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Preparation and ^1H, ^{13}C and ^{15}N NMR Spectra of 1,3-Bis(phenylazo)-2-naphthol and its Precursors

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ABSTRACT

1,3-Bis(phenylazo)-2-naphthol was prepared from 1-phenylazo-2-naphthol in a three-step procedure. The ^1H, ^{13}C *and* ^{15}N *NMR spectra of 1,3-bis(phenylazo)-2-naphthol and its precursors were measured. 1,3-Bis(phenylazo)-2-naphthol exists predominantly as 3-phenylazo-1,2-naphthoquinone 1-phenylhydrazone in deuteriochloroform. Copyright © 1996 Elsevier Science Ltd*

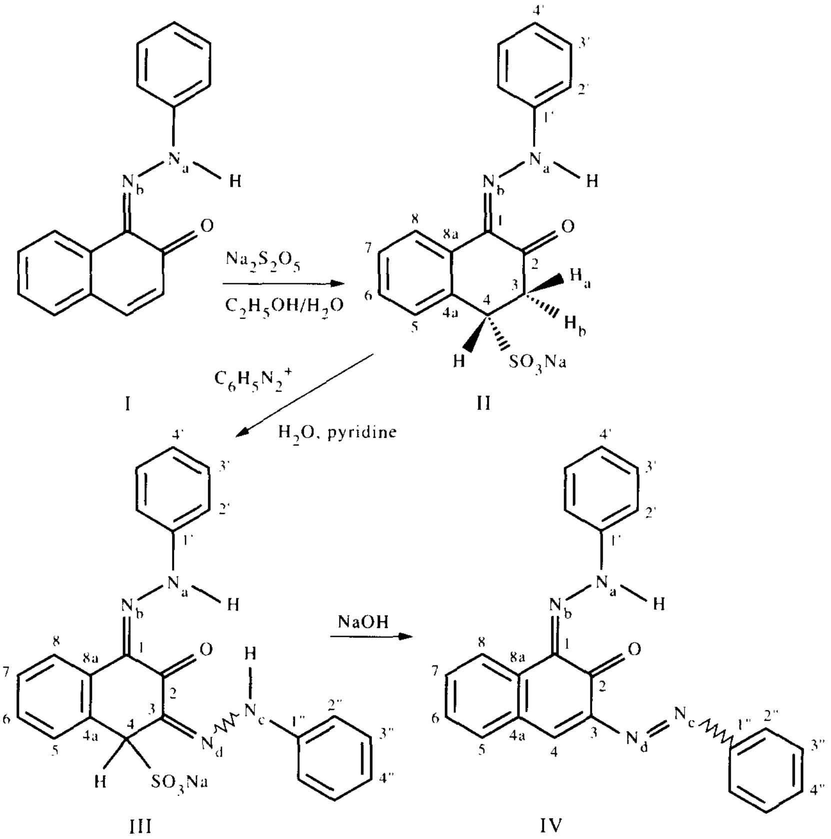
INTRODUCTION

It is well known from the literature[1–5] that it is not possible to prepare 2-naphthols substituted in position 3 by a phenylazo group by a direct coupling reaction. 3-Phenylazo-2-naphthol was synthesized, as reported by Fierz-David *et al.*,[6] from 3-amino-2-naphthol and thionyl chloride, and subsequent reaction with phenylhydroxylamine. On the other hand, activated methylene groups undergo the coupling reaction very easily.[1–7]

The aim of this paper is to report the preparation of 1,3-bis(phenylazo)-2-naphthol by the coupling reaction outlined in Scheme 1, to measure the ^1H, ^{13}C and ^{15}N NMR spectra of this compound and its precursors, and to characterize any relevant azo-hydrazone tautomeric equilibria.

RESULTS AND DISCUSSION

The reaction procedure is shown in Scheme 1 (prevailing tautomers are shown).



Scheme 1.

1-Phenylazo-2-naphthol (**I**) was reacted with with $Na_2S_2O_5$ in an aqueous ethanol mixture to form compound **II** containing an activated methylene group. This compound coupled at the CH_2 group with benzenediazonium chloride in aqueous pyridine, and the resultant product (**III**) was then decomposed with sodium hydroxide to give 1,3-bis(phenylazo)-2-naphthol (**IV**). Details of the syntheses are given in the Experimental section.

^1H, ^{13}C and ^{15}N NMR spectra of compounds **I–IV** were measured and analyzed. Two-dimensional NMR spectra[8] were used with the aim of assigning proton and carbon chemical shifts unambiguously. H,H-COSY, NOESY, H,C-COSY, HMQC and HMBC techniques[9] were applied. ^1H, and ^{13}C chemical shifts are collated in Tables 1–3.

The ^1H, ^{13}C and ^{15}N NMR spectra of compound **I** have been previously related.[10–12]

In the NOESY[13] spectrum of compound **II**, the through-space proximity of proton H-4 with protons H-3a and H-5 was found. This observation allowed us to assign the protons of the prochiral methylene group and to orientate the proton connectivity of the unsubstituted naphthalene ring obtained from the COSY spectrum. The values of $\delta(^{15}N) = -222.0$ (N_a) and -46.5 (N_b), as well as $^{1}J(^{15}N_a, {}^{1}H) = 96.1$ Hz, provide evidence that compound **II** exists completely in a hydrazone configuration.

In the ^{1}H NMR spectrum of compound **III**, there are two acidic protons, which were distinguished on the basis of selective ^{15}N enrichment. The signal with $\delta(^{1}H) = 10.88$ was split into a doublet due to the existence of $^{1}J(^{15}N_c, {}^{1}H) = 96.0$ Hz when the ^{1}H NMR spectrum of the N_cN_d ^{15}N selective labelled compound was measured. $^{1}J(^{15}N_a, {}^{1}H) = 95.7$ Hz was determined from *ca* 0.18% satellites (due to *ca* 0.36% natural abundance of ^{15}N isotope) for the signal at 14.49 ppm. These values are typical of phenylhydrazone groups, as well as $\delta(^{15}N)$ ($\delta(^{15}N_a) = -220.6$, $\delta(^{15}N_c) = -223.6$, $(^{15}N_d) = -30.9$, $^{1}J(^{15}N_c, {}^{15}N_d) = 10.8$ Hz).

The solubility of 1,3-bis(phenylazo)-2-naphthol is very low in chloroform and extremely low in DMSO. HMQC and HMBC techniques therefore had to be used for the assignment of the ^{13}C chemical shifts (Figs 1 and 2).

^{15}N chemical shifts were distinguished using ^{15}N selective labelling. $\delta(^{15}N) = 120.9$ (N_c) and 131.3 (N_d) and $^{1}J(^{15}N, {}^{15}N) = 16.6$ Hz are typical of a

TABLE 1

^{1}H and ^{13}C Chemical Shifts in Sodium Salt of 4-Sulpho-3,4-dihydro-1,2-naphthoquinone 1-phenylhydrazone (**II**) in Hexadeuteriodimethyl Sulfoxide

C/H No.	$\delta(^{1}H)$[a]	$\delta(^{13}C)$	X[c]
1	–	130.09	8
2	–	196.39	3, 4
3	3.18 (H_a)[b]	41.17	–
	3.10 (H_b)[b]	–	–
4	4.07[b]	59.59	–
4a	–	132.67	6, 8
5	7.40	131.52	7
6	7.29	126.70	8
7	7.37	127.56	5
8	7.97	122.62	6
8a	–	134.63	5, 7
1′	–	143.40	3′
2′	7.48	114.36	4′
3′	7.42	129.71	–
4′	7.08	122.62	–

[a] δ(NH/OH) = 13.77.

[b] ^{2}J(H-3a, H-3b) = 17.0 Hz, ^{3}J(H-3a, H-4) = 2.0 Hz, ^{3}J(H-3b, H-4) = 5.9 Hz.

[c] X denotes numbers of the protons for which correlations were found via long-range couplings.

TABLE 2

^{1}H and ^{13}C Chemical Shifts in Sodium Salt of 4-Sulpho-3,4-dihydro-1,2,3-naphthalene-trione 1,3-bisphenylhydrazone(**III**) in Hexadeuteriodimethyl Sulfoxide

C/H No.	$\delta(^1H)^a$	$\delta(^{13}C)$	X^b
1	–	130.22	N_aH, 8
2	–	181.35	4
3	–	133.56	N_cH
4	5.76	61.02	5
4a	–	134.78	–
5	7.46	131.03^c	4
6	7.33	126.64	8
7	7.38	127.52	–
8	7.97	122.57	–
8a	–	131.13^c	4
1′	–	143.26	N_aH
2′	7.54	114.57	–
3′	7.45	129.69	–
4′	7.10	122.91	–
1″	–	144.22	N_cH
2″	7.45^d	114.42	–
3″	7.36^d	129.27	–
4″	7.00^d	121.81	–

[a] $\delta(N_aH)$ = 14.49, $\delta(N_cH)$ = 10.88.

[b] X denotes numbers of the protons for which correlations were found via long-range couplings.

[c] The assignment can be opposite.

[d] Assignment following from the data for deuterated isotopomer.

TABLE 3

^{1}H and ^{13}C Chemical Shifts in 3-Phenylazo-1,2-napthoquinone 1-Phenylhydrazone (**IV**) in Deuteriochloroform

C/H No.	$\delta(^1H)^a$	$\delta(^{13}C)$	X
1	–	130.94	8
2	–	170.98	–
3	–	146.02	4
4	7.96	126.12	–
4a	–	126.72	6
5	7.72	131.06	4, 7
6	7.42	126.42	8
7	7.57	130.04	–
8	8.51	121.74	6
8a	–	134.53	4, 5, 7
1′	–	143.71	3′
2′	7.72	118.31	4′
3′	7.46	129.75	–
4′	7.30	127.53	2′
1″	–	153.05	–
2″	7.99	123.33	4″
3″	7.5	129.11	–
4″	7.5	131.47	2″

[a] δ(NH/OH) = 16.97.

[b] X denotes numbers of the protons for which correlations were found via long-range couplings.

C_6H_5–N_c=N_d– arrangement, while $\delta(^{15}N)$ = −142.4 (N_a) and 15.1 (N_b) correspond to a tautomeric equilibrium which is very similar to that in 1-phenylazo-2-naphthol,[12] i.e. about 70% of hydrazone form and 30% of azo form, their exchange being fast on the NMR time scale. $^1J(^{15}N_c, ^1H)$ = 75.4 Hz is in agreement with this conclusion. This implies that 1,3-bis-(phenylazo)-2-naphthol exists predominantly as 3-phenylazo-1,2-naphthoquinone 1-phenylhydrazone in deuteriochloroform.

EXPERIMENTAL

Sodium salt of 4-sulpho-3,4-dihydro-1,2-naphthoquinone 1-phenylhydrazone (II)

$Na_2S_2O_5$ 20 g (0.105 mol) in 200 ml of water was added to 24.82 g (0.1 mol) of 1-phenylazo-2-naphthol (**I**) in 200 ml of hot ethanol and the mixture was

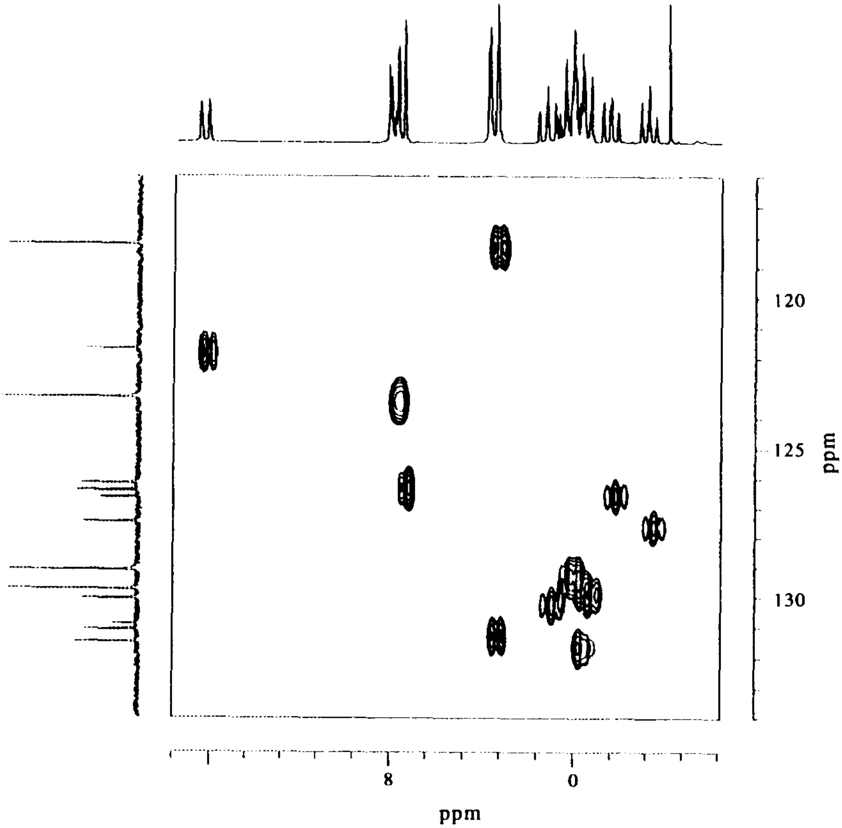


Fig. 1. Part of HMQC spectrum of compound **IV** in deuteriochloroform.

then refluxed on a water bath for 6 h. The reaction mixture was diluted to 800 ml with hot water. After cooling, unreacted 1-phenylazo-2-naphthol (*ca* 3 g) was filtered off and the required reaction product was salted out by addition of NaCl. The resulting precipitate was collected by filtration and washed with 10% aqueous NaCl. For NMR measurements, the compound was crystallized from aqueous ethanol (m.p. 168–170°C).

Sodium salt of 4-sulpho-1,2,3-trioxo-1,2,3,4-tetrahydronaphthalene 1,3-bis(phenylhydrazone) (III)

The crude product (II) was used for the further reaction step, being added to a 0.1 mol solution of benzenediazonium chloride prepared by the standard manner in 200 ml of water. The mixture was cooled to 5°C and 100 ml of pyridine was then added. The reaction mixture was stirred for 2 h maintaining a temperature of 5–10°C. The resulting precipitate was filtered and

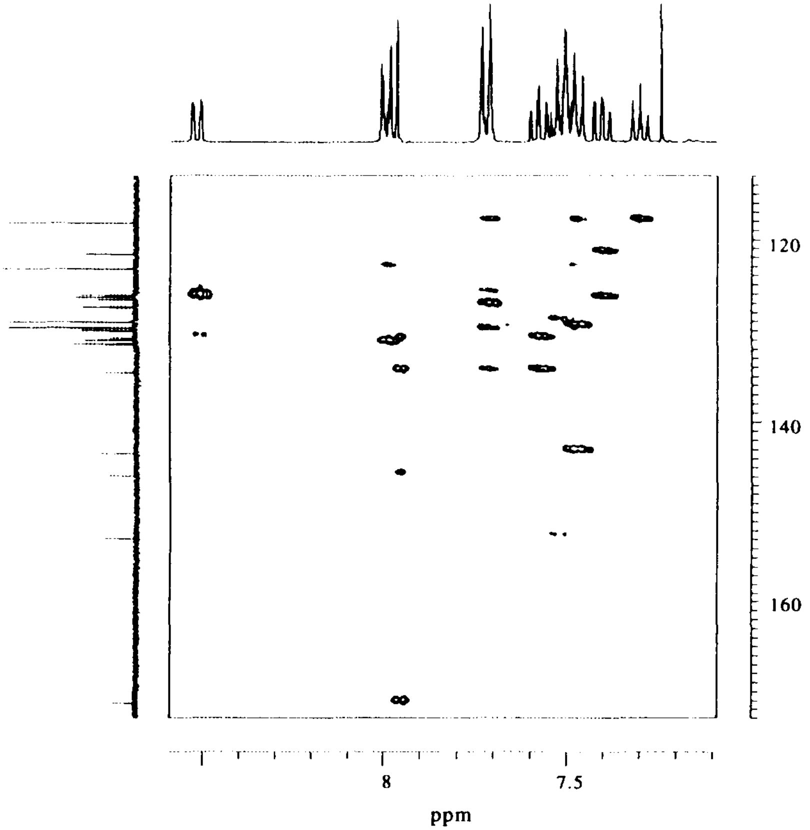


Fig. 2. Part of HMBC spectrum of compound **IV** in deuteriochloroform.

washed with 10% aqueous NaCl. From the ^{1}H NMR spectrum, the crude product contained 1-phenylazo-2-naphthol (**I**) and compound **III** in the ratio of *ca* 1.2 : 1, together with small amounts of other impurities. The crude product was crystallized from benezene/ethanol (m.p. 167–169°C).

$^{15}N_c$ (20% ^{15}N) and $^{15}N_d$ (95% ^{15}N) doubly labelled isotopomer and 3-$NNHC_6D_5$ isotopomer were prepared analogously using aniline-^{15}N (20% ^{15}N) and $Na^{15}NO_2$ (95% ^{15}N) and aniline-D_7, respectively.

1,3-Bis(phenylazo)-2-naphthol (IV)

Compound **III** (10 g) was dissolved in 200 ml of ethanol and the solution poured into 200 ml of 2.5 M NaOH. The separated solid was filtered and washed with 400 ml of 10% NaCl. Yield: 5.2 g. Compound **IV** was recrystallised from toluene, m.p. 225–228°C. Calculated for $C_{22}H_{16}N_4O$: C, 74.98; H, 4.58; N, 15.90. Found: C, 74.93; H, 4.60; N, 15.68%.

The ^{1}H, ^{13}C and ^{15}N NMR spectra were recorded at 300 K on a Bruker AMX 360 spectrometer equipped with a 5 mm broadband probe, 5 mm broadband inverse probe and X32 computer using the UXNMR software (Version 940501.3).

One-dimensional (1D) ^{1}H NMR (360.13 MHz) and ^{13}C NMR (90.566 MHz) spectra were recorded with 64 K data points and a spectral width of 7246.4 Hz and 22 727.3 Hz, respectively. Compounds **II** and **III** were measured in hexadeuteriodimethyl sulfoxide and chemical shifts were referred to the central signal of the solvent (δ = 2.55 (^{1}H) and 39.60 (^{13}C)).

Compound **IV** was dissolved in deuteriochloroform; ^{1}H and ^{13}C chemical shifts were referred to internal TMS (δ = 0.0).

One-dimensional ^{15}N NMR (36.50 MHz) spectra were recorded in 10 mm NMR tubes with 64 K data points and a spectral width of 20 000 Hz using gated and inverse-gated decoupling. ^{15}N chemical shifts were referred to external nitromethane (δ = 0.0) placed in a coaxial capillary.

Positive values of chemical shifts denote down-field shifts with respect to standards.

Experimental conditions of two-dimensional H,H-COSY, NOESY, H,C-COSY and H,C-COSYLR were similar to data reported previously.[14]

Experimental conditions for inverse H/C correlation of compound **IV** were as follows.

HMQC: ^{1}H detected H/C heteronuclear correlation with BIRD pulse sequence to suppress ^{1}Hs connected to ^{12}C. Sequence: d_1-90(^{1}H)-d_2-180(^{1}H)/180(^{13}C)-d_2-90(^{1}H)-d_3-90(^{13}C)-90(^{1}H)-d_2-90(^{13}C)-d_0-180(^{1}H)-d_0-90(^{13}C)-d_2-Acq. Spectral width 1440.9 Hz in F_2 and 7245.3 Hz in F_1, d_1 = 1.5 s, d_2 = 3.1 ms, d_3 = 600 ms, 1 K data points in F_2, 128 experiments in F_1, 4 dummy scans, 4 scans, decoupling during acquisition. Apodization with a $\pi/2$-shifted squared sine-bell function in both dimensions, zero-filling giving a matrix of 1 K × 256 points.

HMBC: ^1H detected H/C heteronuclear correlation optimized on long-range couplings, with low-pass *J*-filter to suppress one-bond correlations.[15] Sequence: d_1-90(^1H)-d_2-90(^{13}C)-d_3-90(^{13}C)-d_0-180(^1H)-d_0-90(^{13}C)-Acq. Spectral width 1440.9 Hz in F_2 and 7245.3 Hz in F_1, $d_1 = 1.5$ s, $d_2 = 3.1$ ms, $d_3 = 62$ ms, 1 K data points in F_2, 256 experiments in F_1, 4 dummy scans, 64 scans, no decoupling during acquisition. Apodization with a $\pi/2$-shifted squared sine-bell function in both dimensions, zero-filling giving a matrix of 1 K × 512 points.

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