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Two-Dimensional ^{1}H- and ^{13}C-NMR Spectra of Two Azo Dyes Derived from S-Acid

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ABSTRACT

Two-dimensional ^{1}H- and ^{13}C-NMR spectra of two products of benzenediazonium chloride coupling with S-acid under alkaline conditions have been measured. It has been found that main product corresponds to ortho *coupling to the hydroxyl group, whilst a minor product is the bisazo dye coupled* ortho *both to hydroxyl and amino groups. Both the dyes exist practically completely in their keto–hydrazone forms in hexadeuteriodimethyl sulfoxide solutions.*

1 INTRODUCTION

It has been generally accepted for many years[1-3] that aminohydroxynaphthalenesulfonic acids (J-, H-, S- and Gamma acids) undergo diazo coupling of benzenediazonium chloride *ortho* to the hydroxyl group at pH > 8. It has been recently concluded however[4] that J-, H- and S-acid undergo diazo coupling exclusively *para* to the hydroxyl group under alkaline conditions. We have found after detailed analysis of two-dimensional spectra[5] that these products are *ortho*-hydroxyazo compounds existing almost totally in their hydrazone forms. Both *ortho-* and *para*-hydroxyazo dyes are obtained after coupling of benzenediazonium salts substituted with electron-withdrawing substituents.[6,7] These results are in agreement with theoretical studies.[8] ^{1}H chemical shifts[4] in the dye prepared by coupling benzenediazonium chloride with S-acid (1-amino-8-naphthol-4-sulfonic acid) do not allow a decisive conclusion[8] about the coupling position of benzenediazonium chloride under alkaline conditions.

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The object of this communication is to determine the coupling position of benzenediazonium chloride with S-acid under alkaline conditions using two-dimensional ^{1}H- and ^{13}C-NMR spectra.

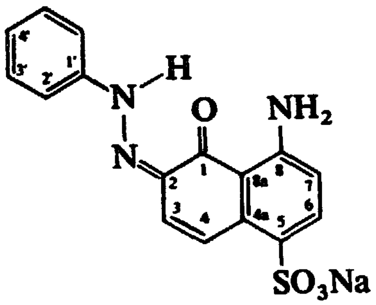
2 EXPERIMENTAL

Equimolar amounts of S-acid and benzenediazonium chloride were coupled at either pH 10 or pH 7 according to Ref. 4. After overnight standing, the pH was adjusted to 6 and the solid was collected by filtration. According to TLC [Silufol UV 254, Kavalier Czechoslovakia silica gel plates, using nitromethane:1-butanol:pyridine:aq.NH_3 (6:6:1:1) as the eluant] the crude product contained two main components: red ($R_f = 0{\cdot}4$) and blue ($R_f = 0{\cdot}6$) in a *ca.* 10:1 ratio in addition to several impurities in negligible amounts. The above-mentioned ratio depended on the concentrations of starting compounds, mixing, pH and rate of addition of benzenediazonium salt. The crude product was crystallized from methanol and the product thus obtained was a mixture of both main components. The blue dye was separated from it by column chromatography (silica gel, eluant the same as that for TLC). Methanol was distilled off from the crystallization liquor and the residue was crystallized from ethanol to give the red dye.

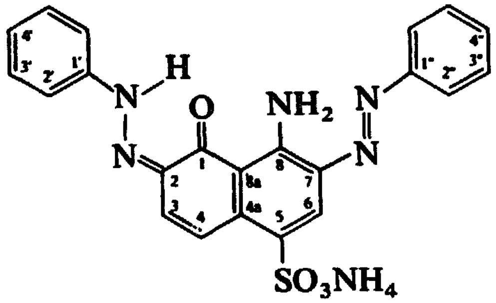
One- (1D) and two-dimensional (2D) ^{1}H- and ^{13}C-NMR spectra of the red and blue dyes in hexadeuteriodimethyl sulfoxide at 300 K were measured on a Bruker AM 400 spectrometer at 400·13 MHz and 100·61 MHz, respectively, as described in Refs 5 and 7.

3 RESULTS AND DISCUSSION

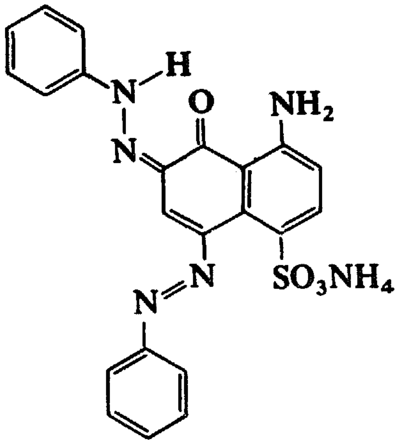
The existence of two main coupling products of S-acid (see the Experimental section) shows, in agreement with the theory,[8] that absolute selectivity of diazo coupling is never obtained. The ^{1}H chemical shifts of the aromatic protons of the red dye are, within experimental error, the same as those described in Ref. 4 and, in addition, a broad signal resonating at 15·58 typical of *ortho*-hydroxyazo dyes[5,7–9] was observed. The H,H-COSY spectrum revealed the connectivity of protons in two AX spin systems (8·01–6·95 and 7·87–6·70). The 1D ^{13}C-NMR spectrum consisted of 14 signals, one of them resonating at 181·58 being typical of the C═O group in dyes which exist almost completely in hydrazone forms.[10] The ^{13}C chemical shifts are temperature-independent. The H,C-COSY spectrum showed correlations of C—H via ^1J(CH). Selective INEPT spectra[11] via ^3J(CH) were used for the assignment of ^{13}C chemical shifts of quaternary carbons. They correlated proton H(3) ($\delta = 6{\cdot}95$) with C(1) ($\delta = 181{\cdot}58$), protons H(4) and H(6) with C(8a) and also protons H(4) and H(7) with C(5). The structure of the major red dye must, consequently, correspond to structure **I**, contrary to the structure given in Ref. 4.



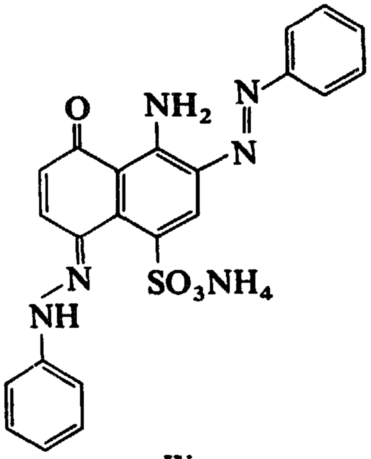
I



III



II



IV

H,H-COSY of the minor blue dye exhibited a singlet ($\delta = 8{\cdot}52$), AX system and signals of two phenyl groups in $C_6H_5NHN{=}$ (7·73–7·53–7·30) and $C_6H_5N{=}N{-}$ (8·04–7·61–7·53). The minor product is therefore a bisazo dye. A hydrazone configuration is indicated by $\delta(^{13}C) = 180{\cdot}25$ and thus there exist three possibilities, **II**–**IV**. The selective INEPT spectrum via the $^3J(CH)$ singlet ($\delta = 8{\cdot}52$) being irradiated gave signals resonating at 150·68 [C(8)] and 138·43 [C(4a)] which excluded structure **II**, which would require the signal at 180·25 [C(1)] to be observed. A broadened signal at 15·98 was found in the 1D ^1H-NMR spectrum of the blue dye and, therefore, this dye has the structure **III**. The ^1H and ^{13}C chemical shifts of red dye **I** and blue dye **III** are given in Table 1.

TABLE 1

^1H and ^{13}C Chemical Shifts of Compounds I and III in Hexadeuteriodimethyl Sulfoxide at 300 K

H/C no.	*Compound I*			*Compound III*		
	$\delta(^1H)^a$	$\delta(^{13}C)$	*Long-range correlations*[b]	$\delta(^1H)^c$	$\delta(^{13}C)^d$	*Long-range correlations*[b]
1	—	181·58	H(3)	—	180·25	H(3)
2	—	132·68	H(4)	—	132·78	H(4)
3	6·95	126·83		7·22	129·76	
4	8·01	122·41		8·14	121·45	
5	—	132·10	H(4), H(7)	—	[e]	
6	7·87	133·95		8·52	124·56	
7	6·70	112·48		—	[e]	
8	—	153·99	H(6)	—	150·68	H(6)
4a	—	134·52	H(3), H(6)	—	138·43	H(3), H(6)
8a	—	112·66	H(4), H(7)	—	115·13	H(4)
1′	—	142·07	H(3′)	—	141·72	H(3′)
2′	7·60	115·93		7·73	116·87	
3′	7·48	129·75		7·53	129·76	
4′	7·21	124·89		7·30	126·11	

[a] $\delta(NN\underline{H}) = 15·58$.

[b] ^1H, ^{13}C long-range shift correlations observed in selective INEPT spectra.

[c] $\delta(NN\underline{H}) = 15·98$; $\delta(N\underline{H}_4^+) = 7·24$; $\delta(H(2'')) = 8·04$; $\delta(H(3'')) = 7·61$; $\delta(H(4'')) = 7·53$.

[d] $\delta(C(1'')) = 152·60$; $\delta(C(2'')) = 122·44$; $\delta(C(3'')) = 129·27$; $\delta(C(4'')) = 130·31$.

[e] 132·53 or 132·33.

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