

42. Spin Densities in Substituted 1,4-Benzosemiquinones.

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The effect of a simple inductive substituent on the odd-electron distribution of substituted 1,4-benzosemiquinones has been calculated by simple molecular-orbital theory, and the results have been applied to the methyl- and chloro-benzosemiquinones. The observed splitting constants of the former are predicted quite well if it is assumed that the only effect of the substituent is to change the coulomb integral of the carbon atom to which it is attached by -0.2β , where β is the carbon-carbon resonance integral. The effect of a chlorine substituent is very much smaller than that of methyl, so that for chlorine the theory is much less satisfactory. The results obtained are used in discussing possible steric effects in *t*-butyl and 2,5- and 2,6-di-*t*-butyl-benzosemiquinone.

THE highly stable semiquinone radical-ions provide a convenient material for the study, by electron-spin resonance, of the effect of structure on the electron distribution in conjugated molecules. A simple molecular-orbital theory of the hyperfine splitting observed in such resonance spectra was developed on the theoretically justifiable assumption that the magnitude of the splitting produced by a proton on an aromatic ring is linearly related to the odd-electron density on the carbon atom to which it is attached.¹ This theory has been since modified to account for the high splitting constant for protons attached to carbon atoms at which the highest occupied orbital has a node.² Nevertheless, in its simple form the original theory gives a good account of the spectra of even-alternant systems such as hydrocarbon positive and negative ions.³

The theoretical description of the spectra of semiquinones is complicated by the presence of the heteroatoms and the consequent necessity to assign values to the coulomb integral of the oxygen atom and the resonance integral of the carbon-oxygen bond. For *p*-benzoquinone it is always possible to achieve agreement between theory and experiment by selecting an appropriate resonance integral for any choice of coulomb integral and *vice versa*; so Vincow and Fraenkel⁴ and Brandon and Lucken⁵ attempted to obtain a unique pair of parameters by studying the spectra and calculating the odd-electron distribution in the 1,4-benzosemiquinone, 1,4-naphthasemiquinone, and 9,10-anthrasemiquinone radical ions. The ranges of parameter values studied by these two groups were different, so that the "best" pair of parameters chosen by them were not the same; in both cases, however, it was observed that a range of values predicted the observed spectra quite well. In fact, it appears that any pair of parameters falling on the curve shown in Fig. 1 will give a satisfactory prediction of the spectrum within the limits of the simple theory.

In the present paper are presented the results of an attempt to account for the splitting

¹ McConnel, *J. Chem. Phys.*, 1956, **24**, 764; McConnel and Chesnut, *ibid.*, 1957, **27**, 984.

² McConnel, *J. Chem. Phys.*, 1959, **28**, 107.

³ De Boer, Thesis, Free University of Amsterdam, 1957.

⁴ Vincow and Fraenkel, *J. Chem. Phys.*, 1961, **34**, 1333.

⁵ Brandon and Lucken, *J.*, 1961, 4273.

constants of the methyl- and chloro-1,4-benzosemiquinones, which was made in the hope that the results will be generally useful in more complex cases. An example of this use is given.

Calculation of Electron Distributions.—The effect of a substituent may be two-fold, inductive and conjugative, so that two parameters are necessary to describe it completely. Experience suggests, however, that it will be possible to obtain agreement between theory and experiment by a series of pairs of such parameters, so that their absolute values have no precise significance. Moreover, the terms “conjugation” or “hyperconjugation” are significant only within the limits of the model of the chemical bond as a pair of electrons shared between two atoms. This model is at its most successful when used to describe properties of the molecule as a whole, but for one-electron properties such as ionisation potential it must be considerably modified, if not abandoned. The electron-spin resonance spectrum of a molecule is such a one-electron property, so that much care must be

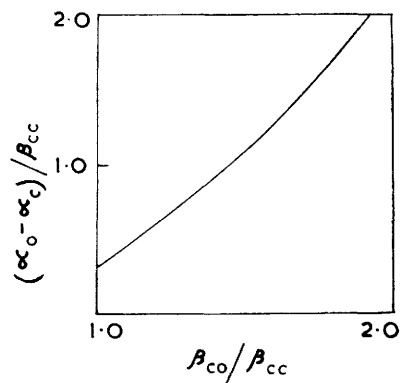


FIG. 1. Molecular orbital parameters for *para*-semiquinones.

exercised when transferring results obtained in this way to, say, chemical reactivity. For this reason we have treated the purely inductive substituent in general and have tried to fit the splitting constants of methyl and chloro-substituents to this model, but we do not claim that its success would necessarily imply that these substituents are purely inductive.

Because of quadrupole relaxation effects, hyperfine splitting has never been observed for the two naturally occurring chlorine isotopes (^{35}Cl , ^{37}Cl ; $I = 3/2$); the hyperfine interaction of the protons of the methyl group is treated in the same way as that of the ring-protons, *i.e.*, its splitting constant is assumed to be proportional to the odd-electron density at the carbon atom to which it is attached.

The calculations were carried out by the simple L.C.A.O.-M.O. method with the following values of parameters for the oxygen atoms: $\alpha_{\text{O}} \equiv$ Coulomb integral of carbon; $\beta_{\text{CO}} \equiv$ carbon-carbon resonance integral; $\alpha + 0.75\beta =$ Coulomb integral of oxygen $\equiv \beta_{\text{CO}}$; $1.3\beta =$ carbon-oxygen resonance integral $\equiv \alpha_{\text{O}}$. These parameters do not correspond to either of the pairs used previously, although, like them, they fall on the curve of Fig. 1. They were chosen, in preference to any other pair, because they gave the minimum least-squares error for the splitting constants of the three polycyclic semiquinones mentioned above; it is not expected, however, that the choice of parameters was critical.

The odd-electron densities at the ring-carbon atoms in monosubstituted and in the three disubstituted and trisubstituted 1,4-benzosemiquinones were calculated for various values of $\Delta\alpha$, the change in coulomb integral at the carbon atom(s) bearing the substituent(s). The resultant ring-proton hyperfine splitting constants are plotted in Fig. 2. In Table I are given the splitting-constant data for the methyl- and chloro-benzosemiquinones, taken from the paper by Venkataraman, Segal, and Fraenkel.⁶

⁶ Venkataraman, Segal, and Fraenkel, *J. Chem. Phys.*, 1959, **30**, 1006.

TABLE I.

Experimental proton splitting constants (gauss) of methyl- and chloro-benzosemiquinones.

Subst.	Ring protons * (a)			Methyl protons * (b)		
	a_1	a_2	a_3	b_1	b_2	b_3
(H)	2.368					
Me	2.462	2.537	1.764	2.045		
2,5-Me ₂	1.836			2.248		
2,6-Me ₂	1.892			2.125		
2,3-Me ₂	2.595			1.714		
Me ₃	1.97			2.24	1.88	1.77
Cl	2.208	2.208	2.453			
2,5-Cl ₂	2.030					
2,6-Cl ₂	2.320					
2,3-Cl ₂	2.319					
Cl ₃	2.163					

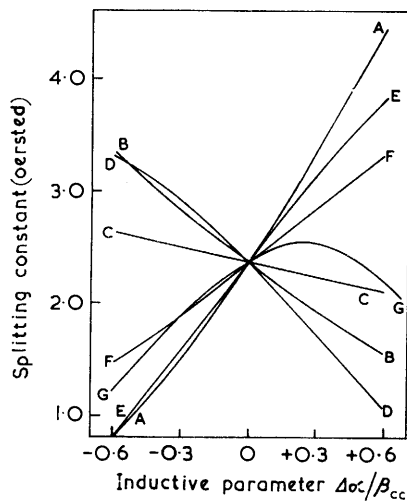


FIG. 2.

FIG. 2. Effect of inductive substituents on ring-proton hyperfine splitting of 1,4-benzosemiquinones.

A = Position 3	monosubstituted	E = Position 3,6	2,5-disubstituted
B = " 5	"	F = " 3,5	2,6- "
C = " 6	"	G = " 6	trisubstituted
D = " 5,6	2,3-disubstituted		

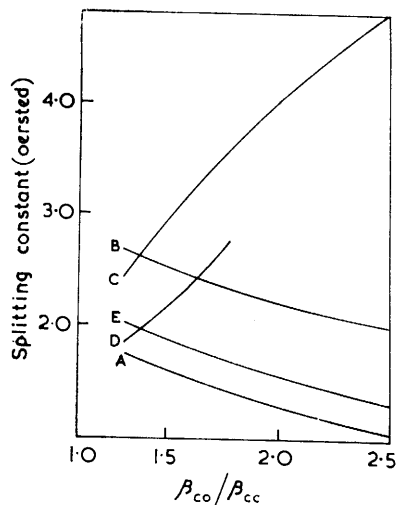


FIG. 3.

FIG. 3. Effect of bond-compression on substituted 1,4-benzosemiquinones. Substituent parameter = -0.3β

A = Position 3	monosubstituted	D = Position 3,6	2,5-disubstituted
B = " 5	"	E = " 3,5	2,6- "
C = " 6	"		

For the monosubstituted and the 2,6-disubstituted derivatives shortening the carbonyl adjacent to the substituent(s) was considered. For the 2,5-derivatives both carbonyl groups were simultaneously shortened.

Discussion.—(a) *Methyl-1,4-benzosemiquinones.* Although three ring-proton splitting constants have been measured for monomethylbenzosemiquinone, it is not known to which protons they are due. By inspection of Fig. 2 a suitable value of the inductive parameter was therefore sought which would account for the unambiguous splitting constants of the di- and tri-substituted compounds. It was obvious that, in accordance with expectation, a negative parameter was necessary: a value $\Delta\alpha = -0.2\beta$ reproduces the observed spectra very well. Moreover, with this value the three predicted coupling

constants for the monomethyl derivative are 1.76 (3), 2.68 (5), 2.46 (6) in excellent agreement with the three experimental values.

By assuming a direct proportionality between the splitting constant of the methyl group and the odd-electron density on the carbon atom to which it is attached, and by evaluating the proportionality constant empirically from the results for monomethylbenzosemiquinone, the splitting constants for the remaining methyl derivatives were calculated for $\Delta\alpha = -0.2\beta$. The agreement with experiment is again good: the results for the methyl derivatives are summarized in Table 2. The standard deviation of the predicted splitting constants is 0.11 oersted. The value $\Delta\alpha = 0.2\beta \approx 0.46$ ev is in good agreement with the value of the inductive parameter (0.42 ev) used by Julg⁷ to explain the spectral shifts of the methylazulenes.

(b) *Chlorobenzosemiquinones.* Table 1 shows that the spread of splitting constant of the chlorobenzosemiquinones is very much less than for the methyl derivatives. A measure of the spread is the standard deviation from the mean splitting constant, which is 0.13 oersted for the chloro- and 0.33 for the methylbenzosemiquinones. It was thus considered unlikely that a theory as simple as the present would be satisfactory for the chloro-compounds, and indeed it is impossible to find a single inductive parameter predicting the observed spectra: it is necessary sometimes to take a slightly negative value and sometimes a slightly positive one. However, the average (2.30) of the observed splitting constants is very close to the splitting constant of benzosemiquinone itself, as the present theory would predict.

In conclusion, the simple model of the benzosemiquinones accounts for their electron-spin resonance spectra as well as can be expected, especially when the substituent effect is reasonably large. Spectra are not available for any complete series of substituted benzosemiquinones except those discussed above. Attempts have been made to measure a number of fluorinated compounds, but as soon as the parent quinone or quinol is converted into the semiquinone it reacts to form more complex radicals whose structures have not been determined.

(c) *Electronic structures of the t-butylbenzosemiquinones.* The splitting constant⁸ of 2,5-di-t-butylbenzosemiquinone (2.13 oersted) is rather higher than that of 2,5-dimethylbenzosemiquinone and, since one would expect the inductive effect of the t-butyl group to be greater than that of methyl (but see, however, ref. 9), considerably greater than the

TABLE 2.
Predicted ring-proton and methyl splitting constants for the methyl-1,4-benzosemiquinones with $\Delta\alpha = -0.2\beta$.

Subst.	Position	Ring proton splitting	Methyl splitting	Error	Subst.	Position	Ring proton splitting	Methyl splitting	Error
Me	2		(2.045)	(0)	2,6-Me ₂	2, 6		2.10	-0.02
	3	1.76		0.00	2,6-Me ₂	3, 5	2.04		+0.15
	5	2.68		+0.14	Me ₃	2		1.61	-0.16
	6	2.46		0.00		3		1.82	-0.06
2,3-Me ₂	2, 3		1.57	-0.17		5		2.40	+0.16
	5, 6	2.76		+0.17		6	2.07		+0.10
2,5-Me ₂	2, 5		2.24	-0.01					
	3, 6	1.81		-0.03					

simple theory would predict. On the other hand, the splitting¹⁰ of 2,6-di-t-butylbenzosemiquinone (1.5 oersted) is very much lower than would be expected. Further, the three splittings observed¹¹ for t-butylsemiquinone (2.85, 2.10, 1.65 oersted) do not fit well with

⁷ Julg, *Compt. rend.*, 1954, **239**, 1498.

⁸ Fraenkel, *Ann. New York Acad. Sci.*, 1957, **67**, 553.

⁹ Heilbronner, *Tetrahedron Epistologue*, "Status of Quantum Chemistry in the Interpretation of Organic Chemistry," in the press.

¹⁰ Beeconsall, Clough, and Scott, *Proc. Chem. Soc.*, 1959, 308.

¹¹ Stock and Suzuk, *Proc. Chem. Soc.*, 1962, 136.

the predictions of Fig. 2. This discrepancy might be due to the bulk of the *t*-butyl group which, as may be seen from a model, would shorten the carbonyl bond and so increase β_{CO} . Calculations were therefore carried out in which β_{CO}/β_{CC} on one (mono, 2,6-) or both (2,5-) carbonyl groups was increased above the value of 1.3 used in the previous calculations, to see if the resultant changes in the predicted hyperfine splitting constants were in the direction indicated by experiment.

The results of these calculations are summarized in Fig. 3, where the inductive parameter of the *t*-butyl group was taken as $\Delta\alpha = -0.3\beta$. Carbonyl-bond compression produces shifts in the right direction, inverting the order of the 2,6- and 2,5-disubstituted derivatives. Much more compression is required for the 2,6- than for the 2,5-derivative if we are to reach agreement with experiment. This is reasonable since in the former the carbonyl group is flanked by two *t*-butyl groups. For the mono-derivative compression does not much improve agreement but it predicts that the proton at position 6 is now the one giving the greatest splitting.

One of the most unsatisfactory aspects of the experimental observations is the uncertainty in the assignments of the proton splitting of the monosubstituted derivatives. For the methyl substituents the assignment given here on the basis of molecular-orbital theory agrees with that of Venkataraman, Segal, and Fraenkel,⁶ based on a simple additivity relation. If, however, the strain theory has any significance for the *t*-butyl derivatives, then here it is the proton at position 6 which has the highest splitting. Deuterium-labelling is needed to check these assignments.

In conclusion then it seems likely that the simple molecular-orbital theory will be suitable for interpreting substituent effects, but that a greater range of substituent types should be studied in order to check the prediction of Fig. 2.

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