectra of S-acid dyes formed at different pH ranges is shown in Figs 8 and 9. The NMR section contains the detailed ^{1}H-NMR data recorded on the azo dyes which were prepared in this investigation.

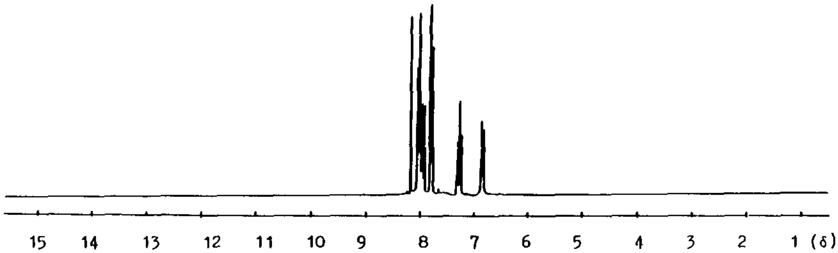
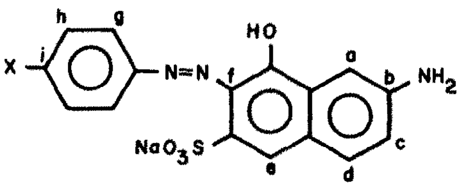


Fig. 9. ^{1}H-NMR spectrum of S-acid coupled with compound **5d** at pH 3·0–3·5.

TABLE 1

Chemical Shifts (δ)[a] and Multiplicities (*M*) for Ring Protons of Some J-Acid and Gamma Acid Dyes



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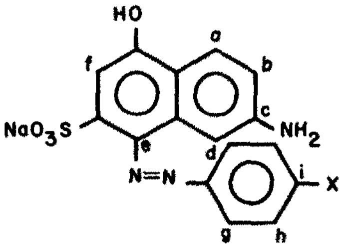

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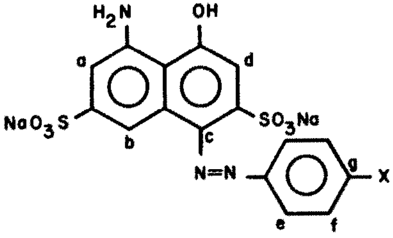
X	$\delta H_a(M)$	$\delta H_b(M)$	$\delta H_c(M)$	$\delta H_d(M)$	$\delta H_e(M)$	$\delta H_f(M)$	$\delta H_g(M)$	$\delta H_h(M)$	$\delta H_i(M)$
6: H	7·45 (m)[b]	—	7·00 (d)	7·45 (m)[b]	7·45 (m)[b]	—	7·97 (d)	7·45 (m)[b]	7·47 (m)[b]
6: CO_2H	7·4	—	6·98 (d)	7·40 (m)[b]	7·40 (m)[b]	—	7·97 (d)	7·66 (d)	—
7: H	7·98 (d)	6·08 (d)	—	7·35 (s)	—	6·78 (s)	7·70 (d)	7·42 (t)	7·17 (t)
7: CO_2H	7·93 (d)	6·71 (d)	—	7·26 (s)	—	6·67 (s)	7·96 (s)	7·56 (d)	—

[a] Chemical shifts are expressed in δ values.

[b] This signal was part of a group of signals centered at the chemical shift indicated.

TABLE 2

Chemical Shifts (δ)[a] and Multiplicities (M) for Ring Protons of Some H-Acid Dyes



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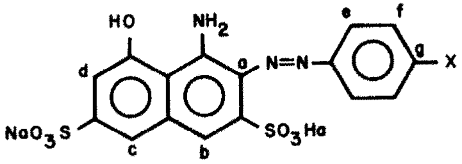

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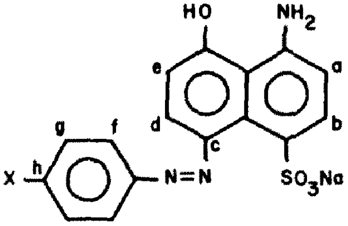
X	$\delta H_a(M)$	$\delta H_b(M)$	$\delta H_c(M)$	$\delta H_d(M)$	$\delta H_e(M)$	$\delta H_f(M)$	$\delta H_g(M)$
8: H	6·91 (s)	7·31 (s)	—	7·08 (s)	7·69 (d)	7·42 (t)	7·15 (t)
8: CO_2H	6·88 (s)	7·28 (s)	—	7·04 (s)	7·92 (d)	7·56 (d)	—
11: CO_2H	—	7·29 (s)	7·90 (d)[b]	6·81 (s)	7·90 (d)[b]	7·76 (d)	—

[a] Chemical shifts are expressed in δ values.

[b] This signal was part of a doublet centered at the chemical shift indicated.

TABLE 3

Chemical Shifts (δ)[a] and Multiplicities (M) for Ring Protons of Some S-Acid Dyes



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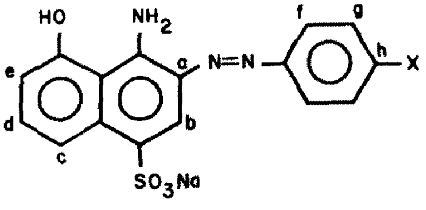

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X	$\delta H_a(M)$	$\delta H_b(M)$	$\delta H_c(M)$	$\delta H_d(M)$	$\delta H_e(M)$	$\delta H_f(M)$	$\delta H_g(M)$	$\delta H_h(M)$
9: H	6·65 (d)	7·82 (d)	—	7·98 (d)	6·88 (d)	7·57 (d)	7·44 (t)	7·18 (t)
9: OMe	6·60 (d)	7·80 (d)	—	7·95 (d)	6·92 (d)	7·55 (d)	7·02 (d)	—
9: NMe_2	6·55 (d)	7·80 (d)	—	7·94 (d)	6·97 (d)	7·49 (d)	6·81 (d)	—
9: CO_2H	6·61 (d)	7·78 (d)	—	7·94 (d)	6·88 (d)	7·98 (d)	7·48 (d)	—
10: CO_2H	—	8·15 (s)	7·93 (d)	7·23 (t)	6·83 (d)	8·00 (d)	7·78 (d)	—
10: NO_2	—	8·22 (s)	8·20 (d)	7·43 (t)	7·02 (d)	8·32 (d)	8·06 (d)	—

[a] Chemical shifts are expressed in δ values.

CONCLUSION

The results of this investigation suggest that the aminohydroxynaphthalenesulfonic acids **1**, **3** and **4a**,**b** undergo selective diazo coupling *ortho* or *para* to the hydroxyl group in weakly acidic (pH 5–6) media as well as in alkaline (pH 9–10) media. It has also been shown that the product distribution of diazo coupling to the sulphonic acids employed is influenced by substituents which are *para* to the diazonium moiety. Thus, electron-withdrawing groups such as CO_2H and NO_2 groups facilitate diazo coupling adjacent to the amino group of an aminohydroxynaphthalenesulfonic acid at pH 3·0–3·5. However, electron-donating groups such as OMe and NMe_2 groups prevent selective diazo coupling in the amino-substituted ring of the sulfonic acids regardless of the pH conditions used. To account for these results, it is suggested that the concentration of free amino groups in acidic media is too low to permit coupling in the amine-containing ring unless a very reactive diazonium salt (e.g. **5d** or **5e**) is employed.

^{1}H-NMR spectra

The chemical shifts and multiplicities for the aromatic ring protons of dyes **6**–**10** are outlined in Tables 1–3. The sulfonic acids which coupled *para* to the hydroxyl groups under alkaline conditions afforded spectra containing two upfield signals between 6·5 and 7·1 ppm that could only be assigned to the beta protons *ortho* to the hydroxyl and amino groups. This observation rules out the possibility of a coupling *ortho* to the hydroxyl group in those cases. Note that only one such signal appears in the spectrum obtained from the coupling of Gamma acid, which does in fact

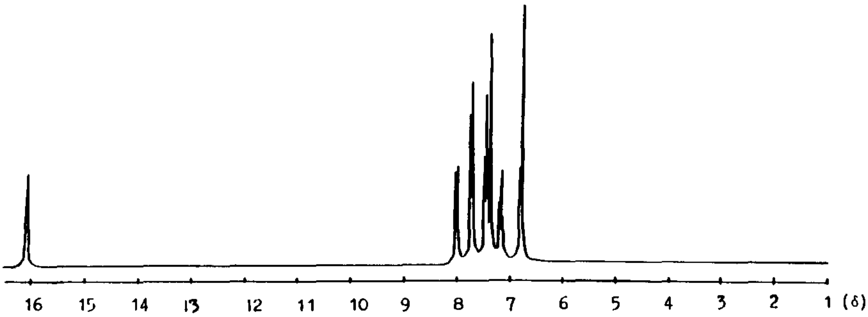

Fig. 10. ^{1}H-NMR spectrum of J-acid coupled with compound **5a** at pH 9–10.

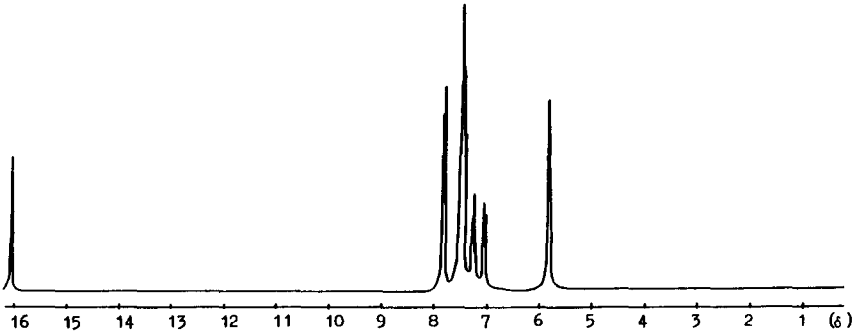

Fig. 11. ^{1}H-NMR spectrum of Gamma acid coupled with compound **5a** at pH 9–10.

gave coupling *ortho* to the hydroxyl group at pH 9–10 (cf. Figs 10 and 11). The dyes resulting from acid (pH 3·0–3·5) versus alkaline coupling to S-acid were readily distinguished by the presence of either a doublet or a triplet for proton H_d (compare **9** with **10**, Table 3).

EXPERIMENTAL SECTION

The naphthalenesulfonic acid derivatives and the anilines employed in this investigation were obtained from commercial sources. The pH of the diazo coupling reactions was monitored with the aid of a Fisher Accumet Model 230 pH/Ion Meter. The ^{1}H-NMR spectra were recorded on a Bruker 250 MHz NMR spectrometer. The TLC data were generated with Eastman Chromagram silica gel plates with 1-butanol:EtOH:aq. NH_3:pyridine(4:1:3:2) as the eluent.

The diazo coupling reactions were conducted in 600 ml beakers equipped with a magnetic stir bar and a pH electrode. The temperature of the reaction was maintained with the aid of a Stir-Kool model SK12 cold plate/stirrer.

6-Amino-4-hydroxy-3-phenylazo-2-naphthalenesulfonic acid (6a) and 6-amino-3-(4-carboxyphenylazo)-4-hydroxy-2-naphthalenesulfonic acid (6b)

A solution of Gamma acid (5·49 g, 0·021 mol) in 200 ml of H_2O was stirred as the pH was adjusted to 10·0 by the addition of 10% NaOH solution. To this solution was added an equimolar amount of benzenediazonium chloride (**5a**; prepared from aniline hydrochloride and $NaNO_2$ at 0 °C) at a rate such that the reaction temperature did not exceed 3 °C. During the addition of **5a**, the pH of the solution was maintained near 10·0 by the periodic dropwise addition of cold 10% NaOH. Coupling was then allowed to proceed for 5 h. At that point, the pH of the solution was lowered to 2·0 by adding concentrated HCl. The precipitated dye was collected by vacuum filtration and suspended in H_2O. The pH was adjusted to 7·0 with the aid of 10% NaOH solution and the resulting solution concentrated. The solid obtained was dried in vacuo at 50 °C for 3 h to give an 85% yield of **6a**. This red dye had an R_f value of 0·55 on silica gel.

Dye **6b** was prepared by substituting 4-aminobenzoic acid for aniline in the above reaction. The amine was diazotized by adding ice, $NaNO_2$, and 2M HCl to a stirred solution of the sodium salt in H_2O. The diazotization was complete (as determined by starch–iodide test paper) within minutes. The coupling reaction was then conducted at pH 10·0 and 0–5 °C. The dye was isolated by the procedure described above for **6a** to give a red dye with $R_f = 0{\cdot}41$.

7-Amino-4-hydroxy-1-phenylazo-2-naphthalenesulfonic acid (7a) and 7-amino-1-(4-carboxyphenylazo)-4-hydroxy-2-naphthalenesulfonic acid (7b)

J-acid (5·49 g, 0·021 mol) was dissolved in water and the pH raised to 10·0 by adding 10% NaOH solution. Ice was added to lower the temperature of the solution to 0 °C. An equimolar amount of benzenediazonium chloride (5% solution) was then added at a rate which kept the temperature of the coupling reaction below 5 °C. The pH of the coupling reaction was maintained near 10·0 by the dropwise addition of cold 10% NaOH. After stirring for about 3 h, the product was isolated by the procedure described above for compound **6a** to give dye **7a** in excellent yield (95%). This orange dye had $R_f = 0{\cdot}53$.

Dye **7b** was prepared from 1·91 g (0·008 mol) of J-acid and 1·10 g (0·008 mol) of 4-aminobenzoic acid by the method described for dye **6b**. Thus was obtained an 80% yield of a pure reddish-orange dye, $R_f = 0{\cdot}32$ on silica gel.

4-Amino-5-hydroxy-8-phenylazo-2,7-naphthalenedisulfonic acid (8a), 4-amino-8-(4-carboxyphenylazo)-5-hydroxy-2,7-naphthalene disulfonic acid (8b) and 4-amino-3-(4-carboxyphenylazo)-5-hydroxy-2,7-naphthalenedisulfonic acid (11)

H-acid (3·68 g, 0·01 mol) was dissolved in H_2O at pH 10·0 and the solution was stirred at 0 °C as 0·01 mol of benzenediazonium chloride

(5 % solution) was added over a period of 15 min. The pH was maintained near 10·0 in the usual way. The coupling reaction was allowed to proceed for 5 h, with vigorous stirring, at 0–5 °C. The dye was precipitated by the slow addition of 2M HCl, collected by centrifugation, and then suspended in 200 ml of H_2O. The pH was raised to 7·0 by adding 10 % NaOH. The resulting solution was concentrated to give a red dye which was in turn dried *in vacuo* at 40 °C. Thus was obtained very pure **8a**, $R_f = 0{\cdot}51$ on silica gel.

The synthesis of dye **8b** utilized diazotized 4-aminobenzoic acid (1·37 g, 0·01 mol) in lieu of benzenediazonium chloride. The diazotization and coupling steps were essentially the same as described above for the preparation of dye **8a**. The red dye obtained (**8b**) had $R_f = 0{\cdot}32$ on silica gel. The yield was 90 %.

Dye **11** was obtained by coupling diazotized 4-aminobenzoic acid (1·37 g, 0·01 mol) to H-acid (3·68 g, 0·01 mol) at pH 2·5–3·0. The coupling step required stirring overnight (16 h) at 5 °C. The solution was centrifuged and the dye collected by filtration. The still-moist dye was suspended in H_2O and the mixture was neutralized (pH 7·0) by adding 10 % NaOH. The dye solution was then concentrated to give a red solid which showed two spots ($R_f = 0{\cdot}20, 0{\cdot}32$) on silica gel. The component of lower R_f clearly predominated and was isolated in pure form by column chromatography using the TLC eluent to give an overall yield of 65 % dye **11**.

4-Amino-5-hydroxy-8-phenylazo-1-naphthalenesulfonic acid (9a), 4-amino-5-hydroxy-8-(4-methoxyphenylazo)-1-naphthalenesulfonic acid (9b), 4-amino-8-(4-dimethylaminophenylazo)-5-hydroxy-1-naphthalenesulfonic acid (9c) and 4-amino-8-(4-carboxyphenylazo)-5-hydroxy-1-naphthalenesulfonic acid (9d)

Aniline (0·93 g, 0·01 mol) was dissolved in dilute HCl and diazotized by adding $NaNO_2$ solution at 0 °C. The diazonium salt was coupled to S-acid (2·53 g, 0·01 mol) at pH 9–10, or at pH 5–6, and a temperature of 0–5 °C. The coupling step was allowed to proceed overnight. The pH was then adjusted to 3·0 and the resulting mixture was centrifuged. The solid was collected and redissolved in H_2O at pH 7 by adding 10 % NaOH. The dye solution was concentrated to give pure **9a** (90 %), $R_f = 0{\cdot}64$ on silica gel.

S-acid (2·11 g, 0·008 mol) and *p*-anisidine (0·98 g, 0·008 mol) were coupled at either pH 10 or pH 5–6, by employing the procedure described for the preparation of dye **9a**, to give the purple–red dye **9b** in 80–90% yield. This dye had $R_f = 0{\cdot}57$ on silica gel.

S-acid (1·26 g, 0·005 mol) and 4-dimethylaminoaniline (0·68 g, 0·005 mol) were coupled at either pH 9–10 or pH 5–6 to give, after stirring overnight and subsequent workup, a modest yield (65%) of reasonably pure **9c**. This purple–red dye had $R_f = 0{\cdot}6$.

S-acid (2·63 g, 0·01 mol) and diazotized 4-aminobenzoic acid were coupled at pH 9–10 and at pH 5–6 to give dye **9d** in yields of 85–90%. The R_f of this red dye was 0·53 on silica gel.

4-Amino-5-hydroxy-3-(4-carboxyphenylazo)-1-naphthalene sulfonic acid (10a) and 4-amino-5-hydroxy-3-(4-nitrophenylazo)-1-naphthalenesulfonic acid (10b)

S-acid (2·63 g, 0·105 mol) and 4-carboxyaniline (1·44 g, 0·105 mol) were coupled at pH 3·0–3·5. The coupling step required stirring overnight (15–18 h) at 0–5 °C to complete the reaction. The dye was subsequently isolated in the usual way (cf. **9a**) to give the violet dye **10a**, $R_f = 0{\cdot}39$ on silica gel. None of the isomeric dye **9d** was obtained as a product of this reaction.

Dye **10b** was prepared selectively by coupling S-acid (2·58 g, 0·01 mol) and diazotized 4-nitroaniline at pH 3·0–3·5. The dye was isolated in the manner previously described for **9a** to give a violet solid, $R_f = 0{\cdot}46$ on silica gel.

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