8908 *J. Phys. Chem. A* **2002,** *106,* 8908−8916

Structure and Proton Reactivity of the Semiquinone Anion and Dianion of Biphenol in Water

G. N. R. Tripathi* and Daniel M. Chipman

Radiation Laboratory, University of Notre Dame, Notre Dame, Indiana 46556

Received: July 11, 2002

Whether the redox intermediate state of 4,4′-biphenol in water, $C_{12}H_8O_2^{-\bullet}$, has a planar or staggered molecular geometry twisted about the inter-ring bond has been examined using time-resolved resonance Raman spectroscopy and electronic structure computation. Hydrogen-bonding effects on the *p,p*′-biphenylsemiquinone radical anion ($C_{12}H_8O_2^{-\bullet}$) structure were incorporated in the calculations by associating two water molecules with each oxygen site. The predicted structure, with inter-ring CC bond length of 1.455 Å and dihedral angle of 17.7°, provides a good description of the spectroscopic observations. Hydrogen bonding slightly elongates the CO bonds, but its effect on the inter-ring twist is negligible. Nonequivalence of the two phenyl rings, which are noncoplanar, is indicated by the resonance Raman spectra of $C_{12}H_8O_2^{-\bullet}$ in liquid water as well as in ethanol matrix at low temperatures. The π-conjugation between the rings is small in the radical anion, but greater than in its reduced dianion ($C_{12}H_8O_2^{2-}$) state, which signifies the role of torsional distortion of the molecular geometry in redox reactions of biphenyl systems. The change in the calculated CO bond length from the parent dianion to the *p,p*′-biphenylsemiquinone radical anion (0.031 Å) is significantly smaller than that for the analogous *p*-benzosemiquinone radical anion system (0.049 Å) and correlates well with the change in acid−base equilibria. The predictive value and limitations of the theoretical structure calculations of molecular ions and radicals containing the $X-C_6H_4O^-$ ($X \neq O$) moiety, which occurs in a wide variety of chemical and biochemical redox systems, are examined.

Introduction

Semiquinones constitute an important class of radical intermediates which play pivotal roles in a variety of chemical and biological processes, such as artificial light energy conversion into chemical energy, natural photosynthesis, cell respiration, and quinoenzyme activity.[1−3] They are qualitatively described through resonance structures conceived by exchanging unpaired and paired electrons on two distant atomic sites of a conjugated system, which make about equal contributions to the radical structure.[1] This simple description of the semiquinone state, introduced by Pauling, has been amply justified by numerous experimental and theoretical studies of the *p*-benzosemiquinone radical anion ($C_6H_4O_2^{-\bullet}$) in recent years.[4−11] Similarities in the CO bond properties and protonation behavior of this radical anion with those of the closed-shell acetate anion can be readily accounted for on that basis.[8,9] Resonance structures similar to those of the *p*-benzosemiquinone radical anion are also commonly used for describing the redox intermediates of bridged aromatics with CC linkage.[7] However, torsional distortion of the molecular geometry about the inter-ring bond can greatly reduce the π-interaction between the rings. In that case, a qualitative structure largely based on electron exchange between the atomic sites on different rings can be inadequate for describing the spectra, bonding and chemical reactivity of the radical intermediates.

Recent measurements on the acid−base properties of the *p,p*′-biphenylsemiquinone radical in water indicate that the pK_a of this radical is about three units higher than that of the *p*-benzosemiquinone radical.[12,13] Obviously, the anion form of the former radical ($C_{12}H_8O_2^{-\bullet}$) is relatively less resonance stabilized.[1] Structurally, this may correspond to greater localization of the extra electronic charge on two equivalent oxygen atoms, which implies weaker CO bonds. Alternatively, one oxygen atom may have more electronic charge than the other. In either case, a lack of effective π-conjugation between the rings is indicated, which can arise from nonplanarity of the molecular configuration in water.

The proton-hyperfine constants of $C_{12}H_8O_2^{-\bullet}$ in solution[14] suggest structural equivalence of the two phenyl groups on the ESR time scale. This equivalence does not necessarily imply a planar configuration. On the other hand, weak satellite bands mostly accompany the principal bands in the resonance Raman (RR) spectrum of the radical in ethanol matrix at 77 K.[7] These secondary spectral features have no analogues in the RR spectrum of $C_6H_4O_2^{-\bullet}$, which might imply a lowering of symmetry. Although the origin of the satellite bands has remained unexplained thus far, it has been clear that resonance structures similar to those of $C_6H_4O_2^{-\bullet}$ do not adequately describe the spectral properties of $C_{12}H_8O_2^{-\bullet}$. It is possible that the radical geometry in rigid matrixes is different from that in liquid water. Biphenyl and some of its 4,4′ derivatives are known to be planar in crystals but twisted by large dihedral angles (45 ± 15°) in liquids and gases.[15]

We have investigated in this work the structural properties of the aqueous *p,p*′-biphenylsemiquinone radical anion, using time-resolved resonance Raman spectroscopy and electronic structure computation with density functional theory (DFT). Vibrational spectroscopic data on the per-deuterated radical ($C_{12}D_8O_2^{-\bullet}$) has been obtained using a novel method of in situ synthesis. Hydration effects on the radical structure have been

---

* To whom correspondence should be addressed.

10.1021/jp021599n CCC: $22.00

modeled in terms of theoretical structures in which each oxygen atom is hydrogen-bound to two water molecules. The calculations give good agreement with the experimental Raman frequencies and their isotope shifts. They also suggest that hydrogen bond interactions have a negligible effect on the inter-ring twist. Comparison of the observed and calculated Raman frequencies, particularly in the low-frequency region, provides strong evidence that the two oxygen atoms in aqueous $C_{12}H_8O_2^{-\bullet}$ are not equivalent on the vibrational time-scale.

Experimental Section

The *p,p′*-biphenylsemiquinone anion radical was prepared by pulse radiolytic oxidation of 4,4′-biphenol ($C_{12}H_{10}O_2$) in basic aqueous solutions. On electron pulse irradiation of N_2O-saturated water, the $^\bullet$OH radical is the main reactive species present in solution on the nanosecond time scale.[15] It was converted into the secondary oxidant, $N_3^\bullet$, by reaction with 0.1 M NaN_3 in solution. The $^\bullet$OH radical reacts with N_3^- at a rate constant of 1.2×10^{10} M^{-1} s^{-1}.[16] Therefore, the formation of the $N_3^\bullet$ radical is complete within the electron pulse duration (<5 ns). The deuterated radical ($C_{12}D_8O_2^{-\bullet}$) was prepared by pulse radiolysis of perdeuterated phenol (C_6D_5OD) in light water. This preparation method is briefly discussed in the following section.

The pulse radiolysis−time-resolved optical absorption and resonance Raman techniques, used in this work, have been previously described.[4,17] Radiolysis by ∼8 MeV, ∼5 ns electron pulses from a linear accelerator, at a dose which produces a radical concentration of $\sim 3 \times 10^{-6}$ M per pulse, was used in optical absorption measurements. In Raman experiments, 2 MeV, ∼100 ns electron pulses, delivered by a Van de Graaff accelerator at dose rates that produced about 10^{-4}−10^{-5} M radical concentration, were applied. The Raman scattering was probed by an excimer-pumped dye laser pulse, tuned in resonance with the optical absorption of the radicals. The spectra were recorded using an optical multichannel analyzer (OMA), accompanied by an intensified gated diode array detector, with the gate pulse synchronized with the Raman signal pulse. Extensive signal averaging was performed to improve the S/N ratio in the Raman spectra, with the accelerator and laser operated at a repetition rate of 7.5 Hz. In both experiments, a flow system was used to refresh the solution between consecutive electron pulses. Raman band positions were measured with reference to the known Raman bands of common solvents, such as ethanol and carbon tetrachloride, and are accurate to within ±2 cm^{-1} for sharp bands and ±5 cm^{-1} for broad and shoulder bands.

Theoretical Procedures

The BPW91 method, which combines Becke's 1988 exchange functional with the Perdew−Wang 91 correlational functional,[18] was used for structural characterization. Although DFT calculations may not give accurate results for either hydrogen-bond distances or binding energies, it has been shown that the BPW91 functional gives a good account of the effect of hydrogen bonding on the vibrational structure of semiquinone and phenoxyl radicals in water.(10) Calculations were performed on the isolated and water bound radical anion ($C_{12}H_8O_2^{-\bullet}$ and $C_{12}H_8O_2^{-\bullet}\cdot 4H_2O$) and the corresponding dianions ($C_{12}H_8O_2^{2-}$ and $C_{12}H_8O_2^{2-}\cdot 4H_2O$). Energetic, geometric, and force field evaluations were obtained using the 6-31+G** basis set[19] having split-valence and polarization functions on all atoms plus diffuse functions on heavy atoms. Vibrational frequencies were obtained from analytical second derivatives evaluated at the computed local minimum geometries. These calculations were carried out with the Gaussian 98 program.[20] The composition of each normal mode in terms of local mode contributions was obtained by the total energy distribution method.[21] Comparison of the hydrogen bonded $C_{12}H_8O_2^{-\bullet}\cdot 4H_2O$ and $C_6H_4O_2^{-\bullet}\cdot 4H_2O$ radicals and their precursor dianion structures ($C_{12}H_8O_2^{2-}\cdot 4H_2O$ and $C_6H_4O_2^{2-}\cdot 4H_2O$), at the same level of theory, was used to gain insight into the nature of the CO bonds and their possible effect on the proton reactivity in water.

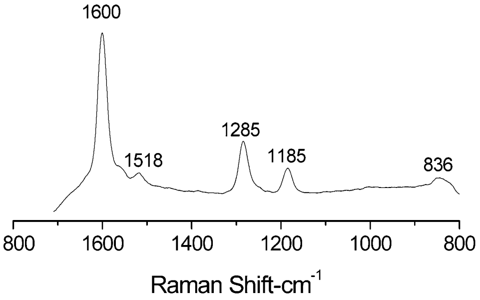

Figure 1. 390 nm Raman spectrum of aqueous $C_{12}H_8O_2^{2-}$ at pH 13.

Results and Discussion

1. Raman Spectrum and Molecular Geometry of the Dianion Form of 4,4′-Biphenol ($C_{12}H_8O_2^{2-}$) in Water. The preresonance Raman spectrum of 4,4′-biphenol in basic aqueous solution (pH 13) obtained using the experimental setup described in previous section is depicted in Figure 1. Excitation was at 390 nm. Fluorescence interferes with spectral acquisition at shorter wavelengths. The spectrum does not change even in strongly basic solutions (3 M KOH). Because of poor solubility of the compound at lower pH, the acid−base equilibrium could not be followed. The second pK_a of dihydroxy aromatics, such as hydroquinone, generally lie in a narrow range of 11 ± 1.[22] On that basis, the spectrum in Figure 1 is ascribed to the dianion form $C_{12}H_8O_2^{2-}$.

The spectrum in Figure 1 is simple, as only those vibrational modes that are preresonance Raman enhanced are observed. They generally represent Franck−Condon-allowed totally symmetric modes. It is convenient to describe these vibrational modes in terms of phenyl vibrations using Wilson notation.[23] Comparison of the spectrum in Figure 1 with those of biphenyl and its derivatives leads to straightforward assignment. The inter-ring CC stretch that appears at 1285 cm^{-1} in liquid biphenyl ($C_{12}H_{10}$)[15] shows as a medium intensity band of similar frequency (1285 cm^{-1}) in aqueous $C_{12}H_8O_2^{2-}$. Similarly, the principal band at 1600 cm^{-1} and weak to moderate intensity bands at 1515 and 1185 cm^{-1} in aqueous $C_{12}H_8O_2^{2-}$ compare well with the Raman frequencies, 1612, 1513, and 1192 cm^{-1}, in liquid $C_{12}H_{10}$.[15] These vibrational modes relate to the in-phase phenyl (Wilson) vibrations: 8a (ring stretch), 19a (CH bend + ring stretch), and 9a (CH bend), respectively. The weak Raman band at 836 cm^{-1} can be readily assigned to the in-phase ring breathing mode (Wilson mode 1), observed at comparable frequencies in para-substituted benzenes (843 cm^{-1} in liquid $C_{12}H_8F_2$).[15,23] These vibrational modes are totally symmetric in $\boldsymbol{D_{2h}}$ (planar) as well as $\boldsymbol{D_2}$ (twisted) molecular symmetry, and their frequencies are known to be insensitive to the inter-ring twist. Therefore, they provide little insight into the rings' orientation. The inter-ring CC bond length in $C_{12}H_8O_2^{2-}$ is expected to be comparable to that of biphenyl (1.48−1.50 Å), based on identical (1285 cm^{-1}) stretching frequencies.

Figure 2A presents the calculated BPW91/6-31+G** structure of $C_{12}H_8O_2^{2-}$, hydrogen-bonded to two water molecules

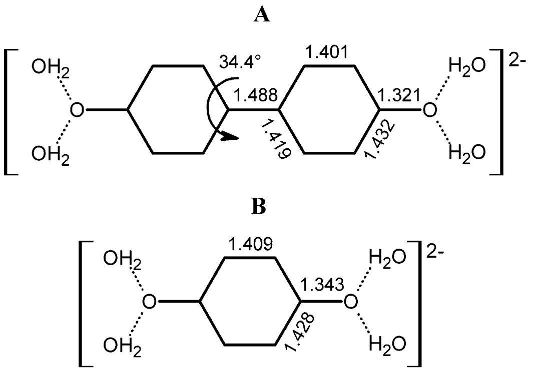

Figure 2. Theoretical (BPW91/6-31+G**) structures of $C_{12}H_8O_2^{2-}\cdot 4H_2O$ (A) and $C_6H_4O_2^{2-}\cdot 4H_2O$ (B).

TABLE 1: Comparison between the 390 nm Raman Frequencies (cm^{-1}) of the Dianion of 4,4′-Biphenol ($C_{12}H_8O_2^{2-}$) in Water and Calculated Frequencies of Totally Symmetric Modes[a]

	$C_{12}H_8O_2^{2-}$			$C_{12}H_8O_2^{2-}$			$C_{12}H_8O_2^{2-}$	
$C_{12}H_{10}$[b] (liquid)	exp	cal	$C_{12}H_{10}$[b] (liquid)	exp	cal	$C_{12}H_{10}$[b] (liquid)	exp	cal
1612	1600	1594	1285	1285	1266	1031	1003	984
1505	1518	1505	1192	1185	1163	*843*	836	831
		1326						

[a] Biphenyl ($C_{12}H_{10}$) frequencies are also given for comparison. [b] Reference 15. Substituent-sensitive frequencies from 4,4′-$C_{12}H_8F_2$ in italics (ref 15).

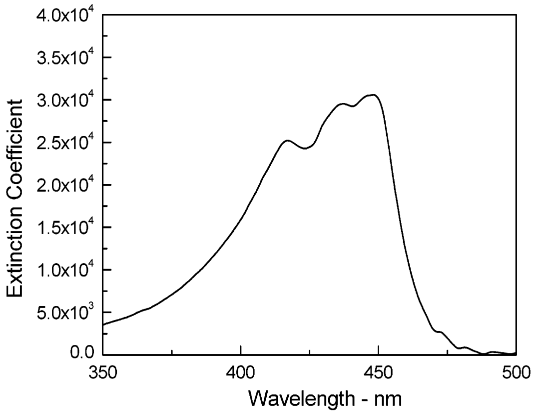

Figure 3. Transient absorption of $C_{12}H_8O_2^{-\bullet}$, observed 2 μs after the electron pulse, in aqueous solution at pH 11 (see text).

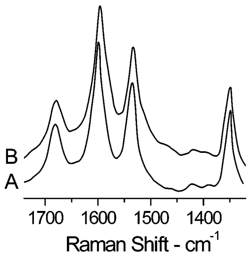

Figure 4. 445 nm Raman spectra of $C_{12}H_8O_2^{-\bullet}$ in the 1400−1800 cm^{-1} region, prepared by $N_3^{-\bullet}$ oxidation of (A) 4,4′-biphenol and (B) phenol in basic solutions.

at each oxygen end. The inter-ring dihedral angle is calculated at 34°, which is comparable to the angle in gas and liquid biphenyl (45 ± 15°). The π-overlap between the rings is negligible, as reflected in the calculated inter-ring CC bond length of 1.488 Å that is typical of a single CC bond. Thus, the predicted ring orientations and bonds are similar to those in liquid biphenyl, which is not surprising. The calculated frequencies 1594 (8a), 1505 (19a), 1163 (9a), and 813(1) cm^{-1} agree well (Table 1) with the observed frequencies for these modes (1600, 1513, 1192, and 836 cm^{-1}).

Hydrogen bonding has very little effect on the calculated inter-ring bond and orientation. However, its inclusion in the calculation elongates the CO bonds by 0.026 Å and leads to a better agreement with the experimental frequencies. The calculation underestimates the inter-ring CC stretching frequency by 20 cm^{-1}. The lower value may be partly a consequence of unusually short calculated CO bonds (1.321 Å), as compared to that in phenols (~1.38 Å). For a short CO bond, the uncoupled stretching frequency becomes higher than that for the inter-ring CC bond, and the resulting mechanical coupling between the two can lower the inter-ring CC frequency. These coupled modes are calculated at 1326 and 1266 cm^{-1}. We observe only one band, at 1285 cm^{-1}, suggesting that the calculation overestimates the degree of coupling. We believe the BPW91/6-31+G** geometry is a reasonable representation of the $C_{12}H_8O_2^{2-}$ molecular geometry in water, as far as the ring orientations are concerned. On the other hand, the CO lengths appear to be shorter than expected, a problem noted previously[24−27] for DFT calculations on phenolate anion ($C_6H_5O^-$).

2. Transient Absorption of *p,p′*-Biphenylsemiquinone Radical Anion ($C_{12}H_8O_2^{-\bullet}$). The transient absorption observed 2 μs after electron pulse irradiation of a N_2O-saturated aqueous solution containing 0.5 mM *p,p′*-biphenol and 0.1 M NaN_3 at pH ~11 is shown in Figure 3. The absorption maximum (λ_{max}) at 443 nm (extinction coefficient ~2.8×10^4 M^{-1} cm^{-1}) is shifted toward the blue by 15 nm with respect to the spectrum in ethanol matrix at 77 K.[7] The p-benzosemiquinone anion and other *p*-substituted phenoxyl radicals ($XC_6H_4O^\bullet$) also absorb in this spectral region.[5] The transition moments for these absorption spectra are directed along the long molecular axis (taken as Z axis). For an electronic transition in $C_{12}H_8O_2^{-\bullet}$ of similar character, the transition moment should be about twice as large and absorption coefficient about four times higher than in $C_6H_4O_2^{-\bullet}$, irrespective of the inter-ring twist. At $\lambda_{max} \sim 430$ nm, $\epsilon_{max} \sim 7.6 \times 10^3$ M^{-1} cm^{-1} for the $B_{2g}-B_{3u}$ transition of $C_6H_4O_2^{-\bullet}$. Thus, one would expect an ϵ_{max} of ~3×10^4 M^{-1} for a corresponding transition in $C_{12}H_8O_2^{-\bullet}$. The observed extinction coefficient is very close to this roughly estimated value.

3. Radiolytic Synthesis of Aqueous $C_{12}D_8O_2^{-\bullet}$. The ring-deuterated radical was synthesized using deuterated phenol (C_6D_5OD) as precursor. It is known[28] that the recombination of phenoxyl radical ($C_6H_5O^\bullet$) leads to formation of $C_{12}H_8O_2^{2-}$, which was verified. The transient Raman spectrum in the 1400−1800 cm^{-1} region, obtained on electron pulse irradiation of a N_2O-saturated aqueous solution containing 0.5 mM 4,4′-biphenol and 0.1 M NaN_3 at pH ~11, is shown in Figure 4A. Excitation was at 445 nm. This spectrum is a difference spectrum of the raw spectra recorded at 1 μs and 100 ms after the pulse. The spectrum in Figure 4B was obtained on pulse radiolysis of a solution containing 2 mM phenol and 0.1 M NaN_3 at pH ~11, using the same excitation wavelength. It can be seen that the two spectra are essentially identical. Thus, it is clear that that the $C_{12}D_8O_2^{-\bullet}$ radical can be conveniently prepared by pulse radiolysis of deuterated phenol (C_6D_5OD) in basic aqueous solutions. This in situ radiolytic synthesis was used to investigate the isotope effects on the resonance Raman spectrum.

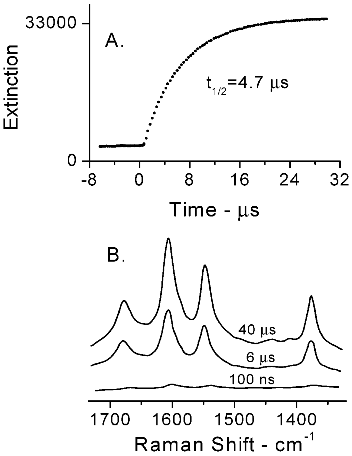

Figure 5. Growth kinetics of $C_{12}H_8O_2^{-\bullet}$ on electron transfer from $C_{12}H_8O_2^{2-}$ to $C_6H_5O^\bullet$ in basic aqueous solution, monitored by (A) 440 nm absorption and (B) 445 nm Raman. (see text).

The mechanism by which $C_{12}H_8O_2^{-\bullet}$ is produced on radiolysis of phenol was briefly examined. It is well recognized that the phenoxyl ($C_6H_5O^\bullet$) radical, the primary intermediate in the oxidation of phenol, undergoes tail−tail bimolecular reaction to produce *p,p′*-dihydroxybiphenyl (biphenol):[28]

$$C_6H_5O^- + {}^\bullet OH/N_3^\bullet \rightarrow C_6H_5O^\bullet + OH^-/N_3^- \qquad (1)$$

$$C_6H_5O^\bullet + C_6H_5O^\bullet \rightarrow C_{12}H_{10}O_2 \rightarrow C_{12}H_8O_2^{2-} + 2H^+ \qquad (2)$$

Electron transfer from $C_{12}H_8O_2^-$ to $C_6H_5O^\bullet$ produces $C_{12}H_8O_2^{-\bullet}$:

$$C_6H_5O^\bullet + C_{12}H_8O_2^{2-} \rightarrow C_{12}H_8O_2^{-\bullet} + C_6H_5O^- \qquad (3)$$

Whether the reaction 3 can indeed occur was investigated. Figure 5A depicts the growth kinetics of $C_{12}H_8O_2^{-\bullet}$ absorption at 440 nm on radiolysis of a N_2O-saturated aqueous solution containing 5 mM phenol and 0.05 mM biphenol at pH ∼11. The absorption grows exponentially, with a half-period of 4.7 µs, which corresponds to a rate constant of 2.9×10^9 M^{-1} s^{-1}. The reaction is complete in less than 20 µs. The transient Raman spectra obtained from this solution 100 ns and 6 and 40 µs after the electron pulse are shown in Figure 5B. The signal intensity at 6 µs is roughly half the intensity of that at 40 µs, giving a rate constant of 2.3×10^9 M^{-1} s^{-1}, in excellent agreement with the rate constant measured by optical absorption. It is clear that recombination of $C_6H_5O^\bullet$ produces $C_{12}H_8O_2^{2-}$, which is subsequently oxidized by $C_6H_5O^\bullet$ to form $C_{12}H_8O_2^{-\bullet}$ in basic solutions.

In Raman studies, the initial radical concentration is fairly high (∼10^{-4}M). Therefore, even if a small fraction of $C_6H_5O^\bullet$ produced on oxidation of phenol converts into biphenol, the latter concentration is high enough to react with $C_6H_5O^\bullet$ to form $C_{12}H_8O_2^{-\bullet}$ on the microsecond time-scale. Any coupling between phenoxyl radicals at the ortho position will produce a different isomer of biphenol. However, there was no evidence that the radicals derived from other isomers are formed. It is likely that the rates of electron transfer from other isomers of biphenol to phenoxyl radical are very low (reaction 3), or do not occur, a possibility that we did not examine. Also, the other isomers may not absorb as strongly as *p,p′*-biphenylsemiquinone radical anion and their absorption may lie in a different spectral region.

4. Resonance Raman Spectra of $C_{12}H_8O_2^{-\bullet}$ and $C_{12}D_8O_2^{-\bullet}$. The resonance Raman spectra of $C_{12}H_8O_2^{-\bullet}$ and $C_{12}D_8O_2^{-\bullet}$ in water, prepared by the methods described in earlier sections, are displayed in Figure 6 and summarized in Table 2. Excitation was at 445 nm. The spectrum in Figure 6A was observed 2 µs after the electron pulse and that in Figure 6B 10µs after the pulse. Prominent bands at 1598, 1530, 1405, 1332, 1201, 982, 842, and 686 cm^{-1} are readily discernible for $C_{12}H_8O_2^{-\bullet}$ in the 1800−600 cm^{-1} region (Figure 6A). Comparatively, many more bands have been reported in the spectra recorded on the radical embedded in ethanol matrix at 77 K.[7] Large downward shifts of 324 and 119 cm^{-1} in frequency occur for the 1201 and 982 cm^{-1} bands in $C_{12}D_8O_2^{-\bullet}$, respectively. On the other hand, the 1332 cm^{-1} band shifts to a higher frequency by 43 cm^{-1}. The remaining Raman bands shift to lower frequencies by about 36 (±7) cm^{-1} on ring deuteration.

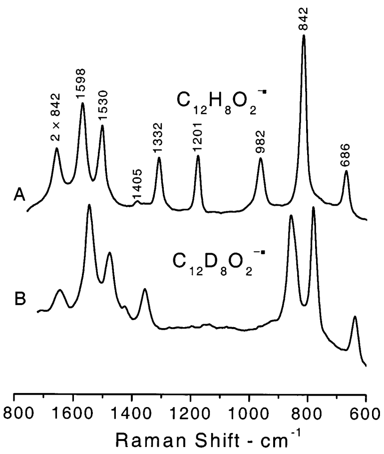

Figure 6. 445 nm Raman spectra of (A) $C_{12}H_8O_2^{-\bullet}$ and (B) $C_{12}D_8O_2^{-\bullet}$.

TABLE 2: Comparison between the 445 nm Resonance Raman Frequencies (cm^{-1}) of the Totally Symmetric Modes (in D_{2h}, D_2, and C_s Symmetries) of $C_{12}H_8O_2^{-\bullet}$ and $C_{12}D_8O_2^{-\bullet}$ in Water and Calculated Frequencies[a]

$C_{12}H_{10}$[b] (liquid)	$C_{12}H_8O_2^{-\bullet}$ exp	$C_{12}H_8O_2^{-\bullet}$ cal	$C_{12}D_8O_2^{-\bullet}$ exp	$C_{12}D_8O_2^{-\bullet}$ cal	$C_{12}H_8O_2^{-\bullet}-C_{12}D_8O_2^{-\bullet}$ exp	$C_{12}H_8O_2^{-\bullet}-C_{12}D_8O_2^{-\bullet}$ cal
1612	1598(1605)[c]	1592	1568	1560	−30	−32
1509	1530(1542)	1525	1494	1492	−36	− 33
	1405	1404		1157		− 247
1285	1332(1337)	1307	1375	1373	+43	+ 66
1192	1201(1204)	1178	877	858	−324	−320
1031	982(982)	969	863	848	−119	−121
843[d]	842(842)	834	797	782	− 43	−52
741	686(688)	675	650	637	−36	− 38
316	298(308)	290		278		− 12

[a] $C_{12}H_{10}$ frequencies are also given for comparison. [b] Reference 15. [c] Frequencies in ethanol matrix (ref 7) in parentheses. [d] Substituent-sensitive frequencies from $C_{12}H_8F_2$ (ref 15) in italics.

The resonant 445 nm transition of the radical is very strong. Therefore, the possibility of observing symmetry-allowed but Franck−Condon forbidden (nontotally symmetric) vibrations in the resonance Raman spectra must be discounted. The ππ* nature of the 445 nm transition requires that these modes involve considerable ring distortion components (implying fundamental frequency below 1800 cm^{-1}) in order to be observably enhanced in the resonance Raman spectra.[29]

Structural equivalence of the two phenyl groups in the radical would be required in a planar $\boldsymbol{D_{2h}}$ point group, as well as in a staggered molecular geometry twisted about the inter-ring bond in a $\boldsymbol{D_2}$ point group. In the case of nonequivalence, the corresponding point group symmetries reduce to $\boldsymbol{C_{2v}}$ and $\boldsymbol{C_1}$ (no symmetry), respectively. In a $\boldsymbol{D_{2h}}$ geometry of $C_{12}H_8O_2^{-\bullet}$, nine fundamentals having totally symmetric character ($\mathbf{a_{1g}}$) can occur below 1800 cm^{-1}. They can be visualized in terms of

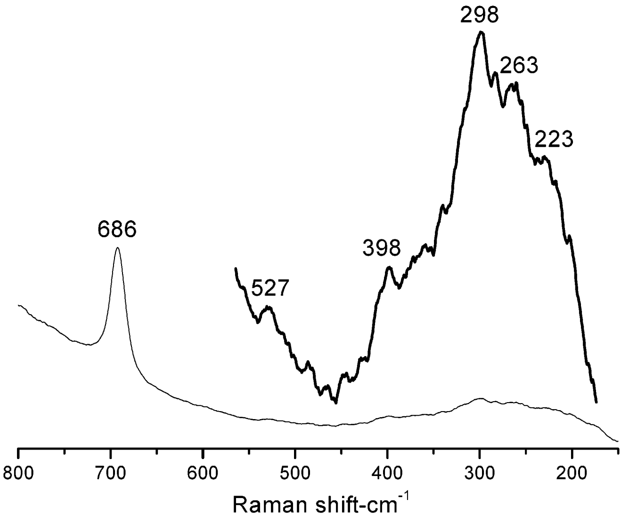

Figure 7. Very weak bands in the low frequency (200−600 cm^{-1}) region in the 445 nm Raman spectrum of $C_{12}H_8O_2^{-\bullet}$.

TABLE 3: Comparison between the 445 nm Resonance Raman Frequencies (cm^{-1}) of the Nontotally Symmetric Modes (in *D_{2h}* Symmetry) of $C_{12}H_8O_2^{-\bullet}$ in Water and Calculated Frequencies[a]

totally symmetric in D_2 structure			nontotally symmetric in D_2 structure (totally symmetric in C_1)		
$C_{12}H_{10}$[b]	$C_{12}H_8O_2^{-\bullet}$		$C_{12}H_{10}$[b]	$C_{12}H_8O_2^{-\bullet}$[c]	
(liquid)	exp	cal	(liquid)	exp	cal[d]
	911	936	1595	(1591)	1605
824		772	1481	(1530)	1495
423	398	398	1158	1150 (1186)	1162
		65	1094	1088	1104/1101
			1007	(969)	960
			806[e]	(798)	768
			515[e]	527 (505)	529/521
			403	(404)	393
			269	263 (277)	235
				223	211

[a] $C_{12}H_{10}$ frequencies are also given for comparison. [b] Reference 15. [c] Frequencies in ethanol matrix (ref 7) in parentheses. [d] Only those calculated nontotally symmetric modes in *D_2* symmetry that are readily assignable to experimental results are cited here. [e] Substituent-sensitive frequencies from 4,4′-$C_{12}H_8F_2$ (ref 15) in italics.

in-phase-coupled motion of the planar a_1 vibrations of the individual phenyl rings (local C_{2v} symmetry)[30] and the inter-ring CC stretch.[15,23] The out-of-phase coupled a_1 vibrations have $\mathbf{b_{3u}}$ symmetry and are Raman-forbidden (infrared active). The latter can acquire totally symmetric character ($\mathbf{a_1}$) and Raman activity in a planar *C_{2v}* geometry. The $\mathbf{a_1(b_{3u})}$ modes derive their intensity by mixing with the $\mathbf{a_1(a_{1g})}$ modes of comparable frequency. In a nonplanar *D_2* geometry, the $\mathbf{a_u}$ (out of ring plane) vibrations become totally symmetric **(A)**. The $\mathbf{A(a_u)}$ vibrations also borrow their intensities from the $\mathbf{A(a_{1g})}$ modes. The borrowed intensity can be very small. Therefore, very weak bands in the RR spectra of the radical are of critical importance in ascertaining the molecular configuration.

Eight fundamentals marked in Figure 6A can be readily attributed to the vibrational modes of $\mathbf{a_{1g}}$ parentage in a *D_{2h}* geometry. They are prominently resonance enhanced and occur at frequencies comparable to those in para-substituted phenoxyl radicals[4] and biphenyl derivatives.[15] The inter-ring CC stretch appears at 1332 cm^{-1}, 47 cm^{-1} higher than in $C_{12}H_8O_2^{2-}$. This is a clear indication of increased π-conjugation between the rings on loss of an electron from $C_{12}H_8O_2^{2-}$ and a consequent decrease in the inter-ring twist. There is a large CH bending component (as in phenyl Wilson mode 19a) in the 1332 cm^{-1} mode, as the frequency increases to 1375 cm^{-1} in the perdeuterated radical. The other fundamentals marked in Figure 6A can be approximately described in terms of in-phase Wilson modes 8a (ring stretch), 7a (CO stretch), 19a (CH bend + ring stretch), 9a (CH bend), 18a (ring distortion + CH bend), 1 (ring breathe), and 12 (trigonal ring distortion), in order of descending frequencies.[4,9,22] The CH bending modes 9a (1201 cm^{-1}) and 18a (982 cm^{-1}) undergo large downward isotope shifts (324 and 119 cm^{-1}, respectively), as expected. These assignments are based on a number of RR studies of radicals produced on oxidation of aqueous phenols and anilines and are consistent with the assignments proposed previously for the spectrum in ethanol matrix.[4,7] The frequencies of these modes are known to be insensitive to the inter-ring twist in biphenyl.[15] The ninth $\mathbf{a_{1g}}$ (*D_{2h}*) vibration is the ring distortion mode (derived from the Wilson phenyl mode 6a), observed at 309 cm^{-1} in liquid biphenyl (15) The corresponding RR band in aqueous $C_{12}H_8O_2^{-\bullet}$ is very weak (Figure 7) and is seen at 298 cm^{-1}.

There are four vibational modes of out-of-ring $\mathbf{a_u}$ parentage in a *D_{2h}* geometry having expected frequencies: ∼900 (Wilson mode 17a; CH bend), ∼800 (Wilson mode 10a; CH bend), ∼400 cm^{-1} (Wilson mode 16a; ring distortion), and a very low frequency for the inter-ring torsion in biphenyl.[15,22] Two of them are observed (at 911 and 398 cm^{-1}) in aqueous $C_{12}H_8O_2^{-\bullet}$ (Table 3). These four vibrations are strictly Raman forbidden in the *D_{2h}* point group. Vibronic coupling between the excited electronic states cannot impart Raman intensity to a "u" (ungerade) vibrational mode in the ground electronic state. Their appearance in the RR spectrum is a clear indication of the lack of center of symmetry in the radical structure. The 911 cm^{-1} mode appears to derive its intensity from the highly enhanced 836 cm^{-1} ring mode and the 398 cm^{-1} mode from the weakly enhanced 298 cm^{-1} ring mode. All of these observations discussed up to this point are consistent with a *D_2* symmetry. However, there are additional very weak bands at 527, 263, and 223 cm^{-1} in Figure 7 that cannot be accounted for by a *D_2* molecular symmetry. In the vibrational spectra of biphenyl and its derivatives, the corresponding vibrations represent modes that are nontotally symmetric in the *D_{2h}* as well as the *D_2* point groups.[15] They can acquire totally symmetric character only in the *C_1* point group (no symmetry). Most of the weakly enhanced vibrational modes observed in the RR spectra of aqueous $C_{12}H_8O_2^{-\bullet}$ are also seen in ethanol matrix.[7]

We conclude from the above analysis of the RR spectra, based on symmetry arguments, that the molecular geometry of the $C_{12}H_8O_2^{-\bullet}$ radical is significantly twisted about the inter-ring CC bond in liquid water as well as in ethanol matrix. The π-conjugation between the rings increases on removal of an electron from the highly twisted $C_{12}H_8O_2^{2-}$. It is logical to assume the structure of the fully oxidized aqueous $C_{12}H_8O_2$ to be planar, and we have corroborated this with BPW91/6-31+G** calculations, but we have no experimental evidence at this point. In that event, the ring orientations in the semiquinone state ($C_{12}H_8O_2^{-\bullet}$) of biphenol should be intermediate between those of its fully oxidized ($C_{12}H_8O_2$) and reduced dianion ($C_{12}H_8O_2^{2-}$) forms.

The spectral evidence further suggests the phenyl moieties in the $C_{12}H_8O_2^{-\bullet}$ radical structure to be nonequivalent. As a consequence, the out-of-phase coupled local a_1 phenyl vibrations should acquire RR activity, as pointed out earlier. In accordance, weak satellite bands accompany the prominent RR band of the radical in ethanol matrix at 77 K. Although nontotally symmetric

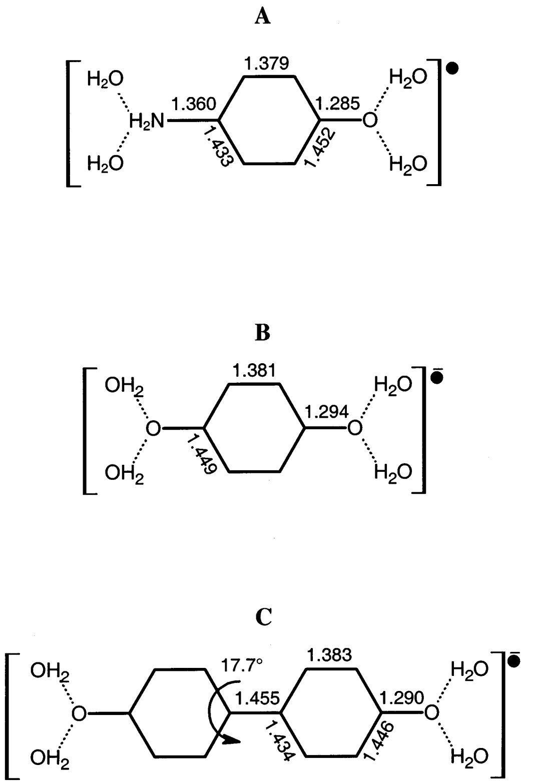

Figure 8. BPW91/6-31+G** CO bond lengths in (A) $H_2NC_6H_4O^{\bullet}\cdot 4H_2O$ and (B) $C_6H_4O_2^{-\bullet}\cdot 4H_2O$. (C) The calculated CO and inter-ring CC lengths and dihedral angle in $C_{12}H_8O_2^{-\bullet}\cdot 4H_2O$.

vibrational modes can appear in the RR spectra of a $\boldsymbol{D_2}$ molecule because of vibronic coupling between the resonant and close by electronic states, they should generally relate to the "g" (gerade) vibrational modes of $\boldsymbol{D_{2h}}$ point group. Also, they should not always accompany the Franck−Condon enhanced vibrational modes of $\mathbf{a_{1g}}$ ($\boldsymbol{D_{2h}}$) parentage. The sidebands seen in ethanol matrix are unlikely to be resolved in aqueous solution, as the bands become considerably broader. However, prominent higher frequency bands (>1200 cm^{-1}) recorded at low slit width (~6 cm^{-1}) of the Raman spectrometer do show considerable asymmetry on the lower frequency side. The structural conclusions based on the observed RR spectra and symmetry arguments are consistent with the calculated frequencies, as discussed in the following section.

5. Calculated Molecular Geometry and Vibrational Frequencies. Figure 8C presents the optimized BPW91/6-31+G** molecular geometry of $C_{12}H_8O_2^{-\bullet}\cdot 4H_2O$. It is nonplanar ($\boldsymbol{D_2}$), with the inter-ring twist (17.7°) reduced to roughly half of its value in the parent dianion (34.4°). The effect of symmetrically associating two water molecules on each oxygen site has small influence on the CO bond lengths (an increase of 0.013 Å) and negligible influence (0.3°) on the inter-ring twist angle and leads to a slightly better agreement with the experimental frequencies in water. The calculated inter-ring CC bond length of 1.455 Å is somewhat shorter than the value 1.488 Å calculated for the parent dianion. Thus, on radical formation there is a small increase in the π conjugation between the rings. The CO bond lengths in hydrogen bonded $C_{12}H_8O_2^{-\bullet}$ (1.290 Å) and $C_6H_4O_2^{-\bullet}$ (1.294 Å), calculated at the same level of theory, are comparable (Figure 8).

The experimental RR spectra suggest a less symmetric molecular geometry of the radical in water than the calculated $\boldsymbol{D_2}$ structure given in Figure 8C. Although one can induce asymmetry in the calculated structure by hydrogen bonding the two oxygen atoms of the radical with different numbers of water molecules, such an exercise would be of little physical significance. The molecular symmetry has only a minor effect on the vibrational frequencies of phenyl systems. It mostly affects the selection rules and RR enhancement pattern. Comparison of the experimental RR frequencies of $C_{12}H_8O_2^{-\bullet}$ in water and calculated $\boldsymbol{D_{2h}}$ symmetry-allowed frequencies of $C_{12}H_8O_2^{-\bullet}\cdot 4H_2O$, given in Table 2, shows good agreement. The predominantly inter-ring CC stretching mode, observed at 1332 cm^{-1}, is calculated at 1307 cm^{-1}. An even better agreement is seen in the frequency of this mode in the perdeuterated radical (1375 vs 1373 cm^{-1}). Several modes in the 1300−1600 cm^{-1} region contain contributions from the in-phase CO stretching motion. The maximum contribution is made to the 1405 cm^{-1} mode, consistent with the calculated CO bond length of 1.290 Å. However, this mode is only weakly enhanced in the RR spectrum, suggesting that the resonant excited state may not involve a large change in the CO bond length. The vibrational modes are approximately similar in composition to those of the single ring systems, such as para-substituted phenoxyl radicals.[4]

The four modes that would be out-of-plane $\mathbf{a_u}$ motions for a planar $\boldsymbol{D_{2h}}$ geometry, but are totally symmetric for a ring-twisted $\boldsymbol{D_2}$ geometry, are of critical importance in ascertaining the nonplanarity of the radical structure. These are calculated at 936, 772, 398, and 65 cm^{-1}. Two of them have been observed at 911 and 398 cm^{-1} (Table 3). Although these bands are extremely weak, as anticipated, the agreement between the calculated and experimental frequencies for these modes supports a twisted molecular configuration for the radical.

The out-of-phase coupled local a_1 phenyl vibrations, calculated at 1605, 1495, 1162, and 768 cm^{-1}, which are nontotally symmetric ($\mathbf{b_1}$) in a twisted $\boldsymbol{D_2}$ geometry, have been seen at 1591, 1530, 1186, and 798 cm^{-1} in ethanol matrix, as weak companions of prominently enhanced in-phase a_1 vibrations (Table 3). The very weak bands observed at 1150, 1088, 527, 263, and 223 cm^{-1} in water, calculated at 1162, 1104/1101, 529/ 521, 235, and 211 cm^{-1}, are also assignable to only nontotally symmetric vibrations in $\boldsymbol{D_2}$ geometry (Table 3). The observation of vibrational modes in the RR spectra of $C_{12}H_8O_2^{-\bullet}$ in water and ethanol matrix that are symmetry-forbidden in $\mathbf{D_{2h}}$ and Franck−Condon-forbidden (nontotally symmetric) in D_2 molecular symmetry is an indication of a lower symmetry ($\boldsymbol{C_1}$) of the radical structure.

The discrepancy noted above between the molecular symmetry of the aqueous radical as determined from the RR spectra ($\boldsymbol{C_1}$) and the DFT predicted symmetry ($\boldsymbol{D_2}$) of the radical hydrate can be readily reconciled. In aqueous solution, the hydrogen bonds are continuously formed and broken, on a time-scale (~10^{-12} s) much longer than the intramolecular vibrational period. The two CO bonds in $C_{12}H_8O_2^{-\bullet}$ can differ by as much as 0.013 Å (the difference between the calculated CO bond lengths in $C_{12}H_8O_2^{-\bullet}$ and $C_{12}H_8O_2^{-\bullet}\cdot 4H_2O$) on the time-scale of molecular vibrations. Fluctuation in the CO bond lengths contributes toward Raman line broadening and relaxation of selection rules. Calculations on the fully hydrogen-bonded radical hydrate essentially model the time-averaged effect of hydrogen bonding on the radical properties in water.

6. Proton Reactivity and the CO Bonds. It has been pointed out in an earlier work that the proximity of the calculated and RR frequencies is not sufficient to ensure reliability of the calculated structures in aromatic oxy radicals; in addition, conformity with some chemical properties is required.[9] In this context, the relationship between the nature of CO bonds and their protonation behavior has been previously discussed.[9,31] In our simple approach, the bond length is expressed in terms of bond number (n), which is empirically related to the protonation pK_a. Thus, it is possible to predict the proton reactivity of a molecule (the probability of forming a proton-bound state, which relates to pK_a) if the CO bond length is known. Conversely, one can use the pK_a to estimate the bond length. Correlation between the calculated bond properties and protonation of closely related systems should establish the predictive value of the theoretical procedures and their limitations.

The BPW91/6-31+G** predictions of CO lengths in $C_6H_4O_2^{-\bullet}\cdot 4H_2O$ (1.294 Å) and p-$H_2NC_6H_4O^{\bullet}\cdot 4H_2O$ (1.285 Å) are consistent with predictions from the proton reactivity models (1.281 Å and 1.267 Å, respectively).[9] For $C_{12}H_8O_2^{-\bullet}\cdot 4H_2O$, the BPW91/6-31+G** CO bond length of 1.290 Å is close to the value estimated from the pK_a of ~7 (1.309 Å).[32,33]

Let us compare the protonation behavior of semiquinone anions, $C_6H_4O_2^{-\bullet}$ and $C_{12}H_8O_2^{-\bullet}$, with their parent dianions. On the basis of the relationship between the bond length (R_{CO} in Å) and bond number (n), given in an earlier paper,[9] R_{CO} changes with n according to the following expression:

$$\delta R_{CO}/\delta n = -0.355/(n + 0.16)[1 - (n - 1)/(0.84n + 0.16)] \tag{4}$$

Implicit in this relationship is $R_{C-O}(n = 1) - R_{C=O}(n = 2)$ difference, taken as 0.193 Å, and the ratio of the C=O and C−O stretching force constants, assumed to be 1.84, based on literature values.[9] A slightly different set of these parameters would have little effect on the analysis that follows. The bond number n is empirically related to the pK_a. For CO bonded systems

$$\delta n = -\delta pK_a/20 \tag{5}$$

based on experimental pK_a for $n = 2$, 1.5, and 1 in aliphatic systems.[9]

The calculated δR_{CO} (0.049 Å) for $C_6H_4O_2^{2-}$ (1.343 Å) to $C_6H_4O_2^{-\bullet}$ (1.294 Å) corresponds to a drop of about six units in pK_a. This agrees well with the experimental finding that $C_6H_4O_2^{-\bullet}$ protonates at about seven units lower pH than its reduced hydroquinone state ($C_6H_4O_2^{2-}$) in water.[11] The change in the calculated CO length ($\delta R_{CO} = 0.031$ Å) from $C_{12}H_8O_2^{2-}$ (1.321 Å) to $C_{12}H_8O_2^{-\bullet}$ (1.290 Å) is relatively smaller. The proton attachment to $C_{12}H_8O_2^{-\bullet}$ is predicted to occur with pK_a ~ 3.5 units lower than for $C_{12}H_8O_2^{2-}$. Considering the protonation behavior of $C_{12}H_8O_2^{2-}$ to be similar to that of $C_6H_5O^-$ and $C_6H_4O_2^{2-}$ (pK_a 11 ± 1), we predict that $C_{12}H_8O_2^{-\bullet}$ should protonate with a pK_a of 7.5 (±1) (measured pK_a ~ 7). These astonishingly good agreements for both semiquinone anions suggest that the BPW91/6-31+G** structures relate well with the proton reactivities of dihydroxy aromatics in their different redox states, using the relationship between the bond length and protonation pK_a given in eqs 4 and 5.

In the above analysis, variation in the proton reactivity from radical anion to parent dianions is correlated with the change in the CO length, which minimizes the effect of systematic errors in calculations. Comparison between the phenyl and biphenyl systems should provide insight into the magnitude of the error. To illustrate this point, we consider the proton reactivity of radicals relative to $C_6H_4O_2^{-\bullet}$. In aqueous $H_2NC_6H_4O^{\bullet}$, the calculated CO bond is 0.009 Å (δR_{CO}) shorter than in $C_6H_4O_2^{-\bullet}$ (Figure 8), which corresponds to $\delta pK_a = -1.2$. Making correction for the statistical factor of 2 for attachment of the proton on either of the oxygen sites in $C_6H_4O_2^{-\bullet}$, a decrease of 1.5 in pK_a is predicted, close to the observed one (1.8).[34] This is a very good agreement between the predicted and experimental values, particularly because the aqueous p-$H_2NC_6H_4O^{\bullet}$ is an extreme case; that is, it is charge neutral. The calculated CO bonds for aqueous $C_{12}H_8O_2^{-\bullet}$ are almost equal (shorter by 0.004 Å; $\delta pK_a \sim -0.5$) to those of $C_6H_4O_2^{-\bullet}$. However, the pK_a of $C_{12}H_8O_2^{-\bullet}$ is about three units higher. This discrepancy may arise due to noncancellation of systematic errors between the calculated bond properties in phenyl and biphenyl systems.

The relationship in eq 5 is empirically derived, but it is rationalized in terms of an electrostatic model of acid−base equilibria.[9,31] It is assumed that the proton encounters the basic form of the molecule (anion/dianion) at a diffusion-controlled rate, but the rate at which it is released depends on the Coulomb interaction energy between the two. Comparison of the charge distributions in $C_6H_4O_2^{-\bullet}$ and $C_{12}H_8O_2^{-\bullet}$, based on Mulliken population analysis, shows almost identical negative electronic charge on the O atoms in the two radicals. Therefore, they are expected to display similar affinity toward the proton, as concluded from the calculated bond lengths.

It is not surprising that the CO lengths and charge on O are lower in the BPW91/6-31+G** geometries of $C_{12}H_8O_2^{-\bullet}$ and $C_{12}H_8O_2^{2-}$, in comparison to those of $C_6H_4O_2^{-\bullet}$ and $C_6H_4O_2^{2-}$. DFT calculations are known to predict a shorter CO bond in $C_6H_5O^-$ than expected from the RR spectra.[24−27] The local symmetry of the phenyl groups in $C_{12}H_8O_2^{-\bullet}$ and in $C_{12}H_8O_2^{2-}$ is similar to that of $C_6H_5O^-$. The proton reactivities suggest that the CO bonds in biphenyl systems may be underestimated, by ~0.02 Å, relative to the bonds in phenyl systems. This difference is small, compared to the spread in calculated bond lengths using different theoretical procedures.[9] However, it is sufficient to produce consistency between the CO bond structure, resonance Raman spectra, and proton reactivity of the semiquinone radical anions and parent dianions containing single as well as biphenyl rings. Exceptions to eq 2 should be considered if the vibrational spectra are correctly predicted but not the reactivity, but that is not the case here. Presently, resonance Raman and theoretical investigations on very few aqueous molecular ions and radicals containing the $-C_6H_4O^-$ moiety are available, which precludes generalization of this critical analysis of the structure and reactivity.

Structural computations have been reported recently on $C_6H_5O^-$ using a number of computational procedures and different basis sets.[27] The lowest predicted CO stretching frequency is about 100 cm^{-1} higher than the experimental frequency. We know from the preceding analysis that the electronic charge on the oxygen atom is underestimated in these computations. To make the predicted CO length and frequency consistent with the spectroscopic observations, calculations have been performed on $C_6H_5O^-Li^+$ and $C_6H_5O^-Na^+$ complexes, as models for aqueous $C_6H_5O^-$ in basic solutions (e.g., pH ~ 13).[27] It can be readily visualized that Coulombic attraction of a positive ion pulls the electronic charge from ring to O. The CO bond can be elongated this way by 0.03−0.05 Å from its vacuum length. Unfortunately, such models are unrealistic for the situation in dilute salt solution, and are inconsistent with the proton reactivity of the aqueous $-C_6H_4O^-$.

Summary

We report, in this work, experimental and theoretical studies of the electronic and vibrational structure of the aqueous p,p'-biphenylsemiquinone radical anion and its reduced dianion state as prototypes of bridged aromatics with CC linkage. These molecular anions provide good model systems for addressing the following questions: (1) In a highly nonplanar biphenyl-type system, the transfer of an electron to an oxidizing species would occur initially from one phenyl site. Does the resulting charge reorganization in the oxidized radical state require coplanarity of the rings and can the charge get equally distributed over them? (2). It is known that DFT calculations do not provide satisfactory description of the bond properties in phenolate anions ($XC_6H_4O^-$) but that they work well for semiquinone anion ($C_6H_4O_2^{-\bullet}$) and dianion ($C_6H_4O_2^{2-}$) of hydroquinone. Does the inadequacy of DFT for structural description of $XC_6H_4O^-$ extend to the semiquinone anion ($C_{12}H_8O_2^{-\bullet}$) and dianion ($C_{12}H_8O_2^{2-}$) of biphenol and to what extent?

This study shows that $C_{12}H_8O_2^{2-}$ is highly nonplanar, with inter-ring dihedral angle similar to that of liquid and gas-phase biphenyl. There is very little π overlap between the rings. On the loss of an electron, the charge gets removed equally from each substituted phenyl component leading to a significant reduction in the torsional distortion of the molecular geometry, which increases π conjugation between the rings and shortens the inter-ring CC bond. However, the radical anion does not attain a strictly planar geometry. The nature of the CO bonds in the *p*,*p*′-biphenylsemiquinone radical anion is closer to that of the *p*-benzosemiquinone radical anion and not to a typical para-substituted phenoxyl radical.

The BPW91/6-31+G** CO stretching frequencies in $C_6H_4O_2^{-\bullet}$ and its parent $C_6H_4O_2^{2-}$ are in excellent agreement with the experimental Raman frequencies. The CO bond lengths also correlate well with the observed acid−base equilibria. On the other hand, the BPW91/6-31+G** CO frequency in $C_6H_5O^-$ is about 100 cm^{-1} higher than the experimental frequency, and the bond is considerably shorter than expected from the proton reactivity of the anion. The BPW91/6-31+G** CO bonds in $C_6H_5O^-$ and $C_{12}H_8O_2^{2-}$ are of nearly the same length. However, there is a good correspondence between the decrease in CO bond length from $C_{12}H_8O_2^{2-}$ to $C_{12}H_8O_2^{-\bullet}$ and drop in pH at which a proton can bond to O. The spectroscopic and chemical evidence taken together indicate that the effective electronic charge on O and the CO bond lengths are underestimated in $C_6H_5O^-$, $C_{12}H_8O_2^{2-}$, and $C_{12}H_8O_2^{-\bullet}$. In other words, the DFT calculations put more electronic charge on the ring and not enough on O in the $XC_6H_4O^-$ ($X \neq O$) moiety, which is common to all three ions. The consequent underestimation in bond length amounts to ∼0.02 Å.

Acknowledgment. The authors thank Professor R. W. Fessenden for confirming an unexpectedly high pK_a of *p*,*p*′-biphenylsemiquinone by ESR and to Professor von Sonntag for bringing this unusual behavior for a semiquinone to our notice. The research described herein was supported by the Office of Basic Energy Sciences of the Department of Energy. This is Contribution No. NDRL 4375 from the Notre Dame Radiation Laboratory.

References and Notes

(1) Pauling, L. *The Nature of the Chemical Bond*; Cornell University Press: Ithaca, New York, 1960.

(2) *The chemistry of Quinonoid Compounds*; Patai, S., Ed.; John Wiley & Sons: New York, 1974. *Functions of Quinones in Energy Converting Systems*; Trumpower, B. L., Ed.; Academic Press: New York, 1982. Okamura, M. Y.; Feher, G. *Annu. Rev. Biochem.* **1992**, *61*, 861. Mason, R. P. In *Free radicals in Biology*; Pryor, W. A., Ed; Academic Press: New York, 1982; Vol. 5. Josephy, P. D.; Eling, T. E.; Mason, R. P. *Mol. Pharm.* **1983**, *23*, 461.

(3) von Sonntag, C. *The Chemical Basis of Radiation Biology*; Taylor and Francis: New York, 1987.

(4) Tripathi, G. N. R. In *Advances in Spectroscopy*, *Vol.18*, *Time-resolved Spectroscopy*; Clark, R. J. H., Hester, R. E., Eds.; John Wiley & Sons: New York, 1989; pp 157−218.

(5) Tripathi, G. N. R. *J. Chem. Phys.* **1981**, *74*, 6044. Tripathi, G. N. R.; Schuler, R. H. *J. Chem. Phys.* **1982**, *76*, 4289. Beck, S. M.; Brus, L. E. *J. Am. Chem. Soc.* **1982**, *104*, 4789. Schuler, R. H.; Tripathi, G. N. R.; Prebenda, M. F.; Chipman, D. M. *J. Phys. Chem.* **1983**, *87*, 5357. Chipman, D. M.; Prebenda, M. F. *J. Phys. Chem.* **1986**, *90*, 5557. Tripathi, G. N. R.; Schuler, R. H. *J. Phys. Chem.* **1987**, *91*, 5881. Tripathi, G. N. R.; Sun, Q.; Schuler, R. H. *Chem. Phys. Lett.* **1989**, *156*, 5881. Bauscher, M.; Mantele, W. *J. Phys. Chem.* **1992**, *96*, 11101. Raymond, K. S.; Wheeler, R. A. *J. Chem. Soc. Faraday Trans.* **1993**, *89*, 665. Tripathi, G. N. R.; Schuler, R. H. *J. Chem. Soc. Faraday Trans.* **1993**, *89*, 4177. Zhao, X.; Imahori, H.; Zhan, C.-G.; Sakata, Y.; Iwata, S.; Kutagawa, T. *J. Phys. Chem.* **1997**, *101*, 622. Nonella, M. *J. Phys. Chem.* **1997**, *101*, 1235. Zhan, C.-G.; Chipman, D. M. *J. Phys. Chem.* **1998**, *102*, 1230 and references cited in these papers.

(6) Dixon, W. T.; Murphy, D. *J. Chem. Soc., Faraday Trans. 2* **1976**, *72*, 1221 and references therein. Venkataraman, B.; Franckel, G. K. *J. Am. Chem. Soc.* **1955**, *77*, 7, 2707.

(7) Hester, R. E.; Williams, K. P. J. *J. Chem. Soc., Faraday Trans. 2* **1982**, *78*, 573.

(8) Tripathi, G. N. R. *J. Am. Chem. Soc.* **1998**, *120*, 5134.

(9) Tripathi G. N. R. *J. Phys. Chem.* **1998**, *102*, 2388.

(10) Chipman, D. M. *J. Phys. Chem.* **2000**, *104*, 11816 and references therein.

(11) Steenken, S.; Neta, P. *Transient Phenoxyl Radicals: Formation and Properties in Aqueous Solution* (Preprint, provided as a private communication).

(12) Das, T. N. *J. Phys. Chem.* **2001**, *105*, 1230.

(13) ESR measurements by Professor R. W. Fessenden in our laboratory on a solution in water mixed with ethanol gave a tentative pK_a value of 6.9, in agreement with the value provided by Professor von Sonntag of Max Planck Institute, Mulheim, Germany (private communication) and also reported in ref 12.

(14) Petránek, J.; Pilaø, J.; Ryba, O. *Collection Czech. Chem. Commun.* **1970**, *35*, 2571.

(15) Barrett, R. M.; Steele, D. *J. Mol. Struct.* **1972**, *11*, 105.

(16) Buxton, G. V.; Greenstock, C. L.; Helman, W. P.; Ross, A. B. *J. Phys. Chem. Ref. Data* **1988**, *17*, 513.

(17) Tripathi, G. N. R. In *Multichannel Image Detectors II*; Talmi, Y., Ed.; ACS Symposium Series 236; American Chemical Society: Washington, DC, 1983; p 171. Patterson, L. K.; Lilie, J. *Int. J. Radiat. Phys. Chem.* **1974**, *6*, 129. Janata, E.; Schuler, R. H. *J. Phys. Chem.* **1982**, *86*, 2078.

(18) Becke, A. D. *Phys. Rev. A* **1988**, *38*, 3098. Perdew, J. P.; Wang, Y. *Phys. Rev. B* **1992**, *45*, 13244.

(19) Hehre, W. J.; Ditchfield, R.; Pople, J. A. *J. Chem. Phys.* **1972**, *56*, 2257. Hariharan, P. C.; Pople, J. A. *Theor. Chim. Acta* **1973**, *28*, 213. Clark, T.; Chandrasekhar, J.; Spitznagel, G. W.; Schleyer, P. v. R. *J. Comput. Chem.* **1983**, *4*, 294.

(20) Frisch, M. J.; Trucks, G. W.; Schlegel, H. B.; Scuseria, G. E.; Robb, M. A.; Cheeseman, J. R.; Zakrzewski, V. G.; Montgomery, J. A., Jr.; Stratmann, R. E.; Burant, J. C.; Dapprich, S.; Millam, J. M.; Daniels, A. D.; Kudin, K. N.; Strain, M. C.; Farkas, O.; Tomasi, J.; Barone, V.; Cossi, M.; Cammi, R.; Mennucci, B.; Pomelli, C.; Adamo, C.; Clifford, S.; Ochterski, J.; Petersson, G. A.; Ayala, P. Y.; Cui, Q.; Morokuma, K.; Malick, D. K.; Rabuck, A. D.; Raghavachari, K.; Foresman, J. B.; Cioslowski, J.; Ortiz, J. V.; Stefanov, B. B.; Liu, G.; Liashenko, A.; Piskorz, P.; Komaromi, I.; Gomperts, R.; Martin, R. L.; Fox, D. J.; Keith, T.; Al-Laham, M. A.; Peng, C. Y.; Nanayakkara, A.; Gonzalez, C.; Challacombe, M.; Gill, P. M. W.; Johnson, B. G.; Chen, W.; Wong, M. W.; Andres, J. L.; Head-Gordon, M.; Replogle, E. S.; Pople, J. A. *Gaussian 98*, revision A.9; Gaussian, Inc.: Pittsburgh, PA, 1998.

(21) Pulay, P.; Torok, F. *Acta Chim. Hung.* **1965**, *47*, 273.

(22) Serjeant, E. P.; Dempsey, P. *Ionization Constants of Organic acids in Aqueous solution*; Pergamon Press: Oxford, U.K., 1979.

(23) Wilson notations are used for convenience. See Dollish, F. R.; Fateley, W. G.; Bentley, F. F. *Characteristic Raman Frequencies of Organic Compounds*; John Wiley and Sons: New York, 1974; for reference.

(24) The CO stretching frequency of 1264 cm^{-1} in the resonance Raman spectrum of aqueous $C_6H_5O^-$ (ref 25) suggests that the CO bond is almost a single bond. The DFT calculation, on the other hand, predicts this frequency in the 1400 cm^{-1} region (ref 26 and 27), which is a consequence of the unusually short calculated CO bond having considerable double bond character.

(25) Mukherjee, A.; McGlashen, Z.; Spiro, T. G. *J. Phys. Chem.* **1995**, *99*, 4912.

(26) Nwobi, O.; Higgins, J.; Zhou, X.; Liu, R. *Chem. Phys. Lett.* **1997**, *272*, 155.

(27) Suter, H. U.; Nonella, M. *J. Phys. Chem. A* **1998**, *102*, 10128.

(28) Nonhebel, D. C.; Walton, J. C. *Free-radical Chemistry. Structure and Mechanism*; Cambridge University Press: New York, 1974.

(29) Albrecht, A. C. *J. Chem. Phys.* **1961**, *34*, 1476

(30) Bold letters are used for representation of the overall molecular symmetry and the symmetry species of all normal modes, whereas regular case letters are used for the local symmetry of each component phenyl group and its associated local modes.

(31) Tripathi, G. N. R.; Su, Y.; Bentley, J. *J. Am. Chem. Soc.* **1995**, *117*, 5540. Tripathi, G. N. R.; Su, Y.; Bentley, J.; Fessenden, R. W.; Jiang, P.-Y. *J. Am. Chem. Soc.* **1996**, *118*, 2245. Tripathi, G. N. R.; Su, Y. *J. Am. Chem. Soc.* **1996**, *118*, 2235. Su, Y.; Tripathi, G. N. R. *J. Am. Chem. Soc.* **1994**, *116*, 4405.

(32) Based on pK_a, the CO bonds in $C_{12}H_8O_2$-• are ascribed to $n = 1.4$ which corresponds to the bond lengths of 1.309 Å in the proton reactivity model (see ref 9).

(33) The proton reactivity model suggests a CO bond of 1.342 Å in $C_6H_5O^-$, 1.355 Å in $C_6H_4O_2^{2-}$ and 1.350 (±0.01) Å in $C_{12}H_8O_2^{2-}$.

(34) Sun, Q.; Tripathi, G. N. R.; Schuler, R. H. *J. Phys. Chem.* **1990**, *94*, 6273.