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^{1}H, ^{13}C and ^{15}N NMR Spectra of Some Anthracenedione Phenylhydrazones

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ABSTRACT

*1,2-Anthraquinone-1-phenylhydrazone (**1**), 1,2-anthraquinone-2-phenylhydrazone (**2**), 1,4-anthraquinone-4-phenylhydrazone (**3**) and 9,10-anthraquinone-9-phenylhydrazone (**4**) were prepared and their* ^{1}*H,* ^{13}*C and* ^{15}*N NMR spectra were measured. Two-dimensional NMR experiments were used to assign* ^{1}*H and* ^{13}*C chemical shifts unambiguously. The values of* $^1J(^{15}N, ^1H)$ *and* ^{15}*N chemical shifts show that these compounds exist almost completely in their hydrazone tautomeric forms under the measurement conditions used. Small amounts of azo forms (<5%) are also very probably present, because of small temperature dependences of* $^1J(^{15}N, ^1H)$ *and* $\delta(^{15}N)$*.*

1 INTRODUCTION

In previous papers we have studied the ^{1}H, ^{13}C and ^{15}N NMR spectra of azo dyes derived from phenolic and naphthoic coupling components.[1-11] The aim of this present work was to measure and assign ^{1}H, ^{13}C and ^{15}N

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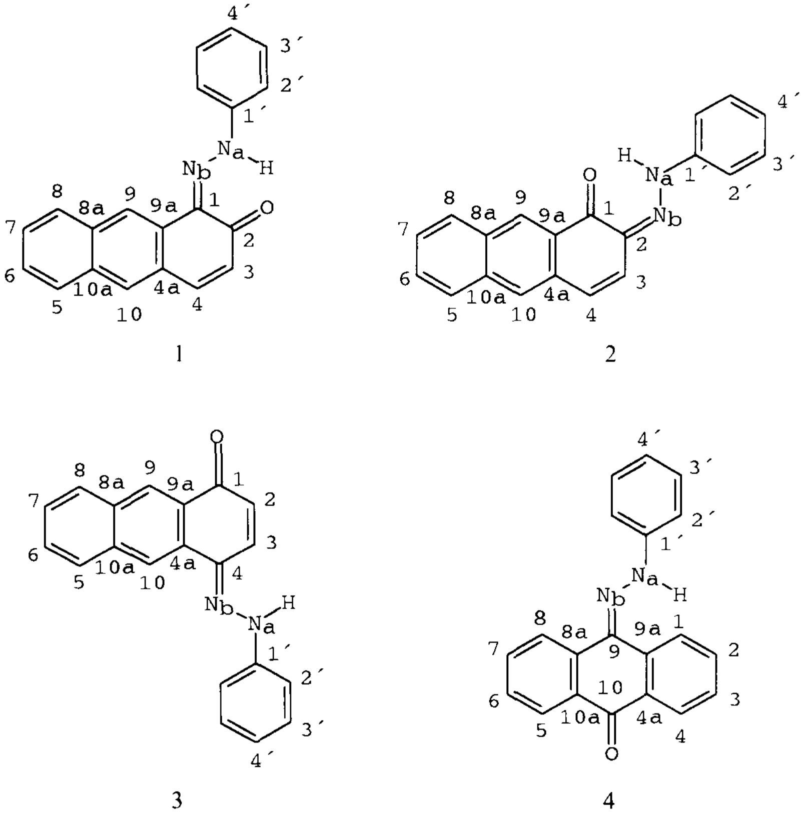
NMR spectra and to determine azo-hydrazone tautomeric equilibria in anthracene analogues.

2 EXPERIMENTAL

1,2-Anthraquinone-1-phenylhydrazone[12] (**1**), 1,2-anthraquinone-2-phenylhydrazone[13] (**2**), 1,4-anthraquinone-4-phenylhydrazone[12] (**3**) and 9,10-anthraquinone-9-phenylhydrazone[14] (**4**) (Scheme 1) were prepared as reported in the literature. ^{15}N (15% $^{15}N_a$, 95% $^{15}N_b$) isotopomers of compounds **1**, **3** and **4** were prepared analogously using ^{15}N-aniline and $Na^{15}NO_2$ (Isocommerz Berlin). ^{15}N (95% $^{15}N_a$, 95% $^{15}N_b$), the isotopomer of compound **2**, was prepared using $C_6H_5{}^{15}NH^{15}NH_2$ (Isocommerz Berlin) and 1,2-anthraquinone.

The ^{1}H and ^{13}C NMR spectra were recorded at 300 K on a Bruker AMX 360 spectrometer equipped with 5 mm broadband probe and 5 mm



Scheme 1. Formulae of compounds measured.

broadband inverse probe, and an 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 7 246·4 Hz and 22 727·3 Hz, respectively. Compounds **1**, **2** and **4** were dissolved in deuterochloroform. ^{1}H and ^{13}C chemical shifts were referred to internal TMS (δ = 0·00). Compound **3** was measured in hexadeuterodimethyl sulfoxide and chemical shifts were referred to the central signal of the solvent (δ = 2·55 (^{1}H) and 39·60 (^{13}C)).

Experimental conditions of 2D NMR measurements[15] have been reported for compound **2**. Other compounds were measured analogously, retaining digital resolution approximately.

H,H-COSY: d_1-90°-d_0-90°-Acq. Spectral width in both dimensions 796·2 Hz, d_1 = 2 s, 512 data points in F_2, 128 experiments in F_1, 8 scans. Apodization with a squared sine-bell function in both dimensions, processing with zero-filling giving a matrix of 256 × 256 points.

NOESY: d_1-90°-d_0-90°-d_m-90°-Acq. Spectral width in both dimensions 796·2 Hz, d_1 = 5 s, d_m = 1·0 s, 512 data points in F_2, 128 experiments in F_1, 32 scans. Apodization with a $\pi/2$-shifted squared sine-bell function in both dimensions, phase-sensitive processing with zero-filling giving a matrix of 256 × 256 points.

H,C-COSY: d_1-90°(^{1}H)-d_0-180°(^{13}C)-d_0-d_2-[90°(^{1}H)/90°(^{13}C)]-d_3-[decoupling/Acq]. Spectral width 7 352·9 Hz in F_2 and 796·2 Hz in F_1, d_1 = 2 s, d_2 = 3·3 ms, d_3 = 2·2 ms. 1 K data points in F_2, 128 experiments in F_1, 4 dummy scans, 32 scans. Apodization with a $\pi/2$-shifted squared sine-bell function in both dimensions, zero-filling giving a matrix of 1 K × 256 points.

H,C-COSYLR: d_1-90°(^{1}H)-d_0-180°(^{13}C)-d_0-d_2-[90°(^{1}H)/90°(^{13}C)]-d_3-[decoupling/Acq]. Spectral width 7 352·9 Hz in F_2 and 796·2 Hz in F_1, d_1 = 2 s, d_2 = 60 ms, d_3 = 40 ms. 1 K data points in F_2, 128 experiments in F_1, 4 dummy scans, 1024 scans. Apodization with a $\pi/2$-shifted squared sine-bell function in both dimensions, zero-filling giving a matrix of 1 K × 256 points.

HMQC (^{1}H detected heteronuclear correlation, with low-pass J-filter to suppress one-bond correlations)[16]: d_1-90°(^{1}H)-d_2-90°(^{13}C)-d_3-90°(^{13}C)-d_0-180°(^{1}H)-d_0-90°(^{13}C)-Acq. Spectral width 1 805·1 Hz in F_2 and 9 056·4 Hz in F_1, d_1 = 1·5 s, d_2 = 3·1 ms, d_3 = 60 ms. 1 K data points in F_2, 256 experiments in F_1, 4 dummy scans, 256 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.

One-dimensional ^{15}N NMR (10·095 MHz) spectra were recorded in 10 mm NMR tubes on a JEOL-FX 100 with 8 K data points and a spectral width of 5 000 Hz using gated and inverse-gated decoupling. ^{15}N chemical shifts were referred to external nitromethane ($\delta = 0{\cdot}0$) placed in a coaxial capillary.

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

3 RESULTS AND DISCUSSION

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

Protons and carbons (except for signals of NH and CO groups) of compounds **1–4** resonate in very narrow ranges of chemical shifts. Application of two-dimensional NMR techniques is thus necessary.[17,18] ^{1}H and ^{13}C chemical shifts were assigned after analysis of H,H-COSY, NOESY, H,C-COSY, H,C-COSYLR and HMQC spectra. The results are given in Tables 1–4.

H,H-COSY spectra revealed proton–proton connectivity patterns.

TABLE 1
^{1}H and ^{13}C Chemical Shifts and $^nJ(^{15}N_b, ^{13}C)$ Coupling Constants in Compound **1** in Deuterochloroform

H/C no.	$\delta(^1H)^a$	$\delta(^{13}C)$	$^nJ(^{15}N_b, ^{13}C)$	X^b
1	—	129·55	2·0	9
2	—	181·01		
3	6·55	127·47		
4	7·58	142·51		10
4a	—	127·10		9
5	7·76	128·25		10
6	7·38	125·76		
7	7·44	127·11		
8	7·86	128·39		9
8a	—	133·54		10
9	8·59	120·40	4·6	
9a	—	130·64	8·9	10
10	7·81	128·60		
10a	—	131·64		9
1'	—	142·51	6·0	
2'	7·52	116·52	2·5	
3'	7·39	129·51		
4'	7·15	125·24		

[a] δ(NH) = 15·91.

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

NOESY[19] spectra showed through-space proximity of appropriate protons. In compounds **1**, **2** and **3**, correlations of proton H-9 with H-8, and of H-10 with the proton in position 5 were found, as well as correlations of H-4 and H-10 in compounds **1** and **2**. A correlation of the NH proton with proton H-1 was observed in compound **4**.

On the basis of known $\delta(^1H)$, ^{13}C chemical shifts were assigned using H,C-COSY and H,C-COSYLR spectra. A much more sensitive ^1H detected heteronuclear correlation technique (HMQC; with low-pass J-filter to suppress one-bond correlations),[16] optimized for long-range couplings (*c.* 8 Hz), was used for the assignment of quaternary carbon signals in compounds **2** and **4**.

3.2 ^{15}N NMR spectra

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

Compounds **1** and **2** possess strong intramolecular hydrogen bonds. Small temperature dependences of $^1J(^{15}N, ^1H)$ coupling constants and

TABLE 2
^1H and ^{13}C Chemical Shifts in Compound **2** in Deuterochloroform

H/C no.	$\delta(^1H)^a$	$\delta(^{13}C)$	X^b
1	—	180·37	9
2	—	132·69	4
3	6·99	128·18	
4	6·99	122·22	10
4a	—	133·56	3, 9
5	7·85	127·87	7, 10
6	7·54	128·56	8
7	7·47	126·22	5
8	8·00	130·01	6, 9
8a	—	131·58	5, 10
9	8·91	129·44	8
9a	—	129·81	4, 10
10	7·86	126·06	4, 5
10a	—	135·88	8, 9
1'	—	142·48	3'
2'	7·50	116·36	4'
3'	7·39	129·81	
4'	7·15	125·18	2'

[a] $\delta(NH) = 15{\cdot}66$.

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

$\delta(^{15}N)$ were found in compounds **1** and **2** (Table 5), and these values were very close to those typical of model hydrazone compounds of this type[18] ($^1J(^{15}N, ^1H) = 96$ Hz; $\delta(^{15}N_a)$ *c.* −205, $\delta(^{15}N_a)$ *c.* −17). Calculated contents of hydrazone forms in compounds **1** and **2** are 94·6–98% using $^1J(^{15}N, ^1H)$ (eqn (1)), and very similar results were obtained using $\delta(^{15}N_a)$ (eqn (2)):

$$\% \text{ hydrazone form} = \frac{^1J(^{15}N_a, H)_{\text{exp.}}}{96} \times 100 \qquad (1)$$

$$\% \text{ hydrazone form} = \frac{\delta[^{15}N(\mathbf{5})] - \delta[^{15}N(\mathbf{x})]}{\delta[^{15}N(\mathbf{5})] - \delta[^{15}N(\mathbf{6})]} \times 100 \qquad (2)$$

where $\delta[^{15}N(\mathbf{x})]$ is an appropriate ^{15}N chemical shift in compounds **1** or **2**, $\delta[^{15}N(\mathbf{5})]$ is the ^{15}N chemical shift in 2-hydroxy-5-*tert*-butylazobenzene (**5**, model azo compound with an intramolecular hydrogen bond), and $\delta[^{15}N(\mathbf{6})]$ is the ^{15}N chemical shift in 3-methyl-1-phenylpyrazole-4,5-dione-4-phenylhydrazone (**6**, model azo compound with an intramolecular

TABLE 3
^1H and ^{13}C Chemical Shifts and $^nJ(^{15}N, ^{13}C)$ Coupling Constants in Compound **3** in Hexadeuterodimethyl Sulfoxide

H/C no.	$\delta(^1H)^a$	$\delta(^{13}C)$	X^b
1	—	184·30	3, 9
2	6·78	127·32	
3	8·35	128·10	
4	—	128·12[c]	2, 10
4a	—	131·94	3, 9
5	8·20	128·55	10
6	7·58	126·64	8
7	7·66	128·55	5
8	8·18	129·65	9
8a	—	131·51	5, 10
9	8·74	126·64	
9a	—	130·64[c]	2, 10
10	9·03	121·55	5
10a	—	134·68	8, 9
1'	—	144·00	3'
2'	7·69	114·62	4'
3'	7·48	129·55	
4'	7·15	122·43	

[a] δ(NH) = 11·55.
[b] *X* denotes numbers of protons for which correlations were found via long-range couplings.
[c] The assignment can be opposite.

TABLE 4
^1H and ^{13}C Chemical Shifts and $^nJ(^{15}N, ^{13}C)$ Coupling Constants in Compound **4** in Deuterochloroform

H/C no.	$\delta(^1H)^a$	$\delta(^{13}C)$	$^nJ(^{15}N_b, ^{15}C)$	X^b
1	8·22	125·25	1·0	2
2	7·30	132·78		1
3	7·48	129·13		4
4	8·34	128·82		3
4a	—	132·57	1·2	2, 4
5	8·16	126·41		7
6	7·43	127·66		8
7	7·62	132·98		
8	8·33	124·13	4·4	6
8a	—	138·71	9·9	6, 8
9	—	131·53	6·7	4, NH
9a	—	129·88	2·1	1, 3
10	—	183·46		1, 8
10a	—	130·04	3·1	5, 7
1'	—	144·18	6·2	3', NH
2'	7·32	114·31	2·4	4'
3'	7·32	129·38		
4'	6·98	122·16		

[a] δ(NH) = 9·18.

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

TABLE 5
Temperature Dependence of ^{15}N Chemical Shifts, $^1J(^{15}N, ^{15}N)$ and $^nJ(^{15}N, ^1H)$ Coupling Constants in Compounds **1**–**4**

Compound	*Temperature*	$\delta(^{15}N_a)$	$\delta(^{15}N_b)$	$^1J(^{15}N_a, ^1H)$	$^2J(^{15}N_b, N_a{}^1H)$	$^1J(^{15}N, ^{15}N)$
1[a]	240	−198·7	−20·9	93·8	1·9	11·3
	270	−196·7	−18·9	93·2	2·1	11·3
	300	−195·0	−17·4	92·5	2·0	11·3
	330	−193·5	−16·2	90·8	2·0	11·3
2[a]	240	−197·5	−11·0	94·1	2·0	11·4
	270	−196·1	−10·0	93·8	2·0	11·4
	300	−195·3	−9·3	93·5	2·0	11·4
	330	−194·3	−8·8	93·3	2·0	11·4
3[b]	300	−219·8[c]	−42·6[c]			
	350	−220·0[c]	−41·5[c]			
4[a]	300	−232·8	−51·4	89·8	2·2	11·6
	330	−233·1	−51·2	89·8	2·2	11·6

[a] CDCl$_3$.

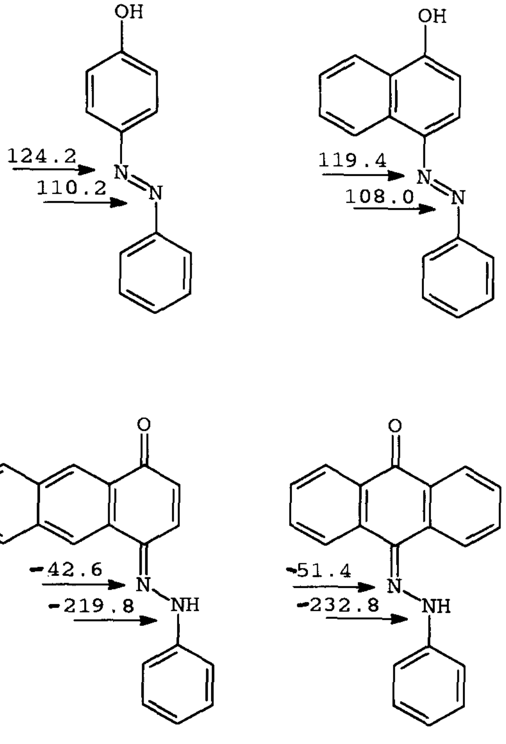
MSO-d$_6$.

adened signals.

hydrogen bond).[2] Chemical shifts of $^{15}N_b$ at 240 and 270 K in compound **1** are shifted even more upfield than those in the model compound 3-methyl-1-phenylpyrazole-4,5-dione-4-phenylhydrazone (**6**).[2,18] Exact calculation of the hydrazone content is difficult in the cases where the content is rather close to 100% (and, analogously, close to 0%) when model compounds are used, because substituent effects are comparable with the influence caused by very subtle changes of tautomeric equilibrium. Annelation of the phenyl ring resulted in *c.* 10–20% increase of the hydrazone contents in compounds **1** and **2** with respect to those in 1,2-naphthoquinone-1-phenylhydrazone and 1,2-naphthoquinone-2-phenylhydrazone[4] (as prevailing tautomeric forms) in deuterochloroform.

A much more dramatic shift in the azo–hydrazone equilibrium can be seen for compounds **3** and **4** (Scheme 2). While 4-hydroxy-azobenzene[3] and 1-hydroxy-4-phenylazonaphthalene[4] exist in DMSO-d_6 as true azo compounds, compounds **3** and **4** are almost completely in the phenylhydrazone forms.

Compounds **3** and **4** have no intramolecular hydrogen bonds, and ^{15}N



Scheme 2. ^{15}N Chemical shifts in 4-hydroxyazobenzene[3], 1-hydroxy-4-phenylazonaphthalene[4] and 1,4-anthraquinone-4-phenylhydrazone measured in DMSO-d_6, and in 9,10-anthraquinone-9-phenylhydrazone measured in $CDCl_3$ at 300 K.

chemical shifts must not therefore be compared with the data for compounds **5** and **6**, but e.g., with the values in benzaldehyde phenylhydrazone, in which $\delta(^{15}N)$ of the —NH— group is $-237{\cdot}0$ and $\delta(^{15}N)$ of —N= is $-54{\cdot}0$ in DMSO.[20]

The results are in agreement both with theoretical considerations and with practical results based on methods other than NMR, i.e. that the hydrazone tautomeric form becomes progressively more stable as the size of the ring system bearing the oxygen atom increases.[12,21–27]

The conclusion, based on our NMR results, is that anthraquinone phenylhydrazones exist in hydrazone forms to more than 95%, but that small amounts of azo forms are also very probably present.

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