Electron Spin Resonance Studies of Hydroxysemiquinone Radicals. Hydrogen–Deuterium Isotope Effects in Intramolecular Hydrogen Bonds[1]

Julien Gendell, William R. Miller, Jr., and George K. Fraenkel

Contribution from the Department of Chemistry, Columbia University, New York, New York 10027. *Received January 22, 1969*

Abstract: Electron spin resonance spectra have been obtained of semiquinone radicals containing intramolecular hydrogen bonds produced by reduction of 1,4-dihydroxy-5,8-naphthoquinone, 1,4-dihydroxy-, 1,5-dihydroxy-, and 1,8-dihydroxy-9,10-anthraquinone, and 6,11-dihydroxy-5,12-tetracenequinone. The same radicals were also investigated with the hydrogen in the hydroxyl position replaced by deuterium. Some of the species were studied in several different solvent systems, and some over a wide temperature range. The proton–deuteron splitting-constant ratios for the protons and deuterons in the hydroxyl positions were found to have values ranging from $(a^{\mathrm{H}}{}_{\mathrm{OH}}/a^{\mathrm{D}}{}_{\mathrm{OD}}) = 7.2$ to 7.8 instead of the value of $(a^{\mathrm{H}}/a^{\mathrm{D}}) = 6.514$ predicted solely on the basis of the magnetic properties of the two isotopes. Substitution of deuterium for hydrogen in the hydroxyl positions was also found to cause significant changes in the ring-proton splitting constants. These two isotope effects have been correlated with changes in the π-electron spin-density distribution determined by the Hückel molecular orbital method. In these calculations, the value of the Coulomb integral for the oxygen atom in the deuterated radicals was chosen to be more negative than the value for the undeuterated species. The deuterium isotope effects in hydrocarbon radicals cannot be accounted for in this way, and the different interpretations are attributed to differences between the structure of carbon–hydrogen bonds and intramolecular hydrogen bonds. An attempt to correlate the hydroxyl-proton splittings with calculated spin densities on the oxygen atoms was not on the whole successful, and the detailed analysis suggests that the σ–π parameters for an intramolecular hydrogen bond vary from radical to radical, and with the solvent employed to study a particular radical, because the structure of these bonds is extremely sensitive to the surroundings. A tentative assignment of the proton splitting constants previously reported for the 1,4-dihydroxyanthrasemiquinone ion has been shown to be incorrect.

I. Introduction

Several years ago, electron spin resonance spectra were reported of the radicals produced by air oxidation of 1,4,5,8-tetrahydroxynaphthalene and 1,4,9,10-tetrahydroxyanthracene.[2] The spectra showed that two of the four hydroxyl protons in the starting materials are retained in the radicals, and that the hyperfine splitting constants of the naphthalene derivative are symmetrically equivalent with respect to a plane passing midway between the pairs of oxygen atoms associated with a particular hydrogen atom, *i.e.*, a plane passing through the carbon atoms at positions 9 and 10. The spectra thus demonstrated that the radicals contain intramolecular hydrogen bonds. In this study, the spectrum of the naphthalene derivative in which hydroxyl protons were replaced by deuterons was also obtained, and the proton–deuteron splitting constant ratio was found to be $(a^{\mathrm{H}}{}_{\mathrm{OH}}/a^{\mathrm{D}}{}_{\mathrm{OD}}) = 7.4$ instead of the value of $(a^{\mathrm{H}}/a^{\mathrm{D}}) = 6.514$ expected solely on the basis of magnetic properties of the two isotopes.[3] In addition, the data indicated that the ring-proton splitting constants in the radical containing deuterium in the hydroxyl position might be different from those in the undeuterated radical.

These preliminary observations of isotope effects are of considerable interest because they indicate that additional investigations could provide information about intramolecular hydrogen bonds[4] and would relate to the studies of the deuterium isotope effects recently observed in the deuterium-substituted benzene[5–7] and naphthalene[8] anion radicals. We have therefore examined the esr spectra of a number of semiquinone radicals containing intramolecular hydrogen bonds. Experiments have been conducted in several solvent systems on radicals with both hydrogen and deuterium in the hydroxyl positions, and two radicals were investigated as a function of temperature. The results have been analyzed in terms of spin-density calculations performed by using Hückel molecular orbital theory.

II. Experimental Section

A. **Materials.** The starting materials employed were 1,4-dihydroxy-5,8-naphthoquinone [di(OH)NQ] (I); 1,4-dihydroxyanthraquinone [1,4-di(OH)AQ] (II); 1,5-dihydroxyanthraquinone [1,5-di(OH)AQ] (III); 1,8-dihydroxyanthraquinone [1,8-di(OH)AQ] (IV); and 6,11-dihydroxy-5,12-tetracenequinone [6,11-di(OH)TQ] (V). Compounds I, III, and IV were obtained from K and K laboratories, and compounds II and V from Eastman Organic Chemicals. All were used as received without purification.

The dideuterio derivatives were prepared by exchange of the hydroxyl protons in the dihydroxyquinones with D_2O. Usually, D_2O was merely added to the solvent before reduction. In one case, that of di(OD)NQ in tetrahydrofuran, deuteration was accomplished by dissolving di(OH)NQ in purified solvent on a vacuum line and then adding the D_2O. After standing and mixing, the solvent was vacuum distilled to near dryness, and subsequent procedures followed those employed for the normal hydrogen-containing radicals.

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[1] This research was supported in part through the Air Force Office of Scientific Research Grants No. AF-AFOSR-285-63 and AF-AFOSR-285-65.

[2] J. H. Freed and G. K. Fraenkel, *J. Chem. Phys.*, 38, 2040 (1963).

[3] T. F. Wimett, *Phys. Rev.*, 91, 499 (1953).

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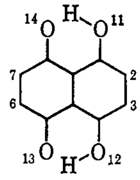
[5] R. G. Lawler, J. R. Bolton, G. K. Fraenkel, and T. H. Brown, *J. Am. Chem. Soc.*, 86, 520 (1964).

[6] M. Karplus, R. G. Lawler, and G. K. Fraenkel, *ibid.*, 87, 5260 (1965).

[7] R. G. Lawler and G. K. Fraenkel, *J. Chem. Phys.*, in press.

[8] R. G. Lawler, J. R. Bolton, M. Karplus, and G. K. Fraenkel, *ibid.*, 47, 2149 (1967).



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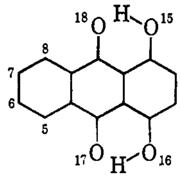

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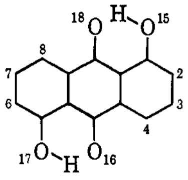

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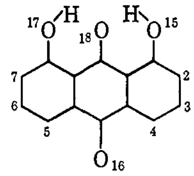

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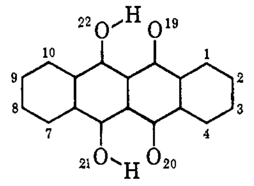

V

The solvents employed were: H_2O, D_2O, N,N-dimethylformamide (DMF), tetrahydrofuran (THF), dimethoxyethane (DME), dimethyl sulfoxide (DMSO), and mixtures of some of them. Purification of the last four was carried out using techniques described elsewhere.[9,10]

B. **Techniques.** In most of the experiments, the radicals were generated by electrolytic reduction of the quinones in the cell described by Dehl and Fraenkel[9] using techniques described by them and by Rieger, *et al.*[11] Radicals generated in THF were prepared under vacuum in the vacuum electrolytic cell described by Bolton and Fraenkel.[10] The electrolysis solutions were between 10^{-3} and 10^{-4} *M* in quinone and 0.1 *M* in the supporting electrolyte, tetra-*n*-propylammonium perchlorate in DMF and DMSO[9,11] and tetra-*n*-butylammonium perchlorate in DME and THF.[10] A silver–silver perchlorate electrode was used as a reference.

All the radicals produced were quite stable, and the esr spectra had narrow lines even under conditions of incomplete reduction.[12]

The X-band superheterodyne spectrometer employed has been described previously.[13-15] Spectra were obtained on strip-chart recordings using a scan rate of about 0.25 G/min. Field calibration marks were made at about every 1.2 G using an appropriately stabilized proton nmr oscillator.[15] Hyperfine splitting constants were obtained from a linear regression analysis of the line positions and of the calibration points as described previously.[10] Errors are given for the 95% confidence level (approximately two standard deviations).

Line widths were measured approximately for some spectra and are given as the difference in magnetic field between the extrema of the first derivative of the spectrum. Relative line widths were also obtained in some instances by employing the usual procedure,[16] based on the assumption of constant line shape for all lines in a spectrum,[14] of measuring the relative amplitudes of the lines from the first derivative of the spectrum. Relative widths were obtained in this way with an over-all precision of about 10%.

III. Results

Part A of this section is devoted to a discussion of the preparation and spectra of each of the radicals studied. The data are presented in Table I. Parts B, C, D, and E are concerned with the assignment of the splittings to positions, the symmetry of the hydrogen bond, and isotope and solvent effects, respectively.

A. Detailed Results for Individual Radicals.

1. 1,4-Dihydroxy-5,8-naphthoquinone [di(OH)NQ]. On reduction at potentials between −0.6 and −1.0 V, the color of solutions of di(OH)NQ changed from red to brown. The initial concentrations of di(OH)NQ ranged from 0.1 to 1.0 m*M*, and the line widths varied from 0.020 G for the most dilute solutions to 0.045 G for the most concentrated.

Measurements of the line widths of the individual hyperfine lines relative to the width of the central line showed that, within the experimental errors of about 10%, there were no variations in width from one line to another.

Spectra of di(OH)NQ$\cdot^-$ (*i.e.*, 1,4-dihydroxy-5,8-naphthosemiquinone) taken at temperatures down to −44° in DMF did not reveal any qualitative changes. Measurements on di(OD)NQ$\cdot^-$ in THF from room temperature to −100° showed only small changes in hyperfine splittings as a function of temperature that were mostly within the experimental errors, and no variation in line width among the hyperfine lines was observed.

2. 1,4-Dihydroxy-9,10-anthraquinone [1,4-di(OH)-AQ]. Upon reduction of this compound at potentials between −0.6 and −1.8 V, the color of the solutions changed from orange to purple. A total of 81 lines are predicted for a nonoverlapping spectrum of 1,4-di(OH)-AQ$\cdot^-$ and 135 are predicted for 1,4-di(OD)AQ$\cdot^-$. At a concentration of 0.2 m*M* in DMF–4.1% H_2O, 75 lines with widths of 0.025 G were observed in the spectrum of the former, while a 0.7 m*M* solution of the latter in DMF–4%D_2O exhibited a 93-line spectrum.

The splittings in the spectrum of 1,4-di(OH)AQ$\cdot^-$ are caused by hyperfine interactions with four groups containing two equivalent protons each, and in DMF–4.1% H_2O the splitting constants are 0.425, 0.483, 0.934, and 2.045 G. Three groups containing two equivalent protons each and one group of two equivalent deuterons cause the splittings in the spectrum of 1,4-di(OD)AQ$\cdot^-$; in DMF–4% D_2O the proton splitting constants are 0.435, 0.932, and 1.999 G, while the deuteron splitting is 0.065 G. One of the two smaller splittings from 1,4-di(OH)AQ$\cdot^-$ therefore arises from the hydroxyl protons. Previously, however, Freed and Fraenkel[2] tentatively assigned a splitting of approximately 0.92 G to the hydroxyl protons on the basis of a comparison with a spectrum reported by Adams, *et al.*,[17] and assumed to be the trinegative ion radical of 1,4-dioxy-9,10-anthraquinone.[18]

Our results for the deuterated species 1,4-di(OD)AQ$\cdot^-$ imply un-

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(9) R. Dehl and G. K. Fraenkel, *J. Chem. Phys.*, **39**, 1793 (1963).

(10) J. R. Bolton and G. K. Fraenkel, *ibid.*, **40**, 3307 (1964).

(11) P. H. Rieger, I. Bernal, W. H. Reinmuth, and G. K. Fraenkel, *J. Am. Chem. Soc.*, **85**, 683 (1963).

(12) In general, reduction potentials were used which produced strong esr signals and no attempt was made to generate radicals at a specific potential. At potentials more negative than −2.0 V, spectra of other radical species were observed. The identification of these species was not pursued. In solvents with added water, esr signals were obtained at lower magnitudes of the reduction potential.

(13) J. M. Hirshon and G. K. Fraenkel, *Rev. Sci. Instr.*, **26**, 34 (1955).

(14) J. Gendell, J. H. Freed, and G. K. Fraenkel, *J. Chem. Phys.*, **41**, 949 (1964).

(15) J. W. H. Schreurs and G. K. Fraenkel, *ibid.*, **34**, 756 (1961).

(16) J. H. Freed and G. K. Fraenkel, *ibid.*, **37**, 1156 (1962).

(17) M. Adams, M. S. Blois, Jr., and R. H. Sands, *ibid.*, **28**, 774 (1958).

(18) Freed and Fraenkel[2] obtained a spectrum of 1,4-di(OH)AQ$\cdot^-$ by air oxidation in alkaline ethanolic solution of 1,4,9,10-tetrahydroxyanthracene. The spectrum was interpreted as arising from two triplet splittings of 0.92 and 2.10 G and one quintet splitting of 0.53 G. They made the tentative assignment $a_5^H = a_6^H = a_7^H = a_8^H = 0.53$ G, $a^H_{OH} = 0.92$ G, and $a_2^H = a_3^H = 2.10$ G, on the basis of a comparison with results obtained by Adams, *et al.*[17] These latter workers reported that reduction of 1,4-di(OH)AQ in alkaline solution produced a radical with a spectrum arising from a 0.49-G quintet and a 2.60-G triplet. Vincow and Fraenkel[19] and later Freed and Fraenkel[2] attributed this spectrum to the trinegative ion radical 1,4-dioxy-9,10-anthracene containing no OH protons. Freed and Fraenkel assumed that the spin-density distribution in this trinegative ion should not differ markedly from that in 1,4-di(OH)AQ$\cdot^-$ since the addition of two protons to the oxygen atoms should not alter the spin-density distribution significantly, especially in the ring not substituted with oxygen atoms. Molecular orbital calculations for the trinegative ion similar to those described in section IV support this assumption. We also note that the ring-proton splittings in the naphthazarin cation (the cation radical of 1,4,5,8-tetrahydroxynaphthalene) are $a_2^H = 2.38$ G,[20] which is the same as the splitting $a_2^H \cong 2.40$ G in di(OH)NQ$\cdot^-$.

Since the ratio a^{H}/a^{D} in the absence of isotope effects[8] is 6.514, and $a^{D}_{OD} = 0.065$ G, one would expect the OH splitting in 1,4-di(OH)AQ$\cdot^{-}$ to be $6.514a^{D}_{OD} = 0.423$ G; *i.e.*, the 0.425-G splitting in this radical might result from the hydroxyl protons. As indicated in Table I, however, we have assigned the splitting of 0.483 G to the hydroxyl protons for two reasons. First, if the 0.425-G splitting in 1,4-di(OH)AQ$\cdot^{-}$ is assigned to the OH protons, the 0.483-G splitting must arise from ring protons; it would then change by 10% to 0.435 G on deuteration of the hydroxyl positions. Alternatively, if the 0.483-G splitting is assigned to the OH protons, the ring-proton splitting of 0.425 G changes by only 2% to 0.435 G on deuteration. Comparison with the other compounds studied (see section III.D) indicates that while a 2% change in a ring-proton splitting as a result of deuteration is typical, a change of 10% is much larger than the other deuterium isotope effects observed. Second, if the 0.483-G splitting is assigned to the OH position, the proton–deuteron splitting ratio becomes $a^{H}_{OH}/a^{D}_{OD} = 7.4$. Although this value is very different from 6.514, it is consistent with ratios of from 7.2 to 7.8 found for the other radicals containing intramolecular hydrogen bonds (see Table II in section III.D, below).

The assignment of ring-proton splittings to positions in the radical is discussed in part B of this section and in section IV.A.

3. **1,5-Dihydroxy-9,10-anthraquinone [1,5-di-(OH)-AQ].** Solutions of this compound are golden yellow, and on reduction at potentials from −0.6 to −0.7 V, the color changes to reddish brown. A 1 m*M* solution in DMSO yielded a spectrum containing 65 out of the 81 lines expected for a nonoverlapping spectrum. The line widths were 0.035 G.

A spectrum of 1,5-di(OD)AQ$\cdot^{-}$ obtained from a 0.8 m*M* solution in DMF–4% D_2O exhibited 27 lines arising from splittings by the three sets of pairs of ring protons, but the deuteron splitting was not resolved. Deuterium splittings were obtained, however, by using a lower initial concentration. The spectrum from a 0.1 m*M* solution contained spurious lines, probably caused by impurities, but the spectrum of 1,5-di(OD)AQ$\cdot^{-}$ was distinguishable and yielded the deuteron splittings given in Table I. The ring-proton splittings from this radical given in the table were obtained from the spectrum of the 0.8 m*M* solution containing 27 lines.

There is no uncertainty in assigning the OH splitting in 1,5-di(OH)AQ$\cdot^{-}$ since the 0.3-G splitting is the only one which is approximately 6.5 times the deuteron splitting in 1,5-di(OD)AQ$\cdot^{-}$. The assignment of ring-proton splittings is discussed in sections III.B and IV.A.

4. **1,8-Dihydroxy-9,10-anthraquinone [1,8-di(OH)-AQ].** Upon reduction at potentials of −0.5 to −0.7 V, solutions of 1,8-di(OH)AQ change from a golden yellow to a red color. At a concentration of 1 m*M* in DMSO, a 49-line spectrum was obtained (81 lines are possible) with line widths between 0.050 and 0.060 G.

1,8-di(OD)AQ$\cdot^{-}$ was generated in a DMF–5% D_2O solution, but the spectrum was not sufficiently well resolved, perhaps because of incomplete reduction, to obtain the deuteron splitting. A well-resolved spectrum (100 lines out of the possible 135) with widths of about 0.025 G was obtained, however, in a DMF–3.8% D_2O solution containing a 0.1 m*M* initial concentration of 1,8-di(OH)AQ.

The 0.2-G splitting from 1,8-di(OH)AQ$\cdot^{-}$ is about 7.2 times the deuteroxyl deuteron splitting from 1,8-di(OD)AQ$\cdot^{-}$. It must therefore be the hydroxyl-proton splitting since all the other splittings from 1,8-di(OH)AQ$\cdot^{-}$ are greater than 0.5 G and are close to the proton splittings in 1,8-di(OD)AQ$\cdot^{-}$. The assignment of ring-proton splittings is discussed in sections III.B and IV.A.

5. **6,11-Dihydroxy-5,12-tetracenequinone [6,11-di-(OH)TQ].** Unreduced solutions of 6,11-di(OH)TQ were violet to transmitted light and brownish green to reflected light. Samples were made up by dissolving 6,11-di(OH)TQ in DMF and in DMF–3.8% D_2O, with concentrations of 1 and 0.52 m*M*, respectively. The DMF–3.8% D_2O solution became reddish on standing. The radicals were generated at between −0.5 and −1.5 V and gave purple solutions.

A 51-line spectrum of 6,11-di(OH)TQ$\cdot^{-}$ was obtained (75 lines are possible for symmetric hydrogen bonds) with line widths of about 0.050 G. The spectrum of 6,11-di(OD)TQ$\cdot^{-}$ contained 55 lines (125 lines are possible) with line widths of about 0.030 G.

The hydroxyl-proton splitting was unambiguously identifiable since it was the only triplet splitting in the spectrum of 6,11-di(OH)TQ$\cdot^{-}$. The assignment of ring-proton splittings is discussed in sections III.B and IV.A.

A sample of 6,11-di(OH)TQ$\cdot^{-}$ was prepared in the vacuum electrolytic cell using as solvent a mixture of THF and DME. Its spectrum was investigated down to −85° and showed no line width variations over this temperature range.

B. Assignment of Splittings to Positions. The assignment of OH-proton splittings has been discussed above, and in all but one instance [1,4-di(OH)AQ$\cdot^{-}$], comparison with the deuterated radicals supplies com-

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ambiguously that the 0.92-G splitting observed by Freed and Fraenkel in the spectrum of 1,4-di(OH)AQ$\cdot^{-}$ is a ring-proton rather than a hydroxyl-proton splitting. Their spectrum must therefore be interpreted as arising from three sets of two equivalent ring protons each with splittings of 0.53, 0.92, and 2.10 G, and a pair of hydroxyl protons with a splitting of 0.53 G; *i.e.*, there is an accidental equivalence between the hydroxyl protons and one pair of ring protons. Consequently, since we believe that the argument cited above to the effect that the ring-proton splittings in the mono- and trinegative ion radicals obtained from 1,4-di(OH)AQ should be similar is indeed correct, we suggest that the interpretation of the results reported by Adams, *et al.*,[17] is in error.

To investigate this discrepancy further, we reduced 1,4-di(OH)AQ in THF containing about 10 drops of tetra-*n*-butylammonium hydroxide in a few milliliters of solution employing vacuum electrolytic techniques. Even though the color of the initial solution was the blue corresponding to the dianion salt of 1,4-di(OH)AQ, the radical obtained was 1,4-di(OH)AQ$\cdot^{-}$. This result suggests that the spectrum reported by Adams, *et al.*, was in fact 1,4-di(OH)AQ$\cdot^{-}$, not the trinegative ion. Unfortunately, these authors did not publish their spectrum, nor did they report the conditions under which it was generated, so that a direct check of their result is not possible. Nevertheless, it is possible that a spectrum of poor quality might have been misinterpreted. We have computed simulated spectra of 1,4-di(OH)AQ$\cdot^{-}$ with two triplet splittings of 0.92 and 2.10 G and a quintet splitting of 0.53 G, corresponding to the splittings obtained by Freed and Fraenkel in ethanol, using different line widths. The 45-line spectrum obtained with narrow widths degenerates into only 17 lines for widths of 0.2 G or more. If, due to a low signal-to-noise ratio, the outside lines were not observed, and if, in addition, insufficient attention was paid to the intensity distribution of the lines, the spectrum could have been erroneously interpreted as containing only 15 lines with the approximate appearance expected from a 0.49-G quintet and a 2.60-G triplet.

(19) G. Vincow and G. K. Fraenkel, *J. Chem. Phys.*, **34**, 1333 (1961).

(20) J. R. Bolton, A. Carrington, and P. F. Todd, *Mol. Phys.* **6**, 169 (1963).

Table I. Hyperfine Splitting Constants

		Hyperfine splittings,[c] G			
		Ring positions		OH or OD positions	
Radical[a]	Solvent[a,b]	Position[d]	a^{H}_{CH}	a^{H}_{OH}	a^{D}_{OD}
I. di(OH)NQ·$^-$	THF	2,3,6,7	2.406 ± 0.003	0.520 ± 0.002	...
	DMF	2,3,6,7	2.390 ± 0.003	0.526 ± 0.002	...
	DMF-3.8% H_2O	2,3,6,7	2.395 ± 0.003	0.534 ± 0.002	...
	DMSO	2,3,6,7	2.387 ± 0.004	0.533 ± 0.003	...
	H_2O[e]	2,3,6,7	2.356 ± 0.001	0.587 ± 0.002	...
di(OD)NQ·$^-$	THF	2,3,6,7	2.376 ± 0.005	...	0.0676 ± 0.0005
	DMF-3.8% D_2O	2,3,6,7	2.368 ± 0.002	...	0.069 ± 0.001
	DMSO-$\sim$5% D_2O[f]	2,3,6,7	2.362 ± 0.003[f]	...	0.070 ± 0.002[f]
	D_2O[e]	2,3,6,7	2.335 ± 0.004	...	0.079 ± 0.002
II. 1,4-di(OH)AQ·$^-$	DMF	2,3	2.034 ± 0.006	0.476 ± 0.003	...
		5,8	0.404 ± 0.002		
		6,7	0.941 ± 0.003		
	DMF-4.1% H_2O	2,3	2.045 ± 0.006	0.483 ± 0.003	...
		5,8	0.425 ± 0.002		
		6,7	0.934 ± 0.004		
	EtOH[e]	2,3	2.104 ± 0.006	0.526 ± 0.005	...
		5,8	0.526 ± 0.005		
		6,7	0.918 ± 0.006		
1,4-di(OD)AQ·$^-$	DMF-4% D_2O	2,3	1.999 ± 0.002	...	0.065 ± 0.001
		5,8	0.435 ± 0.001		
		6,7	0.932 ± 0.002		
III. 1,5-di(OH)AQ·$^-$	DMSO	2,6	1.699 ± 0.004	0.304 ± 0.001	...
		3,7	0.929 ± 0.002		
		4,8	1.160 ± 0.003		
1,5-di(OD)AQ·$^-$	DMF-4% D_2O	2,6	1.661 ± 0.005	...	0.039 ± 0.002
		3,7	0.936 ± 0.004		
		4,8	1.101 ± 0.004		
IV. 1,8-di(OH)AQ·$^-$	DMSO	2,7	1.509 ± 0.007	0.202 ± 0.002	...
		3,6	1.064 ± 0.005		
		4,5	0.515 ± 0.005		
1,8-di(OD)AQ·$^-$	DMF-3.8% D_2O	2,7	1.447 ± 0.004	...	0.028 ± 0.001
		3,6	1.131 ± 0.003		
		4,5	0.575 ± 0.002		
	DMF-5% D_2O	2,7	1.423 ± 0.003	...	*g*
		3,6	1.147 ± 0.003		
		4,5	0.598 ± 0.003		
V. 6,11-di(OH)TQ·$^-$	DMF	1,4,7,10	0.319 ± 0.003	0.752 ± 0.002	...
		2,3,8,9	0.958 ± 0.002		
6,11-di(OD)TQ·$^-$	DMF-3.8% D_2O	1,4,7,10	0.308 ± 0.003	...	0.105 ± 0.005
		2,3,8,9	0.949 ± 0.002		

[a] See section II.A for abbreviations and structural formulas. [b] For mixed solvents, the percentages are given by $100(v/V)$, where v is the volume of H_2O or D_2O added and V is the volume of the final solvent mixture. [c] All data are at room temperature. Errors are at the 95% confidence level. Absolute values of the hyperfine splittings are given. [d] Positions are numbered as in the structural formulas in section II. The assignment of splittings to positions is discussed in sections III.B and IV.A. [e] From a refined analysis of the work reported in ref 2. [f] The D_2O was added to the DMSO during the course of a run so that the exact composition of the solvent is not known. [g] The deuteron splitting was not resolved in this spectrum, perhaps because of incomplete reduction.

pletely unambiguous information. The case of 1,4-di(OH)AQ·$^-$ is somewhat more complicated, as indicated in the foregoing, but there is little reason to doubt the correctness of the assignment made in Table I.

Except for di(OH)NQ·$^-$, for which there is no ambiguity in the assignment of the single ring-proton splitting, assignments of ring-proton splittings were made on the basis of molecular orbital calculations (section IV.A). The splittings in 1,4-di(OD)AQ·$^-$, however, can also be checked by comparison with the splittings in the 9,10-anthrasemiquinone ion. The splittings in this radical (in ethanol) are[21] $a_1^H = 0.550$ and $a_2^H = 0.962$ G. One would expect the splittings in the ring of 1,4-di(OH)AQ·$^-$ not substituted with oxygen atoms to be closer to the splittings in the 9,10-anthrasemiquinone ion than those in the substituted ring, and therefore the 2.1-G splitting in the former radical is caused by the protons at positions 2 and 3. The ordering of the splittings from positions 5,8 and 6,7 in 1,4-di(OH)AQ·$^-$ would also be expected to be the same as the ordering in the 9,10-anthrasemiquinone ion, and thus the 0.5-G splitting arises from the protons at positions 5 and 8 while the 0.9-G splitting is attributable to positions 6 and 7. These assignments are all in agreement with the MO calculations.

C. The Symmetry of the Hydrogen Bond. The esr spectra of di(OH)NQ·$^-$ (I), 1,4-di(OH)AQ·$^-$ (II), and 6,11-di(OH)TQ·$^-$ (V) indicate that, insofar as the hyperfine splittings are concerned, the xz plane is a plane of symmetry. Here, we take the origin of the axis system to be at the center of the molecule with the x and y axes in the molecular plane and with the x axis bisecting the bond between positions 2 and 3. Similarly, for di(OH)NQ·$^-$, 1,8-di(OH)AQ·$^-$ (IV), and 6,11-di(OH)TQ·$^-$ the yz plane is a symmetry plane. The z axis is a twofold axis for di(OH)NQ·$^-$, 1,5-di(OH)AQ·$^-$ (III), and 6,11-di(OH)TQ·$^-$. The same symmetry considerations apply to the species with deuterium in place of hydrogen in the hydroxyl positions.

Since the spectra of both di(OH)NQ·$^-$ and 6,11-di(OH)TQ·$^-$ indicate an xz and a yz symmetry plane,

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(21) G. Vincow and G. K. Fraenkel, *J. Chem. Phys.*, **34**, 1333 (1961).

Table II. Proton–Deuteron Splitting-Constant Ratios (a^{H}_{OH}/a^{D}_{OD})

Species	Solvent[a]		Ratio,[d] (a^{H}_{OH}/a^{D}_{OD})
	OH form[b]	OD form[c]	
I. di(OH)NQ$\cdot^-$–di(OD)NQ$\cdot^-$	THF	THF	7.70 ± 0.05
	DMF–4% H_2O	DMF–4% D_2O	7.7 ± 0.1
	DMSO	DMF–4% D_2O	7.7 ± 0.2
	DMF	DMF–4% D_2O	7.6 ± 0.1
II. 1,4-di(OH)AQ$\cdot^-$–1,4-di(OD)AQ$\cdot^-$	DMF–4% H_2O	DMF–4% D_2O	7.4 ± 0.2
	DMF	DMF–4% D_2O	7.3 ± 0.2
III. 1,5-di(OH)AQ$\cdot^-$–1,5-di(OD)AQ$\cdot^-$	DMSO	DMF–4% D_2O	7.8 ± 0.4
IV. 1,8-di(OH)AQ$\cdot^-$–1,8-di(OD)AQ$\cdot^-$	DMSO	DMF–4% D_2O	7.2 ± 0.3
V. 6,11-di(OH)TQ$\cdot^-$–6,11-di(OD)TQ$\cdot^-$	DMF	DMF–4% D_2O	7.2 ± 0.4

[a] Composition of mixtures (% H_2O or % D_2O) is nominal; see Table I. [b] Solvent used to obtain the hydroxyl form of the radical. [c] Solvent used to obtain the deuteroxyl form of the radical. [d] Data from Table I.

the hydrogen-bonded protons in these two radicals must, on the average, lie on the *yz* plane; *i.e.*, each hydrogen-bonded proton is, on the average, equidistant from its nearest pair of oxygen atoms. The symmetry of the esr spectrum does not imply, however, that the position of minimum potential energy for the hydrogen-bonded protons is equidistant from these two oxygen atoms. For example, there could just as well be two equivalent symmetrically located minima for each proton lying closer to the oxygen atoms provided each proton undergoes sufficiently rapid transitions between its two positions of minimum energy. With two minima for each hydrogen-bonded proton, there would be four different instantaneous states of the radical, and there could be four different instantaneous values for the ring-proton splittings and two for the hydroxyl-proton splittings. If the product of the correlation time τ for the transitions between these different states with the difference in hyperfine splitting Δa between the states (in appropriate units) is small compared to unity, *i.e.*, if $\tau|\gamma_e||\Delta a| \ll 1$, where γ_e is the magnetogyric ratio for the electron and Δa is in gauss, an averaged spectrum would be obtained that is indistinguishable from the spectrum which would result if the position of minimum potential energy for the hydrogen-bonded protons were midway between the oxygen atoms. For slower correlation times or larger splitting-constant differences, on the other hand, the instantaneous inequivalence of the proton splittings would cause anomalous line-width effects similar to the alternating line-width effect observed by several investigators.[22] Other more complicated potential-energy functions may well be more realistic than these simple possibilities, and solvent interactions with the oxygen atoms may also cause large asymmetric perturbations. If there is rapid transfer between various states, all such models would lead to a symmetrical averaged spectrum.

The absence of any detectable line-width variations in the spectra of di(OH)NQ$\cdot^-$, di(OD)NQ$\cdot^-$, 6,11-di(OH)TQ$\cdot^-$, and 6,11-di(OD)TQ$\cdot^-$ indicates that if the hydrogen-bonded protons are undergoing transitions between different potential-energy minima, the rate of this motion must still be quite rapid even at the lowest temperatures for which measurements have been made.

D. Deuterium Isotope Effects. The data in Table I indicate that there are two types of deuterium isotope effects: the ratio of proton to deuteron splittings for the hydrogen isotopes bonded to oxygen, a^{H}_{OH}/a^{D}_{OD}, is anomalous, and the ring-proton splittings are altered when the hydroxyl protons are replaced by deuterons.

Proton–deuteron splitting ratios are listed in Table II using the data in Table I. Identical solvents (except for the substitution of D_2O for H_2O) were employed for the protonated and deuterated species in only three instances: di(OH)NQ$\cdot^-$–di(OD)NQ$\cdot^-$ in THF and DMF–4% $H_2O(D_2O)$, and 1,4-di(OH)AQ$\cdot^-$–1,4-di(OD)AQ$\cdot^-$ in DMF–4% $H_2O(D_2O)$. The values of the ratio a^{H}_{OH}/a^{D}_{OD} for di(OH)NQ$\cdot^-$–di(OD)NQ$\cdot^-$ in the two solvent systems are essentially the same, as are those obtained by comparing a^{H}_{OH} from the protonated form in DMSO or DMF with those for a^{D}_{OD} from the deuterated form in DMF–4% D_2O (see Table II); similar remarks apply to the data for 1,4-di(OH)AQ$\cdot^-$–1,4-di(OD)AQ$\cdot^-$. The a^{H}_{OH}/a^{D}_{OD} ratio is thus not particularly sensitive to the solvent, and meaningful values of this ratio for the other species can be obtained by comparing data for the hydroxyl-proton splittings in DMF, DMSO, and DMF–4% H_2O with data for the deuteron splittings obtained in DMF–4% D_2O.

The ratio a^{H}_{OH}/a^{D}_{OD} for the intramolecular hydrogen-bonded compounds studied varies from 7.2 to 7.8 (Table II), and thus deviates significantly from the expected value, based on the magnetic properties of the two isotopes, of $a^{H}/a^{D} = 6.514$. These data thus indicate that the earlier result obtained by Freed and Fraenkel[2] for di(OH)NQ$\cdot^-$–di(OD)NQ$\cdot^-$ in an aqueous system, namely $a^{H}_{OH}/a^{D}_{OD} = 7.4$, is a general result for semiquinone radicals with strong intramolecular hydrogen bonds; it is not specific to a particular molecule or solvent system.

Freed and Fraenkel[2] reported a small change in the ring-proton splittings on deuteration of the hydroxyl groups in di(OH)NQ$\cdot^-$, although they acknowledged that the change might have been within the experimental errors. Our results (Table I) for di(OH)NQ$\cdot^-$–di(OD)NQ$\cdot^-$ in THF and in DMF–4% $H_2O(D_2O)$ definitely confirm that there is a measurable change in the ring-proton splittings on deuteration, and that the same change occurs in different solvent systems. Thus, the difference between the ring-proton splitting in the deuterated and protonated forms is $\Delta a_2^{H} = -0.030 \pm 0.006$ G with THF as solvent and $\Delta a_2^{H} = -0.027 \pm 0.004$ G with DMF–4% $H_2O(D_2O)$ as solvent. Similar effects were also observed for 1,4-di(OH)AQ$\cdot^-$–

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[22] See, for example, G. K. Fraenkel, *J. Phys. Chem.*, 71, 139 (1967), and references cited therein. The four-jump model appropriate here is analyzed by J. H. Freed and G. K. Fraenkel, *J. Chem. Phys.*, **39**, 326 (1963).

1,4-di(OD)AQ$\cdot^-$: $\Delta a_2^H = -0.046 \pm 0.006$, $\Delta a_5^H = 0.010 \pm 0.002$, and $\Delta a_6^H = -0.002 \pm 0.005$ G.[23]

These changes in ring-proton splittings with deuteration of the hydroxyl positions imply that the substitution of deuterium for hydrogen alters the spin-density distribution in the radical.[8] A possible explanation for these isotope effects is discussed in section IV.C.

E. **Solvent Effects.** di(OH)NQ$\cdot^-$ and di(OD)NQ$\cdot^-$ were generated in a number of different solvent systems, and the results (Table I) found in this work, combined with the results obtained previously by Freed and Fraenkel[2] in aqueous media, show a consistent trend for the changes of both ring-proton and OH-proton or OD-deuteron splittings as the solvent system becomes more polar and protic. The ring-proton splitting for both di(OH)NQ$\cdot^-$ and di(OD)NQ$\cdot^-$ decreases, and the OH-proton and OD-deuteron splitting both increase, as the solvent composition is changed in the sequence THF, DMF, DMF–H_2O(D_2O), DMSO, and H_2O(D_2O).

The data available for 1,4-di(OH)AQ$\cdot^-$ also reveal consistent trends for the splitting constants as the solvent system is altered. On changing from DMF to DMF–4% H_2O to ethanol, the ring-proton splittings for the 2,3 and 5,8 positions increase while that for the 6,7 position decreases, and the hydroxyl-proton splitting increases. Results obtained for 1,8-di(OD)AQ$\cdot^-$ in DMF–3.8% D_2O and DMF–5% D_2O, also show that sizable changes in ring-proton splittings occur when the percentage of D_2O is altered. Solvent effects are discussed further in section IV.D.

IV. Discussion

In the first part of this section, the results of Hückel molecular orbital calculations are presented; they are used throughout the remainder of the discussion. In the latter parts, an attempt is made to apply a simple McConnell-type relationship between hydroxyl-proton hyperfine splittings and oxygen spin densities, and then the MO calculations are applied to the treatment of the two types of deuterium isotope effects observed, one involving a redistribution of spin density on deuteration, and the other an anomaly in the proton–deuteron splitting-constant ratio, $a^H{}_{OH}/a^D{}_{OD}$, for the OH and OD splittings. Finally, the MO calculations are applied to the changes in hyperfine splittings with solvent.

A. **Molecular Orbital Calculations.** Simple molecular orbital calculations of the spin-density distributions in radicals (Hückel LCAO calculations either with or without McLachlan's[24] method of including configuration interaction in an approximate way) have proved to be quite useful in assigning hyperfine splittings to positions in radicals, in correlating trends in a related series of compounds,[25] and in correlating the effects on the spin-density distribution of deuteration,[10] of ion pairing,[26] and of changes in the solvent system.[27] The MO calculations for semiquinone radicals depend on the Coulomb and resonance integrals for the oxygen atom and the oxygen–carbon bond. Coulomb and resonance-integral parameters δ_O and γ_{CO} are defined by

$$\alpha_O = \alpha_C + \delta_O\beta \qquad (1a)$$

$$\beta_{CO} = \gamma_{CO}\beta \qquad (1b)$$

where α_O and α_C are the Coulomb integrals for the oxygen and the carbon atom in a normal aromatic framework, respectively, and β is the carbon–carbon resonance integral for a normal aromatic hydrocarbon. In a number of calculations for semiquinone radicals,[21,27,28] these two parameters have been adjusted to give agreement between calculated and experimental proton hyperfine splittings by using McConnell's relation[29]

$$a^H{}_{CH}(i) = Q^H{}_{CH}\rho(i) \qquad (2)$$

relating hyperfine splittings $a^H{}_{CH}(i)$ to spin densities $\rho(i)$ at the carbon atom i to which the proton is bonded, but recently Das and Fraenkel[30] have shown that this procedure does not adequately predict the spin densities on the carbonyl groups. The spin densities on the carbonyl groups, and on other positions in the radical not bonded to protons, are often quite sensitive to values of the MO parameters, and this is true even when the parameters chosen are confined to those which give good agreement with experimental spin densities at the proton-labeled positions. Nevertheless, in the absence of sufficient data to determine the entire spin-density distribution in a semiquinone radical,[31] MO calculations in which the carbonyl-group parameters are adjusted solely by comparison with proton hyperfine splittings are still likely to be extremely useful for assigning splitting constants, and for giving insight into the trends which accompany solvent changes and deuteration.[32]

In the present application to radicals with intramolecular hydrogen bonds, the analysis is by no means straightforward because little is known about the structure of intramolecular hydrogen bonds. The simplest treatment for symmetrical compounds like di(OH)NQ$\cdot^-$ and 6,11-di(OH)TQ$\cdot^-$ would be to assume that the potential-energy minimum for each hydrogen-bonded proton lies equidistant from the two nearest oxygen atoms. Each oxygen atom and oxygen–carbon bond would then have the same Coulomb and resonance integrals. There is no symmetry requirement, however, which makes it necessary for the two carbonyl groups associated with one hydrogen-bonded proton to be the same in 1,4-di(OH)AQ$\cdot^-$ or 1,5-di(OH)AQ$\cdot^-$. Nor would the middle of the three carbonyl groups (atoms 9 and 15) associated with the two

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[23] The effects of deuteration on the ring-proton splitting constants for 1,5-di(OH)AQ$\cdot^-$, 1,8-di(OH)AQ$\cdot^-$, and 6,11-di(OH)TQ$\cdot^-$ cannot be ascertained from the present data since the deuterated and protonated forms of these radicals were observed in different solvent systems.

[24] A. D. McLachlan, *Mol. Phys.*, 3, 233 (1960).

[25] P. H. Rieger and G. K. Fraenkel, *J. Chem. Phys.*, 39, 609 (1963).

[26] C.-Y. Ling and J. Gendell, *ibid.*, 47, 3475 (1967).

[27] J. Gendell, J. H. Freed, and G. K. Fraenkel, *ibid.*, 37, 2832 (1962).

[28] A. Fairborn and E. A. C. Lucken, *J. Chem. Soc.*, 258 (1963).

[29] H. M. McConnell, *J. Chem. Phys.*, 224, 632, 764 (1956); H. M. McConnell and H. H. Dearman, *ibid.*, 28, 51 (1958); H. M. McConnell and D. B. Chesnut, *ibid.*, 28, 107 (1958), and other papers cited therein.

[30] M. R. Das and G. K. Fraenkel, *ibid.*, 42, 1350 (1965).

[31] To obtain experimental values for the entire spin density distribution in a semiquinone radical, hyperfine splittings from ^{13}C and/or ^{17}O nuclei have to be determined in addition to proton splittings.

[32] Calculated spin densities for the carbonyl group in 9,10-anthrasemiquinone based on reproducing proton splittings only[27] are substantially different from those obtained when the entire spin-density distribution is used.[30] However, splitting constant assignments, and qualitative changes of spin density, both in the ring and in the carbonyl group, with changes in the solvent system, are the same for both calculations.

hydrogen-bonded protons in 1,8-di(OH)AQ$\cdot^-$ necessarily be expected to have the same MO parameters as the two end carbonyl groups (atoms 1 and 17 and 8 and 18), and the single carbonyl group (atoms 10 and 16) not associated with a proton would be expected to have still another set of parameters. Furthermore, an appropriate model for the instantaneous confirmation of symmetrical radicals like di(OH)NQ$\cdot^-$ and 6,11-di(OH)TQ$\cdot^-$ could well be one in which the potential-energy minima are close to the oxygen atoms, thus requiring one set of carbonyl-group parameters for the oxygen atom nearer the proton and another set for the oxygen atom farther away. The two *cis* and *trans* conformations in this model could in principle have different energies, and a weighting of the forms with an appropriate Boltzmann factor might be necessary. Similar considerations would apply to the less symmetrical radicals as well.

In spite of all these complications, we feel that a crude but useful determination of the spin-density distribution can be obtained by treating all the carbonyl groups associated with protons as equivalent. A large number of Hückel calculations were therefore performed for all the radicals studied by using one set of parameters for all the carbonyl groups in all the radicals except 1,8-di(OH)AQ$\cdot^-$, and adjusting these parameters over a wide range. Employing McConnell's relation (eq 2), with $|Q^{H}_{CH}| = 23.7$ G, best agreement between all the experimental ring-proton splittings and spin densities calculated using Hückel theory[33] was obtained with $\delta_O = 0.9$ and $\gamma_{CO} = 1.24$. The results are given in Table III, and the calculated and experimental spin densities differ, on the average, by 11.4%. Comparable results were obtained from McLachlan[24] calculations using somewhat different values of the MO parameters.

Table III. Comparison of Calculated and Experimental Spin Densities[a]

Radical	Position[b]	Spin density, ρ_i Calcd[c]	Spin density, ρ_i Exptl[d]
I. di(OH)NQ$\cdot^-$	2,3,6,7	0.0990	0.1008
II. 1,4-di(OH)AQ$\cdot^-$	2,3	0.1026	0.0858
	5,8	0.0175	0.0170
	6,7	0.0333	0.0397
III. 1,5-di(OH)AQ$\cdot^-$	2,6	0.0760	0.0717
	3,7	0.0327	0.0392
	4,8	0.0556	0.0489
V. 6,11-di(OH)TQ$\cdot^-$	1,4,7,10	0.0148	0.0135
	2,3,8,9	0.0360	0.0404

[a] 1,8-di(OH)AQ$\cdot^-$ not included because of uncertainties in the MO calculations (see text). [b] See structural formulas in section II. [c] From Hückel MO calculations with $\delta_O = 0.9$ and $\gamma_{CO} = 1.24$ for all the carbonyl groups. [d] From the data in Table I with $a^{H}_{CH}(i) = Q^{H}_{CH}\rho(i)$ and $|Q^{H}_{CH}| = 23.7$ G. Data are for DMF solutions with the exception of 1,5-di(OH)AQ$\cdot^-$ for which DMSO was employed.

An additional choice of carbonyl-group MO parameters had to be made for the single oxygen atom in 1,8-di(OH)AQ$\cdot^-$ not associated with hydrogen-bonded protons. The parameters employed previously for semiquinones in DMSO,[27] $\delta_O = 0.4$ and $\gamma_{CO} = 1.40$, were used, together with $\delta_O = 1.06$ and $\gamma_{CO} = 1.19$ for the carbonyl groups associated with protons. The calculated and experimental spin densities are, respectively, 0.0566 and 0.0637 for positions 2,7; 0.0472 and 0.0449 for positions 3,6; and 0.0290 and 0.0217 for positions 4,5. The splitting-constant assignment in Table I is made on the basis of this calculation, which gave reasonably good agreement with experiment, but results of this kind for only one molecule cannot be given too much weight, and other choices of parameters gave a reasonable fit with the assignment of the two larger ring-proton splittings interchanged.

Except for 1,8-di(OH)AQ$\cdot^-$, none of the assignments were sensitive to the choice of MO parameters, and this was also true for sample calculations in which a two-position minimum was employed for the hydrogen bond and in which symmetrically inequivalent carbonyl groups were allowed to have different values of the MO parameters. These latter calculations involve too large a number of adjustable parameters for the detailed results to be meaningful, but the trends are still of significance. Our assignments in 1,8-di(OH)AQ$\cdot^-$ are probably the least certain, and there may be some question also for 1,5-di(OH)AQ$\cdot^-$. We note, moreover, that difficulties recently encountered in the MO description of the methyl-substituted naphthalene negative ions[34] indicate that basing assignments on MO calculations should sometimes be viewed with extreme caution.

B. Hydroxyl-Proton Splittings. The hyperfine splitting a^{H}_{OH} from the proton of a hydroxyl group might be expected to be proportional to the π-electron spin density ρ_O on the oxygen atom in the same way that the proton splitting from a proton attached to a carbon atom in an aromatic framework is related to the spin density on the carbon atom. In analogy with McConnell's relation (eq 2)

$$a^{H}_{OH} = Q^{H}_{OH}\rho_O \qquad (3)$$

and Q^{H}_{OH} would be expected to be negative although of a different magnitude from Q^{H}_{CH}. Similar considerations also apply, for example, to the proton splittings from an NH group.[35] Equation 3 is undoubtedly not sufficient, however, for an OH group attached to an aromatic system, because π-electron spin density on the carbon atom of a COH group will also influence the proton splitting. This occurs in much the same way as the spin density of the carbon atom to which a methyl group is attached affects the proton splitting of the methyl-group protons.[36-38] In addition, the proton splitting will depend on the orientation of the OH group relative to the plane of the π-electron system. The proportionality between the splitting from a hydroxyl proton and the spin densities on the oxygen and adjacent carbon atoms may also be less constant from molecule to molecule, or for a particular molecule in different solvents, than are the analogous proportionality constants for protons bonded to carbon. This greater sensitivity of the "Q" value to environment is to be expected because the oxygen atom usually carries an excess charge and has an unshared

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[33] In performing the MO calculations each O–H–O group contributes three π electrons, corresponding to one π electron for each quinonoid oxygen atom and two for each hydroxyl-group oxygen atom. For example, neutral di(OH)NQ has 16 π electrons and the radical ion di(OH)NQ$\cdot^-$ has 17. Similarly, 1,4-di(OH)AQ$\cdot^-$ and 6,11-di(OH)TQ$\cdot^-$ have 21 and 25 π electrons, respectively.

[34] R. E. Moss, N. A. Ashford, R. G. Lawler, and G. K. Fraenkel, *J. Chem. Phys.*, in press.

[35] B. L. Barton and G. K. Fraenkel, *ibid.*, **41**, 695, 1455 (1964).

[36] R. Bersohn, *ibid.*, **24**, 1066 (1956).

[37] D. B. Chesnut, *ibid.*, **29**, 43 (1958).

[38] A. D. McLachlan, *Mol. Phys.*, **1**, 233 (1958).

Table IV. Hyperfine Splittings and Spin Densities for Hydroxyl Groups[a]

Radical	Solvent	OH-proton splitting,[b] $a^H{}_{OH}$, G	Calcd O-atom spin density[c] ρ_i	ρ_j	$\rho_i + \rho_j$	$Q^H{}_{OH}$[d]
I. di(OH)NQ·⁻	DMF	0.526	$\rho_{12} = 0.0854$	$\rho_{13} = 0.0854$	0.1708	3.08
	DMSO	0.533				3.12
II. 1,4-di(OH)AQ·⁻	DMF	0.476	$\rho_{16} = 0.0599$	$\rho_{17} = 0.0940$	0.1539	3.09
III. 1,5-di(OH)AQ·⁻	DMSO	0.304	$\rho_{16} = 0.1270$	$\rho_{17} = 0.0176$	0.1446	2.10
V. 6,11-di(OH)TQ·⁻	DMF	0.752	$\rho_{20} = 0.0712$	$\rho_{21} = 0.0712$	0.1424	5.28

[a] 1,8-di(OH)AQ·⁻ not included because of uncertainties in MO calculations (see text). [b] From Table I. [c] From Hückel MO calculations with $\delta_O = 0.9$ and $\gamma_{CO} = 1.24$. See structural formulas in section II for numbering of positions. [d] For $a^H{}_{OH} = Q^H{}_{OH}(\rho_i + \rho_j)$; see text section IV.B.

pair of σ electrons so that it interacts strongly with the surroundings.

It is perhaps not surprising, therefore, that proton splittings from ordinary hydroxyl groups in which there is no intramolecular hydrogen bond do not appear to be in good agreement with eq 3, although the amount of data is small[39] and the interpretation not completely without question. Bolton, *et al.*,[40] found that calculated oxygen spin densities for several protonated semiquinone radical cations in acid solution were in the same relative order as the experimental OH-proton splittings, but there was not a linear relation between the spin densities and splittings. More recently, Claxton, *et al.*,[41] generated the monoprotonated durosemiquinone radical in a variety of solvents and were unable to correlate the OH-proton splitting with calculations of the oxygen spin density or the nature of the solvent system.

Still other uncertainties arise in relating proton splittings for intramolecular hydrogen bonds with π-electron spin densities. McConnell's relation is applicable to the proton of a hydrogen atom partaking in a normal σ bond with an atom (carbon, nitrogen, oxygen, etc.) that is part of the π-electron system, but the mechanism of the σ–π interaction in an intramolecular hydrogen bond, depending as it does on the unknown structure of the bond, is by no means clear. Nevertheless, we can explore the possibility of a semiempirical application of eq 3 to radicals with intramolecular hydrogen bonds. The simplest assumption is one of a symmetrically positioned potential-energy minimum for the hydrogen bond in which the π-electron spin density on each oxygen atom contributes to the proton splitting, so that eq 3 becomes

$$a^H{}_{OH} = Q^H{}_{OH}(\rho_i + \rho_j) \tag{4}$$

where ρ_i and ρ_j are the π-electron spin densities on oxygen atoms *i* and *j* sharing in the hydrogen bond.[42]

Equation 4 is undoubtedly most appropriate for the two radicals, di(OH)NQ·⁻ and 6,11-di(OH)TQ·⁻, with symmetrically positioned oxygen atoms. The OH-proton splittings in DMF are 0.526 and 0.752 G, respectively (Tables I and IV), and the spin densities on the oxygen atoms obtained from a Hückel calculation with $\delta_O = 0.9$ and $\gamma_{CO} = 1.24$ are $\rho_i = \rho_j = 0.0854$ and 0.0712, respectively, for the two radicals. The values of $Q^H{}_{OH}$ in eq 4 are 3.08 and 5.28, respectively (Table IV). The spin density on the oxygen atoms in 6,11-di(OH)TQ·⁻ is smaller than in di(OH)NQ·⁻, and as would be expected this is true for all choices of MO parameters in a wide range because in the former radical the spin density is distributed over a larger molecule than in the latter. The OH-proton splitting, however, is considerably larger in 6,11-di(OH)TQ·⁻ than in di(OH)NQ·⁻. This comparison implies that a simple relation such as eq 4 is not valid for intramolecular hydrogen bonds. The functional form may, in fact, be incorrect, or the structure of the hydrogen bond may vary to such an extent from molecule to molecule that the σ–π interactions, and therefore $Q^H{}_{OH}$, are not the same in different radicals.

Table IV also contains the calculated spin densities on the oxygen atoms and the values of $Q^H{}_{OH}$ in eq 4 for 1,4-di(OH)AQ·⁻ and 1,5-di(OH)AQ·⁻. There is considerable variation in the magnitude of $Q^H{}_{OH}$ which may, of course, be a reflection of the crude nature of the spin-density calculations. Not only have we assumed all the oxygen atoms to be equivalent in all of the radicals, and fitted the one set of MO parameters for the carbonyl group to proton splittings alone, but we also have assumed that even in the unsymmetrical molecules the proton is located equidistant from the two adjacent oxygen atoms. As the comparison of the hydroxyl-proton splittings for di(OH)NQ·⁻ and 6,11-di(OH)TQ·⁻ shows, however, the difficulties are probably fundamental, and the inclusion of refinements in the spin-density calculations which employ more realistic assumptions than those just enumerated would not be meaningful without additional knowledge as to the source of the major discrepancy.

C. Deuterium Isotope Effects. Two types of deuterium isotope effects were discussed in section III.D: a redistribution of spin density on deuteration of the hydroxyl protons and an anomalous proton–deuteron splitting ratio, $a^H{}_{OH}/a^D{}_{OD}$. We take these up in turn.

1. Redistribution of Spin Density on Deuteration. Recently Lawler, *et al.*,[8] found that the spin density distribution in the naphthalene negative ion is also altered by deuteration, and were able to obtain good agreement between calculated and experimental changes in proton hyperfine splittings by using a very simple

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(39) G. P. Rabold, R. T. Ogata, M. Okamura L. H. Piette, R. E. Moore, and P. J. Scheuer, *J. Chem. Phys.*, **46**, 1161 (1967), and references cited therein.

(40) J. R. Bolton, A. Carrington, and J. dos Santos-Viega, *Mol. Phys.*, **5**, 465 (1962).

(41) T. A. Claxton, T. E. Gough, and M. C. R. Symons, *Trans. Faraday Soc.*, **62**, 279 (1966).

(42) We note that eq 4 would follow from another extremely simple model. If the instantaneous conformation of an intramolecular hydrogen bond corresponds to an approximately normal σ bond with one oxygen atom, say *i*, and with a negligible interaction with the second oxygen atom, the hyperfine splitting for this conformation (A) would be $a^H{}_{OH}(A) \cong Q^H{}_{OH}\rho_i(A)$. In conformation B in which the hydrogen atom is associated with the other oxygen atom, *j*, the splitting would be $a^H{}_{OH}(B) \cong Q^H{}_{OH}\rho_j(B)$, so that in the rapid exchange limit, the average splitting would be $\langle a^H{}_{OH}\rangle = Q^H{}_{OH}[\rho_i(A) + \rho_j(B)]$. We also note that in general there might be contributions to the splitting proportional to $(c_i + c_j)^2$ where c_i and c_j are the coefficients of the atomic orbitals on atoms *i* and *j* in the LCAO expansion of the (one-electron) wave function of the unpaired electron.

Table V. Changes in Ring-Proton Splittings on Deuteration

Radical	Position[a]	Change in spin density,[b] $\Delta\rho_i$	
		Calcd[c]	Expl[d]
I. di(OH)NQ$\cdot^-$	2,3,6,7	-0.0019	-0.0011 ± 0.0002
II. 1,4-di(OH)AQ$\cdot^-$	2,3	-0.0037	-0.0019 ± 0.0003
	5,8	0.0027	0.0004 ± 0.0001
	6,7	-0.0002	-0.0001 ± 0.0003

[a] See structural formulas in section II. [b] $\Delta\rho_i = \rho_i^{(D)} - \rho_i^{(H)}$ where $\rho_i^{(D)}$ and $\rho_i^{(H)}$ are the spin densities at position i in the deuterated and undeuterated radicals, respectively. [c] From Hückel MO calculations with $\delta_O^{(H)} = 1.0$, $\gamma_{CO} = 1.3$, and $\delta_O^{(D)} = \delta_O^{(H)} + 0.2 = 1.2$. [d] From data in Table I for DMF–4% H_2O and DMF–4% D_2O solutions, using $a^H_{CH}(i) = |Q^H_{CH}|\rho(i)$ with $|Q^H_{CH}| = 23.7$ G.

model. They employed a Hückel MO calculation and took into account the effect of deuterium substitution by slightly increasing the resonance integral for carbon–carbon bonds adjacent to the position of substitution, a procedure which also gives correct results[6] for the deuterium-substituted benzene[5,7] and cyclooctatetraene anion radicals.[43] In contrast, calculations in which the Coulomb integral of the carbon atom at the substituted position was altered gave a number of incorrect predictions. The rationale behind the resonance-integral perturbation is the recognition that the resonance integral actually represents an average over the vibrational motions, and the amplitude of the bending vibrations is smaller, and therefore the resonance integral larger, if deuterium is substituted for hydrogen.

The resonance-integral perturbation model for deuterium substitution is not, however, appropriate for intramolecular hydrogen bonds. These bonds are much weaker than ordinary carbon–hydrogen bonds, and the largest motions are undoubtedly low-frequency vibrations or tunneling in the plane formed by the hydrogen atom and the two oxygen atoms. While we do not have any detailed knowledge of the form of the potential well for the hydrogen bond, we can assume, based on the evidence cited by Rundle,[44] that there are large deuterium isotope effects in hydrogen bonds of intermediate strength with a longer O–D–O than O–H–O bond length. On the other hand, CH bonds are longer than CD bonds, and since deuterium is considered to be slightly electron donating in CD bonds in aromatic systems,[45] it might have an electron-withdrawing effect in intramolecular hydrogen bonds.

Such an effect can be taken into account in a Hückel MO calculation by using a more negative value of the oxygen Coulomb integral for O–D–O than for O–H–O bonds, corresponding to a Coulomb-integral parameter for the deuterium case which is more positive than for the hydrogen case, $\delta_O^{(D)} > \delta_O^{(H)}$. MO calculations performed[46] with $\delta_O^{(D)} = \delta_O^{(H)} + 0.2$ are given in Table V for di(OH)NQ$\cdot^-$–di(OD)NQ$\cdot^-$ and 1,4-di(OH)-AQ$\cdot^-$–1,4-di(OD)AQ$\cdot^-$. The agreement between the calculated and experimental results with respect to both the direction and magnitude of the changes is on the whole satisfactory.

The same model is applied in the following paragraphs as a possible means of accounting for the anomalous proton–deuteron splitting-constant ratio, and the value of $[\delta_O^{(D)} - \delta_O^{(H)}] = 0.2$ was actually chosen on the basis of a comparison with these data rather than by considering the small changes in ring-proton splittings. The value of 0.2 here is quite large. The effects of methyl-group substitution can be accounted for by an inductive effect in which the Coulomb-integral parameter for the carbon atom bonded to the methyl group is about[34,47] $\delta_C^{(Me)} = -0.1$ to -0.3, while for deuterium substitution, the magnitude of $\delta_C^{(D)}$ must be smaller than[8] about 0.008. If the present treatment is meaningful, it implies that there are much larger structural changes in an intramolecular hydrogen bond when a deuterium atom is substituted for a hydrogen atom than for a CH bond.

2. The Anomalous a^H_{OH}/a^D_{OD} Ratio. As discussed in section III.D, the proton–deuteron splitting-constant ratio, a^H_{OH}/a^D_{OD}, for protons and deuterons partaking in intramolecular hydrogen bonds in semiquinone ions is in the range from 7.2 to 7.8, values considerably larger than the ratio $a^H/a^D = 6.514$ predicted solely on the basis of the magnetic properties of the two isotopes. Deuterium isotope effects have been found in other radicals,[48] but usually they are only 1–2%, and the ratio is less than 6.514. In the deuterium-substituted naphthalene negative ions,[8] the ratio was found to be different for the α and β positions, with $(a^H/a^D)_\alpha = 6.451$ and $(a^H/a^D)_\beta = 6.334$, while the average value for a number of deuterium-substituted benzene anions[7] is $a^H/a^D = 6.18$. The only results reported in which the ratio is greater than 6.514 are for the methyl-group splittings in ethyl radicals.[49] The methyl-proton splittings in $CH_3CH_2\cdot$ and $CHD_2CD_2\cdot$ are 26.87 and 29.77 G, respectively, while the methyl-deuteron splitting in the latter is 3.88 G, corresponding to a ratio 18% greater than 6.514.

Schrader and Karplus[50] and Schrader[51] have analyzed the anomalous a^H/a^D ratio in the methyl radical in terms of the vibrational effects on the hyperfine interactions, and Moss,[52] using a much simpler treatment than the other authors, has estimated the ratio in the benzene-1-*d* and benzene-1,3,5-*d*$_3$ anion radicals by including vibrational contributions to the splitting from π-electron spin density on adjacent carbon atoms not bonded to the hydrogen atom. Moss's theory does not account for the entire effect in the deuteriobenzene

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(43) A. Carrington, H. C. Longuet-Higgins, R. E. Moss, and P. F. Todd, *Mol. Phys.*, **9**, 187 (1965).

(44) R. E. Rundle, *J. Phys.* (Paris), **25**, 487 (1964).

(45) See ref 10 above and references contained therein. The evidence for the electron-donating effect of deuterium is not very strong. Independent of the validity of this argument, the results in Table V indicate that the proper choice ($\delta_O^{(D)} > \delta_O^{(H)}$) has been made for the intramolecular hydrogen bonds in the semiquinones.

(46) The MO parameters used for the undeuterated species in Tables V and VI are slightly different from those employed to obtain the data in Tables III and IV, but since small differences (or ratios) are involved, the difference is not of importance.

(47) D. Lazdins and M. Karplus, *J. Am. Chem. Soc.*, **87**, 920 (1965).

(48) See ref 18 for a survey of the available data.

(49) R. W. Fessenden and R. H. Schuler, *J. Chem. Phys.*, **39**, 2147 (1963).

(50) D. M. Schrader and M. Karplus, *ibid.*, **40**, 1593 (1964).

(51) D. M. Schrader, *ibid.*, **46**, 3895 (1967).

(52) R. E. Moss, *Mol. Phys.*, **10**, 339 (1966).

Table VI. Experimental and Calculated Proton–Deuteron Splitting Constant Ratios, a^{H}_{OH}/a^{D}_{OD}, for Hydroxyl and Deuteroxyl Groups

Radical	Proton–deuteron splitting constant ratio, a^{H}_{OH}/a^{D}_{OD} Calcd[a]	Exptl[b]
I. di(OH)NQ$\cdot^{-}$–di(OD)NQ$\cdot^{-}$	7.15	7.7 ± 0.1[b]
II. 1,4-di(OH)AQ$\cdot^{-}$–1,4-di(OD)AQ$\cdot^{-}$	7.19	7.4 ± 0.2[b]
III. 1,5-di(OH)AQ$\cdot^{-}$–1,5-di(OD)AQ$\cdot^{-}$	7.28	7.8 ± 0.4
IV. 1,8-di(OH)AQ$\cdot^{-}$–1,8-di(OD)AQ$\cdot^{-}$	7.56[c]	7.2 ± 0.3
V. 6,11-di(OH)TQ$\cdot^{-}$–6,11-di(OD)TQ$\cdot^{-}$	7.18	7.2 ± 0.4

[a] Calculated $(a^{H}_{OH}/a^{D}_{OD}) = 6.514[\rho_i^{(H)} + \rho_j^{(H)}]/[\rho_i^{(D)} + \rho_j^{(D)}]$ using Hückel MO calculations (see footnotes *b* and *c*, Table V). Compare eq 4 and section IV.B. Positions *i* and *j* refer to oxygen atoms associated with the hydrogen bond (see Table IV). See text, section IV.C. [b] From Table II. The results for radicals I and II are for DMF–4% D_2O solutions. [c] Results for radical IV are not included in some of the earlier tables because of uncertainties in the MO calculations. These uncertainties are unimportant here, however, since they should not markedly affect the difference (or ratios) on deuteration of the calculated oxygen spin densities. The carbonyl-group parameters employed for the protonated species were: for the three oxygen atoms associated with hydrogen bonds (positions 15, 17, and 18), $\delta_O^{(H)} = 0.4$ and $\gamma_{CO} = 1.20$; for the remaining oxygen atom (position 16), $\delta_O^{(H)} = 0.4$ and $\gamma_{CO} = 1.50$.

anions and gives unreasonable results for the β positions in the deuterium-substituted naphthalene negative ions. There are certain questions which remain to be resolved in the Karplus–Schrader treatment as well. Both theories require averaging over the vibrational modes of the radicals and are therefore difficult to apply to complicated molecules.

The Karplus–Schrader and Moss theories attribute the most significant part of the effects of vibrational motions to the out-of-plane bending modes, but, as indicated above, these are probably much less significant for intramolecular hydrogen bonds than for CH bonds. Although Lawler, *et al.*,[8] found that the anomalous a^{H}/a^{D} ratios in the deuterionaphthalene anions could not be explained by a redistribution of the spin density resulting from deuterium substitution, the effects in CH and intramolecular hydrogen bonds may be different, and it is therefore of interest to examine the contributions from the redistribution of spin density in the hydrogen-bonded semiquinone ions. We assume, despite the difficulties indicated in section IV.B, that the OH-proton splittings are given by eq 4, noting, however, that this equation may still be appropriate for a particular molecule in a particular environment. On taking the same change in the oxygen Coulomb integral used above for the change in ring-proton splittings on deuteration $[\delta_O^{(D)} = \delta_O^{(H)} + 0.2]$, we obtain the results[46] shown in Table VI. The calculated ratio is obtained by using eq 4 for both proton and deuteron splittings to give

$$(a^{H}_{OH}/a^{D}_{OD}) = 6.514[\rho_i^{(H)} + \rho_j^{(H)}]/[\rho_i^{(D)} + \rho_j^{(D)}] \quad (5)$$

The spin densities with superscript H refer to those for the protonated form, and those with superscript D to the deuterated form.

In view of the uncertainties discussed above about the description of the intramolecular hydrogen bond and the mechanism of the interactions which cause the proton hyperfine splitting, as well as the approximate nature of the MO calculations, the agreement shown by the results in Table VI is quite remarkable. The over-all trend, in which the a^{H}_{OH}/a^{D}_{OD} ratio is 14% larger than expected from the magnetic properties of the isotopes, is well accounted for by a redistribution of spin density on deuteration. There is less precise agreement between the calculated and experimental values for the individual radicals, but the calculations are much too approximate for a more detailed comparison to be meaningful. There is no reason to believe, however, that changes in the σ–π interactions when deuterium is substituted for hydrogen are not also significant, as was concluded to be the case for the much smaller isotope effects found for the deuterionaphthalene anions.[8]

D. Solvent Effects. In section III.E, it was pointed out that both the ring- and hydroxyl-proton splittings vary with solvent composition in a systematic way. In addition, pursuing the argument employed in section III.B that the ring-proton splittings at positions 5,8 and 6,7 of 1,4-di(OH)AQ$\cdot^{-}$ should be comparable to those at the same positions in the 9,10-anthrasemiquinone ion, one can examine the variation of the splittings with solvent at these positions in the two radicals. On changing the solvent from DMF to ethanol, the splitting at the 5,8 positions of 1,4-di(OH)AQ$\cdot^{-}$ changes from 0.404 to 0.526 G (Table I), while for the 9,10-anthrasemiquinone ion, the splitting at these positions is 0.303 G in DMSO and 0.550 G in ethanol.[27] At the 6,7 positions, the change is in the opposite direction, with values of 0.941 and 0.918 G for 1,4-di(OH)AQ$\cdot^{-}$ and 0.986 and 0.962 G for the 9,10-anthrasemiquinone ion, for the same sets of solvents. The similarity of these changes in splitting constants suggests that the same mechanism causes the solvent dependence of the splitting constants both in the ordinary semiquinone ions and in the semiquinones with intramolecular hydrogen bonds.

Gendell, *et al.*,[27] have shown that the variation of splitting constants with solvent in the semiquinone ions can be accounted for by a simple model in which the changes of splitting constants arise from a redistribution of π-electron spin density resulting from localized complexes between the solvent and the oxygen atoms of the semiquinone ion. This model would thus also appear to be applicable to the effects of solvent variation even when there is an intramolecular hydrogen bond, although the somewhat smaller changes observed at the 5,8 positions of 1,4-di(OH)AQ$\cdot^{-}$ as compared to the 9,10-anthrasemiquinone ion indicate that hydrogen bonding may reduce the ability of the solvent to interact with the oxygen atoms.

Quite good quantitative results were obtained by Gendell, *et al.*,[27] in calculations of changes of splitting constants with solvent that were based on the assumption that the solvent influences the effective electronegativity of the oxygen atoms. Hückel MO calculations were performed in which the Coulomb integral of the oxygen atom was made more negative (larger δ_O) for polar and protic solvents than for aprotic and less polar solvents. The calculations given in Table V are of this type. They show that the spin density at position 2 in di(OH)NQ$\cdot^-$ (or di(OD)NQ$\cdot^-$) decreases as δ_O is made larger, corresponding to a decrease in ring-proton splitting as the polarity of the solvent is increased, in qualitative agreement with the data in Table I. Similarly, an increase in δ_O (with all oxygen atoms equivalent, as in section IV.A) causes the spin density to increase at positions 5,8 and to decrease at positions 6,7 in 1,4-di(OH)AQ$\cdot^-$, again in qualitative agreement with experiment, but the prediction for positions 2,3 is in the wrong direction.

This incorrect prediction for positions 2,3 in 1,4-di(OH)AQ$\cdot^-$ may not be due to a failing in the treatment used to account for the solvent dependence, but rather in too crude a model for the calculation of spin densities. As a first approximation to a more refined treatment, we can abandon the assumption used in section IV.A and the ensuing calculations that all oxygen atoms, even those not at symmetrically related positions in the molecule, can be treated as equivalent. For example, in 1,4-di(OH)AQ$\cdot^-$ we can use a larger Coulomb-integral parameter δ_O for the oxygen atoms attached to positions 1 and 4 (atoms 15 and 16 in the structural formulas of section II) than those attached to positions 9 and 10 (atoms 17 and 18). A larger value of δ_O is appropriate for an oxygen atom bonded to a proton than for a quinonoid oxygen atom, and there is evidence that the oxygen atoms attached to the 9,10 positions are more quinoidal than those attached to the 1,4 positions.[53] This distinction is also consistent with the MO calculations we have performed in which the parameters for all the oxygen atoms are the same, because for this calculation the total π-electron (charge) density on the oxygen atoms attached to positions 1,4 (1.692) is greater than the total density at positions 9,10 (1.636), and therefore the proton is more likely to be bonded to the oxygen atoms attached to positions 1,4. Calculations were performed for DMF with $\delta_{O(15)} = \delta_{O(16)} = 1.20$ and $\delta_{O(17)} = \delta_{O(18)} = 0.85$ and also for ethanol with $\delta_{O(15)} = \delta_{O(16)} = 1.40$ and $\delta_{O(17)} = \delta_{O(18)} = 1.20$. The spin-density differences $\Delta\rho_i = \rho_i(\text{EtOH}) - \rho_i(\text{DMF})$ were calculated to be $\Delta\rho_{2,3} = 0.0033$, $\Delta\rho_{5,8} = 0.0041$, and $\Delta\rho_{6,7} = -0.0010$, while the experimental differences are $\Delta\rho_{2,3} = 0.0030$, $\Delta\rho_{5,8} = 0.0052$, and $\Delta\rho_{6,7} = -0.0010$. Little weight can be given to the detailed agreement found here by varying four parameters to fit three pieces of data, but the procedure we have adopted is certainly not an unreasonable one.

These calculations indicate that the model used previously by Gendell, *et al.*,[27] to account for the solvent dependence of splitting constants is also adequate for explaining the main features of the variation of the ring-proton splitting constants in semiquinone ions having intramolecular hydrogen bonds. More uncertainty appears to arise from the approximations in the model used for the spin-density calculations than in the interactions invoked to explain the solvent effects.

If the same type of calculation is carried out for the solvent dependence of the hydroxyl-proton splittings, however, the predicted changes are in the wrong direction. As pointed out in section III.E, the OH-proton splittings in di(OH)NQ$\cdot^-$ and 1,4-di(OH)AQ$\cdot^-$, and the OD-deuteron splittings in di(OD)NQ$\cdot^-$, increase in a consistent manner as the solvent is made more polar and protic. On the other hand, the model we have employed for the solvent interactions places a larger total charge density on the oxygen atom in a polar or protic solvent than in a less polar or aprotic solvent, and all calculations show that an increase in total charge density on the oxygen atoms results in a *decrease* in the unpaired electron or spin density on these atoms. Thus, even if a simple McConnell-type of relationship is not valid (see section IV.B), this result implies that changes of the total spin density on the two oxygen atoms in the hydrogen bond is not the controlling factor in determining changes of the OH-proton splitting with solvent.

These considerations have led us to surmise that the structure of the intramolecular hydrogen bond is quite sensitive to the nature of the solvent system. Our present uncertain knowledge about the structure of this bond, however, precludes the possibility of a detailed analysis of how the bond changes with fluctuating solvent interactions. Undoubtedly, the potential function which determines the motion of the hydrogen atoms between the two oxygen atoms is strongly influenced by strong solvent interactions with the oxygen atoms, and thus the average position of the hydrogen atom, and perhaps even of the oxygen atoms, can be affected, so that changes in the σ–π interactions which determine the proton hyperfine splitting are perhaps more important than alterations in the spin density on the oxygen atoms.

V. Conclusions

The esr spectrum of 6,11-di(OH)TQ$\cdot^-$, in agreement with the previously observed spectrum[2] of di(OH)NQ$\cdot^-$, indicates a proton hyperfine splitting pattern that is symmetric with respect to a plane midway between the pair of oxygen atoms associated with each hydrogen bond. These observations, coupled with the absence of any detectable line-width variations within a spectrum even at low temperatures for both radicals, implies that either the hydrogen-bonded protons move in potential-energy surfaces with minima on this symmetry plane or they are in *rapid* motion between minima positioned on either side of this plane. These same considerations apply to the species with deuterium in place of hydrogen in the hydroxyl positions.

Two types of deuterium isotope effects were observed. The ratio $a^{\mathrm{H}}_{\mathrm{OH}}/a^{\mathrm{D}}_{\mathrm{OD}}$ of the OH-proton to OD-deuteron splitting was found to be from about 10 to 20% larger (depending on the radical) than the value $a^{\mathrm{H}}/a^{\mathrm{D}} = 6.514$ expected solely on the basis of the magnetic properties of the two isotopes. This large anomaly is thus characteristic of semiquinone radicals with intramolecular hydrogen bonds. Replacing the hydrogen-bonded protons with deuterons also causes significant changes in the ring-proton hyperfine splittings. Both of these isotope effects can be correlated with changes in spin density calculated by the Hückel MO method using a more negative value of the Coulomb integral for the oxygen atom in the deuterated than in the undeuterated species. In deuterium-substituted naphthalene, benzene, and cyclooctatetraene negative ions, on the other hand, calculations with a changed Coulomb integral do not yield results in agreement with experiment, whereas with a resonance-integral perturbation, satisfactory agreement is obtained.[6–8] In addi-

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(53) R. E. Moore and P. J. Scheuer, *J. Org. Chem.*, 31, 3272 (1966).

tion, the anomalous a^H/a^D ratios observed in the deuterium-substituted naphthalene and benzene anions, which are smaller than and in the opposite direction to those found for the intramolecular hydrogen-bonded compounds, cannot be adequately explained by changes in π-electron spin densities and are thought to arise from alterations in the $\sigma-\pi$ interactions when deuterium is substituted for hydrogen. These differences in the isotope effects for hydrocarbon and semiquinone radicals are all in accord with the assumption that the hydrogen atom in an intramolecular hydrogen bond undergoes motions that are primarily confined to the O–H–O plane, whereas in a C–H bond the main effects arise from the out-of-plane bending motion. Presumably, when a deuterium atom is substituted for a hydrogen atom in an intramolecular hydrogen bond, its motion is significantly different from that of a hydrogen atom. This description of the hydrogen bond suggested by the esr studies is consistent with other evidence.[4]

Systematic trends were observed in the changes of ring- and hydroxyl-proton splittings as the degree of polarity and protic character of the solvent were altered. The changes in the ring-proton splitting constants could be satisfactorily accounted for by the same type of model used previously[27] for semiquinone radicals without intramolecular hydrogen bonds, namely one in which there is an interaction between molecules of the solvent and localized sites in the radical which, in the present case, would be the oxygen atoms. The solvent dependence of the hydroxyl-proton splittings, however, was in the opposite direction to that predicted by this type of model. We suggest this probably arises because the structure of the intramolecular hydrogen bond is so sensitive to its surroundings that solvent interactions at the oxygen atoms may alter the structure and therefore the $\sigma-\pi$ parameters. The changes in the OH-proton splittings with solvent would then not be proportional to the changes in the π-electron spin densities on the oxygen atoms.

An attempt to correlate the hydroxyl-proton splittings with the calculated spin densities on the oxygen atoms was unsuccessful. A direct proportionality between the splitting and the sum of the spin densities on the oxygen atoms partaking in the hydrogen bond would be expected if a McConnell type of relationship were valid, and although the inaccuracies in the calculated spin densities might account for part of the difficulty in obtaining a good correlation, the results for the two most symmetrical radicals studied [di(OH)NQ$\cdot^-$ and 6,11-di(OH)TQ$\cdot^-$] are predicted to be in the wrong relative order, and it is unlikely that any refinements in π-electron spin-density calculations would remove this discrepancy. On the other hand, the proton–deuteron splitting-constant ratio for the OH and OD splittings is consistent with our spin density calculations; this result suggests a McConnell type of relationship may still be valid for a particular molecule in a particular environment. These considerations also indicate that the structure of the intramolecular hydrogen bond probably depends strongly on the individual radical and its surroundings, and thus the $\sigma-\pi$ parameters relating the hydroxyl-proton splittings to spin densities are likely to vary considerably from molecule to molecule, and may be particularly sensitive to the environment of the bond.