EPR, ENDOR and TRIPLE Resonance and MO Studies on Ubiquinones (Q-n): Comparison of Radical Anions and Cations of Coenzymes Q-10 and Q-6 with the Model Compounds Q-2 and Q-0†

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Ubiquinone compounds are currently the focus of much biomedical research. Ubiquinones with different numbers (n) of isoprene subunits in the side chain (Fig. 1) are widely found in the tissues of plants and animals. There are many ways in the literature in which the names of ubiquinones are abbreviated, e.g., UQ-n, UQ 5xn, Coenzyme Qn, CoQn, and Q-n. We will use Q for a neutral ubiquinone molecule, because in this way various quinone species can be expressed in an elegant way as can be seen from Scheme 1. Quinones undergo an interesting set of electron and proton transfer reactions. Scheme 1 illustrates a stepwise reaction starting from the neutral quinone molecule and resulting in the neutral aromatic quinol molecule QH₂ having two hydroxy groups (not shown in Fig. 1).

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Scheme 1.

The reactions shown in Scheme 1 are accepted to take place regardless of the length of the side chain. Also, the chemistry of the quinones Q should be very similar, e.g., radical anions can be generated in alkaline media, radical cations in strongly acidic media, and neutral radicals in about neutral solutions. Therefore when we discuss the results obtained for ubiquinones with different numbers of isoprene units in the side chain, we distinguish the species by the use of the abbreviation Q-n. There is considerable confusion in the literature regarding the results for radical ions, partly due to difficulties in the nomenclature of the various species. We want to emphasize that in Scheme 1, one can find a neutral aromatic quinol and its radical cation on the right. In principle the radical cation of the neutral quinone could be
obtained by oxidizing the quinone on the left (not shown in Scheme 1), should it exist.

The function of coenzyme Q-10 in mammalian mitochondria has been closely studied, and it is thought to be responsible for the transport of hydrogen atoms through the bilayer membrane by a pendulum-type movement. On the other hand, ubiquinone Q-7 is found in photosynthetic reaction centers (bRC) of Rhodobacter sphaeroides. To the best of our knowledge only ubiquinones having 6–10 isoprene units are found in Nature as coenzymes, which suggests a certain minimum and maximum length for the side chain of biologically active coenzymes. In this study EPR and ENDOR experiments were carried out for a series of Q-0, Q-2, Q-6 and Q-10 radical ions to find out whether there is a limiting length of the side chain for which the EPR spectra or the dynamic behaviour of the β protons will totally change. PM3 molecular orbital calculations were carried out to obtain fully optimised structures of carefully chosen ubiquinone molecules, Q-3 and Q-7, for comparison.

Das et al. have reported that the EPR and ENDOR spectra of ubiquinone radical anions are temperature-dependent, and that this is due to the relative rotational motion of the aromatic ring and the long side chain around the single bond joining the side chain to the ring. They found that the β protons of the isoprenic side chain are non-equivalent at low temperatures, which causes an alternating linewidth effect. The effect was confirmed by Feher et al., who also found new and smaller hfs, which they suggested could be assigned to the methoxy-protons and the γ proton.

Kasa et al. have measured hfs for the methoxy groups in the 2,3-dimethoxy-5-methyl-1,4-benzoquinone (Q-0) radical anion by ENDOR. Their UMNDO calculations indicated that the methoxy groups are twisted out of the quinone plane by about 80°. Kiste et al. have measured and assigned the proton hfs of the methoxy groups and the hfs of the γ proton of the radical anion of ubiquinone in 2-propanol. Samoilova et al. have measured proton and 13C couplings for the radical anion, neutral radical and radical cation of Q-0 and for the radical anion of Q-10.

Results

Ubiquinone Q-10. The EPR spectrum of the Q-10 radical anion shows a remarkable temperature-dependent alternating linewidth effect due to rotation of the aromatic ring relative to the attached methylene protons of the side chain. Fig. 2 shows ENDOR spectra of the ubiquinone radical anion of the Q-10 sample recorded at different temperatures. In a mixture of chloroform–ethanol at about 250 K there was a clear coalescence point for the signals; two separate values of 3.48 MHz (0.124 mT) and 1.97 MHz (0.070 mT) were measured at temperatures below 250 K while only one value of 2.77 MHz (0.099 mT) was detected above it. The values of hfs in various solvents are shown in Table 1.

By detecting different EPR transitions in the EPR spectrum of a Q-10 sample prepared in an alkaline mixture of chloroform–ethanol, we recorded two ENDOR spectra, indicating the presence of two different radical species. The ENDOR spectrum shown in Fig. 3(b) was obtained from the peak labeled with an asterisk (*) and exhibited hfs of 3.96 MHz (0.141 mT), 1.71 MHz (0.061 mT) and 0.37 MHz (0.013 mT) at 298 K, while the other ENDOR spectrum [Fig. 3(c)] was obtained by saturating the EPR line labeled with a diamond (Δ) and had hfs of 5.71 MHz (0.204 mT) and 2.95 MHz (0.105 mT). The former ENDOR spectrum (*) originated from a secondary radical anion of Q-10 and the latter spectrum (Δ) was confirmed as belonging to the ubiquinone radical anion.
A secondary radical anion of Q-10 and TRIPLE induced EPR (TIE) spectra. The appearance of ENDOR resonance signals of the secondary radical shown in Fig. 3(b) is interesting because they are close to the signals detected for the non-equivalent β protons of the ubiquinone radical anion at low temperature. The secondary radical was detected only at temperatures above 250 K. The reversible appearance and disappearance of the secondary radical depending on temperature may give some hints as to its structure. The secondary radical appeared when alkali-metal ions (from NaOH) were present in the sample. This may indicate the formation of a loose ion-pair and it may explain the influence on the unpaired spin density in the quinone ring.

ENDOR-induced EPR (EIE) spectroscopy is an important technique for obtaining an EPR spectrum of a single species from a mixture of radicals. We measured TIE spectra from both species, because if one detects the enhanced signal of the peak pair in the general TRIPLE experiment by scanning the magnetic field, one can get a better S/N ratio for the induced EPR spectrum. The absorption spectrum obtained was differentiated into the normal first derivative EPR spectrum as shown in Fig. 4. In connection with the analysis shown in Fig. 3 note that the ENDOR lines corresponding to the hfs of 5.71 MHz (0.204 mT) and 2.95 MHz (0.105 mT) belong to the Q-10 radical anion. The TIE spectrum of Q-10 shown in Fig. 4(a) was obtained by pumping the lower field signal with the largest hyperfine appearing at (\(v_H = -5.71/2\)) MHz and detecting the respective line at (\(v_H = 5.71/2\)) MHz. On the other hand the TIE spectrum of the secondary radical shown in Fig. 4(b) was recorded by pumping the

Fig. 2. ENDOR spectra of the radical anion of ubiquinone Q-10 recorded in an alkaline mixture of chloroform-ethanol (3:1 v/v) at different temperatures. Lines marked with an asterisk belong to the secondary radical (conversion factor: 0.03565 mT MHz\(^{-1}\)).

Fig. 3. EPR and ENDOR spectra recorded for the primary and secondary radical anions of Q-10 in a mixture of [\(^1\)H\(_2\)]ethanol-\([\(^2\)H\(_2\)]chloroform-NaOD, D\(_2\)O (1:10:0.5) at room temperature: (a) overlapping EPR spectra, ENDOR spectra of (b) the secondary radical anion and (c) the Q-10 radical anion. Spectra were obtained by saturating the features marked by an asterisk (*) and by a diamond (◇) in the EPR spectrum (a), respectively.

Fig. 4. TIE spectra of primary and secondary radical anions of Q-10 plotted as first derivative spectra. The solid line is the experimental and the dashed line is the simulated spectrum. The noise level of the recorded TIE spectra is estimated by the bars on the left-hand side.

ENDOR feature at (\(v_H = -3.96/2\)) MHz and detecting the feature at (\(v_H + 3.96/2\)) MHz.

According to a special TRIPLE resonance experiment, the two largest hyperfines of the secondary radical showed a proton content ratio of 3:2, which would make the spectrum consistent with a methyl group and a methylene...
Table 1. Hfsc of ubiquinone radical anions determined by ENDOR (in MHz*).

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| **Coenzyme Q-0** |     | MeOH             | 0.14 | 6.79 |     |

*Conversion factor into mT is 0.03565 mT MHz⁻¹. The accuracy of ENDOR measurements was ±0.02 MHz. *The hfsc for the methoxy and γ proton(s) are reversed here. **Calculated with INDO (QCPE, program No. 141). **The IUPAC numbering is different for Q-0 and Q-10; see Fig. 1.

No exchangeable protons were detected in experiments in which deuterated solvents were used. The simulation of the EPR spectrum shown in Fig. 4(b) was in excellent agreement with ENDOR-determined hfsc. On the basis of this analysis it looks as if, in the structure of the secondary radical, there are 3 H with an hfsc of 3.84 MHz (0.137 mT), and 2 H with an hfsc of 2.01 MHz (0.072 mT). There are also smaller hfscs, one for one (γ) proton of 0.48 MHz (0.017 mT), and two very small ones for two groups of three (methoxy) protons of 0.09 MHz (0.003 mT) and 0.05 MHz (0.002 mT). This analysis does not demand a very dramatic change in the geometry of the ubiquinone molecule and it supports the earlier model of a secondary radical as a loose ion-pair comprising an alkali metal and radical anions of the quinone. Hfsc of secondary radical anions of ubiquinones in various solvents are shown in Table 2.

It has been suggested⁴ that chromenols and chromanols may result from the action of a base or acid in solutions of ubiquinones. The hfsc determined in this study in alkaline conditions are different from those tabulated for chromamonoxylys.¹⁰ This does not contradict our earlier hypothesis. On the other hand our MO results suggest that one possible structure for the secondary radical is a quinone structure, in which the folding of the side chain over the quinoid oxygen causes a new distribution of spin density. This is supported by the fact that in the case of the Q-0 we could not find a secondary radical of this type.

**Ubiquinone Q-6.** As can be seen in Table 1, the hfsc of the radical anion of coenzyme Q-6, prepared in a mixture of ethanol–chloroform, were closely similar to those obtained for the coenzyme Q-10. Moreover, the temperature (250 K) at which the hfsc of the β protons became non-equivalent was the same. The same secondary radical anion found with Q-10 was also observed from the Q-6 sample.

**Decylubiquinone (Q-2).** The structure of decylubiquinone, labeled Q-2 in this study, is shown in Fig. 1(b).
ethanol or methanol solutions, both β protons of decyl-
ubiquinone have the same hfs, depending only slightly
on temperature, as shown in Table 1. The relative signs
of the hfs were determined by general TRIPLE reson-
ance spectroscopy. By assuming the positive sign for the
hfs of the methyl group, recorded spectra suggested
positive signs for the hfs of the methoxy groups, in
accordance with Kasa et al.5 The important finding in
the experiments of decylubiquinone was that the hfs of
the β protons remained equivalent even at temperatures
as low as 200 K, indicating that the side chain does not
behave in the same way as in the quinones Q-6 and
Q-10. The β protons had the same hfs in all the solvent
systems studied. A clear triplet could be detected in the
outermost line pair in the EPR spectrum, showing the
hfs of the γ protons, supporting the assignment.

Radical cations of Q-10 and Q-6 in comparison with Q-0.
The radical cation of Q-10 was generated in various
solvents. The ENDOR spectrum was recorded in
HTFMS acid at room temperature (298 K) and four
hfs of 8.05 MHz (0.287 mT), 6.61 MHz (0.236 mT),
1.27 MHz (0.045 mT) and 0.24 MHz (0.009 mT), could
be detected as shown in Fig. 5(a). Simulation of the EPR
spectrum [Fig. 5(a)] was carried out using hfs with the
assignment shown in Table 3, because otherwise the
spectral width of 63.2 MHz (2.25 mT) could not be
obtained. Three methyl protons and two hydroxy protons
having hfs of 6.61 MHz (0.236 mT) and 8.05 MHz
(0.287 mT), were not enough, and two additional hfs
of 6.61 MHz (0.236 mT), and 1.27 MHz (0.045 mT),
corresponding to three (β + γ) and six protons (OCH3),
respectively, had to be added for a successful simulation.
The hfs of 8.05 MHz (0.287 mT), was assigned to
hydroxy protons by using DTFMS acid and deuterated
fuming sulfuric acid in the substitution of OH by OD;
the disappearance of the respective ENDOR signals is
shown in Fig. 5(b). This accidental equivalency of hfs
does not sound reliable, and it is possible that the
generated species is not the aromatic ubiquinol radical
cation of Q-10. A quite similar set of hfs was used for
the simulation shown in Fig. 5(b), except that a deuter-
um hfs of 1.24 MHz (0.044 mT), obtained from the
ENDOR spectrum, replaced the respective hfs of the
OH protons.

The 1H and 13C hfs of the radical cation of Q-0 have
previously been determined at room temperature.7,8 We
also measured a large value, 13.13 MHz (0.468 mT), for
methyl protons. The radical cation of Q-0 did not have
an average hfs for methyl protons (position 5) and for
the single ring-proton (position 6), as was found for the
radical anion of Q-0 in liquid ammonia.5

MO results for ubiquinones (Q-α). Fully optimised theo-
retical structures for the ubiquinone molecules Q-3 and
Q-7 were obtained by performing semiempirical PM3
molecular orbital calculations by means of the
GAUSSIAN 9411 program package for both the neutral
molecules Q and QH2 and the radical anions, neutral
radicals and radical cations shown in Scheme 1 (and in
Fig. 1). Ubiquinones Q-3 and Q-7 were selected for the
following reasons. According to our EPR results
obtained at temperatures under 250 K for the radical
anions of Q-6 and Q-10, the hfs of the β protons were
unequal, whereas the hfs of the β protons were the same
at any temperature for the radical anion of Q-2. PM3
results will provide a solution to the question, what kind
of conformational change forces these β protons to be
in unsymmetrical positions? Calculations for Q-10 would
need a lot more computer time than for Q-6. Q-7 was
chosen instead of Q-6 because Chang et al.5,12 reported
that after adding the co-ordinates of Q-7 to the structural
data of photosynthetic reaction center from Rhodobacter
sphaeroides R-26 they were able to refine the protein and
pigment atoms together. Because the electron density for
the isoprenoid tails of Q4 and Q8 allowed the positioning
of the first four isoprene units of the quinone tail,2 Q-3
was chosen to represent the flexibility of shorter quinones.
PM3 results for fully or partially optimised molecules
are shown in Table 4. Partial optimisation was carried
out for a planar conformation, where only the torsion
angles were constrained to be 180° forcing the side chain
to be planar, i.e., all other parameters were allowed to
relax. Optimised geometries of Q-3 and Q-7 are shown
in Figs. 6 and 7. The side view of the neutral ubiquinone


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Table 2. Hfsc of secondary radical anions of ubiquinones Q-2, Q-6 and Q-10 determined by ENDOR in alkaline solvents (in MHz*).

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<td>Coenzyme Q-6</td>
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<td>Decylubiquinone Q-2</td>
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Hfsc obtained from the simulated EPR spectra differed less than ±0.03 MHz from the ENDOR-determined values. *Conversion factor into mT is 0.03565 mT MHz⁻¹. Numbering was assigned on the assumption that the atomic structure of ubiquinone has not been changed.

Q-3 molecule shown in Fig. 6(b) reveal that when the side chain is planar the quinone ring is in a boat conformation. On the other hand, in all anion and cation radicals the quinone rings are strictly planar. One methoxy group in position 5 is planar, and the other is in an out-of-plane conformation in the cation radical of Q-3, as shown in Fig. 6(g). In our previous study of the alkoxylolation reaction of the Q-0 anion radical, we pointed out that there are many possible conformations very close in energy and with methoxy groups in either planar or out-of-plane conformations. In out-of-plane conformations there is no possibility of hyperconjugation, and only very small hfsc from the methyl protons of the methoxy group could be measured by ENDOR.³ On the other hand, the hfsc of methoxy groups in the cation radicals were easily detectable. The electronic structure of the carbon atoms in the quinone ring in the cation radicals is aromatic, and a redistribution of the charge density has taken place. Therefore one can expect hyperconjugation effects to induce unpaired spin density in the planar methoxy group(s). Solvent molecules are probably loosely hydrogen-bonded to the radicals, causing deviations from the out-of-plane conformation.

Furthermore, both OH hydrogens are in planar cis conformations and are hydrogen-bonded to methoxy oxygen. Unequal hfsc were indeed detected for the methoxy protons and these are listed in Table 3. Molecules having either a twisted (in Q-3) or the folded conformation (in Q-7) of the isoprenyl side chain always had the minimum energy. Folding is so complete in the Q-7 series, that the tip of the side-chain comes into contact with the quinone ring. We emphasise that it was not possible to get the fully optimised structures by means of the PM3 Hamiltonian in the GAUSSIAN 94¹¹ program for all Q-7 molecules; as is indicated by footnote e in Table 4. The calculated energies started to oscillate and no self consistency was obtained, when, e.g., the fully optimised structure of the neutral quinol Q-7 was used as a starting geometry to get the optimised structure for the cation radical. Therefore a damping factor of 0.1 eV (shifts the virtual energy levels up 0.1 eV) was defined for PM3 calculations carried out for the cation radical by MOPAC 7.00¹³ and a self-consistent field was achieved. A single-point calculation was then carried out by GAUSSIAN 94. Because the gradient test was not completely passed, there being no way to reduce the gradient in these cases, the structures obtained are the best ones possible.

Energies of the neutral radicals of Q-7 (also for Q-3) are almost the same indicating that both oxygen atoms in the quinone radical anions are equally susceptible to proton attack. Taking this into account, suggestions¹⁴ that two neutral radicals would disproportionate in the reaction center, generating a neutral quinone and an aromatic quinol is consistent with the data. The tabulated <S^2> values are reasonably small for all the radicals except the neutral ones. The semiempirical UHF level of theory is not good enough for the neutral radicals. The energies of the radical cations of the aromatic quinols Q-3 and Q-7 differ from the energies of the other molecules shown in Table 4. The energy of the folded Q-7 radical cation is so high that it might not be involved in the energy transfer processes taking place in the reaction centers. However, the folded Q-7 radical cation is surprisingly stable compared with the corresponding Q-3 radical cation.

Discussion
X-Ray results³⁻¹² have shown that the side chains of ubiquinones are flexible, but how flexible are they really? How much can they move inside the reaction center, and what conformation can they take on? The PM3 results obtained in this study (gas-phase and 0 K) indicate that the side chains can fold so completely that the ends are over the ring part. The calculated Fermi contact interactions (PM3, UHF) show the presence of small hfsc of the two closest methyl groups and the vinylic proton on
Table 3. Hfsc$^a$ of radical cations generated from Q-n (in MHz) at 298 K.

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<td>H$_2$SO$_4$</td>
<td>7.94</td>
<td>1.28</td>
<td>6.59</td>
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<td>D$_2$SO$_4$</td>
<td>1.24$^a$</td>
<td>1.29</td>
<td>6.62</td>
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<tr>
<td>Coenzyme Q-6</td>
<td>HTFMS</td>
<td>7.93</td>
<td>1.26</td>
<td>6.51</td>
<td>6.51</td>
<td>6.51</td>
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<tr>
<td>Q-6 (Saccharomyces)</td>
<td></td>
<td>1, 4</td>
<td>2, 3</td>
<td>5</td>
<td>5</td>
<td>6$^e$</td>
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<td>Coenzyme Q-0</td>
<td>HTFMS</td>
<td>8.22, 7.53</td>
<td>2.25, 0.90</td>
<td>13.12</td>
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<td>DTFMS$^d$</td>
<td>1.46$^a$, 0.98$^d$</td>
<td>2.25, 0.90</td>
<td>13.12</td>
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<td>D$_2$SO$_4$</td>
<td>9.67, 7.76</td>
<td>1.90, 1.18</td>
<td>13.65</td>
<td>1.90</td>
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<tr>
<td>Samoilova et al.$^7$</td>
<td>HTFMS</td>
<td>8.19, 7.32</td>
<td>2.10, 0.95</td>
<td>13.02</td>
<td>2.10</td>
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$^a$Hfsc obtained by EPR iterations and ENDOR experiments differed by less than ±0.1 MHz. Conversion factor into mT is 0.03565 mT MHz$^{-1}$. $^b$Numbering was assigned on the assumption that the cation radical of Q-n was formed. $^c$Trifluoromethanesulfonic acid is abbreviated to HTFMS and the deuterated acid to DTFMS. $^d$Deuterium coupling. $^e$The IUPAC numberings is different for Q-0 and for Q-n; see Fig. 1.

the tip of the side chain. For example, for the radical anion of Q-7 we obtained hfs of −0.043 MHz (0.002 mT) and −0.037 MHz (0.001 mT) for the methyl protons, but −0.443 MHz (0.016 mT) for the single vinyl proton. Is this a possible new route for electron transfer processes?

In bRC, light-induced electron transfer takes place along the A-branch to the quinones Q$_A$ and Q$_B$ where both Q$_A$ and Q$_B$ are Q-10 ubiquinones. According to Okamura et al.,$^{15}$ Q$_A$ can accept only one electron but cannot receive any protons H$^+$, while Q$_B$ can be doubly reduced and protonated to form a neutral aromatic quinol molecule as shown in Scheme 1. The protein environment therefore has a strong effect on the electron structure of the quinones, and probably Nature has modified their geometry to optimise the efficiency of the electron and proton transfer processes as discussed by Okamura and Feher$^{16}$ and Shinkarev and Wraight.$^{17}$ Isaacson et al.$^{18}$ determined the magnitude and orientation of the electronic $g$-tensor of the radical anion of Q$_A$ in single crystals of zinc-substituted Rhodobacter sphaeroides R-26 by EPR spectroscopy. The orientation of the radical anion as determined by the $g$-tensor axes deviated by only a few degrees from the orientation of the neutral Q$_A$ molecule obtained from an average of four different X-ray structures. They do not consider the deviation to be significant. According to our MO calculations the neutral ubiquinone molecules Q did differ structurally substantially from the corresponding radical anion, because the boat conformation changed to a planar one. However, no big conformational changes took place in the side chains of the quinones. To the best of our knowledge there are no fully optimised theoretical structures for ubiquinones of this size. In any case, ab initio calculations are needed. The side chain of bioactive ubiquinones appears to have only limited freedom to move in the protein network, as if the tail is wagging the dog; i.e., it is the quinone ring that moves the most. Since the side chains of ubiquinones are situated on the cytoplasmic side of the reaction center, with the side

![Fig. 6.](image1)

![Fig. 7.](image2)
chain parallel to the membrane and the quinone plane at the centre of the protein, the occasional immobility of the quinone plane of the radical would be of considerable importance for the electron transfer.

**Experimental**

*Materials.* Super CoQ10 or Q-10 (Livsenergi, 30 mg/capsule) was obtained from Vitamex AB, Sweden; BioQinon or Q-10 (30 mg/capsule) from Pharma Nord, Denmark; synthetic coenzyme Q-10, dehydroquiunone (98%) and coenzyme Q-6, or 2,3-dimethoxy-5-methyl-6-[all trans]farnesylfarnesyl-1,4-benzoquinone, separated from the yeast *Saccharomyces*, were from Sigma. KOH (*pro analysi*), methanol, [1H]chloroform, and NH₃ (99.99%) were obtained from Merck. Ethanol (99.9%, AaS) was from Alko Oy, Finland, chloroform from Riedel-de-Haén (freshly distilled), and solid sodium metal from Baker. CH₃CH₂OD and NaOD (40% in D₂O, 99.5%) were Merck products. Fuming sulfuric acid was a Riedel-de-Haén product and [1H]H₂SO₄ was from Merck. Trifluoromethanesulfonic acid (HTFMS) and [1H]TFMS (DTFMS) were Fluka products and were obtained in sealed ampoules.

*Equipment and MO calculations.* Spectra were recorded on a Bruker ER 200 D-SRC spectrometer equipped with a Varian E-12 magnet and a Bruker ER 033 M FF lock. EPR spectra were simulated either with a Bruker program or iteratively with an EPRFT program developed by Kirsch.²⁹ SYBYL 6.0 was run on a Sun SPARC 10 workstation. Semiempirical PM3 molecular orbital calculations were carried out by means of GAUSSIAN 94³¹ and MOPAC 7.0³² program packages, run on Digital Alpha (OSF/1) and Silicon Graphics Power Onyx computers.

*Sample preparation.* Anion radicals were prepared under high-vacuum conditions in alkaline ethanol or in liquid ammonia, with solid sodium as the reducing agent. Ammonia was distilled into a sample tube under an atmosphere of nitrogen and degassed with freeze–pump–thaw cycles under conditions of high vacuum. The CoQ10 sample was prepared in chloroform and ethanol (3:1 v/v) and by adding a tiny fragment of dry KOH pellet. The BioQinon sample was prepared in a mixture of CDCl₃–CH₃CH₂OD–NaOD (1:10:0.5 v/v). Radical cations of ubiquinones Q-n were prepared by reaction with sodium dithionite (Na₂S₂O₅) in trifluoromethanesulfonic acid and in a mixture of fuming sulfuric acid–sulfuric acid (in various ratios) or in the respective deuterated acids.

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