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THE PREPARATION, SPECTRA AND TAUTOMERISM OF SOME 4(N-ARYLAMINO)-1,2-NAPHTHOQUINONES

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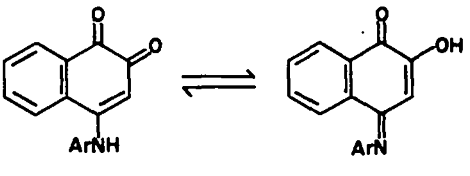
Abstract—Twelve 4(N-arylamino)-1,2-naphthoquinones (**1**) have been prepared by the direct addition of substituted anilines to 1,2-naphthoquinone, and their spectra have been studied. In the solid and in ethanol solution the 1,2-naphthoquinone tautomer (**1a**) predominates, but in trifluoroacetic acid the 2-hydroxy-1,4-naphthoquinone-4-aryliminium (**2a**) is the major species.

The spectra of a number of halogen substituted 1,2-naphthoquinones were studied by Oliver *et al.*[1] in 1968 and in the following year Harmon *et al.*[2] described the preparation and UV spectra of a number of 4-arylamino-1,2-naphthoquinones. The latter workers made a particular study of the effect acidity had on the UV spectra and concluded that in non-acidic media the 1,2-naphthoquinone tautomer (**1a**) predominated. In strongly acidic media however they concluded that the 1,4-naphthoquinone-4-iminium ion (**2a**) predominated.

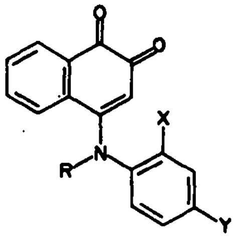


Ia **Ib**

The present work arose from our studies on the displacement of alkyl groups from alkyl-1,2-benzoquinones, which we extended to 4-methyl-1,2-naphthoquinone.[3] Previous workers prepared 4(N-arylamino)-1,2-naphthoquinones by treating 1,2-naphthoquinone-4-sulphonate with the appropriate amino compound.[2,4] In the present study following our earlier work all the amino-quinones have been prepared by the direct addition of the amines to 1,2-naphthoquinone.

Table 1 lists the UV spectra of the twelve 4(N-arylamino)-1,2-naphthoquinones synthesised. Two of these (for compounds **d** and **j**) have been previously reported by Harmon *et al.*[2] All the present spectra have a single peak in the 240–250 nm region which Harmon *et al.* attribute to the 1,2-naphthquinone tautomer (**1a**), in

Table 1. Ultra-violet/visible spectra of 4-aminonaphtho-1,2-quinones



SOLVENT: Methanol

Ref. letter	R	X	Y	λ_1	$\log \epsilon_1$	λ_2	$\log \epsilon_2$	λ_3	$\log \epsilon_3$	λ_4	$\log \epsilon_4$
a	H	Cl	Cl	239	4.30	284	4.17	335	3.77	447	3.56
b	H	CH_3	CH_3	240	4.33	277	4.14	325–345(sh)	3.70	455	3.64
c	H	H	CH_3	242	4.40	277	4.16	325–234(sh)	3.82	460 ± 10	3.72
d	H	H	H	243	4.48	282	4.27	325–350(sh)	3.86	459	3.89
e	H	H	Br	243	4.37	282	4.12	330	3.82	470	3.66
f	H	H	OCH_3	245	4.40	279	4.20	345	3.73	475	3.74
g	H	H	$NHCOCH_3$	249	4.50	275	4.22	345	3.79	476	3.76
h	H	H	NH_2	252	4.39	282	4.14	—	—	500	3.66
i	H	H	$N(CH_3)_2$	262	4.50	285	4.05	—	—	520	3.77
j	CH_3	H	H	244	4.31	272	4.06	322	3.81	456	3.83
k	C_2H_5	H	H	246	4.38	278	4.08	322	3.80	476	3.88
l	H	H	N = NPh	240	—	—	—	354	—	474	—
m	N-(n-hexyl)-4-Aminonaphtho-1,2-Quinone			238	4.27	275	4.23	300(sh) 325(sh)	4.00 3.64	445	3.68

Notes. 1. The minimum absorption in the range between λ_2 and λ_3 was little less than the absorption at λ_3. In the spectra of 'h' and 'i' no shoulder near 330 nm was visible. 2. 'l' was too insoluble to allow extinction coefficient determination. 3. (sh)–shoulder or inflexion.

contrast to 2 - methoxy - 4 - (N - arylimino) - 1,4 - naphthoquinone which has a doublet peak λ_h = 246,251 nm and which is fixed in a 1,4-naphthoquinonoid form.

Table 2 lists the IR spectra (Nujol mull). The important bands are in the region 3200–3300 cm^{-1} and in the CO region *ca.* 1690 cm^{-1} and *ca* 1600 cm^{-1}. The shorter wave length absorptions at 3200–3300 cm^{-1} are exactly in the region expected for the N–H band, and could therefore be considered as evidence for the predominence of tautomer (**1a**). However in tautomer **1b** the hydroxyl H atom would be expected to be H-bonded and this would shift the O–H absorption from the 3600 cm^{-1} region characteristic of a phenol to the 3100–3300 cm^{-1} region. Such H-bonding, which occurs in tropolone and *ortho*-hydroxyaryl ketones, also causes a very substantial lengthening of the wave length attributable to the CO stretching frequency (e.g. 1600 cm^{-1} for tropolone and

Table 2. Positions of absorption peaks in IR spectra of 4(N-arylamino)-1,2-naphthoquinones (ν_{max} in cm^{-1})

Quinone (see Table 1)	N–H/O–H	C=O	Others
a	3200(w, b)	1680(m, s)	1600(i, fb)
b	3200(w, b)	1685(m, s)	1610, 1580(m, s), 1520(i, fs)
c	3300(m, b)	1690(i, s)	1590–70(i, doublet), 1540 → 1490(mult.)
d	3300(m, s)	1690(m, s)	1590, 1580 (i, s)
e	3250(w, b)	1680(w, s)	1600, 1590–70(i, multiplet), 1515(i, fb)
f	3200(w, b)	1690(m, s)	1610, 1590(i, fs)
g	3300(w, b)	1690(m, s) 1670(m, s)	1610(i, s), 1560(i, s), 1540
h	3340(w, s) 3200(w, b)	16780(m, s)	1570(i, b), 1510, 1520
i	3290(w, b)	1680(m, s)	1605, 1580(i, fs)
j	3050(v, w)	1685(i, s)	1630(i, s), 1560(i, s), 1580(i, fb)
k	—	1690(i, s)	1620(i, fb), 1575(i, s), 1530(i, s)
l	3300(w, s) 3280–3120(b)	1690(m, s) 1650(i, s)	1605, 1590, 1580(i, s), 1520(i, multiplet)

Key. Where there are brackets after a given wavelength, the letters enclosed thereby indicate the intensity and width of the absorption.
i, intense; m, medium; w, weak; s, sharp; b, broad; f, fairly; v, very.
Note. Minor errors in calibration have not been corrected.

Table 3. PMR spectra of N-Aryl-4-aminonaphtho-1,2-quinones

Ref. letter	Solvent		Protons 5,8	Protons 6,7	Aryl ring protons		Alkyl protons on X and/or Y
b	TFA		br 1.6	br 2.0	s 2.68, s 2.76, tiny peak 2.86	s 3.48	s 7.56, s 7.69
b	DTFA		br 1.6	br 2.0	slightly more complex but very similar to above	Absent	as above but more complex
c	TFA		br 1.63(2)	br 2.04(2)	br 2.58(4)	br s 3.18(1)	br s 7.52(3)
d	TFA		q 1.56	q 1.96	m 2.28, m 2.52	s 3.19	
e	TFA		br m 1.63	br m 2.0	AA 'XX' pattern 2.20 and 2.62 (J = 8 Hz)	s 3.26	
f	TFA		br m 1.58(2)	br m 1.96(2)	AA 'XX' pattern 2.50 and 2.76(2:2) (J = 9 Hz)	s 3.10(1)	s 5.99(3)
g	TFA	s 0.87	m 1.56	m 2.0	AA 'XX' pattern 2.1 and 2.44 (J = 8 Hz)	s 3.16	s 7.54
i	TFA		br s 1.6		v.br.m. 2.0	br s/d 3.33	s 6.44
l	TFA		br m 1.6	br m 2.2	s 3.0	s 3.15	
			Proton 8		Protons 5, 6, 7 aryl ring protons	Proton 3	Protons on R
j	CDCl$_3$		br m 1.95(l)		v br m 2.8(8)	br s 3.72(1)	s 6.5(3)
k	CDCl$_3$		m 1.9(1)		m 2.75(8)	s 3.68(1)	1:3:3:1 q 6.0 (J = 7 Hz)(2) 1:2:1 t 8.68 (J = 7 Hz)(3)
					Protons 3,5,6,7, + aryl ring protons		
j	TFA		br m 1.6(1)		br m 2.3(9)	—	s 5.63(3)
k	TFA		m 1.7		m 2.45	—	q 5.4, q 6.2, t 8.4, t 8.68

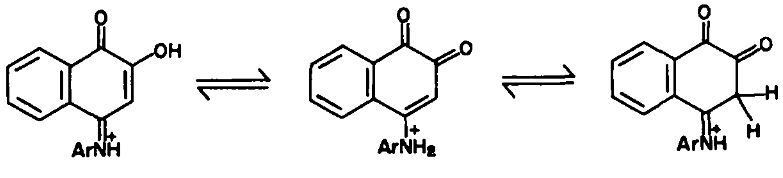
All positions are given in ppm using the τ system. Integrals, where available, are given in parentheses.
Key. br, broad; d, doublet; m, multiplet; s, singlet; q, quartet; t, triplet; v, very.

Table 4. 4-Aminonaphtho-1,2-quinones experimental data

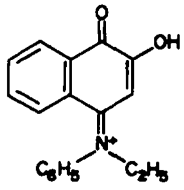
Ref. letter	Formula	Analysis Calc./required %C	%H	%N	Found %C	%H	%N	Molecular weight Calc/required		Found	Melting point Lit.	Found	Yield
a	$C_{16}H_9NO_2Cl_2$	60.38	2.83	4.40	60.22	2.97	4.43				—	245–50 (decomp)	29%
b	$C_{18}H_{15}NO_2$	77.98	5.42	5.05	77.34 78.42	5.39 5.15	4.82 5.15	277.110272		277.110367	—	254 decomp; 264 residue.	76%
c	$C_{17}H_{13}NO_2$	77.57	4.94	5.32	76.65	4.87	5.01	263.094623		263.095255	—	259	31%
d	$C_{16}H_{11}NO_2$	77.11	4.42	5.67	77.09	4.57	5.53	249.078973		249.078727	258–61	246–50 decomp, 254–56 residue.	69%
e	$C_{16}H_{10}NO_2Br$	58.54	3.05	4.27	58.15	2.93	4.24	—		—		275–7 decomp.	—
f	$C_{17}H_{13}NO_3$	73.12	4.66	5.02	73.20	4.93	5.08	279.089537		279.089747	252–53 232	238–40	56%
g	$C_{18}H_{14}N_2O_3$	70.59	4.58	9.15	69.49	4.82	8.58	306.100435		306.100849	—	311–13	45%
h	$C_{16}H_{12}N_2O_2$	72.73	4.55	10.61	72.09	4.67	10.88	264.089872		264.090055	147	>360	68%
i	$C_{18}H_{16}N_2O_2$	—	—	—	—	—	—	292.121170		292.121155	—	239–41	64%
j	$C_{17}H_{13}NO_2$	—	—	—	—	—	—	265.110277	†	265.110893	173	160 shrinkage 165–69°C	
k	$C_{18}H_{15}NO_2$	77.98	5.42	5.05	77.58	5.64	4.87	—	†	—	—	172–4	
l	$C_{22}H_{15}N_3O_2$	74.79	4.25	11.90	74.96	4.53	12.08	—		—	—	205 decomp. 238–43 residue	*ca.* 100%
m	$C_{16}H_{19}NO_2$	74.71	7.39	5.45	74.13	7.68	5.23	—		—	236–7	218–9	—

†Both "j" and "k" showed an absorption at *ca.* 1685 cm^{-1}, and condensed with 1,2-diaminobenzene to give benzo[a]phenazines, but in their mass spectra the main peak of highest mass was at M+2, i.e. "j" Calc. for $C_{17}H_{15}NO_2$: 265.110277. Found: 265.110893 M.P. 165–69 (lit. 173) Yield 52%; "k" Req. for $C_{18}H_{17}NO_2$: 279.125921 Found: 279.126496.

The compounds were recrystallized from methanol except as follows: a, g, k: 2-methoxyethanol; e: 2-ethoxyethanol; g: N,N-dimethylformamide. N-(n-hexyl)-4-aminonaphtho-1,2-quinone; purified by chromatography.



2a **2b** **2c**



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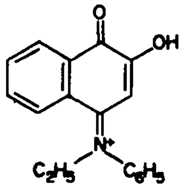

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1635 cm^{-1} for hydroxylaryl ketones). On the basis of the assignments made by Oliver *et al.* the observed absorptions 1670–1690 cm^{-1} may possibly be attributed to the CO in the 2-position and clearly there is no evidence of H-bonding in the spectra in Table 2 (cf. 1,2-naphthoquinone ν_{max} 1685 cm^{-1}, 1650 vs, 1648 (sh), 1586 cm^{-1}). The evidence from the IR spectra provides therefore strong evidence for the predominance of tautomer (**1a**) in the solid phase.

Table 3 lists the ^{1}H NMR spectra of the arylaminonaphthoquinones. These were run in trifluoroacetic acid because they were too insoluble to run in ordinary solvents. There is no doubt that the compounds were protonated. There are three possible tautomers with the positive charge on the nitrogen. Protons bonded to nitrogen or oxygen exchange too rapidly with the solvent and are not therefore observed.

In the NMR spectrum of 4-chloro-1,2-naphthoquinone, the H atoms at the 6 and 7 positions, (τ 1.98–2.24 complex) could not be separated but the H atoms at the 5 and 8-positions were clearly distinguished ([5]-2.26–3.36 quartet; [8]-1.74–1.87 quartet). In 1,4-naphthoquinone the 5 and 8-positions are identical (τ 1.93) and the 6 and 7-positions are also identical (τ 2.23). The fact that in trifluoroacetic acid the 4(N-arylamino)1,2-naphthoquinone-iminium ions' absorptions at τ 1.6 correspond to two protons, provides very strong evidence that **2a** is the predominant tautomeric form for these ions. This provides confirmation of the proposals of Harmon *et al.*, namely that in acidic media the 1,4-naphthoquinone-imine structure (**2a**) predominates. However evidence for the transient existence of tautomer (**2c**) comes from the loss of the signal attributable to the H atom at the 3-position when the spectra are run in deuterio-trifluoroacetic acid.

The 4(N-alkyl-N-arylamino)-1,2-naphthoquinones (**j** and **k**) are soluble in chloroform. If there is conjugation between the amino-group and the CO, the N-alkyl or N-phenyl group must lie close to the H atom at position 5, so that protons 5 and 8 are no longer in similar environments. In trifluoroacetic acid the signal attributed to the proton at the 3-position develops a high field tail due to exchange with the solvent. The N-ethyl compound (**k**) shows two sets of signals due to the two isomeric ions 3 and 4.

The mass spectra of both the 4(N-alkyl-N-arylamino)-1,2-naphthoquinones both gave a principle peak of highest mass at M + 2 of that expected. Oliver and coworkers noticed a similar effect in some of their halogeno-1,2-naphthoquinones.

EXPERIMENTAL

The spectra were run on: IR a "Perkin Elmer 257", UV on a "Unicam SP800", NMR on a "Varian HA100" and mass spectra on an "A.E.I. MS902".

General procedure for the preparation of 4(N-arylamino)-1,2-naphthoquinones. 1,2-Naphthoquinone was treated with excess amine in MeOH soln. The primary aromatic amines gave products of low solubility which could be separated by filtration and recrystallised. The aminoquinones derived from the secondary aromatic amines and hexylamine were obtained by evaporation of the solvent followed by column chromatography.

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