842. *The Electron-spin Resonance Spectra and Odd-electron Distribution of a Number of Polycyclic Semiquinones and Their Derivatives.*

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The electron resonance spectra of p-benzosemiquinone, 1,4-naphthasemiquinone, 9,10-anthrasemiquinone, 9,10-phenanthrasemiquinone, 1,2-acenaphthasemiquinone, and of some of their alkyl, chloro-, and nitro-derivatives have been measured on an X-band spectrometer. It has thus been possible to assign unambiguously the measured splitting constants to the different protons of the parent semiquinones. Odd-electron densities in these compounds have been calculated by the L.C.A.O.-M.O. method and the splittings in the three *para*-semiquinones explained in terms of a unique pair of values for the coulomb integral of the oxygen atom and the carbon–oxygen resonance integral, $\alpha_O = \alpha_C + 0.39\beta_{C-C}$, $\beta_{C-O} = 1.06\beta_{C-C}$. The results for the *ortho*-semiquinones are explained with a variety of pairs of values for α_O and β_{C-O}, none of which however, corresponded to the *para*-semiquinone parameters.

VALUES of proton hyperfine splitting constants in electron-spin resonance spectra of conjugated organic radicals provide, in principle, a measure of the π-electron spin density

at the proton-bearing carbon atoms of the conjugated system.[1] A sensitive method is thus afforded for testing theoretical predictions of π-electron distribution, and Weissman and de Boer [2] have used it to show that the π-electron distribution in aromatic negative ions agrees well with that calculated by the simple Hückel molecular-orbital method. It has also been shown to account qualitatively for the spectra of *ortho-* and *para-*benzosemiquinones,[1] but here there arises the difficulty that values must be guessed for the oxygen coulomb integral, α_O, and the carbon–oxygen resonance integral, β_{C-O}, and that for any choice of coulomb integral it is usually possible to obtain satisfactory agreement with experiment by an appropriate choice of resonance integral.

It therefore seemed to us worth while to measure the electron-spin resonance spectra of a number of polycyclic semiquinones to see if the results could be explained in terms of a unique pair of parameters α_O and β_{C-O}. We have confirmed previous results on 1,4-naphthasemiquinone,[3] 9,10-anthrasemiquinone,[4] 9,10-phenanthrasemiquinone,[4] and acenaphthenesemiquinone,[4] and have measured the electron-spin resonance spectra of a number of their derivatives; thereby we have been able to assign splitting constants to the different protons in the parent compounds with reasonable certainty.

<center>EXPERIMENTAL</center>

1. *Preparation of the Semiquinones.*—The starting materials were the corresponding quinones. With the following exceptions they were commercially available: 2-Chloro-1,4-naphthaquinone was prepared by oxidation of 2-chloronaphthalene supplied by Dr. P. M. G. Bavin (formerly of this College); 2- and 4-nitro- and 2- and 3-chloro-phenanthraquinone by oxidation of the substituted hydrocarbons (2- and 3-chloro-phenanthrene were prepared by the method of Bachmann and Boatner [5] from the corresponding amines which were supplied by Dr. E. W. T. Warford, formerly of this College, who also supplied the two nitrophenanthrenes). An attempt was made to prepare 5,8-dichloro-1,4-naphthaquinone by oxidation of 1,4-dichloronaphthalene: the electron-spin resonance spectrum of the derived semiquinone showed however that the product was probably 4-chloro-1,2-naphthaquinone. Oxidations were carried out by slowly adding a solution of chromic oxide in acetic acid to one of the hydrocarbon in glacial acetic acid at 100°; the mixture was then poured into water; the precipitated quinone was filtered off, washed with dilute sodium hydroxide and water, and used for preparation of the semi-quinone without purification.

The semiquinones were prepared from the corresponding quinones by one or both of the following methods.

(*a*) To a $\sim 10^{-2}$M-solution of the quinone in ethanol two drops of concentrated alcoholic potassium hydroxide were added, with immediate formation of semiquinone radical-ions. The reaction is presumably oxidation of the alkoxide ion to the peroxide radical although it does not seem to have been previously reported. The nature of the alkoxide ion does not seem to be important, the systems methanol–sodium methoxide and t-butyl alcohol–potassium t-butoxide seeming to be equally efficient.

(*b*) In a number of cases, *e.g.*, 1,4,5,8-tetrachloroanthraquinone, the above reaction failed to produce semiquinones. The following method produced semiquinones in every case. Methyl quinol-2-carboxylate is autoxidised very rapidly in alkaline solution, the half-life of the intermediate semiquinone being a few minutes. To a solution in ethanol ($\sim 10^{-2}$-M each in the above quinol, and the quinone under study) were added 2 drops of concentrated alcoholic potassium hydroxide. The spectrum of the ester semiquinone at once appeared, then rapidly decayed and was replaced by that of the desired semiquinone. The sequence of reactions is presumably as annexed. It may be that the oxidising agent in stage (1) is the quinone, Q, itself. It is possible to substitute quinol for the quinol ester, but the unwanted benzosemiquinone radical disappears much more slowly.

[1] McConnel, *J. Chem. Phys.*, 1956, **24**, 764.
[2] Weissman and de Boer, *J. Amer. Chem. Soc.*, 1958, **80**, 4549.
[3] Wertz and Vivo, *J. Chem. Phys.*, 1956, **24**, 479.
[4] Adams, Blois, and Sands, *J. Chem. Phys.*, 1958, **28**, 774.
[5] Bachmann and Boatner, *J. Amer. Chem. Soc.*, 1936, **56**, 2194.

Measurement of Electron-spin Resonance Spectra.—The spectra were measured on an X-band spectrometer, constructed in this laboratory, having a H_{012} rectangular sample-cavity in one arm of a magic-tee bridge and employing 470 kc./sec. field modulation and phase-sensitive detection to increase sensitivity. A " Clarendon " electromagnet, supplied by Newport
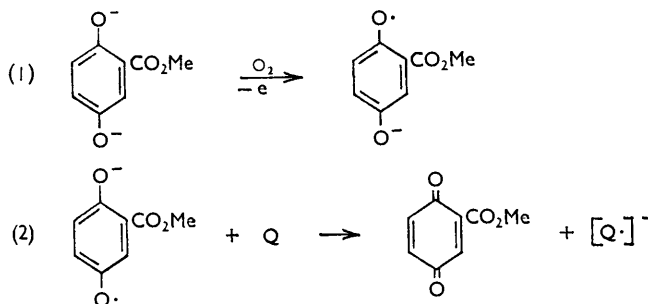
Instruments Ltd., with a 3 cm. gap and shimmed polefaces provided the main magnetic field. The current for the magnet was obtained from a bank of heavy-duty lead accumulators, and the field was swept by passing an electronically generated saw-tooth current through a pair of Helmholtz coils mounted on the pole-pieces. The sweep was calibrated daily against a solution of peroxyaminedisulphonate ion in water. The resolving power of the spectrometer was ~0·25 oersted.

The number of hyperfine components and the splitting constants of all the semiquinones measured are shown in Table 1. The spectra of selected quinones are shown in Fig. 1.

Calculations of Electron-distribution by the Hückel Method.—The standard assumptions of the Hückel method were made, *i.e.*, $\Psi_a = c_{oi}\psi_i$, where Ψ_a is a molecular orbital, c_{oi} is a numerical coefficient, and ψ_i is the $2p_z$-atomic orbital of atom " i " in the conjugated system. Application of the variation principle gives the secular determinant

$$|H_{ij} - ES_{ij}| = 0$$

where

$$H_{ij} = \int \psi_i H \psi_j{}^* \, dr$$

$$S_{ij} = \int \psi_i \psi_j{}^* \, dr,$$

H being an effective one-electron Hamiltonian operator for the system. Overlap was neglected, *i.e.*, $S_{ij} = \delta_{ij}$, where δ_{ij} is the Krönecker delta. All carbon atoms were supposed to have the same value of the coulomb integral H_{ii} ($\equiv\alpha$), and the resonance integral H_{ij} between neighbouring carbon atoms i and j was likewise presumed to be constant (β). Resonance integrals between non-neighbours were set equal to zero. The oxygen coulomb integral was given the value $\alpha + \rho\beta$ and the carbon–oxygen resonance integral the value $\gamma\beta$, where ρ and γ are parameters. ρ was allowed to take on values 0·0—1·4 inclusive and γ values 0·8—1·2 inclusive in steps of 0·1. The equations were solved by the courtesy of Imperial Chemical Industries Limited on their computer.

For this investigation it was supposed that the spin density was equal to the odd-electron density, *i.e.*,:

$$\Delta H_i = Q_p c_{oi}{}^2$$

where ΔH_i is the splitting produced by the proton on carbon atom " i," c_{oi} is the coefficient of ψ_i in the highest occupied orbital, *i.e.*, containing the odd electron, and Q_p is the proton splitting constant. This is now known to be incorrect, but probably not too important for the even-alternant systems considered here. De Boer and Weissman [2] were able with this assumption to explain the splitting constants of the different protons in a particular hydrocarbon radical-ion, but in order to compare different ions it was necessary to use a different value of Q_p for each molecule.

The results of these calculations are shown graphically in Figs. 2—7. The graphs are of two types: (*a*) The ratios of orbital coefficients of two different carbon atoms within the same molecule are plotted against the parameters ρ and γ; and (*b*) the ratio of a coefficient of one

<div align="center">

TABLE 1.

Hyperfine components and splitting constants of semiquinones.

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Semiquinone	No. of hyperfine components	Splitting constant(s) (oersted)
1,4-Benzo-	5 †	2·37 ± 0·04
2-Chloro-1,4-benzo- [a]	4 †	2·27 ± 0·04
2,6-Dimethyl-1,4-benzo- [a]	9 †	2·13 ± 0·04
1,4-Naphtha- [b]	15 † (three quintuplets)	3·19 ± 0·4; 0·58 ± 0·04
2-Methyl-1,4-naphtha- [b]	25 † (five quintuplets)	3·31 ± 0·04; 0·66 ± 0·04
2-Chloro-1,4-naphtha-	10	0·66 ± 0·4
2,3-Dichloro-1,4-naphtha-	5 †	0·65 ± 0·04
[Oxidation product of 1,4-dichloronaphthalene	4 (two doublets)	0·86 ± 0·4; 0·62 ± 0·04]
9,10-Anthra- [c]	13	0·58 ± 0·04
1-Chloro-9,10-anthra-	>8	~0·7
2-Chloro-9,10-anthra-	>8	~0·7
1,4,5,8-Tetrachloro-9,10-anthra-	5 †	1·13 ± 0·04
2-Methyl-9,10-anthra-	Broad and unresolved	Line width $\begin{cases} \sim2\cdot8 \\ \sim2\cdot6 \end{cases}$
2-Ethyl-9,10-anthra-	Broad and unresolved	
9,10-Phenanthra- [c]	5 †	1·66 ± 0·1
2-Nitro-9,10-phenanthra-	5 †	1·60 ± 0·1
4-Nitro-9,10-phenanthra-	5 †	1·65 ± 0·1
2-Chloro-9,10-phenanthra-	5 †	1·58 ± 0·1
3-Chloro-9,10-phenanthra-	4 †	1·60 ± 0·1
3-Isobutyl-9,10-phenanthra-	4 †	1·52 ± 0·1
3-Acetyl-9,10-phenanthra-	4 †	1·33 ± 0·1
3-Cyclohexyl-9,10-phenanthra-	4 † (traces of fine structure)	1·65 ± 0·1
1,2-Acenaphtha- [c]	5 †	1·30 ± 0·04

[a] See also ref. 6.   [b] See also ref. 3.   [c] See also ref. 4.

† The intensity ratio of the lines of the multiplet are approximately proportional to the coefficients of a in the binomial expansion of $(1 + a)^{n-1}$ where n is the number of lines.
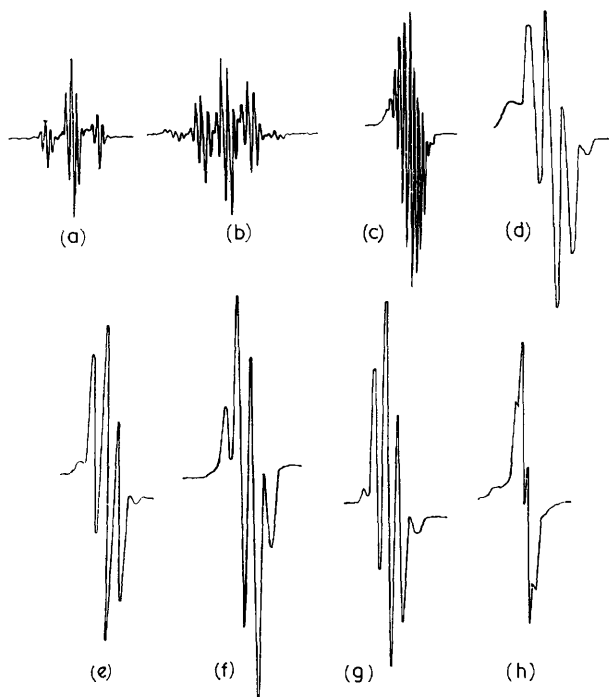

FIG. 1.   Electron-spin resonance spectra of semiquinones, from (a) 1,4-naphthaquinone, (b) 2-methyl-1,4-naphthaquinone, (c) anthraquinone, (d) phenanthraquinone, (e) 2-chlorophenanthraquinone, (f) 3-chlorophenanthraquinone, and (g) 4-nitrophen-anthraquinone, and from (h) the oxidation product from 1,4-dichloronaphthalene.

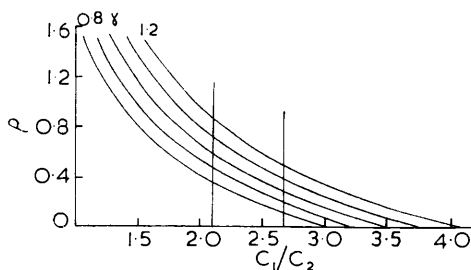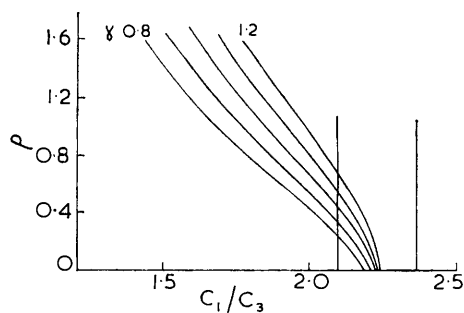6 Venkataraman, Segal, and Fraenkel, *J. Chem. Phys.*, 1959, **30**, 1006.

FIG. 2.

FIG. 3.

FIGS. 2 and 3. Ratios of orbital coefficients for (Fig. 2) $C_{(1)}$ and $C_{(2)}$, and (Fig. 3) $C_{(1)}$ and $C_{(3)}$ of 1,4-naphthaquinone, plotted against the parameters ρ and γ.

Here, and in Figs. 4—7, successive plots for γ are at intervals of 0·1. Throughout, for naphthaquinone, C_1, C_2, and C_3 refer to positions 1(= 2), 5(= 8), and 6(= 7) respectively; other molecules are numbered as usual.
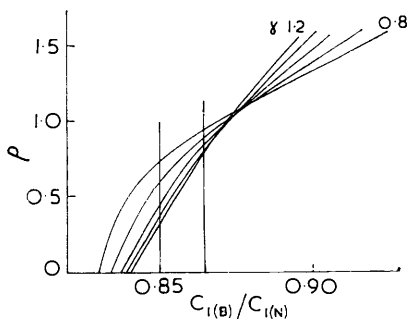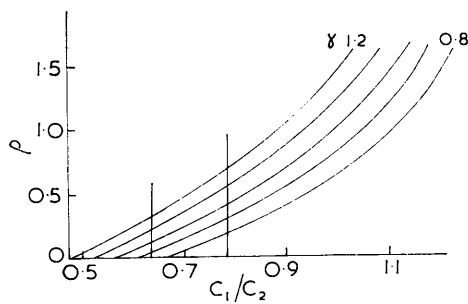
FIG. 4.

FIG. 5.

FIG. 4. Ratio of orbital coefficients of $C_{(1)}$ of 1,4-benzoquinone (C_{1B}) and 1,4-naphthaquinone (C_{1N}) plotted against the parameters ρ and γ.

FIG. 5. Ratio of orbital coefficients for $C_{(1)}$ and $C_{(2)}$ of 9,10-anthraquinone, plotted against the parameters ρ and γ.
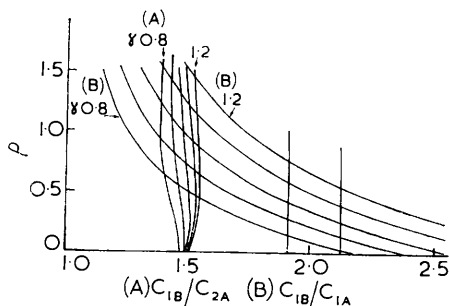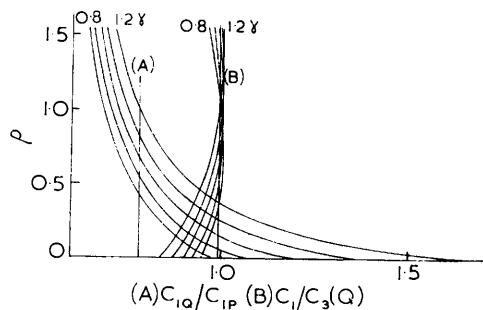
FIG. 6.

FIG. 7.

FIG. 6. Ratio of orbital coefficients for $C_{(1)}$ of 1,4-benzoquinone (C_B) and (A) $C_{(2)}$ and (B) $C_{(1)}$ of 9,10-anthraquinone (C_A) plotted against the parameters ρ and γ.

FIG. 7. Ratio of orbital coefficients for (A) $C_{(1)}$ of acenaphthaquinone (C_Q) and phenanthraquinone (C_P), and (B) $C_{(1)}$ and $C_{(3)}$ of acenaphthaquinone, plotted against the parameters ρ and γ.

molecule to the coefficient of another molecule, usually benzosemiquinone, is plotted against the parameters ρ and γ.

DISCUSSION

Experimentally Determined Splitting Constants.—(a) *Naphthasemiquinones.* 1,4-Naphthasemiquinone has three pairs of equivalent protons and the spectrum consists of three groups of five lines, as would be expected if it arose from the interaction of the electron-spin with one pair of protons with a large splitting constant and four protons with a much smaller splitting constant. Two of the pairs of protons in the semiquinone are thus approximately equivalent. The spectrum of 2-methyl-1,4-naphthasemiquinone consists of five groups of overlapping quintuplets and it is known[6] from measurements on the methylbenzosemiquinones that the splitting produced by a proton in a methyl group attached to a conjugated carbon atom is approximately the same as would be produced by a proton directly attached to the same atom. These spectra are then at once explicable if we assume that in naphthasemiquinone the larger splitting constant is due to protons 2 and 3 while the smaller constant is due to the set 5, 6, 7, and 8. Had protons 2 and 3 belonged to the set giving the smaller constant, the spectrum of the 2-methyl derivative would have consisted of three overlapping groups of seven lines. This conclusion is wholly confirmed by the five-line spectrum of 2,3-dichloro-1,4-naphthasemiquinone and the ten-line spectrum of the 2-chloro-derivative.

The spectrum of the semiquinone derived from the oxidation product of 1,4-dichloronaphthalene consists of a pair of doublets and therefore cannot be due to 5,8-dichloro-1,4-naphthasemiquinone whose spectrum would consist of three triplets. The splitting presumably comes from two inequivalent protons and it is suggested that the product is 4-chloro-1,2-naphthaquinone, the 3-proton giving the larger and the 8-proton the smaller of the observed splitting constants.

(b) *Anthrasemiquinones.* Anthrasemiquinone has two groups of four protons, and the derived semiquinone would thus be expected to have a spectrum consisting of five groups of five, probably overlapping, lines. The observed thirteen-line spectrum of anthrasemiquinone would arise if the splitting constant of one group of protons were approximately twice that of the other group, *i.e.*, 1·16 and 0·58, respectively. The spectrum of 1,4,5,8-tetrachloroanthrasemiquinone strongly supports this interpretation, the observed splitting of 1·13 oersted being almost exactly twice that in the unsubstituted compound, and shows moreover that the 2-, 5-, 6-, and 7-protons are responsible for the larger of the splitting constants. The spectra of the remaining four anthrasemiquinone derivatives are not well resolved; in particular the spectra of the chloro-derivatives suffer from the relaxation time asymmetry noted by Ebsworth and Weil[7] for peroxydicobalt compounds; it is impossible to say more than that they do not contradict the hypothesis above.

(c) *Phenanthrasemiquinones.* Despite the fact that phenanthrasemiquinone has four pairs of protons the electron-spin resonance spectrum is relatively simple, showing that two of the pairs of protons are approximately equivalent and that the splitting produced by the other two pairs is small. The protons responsible for the splitting are readily identified from the spectra of the substituted compounds. 2- and 4-Substituted derivatives have a five-line spectrum resembling that of 9,10-phenanthrasemiquinone, while the spectra of 3-substituted derivatives have only four lines. No 1-substituted derivatives were measured, but they also would presumably have four-line spectra. The splitting in 9,10-phenanthrasemiquinone is thus attributed to the 1-, 3-, 6-, and 8-protons.

(d) *Acenaphthasemiquinone.* The spectrum of this compound resembles that of 9,10-phenanthrasemiquinone, consisting of five lines. No derivatives of acenaphthaquinone were measured and the results of the molecular-orbital calculations must be anticipated in assigning the splitting to the 1-, 3-, 4-, and 6-protons. The splitting due to the 2- and 5-protons is expected to be small, in agreement with the observed spectrum.

[7] Ebsworth and Weil, *J. Phys. Chem.*, 1959, **63**, 1890.

TABLE 2.

Ratios of splitting constants of benzosemiquinone, naphthasemiquinone, and anthrasemiquinone.

Semiquinone	ΔH_1	$\Delta H_2, \Delta H_3$	$\dfrac{\Delta H_1}{\Delta H_2}, \dfrac{\Delta H_1}{\Delta H_3}$	$\sqrt{\dfrac{\Delta H_1}{\Delta H_2}}$	$\sqrt{\dfrac{\Delta H_{\text{Benzosemiquinone}}}{\Delta H_1}}$
1,4-Naphtha-	3·19 (±0·04)	0·45—0·71	7·08—4·4	2·66—2·10	0·865—0·850
9,10-Anthra-	0·52—0·64	1·28—1·04	0·406—0·615	0·637—0·784	2·13—1·92

The results of the foregoing discussion are summarised in Table 2. If it is assumed that the resolution of the spectrometer is 0·25 oersted, then, provided the splitting constants of two protons in a molecule differ by less than 0·25 oersted, they will not be differentiated in the spectrometer. The same applies to two non-equivalent pairs of protons, which means that the splitting constants of the (6,7)- and (5,8)-protons may lie anywhere in the region 0·45—0·71 oersted, the average of the two constants being equal to the observed 0·58 oersted. A similar argument leads to the conclusion that the splitting constant (ΔH_1) of the (1,4,5,8)-protons in anthrasemiquinone lies between 0·52

FIG. 8.   Plots of ρ against γ (for connotation of A—F see text).
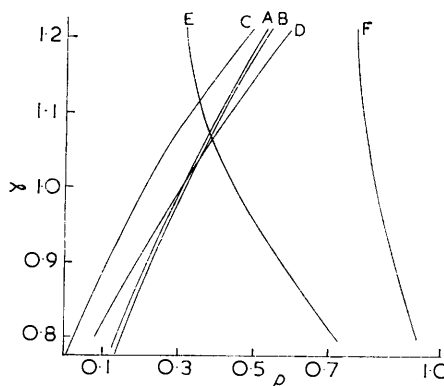
and 0·64 oersted, and that of the (2,3,6,7)-protons (ΔH_2) between 1·04 and 1·28 oersted in the weighted mean of the splitting constants, the value of $(2\Delta H_1 + \Delta H_2)/2$ being 1·16 oersteds. On this basis the limits of the mutual ratios of the various constants corresponding to the ratios of the orbital coefficients plotted in Figs. 2—7 are shown in Table 2. Since the ratio of the orbital coefficients should be equal to the square root of the ratio of the splitting constants, these are also given and correspond to the pairs of vertical lines plotted in Figs. 2—7.

Molecular-orbital Calculations.—The approximations involved in the theory make it likely that different parameters will be necessary for *ortho-* and *para*-semiquinones and therefore these are considered separately.

(a) para-*Semiquinones.*   Consideration of Fig. 3 shows that if the Hückel theory has any value in this application, then ΔH_3 for naphthaquinone must lie in the upper quarter of its range of possible values, *i.e.*, $2\cdot10 < \sqrt{(\Delta H_1/\Delta H_3)} < 2\cdot25$ and hence $2\cdot45 < \sqrt{(\Delta H_1/\Delta H_2)} < 2\cdot66$. By trial and error it is found that, if $\sqrt{(\Delta H_1/\Delta H_3)} = 2\cdot15$ and hence $\sqrt{(\Delta H_1/\Delta H_2)} = 2\cdot61$, then two almost coincident curves relating ρ and γ are obtained from Figs. 2 and 3. These are shown in Fig. 8 as curves A and B. Any other choice of ΔH_2 and ΔH_3 produces two almost parallel curves.

Similar consideration of Figs. 5 and 6 for anthraquinone shows that only the choice of $\Delta H_1 = 0\cdot56$ (and hence $\Delta H_2 = 1\cdot20$) gives a pair of coincident curves relating ρ and γ, which also coincide with those derived from naphthasemiquinone. These are labelled C and D in Fig. 8.

The results thus far considered do not provide a unique pair of parameters ρ and γ. Fortunately, however, Fig. 4 produces a curve relating ρ and γ which crosses the previous

set. Unfortunately, the ratio $\sqrt{(\Delta H_B/\Delta H_1)}$ (where B denotes benzosemiquinone) for naphthalene is not very sensitive to ρ and γ, and the uncertainty in the experimental ratio $\sqrt{(\Delta H_B/\Delta H_1)}$ becomes very serious, the curves for the limiting ratios being shown as E and F in Fig. 8. Curve F, however, crosses A, B, C, and D at points where they are already diverging significantly from each other, while curve E crosses them in the region where they coincide the most (*i.e.*, $\rho = 0.49$; $\gamma = 1.06$). Rather laborious trial and error shows that no other values for the ratios of the splitting constants provide a unique pair of ρ and γ. In view of the approximation of equating spin-density and odd-electron density, this may not necessarily be an argument in favour of their adoption. They are, however, the best values obtainable within the scope of the present work. Since, however, this was completed, precise measurements by Vincow[8] of the splitting constants of the semiquinones discussed here have come to our attention. These are compared in Table 3 with our predictions from molecular orbital theory for the values $\rho = 0.39$ and $\gamma = 1.06$ derived from our less precise measurements, with ΔH for benzosemiquinone assumed as 2.37 oersteds. Agreement is remarkably good, demonstrating the general adequacy of our method in this application.

TABLE 3.

Predicted and precise experimental values of splitting currents.

	Predicted			Vincow's data		
	ΔH_1	ΔH_2	ΔH_3	ΔH_1	ΔH_2	ΔH_3
1,4-Naphthasemiquinone ...	3.28	0.62	0.50	3.23 ± 0.01	0.635 ± 0.005	0.513 ± 0.003
9,10-Anthrasemiquinone ...	0.56	1.01	—	0.55 ± 0.004	0.962 ± 0.005	—

If these values of ρ and γ are used, a value of 0.076 is obtained for the odd-electron density at the carbon atoms in 1,4-benzosemiquinone and hence Q_p equals 31 oersted. This is in reasonable accord with the range found by Weissman and de Boer for hydrocarbon negative ions.

(b) ortho-*Semiquinones.* It is impossible, from the data presented here, to derive a unique pair of values of ρ and γ for the *ortho*-semiquinones. Qualitatively, theory agrees well with experiment: the odd-electron densities at the (1,8)- and (3,6)-positions of 9,10-phenanthrasemiquinone are approximately equal and large; those at the (2,7)- and (4,5)-positions are always much smaller. Similarly the (2,7)- and (4,5)-odd-electron densities in acenaphthasemiquinone are always approximately the same (Fig. 7B) while the density at the (2,6)-positions is very small indeed. The ratio between the splitting constants for phenanthrasemiquinone and acenaphthasemiquinone (Fig. 7A) shows, as expected, that the values obtained for the *para*-quinones will not be suitable for *ortho*-semiquinones.

In sum, our results show that simple molecular-orbital theory suffices to explain the electron-spin resonance spectra of the semiquinones and that a unique pair of parameters, $\rho = 0.39$ and $\gamma = 1.06$, account for the observed spectra of *para*-semiquinones. Calculations are in progress to see whether allowing for the inductive effect of the oxygen atoms will produce a pair of parameters suitable for both *para*- and *ortho*-quinones and whether these are modified by calculations of actual spin-densities rather than odd-electron densities.

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[8] Vincow, *Diss. Abs.*, 1960, **20**, 3973.