Conformational Analysis of Quinone Anion Radicals in Photosystem II and Photosynthetic Bacteria

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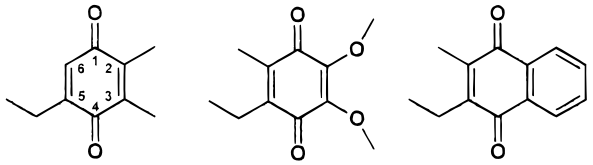
Using density functional theory (DFT) techniques, we have investigated possible conformers of the radical anions of plastoquinone (psQ), ubiquinone (ubQ), and menaquinone (mnQ), which are formed in the reaction centers of photosynthetic bacteria, blue-green bacteria, and green plants. Replacing the hydrocarbon tail connected to the quinone ring by an ethyl group, we have computed the rotational potential energy surfaces for psQ^- and ubQ^-. Our results show that in the absence of environmental effects both systems have global minima for near-perpendicular orientations of the γ-carbon relative to the quinone ring. For psQ^-, however, a low-lying local minimum is also observed for an in-plane arrangement with Cγ pointing away from the O4 oxygen. These differences in head-to-tail rotational energy surfaces may explain the experimentally observed differences in β-proton hyperfine couplings of psQ^- vs ubQ^- and mnQ^-, and their corresponding model compounds. By replacing the C6 methyl group in ubQ and mnQ by hydrogen, or the C6 hydrogen in psQ by methyl, we show that the crucial factor determining the rotational arrangements of the quinones in biological systems (planar psQ in green plants; perpendicular ubQ and mnQ in bacteria) is the presence or absence of this methyl group. The computed barrier height to rotation in ubQ^-, ca. 6 kcal/mol, and the β-proton hyperfine coupling constants for the planar vs perpendicular arrengements are in excellent accord with experimental data. Finally, we show that the methoxy group at the C2 position in ubiquinone displays a conformational preference as a result of the electron addition process, which may effect the hydrogen bonding pattern and hence promote the electron-transfer processes.

Introduction

The importance of quinones (Q) as electron mediators in photosynthesis and respiration is well-recognized.[1] In photosynthetic centers of green plants (photosystem II, PSII) and photosynthetic bacteria, a quinone pair Q_A and Q_B plays an active role in the process of building up the proton gradient across the thylakoid membrane. In key steps of the process, an electron is transferred after light absorption by the reaction center chlorophyll chromophores to Q_A, which in turn transfers the electron to the second quinone Q_B. Graige et al.[2] have recently shown that, in the reaction centers of *Rhodobacter sphaeroides*, Q_B^- will consecutively take up a proton from the stroma, receive a second electron via Q_A and then add a second proton. This is followed by migration of the neutral Q_BH_2 through the membrane, and subsequent electron donation to the cytochrome $\mathbf{b_6f}$ complex and proton release to the lumen. In previous theoretical work, we could confirm this proposed reaction sequence by comparing electron and proton affinities of Q, Q^-, QH, and QH^-.[3]

The ring substitution patterns in quinones that are utilized by green plants differ from those employed by photosynthetic bacteria, and several studies have appeared in which plastoquinones (psQ) of green plants, or models thereof, have been introduced into bacterial reaction centers, and vice versa.[4−10] In Scheme 1 we show the basic quinoid structure of plastoquinone (green plants), and ubiquinone (ubQ) and menaquinone (mnQ) of bacterial reaction centers. As shown already some 35 years ago by Krogmann et al.[4] and by Trebst et al.,[5] the C6 methyl group must be absent for the quinone to function in PSII. Klimov and co-workers showed that vitamin K1 (6-methyl-5-phytyl-1,4-naphthoquinone) does not bind correctly to the PSII reaction center.[6] Okamura et al. managed to force a psQ model into the reaction center of *Rb. sphaeroides* using a concentration 5−20 times higher than that required for the corresponding ubQ models,[7] whereas for the reverse replacement (ubQ model into PSII) a 20 times higher concentration was required for a 50% restored activity.[8] This implies that psQ fits in slightly easier in bacterial reaction centers than ubQ does in PSII, although there is still a very strong specificity at both reactions centers. Recent work by Tang et al.[9] and Astashkin et al.[10] suggests that the two types of centers host different protein conformations to accommodate different quinone head rotations, and Zheng and Dismukes have demonstrated that the C6 methyl group causes a rotation to a perpendicular head-to-tail orientation,

SCHEME 1



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whereas in the quinone systems with a C6 hydrogen the preferred conformation is planar.[11] This is supported by the solution conformations of different type I and type II quinone anion radicals (with and without the C6 methyl group, respectively).[12] On the basis of EPR line width effects, the barrier to rotation has been determined to be 5−7 kcal/mol for vitamin K1 and UQ-10 anion radicals in solution,[12] whereas for PQ-9 an energy difference of only ca. 1.4 kcal/mol is estimated between the planar and the perpendicular conformation.[11]

The conformational analysis above is based on the hyperfine coupling constants of the two β-protons of the hydrocarbon tail. Since the radical anions of quinones have ring-localized singly occupied molecular orbitals (SOMO) of π symmetry, the induced hyperfine couplings of these protons will vary markedly depending on rotational angle to the ring plane. For a perpendicular head-to-tail arrangement, the isotropic components of the radical anion β-protons (located on the same side of the ring plane) are generally 2.0−3.5 MHz, whereas for the planar conformers (the two protons located symmetrically on each side of the ring) they are considerably larger; 7−8 MHz. This is directly related to the different oritentaion of the β-protons relative to the ring-centered SOMO of π-symmetry. The torsional angles relative to the ring plane are 30° and 150° for the perpendicular arrangement and ±60° for the planar conformations.

Of previous theoretical studies of properties of quinones, we in particular mention the recent accurate hybrid Hartree−Fock density functional theory (HF-DFT) work by O'Malley et al.[13−16] and Spanget-Larsen,[17] exploring the effects of different solvents, either as polarizable continuum models or via direct formation of hydrogen bonds to the quinoid oxygens, on the hyperfine properties of benzoquinone anions and related model compounds. Nonelli has investigated the orientation of the methoxy groups in ubiquinone models,[18] and Wheeler and coworkers have undertaken very detailed studies of structures and properties of plasto-,[19] ubi-,[20] and menaquinone models,[21] employing tools similar those utilized in the present work. In essentially all previous work, however, the hydrocarbon tail has been replaced by hydrogen or methyl, thereby neglecting to address the important issue of the head-to-tail orientation of different types of quinones.

We have in the present study explored the rotational energy surfaces for plastoquinone and ubiquinone radical anion models, and also investigated the effects of CH_3/H substitution at the C6 position on the equilibrium structures and electron affinities for plastoquinone, ubiquinone, and menaquinone models. For each system we have computed the hyperfine couplings of the β-protons and compare these with available experimental data.

Methods

All calculations were performed by using the hybrid HF-DFT functional B3LYP,[22] as implemented in the Gaussian 94 program package.[23] Rotational energy curves for the radical anions were computed with the 6-31G(d,p) basis[24] by freezing the Cγ−Cβ−C5−C6 dihedral angle in steps of 10° and performing full geometry optimizations of the remaining geometric parameters at each point. The energetics of the minima and maxima were subsequently recalculated in single point calculations by using the larger 6-311G(d,p) basis set.[25] Full geometry optimizations of the equilibrium structures (local minima) of the neutral and anionic systems were also performed at the B3LYP/6-311G(d,p) level.

The isotropic hyperfine parameters of the β-protons were obtained from the unpaired spin densities at the nuclei ($\rho(0)^{\alpha-\beta}$), the Fermi contact terms, multiplied by the appropriate conversion factor for hydrogen, 4474.93 MHz/au. The level of theory employed has previously been used extensively for hyperfine coupling calculations and is known to generate proton couplings of high accuracy.[26−28]

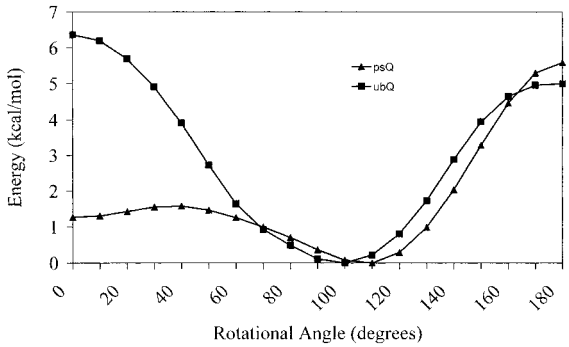

Figure 1. Head-to-tail rotational energy surfaces (kcal/mol) of the radical anions of psQ and ubQ.

Rotational Energy Surfaces of psQ− and ubQ−

In Figure 1 we show the B3LYP/6-31G(d,p) computed potential energy curves for rotation about the Cβ-C5 bond in the ubQ and psQ radical anion models depicted in Scheme 1. For the ubiquinone anion, the potential displays a well-defined single minimum at a Cγ−Cβ−C5−C6 dihedral angle of 90−100°, in agreement with solution structure data,[12] X-ray data for UQ-10 in *Rb. sphaerodies*,[29] and semiempirical estimates by Burie et al.[30] The two possible in-plane positions correspond to transition states on the surface caused by steric repulsion between the terminal methyl group protons and O4 (180°) or the C6 Me group (0°), respectively. Due to the repulsive interactions between the hydrogens on the two methyl groups, the largest barrier, 6.3 kcal/mol, is found at low values of the rotational angle. On the oxygen side, ΔE is slightly lower: 5.0 kcal/mol. The single point energy calculations with the larger basis set yielded barriers that are 0.2−0.3 kcal/mol higher. The rotational barrier agrees perfectly with the 5−7 kcal/mol estimate,[12] obtained from line width effects in β-proton EPR measurements on UQ-10 and vitamin K1 anion radicals. Due to symmetry, all systems were investigated in the range 0−180° rotational angle only.

Plastoquinones lack the C6 methyl group, and so the rotational energy surface shows a different behavior from that of ubiquinone. Removal of the C6 methyl group leads to a drastically reduced barrier height to rotation at low angles. The global minimum is at a perpendicular arrangement of the hydrocarbon tail also in this case, but with a slightly larger energy barrier to rotation at the oxygen side (ΔE = 5.5 kcal/mol). At the in-plane arrangement with the dihedral angle equal to zero we note a second minimum, located ca. 1.3 kcal/mol above the global one. The barrier to reach this minimum is very small and lies only a few tenths of a kcal above the local minimum. In solution, the plastoquinones may hence be assumed to perform a wagging motion between +90° ← (0°) → −90° quite readily, rather than performing a full rotation. It should be noted that, whereas density functional methods in general are known to underestimate transition barriers by a few kcal/mol, rotational barriers about single bonds are reproduced to very high accuracy at the present level of theory.[31]

The energy curves computed here provide a likely explanation for the different behavior observed for the two types of quinones. The occurrence of a single minimum with a perpendicular

TABLE 1: B3LYP/6-311G(d,p) Computed Adiabatic Electron Affinities (eV) of the Quinone Models Listed in Scheme 1

quinone model	C6−CH_3 (this work)	theor[a] (exp)[b]	C6−H (this work)	theor[a] (exp)[b]
plastoquinone	1.64		1.65	1.66 (1.63)
menaquinone	1.64	1.69 (1.67−1.74)	1.70	1.75 (1.73−1.81)
ubiquinone	1.77	(1.86)	1.76	1.68−2.01

[a] Refs 18, 20, and 21. [b] Refs 32 and 33.

arrangement in type I quinones (C6 Me group present) leads to the observed higher specificity of these quinones compared to the plastoquinone systems.[4−9] The local minimum for the planar arrangement in the type II quinones, and the low barrier between the perpendicular and the planar arrangements, 1.5 kcal/mol, also explains the (at least) 10-fold difference in the relative population of these two minima, as suggested by Zengh and Dismukes.[11] Again, increasing the basis set to the triple-ζ valence family (6-311G(d,p)) but retatining the 6-31G(d,p) optimized structures, raises the barriers somewhat and reduces the energy difference between the two minima to only 0.9 kcal/mol.

Electron Affinities and Equilibrium Geometries

As mentioned above, not only the C6 group, but also the remaining ring substituents differ in the various quinones utilized in photosynthesis in green plants vs photosynthetic bacteria. To gain a more complete understanding of the differences in the detailed interactions of these systems, we need to clarify the role of the additional side groups at the C2/C3 positions. We thus performed fully unconstrained equilibrium geometry optimizations for the plastoquinone, ubiquinone, and menaquinone anions displayed in Scheme 1, using either methyl or hydrogen at the C6 position. All optimizations were performed at the B3LYP/6-311G(d,p) level and were intitated by assuming a planar conformation, with Cγ oriented toward C6. Additional optimizations were also performed for the C6−H systems, starting from a near-perpendicular orientation of Cγ.

All systems in which the C6 methyl group was absent, irrespective of C2/C3 substitution, remained in the initial planar arrangement, indicating a local minimum, whereas when the optimizations were initiated at the perpendicular arrangement, a 1−1.5 kcal/mol lower lying minimum was obtained. For the three systems in which the C6 methyl group was added, on the other hand, the ethyl group was always rotated so as to attain a perpendicular orientation of Cγ vs the ring plane. From this limited study, we conclude that one of the key specificity factors in biologically active quinones is the interaction between the C6 substituent and the C5 hydrocarbon tail.

The choice of C2/C3 substituent, on the other hand, appears to play a small role both in terms of head-to-tail arrangement and in the electron-transfer capabilities of the quinones, as displayed in Table 1. This compilation shows the calculated adiabatic electron affinities (EA) of the six quinones (psQ, ubQ, mnQ with and without the C6 methyl group), again at the B3LYP/6-311G(d,p) level. Although this level of theory will provide quinone electron affinities that are a few tenths of an eV too low,[3] the relative EA's should be sufficiently accurate to allow for an assessment of the roles of the different substituents. The present data are in close accord with previous experimental and theoretical studies on related model compounds (generally lacking the hydrocarbon tail at C5 position).[18−21,32−34]

From the data obtained, we can conclude that the C6 methyl group is of very little importance to the electron-transfer properties of the quinones and that the two systems with pure hydrocarbon substituents at C2/C3 (psQ and mnQ models) have identical EA's. The ubQ systems all exhibit EA values that are 0.1 eV higher than the other systems. In our previous work,[3] we found that the presence of hydrogen bonding water molecules increased the EA's of psQ by ca. 0.6 eV. Since the methoxy groups in ubQ may enable further hydrogen bonding via the additional oxygens, it is possible that the EA of ubQ in solution or in a protein environment is increased even further.

TABLE 2: Methoxy Group Dihedral Angles[a] of the Optimized Neutral and Anionic Ubiquinones with and without C6 Methyl Group Present

system	C6 subst	C2 methoxy	C3 methoxy
neutral	H	−35.3	60.6
anion	H	58.5	60.8
neutral	CH_3	38.3	43.9
anion	CH_3	60.3	59.9

[a] The angles are defined such that 0° corresponds to an in-plane arrangement with the methoxy carbon pointing toward the nearest semiquinone oxygen ($C_{Me}-O_{Me}-C2-C1$ and $C_{Me}-O_{Me}-C3-C4$, respectively). Positive value, methoxy above ring plane; negative value, methoxy below ring plane.

The reaction centers of the photosynthetic bacteria *Rb. sphaeroides* and *Rhodopseudomona viridis* differ from each other in that *Rb. sphaeroides* uses a ubiquinone at the Q_A position, whereas *Rps. viridis* uses a menaquinone. In *Rps. viridis*, the basis for the use of the slightly more electronegative ubiquinone, rather than menaquinone, in the B-position could be to ensure that the electron is eventually trapped at this position and, hence, not back-donated to the slightly less electronegative menaquinone at Q_A. The question remains, however, as to why nature has chosen to use ubiquinones at both A and B positions in *Rb. sphaeroides*. In this context, the relative orientations of the methoxy groups may play an important role.

The optimized, neutral closed shell conformers of ubiquinone have the methoxy groups aligned such that one (C2) has a smaller out-of-plane angle (ca. 30°) whereas the second (C3) is in a more distinct out-of-plane orientation (Table 2). This is in accordance with crystal structure data[34−36] and with recent semiempirical data by Burie et al.,[30] although the latter give a clearer differentiation between the planar/perpendicular orientations. After the electron uptake, however, both methoxy groups align in out-of-plane orientations and reside on the same side of the ring plane. The electron addition reaction thus leads to a different ground-state geometry. As shown by Burie et al.,[30] the rotation of the C2 methoxy group increases the EA of ubQ by ca. 0.16 eV.

The data are in accord with the detailed studies by Nonelli[18] and by Boesch and Wheeler,[20] although also other methoxy group arrangements were noted in those studies.

In the protein, the rotation of the C2 methoxy group in the anionic system may cause a slight distortion of the molecular orientation relative to its surrounding and hence modify the hydrogen bonding pattern. As mentioned above, this could lead to a large change in EA, which, in turn, could act as a driving force for the Q_A to Q_B electron-transfer mechanism. It is also possible that a modified spatial arrangement of ubQ_A^- vs ubQ_A, caused by the methoxy group rotation, orients the quinone such that it enhances electron donation to a position different from that at which electron uptake occurred.

TABLE 3: B3LYP/6-311G(d,p) Calculated Isotropic β-Proton Hyperfine Coupling Constants (MHz) for the Planar and Perpendicular Head-to-Tail Orientations of the Quinone Radical Anions of Scheme 1[a]

system	C6 subst	head-to-tail	Hβ1/Hβ2 (av)	exp[a]
psQ$^-$	H	planar	7.8/8.0 (7.9)	(6.9)−(7.1)
	H	perp	4.2/0.6 (2.4)	(2.3)
	CH_3	perp	3.2/1.4 (2.3)	(2.6)
ubQ$^-$	H	planar	9.6/8.9 (9.2)	
	H	perp	5.1/0.7 (2.9)	
	CH_3	perp	3.9/1.5 (2.7)	3.8/2.1 (2.6)−(2.9)
mnQ$^-$	H	planar	10.3/10.3 (10.3)	
	H	perp	5.4/0.8 (3.1)	
	CH_3	perp	4.4/1.8 (3.1)	(3.1), (3.6)

[a] Averaged experimental data for model systems PQ-9 (psQ), vitamin E and ubQ (ubQ), vitamin K1 (mnQ). For ubQ, frozen matrix data giving two unequivalent couplings are also listed. From refs 11, 12, and 40.

In the case of *Rb. spheorides*, ubQ_B is known to undergo a propellar motion upon reduction, in the form of a 180° twist around the first double bond of the ubQ isopropyl tail.[37] Also in *Rps. viridis*, different positions of ubQ_B have been noted, indicating a similar behavior also for this system.[38] The presently observed rotations of the methoxy groups upon reduction could possibly serve as a driving force for this propellar motion. It is very likely that these types of "sterical switching functions" are crucial for the functionality of the entire photosynthetic sequence in bacterial reaction centers.

β-Proton Hyperfine Structures

The hyperfine coupling constants of the β-protons provide an incisive tool for determining the tail-to-head dihedral angle. As mentioned above, there is a considerable difference in the isotropic Hβ hyperfine couplings of the type I and type II quinone anion radicals (ca. 3 and 7 MHz, respectively). In Table 3 we list the B3LYP/6-311G(d,p) computed isotropic β-proton HFCC's at the optimized minima on the rotational energy surfaces. Since these are slightly distorted from the totally symmetric conformations, the HFCC's of the two protons differ from each other. In solution, or even in the protein or frozen solution environments at temperatures above 30−50 K, one can, however, expect to have a certain degree of vibrational averaging between the two.[39] We note a very close agreement between the data for the planar plastoquinone model with hydrogen at the C6 position and the data recorded for PQ-9 anion in solution and psQ$^-$ in PSII. Moreover, the other two quinones that have a C6 hydrogen display large average values of Hβ. For the entire rotational motion, the isotropic Hβ couplings lie within the range 0−12 MHz, as displayed in Figure 2A (psQ) and 2B (ubQ).

For the perpendicular arrangements, on the other hand, all systems, including the normal plastoquinone at the perpendicular minimum and the C6 Me modified plastoquinone model, have average isotropic HFCC's in the 2−3.5 MHz range. This is in excellent agreement with available data for the radical anions of ubiquinone model UQ-10, ubiquinone in bacterial reaction centers, vitamin K_1, and vitamin E. The C2/C3 side groups appear to be of some significance in terms of the magnitudes of the couplings, although the effects are small in comparison with the influence of the Cγ rotational angle.

Feher et al. investigated the HFCCs of ubQ-10 anion models in liquid solution at −3 and −68 °C.[40] At −3 °C, the two methylene protons were found to be equivalent (A_{iso} = 2.9 MHz), whereas at the lower temperature the two unequivalent couplings 3.7 and 2.1 MHz were detected. These data agree well with the presently computed ones, assuming a vibrationally averaged structure at the higher temperature, whereas at −68 °C, the geometry is frozen in the somewhat unsymmetric equilibrium geometry. The EPR spectrum of ubQ in the reaction center of *Rps. sphaeroides* was also recorded in the above study and was found to exhibit only one, relatively large methylene coupling (A_{iso} = 6.2 MHz). From Figure 2, we see that the HFCC pair 6.2 and 0 corresponds to torsional angles of ca. 70 and 120°, and we may conclude that the protein environment in this case causes a slight distortion away from the equilibrium geometry. From the energetic curve, Figure 1, these distortions lie well within 1 kcal/mol and should hence be energetically easy to accomplish through hydrogen bonding or steric repulsions.

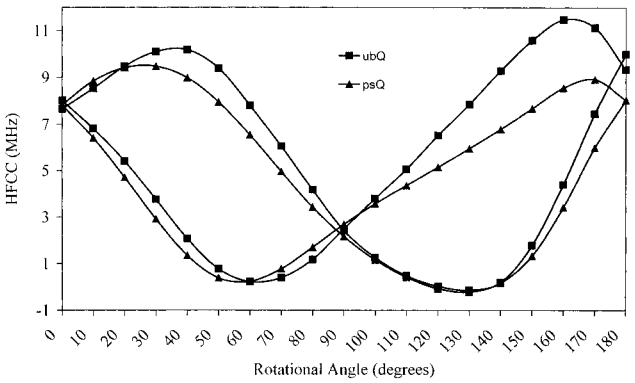

Figure 2. Variation in isotropic β-proton HFCCs (MHz) in psQ$^-$ and ubQ$^-$ as functions of head-to-tail rotational angle.

Concluding Remarks

The conformational arrangement controlling biological activity of quinones involved in the photosynthetic processes in PSII and photosynthetic bacteria have been investigated by means of hybrid HF-DFT theory. The calculations show that the presence or absence of the C6 methyl group drastically modifies the head-to-tail rotational energy surfaces. The quinones of type I, used in photosynthetic bacteria, require the C6 methyl group in order to attain a perpendicular arrangement of the ring relative to the hydrocarbon tail. For the plastoquinones, used by green plants, the C6 methyl group is absent, leading to a local minimum in a planar arrangement. The difference in energetics provides an important explanation for experimental observations of differences in the capability to incorporate psQ models in bacterial reaction centers relative to using ubiquinones or menaquinones in PSII.

For systems with and without the C6 methyl group, we report the computed β-proton hyperfine couplings. The data for planar vs perpendicular structures correlate very well with the experimentally observed results for the type I and II quinones, supporting the assumption that the plastoquinones may be arranged in a planar conformation in photosynthetic centers of green plants but that the quinones employed by photosynthetic bacteria are in a perpendicular head-to-tail orientation. The observation of only one methylene coupling (6.2 MHz) of ubQ_A^- in *Rb. sphaeroides*[40] is explained in terms of a low-energy distortion to a dihedral angle of 70 or 120° by the protein surrounding.

The C2 methoxy group in ubiquinone is found to orient differently in the neutral and in the anionic state of the quinone. This electron-induced conformational modification may cause a modified influence from surrounding hydrogen bonding groups to the anion. We have in previous work shown the strong effects in the EA of plastoquinone anions upon formation of hydrogen

bonding.[3] Thus, upon electron capture at ubQ_A in *Rb. sphaeroides* the quinone may rotate slightly as a result of the methoxy group reorientation. This could, in turn, modify the electron affinity due to modified H-bonding, and also modify the ability for electron donation/uptake and proton uptake relative to the neutral system. Or, in the case of ubQ_B in *Rb. spaeroides* and *Rps. viridis*, to promote the observed propellar motion upon reduction.[37,38]

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