EPR and ENDOR spectroscopy studies on α-aminoanthraquinone radical cations in solution

Virpi Vatanen,* Jussi M. Eloranta and Mikko Vuolle

Department of Chemistry, University of Jyväskylä, PO Box 35, FIN-40351, Jyväskylä, Finland

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EPR and ENDOR spectra of the radical cations of 1,4-diamino-9,10-anthraquinone, 1,4-bis(methylamino)-9,10-anthraquinone, 1,4-bis(ethylamino)-9,10-anthraquinone, 1,4-bis(butylamino)-9,10-anthraquinone and 1,4-bis(hexylamino)-9,10-anthaquinone were measured in 1,1,1,3,3,3-hexafluoropropan-2-ol (HFP), with (bis(trifluoroacetoxy)iodo)benzene (PIFA) as oxidizing agent, in the temperature range 260–300 K. The isotropic hyperfine coupling constants (hcc) of the labile amino protons were assigned by deuterium exchange with deuterated trifluoroacetic acid (*d*-TFA) in HFP as solvent. The results are compared with the radical cations of 1,4-diamino-9,10-anthraquinone and 1,4-bis(methylamino)-9,10-anthraquinone produced in acetonitrile by electrolytic oxidation. A tentative assignment of the hcc constants by MO calculations was made for 1,4-diamino-9,10-anthraquinone. The results indicate that deuteration is restricted entirely to the amino protons and that the obtained radical cation of aminoanthraquinone occurs in the non-protonated form ($Q^{+\bullet}$).

Introduction

Despite the availability of several methods to produce quinone radical cations,[1] their chemical properties have not been as thoroughly studied as those of quinone radical anions.[2] A number of techniques have been developed for observing the EPR spectra of radical cations in solution.[3] Many of the studies on quinone radical cations have been made in strongly acidic conditions, often combined with UV radiation. The disadvantage of acidic systems is that some undesired acid-catalysed rearrangements may occur before oxidation. Quinone radical cations in acidic medium are assigned as protonated radical cations,[4] $QH_2^{\bullet +}$, whereas radical cations derived by electrolytic oxidation from quinones under neutral conditions are designated as non-protonated quinone radical cations,[5] $Q^{\bullet +}$. The oxidation potential of quinone radical cation is usually higher than the reduction potential of the corresponding radical anion.[6] Oxidation potentials for some 1-amino- and 1,4-diamino-substituted anthraquinones in acetonitrile have been found to be less than 1.5 V (see Table 1),[7] and for anthraquinone in HFP 2.25 V.[8]

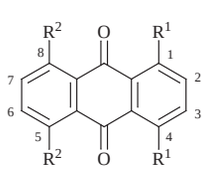
Recent studies on the relatively new anthracycline antitumour agents mitoxantrone and ametantrone (Fig. 1A) have focused on the biologically relevant properties of these agents, including their possible redox activity and oxidative enzymatic metabolism.[9] Diminished redox activity of mitoxantrone has been postulated to be responsible for the reduced cardiotoxicity relative to adriamycin.[10] Several anthraquinones and naphthoquinones have been used as simple model compounds of anthracycline drugs,[11] and in this event we chose α-amino-anthraquinone dyes as model compounds for studying the oxidation processes of these new anticancer agents.

The hcc constants for magnetic nuclei in DV1, DB14, SB59, SB35 and OBN were measured by EPR and ENDOR. Deuterated solvent was used in order to assign the amino proton hcc constants. The results are discussed with reference to data obtained earlier by electrolytic oxidation.[7b] MO calculations were performed for DV1 in order to assign the hcc constants at specific positions and to test the reliability of the applied density functional (DFT) method. In view of its partial similarity in structure to aminoanthraquinones, *p*-phenylenediamine (PPD, Fig. 1B) was used as model compound in discussion of the amino proton hcc's.

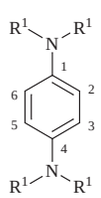
Table 1 Standard oxidation potentials of some amino-substituted 9,10-anthraquinone radical cations

Compound	E_{ox}/V
AQ	1.21,[a] 2.25[b]
1-Amino-AQ	1.33[a]
1-Amino-4-hydroxy-AQ	1.01[a]
1-Methylamino-AQ	1.16[a]
1,4-Diamino-AQ	0.72[c]
1,4-Bis(dimethylamino)-AQ	0.54[c]

[a] Ref. 7*a* in acetonitrile. [b] Ref. 8 in HFP. [c] Ref. 7*b* in acetonitrile.



A



B

Compound	R^1	R^2
Disperse Violet 1 (DV1)	NH_2	H
Disperse Blue 14 (DV14)	$NHCH_3$	H
Solvent Blue 59 (SB59)	$NHCH_2CH_3$	H
Solvent Blue 35 (SB35)	$NH(CH_2)_3CH_3$	H
Oil Blue N (OBN)	$NH(CH_2)_5CH_3$	H
Mitoxantrone (MX)	$NH(CH_2)_2NH(CH_2)_2OH$	OH
Ametrantrone (AM)	$NH(CH_2)_2NH(CH_2)_2OH$	H
p-Phenylenediamine (PPD)	H	H

Fig. 1 The structures of some α-amino-9,10-anthraquinones.

Experimental

Materials

9,10-Anthraquinone, 1,4-diamino-, 1,4-bis(methylamino)-, 1,4-bis(ethylamino)- and 1,4-bis(butylamino)-9,10-anthraquinone

Table 2 Hccs (a/mT) for studied radical cations obtained by ENDOR measurements (e) and by xemr simulation program (s)

Compound	a_N	a_{NH_2}	a_{NH_2}	a_{CH_3}	$a_{2,3}$	$a_{5,8}$	$a_{6,7}$	Lw/μT
DV1 (e)	0.4605	0.5730	0.5507	—	0.1047	n.d.	0.0074	
DV1 (s)	0.4599	0.5719	0.5508	—	0.1040		0.0069	13.1
DB14 (s)[a]	0.5380	0.6081	—	0.6744	0.1115	—	0.0107	23.4
SB59 (e)[b]	n.d.	n.d.	—	0.6404	0.1043	n.d.	0.0117	
SB59 (s)	0.5308	0.5989	—	0.6359	0.1056		0.0135	23.7
SB35 (e)	0.5365	0.5973	—	0.6346	0.1048	n.d.	0.0125	
SB35 (s)	0.5275	0.5978	—	0.6357	0.1002		0.0191	32.7
OBN (e)	0.5367	0.6004	—	0.6360	0.1097	n.d.	0.0083	
OBN (s)	0.5302	0.5991	—	0.6381	0.1019		0.0130	17.4

n.d. = not detected. [a] ENDOR not obtained. [b] Measured at 260 K.

Table 3 Hccs (a/mT) for the deuterated DV1 radical cation obtained by simulation program

Compound	am. of D	Ratio	a_N	a_{NH_2}	a_{NH_2}	a_{NH}	a_{ND_2}	a_{ND_2}	a_{ND}	$a_{2,3}$	$a_{6,7}$	LW/μT
DV1	0	7.6	0.4470	0.5484		—	—	—	—	0.0917	0.0103	14.9
	1	19.8	0.4433	0.5422	0.5249	0.5277	—	—	0.0805	0.0988	0.0097	16.0
	2	34.2	0.4373	0.5305	—	—	0.0828	—	—	0.1039	0.0096	16.4
	3	26.6	0.4409	—	—	0.5156	0.0916	—	0.0850	0.1031	0.0110	15.1
	4	11.8	0.4452	—	—	—	0.0921	0.0864	—	0.1043	0.0143	15.1

were purchased from Aldrich, and 1,4-bis(hexylamino)-9,10-anthraquinone was obtained from ACRO. The other chemicals were 1,1,1,3,3,3-hexafluoropropan-2-ol from Sigma, (bis-(trifluoroacetoxy)iodo)benzene from Aldrich and deuterated trifluoroacetic acid (99% of D) from Merck.

Equipment

EPR spectra were recorded on a Bruker ESP-300 spectrometer with a modulation frequency of 12.5 or 25 kHz. ENDOR spectra were recorded on a Bruker 200 D-SRC spectrometer as described earlier.[12] A temperature of 260–300 K was maintained by a liquid nitrogen cooling system.

Sample preparation

High-vacuum samples were prepared by a method described elsewhere.[12] After freezing the solvent in the cuvette a small amount of the parent anthraquinone was added, so that the final concentration of the radicals was in the range 0.1–0.5 mmol dm^{-3}. Finally a small quantity of the oxidizing agent was added to the cuvette in a glass capillary. All the samples were prepared in HFP, and deuterated samples in HFP with a small amount of *d*-TFA added.

Computational methods

EPR simulations. The root-mean-square (RMS) error between the experimental and first-order simulated EPR spectra was minimized by the Monte Carlo and simplex procedures provided in the xemr software package.[13,14] Given a suitable initial guess of the spectral parameters, this process yields estimates for the variables with good accuracy. The ENDOR derived hcc values were used as starting data. In the case of deuterated DV1, the simulations consisted of five spectra differing in degree of deuteration, which were summed before the RMS error was calculated. All the simulated spectra were computed using first order approximation and exhibited Lorentzian lineshape and a constant linewidth for all the lines.

MO calculations. The hccs were computed using Gaussian 94 on Sun Sparc Station 10 (SunOS 4), Intel Pentium Pro (Linux), and Digital AXP (OSF/1) systems.[15] Geometry optimizations were performed by the UB3LYP/6-31G* DFT method with no geometry constraints. The UB3LYP method consists of unrestricted Becke's three-parameter hybrid method for exchange and Vosko–Wilk–Nusair local and Lee–Yang–Parr non-local functionals for correlation.[16] The standard parameter values given by Becke were used. The hcc data were derived from the last point of the optimization runs by the UB3LYP/6-31G* method. The hcc constants were calculated by the Fermi contact term in the DFT calculations.[17] The initial molecular modelling and Gaussian Z-matrices were generated with SYBYL 6.1.[18] The dielectric solvent effects were included in the calculation by the self-consistent isodensity polarized continuum model (SCI-PCM).[19]

Results

EPR spectra

Resolved EPR spectra of DV1, DB14, SB59, SB35 and OBN were obtained in the HFP–PIFA system. All the radical cations measured exhibited surprisingly long lifetimes. Well-resolved spectra of the same radical cation could be detected even after two months. The spectra recorded from DV1 and DB14 were identical with electrolytically generated radical cations.[7b] EPR spectra for the radical cations of SB59 and OBN are presented in Fig. 2 along with the corresponding simulations. The parameters from the ENDOR experiments and xemr simulations are presented in Table 2.

d-TFA was added to the solution to deuterate the labile amino protons for DV1, DB14 and SB35. The simulation parameters for the radical cations of DV1 in deuterated solvent are shown in Table 3.

ENDOR spectra

The ENDOR spectra of SB35 at 260 and 300 K are presented in Fig. 3. The ENDOR spectra recorded from other studied radical cations with aminoalkyl substituents exhibited similar features to the spectrum of SB35.

The ENDOR measurements revealed temperature-dependent relaxation effects on the proton and nitrogen lines, as shown in Fig. 3a and b. The amino proton ENDOR lines disappeared when the temperature was lowered, and simultaneously the intensity of the smallest proton lines diminished considerably. Although the temperature scale in our measurements is too limited to reveal a clear temperature dependence, the effect of temperature is evident. ENDOR experiments on deuterated samples were successful only for DV1 and gave the same hcc values as the simulation.

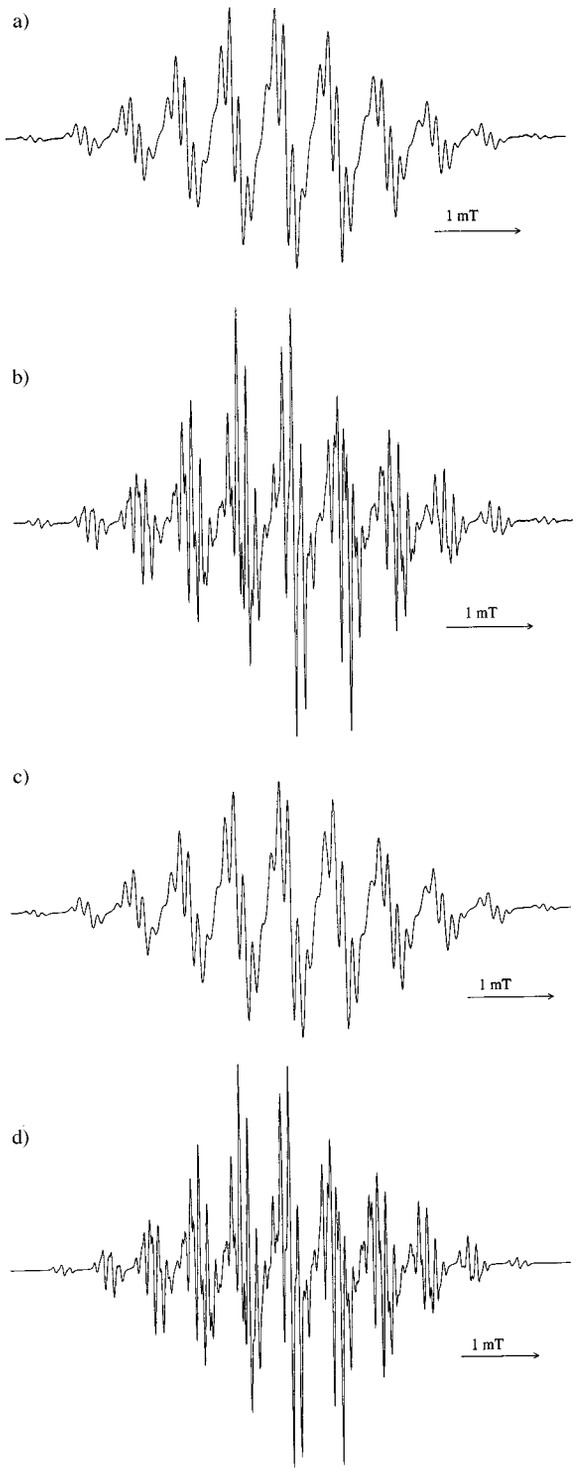


Fig. 2 EPR spectra of a) SB59 and b) OBN in HFP at room temperature. The simulated counterparts are shown in c) and d).

MO calculations

The results of the MO calculations for DV1 radical cation are presented in Table 4. Calculations were executed for doubly protonated hydroquinone ($QH_2^{+\bullet}$) and non-protonated quinone ($Q^{+\bullet}$) radical cations under vacuum conditions, and for the latter also with a dielectric solvent effect ($\varepsilon = 16.7$) included. The studied cation radicals had an electronic doublet state and a total charge of +1.

The geometry optimization showed that the amino protons lie in the AQ ring plane in both considered radical cations. The solvent slightly decreases all the hccs but does not change the radical geometry significantly. In the case of $Q^{+\bullet}$ the calculation by the SCI-PCM model showed improved agreement with the experimental.

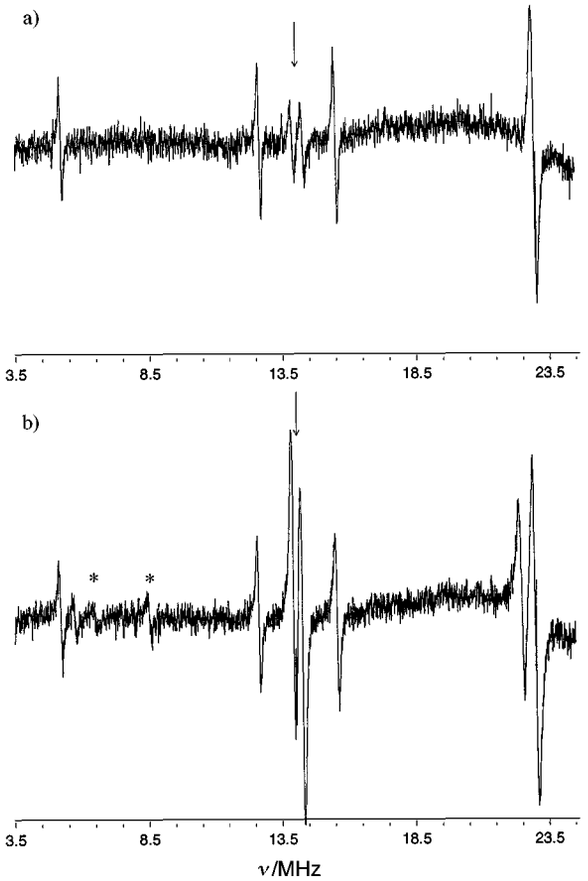


Fig. 3 The ENDOR spectra of SB35 in HFP a) at 260 K and b) 300 K; the proton ν_H is 14.0 MHz. The nitrogen ENDOR lines are marked with asterisks, the nitrogen ν_N is 1.02 MHz.

Discussion

The chemical system HFP and PIFA, had earlier proved a highly effective way to produce radical cations.[21] PIFA has been widely used as an oxidizing agent[22] in organic synthesis and has been found to be comparable to thallium(III) trifluoroacetate.[23] Consistent with the proposed oxidation capability of PIFA[21] no EPR spectrum could be recorded from the AQ radical cation in the HFP–PIFA system.

From the experimental parameters in Table 2, it can be seen that the hccs for SB59, SB35 and OBN are almost identical. Tentative assignment for the hccs follows that made in earlier studies.[7b] The two largest proton hccs were assigned to the amino group protons in 1,4-diaminoanthraquinone. Replacing the amino proton with an alkyl group did not appreciably alter the remaining proton hcc. Hccs of ~0.1 mT were assigned to the protons at C2 and C3 and ~0.01 mT to the protons at C6 and C7; no hcc was detected from the protons at C5 and C8. The linewidths of the spectra appear to be related to the length of the amino side chain. The increment in the linewidth may have at least two explanations: i) the rotation of the radical cation molecule becomes slower and more difficult as the size of the molecule increases and ii) the unresolved hccs from the alkyl side chain and from the unsubstituted quinone ring contribute to the linewidth. From the alkyl chain only protons attached to the α-carbon can be detected by EPR. The unpaired electron can be considered to be localized on the substituted and quinoid rings and thus the cations from 1,4-diaminoanthraquinones can be regarded as aromatic diamino radicals.

Analysis of the deuterated spectrum from DV1 gave evidence of five radical cations with various degrees of deuteration.

Table 4 Calculated hccs (a/mT) for DV1 and PPD radical cations

Cation	a_N	a_{NH_2}	a_{NH_2}	a_2	a_3	a_5	a_6	a_{OH}
Exp.	0.461	0.573	0.551	0.105	0.105	0.007	—	—
$QH_2^{+\bullet}$	0.342	−0.528	−0.512	−0.308	−0.308	−0.046	−0.047	−0.019
$Q^{+\bullet}$	0.481	−0.684	−0.718	−0.130	−0.130	−0.008	0.002	—
$Q^{+\bullet}$ [a]	0.454	−0.661	−0.693	−0.097	−0.097	−0.007	0.001	—
$PPD^{+\bullet}$ exp. [b]	0.529	0.588	0.588	0.213	0.213	0.213	0.213	—
$PPD^{+\bullet}$	0.488	−0.734	−0.734	−0.204	−0.204	−0.204	−0.204	—

[a] Dielectric solvent effect, $\varepsilon = 16.7$. [b] Ref. 20.

Ratios for the radicals were calculated from the spectral amplitudes of Table 3. The nitrogen hcc was lowest when the ratio was at a maximum, *i.e.* half of the protons had exchanged. Calculated value for the magnetogyric ratio ${}^{D}a_{ND}/{}^{H}a_{NH}$ was 0.163, which is higher than the theoretical value of 0.153. The high hcc ratio has also been observed in the case of hydroxy hccs.[24,25] The amino proton hcc decreases and the deuteron hcc increases in magnitude as the number of deuterons present grows.[7b] These observations indicate that protons/deuterons are in out-of-plane movement.

However, deuteration creates a problem regarding the radical in question. Since we now have an acid (*d*-TFA) in the system, the possibility arises of having a doubly-protonated quinone radical cation ($QD_2^{+\bullet}$), which would alter the electronic structure of the quinone. Protonation of aminoanthraquinone dyes can occur either at nitrogen or at oxygen where two resonance stabilized cations may form.[26] In this work, protonation by HFP can be excluded since the aminoanthraquinone dyes are weak bases in aqueous media, and several studies[27–29] indicate an intramolecular hydrogen bond between the hydrogen atom in the amino group and the carbonyl oxygen. The MO calculations suggest that in the case of the doubly-protonated quinone cation the hccs of the nitrogen and the protons in the substituted ring would be different, and this respect the current radical appears to be the non-protonated ($Q^{+\bullet}$) rather than the doubly-protonated ($QD_2^{+\bullet}$). Furthermore, the deuteration is solely confined to the amino protons.

The applied DFT method has been used with some success for quinone radicals.[30–33] Improvement of the hccs is apparent in the α-positions of the calculated quinone radicals when comparing calculations in solvent induced model *versus* vacuum conditions. In the case of $QH_2^{+\bullet}$, the calculated hccs of the nitrogen and the protons in the substituted ring differ considerably from the experimental values, but for $Q^{+\bullet}$ disagreement is evident only for the amino proton hccs. For $PPD^{+\bullet}$ the differences in the amino proton hccs between the experimental and calculated values are of the same order as for $Q^{+\bullet}$ in this work. This similarity in behaviour would imply that in both molecules the amino protons are in out-of-plane movement and form a hydrogen bond between the amino proton and the carbonyl oxygen. The hccs from the unsubstituted ring are quite small and within computational accuracy for both and thus the assignment of these hccs is tentative. The differences of the amino proton hccs in $Q^{+\bullet}$ model arises from the out-of-plane movement of the amino protons[34] as suggested by the a_H/a_D ratio and the MO calculations for $PPD^{+\bullet}$.

Conclusion

Despite the relatively high oxidation potential of the aminoanthraquinone radical cations the HFP–PIFA system proved to be a very effective way to generate these cations. The hyperfine structure of the 1,4-diamino-substituted anthraquinone radical cation remains nearly unchanged when the amino proton is replaced by an alkyl group containing more than two carbons. The amino protons are in out-of-plane movement, as was evident from the higher deuteron hccs than the magnetogyric ratio predicts and from the MO calculations. Hccs could be assigned and the structures of the radicals determined on the basis of MO calculations and deuteration of the samples. The results indicate that deuteration is restricted entirely to the amino protons and that the obtained radical cation of aminoanthraquinone occurs in the non-protonated form ($Q^{+\bullet}$).

Acknowledgements

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