Adducts formed by some 1,4-Benzoquinones in Liquid Ammonia

John A. Chudek, Roy Foster,* and Francis J. Reid

Chemistry Department, University of Dundee, Dundee DD1 4HN, U.K.

N.m.r. spectra of fresh solutions of 1,4-benzoquinone and various, mainly chloro-substituted, derivatives in liquid ammonia are consistent with nucleophilic addition at one or both carbonyl carbon atoms and not at C(2), or equivalent positions, expected in Michael-type addition.

Most nucleophilic addition reactions involving amines with 1,4-benzoquinones are of the Michael type resulting from initial attack at C(2) or an equivalent position.[1] We have now established that for a series of 1,4-benzoquinones in liquid ammonia the first adduct that is formed is by attack on a carbonyl carbon.

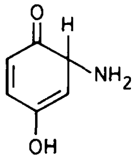
The structures of a number of adducts formed by attack of NH_2^- on nitroaromatics[2] and cyanoaromatics[3] in liquid ammonia solution have recently been determined using ^1H n.m.r. spectroscopy. Using the same technique, we have observed an AB spectrum for the ring protons of 1,4-benzoquinone in liquid ammonia at 240 K (Table 1). This is not consistent with the Michael adduct (**1**). Although an AB spectrum would be expected for the di-adduct (**2**), the line positions and large coupling constant (*J* 10 Hz) make this unlikely. We propose the alternative structure (**3a**). Confirmation of this structure is provided by the ^{13}C n.m.r. spectrum: four lines are observed, two in the olefin region, one in the carbonyl region, and one at high field, the last corresponding to C(1) in (**3a**). The ^{13}C n.m.r. assignments (Table 2) are based on the unambiguous assignments for cyclohex-2-en-1-one.[4] In particular, the higher field methine line in the 1,4-benzoquinone adduct can be assigned to C(3) and C(5) in (**3a**). The ^1H n.m.r. assignments (Table 1) are consistent with those for cyclohex-2-en-1-one.[5] The structures have been written as the protonated forms rather than as the alkoxide ions on the basis of preliminary conductivity measurements (*e.g.*, *ca.* 3 Ω^{-1} cm^2 mol^{-1} for the molar conductivity of a 0.9 M solution of the 1,4-benzoquinone adduct).[6]

Table 1. ^1H N.m.r. spectra of (**3**) and (**4**) in liquid ammonia[a] at 220 K.

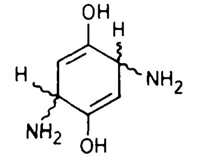
Compound	Chemical shifts[b]			
	R^1	R^2	R^3	R^4
(**3a**)	6.4 (d)	5.4 (d)	5.4 (d)	6.4 (d)
(**3b**)	—	5.8	5.5 (d)	6.4 (d)
(**3c**)	—	5.9	5.9	—
(**3d**)	—	—	5.6 (d)	6.5 (d)
(**3e**)	—	—	5.7 (d)	6.4 (d)
(**3f**)	—	6.0	—	6.8
(**3g**)	—	—	6.0	—
(**4a**)	—	—	5.1	5.1
(**4b**)	—	5.4	—	5.4
(**4c**)	—	—	5.4	—

[a] Measured at 60 MHz. [b] In p.p.m. from Me_4Si (TMS) using CH_2Cl_2 as internal reference; d = doublet, all *J* values 10 Hz.

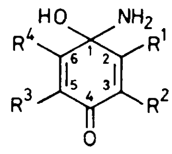
The ^{13}C n.m.r. spectrum of the adduct from chloro-1,4-benzoquinone has six lines which are assigned as in Table 2. The argument for it having structure (**3b**) rather than (3, $R^1 = R^3 = R^4 = H$, $R^2 = Cl$) is that, of the three methine lines in the ^{13}C n.m.r. spectrum, two are at higher field; therefore by analogy with the adduct from 1,4-benzoquinone, this adduct must have two methine carbons adjacent to the carbonyl.

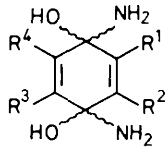


(**1**)



(**2**)





(**3**) **a**; $R^1 = R^2 = R^3 = R^4 = H$
b; $R^1 = Cl$, $R^2 = R^3 = R^4 = H$
c; $R^1 = R^4 = Cl$, $R^2 = R^3 = H$
d; $R^1 = R^2 = Cl$, $R^3 = R^4 = H$
e; $R^1 = R^2 = CN$, $R^3 = R^4 = H$
f; $R^1 = R^3 = Cl$, $R^2 = R^4 = H$
g; $R^1 = R^2 = R^4 = Cl$, $R^3 = H$

(**4**) **a**; $R^1 = R^2 = Cl$, $R^3 = R^4 = H$
b; $R^1 = R^3 = Cl$, $R^2 = R^4 = H$
c; $R^1 = R^2 = R^4 = Cl$, $R^3 = H$

Table 2. ^{13}C N.m.r. spectra of (**3a**—**c**) in liquid ammonia.[a]

Compound	δ/p.p.m.					
	C(1)	C(2)	C(3)	C(4)	C(5)	C(6)
(**3a**)	75.5	153.5	125.1	189.0	125.1	153.5
(**3b**)	76.6	160.5	124.0[b]	186.5	124.7[c]	152.9
(**3c**)	79.5	161.1	124.9	184.6	124.9	161.1

[a] Measured at 15.08 MHz, chemical shifts in p.p.m. from TMS. [b] May alternatively be assigned to C(5). [c] May alternatively be assigned to C(3).

The principle that nucleophilic attack occurs at the carbonyl adjacent to the maximum number of chlorinated carbon atoms is maintained in the di- and tri-chloro-1,4-benzoquinones (Tables 1 and 2). In particular the methine carbon resonance for the adduct from 2,6-dichloro-1,4-benzoquinone at δ 124.9 p.p.m. corresponds to (**3c**) rather than (**3**, $R^1 = R^4 = H$, $R^2 = R^3 = Cl$). 2,3-Di-, 2,5-di-, and tri-chloro-1,4-benzoquinones were not sufficiently soluble for ^{13}C n.m.r. spectra to be obtained. However, the structural assignments of their adducts have been made from their ^{1}H n.m.r. spectra [(**3d,f,g**), Table 1].

On cooling the liquid ammonia solutions to 220 K, new singlets are observed in the ^{1}H n.m.r. spectra of solutions of 2,3-di-, 2,5-di-, and tri-chloro-1,4-benzoquinone. These develop at the expense of the original lines. The effect is reversed by raising the temperature again. These new lines are assigned to the di-adducts (**4a**—**c**) (Table 1).

Initially, it is possible to recover the various solutes by addition of dichloromethane followed by the removal of ammonia by pumping. With time, irreversible reaction occurs. For unsubstituted 1,4-benzoquinone the initial spectra persist for *ca.* 12 h; the chlorinated quinones react faster.

All measurements were made on a Bruker WP60 spectrometer, part of the facilities of which were provided by S.E.R.C.

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6 We are grateful to one of the referees for comments on this point.