11816 *J. Phys. Chem. A* **2000,** *104,* 11816−11821

Hydrogen-Bonding Effects on Free-Radical Properties

Daniel M. Chipman*

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

Received: August 23, 2000; In Final Form: October 3, 2000

Hydrogen-bonding effects on structures, vibrational frequencies, and isotropic hyperfine coupling constants are investigated in semiquinone, phenoxyl, and closely related amine-substituted radicals. Included are the disubstituted isoelectronic series of *p*-benzosemiquinone anion, *p*-phenylenediamine cation, and *p*-aminophenoxyl neutral radicals, as well as the corresponding monosubstituted isoelectronic series of phenoxyl and aniline cation radicals. Computational studies that include all hydrogen-bound first shell water molecules, corresponding to two water molecules coordinated at each oxygen substituent and two coordinated at each amine substituent, give satisfactory agreement with aqueous experimental results in nearly all cases. In those instances where experimental results are also available in non-hydrogen-bonding environments for comparison, the calculations rationalize the signs and most approximate magnitudes of the experimental shifts attributable to hydrogen bonding. Asymmetric solvation structures, corresponding to fewer than the maximum number of hydrogen-bound water molecules, are also investigated. These show that the influences of individual water molecules are often, but not always, additive in determining vibrational frequency shifts. Asymmetric solvation can have a large influence on the spin distribution, where individual effects from each water are often largely canceled out to yield smaller net shifts when the hydrogen-bonding shell is completed.

Introduction

Hydrogen-bonding effects are believed important in dictating the very different roles of apparently similar semiquinones in the fundamental electron transfer steps of photosynthesis.[1−3] To improve basic understanding of such phenomena, this work computationally examines the way hydrogen bonding influences the structures, vibrational frequencies, and isotropic hyperfine coupling constants (hfc) in a series of semiquinone, phenoxyl, and closely related related amine-substituted radicals. Included are the three disubstituted isoelectronic radicals *p*-benzosemiquinone anion $C_6H_4O_2^-$, *p*-phenylenediamine cation $C_6H_4(NH_2)_2^+$, and *p*-aminophenoxyl neutral $C_6H_4ONH_2$, as well as the corresponding two monsubstituted isoelectronic radicals phenoxyl C_6H_5O and aniline cation $C_6H_5NH_2^+$.

A number of recent calculations have given satisfactory accounts of vibrational frequencies[4−7] and hfc[4−7] in phenoxyl, of vibrational frequencies[8−12] and hfc[10,13,14] in *p*-benzosemiquinone anion, of vibrational frequencies[15] in *p*-phenylenediamine cation, and of vibrational frequencies[16] and hfc[16] in *p*-aminophenoxyl radical. Hydrogen-bonding effects have also been investigated in several of these studies, by examining shifts of vibrational frequencies[12] and hfc[13,14] in *p*-benzosemiquinone anion and of vibrational frequencies[16] and hfc[16] in *p*-aminophenoxyl radical.

Of course, static models are oversimplified since hydrogen bonds are continually being formed and broken in solution. In this regard, the present contribution augments these previous studies by further considering in more detail how the properties of interest change with varying numbers of hydrogen bonds. In addition, this study is also designed to provide facile comparisons among isoelectronic series of radicals. By calculating all these related systems with a uniform and satisfactory level of theory, further insight is obtained on trends that might otherwise escape notice.

Computational Methods

The BPW91 method, which combines Becke's 1988 exchange functional[17] with the Perdew−Wang 91 correlation functional,[18] was used for structural characterization. This method has previously been found to provide a good description of the vibrational frequencies in *p*-benzosemiquinone anion[11,12] and in *p*-aminophenoxyl.[16] We have previously emphasized the difficulties in obtaining proper structures for the phenoxyl[4] and *p*-aminophenoxyl[16] radicals from traditional Hartree−Fock and multiconfiguration self-consistent-field methods. The BPW91 energetic, geometric, and force field evaluations were obtained with the split-valence plus heavy-atom polarization 6-31G* basis set.[19,20] We have previously reported[12] analogous calculations on *p*-benzosemiquinone anion using a larger basis set including polarization functions on hydrogens and diffuse functions on oxygens. The larger basis set led to generally even better agreement with experimental vibrational frequencies than does the smaller calculation reported here.

Vibrational frequencies were obtained from analytic second derivatives evaluated at the computed local minimum geometry. The composition of each normal mode in terms of local mode contributions was obtained by the total energy distribution method.[21]

Neither the BPW91 method nor the 6-31G* basis set[22] is very reliable for spin densities. Therefore, hfc were determined instead using the B3LYP method,[23,24] which is known to often perform well for this property,[22,25,26] together with a [631|41] basis set[27] that has previously been specially designed for the purpose. These were single-point calculations carried out at the respective BPW91/6-31G* geometries.

Hydrogen bond energies, obtained as the energies required to remove the bound water molecules, were corrected for basis set superposition error by the widely accepted full counterpoise method.[28,29] This procedure gives the dominant electronic

10.1021/jp003039z CCC: $19.00

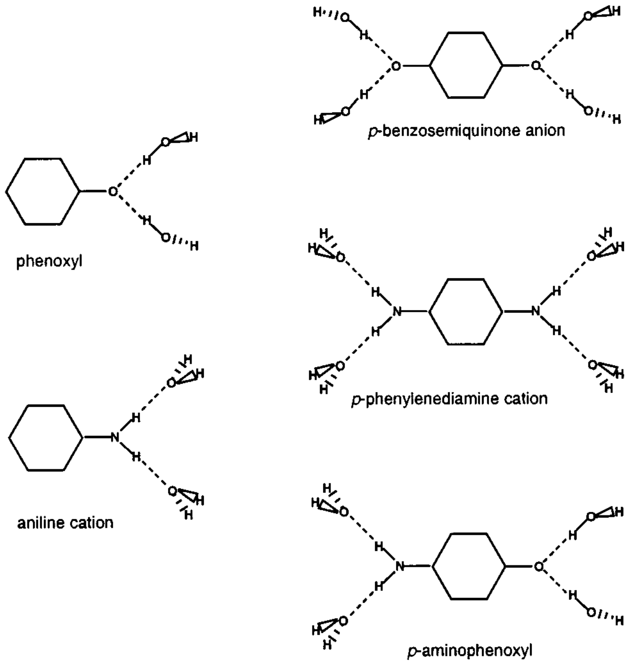

Figure 1. Structures of radicals with the maximum number of first-shell hydrogen bonds at the heteroatom substituents.

contributions to the hydrogen bond strengths; no attempt was made to include vibrational contributions.

The calculations were carried out with the Gaussian-94 program.[30]

Pilot studies indicated that each oxygen and/or amine substituent could hydrogen bond with up to two water molecules. An amine substituent acts as a hydrogen bond donor by coordinating to the oxygen atom of a water molecule, generally leading to only one possible local minimum structure. In contrast, an oxygen substituent acts as a hydrogen bond acceptor by coordinating to one hydrogen atom of a water molecule, often leaving several possible local minima of nearly equal energy for various relative out-of-plane orientations of the remaining dangling hydrogen atoms. A published study on *p*-benzosemiquinone anion[12] and our unpublished exploratory studies on the other species considered have indicated that the orientations of such dangling hydrogens have little effect on any of the properties of interest here. In the present work the only possibility reported corresponds to the most highly symmetric local minimum overall structure that could be obtained for each system.

The resulting supermolecule complexes are designated as $C_6H_5O{\cdot}2w$, $C_6H_5NH_2^+{\cdot}2w$, $C_6H_4O_2^-{\cdot}4w$, $C_6H_4(NH_2)_2^+{\cdot}4w$, and $C_6H_4ONH_2{\cdot}4w$, where the notation *n*w indicates the total number of hydrogen bound water molecules. Structures obtained for each radical with the maximum number of hydrogen-bound water molecules are sketched in Figure 1.

Further calculations were carried out on each radical with fewer than the maximum number of hydrogen bonds. In a given radical, such asymmetric solvation often caused significant differences in properties at the two ends of the molecule, especially at the heteroatoms, but generally caused only modest changes in properties at the nominally equivalent lateral positions, e.g., properties about C_2 remained nearly equivalent to those about C_6 and similarly C_3 to C_5. In the interest of brevity, we therefore present for the most part detailed results only for those partially solvated structures in the disubstituted radicals that have two water molecules both coordinated at the same substituent, thus maximizing the asymmetry of interest.

TABLE 1: Average Hydrogen Bond Strengths (in kcal/mol) and Amount of Charge Transfer to Each Hydrogen-Bonded Water Molecule

	H-bond energy	charge transfer
$C_6H_5O{\cdot}2w$	4.2	0.01
$C_6H_5NH_2^+{\cdot}2w$	15.1	−0.09
$C_6H_4O_2^-{\cdot}4w$	9.3	0.06
$C_6H_4(NH_2)_2^+{\cdot}4w$	11.4	−0.08
$C_6H_4ONH_2{\cdot}4w$	5.4	0.03 (at O) −0.07 (at NH_2)

Structures of monosubstituted radicals with one water molecule and structures of disubstituted radicals with either one or three water molecules generally gave results intermediate between those found for the structures that are presented here in detail.

Results and Discussion

Hydrogen Bond Characteristics. The average hydrogen bond strength in a given complex can be defined as the energy required to remove all the bound water molecules, divided by the number of such water molecules. The calculations give average hydrogen bond strengths shown in the second column of Table 1. Further calculations, not reported in detail, were also carried out to determine individual hydrogen bond strengths for stepwise addition of water molecules. The first water to be added is always bound more strongly than the average, and the last less strongly than the average. But the differences are not large, and the individual hydrogen bond strengths in any given radical never deviate by more than 20% from the reported average. It may be concluded that the individual hydrogen bond strengths are roughly additive.

The average hydrogen bond strengths are quite substantial in each of the ions, being highest at amine sites and also quite high at oxygen sites. Comparing the two neutral radicals, the average hydrogen bond strength is larger in the radical having both oxygen and amine sites than in the radical having only an oxygen site. In light of this, it is surprising that within the $C_6H_4ONH_2{\cdot}4w$ radical that has both oxygen and amine sites the individual hydrogen bond strengths at the oxygen substituent are higher than the average, while the individual hydrogen bond strengths at the amine substituent are lower than the average. Therefore, no simple conclusion can be made regarding the relative strengths of hydrogen bonds to oxygen and amine sites in the neutral radicals.

Analogous BPW91/6-31G* calculation gives the hydrogen bond strength in water dimer to be 4.5 kcal/mol, which compares favorably to the semiexperimental result for the electronic contribution[31] of 5.4 kcal/mol. Thus, the average hydrogen bond strength in each of the radicals is comparable to or larger than that in water dimer. This suggests that the structures considered here can be taken as representative of those occurring in the actual aqueous phase.

Mulliken population analysis can be used to examine charge transfer to or from the substituents and their respective bound water molecules, giving results reported in the third column of Table 1. Because of uncertainties associated with Mulliken analysis, the actual numbers should be taken to have only qualitative significance and will be used only to indicate trends. Oxygen substituents are found to donate electron density to water, whereas amine substituents accept electron density from water. This effect is larger at amine substituents than at oxygen substituents. For a given type of substituent, it is larger in the ionic radicals than in the neutral radicals, this contrast being greater with oxygen than with amine substituents.

TABLE 2: Selected Bond Distances (in Å)[a]

	R(CO)	*R*(CN)	*R*(C_1C_2)	*R*(C_2C_3)	*R*(C_3C_4)
		Phenoxyl			
C_6H_5O	1.265		1.462	1.385	1.416
$C_6H_5O\cdot 2w$	1.279		1.457	1.384	1.418
		Aniline Cation			
$C_6H_5NH_2^+$		1.345	1.441	1.382	1.421
$C_6H_5NH_2^+\cdot 2w$		1.342	1.442	1.384	1.418
		p-Benzosemiquinone Anion			
$C_6H_4O_2^-$	1.276		1.460	1.381	1.460
$C_6H_4O_2^-\cdot 2w$ (at C_1-O)	1.300, 1.272		1.448	1.380	1.461
$C_6H_4O_2^-\cdot 4w$	1.294		1.450	1.379	1.450
		p-Phenylenediamine Cation			
$C_6H_4(NH_2)_2^+$		1.352	1.434	1.377	1.434
$C_6H_4(NH_2)_2^+\cdot 2w$ (at C_1-NH_2)		1.346, 1.357	1.437	1.377	1.432
$C_6H_4(NH_2)_2^+\cdot 4w$		1.350	1.436	1.377	1.436
		p-Aminophenoxyl			
$C_6H_4ONH_2$	1.263	1.378	1.462	1.379	1.428
$C_6H_4ONH_2\cdot 2w$ (at C_1-O)	1.281	1.369	1.454	1.378	1.429
$C_6H_4ONH_2\cdot 2w$ (at C_4-NH_2)	1.264	1.362	1.462	1.379	1.432
$C_6H_4ONH_2\cdot 4w$	1.284	1.357	1.453	1.377	1.433

[a] In cases where asymmetric solvation causes otherwise equivalent values of *R*(CO) or *R*(CN) to differ at the C_1 and C_4 positions, the value at the C_1 position is listed first.

Geometrical Parameters. In all but one case the rings and substituents are found to be planar. The lone exception is *p*-aminophenoxyl radical, where the issue of planarity has been discussed at length previously.[16] To summarize, it was found[16] in isolated *p*-aminophenoxyl radical that pyramidalization occurs at nitrogen to give a nonplanar equilibrium structure. However, the barrier to planarity is less than the zero-point vibrational energy in the corresponding inversion mode, so the actual structure should be regarded as quasiplanar. When four hydrogen-bonded water molecules are included in the calculation, the equilibrium structure becomes strictly planar.

The effects of hydrogen-bonded water molecules on selected bond distances in each of the radicals are shown in Table 2.

First we consider the structural implications of forming hydrogen bonds at only one oxygen substituent. They are found to weaken the associated CO bonds, which become longer by 0.014 Å in $C_6H_4O\cdot 2w$, by 0.024 Å in $C_6H_4O_2^-\cdot 2w$, and by 0.018 Å in $C_6H_4ONH_2\cdot 2w$. They strengthen the adjacent C−C bonds, which become shorter by amounts ranging from 0.005−0.012 Å. Only small effects of ≤ 0.002 Å are found on any of the more remote C−C bonds. It is therefore interesting that the bonds to the remote para substituents are significantly strengthened, the distances becoming shorter by 0.004 Å for the remote CO bond in $C_6H_4O_2^-\cdot 2w$, and by 0.009 Å for the remote CN bond in $C_6H_4ONH_2\cdot 2w$.

Next we take up the implications of forming hydrogen bonds at only one amine substituent. They are found to strengthen the associated CN bonds, which become shorter by 0.003 Å in $C_6H_5NH_2^+\cdot 2w$, by 0.006 Å in $C_6H_4(NH_2)_2^+\cdot 2w$, and by 0.016 Å in $C_6H_4ONH_2\cdot 2w$. Only small effects of ≤ 0.004 Å are found on any of the ring C−C bonds. The bonds to the remote para substituents are weakened, the distances becoming longer by 0.005 Å for the remote CN bond in $C_6H_4(NH_2)_2^+\cdot 2w$, and by 0.001 Å for the remote CO bond in $C_6H_4ONH_2\cdot 2w$.

Finally, we consider forming hydrogen bonds simultaneously at both substituents. The CO bonds are weakened in $C_6H_4O_2^-\cdot 4w$, becoming longer by 0.018 Å. The CN bonds are slightly strengthened in $C_6H_4(NH_2)_2^+\cdot 4w$, becoming shorter by 0.002 Å. In $C_6H_4ONH_2\cdot 4w$ the CO bond is weakened, becoming longer by 0.019 Å, and the CN bond is strengthened, becoming shorter by 0.021 Å. These trends are all consistent with qualitatively additive contributions from the various tendencies noted above for forming hydrogen bonds at the individual sites.

It may be concluded that formation of hydrogen bonds at an oxygen substituent weakens the associated CO bond and strengthens a remote para CO or CN bond, whereas formation of hydrogen bonds at an amine substituent strengthens the associated CN bond and weakens a remote para CO or CN bond. These effects are larger for hydrogen bonds to oxygen than for hydrogen bonds to amine, and are larger at the immediate hydrogen-bonding site than at the remote site.

It should be mentioned that the CO bond lengths calculated here for the fully hydrogen-bonded radicals are in qualitative but not quantitative agreement with a simple model[32] based on use of aqueous experimental pK_a data to estimate bond order.

Vibrational Frequencies. The most powerful experimental tool for observation of free-radical vibrational frequencies is resonance Raman spectroscopy. In the interests of brevity we therefore present, for the most part, detailed results only for modes that are good candidates for resonance Raman observation. These are generally all the totally symmetric modes other than hydrogenic stretches. However, for completeness we also include for the high symmetry *p*-benzosemiquinone anion and *p*-phenylenediamine cation radicals non-totally symmetric modes of b_{1u} symmetry, which derive from totally symmetric modes examined in the other lower symmetry radicals.

For several of the vibrational modes being examined here there is strong mixing among various local atomic motions. This makes it very difficult to obtain a set of Wilson mode designations that consistently describes the proper correlation among corresponding modes in the various radicals. Indeed, somewhat arbitrary choices occasionally have been made in the experimental literature on these systems. To minimize confusion, we therefore eschew the Wilson designations and give only the dominant stretching or bending motion actually found in each calculated mode. It is emphasized that the oversimplified descriptions used here should not be taken too seriously.

Vibrational frequency results are reported and compared with experimental values in Table 3. The overall agreement between experimental and calculated freqencies is quite good. With only two exceptions (which are discussed and rationalized immediately below) the agreement is always within 25 cm^{-1}, and in the majority of cases the agreement is within 10 cm^{-1}.

The largest discrepancy between calculation and experiment comes with the CH bending mode in aniline cation that was experimentally assigned[37] to a weak band observed at 1338 cm^{-1} but is calculated to be above 1370 cm^{-1}. This suggests a possible reassignment of the experimental spectrum to make this totally symmetric mode correspond instead to the previously unidentified[37] medium intensity band observed at 1380 cm^{-1}. The weak experimental band at 1338 cm^{-1} may then correspond to a non-totally symmetric b_2 fundamental calculated at 1338 cm^{-1} in $C_6H_5NH_2^+$ (1346 cm^{-1} in $C_6H_5NH_2^+\cdot 2w$). Furthermore, the weak unidentified band observed[37] at 1458 cm^{-1} likely corresponds to a non-totally symmetric b_2 fundamental mode calculated at 1448 cm^{-1} in $C_6H_5NH_2^+$ (1462 cm^{-1} in $C_6H_5NH_2^+\cdot$ 2w).

The next largest discrepancy between calculation and experiment comes with the ring-breathing mode in *p*-benzosemiquinone anion observed at 830 cm^{-1} but calculated to be at or below 805 cm^{-1}. But here the calculated 804 cm^{-1} result for

TABLE 3: Calculated and Experimental Vibrational Frequencies (in cm^{-1})[m]

	CCC bend	CC stretch	CCC bend	CC stretch	CH bend	CH bend	CX stretch[a]	CX stretch[b]	CC stretch	NH_2 scissor
Phenoxyl										
calculation on C_6H_5O	514	788	958	996	1150	1398		1485	1566	
calculation on $C_6H_5O{\cdot}2w$	519	800	962	1001	1171	1391		1490	1575	
experiment in water[c]	528	801		990	1163	1398		1505	1557	
Aniline Cation										
calculation on $C_6H_5NH_2^+$	516	808	968	995	1191	1371*	1488*		1605	1657
calculation on $C_6H_5NH_2^+{\cdot}2w$	518	812	970	1002	1184	1375*	1495*		1596	1643
experiment in gas[d]	516	798	976		1169	1347			1581	
experiment in water[e]	521	820		1001	1175	1338[f]	1494		1574	
p-Benzosemiquinone Anion										
calculation on $C_6H_4O_2^-$	454	801	767*	938*	1128	1343	1480	1531	1617	
calculation on $C_6H_4O_2^-{\cdot}2w(\text{at } C_1{-}O)$	462	805	772*	952*	1147	1340	1455	1527	1617	
calculation on $C_6H_4O_2^-{\cdot}4w$	467	804[g]	777*	964*	1165	1341	1445	1514	1626	
experiment in acetonitrile[h]	470	819	780		1143	1347	1452		1609	
experiment in water[i]	484	830			1162		1434		1620	
p-Phenylenediamine Cation										
calculation on $C_6H_4(NH_2)_2^+$	457	834	772	974	1196	1344	1414	1529	1641*	1667*
calculation on $C_6H_4(NH_2)_2^+{\cdot}2w(\text{at } C_1{-}NH_2)$	459	834	773	978	1192	1343	1419	1533	1640*	1663*
calculation on $C_6H_4(NH_2)_2^+{\cdot}4w$	461	833	774	980	1190	1346	1425	1537	1644*	1662*
experiment in water[j]	467	840			1184		1423	1524	1644	1658
p-Aminophenoxyl										
calculation on $C_6H_4ONH_2$	454	810	766*	959*	1157	1320	1437	1527	1611	1647
calculation on $C_6H_4ONH_2{\cdot}2w(\text{at } C_1{-}O)$	458	823	772*	972*	1179	1329	1430	1521	1622	1649
calculation on $C_6H_4ONH_2{\cdot}2w(\text{at } C_4{-}NH_2)$	457	813	769*	959*	1152	1335	1451	1535	1624	1677
calculation on $C_6H_4ONH_2{\cdot}4w$	462	827	778*	973*	1174	1339	1441	1526	1634	1677[k]
experiment in water[l]	474	824			1168		1434	1518	1636	1673

[a] The first CX stretch mode listed corresponds to CN in $C_6H_5NH_2^+$, to CO + CO in $C_6H_4O_2^-$, to CN + CN in $C_6H_4(NH_2)_2^+$ and to CN in $C_6H_4ONH_2$. [b] The second CX stretch mode listed corresponds to CO in C_6H_5O, to CO−CO in $C_6H_4O_2^-$, to CN−CN in $C_6H_4(NH_2)_2^+$, and to CO in $C_6H_4ONH_2$. [c] From resonance Raman results in refs 33−35. [d] From photoelectron results in ref 36. [e] From resonance Raman results in ref 37. [f] This mode could be reassigned to a band at 1380 cm^{-1}. See text for discussion. [g] This frequency is artificially lowered by an accidental near degeneracy with a water mode. See text for discussion. [h] From infrared and resonance Raman results in ref 38. [i] From resonance Raman results in ref 38. [j] From resonance Raman results in ref 15. [k] This was previously assigned in ref 16 to a mode calculated at 1669 cm^{-1}, but that mode is actually dominated by solvent motions. A better assignment is to a mode calculated at 1677 cm^{-1} in which the NH_2 scissor motion is more prominent. [l] From resonance Raman results in ref 39. [m] In adjacently listed calculated modes marked with an asterisk the local atomic motions that are used for oversimplified labelling purposes are very strongly mixed.

$C_6H_4O_2^-{\cdot}4w$ is artificially depressed due to an accidental near degeneracy with a mode primarily composed of water molecule librations. This mixing was also noted in a previous calculation[12] with a larger basis set. Because no second shell water molecules are included in the calculation, this librational water mode is not representative of the actual aqueous environment. Thus, a somewhat higher unperturbed frequency should be taken for the mode calculated at 804 cm^{-1}, and this would improve agreement with experiment.

In most cases the agreement with experimental frequencies measured in water is better for the frequencies calculated in the hydrogen bonded species than in the isolated radicals. For aniline cation and *p*-benzosemiquinone anion, experimental data is available in non-hydrogen-bonding environments to allow closer examination of the actual shifts due to hydrogen bonding.

In aniline cation, comparison of $C_6H_5NH_2^+$ to $C_6H_5NH_2^+{\cdot}2w$ gives calculated hydrogen-bonding shifts of the same sign as seen in comparing gas to aqueous phase experimental results for the two lowest and one highest frequency mode where comparison is possible. However, the shifts disagree in sign for the two CH bending modes, or rather for just one if the reassignment of the higher frequency CH bending mode that was suggested above is accepted.

In *p*-benzosemiquinone anion the shifts due to hydrogen bonding can be judged by comparing experimental results in the non-hydrogen-bonding solvent acetonitrile to those in water. Since both acetonitrile and water are high dielectric solvents, long-range electrostatic interactions with solvent should largely cancel out in this comparison, thus focusing even more closely on the specific effects of hydrogen bonding than is possible in a gas−aqueous comparison. For this radical, the signs of hydrogen bonding shifts agree between calculation and experiment for all five modes where comparison is possible.

It should also be pointed out that the calculated hydrogen-bonding shifts in CO and CN stretching motions are generally consistent in sign with that expected from the bond weakening and/or strengthening effects noted in the previous section on structural considerations. Exceptions occur only for *p*-aminophenoxyl in the two intermediate structures each having two bound water molecules. Thus, binding two waters at the oxygen substituent gives the expected lowering of the CO stretch frequency but an unexpected lowering of the remote CN stretch frequency, and binding two waters at the amine substituent gives the expected raising of the CN stretch frequency but an unexpected raising of the remote CO stretch frequency. These individual influences lead to some partial cancellations, so that the net shifts in going from isolated $C_6H_4ONH_2$ to $C_6H_4ONH_2{\cdot}4w$ are rather small for the CO and CN stretching modes.

Isotropic Hyperfine Coupling Constants. Electron spin resonance spectra have been obtained for each of the radicals considered here, giving isotropic hyperfine coupling constants (hfc) for all hydrogen and nitrogen nuclei, and in *p*-benzosemiquinone anion for carbon-13 and oxygen-17 nuclei as well. Results are presented and compared to experimental values in Table 4. In phenoxyl and aniline cation radicals the hfc signs have not been determined experimentally, and consequently the results are shown as absolute values. However, comparison to the present as well as to most previous calculated results

TABLE 4: Isotropic Hyperfine Coupling Constants (in gauss)[a]

	$^{13}C_1$	$^{13}C_2$	$^{13}C_3$	$^{13}C_4$	^{17}O	^{14}N	H_2	H_3	H_4	H_N
Phenoxyl										
calculation on C_6H_5O	−13.4	8.4	−9.7	12.6	−9.1		−6.9	2.7	−8.8	
calculation on $C_6H_5O{\cdot}2w$	−10.8	7.4	−9.2	12.4	−9.3		−6.6	2.4	−8.9	
experiment in water[b]							$\lvert 6.6 \rvert$	$\lvert 1.9 \rvert$	$\lvert 10.2 \rvert$	
Aniline Cation										
calculation on $C_6H_5NH_2{}^+$	−5.3	5.0	−7.5	11.9		5.4	−5.1	1.5	−9.3	−9.3
calculation on $C_6H_5NH_2{}^+{\cdot}2w$	−8.0	6.3	−8.1	11.7		6.1	−5.6	1.9	−8.8	−10.2
experiment in methylene chloride[c]						$\lvert 7.7 \rvert$	$\lvert 5.8 \rvert$	$\lvert 1.5 \rvert$	$\lvert 9.6$	$\lvert 9.6 \rvert$
p-Benzosemiquinone Anion										
calculation on $C_6H_4O_2{}^-$	−3.2	−0.2	−0.2	−3.2	−7.4		−2.2	−2.2		
calculation on $C_6H_4O_2{}^-{\cdot}2w(\text{at } C_1{-}O)$	1.1	−2.5	1.7	−5.4	−6.8,−7.7		−1.1	−3.3		
calculation on $C_6H_4O_2{}^-{\cdot}4w$	−1.1	−0.6	−0.6	−1.1	−7.3		−2.1	−2.1		
experiment in DMSO[d]	−2.1	(−0.1)	(−0.1)	−2.1	−9.5		−2.4	−2.4		
experiment in water[d]	0.2	−0.7	−0.7	−0.2	−8.7		−2.4	−2.4		
p-Phenylenediamine Cation										
calculation on $C_6H_4(NH_2)_2{}^+$	0.4	−0.6	−0.6	0.4		3.7	−1.9	−1.9		−6.8
calculation on $C_6H_4(NH_2)_2{}^+{\cdot}2w(\text{at } C_1{-}NH_2)$	−2.4	1.2	−2.2	2.2		4.5,3.2	−2.8	−1.0		−7.8,−5.9
calculation on $C_6H_4(NH_2)_2{}^+{\cdot}4w$	−0.4	−0.4	−0.4	−0.4		3.9	−1.9	−1.9		−6.9
experiment in DMSO[e]						5.3	−2.1	−2.1		−6.0
experiment in methanol[e]						5.3	−2.1	−2.1		−6.0
p-Aminophenoxyl										
calculation on $C_6H_4ONH_2$	−10.0	5.5	−6.6	7.6	−8.3	3.7	−5.3	1.1		−1.5
calculation on $C_6H_4ONH_2{\cdot}2w(\text{at } C_1{-}O)$	−6.4	3.6	−5.0	5.8	−8.3	3.0	−4.4	0.3		−3.7
calculation on $C_6H_4ONH_2{\cdot}2w(\text{at } C_4{-}NH_2)$	−8.6	4.2	−4.9	4.6	−8.0	2.6	−4.6	0.3		−5.1
calculation on $C_6H_4ONH_2{\cdot}4w$	−4.7	2.2	−3.2	2.9	−7.9	3.1	−3.6	−0.5		−5.7
experiment in water[f]						5.2	−2.7	−1.8		−5.6

[a] In cases where asymmetric solvation causes otherwise equivalent values at the 1 and 4 positions to differ, the value at the 1 position is listed first. [b] From ref 40. [c] From ref 41. [d] From refs 42−44 (with estimated values in parentheses). [e] From ref 45. [f] Magnitudes from ref 46, signs from ref 47.

removes any reasonable doubt about the appropriate sign choices in those systems. The overall agreement with experimental hfc values is generally satisfactory in all the radicals considered.

In phenoxyl radical, the calculations predict that hydrogen bond formation leads to significant changes in several of the carbon-13 hfc, but only small effects at oxygen-17 and at the hydrogens.

In aniline radical cation, the calculations again predict that hydrogen bond formation leads to significant changes in several of the carbon-13 hfc and only small changes at the ring hydrogens. Modest changes are predicted for nitrogen and for the amine hydrogens.

In *p*-benzosemiquinone anion, comparison of calculated $C_6H_4O_2{}^-$ and $C_6H_4O_2{}^-{\cdot}4w$ results correctly rationalizes the directions of the modest changes found in experimental carbon-13 and oxygen-17 values between the non-hydrogen-bonding solvent DMSO and water, and also rationalizes the corresponding negligible change in the experimental hydrogen value.

In view of the generally modest changes found, it would be tempting to conclude that the spin density in *p*-benzosemiquinone anion is not very highly sensitive to hydrogen bonding. But that notion is dispelled by examination of calculated results for the asymmetrically solvated $C_6H_4O_2{}^-{\cdot}2w$. The overall +2 G increase from hydrogen bonding in the nominally equivalent $^{13}C_1$ and $^{13}C_4$ values is seen to arise from a large +4 G increase caused by hydrogen bonding at the nearby site that is partially canceled by a decrease of −2 G caused by hydrogen bonding at the more remote site. Similarly, the small decrease from overall hydrogen bonding in the nominally equivalent $^{13}C_2$ and $^{13}C_3$ values arises from near cancellation of changes by ±2 G or more from individual hydrogen-bonding effects at the two different sites. The almost negligible changes from overall hydrogen bonding at oxygen-17 and at hydrogen are also due to cancellations from significant nearby and remote influences.

In *p*-phenylenediamine cation the calculations also predict modest overall changes from hydrogen bonding at the carbons. The calculations agree with experiment in finding small or negligible overall changes attributable to hydrogen bonding in the hfc at nitrogen and at all of the hydrogens. But the overall small calculated decrease of −1 G at $^{13}C_1$ and $^{13}C_4$ arises from partial cancellation of larger effects, coming from a −3 G decrease due to hydrogen bonding at the nearby site and a +2 G increase due to hydrogen bonding at the remote site. Similarly, the very small overall decrease in $^{13}C_2$ and $^{13}C_3$ values arises from near cancellation of changes by about ±2 G from individual hydrogen bonding effects at the two different sites. Analogous partial cancellation effects of smaller magnitude are also seen for the overall nitrogen and hydrogen values.

In *p*-aminophenoxyl radical the calculations predict substantial changes from hydrogen bonding for all of the carbon-13 values. Examination of values in the two intermediate 2w structures shows that these large changes arise because of mutually reinforcing and approximately additive changes due to hydrogen-bonding effects at the two sites. The small overall decrease in the value calculated for oxygen-17 is nearly all due to hydrogen-bonding effects from the remote site. The modest overall decrease in the nitrogen value is smaller than the decrease attributable to the influence of either hydrogen-bonding site alone, implying nonadditive effects in this case. This nitrogen hfc shows the largest error (2.1 G) between calculation and experiment found in all of the couplings examined in this work. The significant overall decreases in both of the ring hydrogen values can be interpreted as reinforcing additive effects from hydrogen bonding at the two sites. The large overall decrease in the amine hydrogen value is consistent in sign with decreases attributable to hydrogen bonding at both sites, but the magnitude is smaller than simple additivity would predict.

The complex nonadditive behavior of the nitrogen and amine hydrogen couplings in *p*-aminophenoxyl radical is probably associated in part with the change in structure from pyramidal to planar nitrogen upon hydrogen bond formation. Further discussion regarding vibrational averaging of the hfc over motions corresponding to pyramidalization and to torsion at the amine substituent in this radical can be found elsewhere.[16]

To summarize, hydrogen-bonding effects are generally largest for hfc at the apex carbons, and in some of the radicals are significant at various other nuclei as well. In the highly symmetric *p*-benzosemiquinone anion and *p*-phenylenediamine cation radicals large changes potentially caused by hydrogen bonding at either of the two substituents are largely canceled out because the contributions are of opposite sign. In the less symmetric *p*-aminophenoxyl radical the effects of hydrogen bonding at the two substituents instead generally produce changes of the same sign, although the magnitudes are usually not even qualitatively additive.

Conclusions

Hydrogen bonding can have significant effects on the structures, vibrational frequencies, and hfc of these radicals. The present calculations give a generally satisfactory account of nearly all the experimental data that is available on these properties. Those calculations that include the maximum number of hydrogen-bound water molecules generally give better agreement with experimental results in water than do calculations on the isolated radicals. Furthermore, in those cases where experimental results are available for comparison either in gas or in non-hydrogen-bonding solvents, the calculations provide successful accounts of nearly all the signs and most of the approximate magnitudes of the observed shifts attributable to hydrogen bonding. It is concluded that the level of theory employed here is quite adequate for this study.

Up to two hydrogen bonds can be formed at each oxygen and at each amine substituent in these radicals. The individual hydrogen bond strengths in a given radical are approximately additive, although the first hydrogen bonds to be formed are a little stronger than the last. Oxygen substituents accept hydrogen bonds and donate electron density to water. This leads to some weakening of the associated CO bonds and, to a lesser extent, to some strengthening of any para CO or CN bond. In contrast, amine substituents donate hydrogen bonds and accept electron density from water. This leads to some strengthening of the associated CN bonds and, to a lesser extent, to some weakening of any para CO or CN bond. These effects are larger for hydrogen bonds to oxygen than to amine substituents.

The consequences of these influences are manifest in the geometries of the radicals and explain many of the significant effects of hydrogen bonds on vibrational frequencies. However, some exceptions to expectations based on simple additivity of these individual influences are found in the *p*-aminophenoxyl radical that contains both kinds of substituents.

Hydrogen bonding can particularly affect carbon-13 hfc at the apex carbon sites, and is often significant at other nuclei as well. Contributions from individual hydrogen bonds sometimes reinforce and sometimes cancel one another. As a consequence, asymmetric hydrogen-bonding arrangements can have especially strong influences that are not evident in the net results from higher symmetry arrangements. To the extent that relative reactivities at different sites are correlated with the spin density distribution, this may have important chemical ramifications in solution where hydrogen bonds are constantly forming and breaking. Similar investigations need to be carried out on a wider range of systems to give improved understanding of this matter.

Acknowledgment. The research described herein was supported by the Office of Basic Energy Sciences of the Department of Energy. This is Contribution No. NDRL-4256 from the Notre Dame Radiation Laboratory.

References and Notes

(1) Okamura, M. Y.; Feher, G. *Annu. Rev. Biochem.* **1992**, *61*, 881.
(2) Ding, H.; Moser, C. C.; Robertson, D. E.; Tokito, M. K.; Daldal, F.; Dutton, P. L. *Biochemistry* **1995**, *34*, 15979.
(3) Hayashi, T.; Miyahara, T.; Koide, N.; Kato, Y.; Masuda, H.; Ogoshi, H. *J. Am. Chem. Soc.* **1997**, *119*, 7281.
(4) Chipman, D. M.; Liu, R.; Zhou, X.; Pulay, P. *J. Chem. Phys.* **1994**, *100*, 5023.
(5) Qin, Y.; Wheeler, R. A. *J. Chem. Phys.* **1995**, *102*, 1689.
(6) Nwobi, O.; Higgins, J.; Zhou, X.; Liu, R. *Chem. Phys. Lett.* **1997**, *272*, 155.
(7) Adamo, C.; Subra, R.; di Matteo, A.; Barone, V. *J. Chem. Phys.* **1998**, *109*, 10244.
(8) Chipman, D. M.; Prebenda, M. F. *J. Phys. Chem.* **1986**, *90*, 5557.
(9) Nonella, M. *J. Phys. Chem. B* **1997**, *101*, 1235.
(10) Grafton, A. K.; Boesch, S. E.; Wheeler, R. A. *J. Mol. Struct. (THEOCHEM)* **1997**, *392*, 1.
(11) Zhan, C.-G.; Iwata, S. *Chem. Phys.* **1998**, *230*, 45.
(12) Zhan, C.-G.; Chipman, D. M. *J. Phys. Chem.* **1998**, *102*, 1230.
(13) O'Malley, P. J. *J. Phys. Chem.* **1997**, *101*, 6334.
(14) Eriksson, L. A.; Himo, F.; Siegbahn, P. E. M.; Babcock, G. T. *J. Phys. Chem.* **1997**, *101*, 9496.
(15) Chipman, D. M.; Sun, Q.; Tripathi, G. N. R. *J. Chem. Phys.* **1992**, *97*, 8073.
(16) Chipman, D. M. *J. Phys. Chem.* **1999**, *103*, 11181.
(17) Becke, A. D. *Phys. Rev. A* **1988**, *38*, 3098.
(18) 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.
(20) Hariharan, P. C.; Pople, J. A. *Theor. Chim. Acta* **1973**, *28*, 213.
(21) Pulay, P.; Torok, F. *Acta Chim. Acad. Sci. Hung.* **1965**, *47*, 273.
(22) Cohen, M. J.; Chong, D. P. *Chem. Phys. Lett.* **1995**, *234*, 405.
(23) Becke, A. D. *J. Chem. Phys.* **1993**, *98*, 5648.
(24) Lee, C.; Yang, W.; Parr, R. G. *Phys. Rev. B* **1988**, *37*, 785.
(25) Barone, V. In *Recent Advances in Density Functional Methods*; Chong, D. P., Ed., World Scientific Publishing: Singapore, 1995.
(26) Wetmore, S. D.; Boyd, R. J.; Eriksson, L. A. *J. Chem. Phys.* **1997**, *106*, 7738.
(27) Chipman, D. M. *J. Chem. Phys.* **1989**, *91*, 5455. In that work the [631|41] basis was labeled as [5s 2p 1d|3† s 1p]+ diffuse sps.
(28) Boys, S. F.; Bernardi, F. *Mol. Phys.* **1970**, *19*, 553.
(29) van Duijneveldt, F. B.; van Duijneveldt-van de Rijdt, J. G. C. M.; Lenthe, J. H. *Chem. Rev.* **1994**, *94*, 1873.
(30) Frisch, M. J.; Trucks, G. W.; Schlegel, H. B.; Gill, P. M. W.; Johnson, B. G.; Robb, M. A.; Cheeseman, J. R.; Keith, T.; Petersson, G. A.; Montgomery, J. A.; Raghavachari, K.; Al-Laham, M. A.; Zakrzewski, V. G.; Ortiz, J. V.; Foresman, J. B.; Cioslowski, J.; Stefanov, B. B.; Nanayakkara, A.; Challacombe, M.; Peng, C. Y.; Ayala, P. Y.; Chen, W.; Wong, M. W.; Andres, J. L.; Replogle, E. S.; Gomperts, R.; Martin, R. L.; Fox, D. J.; Binkley, J. S.; Defrees, D. J.; Baker, J.; Stewart, J. P.; Head-Gordon, M.; Gonzalez, C.; Pople, J. A., *Gaussian 94*, Revision D.2; Gaussian, Inc.: Pittsburgh, PA, 1995.
(31) Curtiss, L. A.; Frurip, D. J.; Blander, M. *J. Chem. Phys.* **1979**, *71*, 2703.
(32) Tripathi, G. N. R. *J. Phys. Chem. A* **1998**, *102*, 2388.
(33) Johnson, C. R.; Ludwig, M.; Asher, S. A. *J. Am. Chem. Soc.* **1986**, *108*, 905.
(34) Tripathi, G. N. R.; Schuler, R. H. *J. Phys. Chem.* **1988**, *92*, 5129.
(35) Mukherjee, A.; McGlashen, M. L.; Spiro, T. G. *J. Phys. Chem.* **1995**, *99*, 4912.
(36) Meek, J. T.; Sekreta, E.; Wilson, W.; Viswanathan, K. S.; Reilly, J. P. *J. Chem. Phys.* **1985**, *82*, 1741.
(37) Tripathi, G. N. R.; Schuler, R. H. *J. Chem. Phys.* **1987**, *86*, 3795.
(38) Zhao, X.; Imahori, H.; Zhan, C.-G.; Sakata, Y,; Iwata, W.; Kitagawa, T. *J. Phys. Chem.* **1997**, *101*, 622.
(39) Sun, Q.; Tripathi, G. N. R.; Schuler, R. H. *J. Phys. Chem.* **1990**, *94*, 6273.
(40) Neta, P.; Fessenden, R. W. *J. Phys. Chem.* **1974**, *78*, 523.
(41) Neugebauer, F. A.; Bamberger, S.; Groh, W. R. *Chem. Ber.* **1975**, *108*, 2406.
(42) Stone, E. W.; Maki, A. H. *J. Am. Chem. Soc.* **1965**, *87*, 454.
(43) Das, M. R.; Fraenkel, G. K. *J. Chem. Phys.* **1965**, *42*, 1350.
(44) Gulick, Jr., W. M.; Geske, D. H. *J. Am. Chem. Soc.* **1966**, *88*, 4119.
(45) Bullock, A. T.; Howard, C. B. *J. Chem. Soc., Faraday Trans. 2* **1975**, *71*, 1008.
(46) Tripathi, G. N. R.; Schuler, R. H. *J. Phys. Chem.* **1984**, *88*, 1706.
(47) Scheffler, K.; Stegmann, H. B.; Ulrich, C.; Schuler, P. *Z. Naturforsch.* **1984**, *39a*, 789.