

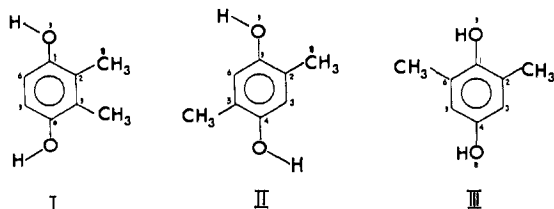
An Electron Spin Resonance Study of the Cation Radicals of Dimethylhydroquinones^{1a}

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Abstract: The electron spin resonance spectra (esr) of the 2,3-, 2,5-, and 2,6-dimethylhydroquinone cations have been obtained by oxidation of the hydroquinones both in an $\text{AlCl}_3\text{-CH}_3\text{NO}_2$ solution and in concentrated sulfuric acid. The esr spectrum of the 2,6-dimethylhydroquinone cation exhibits line-width alternation phenomena characteristic of the hindered rotation of the OH groups. However, neither the 2,3- nor the 2,5-dimethylhydroquinone cation radical esr spectra show any sign of an alternating line-width effect. This behavior is interpreted by assuming that the 2,3- and 2,5-dimethylhydroquinone cations are stabilized in the *cis* and *trans* conformations, respectively. Comparison of the hyperfine splittings with molecular orbital calculations and with the hyperfine splittings in the corresponding *p*-benzosemiquinone anions supports this view. Also, the changes are consistent with the assignments made for the hyperfine splittings in the *cis* and *trans* isomers of the unsubstituted hydroquinone cation.

Previous esr studies on the cation radicals of hydroquinone,^{2a} *p*-dimethoxybenzene,^{2b} and duroquinol³ have shown that these compounds exist as *cis* and *trans* isomers. Splitting constants were assigned by empirical molecular orbital calculations, but these assignments could not be confirmed unambiguously by direct experiment. By studying the 2,3- (I) and 2,5-dimethylhydroquinone (II) cations, which might be expected to exist predominantly in the *cis* and *trans* forms, respectively, it should be possible to confirm the initial assignments. The 2,6-dimethylhydroquinone (III), on the other hand, is expected to exist as both *cis* and *trans* isomers because of the symmetrical substitution, and thus serves as an additional reference compound.



Experimental Section

The cation radicals were prepared from the corresponding hydroquinones by oxidation with concentrated H_2SO_4 or with AlCl_3 in CH_3NO_2 . Spectral analyses and computer programming were carried out as described previously.⁴ 2,5-Dimethylhydroquinone was obtained from K & K Laboratories and was used without purification. The 2,3- and 2,6-dimethylhydroquinones were prepared by the reduction of the corresponding quinones obtained from Sapon Chemical Co.

Results

The 2,5-Dimethylhydroquinone Cation (II). The esr spectrum of the cation radical of II was first reported when *p*-xylene was oxidized by potassium persulfate in sulfuric acid. It was also observed when the parent

compound was dissolved in sulfuric acid.⁵ The spectrum was analyzed in terms of six equivalent protons (3.89 G) and four equivalent protons (3.00 G). Another investigation⁶ analyzed the spectrum in terms of six protons (3.70 G), two protons (2.98 G), and two protons (0.90 G). In both studies the wings of the spectrum were of low intensity, and the outside lines were too weak to be observed.

In the present study, the cation radical was prepared by three methods: (a) by dissolving II in concentrated H_2SO_4 or a 50:50 mixture of CF_3COOH and H_2SO_4 ; (b) by dissolving *p*-xylene in $\text{CF}_3\text{COOH-H}_2\text{SO}_4$ followed by irradiation with 2537-Å light; (c) reaction of II with AlCl_3 in CH_3NO_2 . In each case the radical was relatively stable; however, the line width varied considerably, (a) giving a line width of 0.25–0.30 G, (b) 0.15–0.20 G, and (c) 0.07–0.10 G. The spectra obtained by methods b and c (see Figure 1) were strong and well resolved, and a close examination of the wings lead to an interpretation in agreement with the analysis reported by Goodman⁶ (see Table I). Spectra in D_2SO_4 were also found to support this assignment.

Line-width asymmetries were noted in the spectra and were most pronounced when the radical was prepared by methods a and b. However, all three methods led qualitatively to the same conclusions; namely, that the lines associated with the ring and hydroxyl protons broaden to high field, whereas the lines due to the methyl protons broaden to low field. The magnitude of these effects followed the order $\text{OH} > \text{CH} > \text{CH}_3$. The interpretation of this broadening is consistent with previous results,^{2a,3,7} suggesting again that the signs of the isotropic splitting constants for OH, CH, and CH_3 are most probably negative, negative, and positive, respectively.

2,3-Dimethylhydroquinone (I). The cation radical of I was prepared both in $\text{AlCl}_3\text{-CH}_3\text{NO}_2$ and in concentrated H_2SO_4 . The esr spectrum in $\text{AlCl}_3\text{-CH}_3\text{NO}_2$ (Figure 2) was analyzed in terms of only one species. The splitting constants in both solvents are shown in Table I, and assignments were made by comparison with the MO calculations (Table II) and were confirmed by

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Table I. ESR Hyperfine Splitting Constants for the Dimethylhydroquinone and Dimethyl-1,4-dimethoxybenzene Cation Radicals

Compound	Position	Hyperfine splittings, G		<i>g</i> factor		
		AlCl ₃ -CH ₃ NO ₂ ^a	H ₂ SO ₄ ^a			
2,3-Dimethylhydroquinone	<i>a</i> ^H _{OH}	3.13	3.11	2.00343 ±		
	<i>a</i> ^H _{CH₃}	1.83	1.83	0.00002		
	<i>a</i> ^H _{CH}	2.58	2.58			
2,3-Dimethyl-1,4-dimethoxybenzene	<i>a</i> ^H _{OCH₃}	3.07				
	<i>a</i> ^H _{CH₃}	1.48				
	<i>a</i> ^H _{CH}	2.90				
2,5-Dimethylhydroquinone	<i>a</i> ^H _{OH}	3.11	3.00	2.00338 ±		
	<i>a</i> ^H _{CH₃}	3.81	3.82	0.00002		
	<i>a</i> ^H _{CH}	0.95	0.86			
2,5-Dimethyl-1,4-dimethoxybenzene	<i>a</i> ^H _{OCH₃}	3.22	3.19	2.00353 ±		
	<i>a</i> ^H _{CH₃}	4.29	4.45	0.0002		
	<i>a</i> ^H _{CH}	0.59	0.49			
2,6-Dimethylhydroquinone	<i>a</i> ^H _{OH} (1)	<i>cis</i> isomer	2.99	3.01	2.00337 ± 0.00002	
		<i>trans</i> isomer	2.99			
	<i>a</i> ^H _{OH} (4)	<i>cis</i> isomer	3.11	3.11		
		<i>trans</i> isomer	3.11			
	<i>a</i> ^H _{CH₃} (2)	<i>cis</i> isomer	2.11	2.55		2.18
		<i>trans</i> isomer	2.55			
	<i>a</i> ^H _{CH₃} (6)	<i>cis</i> isomer	2.26	1.82		1.81
		<i>trans</i> isomer	1.82			
<i>a</i> ^H _{CH} (3)	<i>cis</i> isomer	1.87	1.70	1.99		
	<i>trans</i> isomer	1.70				
<i>a</i> ^H _{CH} (5)	<i>cis</i> isomer	2.12	2.29	1.81		
	<i>trans</i> isomer	2.29				

^a Error in splitting constants is $\pm 0.5\%$ for $a_i > 1$ G.

Table II. Summary of Molecular Orbital Calculations for the Dimethylhydroquinone Cation Radicals^a

Compound	Position	ρ_i (calcd)	ρ_i (calcd) ^b	a_i (calcd)	a_i (calcd) ^b	a_i (exptl)
2,3-Dimethylhydroquinone	1	0.1889	0.1869			
	2	0.0706	0.0689	1.90 ^c	1.86 ^c	1.83 (1.81) ^e
	5	0.0937	0.0970	-2.62 ^d	-2.72 ^d	-2.58 (2.57)
	7	0.1425	0.1428			-3.13 (3.11)
2,5-Dimethylhydroquinone	1	0.1882	0.1849			
	2	0.1300	0.1447	3.51 ^c	3.91 ^c	3.81 (3.82)
	3	0.0343	0.0229	-0.96 ^d	-0.64 ^d	-0.95 (0.86)
	7	0.1394	0.1384			-3.11 (3.00)
2,6-Dimethylhydroquinone	1	0.2058				
	2	0.0967		2.61 ^c		2.18 (2.41)
	3	0.0661		-1.85 ^d		-1.99 (1.81)
	7	0.1725				-3.11 (3.01)
	8	0.1582				-2.99 (3.01)

^a Parameters used were $h_o = 1.65$, $k_{oc} = 1.20$; for the methyl groups the inductive model was used $>C-C'-X$; $h_c = -0.10$, $h_{c'} = -0.10$, $h_x = 0.50$, $k_{cc'} = 0.70$, $k_{cx} = 2.50$. ^b Calculated using the additional parameters $h_c(5) = h_c(6) = 0.03$ for the 2,3 isomer and $h_c(3) = h_c(6) = 0.05$ for the 2,5 isomer. ^c Calculated using $Q^{\text{HCH}_3} = 27$. ^d Calculated using $Q^{\text{HCH}} = -28$. ^e Results in parentheses are for H₂SO₄ solutions.

dissolving the hydroquinone in concentrated D₂SO₄. The spectrum in AlCl₃-CH₃NO₂ was found to be slightly temperature dependent due to a small variation of the

2,6-Dimethylhydroquinone (III). The esr spectrum of the cation radical of III in AlCl₃-CH₃NO₂ is extremely complicated and is temperature dependent

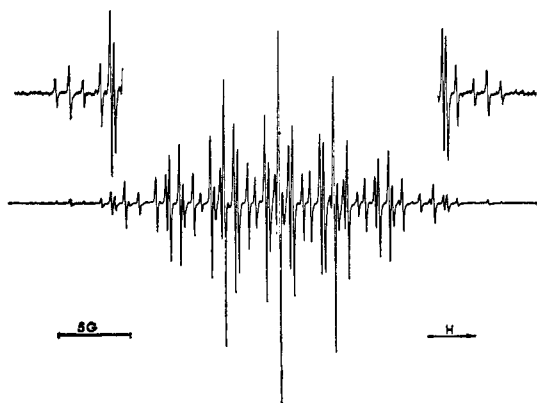


Figure 1. The esr spectrum of the 2,5-dimethylhydroquinone cation radical in AlCl₃-CH₃NO₂ at -50°.

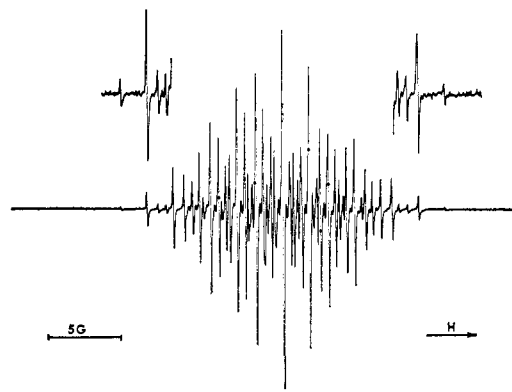


Figure 2. The esr spectrum of the 2,3-dimethylhydroquinone cation radical in AlCl₃-CH₃NO₂ at -50°.

hydroxyl splitting constant. Line-width asymmetries in the spectrum were again noted and were qualitatively similar to those observed for II.

(Figure 3a, c, d). At -60° (Figure 3a) the spectrum can be analyzed in terms of two species (see Table I), and a computer simulation using these parameters is

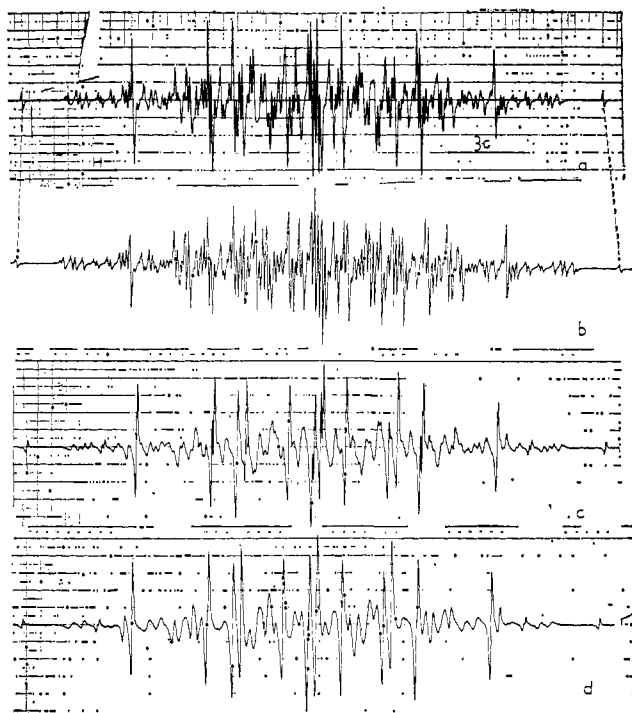


Figure 3. The esr spectrum of the 2,6-dimethylhydroquinone cation radical in $\text{AlCl}_3\text{-CH}_3\text{NO}_2$ at (a) -60° , (c) -25° , and (d) $+25^\circ$. Figure 3b shows a computer-simulated spectrum of Figure 3a using the parameters given in Table I.

shown in Figure 3b. As the temperature is increased line-width alternation effects are observed. At -25° (Figure 3c), the main lines of the spectrum can be analyzed in terms of three equivalent protons of 4.361 G, and three nonequivalent protons of 2.985, 3.089 and 4.017 G, respectively. The line intensities do not, however, obey the binomial intensity distribution; in particular, the lines due to the three equivalent protons are in the approximate ratios 1:9:9:1. This result is consistent with a line-width alternation of the methyl and ring protons. In the limit of maximum alternation, only four lines from the methyl groups and two lines from the ring protons are expected. (The two other nonequivalent protons are the hydroxyl protons.) This parallels the behavior of duroquinol³ except that in this case, the alternation is complicated by the nonequivalence of the methyl groups and the ring protons. A four-jump process, similar to that for the hydroquinone cation, can be postulated to account for the changes in the spectra which are observed. At higher temperatures one anticipates a time-averaged spectrum due to rapid interconversion between the four conformations. At $+25^\circ$ (Figure 3d), the lines are broadened considerably, but it is obvious that the rapid-rotation limit has not yet been reached. Higher temperatures are precluded due to the rapid decay of the radical.

In concentrated H_2SO_4 line widths were considerably broader (~ 0.3 G) so that no anomalous line-width effects could be observed; however, the spectrum resembled that of III in $\text{AlCl}_3\text{-CH}_3\text{NO}_2$ at the highest temperature. The hyperfine splittings are given in Table I. Assignment of the OH hyperfine splitting was confirmed by dissolving III in concentrated D_2SO_4 .

Methylhydroquinone and Trimethylhydroquinone.

On reaction with $\text{AlCl}_3\text{-CH}_3\text{NO}_2$ both compounds gave their respective cation radicals, the esr spectra of which were extremely complex and temperature dependent. At lower temperatures the spectra are probably composed of *cis* and *trans* isomers. Because of the expected nonequivalence of all ring positions, the spectra are unduly complicated and therefore have not been analyzed in detail. Solution of the hydroquinones in concentrated H_2SO_4 also gave complex spectra which could not be interpreted.

Discussion

1. Conformations. For the duroquinol cation it has been observed that the separation of lines in the esr spectrum attributable to *cis* and *trans* isomers occurs at a lower temperature than is the case for the hydroquinone cation.^{2a} In addition, the barrier to rotation is lower in duroquinol (4 kcal mol⁻¹ vs. 10 kcal mol⁻¹ in the hydroquinone cation). These facts indicate that the methyl group is probably interacting sterically with the hydroxyl group. Thus it might be argued that the preferred conformation for the hydroxyl group will be *anti* to a methyl group. This then suggests that the more stable conformations of the 2,3- and 2,5-dimethylhydroquinone cations are the *cis* (I) and *trans* (II) forms, respectively. Similar arguments may also be applied to the cation radicals of 2,3- and 2,5-dimethyl-1,4-dimethoxybenzene and results for these compounds are given for comparison in Table I. For the 2,6-dimethylhydroquinone cation, the substitution is symmetrical and no stabilization should occur. At low temperatures, line-width alternation phenomena should be observed and are found experimentally. The magnitudes of the splitting constants of I and II may be compared with those found for the *cis* and *trans* isomers of hydroquinone^{2a} and *p*-dimethoxybenzene.^{2b} The agreement is good, suggesting that the assignment based on the empirical molecular orbital approach which was used to simulate the spin densities in the isomers of hydroquinone and *p*-dimethoxybenzene was essentially correct.

2. Molecular Orbital Calculations. Calculations were carried out using the McLachlan perturbation corrections to the Hückel LCAO-MO method;⁸ $\lambda = 1.20$ was used. The methyl group was treated according to the inductive model of Lazdins and Karplus.⁹ The Coulomb and resonance integral parameters of oxygen were varied over a wide range and the results of the spin-density dependencies are shown in Figures 4 and 5 for the 2,3- and 2,5-dimethyl substituents. Assuming that the McConnell equations, $a^{\text{H}_{\text{CH}}} = Q^{\text{H}_{\text{CH}}}\rho_{\text{C}}$, $a^{\text{H}_{\text{CH}_3}} = Q^{\text{H}_{\text{CH}_3}}\rho_{\text{C}}$, hold and that $Q^{\text{H}_{\text{CH}}} = -28$ G and $Q^{\text{H}_{\text{CH}_3}} = 27$ G, it was found possible to obtain good agreement for the cation radicals of I and II with $h_{\text{O}} = 1.65$, $k_{\text{OC}} = 1.20$ (see Table II). These parameters were obtained by minimizing the deviations between the experimental and calculated spin densities of I and II. The agreement for III using the same parameters was also found to be reasonable.

Inclusion of the empirical parameters previously employed to reproduce the asymmetry in the *cis* and *trans* isomers of the hydroquinone cation gave slightly

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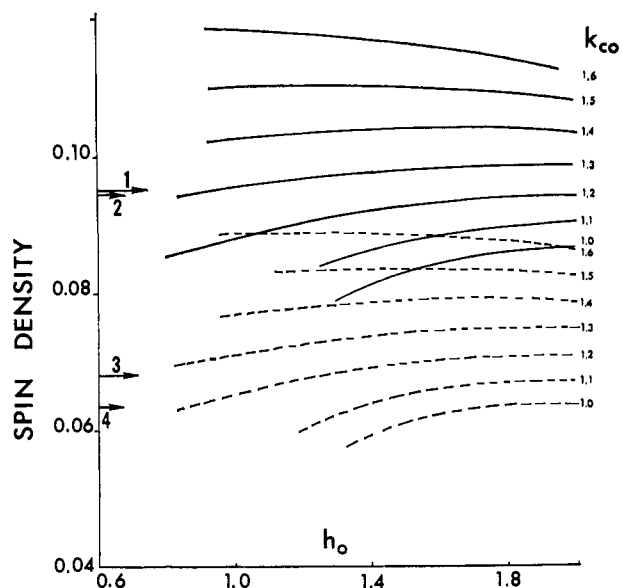


Figure 4. The dependence of the calculated spin densities for the 2,3-dimethyl-substituted compounds as a function of the h_o and k_{CO} parameters. The full lines are the spin densities at carbon atoms 5 and 6, the numbers 1 and 2 on the spin density axis are the experimental spin densities for the hydroquinone cation and semiquinone anion at these positions. The dotted lines are the spin densities at carbon atoms 2 and 3, while numbers 3 and 4 on the spin density axis are the experimental spin densities at these positions for the semiquinone anion and hydroquinone cation, respectively.

different results as seen in columns 4 and 6 of Table II. From the calculated spin densities (Table II), assuming that the relationship $a^H_{OH} = Q^H_{OH}\rho_O$ holds, a value of $Q_{OH} = -22$ G is found for I and II. This is in good agreement with the earlier suggestion that $Q^H_{OH} \approx -20$ G.^{2a}

3. Comparison of the Hyperfine Splittings in the Dimethyl-*p*-benzosemiquinone Anions¹⁰ with Those in the Hydroquinone Cations. It is interesting to compare the effect of the methyl group in the anion and cation radicals (Table III). As can be seen, very little difference in the ring proton splitting constants is found for I and III; however, a large difference is observed for II.

Table III. Comparison of the Hyperfine Splittings for the Dimethyl-*p*-semiquinone Anions and the Dimethylhydroquinone Cations

Positions of methyl substitution	Hyperfine splittings, G	
	Semiquinone anion ^a	Hydroquinone cation
2,3	$a^H_{CH} = 2.595$	2.58 (2.57) ^b
	$a^H_{CH_3} = 1.714$	1.83 (1.81)
2,5	$a^H_{CH} = 1.836$	0.95 (0.86)
	$a^H_{CH_3} = 2.248$	3.81 (3.82)
2,6	$a^H_{CH} = 1.892$	1.99 ^c (1.81)
	$a^H_{CH_3} = 2.125$	2.18 ^c (2.41)
Unsubstituted	$a^H_{CH} = 2.368$	2.25 (2.36)

^a Taken from ref 10. ^b Numbers in parentheses are the results for H₂SO₄. ^c Averaged values.

Qualitatively, the results may be explained as follows. The spectra of the *p*-benzosemiquinone anion

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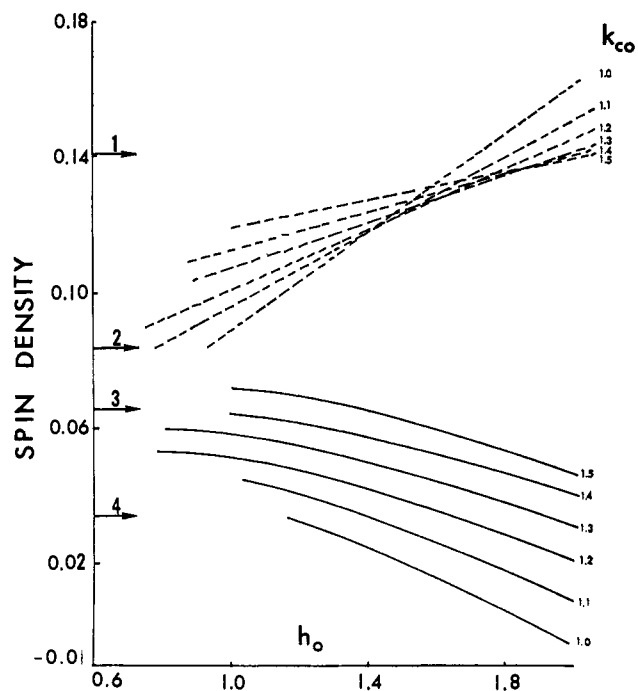
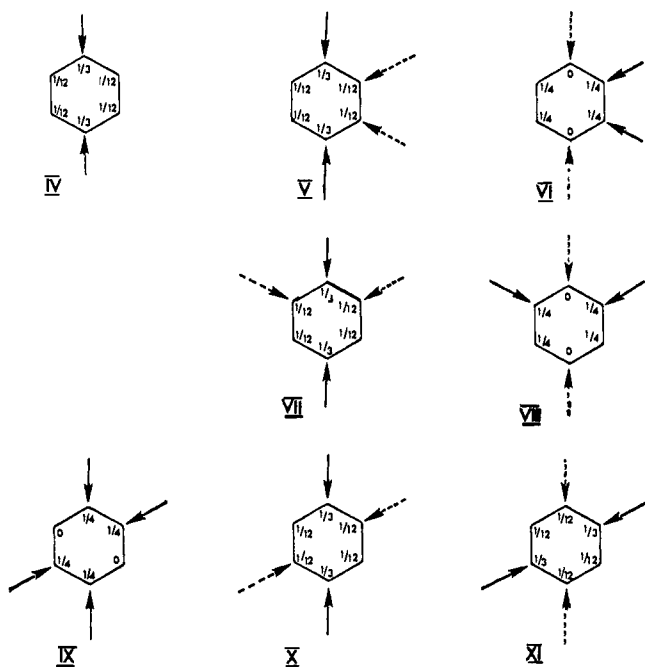


Figure 5. The dependence of the calculated spin densities for the 2,5-dimethyl-substituted compounds as a function of the h_o and k_{CO} parameters. The dotted lines are the spin densities at carbon atoms 2 and 5, the numbers 1 and 2 on the spin density axis are the experimental spin densities for the hydroquinone cation and semiquinone anion at these positions. The full lines are the spin densities at carbon atoms 3 and 6, while numbers 3 and 4 on the spin density axis are the experimental spin densities at these positions for the semiquinone anion and hydroquinone cation, respectively.

and the hydroquinone cation show that the unpaired electron is in the same orbital in both; namely, the highest unfilled symmetric bonding orbital (IV), assuming that both are considered as perturbed benzene cation radicals and that the electron-donating effects of the O⁻ and OH groups are predominant. Thus one actually observes a radical with an electron hole. The effect of 2,3- and 2,6-electron-donating substituents will depend upon their strength. If they are much stronger than the 1,4 substituents, a switch to the antisymmetric orbitals (VI and VIII) might occur. If all four substituents were equally strong, the symmetric orbital would still be favored. The effect of 2,3- and 2,6-dimethyl substituents is therefore predicted to be small since the electron-donating effects of O⁻ and OH are greater than that of a methyl group. For 2,5 substituents a slightly different situation exists (IX → XI); if all four substituents are equally electron donating, a switch in orbitals will occur to the antisymmetric orbital with a node at the unsubstituted positions (IX) (for example, compare 1,2,4,5-tetramethoxybenzene¹¹). Therefore, as the effects of the 1,4 and 2,5 substituents become nearly equal, one might expect to observe a mixing of orbitals IX and X. The experimental data suggest that this is an actuality for the 2,5-dimethylhydroquinone cation since the ring proton splittings decrease and the methyl splittings increase relative to the unsubstituted hydroquinone. That this situation is not observed for the 2,5-dimethylsemiquinone anion may

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be due to the greater electron-donating ability of O⁻ relative to OH which thus prevents any significant contributions from orbital X. Assuming that the 2,5-dimethylhydroquinone is a linear combination of IX and X and taking 1,4-dimethoxybenzene^{2b} and 1,2,4,5-tetramethoxybenzene¹¹ as limiting cases, it can be estimated that the contribution of structure IX is about 40%.



Quantitatively, since the unpaired electron is in the same molecular orbital for both sets of radicals, it seems feasible that the changes can be simulated by molecular orbital calculations. This may be done by changing the Coulomb and resonance integrals of the oxygen atoms and assuming that the $Q^{\text{H}_{\text{CH}}}$ and $Q^{\text{H}_{\text{CH}_2}}$ parameters are the same for both the semiquinone anions and hydroquinone cations. This was done systematically for I and II and the results are shown graphically in Figures 4 and 5. The 2,3-dimethyl compound is seen to be relatively insensitive to the choice of h_{O} over a fairly wide range; this parallels the behavior found for the unsubstituted compound.^{2a} On the other hand, the k_{OC} parameter need not be changed very greatly to obtain good agreement for both the semiquinone anion and hydroquinone cation. This is physically realistic and reflects the effect of the proton on the electronegativity of the oxygen atom, the bond length being relatively unaffected.

The 2,5-dimethyl-substituted compound (Figure 5) shows a large dependence on both the h_{O} and k_{OC} parameters. In general, high values of h_{O} most closely approach the cation spin densities while low values of h_{O} approach the anion spin densities. A separate analysis was made for both the cation and anion radicals of I and II. The best values for the cation radicals as already mentioned are $h_{\text{O}} = 1.65$, $k_{\text{OC}} = 1.20$. In a similar manner, the best set for the anion radicals were found to be $h_{\text{O}} = 0.80$, $k_{\text{OC}} = 1.25$. Significantly, the k_{OC} parameter is found to be very similar for both groups,

whereas the h_{O} parameter is dramatically different. The calculated spin densities for the anion radicals are shown in Table IV; the agreement for I is good, but for II only poor agreement is found and under *no* conditions can this situation be improved while still giving reasonable results for II. The spin densities on the oxygen atoms are seen to change by almost a factor of 2 (as compared to the results in Table II). This can be related to the change in *g* factor from $\cong 2.0034$ (Table I) for the hydroquinones, to $\cong 2.0045$ for the semiquinone anions.¹² This corresponds to a deviation from the free spin value of ~ 0.0009 and ~ 0.0020 , respectively.

Table IV. Summary of Molecular Orbital Calculations for the Dimethylsemiquinone Anions^a

Compound	Position	ρ_i (calcd)	a_i (calcd)	a_i (exptl)	% dev
2,3-Dimethyl-semiquinone	1	0.0607			
	2	0.0661	1.784	1.714 ^b	+4.1
	5	0.0898	-2.514	2.595 ^c	-3.1
	7	0.2803			
2,5-Dimethyl-semiquinone	1	0.0615			
	2	0.0982	2.651	2.248 ^b	+17.9
	3	0.0566	-1.585	1.836 ^c	-13.7
	7	0.2789			
2,6-Dimethyl-semiquinone	1	0.0637			
	2	0.0900	2.43	2.125 ^b	+14.3
	3	0.0646	-1.808	1.892 ^c	-4.4
	7	0.3095			
	8	0.2503			

^a Parameters used were $h_{\text{O}} = 0.80$, $k_{\text{OC}} = 1.25$, plus methyl parameters as indicated in Table II. ^b Calculated using $Q^{\text{H}_{\text{CH}_3}} = 27$. ^c Calculated using $Q^{\text{H}_{\text{CH}}} = -28$.

The h_{O} parameter found for the semiquinone anions is different from those suggested by Das and Frankel¹¹ ($h_{\text{O}} = 1.20 \rightarrow 1.60$, $k_{\text{OC}} = 1.20 \rightarrow 1.60$) and by Broze, Luz, and Silver¹³ ($h_{\text{O}} = 1.17$, $k_{\text{OC}} = 1.46$). It seems probable that more intensive carbon-13 and oxygen-17 studies are necessary to completely resolve the problem.

Conclusions

The esr spectra of the dimethylhydroquinone cation radicals indicate that in the 2,3- and 2,5-dimethylhydroquinone cations, the molecules are stabilized in the *cis* and *trans* conformations, respectively. The splitting constants are consistent with the assignments for the splittings in the *cis* and *trans* isomers of the hydroquinone cation. On the other hand, the esr spectrum of the 2,6-dimethylhydroquinone cation exhibits a line-width-alternation phenomena characteristic of hindered rotation of the OH groups. Changes in the hyperfine splittings between the dimethyl-*p*-benzosemiquinone anions and the corresponding hydroquinone cations are consistent with qualitative molecular orbital predictions.

Acknowledgments. We wish to thank Mr. Douglas Berkner for his help in taking some of the esr spectra.

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(13) M. Broze, Z. Luz, and B. L. Silver, *ibid.*, **46**, 4891 (1967).