

Proton magnetic resonance and polarographic studies of some aminated naphthoquinones

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Variable temperature n.m.r. and polarographic measurements have been performed on a series of cyclic secondary aminonaphthoquinones. The results indicate that ring strain is not the only factor which would explain the order of effective electron donation by the various amines to the quinone nucleus.

S. Afr. J. Chem., 1978, 31, 37-39

Veranderlike temperatuur k.m.r.- en polarografiese metings is op 'n reeks sikliese sekondêre geamineerde naftokinone uitgevoer. Die resultate toon aan dat ringspanning nie die enigste faktor is wat die orde van effektiewe elektrondonasie van verskillende amiene na die kinoonkern kan verklaar nie.

S.-Afr. Tydskr. Chem., 1978, 31, 37-39

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Received 13 September 1977

Earlier workers¹⁻⁴ have shown that 2,5-bisaminated benzoquinones exist as resonance hybrids of the two extreme canonical forms (1) and (2), there being a significant contribution by the quadrupolar form (2) towards these hybrids. A convenient method has been developed for observing the existence of the quadrupolar forms (2) by n.m.r. spectroscopy. The chemical shifts of the quinonoid hydrogen signals undergo an upfield shift (*ca* τ 4,60 relative to 1,4-benzoquinone, τ 3,24) which implies a strong shielding effect. This diamagnetic anisotropy has been ascribed to a high degree of quinone-nitrogen double bond character in the immediate vicinity of the quinone hydrogens.²

Variable temperature n.m.r. studies⁵ have been carried out on a series of cyclic 2,5-bisaminated-1,4-benzoquinones (Table 1) in order to determine the coalescence temperatures, T_c .⁶ This observation made possible the assessment of the relative importance of the resonance hybrids (2) as a function of the series of cyclic amines. The order of importance of effective electron donation of the different amino-substituents in the bisaminated benzoquinone series was found to be: azetidino > pyrrolidino > hexamethyleneimino⁷ > piperidino > aziridino. The mono- and dimethylamino-analogues are included in both series (Tables 1 and 2) for comparative purposes. The chemical shifts of the quinonoid protons in the series decreases in the same order (Table 1).

Measurement of the half-wave potentials⁸ for the bisaminated benzoquinones gave an order (Table 1) which was in qualitative agreement with that obtained from T_c measurements and quinonoid proton chemical shifts, with the exception that the relative order of amines (1, NR_2 = azetidino) and (1, NR_2 = pyrrolidino) was reversed.

It was expected that if the series was extended to include 2-aminated naphthoquinones, a similar order of effective electron donation within the series of cyclic secondary amines would be observed. Thus the effects of these amino-substituents on the 1,4-naphthoquinone nucleus (3) i.e. the relative importance of dipolar contributors (4), have been examined in terms of the same three criteria that have previously been employed,^{5,8} viz polarographic half-wave potential measurements, $E_{1/2}^0$, approximate coalescence temperatures, T_c , and shielding of the quinonoid proton by

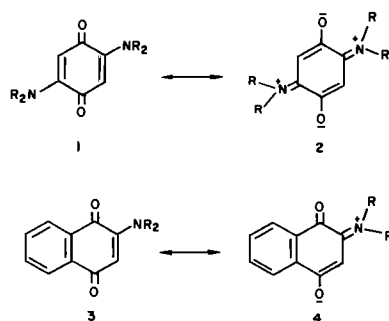
Table 1 Variable temperature n.m.r. studies on 2,5-bisaminated benzoquinones (1)

NR ₂	T _c (°C)	Quinone H (τ)	ΔE _{1/2} ^{0 a}
Azetidino	65	5,08	-0,463
Pyrrolidino	25	4,75	-0,481
Hexamethyleneimino	-10	4,62	-0,442
Piperidino	< -60	4,50	-0,299
Aziridino	< -60	4,05	-0,199
Monomethylamino	-	4,72	-0,510
Dimethylamino	< -45	4,67	-0,346

^aΔE_{1/2}⁰ = ΔE_{1/2}⁰(NR₂) - E_{1/2}⁰(H) i.e. the difference in half-wave potential for bisaminated benzoquinones and benzoquinone measured at pH = 7.

the adjacent nitrogen substituents.

Comparison of the n.m.r. results for the 2-amino-1,4-naphthoquinone series (Table 2) indicates that the relative effects of the various secondary amino-substituents are the same as in the aminated benzoquinone series. The chemical shifts of the signals for the quinonoid protons closely parallel the findings obtained from T_c measurements, and may perhaps be used as a more reliable guide in deducing the relative order of effective electron donation by the various cyclic secondary amino-substituents since they give a direct indication of the relative importance of the hybrid (4). Thus by n.m.r. criteria the apparent order of effectiveness of electron donation for the different cyclic amines in the aminated naphthoquinone series is: azetidino > pyrrolidino > hexamethyleneimino > piperidino > aziridino, whereas by the polarographic half-wave potential criterion the trend is similar except that the order of the first two amines is reversed. This order is the same as that found in the benzoquinone series.



Comparison of the n.m.r. data for the corresponding members of the aminated benzoquinone and naphthoquinone series shows that the latter series exhibits both a lower degree of shielding of the quinonoid hydrogens and lower coalescence temperatures than the former. This leads us to conclude that for a particular secondary amino-substituent the dipolar contributor (4) was of less significance to an aminated naphthoquinone than was the analogous quadrupolar contributor (2) to a bisaminated benzoquinone. It is also noteworthy that polarographically, the effect of a particular amino substituent is remarkably similar in the two series. This is exemplified by comparison of the ΔE_{1/2}⁰ values for corresponding members of the two series, where it is evident that the values found for the aminated naphthoquinones were approximately half the values for the bisaminated benzoquinones.

Table 2 Variable temperature n.m.r. studies on aminated naphthoquinones (3)

NR ₂	T _c (°C)	Quinone H (τ)	ΔE _{1/2} ^{0 a}
Azetidino	30	4,58	-0,221
Pyrrolidino	20	4,30	-0,264
Hexamethyleneimino	-30	4,14	-0,214
Piperidino	< -60	3,94	-0,149
Aziridino	< -60	3,67	-0,089
Monomethylamino	-	4,32	-0,274
Dimethylamino	-60	4,19	-0,194

^aΔE_{1/2}⁰ = ΔE_{1/2}⁰(NR₂) - E_{1/2}⁰(H) i.e. the difference in half-wave potential for bisaminated benzoquinones and benzoquinone measured at pH = 7.

In attempts to rationalize the differing effects of the series of cyclic secondary amino-substituents, the influence of ring strain was regarded as a contributing factor. However, the similar effects operating on the quinone nucleus through the azetidino- and pyrrolidino-groups are apparent, even though they would not have been predicted from the considerable differences existing between cyclobutyl and cyclopentyl ring systems.⁹ Furthermore, appreciable differences were observed between the influences of the pyrrolidino- and hexamethyleneimino-moieties, which would also not have been expected by comparison of the data quoted for cyclopentyl and cycloheptyl ring system.⁹ A comparison with the pyrrolidino-group showed that, in both cases, there was a greater contribution to the hybrids (2) and (4) by the azetidino-substituent and a lesser contribution by the hexamethyleneimino-substituent than would possibly have been predicted on the grounds of ring strain alone. It is suggested that the hydrogens alpha to the nitrogen atom may sterically interact with the neighbouring quinonoid oxygen and hydrogen, thereby providing a supplementary destabilizing factor in the hybrids (2) and (4) as the ring size of the cyclic amine is increased.

On the other hand, in the quinones (3, NR₂ = pyrrolidino) and (3, NR₂ = piperidino) the greater contribution of the dipolar form (4) in the former relative to the latter case, may be explained in terms of the quinone-nitrogen double bond of dipolar form (4) being *exo* to a five and a six membered ring respectively. Brown has shown that double bonds *exo* to five membered rings are both less reactive and more stable, relative to the saturated analogues, than the corresponding double bonds *exo* to six membered rings.¹⁰

The markedly anomalous nature of the aziridino-analogue in both series, (1, NR₂ = aziridino) and (3, NR₂ = aziridino), where T_c is very low and the shielding of the quinonoid hydrogen is smallest, could in part be due to the nitrogen lone pair orbital having more s character in the aziridino-ring, compared to the other members; this would inhibit delocalization of these electrons over the quinonoid ring system.

Experimental

All melting points, which are uncorrected, were determined on a Fisher-Johns apparatus. Infrared spectra were measured as nujol mulls on a Perkin Elmer 237 spectrometer and ultraviolet spectra were measured in 95% ethanol on a Beckman D.B. spectrophotometer. ¹H-n.m.r. spectra were measured in deuteriochloroform on a Varian XL-100 spectrometer using deuterium as the lock signal.

2,5-Bis(2-hexamethyleneimino)-1,4-benzoquinone

A solution of hexamethyleneimine (23 ml) in ethanol (25 ml) was added to a mixture of hydroquinone (5 g) in water (30 ml) and the mixture was aerated for 8 h. The red solution was filtered and the filter cake was washed with chloroform to leave a residue of unreacted hydroquinone (1 g). The filtrate was evaporated to dryness and treated with aqueous H_2SO_4 (6 ml acid in 180 ml water). Chloroform extraction gave the *bis(2-hexamethyleneimino)-benzoquinone* (40%) as bright red needles, m.p. 159° (from methanol), ν_{max} 1614 (C=O) and 1551 cm^{-1} (C=C), λ_{max} 523, 379 and 228 nm (log ϵ 2,66, 4,35 and 4,38), τ 4,62 (2H, s, 3-H and 6-H), 6,29 (8H, t, $J_{2,3}$ 5,2 Hz, 2'- and 7'-H), 8,33 (16H, br, 3'-, 4'-, 5'- and 6'-H) (Found: C, 71,8; H, 8,7; N, 9,2. Calc. for $C_{18}H_{26}N_2O_2$: C, 71,5; H, 8,6; N, 9,3%).

2-Aziridino-1,4-naphthoquinone

The product was prepared as described,¹¹ to give yellow-brown needles, m.p. 170° - 178° (decomp.), [lit.,¹¹ m.p. 175 - 182° (decomp.)].

2-Azetidino-1,4-naphthoquinone

Azetidine¹² (4,0 ml) was added to a mixture of copper (II) acetate (2,4 g) and methanol (60 ml), and the resulting mixture was aerated for 5 min. A solution of 1,4-naphthoquinone (2,0 g) in methanol (80 ml) was added and aeration was continued for 3 h. The solution was evaporated to dryness and treated with 3M- H_2SO_4 (150 ml). Filtration of the aqueous mixture gave the *azetidino-quinone* (41%) as red needles, m.p. 174° (from methanol), ν_{max} 1680 (C=O) and 1613 cm^{-1} (C=C), λ_{max} 437, 277 and 239 nm (log ϵ 3,68, 4,40 and 4,18), τ 2,00 (2H, m, 5- and 8-H), 2,40 (2H, m, 6- and 7-H), 4,58 (1H, s, 3-H), 5,70 (4H, br. d, 2'- and 4'-H), 7,54 (2H, m, 3'-H) (Found: C, 73,1; H, 5,3; N, 6,5. Calc. for $C_{13}H_{11}NO_2$: C, 73,2; H, 5,2; N, 6,6%).

2-Pyrrolidino-1,4-naphthoquinone

Freshly distilled pyrrolidine (1,7 ml) in ethanol (5 ml) was added to a solution of 1,4-naphthoquinone (1,0 g) in ethanol (30 ml) and the resulting red solution was stirred for 20 h in the dark. The reaction mixture was chilled and the resultant red solid was filtered to give the *pyrrolidino-quinone* (63%) as long red plates, m.p. 159° (from aqueous methanol), ν_{max} 1672 (C=O) and 1616 cm^{-1} (C=C), λ_{max} 474, 277 and 238 nm (log ϵ 3,74, 4,40 and 4,22), τ 2,00 (2H, m, 5- and 8-H), 2,40 (2H, m, 6- and 7-H), 4,30 (1H, s, 3-H), 6,36 (4H, br. s, 2'- and 5'-H), 8,02 (4H, m, 3'- and 4'-H) (Found: C, 73,7; H, 5,6; N, 6,0. Calc. for $C_{14}H_{13}NO_2$: C, 74,0; H, 5,7; N, 6,2%).

2-Piperidino-1,4-naphthoquinone

The product was prepared as described,¹³ to give deep purple needles m.p. 95° (lit.,¹³ m.p. 94 - 96°).

2-Hexamethyleneimino-1,4-naphthoquinone

Hexamethyleneimine (8 ml) was added to a solution of 1,4-benzoquinone (0,9 g) in ethanol (30 ml) and the resulting red solution was stirred for 15 h and then evaporated to give a deep red oil. Ether (50 ml) was added followed by 3M- H_2SO_4 (60 ml). The aqueous layer was rapidly extracted with ether. The dried extracts were evaporated to a red oil which was extracted with boiling cyclohexane to give the *hexamethyleneimino-quinone* (73%) as red needles, m.p. 98° (from aqueous methanol), ν_{max} 1669 (C=O) and 1615 cm^{-1} (C=C), λ_{max} 469, 278 and 241 nm (log ϵ 3,72, 4,35 and 4,19), τ 2,02 (2H, m, 5- and 8-H), 2,42 (2H, m, 6- and 7-H), 4,14 (1H, s, 3-H), 6,36 (4H, t, $J_{2,3}$ 4 Hz, 2'- and 7'-H), 8,14 and 8,38 (8H, each br. s, 3'-, 4'-, 5'- and 6'-H) (Found: C, 75,2; H, 6,9; N, 5,4. Calc. for $C_{16}H_{17}NO_2$: C, 75,4; H, 6,7; N, 5,5%).

2-Monomethylamino-1,4-naphthoquinone

The compound was prepared as described,¹⁴ to give long red needles, m.p. 240° (lit.,¹⁴ m.p. 232°).

2-Dimethylamino-1,4-naphthoquinone

The compound was prepared as described,¹⁵ to give orange needles, m.p. $121,6^\circ$ (lit.,¹⁵ m.p. $121,5^\circ$).

Acknowledgement

The authors thank the Council for Scientific and Industrial Research for financial support.

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