radicals A and B). From the slope of the plot in Figure 4, a difference in the Arrhenius activation energies of 1.8 kcal for these two products can be determined.

Experimental Section

Apparatus and Methods of Analysis. γ-Butyrolactone was irradiated in a cyclindrical Cary quartz cell of 1-cm path length. The Teflon stopper of the cell was provided with a small hole through which a syringe needle could be inserted for withdrawing samples for gas chromatographic analysis. With this arrangement, a single injection into a chromatograph equipped with a flame detector and a cyanosilicone XF 1500 column (60°, 10 ft × $^1/_8$ in.) permitted the analysis of allyl formate, cyclopropane, and ethylene. A Carbowax 20M (155°, 10 ft × $^1/_8$ in.) column was used for the analysis of succinaldehyde. The solutions were all flushed with nitrogen prior to irradiation. This procedure was found to be more than sufficient since the same results were obtained when the solutions were degassed by repeated freeze–thaw cycles or when air saturated.

For the analysis of carbon monoxide and carbon dioxide, a different procedure was used. The volatile fraction at $-196°$ was removed with a Toepler pump and its volume determined with a calibrated gas buret. Mass spectrometric analysis showed this fraction to consist entirely of carbon monoxide. A second fraction was taken at $-78°$. This fraction consisted of cyclopropane, carbon dioxide, and ethylene. Mass spectrometric analysis yielded the mole ratio of cyclopropane to carbon dioxide. The cell employed for irradiations in which carbon monoxide and carbon dioxide analyses were performed was larger (3-cm diameter and 0.5-cm path length) and equipped with an approprirate arrangement for degassing.

The experiments were performed with a Hanovia low-pressure mercury lamp (type) emitting mainly the 2537-Å resonance line and with the 2380-Å line of a medium-pressure mercury lamp (Hanovia Type A, 500 w). The beam of the resonance lamp was concentrated with a lens and passed through a 3-cm chlorine filter to remove radiation at higher wavelengths, and the light from the medium pressure lamp was rendered monochromatic with a Bausch and Lomb monochromator. For runs above room temperature, the cell was enclosed in an aluminum block furnace.

The identification of products was accomplished by the usual instrumental method, and in each case the spectral properties were compared to those of authentic samples. The actinometry employed was ferrioxalate.

Materials. The γ-butyrolactone was obtained from the Matheson Co. and was fractionated with a spinning-band column, retaining the middle fraction. Examination of the absorption spectrum of the neat lactone (1-cm path length) showed a shoulder beginning at 3100 Å. Since this absorption was suspected as being due to impurities, the lactone was subjected to charcoal treatment until all absorption above 2700 Å was virtually eliminated. The lactone thus purified shows a sharp rise in absorption beginning at 2600 Å. After the charcoal treatments, the lactone was again subjected to a fractionation, the middle fraction being retained. Glpc analysis showed the remaining impurities to be 0.1%.

The cyclohexene was purified by fractionation and chromatography over alumina; *cis*- and *trans*-butene (Phillips) were used without further purification. Biacetyl and isopropyl alcohol were purified by fractionation. The acetonitrile used was Matheson "chromato" quality. All solutions were made up immediately after purification and used without delay.

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Electron Spin Resonance in *t*-Butyl-Substituted Semiquinones. The Hyperfine Structure of *t*-Butyl Protons

Charles Trapp, Charles A. Tyson,[1] and G. Giacometti[2]

Contribution from the Department of Chemistry, Illinois Institute of Technology, Chicago, Illinois 60616. *Received September 11, 1967*

Abstract: The electron spin resonance spectra of three *p*-benzosemiquinones and four *o*-benzosemiquinones with *t*-butyl substituents have been obtained. Resolution of *t*-butyl proton hyperfine splittings has been accomplished in all but one of the radicals. The most reasonable interpretation of the splittings is in terms of carbon–carbon hyperconjugation which produces unpaired spin density in the β-carbon atom tetrahedral orbitals. Spin density is then transferred to the protons by a spin-polarization mechanism. The Q value for the latter mechanism is approximately 44 gauss, which indicates that tetrahedral orbitals are more effective than p_z orbitals in polarizing hydrogen 1s orbitals. Hückel molecular orbital calculations are performed to fit the data; the results indicate that the *t*-butyl group is probably more inductive than the methyl group and that an interaction between the carbonyl group and a *t*-butyl group *ortho* to it may occur.

The effect of ring substitution on the electron spin resonance (esr) spectra of semiquinone radical anions has been the subject of a number of papers.[3-10] The effect of chloro and methyl substitution in *p*-benzosemiquinone on the ring proton hyperfine splitting (hfs) can be accounted for by the additivity rules of Venkataraman and Fraenkel.[6] The hfs of the methyl protons has been explained in terms of hyperconjugation by Bersohn.[5] Vincow and Fraenkel[7] did a Hückel molecular orbital (HMO) calculation on *p*-benzosemiquinones in which the parameters were varied to obtain the best fit for the ring proton hfs. This calculation

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(1) Department of Medical Chemistry, Kyoto University, Sakyo, Kyoto, Japan.

(2) National Science Foundation Senior Foreign Scientist Fellow, 1967. University of Padua, Padua, Italy.

(3) B. Venkataraman and G. K. Fraenkel, *J. Am. Chem. Soc.*, 77, 2707 (1955).

(4) R. Hoskins, *J. Chem. Phys.*, 23, 1975 (1955).

(5) R. Bersohn, *ibid.*, 24, 1066 (1956).

(6) B. Venkataraman, B. G. Segal, and G. K. Fraenkel, *ibid.*, 30, 1006 (1959).

(7) G. Vincow and G. K. Fraenkel, *ibid.*, **34**, 1333 (1961).

(8) A. Fairbourn and E. A. C. Lucken, *J. Chem. Soc.*, 258 (1963).

(9) T. J. Stone and W. A. Waters, *ibid.*, 1488 (1965).

(10) L. M. Stock and J. Suzuki, *J. Am. Chem. Soc.*, **87**, 3909 (1965).

was moderately successful for 2-methyl-*p*-benzosemiquinones. Fairbourn and Lucken[8] considered the inductive effect of methyl and *t*-butyl substitution on ring carbon atom spin densities in *p*-benzosemiquinone using HMO theory. Good agreement of the calculated values with experimental results was not obtained, but their treatment did indicate that the inductive effect of the *t*-butyl group was slightly greater than that of methyl and that an interaction of the substituent with the carbonyl group might account for some of the observed discrepancies. This "*ortho*" interaction effect would essentially result in a shortening of the carbon–oxygen bond distance.

Stone and Waters[9] noted that very few substituted *o*-semiquinones had been studied by esr. They report results on a large number of compounds, some of which were methyl- and *t*-butyl-substituted *o*-semiquinones. They did not, however, attempt a theoretical interpretation of the spectra. Stock and Suzuki[10] have done esr on 2-*t*-butyl-C^{13}- and 2-trifluoromethyl-*p*-benzosemiquinone and have shown that spin density is transferred to β nuclei presumably by way of a hyperconjugative mechanism. They observed β-C^{13} hyperfine splittings in enriched samples and were able to estimate the spin density in 2s orbitals of the β-carbon atoms. They concluded that carbon–carbon hyperconjugation is only slightly less effective than carbon–hydrogen hyperconjugation.

Hoskins[4] has observed an esr spectrum of 4-*t*-butyl-*o*-benzosemiquinone. The large number of lines in the spectrum indicated the presence of *t*-butyl proton splittings, but because of limited resolution the splitting constant could not be obtained. Fraenkel[11] has reported that it is possible to resolve the proton hfs in 2,5-di-*t*-butyl-*p*-benzosemiquinone. In view of this we conclude that it may be possible to observe *t*-butyl splittings in a larger number of *t*-butyl-substituted *p*- and *o*-benzosemiquinones.

In this paper we report the esr spectra of seven *t*-butyl-substituted benzosemiquinones. The *t*-butyl proton hfs has significance from the point of view of carbon–carbon hyperconjugation. At present very little good experimental data are available which are directly associated with this effect. Any *t*-butyl proton hfs in one of the radicals, 2-*t*-butyl-*p*-benzosemiquinone, may be related to the β-C^{13} hfs observed in the same radical by Stock and Suzuki.[10] The mechanism of the transfer of spin density from the β-carbon atoms to the *t*-butyl protons is probably through a spin-polarization mechanism of the type which is effective for ring protons. We will attempt to determine a Q value for this interaction from our experimental data in conjunction with the data of Stock and Suzuki on β-C^{13} hfs splittings and also from a Hückel molecular orbital model.

The presence of an interaction between the *t*-butyl group and the carbonyl group, when they are *ortho* to each other, should probably affect the nature of the *t*-butyl hfs, and we should find some evidence for this in the spectra and in the HMO parameters used to fit the hfs data. In addition we shall attempt to determine whether the additivity relationships of Venkataraman and Fraenkel,[3] which apply to methyl-substituted benzosemiquinones, will work in the case of *t*-butyl substitution. Finally, we shall attempt to fit the experimental data on both methyl and *t*-butyl-substituted *o*- and *p*-benzosemiquinones using HMO theory and a conjugative model for the substituent.

Experimental Section

The esr spectra were all taken on a Varian Associates V-4502-12 epr spectrometer. All measurements were made at 25° in alkaline methanol–water solutions. The methanol concentration was generally 50% by weight, but in some cases lower methanol concentrations were necessary to get full resolution. The splitting constants changed only slightly with change in methanol concentration. The *p*- and *o*-semiquinones were generated from the corresponding hydroquinone or catechol in a Pyrex cell by bubbling air through the alkaline solutions. The reaction mixture was circulated through 1.5-mm i.d. Pyrex tubing in the microwave cavity using a peristaltic pump. Flow rate was 30 ml/min, and the pH reading was kept constant at about 10.0–10.5, relative to standardization in $-\log [H^+]$ units in 50% methanol.[12] Concentrations of the radicals were estimated at about 10^{-3} *M*.

Chemicals were all commercially available: 2-*t*-butylhydroquine from Eastman Organic Chemicals; 2,5-di-*t*-butylhydroquinone, 4-*t*-butylpyrocatechol, 3,5-butyl-5-methylpyrocatechol, and 5-*t*-butyl-3-methylpyrocatechol from Aldrich Chemical Co.; 2,6-di-*t*-butyl-*p*-benzoquinone, a gift from the Ethyl Corp., and 3-5-di-*t*-butylpyrocatechol from Gallard-Schlesinger, Long Island City, N. Y. All were used without further purification except for the last item which was recrystallized twice from benzene. The hydroquinone of 2,6-di-*t*-butyl-*p*-benzoquinone was prepared by zinc–HCl reduction of the *p*-quinone.[13]

A frequency meter and an nmr gaussmeter were used to measure *g* values of the radicals studied. It was not felt that the *g* values of these radicals were significant so that they were measured to an accuracy of only one part in 3000. The *g* values of all the radicals were constant at 2.0042 ± 0.0007.

The HMO calculations were performed on an IBM Model 360-40 data-processing system with a Jacobi diagonalization routine.

Results

2-*t*-Butyl-*p*-benzosemiquinone. Our results are very close to those reported by Stock and Suzuki[10] for the ring protons. The splitting constants are given in Table I. The subscripts on the splitting constants refer to the ring carbon atom to which the hydrogen atom is attached. The coupling constants are assigned on the basis of the results of the HMO calculations described in the next section and are, therefore, not unambiguous. a_3 and a_6 tend to decrease about 10% from the values given in the table when the methanol concentration is reduced to 12.5%, whereas a_5 is unaffected. The spectrum consists of eight main lines as previously reported.[10] Upon higher resolution each main line is split into a number of lines. This latter splitting is produced by the *t*-butyl protons, and the splitting constant is $a_2^{t\text{-Bu}} = 0.060 \pm 0.005$ gauss. The three main lines on the low-field side of the center of the spectrum are shown in Figure 1. The presence of a center line in the group associated with each main line may indicate that the *t*-butyl group is not freely rotating. This lack of free rotation may be evidence of an interaction between the *t*-butyl group and the carbonyl group *ortho* to it.

2,5-Di-*t*-butyl-*p*-benzosemiquinone. Fraenkel[11] reports the observation of *t*-butyl proton hfs in this radical, and Adams, Blois, and Sands[14] determined the ring proton hfs splittings. Our experimental values are given in Table I and agree with those previously reported. The spectrum is shown in Figure 2 and is a

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(11) G. K. Fraenkel, *Ann. N. Y. Acad. Sci.*, **67**, 546 (1957).

(12) C. A. Tyson and A. E. Martell, *J. Am. Chem. Soc.*, in press.

(13) A. I. Vogel, "A Textbook of Practical Organic Chemistry," 3rd ed, John Wiley and Sons, Inc., New York, N. Y., 1956, p 748.

(14) M. Adams, M. S. Blois, and R. H. Sands, *J. Chem. Phys.*, **28**, 774 (1958).

Table I. Hfs Splitting Constants of *t*-Butyl- and Methyl-Substituted Benzosemiquinones[a]

Radical	Solvent[b]	a_2	a_3	a_4	a_5	a_6
			A. This Work			
2-*t*-Butyl-*p*-	50% CH_3OH	0.060 ± 0.005	1.55 ± 0.02	...	2.82 ± 0.02	2.07 ± 0.02
2-*t*-Butyl-*p*-	12.5% CH_3OH	0.060 ± 0.005	1.41 ± 0.02	...	2.82 ± 0.02	1.91 ± 0.02
2,5-Di-*t*-butyl-*p*-	50% CH_3OH	0.060 ± 0.005	2.07 ± 0.02	...	0.060 ± 0.005	2.07 ± 0.02
2,6-Di-*t*-butyl-*p*-	50% CH_3OH	0.055 ± 0.005	1.17 ± 0.02	...	1.17 ± 0.005	0.005 ± 0.005
4-*t*-Butyl-*o*-	50% CH_3OH	...	0.3 ± 0.1	0.32 ± 0.03	3.80 ± 0.02	1.17 ± 0.02
3,5-Di-*t*-butyl-*o*-	50% CH_3OH	...	<0.03	2.67 ± 0.02	0.31 ± 0.03	0.3 ± 0.1
3-Methyl-5-*t*-butyl-*o*-	50% CH_3OH	...	0.3 ± 0.1	3.07 ± 0.02	0.29 ± 0.03	0.3 ± 0.1
3-*t*-Butyl-5-methyl-*o*-	50% CH_3OH	...	<0.03	2.50 ± 0.02	5.35 ± 0.02	0.35 ± 0.02
			B. Previous Work[c]			
2-Methyl-*p*-[d]	70% CH_3CH_2OH	2.045	1.764	...	2.537	2.462
2-*t*-Butyl-*p*-[e]	Acetonitrile	...	1.65	...	2.85	2.10
2,5-Dimethyl-*p*-[d]	70% CH_3CH_2OH	2.248	1.836	...	2.248	1.836
2,6-Dimethyl-*p*-[d]	70% CH_3CH_2OH	2.125	1.892	...	1.892	2.125
2,5-Di-*t*-methyl-*p*-[f]	Ethanol–water	...	2.13	...	...	2.13
4-Methyl-*o*-[g]	Water	...	0.25	5.1	4.0	1.0
4-*t*-Butyl-*o*-[h]	Ethanol–water	...	...	...	4.1	...
3,5-Di-*t*-butyl-*o*-[i]	Acetone	...	...	2.5	...	...
3-*t*-Butyl-5-methyl-*o*-[g]	Water	...	...	2.65	5.4	0.3

[a] All splitting constants are in gauss. [b] Other component of the solvent was in all cases water. [c] Only compounds of direct interest to this research are listed. [d] Reference 6. [e] Reference 10. [f] Reference 14. [g] Reference 9. [h] Reference 4. [i] Reference 16.

good example of the resolution obtained in our experiments.

2,6-Di-*t*-butyl-*p*-benzosemiquinone. This radical has been observed before only at low resolution.[15] We had no difficulty in resolving the *t*-butyl proton hfs. The splitting constants are given in Table I and differ somewhat from those previously reported. The spectrum is similar in appearance to the spectrum shown in Figure 2, but with a smaller ring proton splitting.

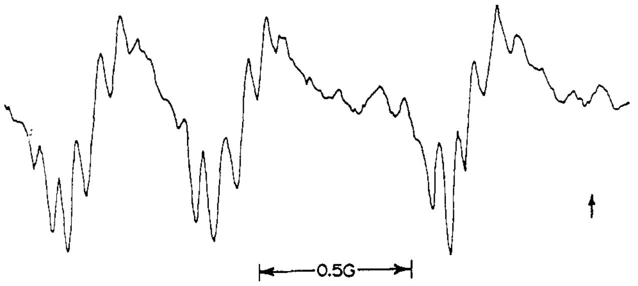

Figure 1. Part of the esr spectrum of 2-*t*-butyl-*p*-benzosemiquinone. The arrow represents the position of the center of the spectrum.

4-*t*-Butyl-*o*-benzosemiquinone. The esr spectrum of this radical has been previously observed by Hoskins.[4] However, he was able to obtain only one splitting constant due to limited resolution. Our results are presented in Table I and Figure 3. The ring proton splitting constants are assigned on the basis of the HMO calculations described in the next section. The value given in the table for a_3 is somewhat uncertain because of the complicated nature of the spectrum. The splitting from the *t*-butyl protons is clearly evident in the figure and has the value $a_4^{t\text{-Bu}} = 0.32 \pm 0.03$ gauss. This is 5.3 times greater than the *t*-butyl splitting in 2-*t*-butyl-*p*-benzosemiquinone. In the analogous methyl compounds the ratio between the methyl proton splittings is 2.5. Splitting constants for the methyl-substituted semiquinones analogous to the *t*-butyl-substituted compounds studied in this research are also presented in Table I for comparison purposes. The significance of the difference between the ratios 5.3 and 2.5 is discussed in the next section. Examination of Figure 3 shows that, in contrast to the case of 2-*t*-butyl-*p*-benzosemiquinone, there is no evidence of hindered rotation of the *t*-butyl group. This is reasonable as there are no carbonyl groups *ortho* to the *t*-butyl group.

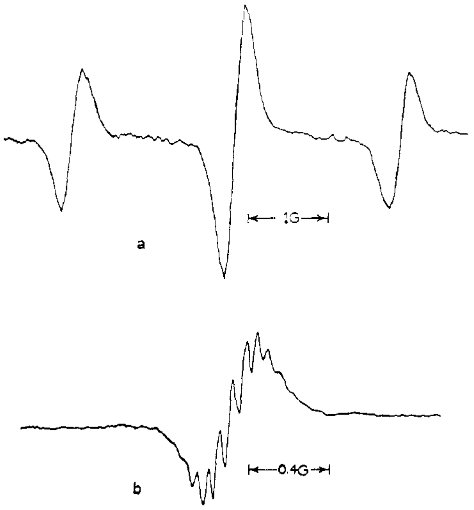

Figure 2. The esr spectrum of 2,5-di-*t*-butyl-*p*-benzosemiquinone: (a) the complete spectrum at low resolution, and (b) the central line at high resolution.

3,5-Di-*t*-butyl-*o*-benzosemiquinone. The esr spectrum of this radical has been observed before at low resolution.[16] Our results are given in Table I and the spectrum is shown in Figure 4. The assignment of the splitting constants is once again done on the basis of the HMO calculations. Resolution of the *t*-butyl group protons in the 5 ring position has been accomplished, but the proton splittings of the *t*-butyl group

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(15) J. K. Becconsall, S. Clough, and G. Scott, *Proc. Chem. Soc.*, 308 (1959).

(16) J. J. Conradi and G. A. Maclaren, *J. Am. Chem. Soc.*, **82**, 4745 (1960).

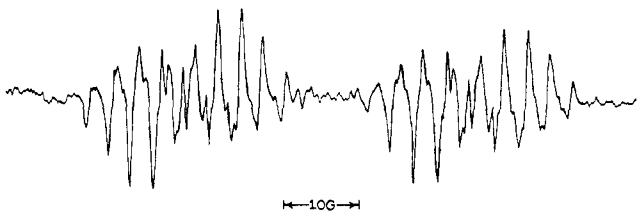

Figure 3. The esr spectrum of 4-*t*-butyl-*o*-benzosemiquinone.

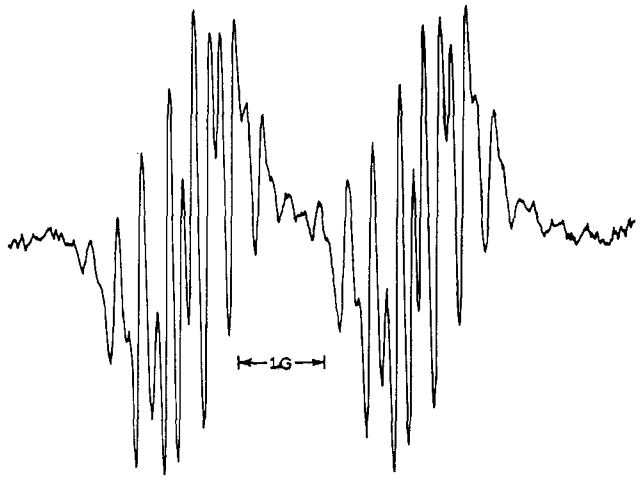

Figure 4. The esr spectrum of 3,5-di-*t*-butyl-*o*-benzosemiquinone.

in the 3 position could not be resolved. We estimate that they are less than 0.03 gauss.

3-Methyl-5-*t*-butyl-*o*-benzosemiquinone. There are no previous esr spectra of this compound. Our results are shown in Table I and Figure 5. There is a somewhat greater uncertainty in the splitting constants in this compound as the methyl proton, *t*-butyl proton, and ring proton splittings are quite close in magnitude, making their evaluation from the spectrum somewhat more difficult.

3-*t*-Butyl-5-methyl-*o*-benzosemiquinone. The esr spectrum of this radical has previously been observed by Stone and Waters.[9] Our results do not differ substantially from theirs. We were not able to observe *t*-butyl proton splittings. We can, however, estimate that these splittings are less than 0.03 gauss.

Discussion

In order to aid in the interpretation of the results, we have performed simple Hückel molecular orbital calculations with neglect of overlap based on the structures shown in Figure 6. The substituent Y–Z in the figure represents either the methyl group or the *t*-butyl group. We treat the substituent as having both inductive and conjugative effects, and we assume that the principal mechanism for transfer of unpaired spin to the protons (when Y–Z is methyl) and to the β-carbon nuclei (when Y–Z is *t*-butyl) is a hyperconjugative mechanism. Thus, in practice, for the purpose of the calculation, the methyl group is treated as a modified attached vinyl group and the *t*-butyl group as a modified attached isocrotyl group. For Y–Z equal to methyl, Y represents the α-carbon atom and Z the hydrogen group pseudo-atom (H_3); for Y–Z equal to *t*-butyl, Y represents the α-carbon atom and Z the carbon group pseudo-atom (C_3).

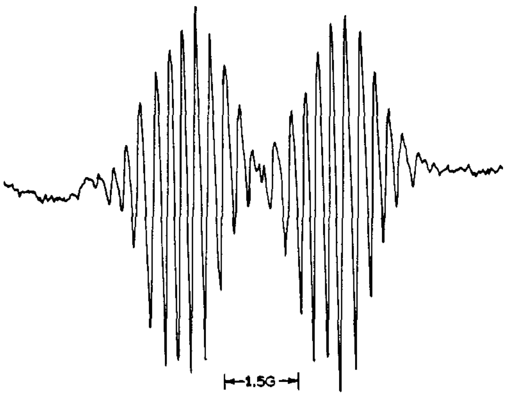

Figure 5. The esr spectrum of 3-methyl-5-*t*-butyl-*o*-benzosemiquinone.

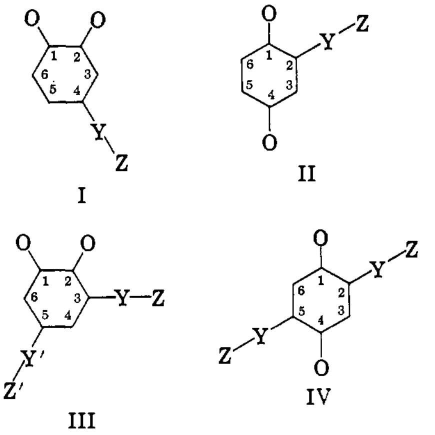

Figure 6. Model structures for HMO calculations and numbering system for the ring positions

We have adopted the usual notation[17] for the Coulomb integral of atom X and the resonance integral between atoms X and X′, that is

$$\alpha_X = \alpha_C + h_X\beta_{CC} \tag{1}$$

$$\beta_{X-X'} = k_{X-X'}\beta_{CC} \tag{2}$$

α_C is the coulomb integral of carbon and β_{CC} is the resonance integral between carbon atoms in a conjugated system. The HMO calculations were performed in the following order: (1) the esr data of Stone and Waters[9] on 4-methyl-*o*-benzosemiquinone were fitted by variation of the Hückel parameters as described below; (2) our esr data on 4-*t*-butyl-*o*-benzosemiquinone were then fitted with the same parameters as in step 1 except for parameters pertaining directly to the *t*-butyl group; (3) the parameters determined in steps 1 and 2 were then applied to the analogous *p*-benzosemiquinones to see in what manner they needed to be changed to take accout of any "*ortho*" interaction effect; and, finally, (4) the results of steps 1, 2, and 3 were used on structures III and IV of Figure 6 which represent the disubstituted radicals listed in Table I.

For structure I of Figure 6 the only *h*'s and *k*'s which are likely to be different from 0 and 1 are the following: h_O, k_{CO}, h_C^{CO}, h_C^{CY}, k_{C-Y}, h_Y, k_{Y-Z}, and h_Z. Systematic variation of all these parameters in order to obtain a best fit with the experimental data would be an im-

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[17] A. Streitwieser, Jr., "Molecular Orbital Theory for Organic Chemists," John Wiley and Sons, Inc., New York, N. Y., 1961, p 117.

Table II. HMO Parameters, Calculated Spin Densities, and Hfs Splitting Constants for Substituted Benzosemiquinones

A. Monosubstituted Benzosemiquinones

Radical	k_{CO} 1	k_{CO} 2	k_{Y-Z}	h_C^{CY}	k_{C-Y}	ρ_2	ρ_3	ρ_4	ρ_5	ρ_6	ρ_Z	a_2	a_2	a_3	a_4	a_4	a_5	a_6	Q	Q_t
4-Methyl-*o*-	1.0	1.0	3.0	−0.3	0.95	...	~0	0.175	0.158	0.0388	0.0201	...	...	~0.0	5.08[b]	5.10[c]	3.95	0.97	25	
Exptl[a]														0.25	5.1	5.1	4.0	1.0		
4-*t*-Butyl-*o*-	1.9	1.0	2.0	−0.45	1.0	...	0.0110	0.171	0.163	0.045	0.0556	...	...	0.29	...	...	3.99	1.10	24.5	44[d]
Exptl[a]														0.3	0.32	0.32	3.80	1.17		
2-Methyl-*p*-	1.66	1.56	3.8	−0.10	0.95	0.120	0.0786	...	0.111	0.112	0.0076	3.47[b]	1.94[c]	1.81	...	...	2.55	2.58	23	
Exptl[a]												2.04	2.04	1.76	...	...	2.46	2.54		
2-*t*-Butyl-*p*-	1.46	1.56	3.0	−0.20	0.95	0.107	0.0704	...	0.132	0.091	0.0112	...	...	1.55	...	...	2.90	2.00	22	44[d]
Exptl[a]												0.060	0.060	1.55	...	...	2.82	2.07		

B. Disubstituted Benzosemiquinones

Radical	ρ_2	ρ_3	ρ_4	ρ_5	ρ_6	ρ_Z[e]	$\rho_{Z'}$[e]	a_2	a_2	a_3	a_3	a_4	a_5	a_5	a_6	Q
3-Methyl-5-*t*-butyl-*o*-	...	0.0645	0.125	0.172	0.0178	0.0043	0.0542	...	...	1.87[b]	1.09[c]	2.88	0.30	0.30	0.40	23
Exptl[a]										0.3	0.3	3.07	0.29	0.29	0.3	
3-*t*-Butyl-5-methyl-*o*-	...	0.051	0.119	0.181	0.0059	0.0210	0.0059	...	...	0.03	0.03	2.62	5.25[b]	5.33[c]	0.13	22
Exptl[a]										<0.03	<0.03	2.50	5.35	5.35	0.35	
2,5-Dimethyl-*p*-	0.124	0.085	...	0.124	0.085	0.0079	...	3.60	2.00[c]	1.96	...	...	3.60[b]	2.00[c]	1.96	23
Exptl[a]								2.25	2.25	1.84	...	...	2.25	2.25	1.84	
2,5-Di-*t*-butyl-*p*-	0.136	0.0537	...	0.136	0.0537	...	0.0142	...	0.078[f]	1.18	...	...	...	0.078[f]	1.18	22
Exptl[a]									0.060	2.07	2.07	...	...	0.060	2.07	

[a] These are the same experimental values that appeared in Table I but without error limits and with some rounding off. [b] Calculated from eq 4. [c] Calculated from eq 5. [d] Calculated from eq 7. [e] Z represents methyl and Z′ represents *t*-butyl. [f] Calculated from eq 7 with $Q_t = 44$ as determined from the monosubstituted radicals.

mense task, and, perhaps, one would find that more than one set of parameters fit the data. In order to reduce the complexity of the fitting procedure and to be able to compare our calculations with previous calculations, we have used Vincow's[18] parameters for h_O, k_{CO}, and h_C^{CO} and Streitwieser's[19] parameters for h_Y, k_{Y-Z}, and h_Z when Y–Z is methyl. Thus for step 1 above, it is only necessary to vary h_C^{CY}, the Coulomb integral of the ring carbon atom attached to the substituent, and k_{C-Y}. The best fit is obtained with $h_C^{CY} = -0.3$ and $k_{C-Y} = 0.95$. The calculated values of the spin densities and hfs constants using the above parameters are given in Table IIA along with the experimental data. The spin densities are converted into hfs constants using McConnell's relationship[20] for the ring protons, *i.e.*

$$a_i = Q\rho_i \qquad (3)$$

and a similar relationship[21] for methyl protons

$$a_i = 29\rho_i \qquad (4)$$

ρ_i represents the spin density on the adjacent ring carbon atom i. The methyl proton hfs constants may also be calculated from ρ_Z by the relationship

$$a^{me} = \frac{1}{2}508\rho_Z \qquad (5)$$

The factor 508 is the hfs constant in gauss of an unpaired electron in a hydrogen atom 1s orbital and the factor of $^1/_2$ arises because of the free rotation of the methyl group. From the table one can see that the agreement between the calculated values and the experimental values for this choice of parameters is very good.

When Y–Z is *t*-butyl in structure I, some of the parameters determined above will need to be changed. To a good first approximation only those parameters associated with the *t*-butyl group itself, and the ring carbon atom to which it is attached, need be varied. Five parameters are involved; they are h_C^{CY}, k_{C-Y}, h_Y, k_{Y-Z}, and h_Z. In order to simplify the variation process, we have used the same values for h_Y and h_Z as above. Atom Y is in both cases a tetrahedral carbon atom, and it would be surprising if h_Y were different in methyl and *t*-butyl groups. In any case, variation of h_Y does not affect significantly the spin density at any position capable of experimental verification. Likewise, variation of h_Z does not affect the verifiable positions to any measurable extent and affects ρ_Z only slightly, although one might expect that h_Z itself would be significantly different in the methyl and *t*-butyl groups. Throughout all our calculations we have kept h_Y and h_Z constant at the values suggested by Streitwieser for methyl. For 4-*t*-butyl-*o*-benzosemiquinone, it was only necessary then to vary h_C^{CY}, k_{C-Y}, and k_{Y-Z}. The variation of parameters was performed subject to the restriction that k_{Y-Z} for the *t*-butyl group would be less than k_{Y-Z} for the methyl group. This is based on the result of Stock and Suzuki[10] that carbon–carbon hyperconjugation is somewhat less effective than carbon–hydrogen hyperconjugation. Good agreement with experiment is obtained for $h_C^{CY} = -0.45$, $k_{C-Y} =$

(18) G. Vincow, *J. Chem. Phys.*, **38**, 917 (1963).
(19) A. Streitwieser, Jr., ref 17, p 135.
(20) H. M. McConnell, *J. Chem. Phys.*, **24**, 764 (1956).
(21) A. D. McLachlan, *Mol. Phys.*, **1**, 233 (1958).

1.0, and $k_{Y-Z} = 2.0$. This is consistent with the expectation that the inductive effect of the *t*-butyl group is greater than that of the methyl group.

Structure II of Figure 6 represents 2-methyl-*p*-benzosemiquinone and 2-*t*-butyl-*p*-benzosemiquinone. Once again we use the parameters of Vincow for h_O, k_{CO}, and h_C^{CO} although we will vary k_{CO} for a carbonyl group *ortho* to methyl and *t*-butyl groups. The parameters which give best fit with the experimental data are given in Table IIA. The values of the parameters k_{Y-Z} and h_C^{CY} which worked best for the *o*-semiquinones described above give poor results for the *p*-semiquinones. The changed values of these parameters may indicate the presence of an interaction between the carbonyl group and the substituent *ortho* to it. In terms of the parameters which give the best fit, we may describe this interaction as a reduction of the inductive effect of the substituent and a lengthening of the Y–Z bond. From the modified value of k_{CO}, we may describe the effect on the carbonyl group as a lengthening of the bond when the substituent is the *t*-butyl group and a shortening of the bond when the substituent is methyl. The latter effect, however, must be considered highly tentative as the difference in k_{CO} involved is quite small.

Finally, we have used the parameters determined for the methyl and *t*-butyl groups in structures I and II and applied them without change to the radicals listed in Table IIB which correspond to structures III and IV of Figure 6. These are all disubstituted radicals and the results of the calculations are not as good as for the monosubstituted radicals. In general we may note that the parameters obtained from a HMO calculation should not be interpreted too literally. The parameters which give good agreement with experiment for the monosubstituted radicals are expected to give somewhat poorer agreement for the disubstituted radicals. In addition good agreement between the calculated and experimental values for the 3 and 6 positions in *o*-benzosemiquinones is not expected as the spin density in these positions is usually negative.[18] Simple HMO calculations can produce only positive spin densities. However, the approximate agreement obtained for hfs constants in the 2 and 5 positions in the disubstituted radicals probably indicates that the substituent group parameters are reasonably constant from one compound to the next.

From the calculated spin densities given in Table IIA and the experimental results, we may determine the Q's of eq 3 for each of the monosubstituted radicals. The values of Q in gauss which gave the best fit to the experimental data are also given in Table IIA. The Q values range between 22 and 25 and are quite reasonable for ring protons. In Table IIB the Q values obtained for the corresponding monosubstituted radicals are used to calculate the hfs constants for the disubstituted radicals. The agreement with experiment is only fair.

The usual theory of hyperconjugation[22,23] gives the result that unpaired spin density is transferred to the β-carbon atoms in the *t*-butyl-substituted compounds. In this research we have demonstrated that unpaired spin density is in addition transferred to the protons in the *t*-butyl group. The observation of the hfs splittings due to these protons can be explained by the hyperconjugative mechanism which produces unpaired spin on the carbon atoms to which the protons are attached. Thus, the results presented here are additional evidence for the effectiveness of hyperconjugation in free radicals. The mechanism of the transfer of unpaired spin to the protons from the tetrahedral β-carbon atom is presumably very similar to the spin-polarization mechanism[20] which adequately explains the hfs of ring protons. The difference in the tetrahedral β-carbon atom situation is that spin density is present not only in the $2p_z$ orbital but also in the $2p_x$, $2p_y$, and 2s orbitals. Assuming that a similar mechanism operates for each orbital we may write for the hfs constant of a *t*-butyl proton

$$a^{t\text{-Bu}} = \frac{1}{2}[Q_{2s}\rho_{2s} + Q_{2p_x}\rho_{2p_x} + Q_{2p_y}\rho_{2p_y} + Q_{2p_z}\rho_{2p_z}]$$

The factor of $^1/_2$ arises because of the rotation of the protons. Since $\rho_{2s} = \rho_{2p_x} = \rho_{2p_y} = \rho_{2p_z} = {}^1/_4\,\rho_Z$ in a tetrahedral orbital, we may rewrite the above equation as

$$a^{t\text{-Bu}} = \frac{1}{8}(Q_{2s} + Q_{2p_x} + Q_{2p_y} + Q_{2p_z})\rho_Z \qquad (6)$$

Without detailed calculations of the type performed by McConnell for ring protons,[20] it would be difficult to say much about the magnitudes of the individual Q's so that we prefer to write eq 6 as

$$a^{t\text{-Bu}} = \frac{1}{8}Q_t\rho_Z \qquad (7)$$

In Table IIA, Q_t is determined from the experimental value of $a^{t\text{-Bu}}$ and the calculated value of ρ_Z in the mono-*t*-butyl-substituted semiquinones. The value obtained is approximately 44 gauss and indicates that a tetrahedral orbital is more effective in polarizing the 1s hydrogen orbital than the $2p_z$ orbital of ring carbon atoms, where the Q value is approximately 25 gauss. This is not unexpected as the $2p_x$ and 2s orbital contribution to spin polarization is likely to be larger than the $2p_z$ contribution because the former orbitals are spatially closer to the hydrogen 1s orbital.

We may note that the values of ρ_Z calculated in our HMO model are not proportional to the spin density on the ring carbon atom to which the *t*-butyl group is attached. Thus this model adequately explains the fact that the *t*-butyl proton splitting increases by a factor of 5.3 in going from 2-*t*-butyl-*p*-benzosemiquinone to 4-*t*-butyl-*o*-benzosemiquinone, whereas for the analogous methyl compound the ratio is only 2.5. As a result eq 4, which is experimentally well established for methyl protons in alkyl radicals, gives erratic results in our compounds as shown in Table II. This is not surprising as the conjugation model which we have used is likely to give poorer results for the ring carbon atom to which the substituent is attached.

It is also of interest to compare the value of ρ_{2s} in the β-carbon atom of 2-*t*-butyl-*p*-benzosemiquinone determined by Stock and Suzuki[10] with ρ_{2s} obtained from our HMO treatment. We obtain $\rho_{2s} = 0.0014$, whereas Stock and Suzuki obtained $\rho_{2s} = 0.00067$. The results differ considerably. Stock and Suzuki based their determination on the equation

$$a^{C^{13}} = \rho_{2s}a_0^{2s} \qquad (8)$$

where a_0^{2s} is the hyperfine splitting that would be ob-

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[22] A. Streitwieser, Jr., ref 17.

[23] L. Salem, "The Molecular Orbital Theory of Conjugated Systems," W. A. Benjamin, Inc., New York, N. Y., 1966.

served if the carbon atom 2s orbital contained one unit of unpaired spin density. The difficulty with this approach is that there is very likely a contribution to $a^{C^{13}}$ from the 1s orbital of the carbon atom. Karplus and Fraenkel[24] have estimated this contribution for sp^2-hybridized carbon atoms and found that it is approximately two-thirds as large as the 2s contribution and of opposite sign. For tetrahedral carbon atoms there is undoubtedly a similar contribution, although not necessarily of the same magnitude. As a result the estimate of ρ_{2s} by Stock and Suzuki is likely to be too low, perhaps by as much as a factor of 2. Spin densities produced in the C^{13} 1s orbital will not affect significantly the proton hfs so we are correct in using the value of ρ_Z determined in our Hückel calculations to estimate Q_t.

Finally, we have examined the effect of *t*-butyl substituents on the ring proton hyperfine splittings from the point of view of the additivity rules of Venkataraman and Fraenkel.[3] These rules work reasonably well for methyl substitution in *p*-benzosemiquinones. We have attempted to fit our data on 2-*t*-butyl-*p*-, 2,5-di-*t*-butyl-*p*-, and 2,6-di-*t*-butyl-*p*-benzosemiquinone and have found that it is not possible to obtain a set of additivity constants which give good agreement with the experimental values of the splitting constants. This may be a further indication of a direct interaction between the *t*-butyl groups and the carbonyl group.

Conclusions

We have obtained the esr spectra of seven *t*-butyl-substituted semiquinones and have resolved the *t*-butyl proton splittings in six of these radicals. In the *p*-benzosemiquinones this splitting is 0.060 gauss and in the *o*-benzosemiquinones it is 0.3 gauss in the fourth and fifth ring position but less than 0.03 gauss in the third and sixth position. The most reasonable mechanism whereby *t*-butyl proton splittings may arise is a transfer of spin density to the β-carbon atoms *via* carbon–carbon hyperconjugation and thence to the *t*-butyl protons *via* the usual spin-polarization mechanism. Based on this model we estimate that the Q value for the spin-polarization mechanism is approximately 44 gauss. This quite reasonable value for Q probably indicates the essential correctness of the model and provides the expected result that tetrahedral obitals are more effective than p$_z$ orbitals in polarizing hydrogen 1s orbitals. The parameters used in our HMO calculations indicate that carbon–carbon hyperconjugation is somewhat less effective than carbon–hydrogen hyperconjugation. In addition the HMO calculations suggest that the *t*-butyl group has a larger inductive effect upon the aromatic ring than the methyl group and that an interaction between the substituent (either methyl or *t*-butyl) and adjacent carbonyl groups may occur, although the nature of this interaction is somewhat uncertain. The fact that the additivity relationships of Venkataraman and Fraenkel do not apply to *t*-butyl substitution in *p*-benzosemiquinones may suggest a stronger interaction of the carbonyl group with the *t*-butyl group than with the methyl group.

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[24] M. Karplus and G. K. Fraenkel, *J. Chem. Phys.*, **35**, 1312 (1961).

Carbon-13 Magnetic Resonance. XI.[1a] Structural and Electronic Effect on the Carbon-13 Nuclear Magnetic Resonance Spectra of the Halogen-Substituted Methanes[1b]

William M. Litchman and David M. Grant

Contribution from the Department of Chemistry, University of Utah,
Salt Lake City, Utah 84112. *Received September 30, 1967*

Abstract: The carbon-13 chemical shifts of the halomethanes exhibit anomalous trends which cannot be explained by any simple additive relationship in the number of halogen substituents. The addition of a pair-interaction term in a linear expression, however, allows reasonable correlation of the chemical shift data. These parameters are discussed theoretically in terms of charge polarization, the steric influence of halogen substituents on the effective orbital radii, and deviations from the classical bond structure. Polarization effects upon the chemical shift are attributed to changes in the effective nuclear charge and its accompanying alteration of the $\langle 1/r^3 \rangle$ term in the paramagnetic screening expression. Steric effects produce changes in the bond lengths which are reflected in the effective radius of the electron as shown by further changes in the $\langle 1/r^3 \rangle$ term. Deviation from perfect pairing alters the extent of spin pairing of two interacting electrons on the same carbon, and this affects the preferential admixture by the magnetic field of excited states having intrinsic angular momentum into the ground state of the molecules.

The carbon-13 chemical shifts of the halogen-substituted methanes were reported quite early by Lauterbur,[2] but a satisfactory theoretical explanation of the somewhat anomalous experimental values has been needed. The chemical shifts of the iodine and chlorine series, $CH_{4-n}X_n$, were found[2] to exhibit values above and below, respectively, that of methane, while the trend in chemical shift values reverses itself at CH_2Br_2 in the

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[1] (a) Previous paper in this series: R. J. Pugmire and D. M. Grant, *J. Am. Chem. Soc.*, 90, 697 (1968). (b) This is an essential portion of a thesis submitted to the Department of Chemistry, University of Utah, in partial fulfillment of the requirements for a Ph.D. degree.

[2] P. C. Lauterbur, *Ann. N. Y. Acad. Sci.*, 70, 841 (1958).