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^{15}N, ^{13}C and ^{1}H NMR spectra and azo-hydrazone tautomerism of some dyes prepared by coupling of 1-naphthalenediazonium salt

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Abstract

2-(1-Naphthyl)azo-5-tert.butylphenol (**1**), 3-methyl-1-phenylpyrazole-4,5-dione 4-(1-naphthyl)hydrazone (**2**), 1-(1-naphthyl)azo-2-naphthol (**3**), and 4-(1-naphthyl)azo-1-naphthol (**4**) were prepared by coupling naphthalene-diazonium chloride with the appropriate passive components and their ^{1}H, ^{13}C and ^{15}N NMR spectra were measured and analysed. Two-dimensional NMR experiments were used to assign ^{1}H and ^{13}C chemical shifts unambiguously. The values of $^{1}J(^{15}N,^{1}H)$ and ^{15}N chemical shifts show that compounds **1** and **4** exist almost completely in azo tautomeric forms, whilst compound **2** exists completely in the hydrazone form and compound **3** predominantly in the hydrazone form. The increase of hydrazone content in compound **3** compared with the hydrazone content in 1-phenylazo-2-naphthol is in the range 1–2.7%, calculated from $\delta(^{15}N_a)$ and $\delta(^{15}N_b)$ chemical shifts and 1.2–1.6% using $^{1}J(^{15}N,^{1}H)$, i.e. the annelation of the benzene ring in the active component has, contrary to the annelation of the benzene ring in the passive component, practically negligible influence on the azo-hydrazone equilibrium in compounds studied. © 1999 Elsevier Science Ltd. All rights reserved.

Keywords: ^{1}H; ^{13}C and ^{15}N NMR; Azo and hydrazone compounds; Azo-hydrazone equilibrium

1. Introduction

In previous papers [1–4] we have reported the effect of the annelation of the benzene ring in passive components of model azo dyes on the azo-hydrazone tautomeric equilibria [5–10]. Whilst 2-hydroxy-5-tert.butylazobenzene exists as a true azo compound [1,2], annelation of the benzene ring results in 1,2-naphthoquinone 1-phenylhydrazone and 1,2-naphthoquinone 2-phenylhydrazone [1,2] being in a prevailing tautomeric form in compounds derived from 1- and 2-naphthol and an additional increase (ca. 10–20%) of hydrazone content [3,4] was observed in 1,2-anthraquinone 1-phenylhydrazone and 1,2-naphthoquinone 2-phenylhydrazone in deuteriochloroform. Similarly, 4-hydroxyazo-benzene and 1-hydroxy-4-phenylazo-naphthalene exist in DMSO-D_6 as true azo compounds but 1,4-naphthoquinone 4-phenylhydrazone and 9,10-naphthoquinone 9-phenylhydrazone are essentially completely in the appropriate phenylhydrazone forms [1–4].

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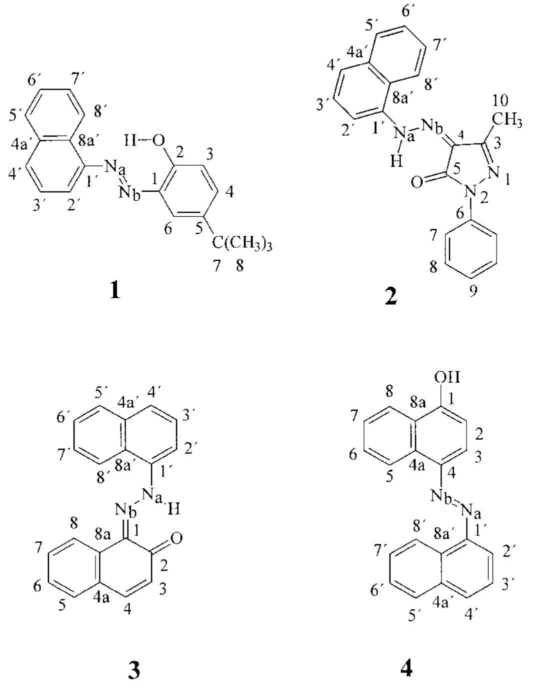
The objective of this investigation was to prepare compounds **1–4** by the 1-naphthalenediazonium salt coupling reaction, and to measure ^{1}H, ^{13}C and ^{15}N NMR spectra of these compounds and to characterise quantitatively the influence of the benzene ring annelation in passive component on the azo-hydrazone tautomeric equilibrium, comparing the results with data for analogous compounds prepared by coupling benzenediazonium chloride with the same passive components.

2. Experimental

The compounds **1–4** shown in Scheme 1 were prepared as described previously [11]. $^{15}N_a$ (96% ^{15}N) and $^{15}N_b$ (20% ^{15}N) doubly labelled isotopomers of compounds **1–3** were prepared analogously using 1-naphthylamine-^{15}N (96% ^{15}N) and $Na^{15}NO_2$ (20% ^{15}N).

^{1}H (360.13 MHz), ^{13}C (90.566 MHz) and ^{15}N NMR (36.50 MHz) NMR spectra were recorded at 300 or 330 K on a Bruker AMX 360 spectrometer equipped with a 5 mm broadband probe and a 5 mm broadband inverse z-shielded probe and Silicon Graphic Indy computer using the UXNMR software. Compounds **1–3** were measured in deuteriochloroform and compound **4** in hexadeuteriodimethyl sulfoxide. The ^{1}H and ^{13}C chemical shifts were referred to internal TMS ($\delta = 0.00$) and ^{15}N chemical shifts to external nitromethane ($\delta = 0.0$) placed in a coaxial capillary.



Scheme 1. Formulae of compounds measured (prevailing tautomers are shown).

Positive values of chemical shifts denote downfield shifts with respect to standards.

Two-dimensional H,H-COSY, H,H-COSYLR, NOESY, gs-HMQC, gs-HMBC, gs-HMQC-RELAY and gs-HMQC-RELAY spectra [12–15] were measured using microprograms provided by Bruker.

3. Results and discussion

3.1. ^{1}H and ^{13}C NMR spectra

^{1}H, ^{13}C and ^{15}N NMR spectra of compounds **1–4** were measured and analysed. The assignment is more complicated compared with that of analogous derivatives prepared by coupling benzenediazonium chloride with the same passive components, as previously published [1]. The phenylazo group gives a typical pattern of a monosubstituted phenyl group in the ^{1}H NMR spectrum and four signals in the ^{13}C NMR spectrum, two of them having two-fold intensity [1]. The 1-naphthyl group provides seven ^{1}H and ten ^{13}C NMR signals resonating in relatively very narrow spectral regions. Some signals coincide with the signals of the passive components. For this reason, two-dimensional NMR spectra need to be used with the aim of assigning the proton and carbon chemical shifts unambiguously. H,H-COSY, H,H-COSYLR, NOESY and gradient-selected HMQC, HMBC, HMQC-RELAY and HMQC-TOCSY techniques were applied. ^{1}H and ^{13}C chemical shifts are shown in Tables 1–4.

Analysis of the H,H-COSY and H,H-COSYLR spectra revealed the proton–proton connectivity patterns (Fig. 1).

In the NOESY spectra, the through-space proximity of protons H-4 with H-5 and H-4′ with

Table 1
^{1}H and ^{13}C chemical shifts for compound **1** in deuteriochloroform
10

H/C	δ(^{1}H)	δ(^{13}C)	H/C	δ(^{1}H)	δ(^{13}C)
1	–	137.73	1′	–	146.35
2	–[a]	150.38	2′	7.93	113.21
3	7.06	117.65	3′	7.58	126.76
4	7.46	131.13	4′	7.93	129.37
5	–	143.06	4a′	–	134.26
6	8.05	129.77	5′	7.97	131.29
7	–	34.17	6′	7.58	126.69
8	1.41	31.39	7′	7.63	127.51
			8′	8.49	122.18
			8a′	–	129.47

[a] δd(OH) = 13.08.

Table 2
^{1}H and ^{13}C chemical shifts for compound **2** in deuteriochloroform

H/C	δ(^{1}H)	δ(^{13}C)	H/C	δ(^{1}H)	δ(^{13}C)
3	–	148.52	1′	–[a]	136.01
4	–	129.86	2′	7.69	111.29
5	–	158.05	3′	7.52	126.01
6	–	137.98	4′	7.91	125.89
7	7.99	118.78	4a′	–	134.04
8	7.48	128.97	5′	7.87	128.81
9	7.22	125.29	6′	7.53	126.58
10	2.38	11.83	7′	7.61	127.08
			8′	8.05	119.37
			8a′	–	123.12

[a] δ(NH) = 14.49.

Table 3
^{1}H and ^{13}C chemical shifts for compound **3** in deuteriochloroform

H/C	δ(^{1}H)	δ(^{13}C)	H/C	δ(^{1}H)	δ(^{13}C)
1	–	131.28	1′	–	139.69
2	–[a]	172.91	2′	8.21	112.93
3	6.92	124.97	3′	7.60	126.15
4	7.74	140.46	4′	7.81	127.51
4a	–	128.12	4a′	–	134.17
5	7.61	128.71	5′	7.91	128.64
6	7.41	125.91	6′	7.57	126.56
7	7.57	129.99	7′	7.66	127.24
8	8.64	121.83	8′	8.33	120.75
8a	–	133.52	8a′	–	125.24

[a] δ(OH/NH) = 17.24.

Table 4
^{1}H and ^{13}C chemical shifts for compound **4** in hexadeuteriodimethyl sulfoxide

H/C	δ(^{1}H)	δ(^{13}C)	H/C	δ(^{1}H)	δ(^{13}C)
1	–[a]	158.07	1′	–	147.67
2	7.16	108.72	2′	8.01	111.86
3	8.18	114.63	3′	7.74	126.64
4	–	140.55	4′	8.12	130.56
4a	–	132.96	4a	–	134.12
5	9.06	122.78	5′	8.11	128.13
6	7.79	127.97	6′	7.71	126.08
7	7.65	125.59	7′	7.77	127.01
8	8.33	122.57	8′	9.01	123.13
8a	–	124.55	8a′		130.66

[a] δ(OH) = 11.34.

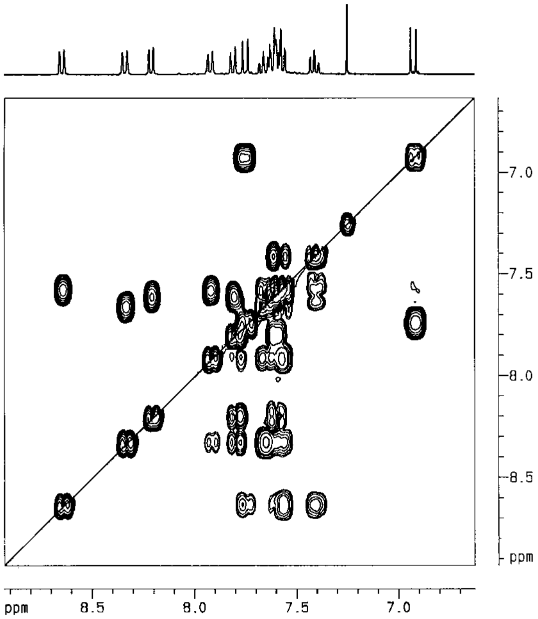


Fig. 1. H,H-COSY (upper left part) and H,H-COSYLR (bottom right part) spectra of compound **3** in deuteriochloroform.

H-5′ in compounds **1**–**4** were found. Gradient-selected HMQC spectra were used to correlate protons and appropriate carbons via ^{1}J(^{13}C,^{1}H) and HMBC via ^{3}J(^{13}C,^{1}H) coupling constants. Gradient-selected HMQC-RELAY and HMQC-TOCSY techniques were applied during the measurement of compounds **3**,**4** because of the complexity of the ^{1}H and ^{13}C NMR spectra. Starting from the HMQC cross-peak, one can find in the same row in F$_1$ additional signals which are caused by a RELAY transfer (showing –CH–CH– arrangement) or by a TOCSY transfer (showing –CH–CH–CH... arrangement). The spectra are shown in Fig. 2–4.

3.2. ^{15}N NMR spectra

^{15}N chemical shifts and coupling constants in **1**–**4** are shown in Table 5.

^{15}N chemical shifts are shifted ca. 3–5 ppm upfield for compounds **1**–**4** compared with data for phenyl analogues. This fact is mainly caused by the fact that phenyl compounds were measured using an NMR spectrometer an having electromagnet [2] whilst the ^{15}N chemical shifts in compounds **1**–**4** were determined using a superconducting magnet. The relative orientation of the magnetic field with respect to a sample differs by 90° for the above-mentioned two possible types of measurements (the orientation of the direction of the external magnetic field with respect to sample tube axis is parallel in superconducting magnet systems and perpendicular in electromagnet systems [16]) and the data are not corrected for the magnetic susceptibility effect. On the other hand, this fact cannot affect the

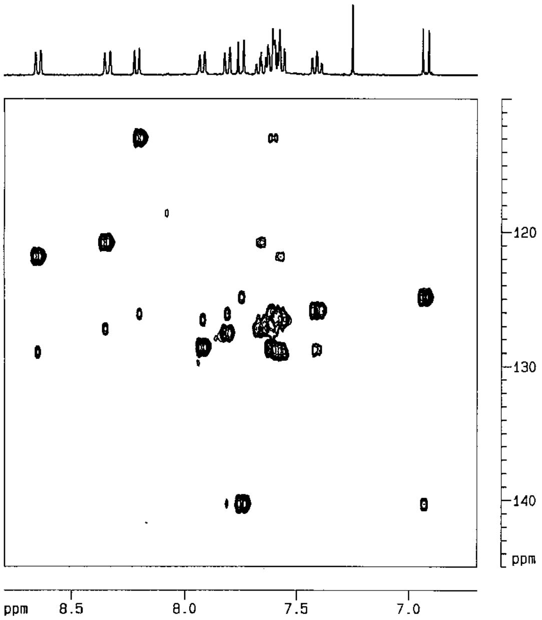


Fig. 3. Gradient-selected HMQC-RELAY spectrum of compound **3** in deuteriochloroform.

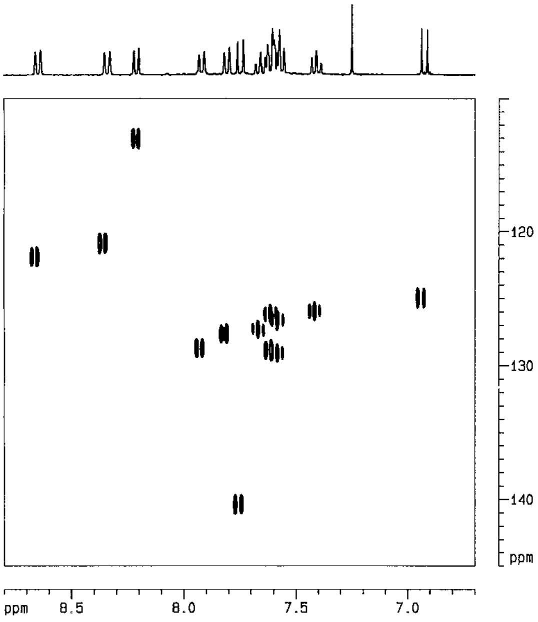


Fig. 2. Gradient-selected HMQC spectrum of compound **3** in deuteriochloroform.

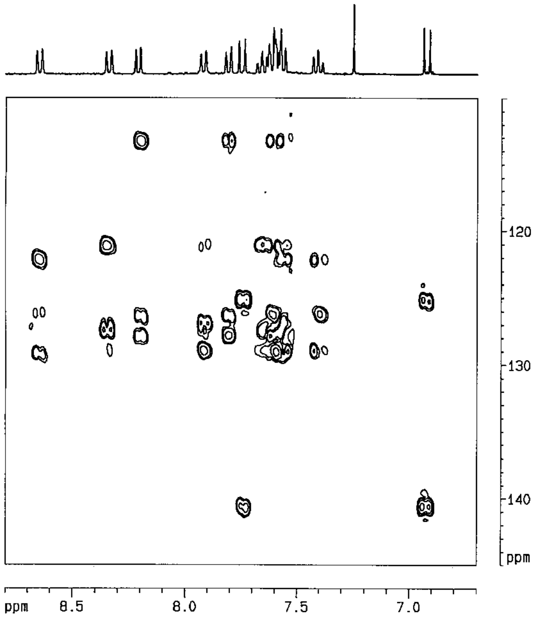


Fig. 4. Gradient-selected HMQC-TOCSY spectrum of compound **3** in deuteriochloroform.

Table 5

^{15}N Chemical shifts and $^{1}J(^{15}N_a, H)$ and $^{1}J(^{15}N_a, N_b)$ coupling constants for compounds **1**–**4**

Compound	Temperature (K)	$\delta(N_a)$	$\delta(N_b)$	% Hydrazone calc. from $\delta(^{15}N_a)$	% Hydrazone calc. from $\delta(^{15}N_b)$	$^{1}J(^{15}N_a, H)$ (Hz)	% Hydrazone calc. from $^{1}J(^{15}N_a, H)$	$^{1}J(^{15}N_a, ^{15}N_b)$
1	300	62.6	123.5	0	0	n.o.	0	15.1
	330	64.7	124.6	0	0	n.o.	0	15.1
2	300	−210.1	−20.1	100	100	95.7	100	11.1
	330	−210.9	−19.2	100	100	95.6	100	11.1
3	300	−134.1	18.6	72.1	73.1	67.5	70.5	12.5
	330	−119.1	27.4	66.7	67.6	62.1	65	12.8
4	300	118.3	102					

azo-hydrazone content determination because both model azo and hydrazone compounds as well as tautomeric systems were measured under uniform conditions, and the relative weighted average is independent of the absolute values of the ^{15}N chemical shifts.

The values of the $^{1}J(^{15}N,^{1}H)$ and ^{15}N chemical shifts show that compounds **1** and **4** exist almost completely in the azo tautomeric form, while compound **2** exists completely in the hydrazone form and compound **3** predominantly in the hydrazone form [10].

Compounds **1**–**3** possess strong intramolecular hydrogen bonds. For calculation of the hydrazone form content, Eqs. (1) and (2) were used:

$$\%\ \text{hydrazone form} = \frac{^{1}J(^{15}N_a, H)_3}{^{1}J(^{15}N_a, H)_2} \times 100 \qquad (1)$$

$$\%\ \text{hydrazone} = \frac{\delta[^{15}N(\mathbf{1})] - \delta[^{15}N(\mathbf{3})]}{\delta[^{15}N(\mathbf{1})] - \delta[^{15}N(\mathbf{2})]} \qquad (2)$$

where

(i) $^{1}J(^{15}Na,H)_3$ is the one-bond nitrogen coupling constant in compound **3**, (ii) $^{1}J(^{15}Na,H)_2$ is the one bond nitrogen coupling constant in 3-methyl-1-phenyl-pyrazole-5-dione 4-(1-naphthyl)-hydrazone **2** (model hydrazone compound with an intramolecular hydrogen bond), (iii) $\delta[^{15}N(\mathbf{3})]$ is an appropriate ^{15}N chemical shift (N_a or N_b) in compound **3**, (iv) $\delta[^{15}N(\mathbf{1})]$ is the ^{15}N chemical shift in **1**, 2-(1-naphthyl)azo- 5-tert.butylphenol (model azo compound with an intramolecular hydrogen bond), and (v) $\delta[^{15}N(\mathbf{2})]$ is the ^{15}N chemical shift in 3-methyl-1-phenylpyrazole-4,5-dione 4-(1-naphthyl)hydrazone **2**.

Calculated contents of the hydrazone forms in compound **3**, using $^{15}N_a$ and $^{15}N_b$ chemical shifts (Table 5), are practically the same (the difference is 1% or less), and very similar results were obtained using $^{1}J(^{15}N,^{1}H)$ [Eq. (1)]. The increase of hydrazone content in compound **3** compared with the hydrazone content in 1-phenylazo-2-naphthol [3] is in the range 1–2.7%, calculated from $\delta(^{15}N_a)$ and $\delta(^{15}N_b)$ chemical shifts and 1.2–1.6% using $^{1}J(^{15}N,^{1}H)$ [17]. The ^{15}N chemical shifts in 4-(1-naphthyl)azo-1-naphthol (**4**) are 102 and 118.3, and in 4-phenylazo-1-naphthol are 108 and 119.2 [3]. Compound **4** has no intramolecular hydrogen bonds, and ^{15}N chemical shifts must not therefore be compared with the data for above-mentioned compounds **1** and **2** but, e.g. with the values in 4-hydroxyazobenzene in DMSO [18] ($\delta(^{15}N_a) = 110.2$ and $\delta(^{15}N_b) = 124.2$) and benzaldehyde phenylhydrazone, in which $\delta(^{15}N)$ of the NH group is −237.0 and $\delta(^{15}N)$ of −N= is −54.0 in DMSO [19].

Annelation of the benzene ring in the active component has, contrary to the annelation of the benzene ring in the passive component, practically negligible influence on the azo-hydrazone equilibrium in the compounds studied.

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