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Paramagnetic Resonance of Methyl- and Chloro-Substituted *p*-Benzosemiquinones^{*}

BALU VENKATARAMAN, † BERNICE G. SEGAL, AND GEORGE K. FRAENKEL

Department of Chemistry, Columbia University, New York 27, New York

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Detailed measurements, made under conditions of high resolution, of the paramagnetic resonance spectra of the negative radical ions of all the methyl- and chloro-substituted p-benzosemiquinones are reported. All the spectra exhibited hyperfine structure which is accounted for in terms of interactions between the unpaired electron and all the protons in the radicals; no chlorine hyperfine splittings were observed. In some of the chlorine compounds anomalous lines, not attributable to the chloro-substituted p-benzosemiquinone ion, appeared; these presumably arise from radicals produced by side reactions. Microwave power saturation was encountered in all the spectra examined. Line widths of all the spectra were observed to depend markedly on the microwave power and on the concentration of the hydroquinone from which the semiquinone was prepared. Separations of the hyperfine components were measured to a high degree of accuracy and splitting constants for individual protons were calculated from the measurements using the method of least squares. Proton splitting constants ranged from a minimum of 1.714 gauss for the methyl group protons in 2,3-dimethyl semiquinone ion to a maximum of 2.595 gauss for the ring protons in that same compound. The variation of the splitting constants with chlorine and methyl group substitutions are shown to obey a nearly additive relation.

I. INTRODUCTION

NUMBER of studies of the paramagnetic res-A onance spectra of solutions of methyl-substituted p-benzosemiquinone ions¹⁻³ have indicated that the rather complex splitting patterns of the spectra can be interpreted in terms of proton hyperfine interactions with all the protons in the ion, both the methyl group protons and the ring protons. These studies have also shown that there were relatively large variations in the splittings attributable to different protons within a given compound and from one compound to another. Preliminary measurements indicated that the variations in the splitting constants with substituents obeyed an additive law, but there were some discrepancies in cases of apparent accidental degeneracy.³ It also appeared that improving the resolution and the precision of the measurements would remove these discrepancies. In the present investigation, experimental conditions have been carefully studied and controlled to give a very high degree of resolution and a method has been devised for making precise measurements of the separations between hyperfine components. These procedures have permitted detailed study of the variations in the splitting constants in the entire series of methyl- and chloro-substituted *p*-benzosemiquinone ions.

The splitting in a paramagnetic spectrum arising from the isotropic hyperfine interaction between the unpaired electron and a particular proton is proportional to the odd-electron density at this proton,⁴ and

therefore an electron density map at the average positions of the protons can be obtained from the paramagnetic resonance spectrum. The number of points at which the densities can be measured is so small, however, that the detail of the electron density map is not very great, and theoretical estimates of the splittings must be made to obtain appreciable knowledge of the distribution of the molecular wave functions.

Bersohn⁵ has shown how to account for the magnitude of the splittings on methyl group protons by using a calculation based on the molecular orbital theory of hyperconjugation. This theory also predicts approximately the variations to be expected among different protons in the different methyl-substituted compounds. The detailed understanding of the splitting arising from the ring-substituted protons, however, has proved to be a complicated problem, and only the main features of the theory have been developed. The principal contributors to this theory have been McConnell,⁶⁻⁹ Bersohn,⁵ Weissman,¹⁰ and Jarrett.¹¹ McConnell originally proposed⁶ that the odd-electron density at the ring protons, and therefore the splitting constant, was proportional to the unpaired π -electron density on the adjacent carbon atom in the aromatic ring, and experiments by Weissman, et al.12 and de Boer,13 on even-alternate hydrocarbon negative and positive ions are in good agreement with this theory. Preliminary measurements on the methyl-substituted p-benzosemiquinone ions did not appear to agree with this theory, but recently McConnell has refined the theory, introducing the concept of unpaired spin density on the ad-

⁹ See reference 8, page 1188.
¹⁰ S. I. Weissman, J. Chem. Phys. 25, 890 (1956).
¹¹ H. S. Jarrett, J. Chem. Phys. 25, 1289 (1956).
¹² Weissman, Tuttle, and de Boer, J. Phys. Chem. 61, 28 (1957).
¹³ E. J. Boer, thesis, Free University of Amsterdam (1957).

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[†] Present address: Atomic Energy Establishment, Apollo Pier Road, Bombay, India. ¹ B. Venkataraman and G. K. Fraenkel, J. Am. Chem. Soc.

^{77, 2707 (1955).} ² B. Venkataraman and G. K. Fraenkel, J. Chem. Phys. 23,

^{588 (1955).} ³ B. Venkataraman, thesis, Columbia University, New York,

New York (1955).

⁴S. I. Weissman, J. Chem. Phys. 22, 1378 (1954).

 ⁶ R. Bersohn, J. Chem. Phys. 24, 1066 (1956).
 ⁶ H. M. McConnell, J. Chem. Phys. 24, 764 (1956).
 ⁷ H. M. McConnell and D. B. Chesnut, J. Chem. Phys. 27, 984 (1957) ⁸ H. M. McConnell, J. Chem. Phys. 28, 107 (1958).

¹³ E. de Boer, thesis, Free University of Amsterdam (1957).

jacent carbon atom, and has extended the theory to odd-alternate hydrocarbons.^{8,9}

The present series of experiments serves to test the general features of Bersohn's theory for the variation of proton hyperfine splitting constants of methyl group protons and of McConnell's theory for the dependence of ring-proton splitting constants on the unpaired spin density in the aromatic ring.

II. MATERIALS

Hydroquinone.—cp grade hydroquinone was obtained from Eimer and Amend; m.p. 170.5–173.0°.

p-Toluhydroquinone.—Reagent grade *p*-toluhydroquinone was obtained from Eastman Kodak Company; m.p. 125–128°.

Monochlorohydroquinone.—Practical grade monochlorohydroquinone, obtained from Eastman Kodak Company, was recrystallized from ligroin; m.p. 103–104°.

2,5-Dichlorohydroquinone.—Eastman Kodak Company, 2,5-dichloroquinone was reduced with Zn dust in glacial acetic acid¹⁴; m.p. 171.5–173.0°.

2,6-Dichlorohydroquinone.—Eastman Kodak Company, 2,6-dichloroquinone was reduced with SnCl₂ in concentrated HCl¹⁵; m.p. 166.0–166.5°.

2,3-Dichlorohydroquinone.—2,3-Dichloroquinone was donated by Professor L. F. Fieser of Harvard University, who prepared it by the method of Eckert and Endler.¹⁶ It was reduced to the hydroquinone in ether solution by means of an aqueous solution of $Na_2S_2O_4$.¹⁷ The product obtained was recrystallized from ligroin; m.p. 146–148°.

Trichlorohydroquinone.—Trichlorohydroquinone was prepared from Eastman Kodak Company, 2,5-dichloroquinone by the method of Thomson.¹⁸ The product was recrystallized from ligroin; m.p. 139–140°. The results of microchemical analysis of the trichlorohydroquinone were: Calculated for C₆H₃O₂Cl₃: C, 33.76; H, 1.42; Cl, 49.83. Found: C, 34.04; H, 1.64; Cl, 50.04.

2,5-Dimethylhydroquinone.—Eastman Kodak Company, 2,5-dimethylquinone was reduced to the corresponding hydroquinone by 85% hydrazine hydrate solution, according to the method of LuValle and Weissberger¹⁹; m.p. 214–219°.

2,6-Dimethylhydroquinone.—2,6-Dimethylquinone was donated by Professor G. Stork of Columbia University, and was reduced to the corresponding hydroquinone by two methods; (a) with 85% hydrazine hydrate solution¹⁹; m.p. 150–152°; and (b) with an aqueous solution of Na₂S₂O₄¹⁷; m.p. 151.5–152.5°. 2,3-Dimethylhydroquinone.—A crude sample of the 2,3-dimethylquinone, donated by Dr. A. Weissberger of Eastman Kodak Company, was purified by sublimation under reduced pressure and then reduced with aqueous $Na_2S_2O_4$ solution¹⁷; m.p. 217°.

Durohydroquinone.—Duroquinone was prepared from Eastman Kodak Company durene by the method of Smith and Dobrovolny²⁰ and was recrystallized from 95% ethanol. It was reduced to durohydroquinone with Zn dust and glacial acetic acid¹⁴; m.p. 237–240°.

2,3,5-*Trimethylhydroquinone.*—This was obtained from Dr. J. E. LuValle of Technical Operations, Inc.

All of the inorganic chemicals used were of reagent grade.

III. DESCRIPTION OF THE EXPERIMENTS

Preparation of radicals.—All the semiquinone radicals studied were obtained by air oxidation of the corresponding hydroquinone in alkaline medium. The spectrometer used for the paramagnetic resonance measurements, which has been described elsewhere,²¹ operates at a wavelength of 3.2 cm.

Most of the radicals investigated were unstable and, since it was desired to maintain a steady concentration of radical in the spectrometer during the course of the measurements, a flow system similar to that described in reference 1 was used. One reservoir of the flow system contained an alcoholic solution of the appropriate hydroquinone, the other a 70-30 ethanol-water solution containing approximately 0.1 mole of NaOH per liter. The concentration of the alcoholic solution used in the reservoir for a given hydroquinone was determined by the following considerations: the line widths, and therefore the resolution of the spectra, were found to depend on the radical concentration; accordingly, for each radical, spectra were observed using several different concentrations of the appropriate hydroquinone, and the concentration which resulted in the narrowest lines consistent with adequate signal strength was the one used for the measurements. In order to prevent clogging the flow system with dust particles, all solutions were filtered immediately before filling of the reservoirs. The rate of flow from the flow-system capillary ranged from 0.10 to 0.15 ml/min.

The spectra of the semiquinone ions of the duro, 2, 5dimethyl, and 2, 3-dimethyl hydroquinones, were sufficiently stable and well resolved to permit operation without a flow system. For these substances, a solution of the radical was prepared by dissolving approximately 5 mg of the hydroquinone in about 1.5 ml of 95% ethanol and then adding 2 drops of 0.1M NaOH. A thin-walled melting-point capillary tube was filled

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¹⁴ T. H. James and A. Weissberger, J. Am. Chem. Soc. **60**, 98 (1938).

 ¹⁵ J. B. Conant and L. F. Fieser, J. Am. Chem. Soc. 45, 2194 (1923).
 ¹⁶ A. Eckert and R. Endler, J. prakt. Chem. 104, 81 (1922).

¹⁷ L. I. Smith and F. L. Austin, J. Am. Chem. Soc. 64, 528 (1942).

¹⁸ R. H. Thomson, J. Chem. Soc. 1953, 1196.

¹⁹ J. E. LuValle and A. Weissberger, J. Am. Chem. Soc. 69, 1576 (1947).

²⁰ L. I. Smith and F. J. Dobrovolny, J. Am. Chem. Soc. 48, 1420 (1926).

²¹ Hirshon, White, and Fraenkel, Rev. Sci. Instr. **23**, 772 (1952); J. M. Hirshon and G. K. Fraenkel, Rev. Sci. Instr. **26**, 34 (1955).

with this solution and inserted through the microwave cavity of the spectrometer.²¹

Magnetic field homogeneity.-The homogeneity of the magnetic field was checked by observing the spectrum of the 2,5-ditertiary-butyl semiquinone ion, a relatively stable radical with a paramagnetic spectrum containing hyperfine structure components as closely spaced as 0.06 gauss.^{3,22} The magnet used had an adjustable air gap spacing,²¹ and it was found that the homogeneity of the magnetic field could be improved by adjusting the force on spacers placed between the magnet pole faces. Adjustment of the homogeneity was required each day.

Microwave power saturation.-Microwave power saturation was observed in all the spectra examined. The power level employed was either sufficiently low to avoid saturation, or at as low a level of power as was consistent with adequate signal strength. The power incident on the microwave cavity was generally in the range of 0.1 milliwatt. The rectangular cavity employed was operated in the TE_{102} mode and had a loaded Q with the sample present of approximately 1800.

Measurement of hyperfine separations .--- The separations of the hyperfine components were measured in terms of the proton resonance frequency using a circuit of the type described by Knoebel and Hahn.²³ The magnetic field and the proton-oscillator frequency were adjusted until the crossover zero-slope point at a line center was observed simultaneously for both the electron and proton resonance lines. The first derivatives (slopes) of the resonances were obtained by using small-amplitude field modulation (at 38 cps) and by amplifying the absorption signals with narrow-band amplifiers. The amplifier outputs were displayed on the vertical axes of two oscilloscopes, one for the electron and one for the proton resonance, using synchronous 38-cps signals of the proper phase for the horizontal axes. The amplitude of the field modulation was held at as low a value as possible when observing narrow and overlapping components. Since decreasing the amplitude of the field modulation decreases the intensity of the signal, the lowest value which could be used varied from spectrum to spectrum. The range of peak-to-peak magnitudes of the amplitude of the field modulation for all the spectra examined was from 0.01 to 0.05 gauss.

The Knoebel-Hahn circuit was actually not stable enough for these measurements and, presumably because of anomalous dispersion, its frequency changes abruptly when resonance is approached. These difficulties were overcome by locking the proton oscillator to a stable adjustable frequency source obtained from a combination of a General Radio Type 805-C Standard Signal Generator and a BC-221 frequency meter. The output of the frequency meter was used to amplitude modulate the signal generator at from 150 to 175 kc/sec and the signal generator was adjusted so that the lower side band of its output, at approximately 14 Mc/sec, locked the proton oscillator. The use of the frequency meter to modulate the signal generator was essentially a makeshift method of obtaining extremely fine tuning of the signal generator output. The center frequency of the signal generator was monitored by beating it against the harmonics of the 10-kc/sec output of a General Radio Type 1213-A Unit Crystal Oscillator in a radio receiver, and the audio beat note was measured with a Hewlett-Packard Type 200 CD Wide Range Oscillator, thus allowing corrections to be made for drift in the signal generator. The BC-221 dial was calibrated by standard methods at every 0.5 kc/sec point over the range used. The signal generator was just barely stable enough for these measurements, had to be left running continuously, had to be insulated from thermal gradients, and required frequent replacement of the type 1614 oscillator tube. Modulation well above the highest nominal modulation frequency of the signal generator presented no difficulties.

The frequency of the microwave power was monitored with a conventional TE_{011} wave meter. The wave meter was kept at a fixed setting and the power transmitted in the neighborhood of its resonance was measured with a crystal and microammeter. If appreciable changes in the crystal current were observed during a run, indicating a shift in microwave frequency or power, the results were discarded. Although this method is not adequate for measuring the frequency with the required accuracy of about 1 part in 10⁶, it is sufficiently sensitive to detect short-time changes of this magnitude.

The proton-containing probe of the proton oscillator and the sample of paramagnetic material were not at identical positions in the magnetic field, but errors in the measured separations between hyperfine components resulting from possible differences in magnetic field at the two different regions were judged to be negligible.

IV. GENERAL FEATURES OF THE SPECTRA

All the spectra examined, except that of the tetrachlorosemiquinone ion, exhibited hyperfine structure, and in almost all cases the structure could be completely interpreted in terms of hyperfine interactions between the unpaired electron and protons in the negative semiquinone ion of the oxidized hydroquinone.[‡] No splitting attributable to Cl³⁵ or Cl³⁷, both

$$B_i = B_0 - \Sigma a_i m_i,$$

 ²² G. K. Fraenkel, Ann. N. Y. Acad. Sci. 67, 546 (1957).
 ²³ H. W. Knoebel and E. L. Hahn, Rev. Sci. Instr. 22, 904 (1951).

[‡] The spectrum at a fixed microwave frequency is described on the basis of isotropic hyperfine interaction by the equation (for the magnetic field corresponding to a particular component B_i)

where B_0 is the magnetic field at the center of the spectrum, a_i is the splitting constant in gauss of the *i*th proton, and m_i is the z component of the angular momentum of the *i*th proton in units of $\hbar(m_i = \pm \frac{1}{2})$. All possible combinations of the m_i must be included to obtain the spectrum.

of which have spin 3/2, was observed. All spectra of the methyl-substituted compounds could be interpreted by assuming that the three protons in a given methyl group are equivalent to each other, although they are not necessarily equivalent to the protons in another methyl group. Any intramolecular bonding between the methyl-group hydrogen atoms and the oxygen atoms must therefore average out with respect to the times observable in these measurements, as do any of the effects of the gear-type interleaving or meshing which must occur between methyl groups at positions ortho with respect to one another.

Anomalous lines not interpretable in terms of proton hyperfine interactions in the radical ion of the appropriate oxidized hydroquinone were found in some of the chloro-substituted compounds and in the oxidation products from durohydroquinone. The anomalous lines in the chloro-substituted compounds are interpreted as arising from radical species other than the simple semiquinone ion of the hydroquinone,²⁴ but the extra lines in durohydroquinone have not been explained (see below).

Absence of chlorine splitting.—The absence of resolved chlorine hyperfine structure has not been adequately explained. The spectra were obtained in nonviscous solutions where the rapid tumbling of the molecules averages out anisotropic interactions⁴; only the isotropic Fermi or contact type of hyperfine structure (except for possible second-order isotropic effects) can survive this tumbling.⁴ The absence of a resolvable chlorine hyperfine structure therefore implies only that there is a small odd electron density at the site of the chlorine nucleus itself, i.e., the odd electron is in an orbital which has a small s-type contribution with respect to the chlorine. The hyperfine structure observed for in-plane aromatic protons may be considered as arising from a small contribution of valence structures in which the carbon-hydrogen σ bond is unpaired while the σ and π orbitals of the carbon are paired.⁵⁻¹¹ If a similar mechanism were involved in producing chlorine hyperfine structure, only the s character of the carbonchlorine bond would make a contribution. The percentage of s character in a bond of this type is probably less than about 20%,²⁵ the density of a 3s chlorine orbital at the chlorine nucleus is about eight times that of a hydrogen 1s orbital at the proton, and the magnetic moment of the chlorine isotopes is about onefourth that of the proton. The chlorine splittings would thus be expected to be of the order of (0.2)(8)(1/4) = 0.4 times that of the proton splitting, or about 0.8 gauss. Splittings of this magnitude should be clearly resolvable and we must conclude that the present estimate is incorrect or that perhaps a relaxation of the chlorine nuclear-spin states through a mechanism involving the quadrupole moment causes the averag-

TABLE I. Half-widths at half-maximum (gauss).

Tolusemiquinone ion	0.045
2.6-Xylosemiquinone ion	0.092
Durosemiquinone ion	0.048
Monochlorosemiquinone ion	0.074
2.5-Dichlorosemiquinone ion	0.14
Trichlorosemiquinone ion	0.14

^a The two lines had slightly different widths. This value is an average.

ing to zero of the chlorine hyperfine splitting. Further investigation is required to explain both the absence of the hyperfine structure in the spectra and the variation of line widths from compound to compound (cf. below).

Line widths.-The line widths of all spectra depended on microwave power and the concentration of hydroquinone. Line widths, which were determined for only a small number of the compounds, were measused under the same experimental conditions as for the measurements of the splitting constants. The results are given in Table I. The narrowest lines may have been broadened by magnetic field inhomogeneity. Marked changes in width with variation of power and hydroquinone concentration did not occur in the region used so that appreciably smaller widths at lower concentrations or powers are not expected. It is believed that the dependence of width on concentration was not caused by interradical dipolar broadening because the concentrations were too low.²⁶ A possible source of broadening is the chemical reactivity of the semiquinone ion: exchange reactions are possible between the semiquinone and the hydroquinone or quinone, and many other reactions, some of which are irreversible, undoubtedly take place. If the chemical reactivity limits the lifetime sufficiently, and the spinstate lifetime is determined by the chemical reaction, line broadening will occur.^{22,27,28}

The large widths in the spectra of the chlorine compounds may be the result of unresolved chlorine hyperfine splitting, but an attempt to account for all the line widths as the result of a superposition of unresolved components was unsuccessful, the observed line width increasing more rapidly with an increase in the number of chlorine atoms than the calculated width. (In making this calculation it was assumed that the unresolved components were of constant width and that the widths of the observed line were the result of a hyperfine splitting of approximately constant amount from compound to compound.) Apparently factors other than unresolved chlorine hyperfine structure contribute to the width of these spectra.

²⁶ From the work of Kittel and Abraham [Phys. Rev. 90, 238 (1953)], it is possible to estimate that the width is of the order of 60M gauss, where M is the radical concentration in moles per liter. ²⁷ R. L. Ward and S. I. Weissman, J. Am. Chem. Soc. **76**, 3612

⁽¹⁹⁵⁴⁾

²⁸ D. M. Gardner and G. K. Fraenkel, J. Am. Chem. Soc. 78, 3279 (1956).

²⁴ Similar observations were made by J. L. Vivo [thesis, University of Minnesota (1956)].

²⁵ B. P. Dailey (private communication).

			Splitting cons	tants (gauss)		
Derivative of the angegrami	R	ing protons ^a (a)	ı	Methy	l group protor	$ns^a(b)$
quinone ion	a_1	a_2	a_3	b_1	b_2	b_3
Unsubstituted	2.368 ^b					
Monomethyl	2.462°,d	2.537c.d	1.764 ^{c,b}	2.045 ^{c,b}		
2,5-Dimethyl	1.836 ^d			2.248 ^d		
2,6-Dimethyl	1.892°,d			2.125°,d		
2,3-Dimethyl	2.595 ^b			1.714 ^b		
Frimethyl	1.97°			2.24e	1.88 ^e	1.77e
Fetramethyl				1.897 ^b		
Monochloro	2.208°,b	2.208 ^{c,b}	2.453 ^{c,b}			
,5-Dichloro	2.030 ^b					
,6-Dichloro	2.320ь					
,3-Dichloro	2.319 ^b					
Frichloro	2.163 ^{e,d}					

TABLE II. Results.

^a See footnote ‡ in Sec. IV for the definition of the splitting constants.

^b Limit of error: ±0.001.

^e Indicates values which include overlap corrections.

^d Limit of error: ± 0.002 .

^e Limit of error: ± 0.01 .

g values.—Spectroscopic splitting factors (g values) were determined by measuring the difference between the values of the magnetic field at which resonance occurred for the compound under investigation and for a standard. The standard was a polycrystalline sample of 1,1-diphenyl-2-picrylhydrazyl, the g value of which was taken to be $2.0037.^{29}$ No attempt was made to obtain accurate absolute or relative g values for the compounds studied and all the spectra had g values which were indistinguishable from $g=2.005\pm$ 0.001. There is some evidence to indicate that more precise measurements would show differences between these compounds.³⁰

V. DETAILS OF INDIVIDUAL SPECTRA

The detailed analysis of the spectra is summarized in Table II. The splitting constants were calculated by the method of least squares and, where necessary, corrections were made for overlap of individual components according to procedures outlined in Appendix I. The relative intensities of the components were not measured carefully except in the case of unsubstituted p-benzosemiquinone ion. In all other compounds, the relative intensities were in qualitative accord with the values predicted from a knowledge of the number of protons and their respective splitting constants, but in general the relative intensities depended on the level of microwave power. Insofar as could be determined, the magnitude of the splitting constants did not depend on the power level over the range used.

p-Benzosemiquinone ion.—Four equivalent ring protons; predicted spectrum of five lines with relative intensities 1:4:6:4:1. The relative intensities reported in reference 1 are found only at a particular level of microwave power, and measurements at a low enough power to yield an asymptotic approach to the theoretical intensity ratios have not been performed. The concentration of hydroquinone in the flow system reservoir was $2 \times 10^{-3}M$.

p-Tolusemiquinone ion .- Three equivalent methylgroup protons and three nonequivalent ring protons. The spectrum, shown in Fig. 1, contains seven main lines indicating that the six protons are roughly equivalent. Under conditions of high resolution, 32 components are observed, some of which are incompletely resolved. The best resolution was obtained when the concentration of toluhydroquinone in the flow system reservoir was from 2×10^{-3} to $4 \times 10^{-3}M$. The spectrum predicted for a molecule with 6 protons, three equivalent and three nonequivalent, consists of 32 lines, 16 of which are triply degenerate. The predicted relative intensities for one-half of the spectrum are(1):(1:3:1:1):(3:3:1:1:3:3:1):(3:1:3:3- (no center line). The grouping indicates the seven main lines. A detailed analysis of this spectrum is given in Appendix II.

2,5-Dimethylsemiquinone ion.—Six equivalent methyl-group protons (two equivalent methyl groups) and two equivalent ring protons (Fig. 2). The predicted spectrum contains 21 lines. The observed spectrum contains nine major lines, indicating that the eight protons are roughly equivalent, but under high resolution 21 completely resolved components are seen. The predicted relative intensities for one-half of the spectrum are (1):(2:6):(1:12:15):(6:30:20):(15:40) (including the center line).

2,6-Dimethylsemiquinone ion.—The general features of the spectrum, including the predicted relative intensities, are the same as for the 2,5-dimethyl radical, except that in this spectrum some of the lines are not completely resolved. The best resolution was obtained when the concentration of 2,6-dimethylhydroquinone

 ²⁹ Holden, Kittel, Merritt, and Yager, Phys. Rev. 77, 147 (1950); C. H. Townes and J. Turkevich, *ibid.*, 77, 148 (1950).
 ³⁰ J. L. Vivo, thesis, University of Minnesota (1956).

in the flow system reservoir was $4 \times 10^{-3}M$. In addition, an apparent asymmetry was observed: the average value of a given separation on the high-field side of the spectrum differed from the average value of the equivalent separation on the low-field side by an amount greater than the average deviation for either of the two groups of measurements. The line width of the extreme line on each side of the spectrum was also different. The asymmetry, although slightly greater than the experimental error, was very small, and no explanation was found. In calculating the splitting constants, the observed values for the separations and widths of the two sides of the spectrum were averaged. One spacing was omitted from the least squares calculation because the asymmetry for this spacing was fairly large.

2,3-Dimethylsemiquinone ion.—Just as for the 2,5and 2,6-dimethyl compounds, 21 lines are observed. They are completely resolved. The predicted relative intensities for this radical, however, for one-half of the spectrum are (1):(6:2):(15:12:1):(20:30:6):(15:40)(including the center line).

Trimethylsemiquinone ion.-The spectrum of trimethylsemiquinone ion contains a great many lines, all of which overlap considerably, and it was not possible to measure the majority of the spacings. The line width is exceedingly dependent on the concentration of trimethylhydroquinone in the flow system reservoir; the best resolution was obtained when this concentration was $4 \times 10^{-3} M$. In all, some 60 lines were distinguished. Assuming that there are three nonequivalent methyl groups and one ring proton, not equivalent to any of the methyl group protons, a spectrum of 128 lines is expected. The positions of these 128 lines can be predicted using the values of o', m', p' and o'', m'', p'' calculated from the experimental data on the three xylosemiquinones by using an additivity theory (see Sec. VI). A plot of the predicted spectrum was compared with the observed spectrum and gave excellent qualitative agreement.

Because of the extremely large amount of overlap, it was only possible to measure spacings between six different pairs on each side of the spectrum, and these data were all the information available from which to determine the four splitting constants. It was not possible to measure the line width (all of the observed lines overlapped considerably) and therefore no overlap corrections were applied to the measured spacings. For these reasons, the splitting constants of this radical are less accurately known than for any of the other compounds investigated.

Durosemiquinone ion.—Twelve equivalent protons (four equivalent methyl groups). The expected spectrum of thirteen equally spaced lines is observed. The predicted relative intensities for half of the spectrum are 1:12:66:220:495:792:924. In addition to the thirteen lines, small lines were frequently observed between the intense central components of the duro-



FIG. 1. Paramagnetic resonance spectrum of p-tolusemiquinone ion; (A) entire spectrum; (B), (C), (D), and (E) show the detailed spectra of the regions marked in (A). The magnetic field increases from left to right.

semiquinone ion. These are unexplained. It was expected that the thirteen lines would be equally spaced, but it was found that the splitting constants obtained from measurements of the separation of different pairs of lines differed from each other by an amount greater than the average deviation obtained for replicates on a given pair. This small apparent nonuniformity is unexplained. The average of all the measurements on many different pairs of lines is reported in Table II.

Monochlorosemiquinone ion.-Three inequivalent ring protons. Under most conditions, the observed spectrum consists of 6 lines, two of which are doublets. A spectrum such as this is expected for two equivalent and one inequivalent proton. When the spectrum is observed under conditions of high resolution, however, and with an extremely low concentration of monochlorohydroquinone (less than $1 \times 10^{-3}M$) in the flow system reservoir, the doublet is partially resolved. It was not possible to measure this splitting accurately but it is estimated to be of the order of 0.06 gauss. The measurements of the major spacings were performed with a concentration of monochlorohydroquinone in the flow system reservoir in the range from 4×10^{-3} to $5 \times 10^{-2} M$ and therefore only the splitting constants assuming two equivalent and one inequivalent proton are given in Table II.

2,5-Dichlorosemiquinone ion.—Two equivalent protons. Three lines with relative intensities 1:2:1. The splitting constant was measured with the concentration of 2,5-dichlorohydroquinone in the flow system reservoir in the range from 6×10^{-3} to $2 \times 10^{-2}M$.

2,6-Dichlorosemiquinone ion.-The features of the



FIG. 2. Paramagnetic resonance spectrum of 2,5-dimethylsemiquinone ion; (A) entire spectrum, (B), (C), (D), (E), and (F) show the detailed spectra of the regions marked in (A). The magnetic field increases from left to right.

spectrum are the same as for 2,5-dichlorosemiquinone ion. The splitting constant was measured with the concentration of 2,6-dichlorohydroquinone in the flow system reservoir in the range from 8×10^{-3} to $2 \times 10^{-2} M$.

2,3-Dichlorosemiquinone ion.—The general features of the splitting pattern are the same as for the other dichlorosemiquinone ions. If a solution of the 2,3dichlorosemiquinone ion is placed in a capillary sample tube and the spectrum observed over a period of many hours, however, additional lines are observed, the first appearing after an hour or more has elapsed. These anomalous lines are unexplained, but are thought to arise from another radical species which is produced by some side reaction. Their appearance causes no difficulty in measuring the splitting constant of the 2,3dichlorosemiquinone ion because the measurement was done using a (relatively fast) flow system. The concentration of the 2,3-dichlorohydroquinone in the flow system reservoir was $5 \times 10^{-3}M$.

Trichlorosemiquinone ion.—One ring proton. A spectrum of two lines of equal intensity is expected. It is not observed, however, except under particular conditions. If a solution of trichlorosemiquinone is placed in a capillary sample tube (rather than in a flow system) the spectrum observed within five minutes of preparation of the radical consists of two main lines of equal intensity and a small third line between the two, but overlapping the high field peak. This third line grows with time until, at the end of an hour and a half, while the relative heights of the original two peaks remain

essentially constant, the third line has become more intense than these two. It is also the narrowest line. The spectrum is very dependent on the concentrations of base and trichlorohydroquinone; the higher the concentration of either of these, the more quickly does the anomalous line appear and grow. The line width also depends strongly on these concentrations. The sample of trichlorohydroquinone was recrystallized several times and analyzed. From the analysis (see Sec. II) it seems likely that the anomalous lines are due to the production of other radicals by side reactions. The spacing reported for trichlorosemiquinone ion in Table II was measured with a flow system using that concentration of trichlorohydroquinone in the flow system reservoir which produced a spectrum of only two, equally intense, lines. It was not possible to resolve these two lines completely. The measured line widths of these two lines were slightly different. An average line width was used to make the overlap correction. Because of the large uncertainty in the overlap correction and the possibility that the anomalous line was too weak to be observed but still contributed to the spectrum, it is considered that this spacing is not as reliable as the others.

Tetrachlorosemiquinone ion.—There are no protons in this molecule, and only one line is observed. After several hours, additional lines begin to appear, presumably resulting from radicals produced by side reactions.

VI. INTERPRETATION OF VARIATIONS IN SPLITTING CONSTANTS

McConnell has related proton hyperfine coupling constants to the unpaired spin density at the carbon atom adjacent to the proton.^{6–9} It is therefore of interest to explore the possibility that the differences observed in the proton hyperfine interaction constants for the various semiquinones studied might be indicative of directive effects of the substituents.

In order to obtain a quantitative measure of substituent effects, it is convenient to choose the unsubstituted semiquinone ion as a reference and to let the quantities o, m, and p measure the changes, on chlorine substitution, in the splitting constants of ring protons which are, respectively, *ortho*, *meta*, and *para* to the chlorine atom. In general the quantities o, m, and p could vary from compound to compound, (thus making it impossible to evaluate the parameters), but it will be assumed as a first approximation that these quantities are constant and that in compounds with more than one chlorine atom, the effect at any particular ring proton is the sum of the effects produced by the individual chlorine atoms, acting independently of one another.

With this assumption of additivity, the values of o, m, and p can be determined from the ring-proton splitting constants for the three dichloro-p-benzosemi-

quinone ions by means of the equations

2,3 ion:	2.368 + m + p = 2.319,
2.5 ion:	2.368 + o + m = 2.030.

2,5 ion: 2.368 + o + m = 2.030,

2,0 ion:
$$2.368 + o + p = 2.320$$
,

where 2.368 is the splitting constant for the unsubstituted p-benzosemiquinone ion.

Solution of these equations yields

$$o = -0.169$$

 $m = -0.170$
 $p = +0.120.$

These values of o, m, and p can now be used to predict the ring proton splitting constants for the monoand trichloro-p-benzosemiquinone ions. A comparison with the observed values will serve to test the assumption of additivity. In order to identify the different protons in the monochloro ion, the Cl is assigned to the 2 position and the three ring protons to the 3, 5, and 6 positions. The predicted values for these two radicals are given in Table III.

A similar calculation can be made for the effects produced by methyl substitution. Define o', m', and p' as the changes, on methyl substitution, in the splitting constants of ring protons which are, respectively, *ortho*, *meta*, and *para* to the methyl group, and again assume that the effects of the individual methyl groups are additive. The values of o', m', and p' can then be obtained from the ring-proton splitting constants for the three dimethyl-*p*-benzosemiquinone ions.

The results are

$$o' = -0.618$$

 $m' = +0.086$
 $p' = +0.142.$

In order to identify the different protons in the tolucompound for comparison of the predicted and experimental values, the methyl group is assigned to the 2 position and the three ring protons to the 3, 5, and 6 positions. See Table IV for a comparison of predicted and experimental values.

TABLE	III.ª
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	Position of proton	Predicted a	Experi- mental a
Monochlorosemiqui- none	3 6 5	$2.368 + o = 2.200 \\ 2.368 + m = 2.199 \\ 2.368 + p = 2.488$	$\begin{cases} 2.208 \\ 2.208 \\ 2.453 \end{cases}$
Trichlorosemiqui- none	2.36	$b^{+} b^{+} m^{+} p^{-} 2.151$	2.163

^a For the monochlorosemiquinone ion, the measurements made do not indicate how the three constants are to be assigned to the different positions; assignment of the experimental values has been made on the basis of the predicted values.

TABLE IV.ª

(Position of proton	Predicted a	Experi- mental a
Tolusemiquinone	3 6 5	2.368+o' = 1.7502.368+m' = 2.4542.368+p' = 2.510	$ \begin{cases} 1.764 \\ 2.462 \\ 2.537 \end{cases} $
Trimethylsemiquinon	e 2.36	$b^{0}8 + o' + m' + p' = 1.978$	1.97

^a Since the experiments performed do not indicate how the three ring proton constants of tolusemiquinone are to be assigned, we were guided by the predicted values in making the assignment of the experimental values.

In a similar manner, the effects of substituents on the methyl group splitting constants can be determined. The quantities o'', m'', and p'' are defined as the changes in a methyl-group splitting constant when another methyl group is substituted for a proton in a position ortho, meta, or para, respectively, to the methyl group under consideration. It is also necessary to introduce a quantity q to account for the difference between the splitting constant at a methyl group proton and a ring proton. To the degree of approximation used in the present analysis, q is a constant. From the semiquinone ions of duroquinone and the xyloquinones one finds

duroquinone ion:	o"+m"+	p'' + q + 2.368 = 1.897
2,5 ion:		p'' + q + 2.368 = 2.248
2,6 ion:	<i>m</i> ″	+q+2.368=2.125
2,3 ion:	0"	+q+2.368=1.714

The solutions of these equations yields

$$q = -0.273$$

 $o'' = -0.381$
 $m'' = +0.030$
 $p'' = +0.153.$

In order to compare these results with the observed values in the tolu- and trimethyl compounds, the different methyl groups in the trimethyl radical are identified by assigning the proton to the 2 position and the three methyl groups to the 3, 5, and 6 positions. The comparison between the predicted and experimental values is shown in Table V.

It has been shown above that an additivity law predicts the variation in odd-electron density at a proton when substitutions are made on the ring with considerable success. The odd-electron density at a ring proton decreases when a methyl group is attached to the ring at the *ortho* position and increases slightly when the methyl group is *meta* or *para* to the proton. When a chloro group is substituted either *ortho* or *meta* to a proton, the odd electron density at the proton decreases, but if the chloro group is substituted *para* to the proton, the odd-electron density at the proton in-

	Positio of meth group	pn yl b Predicted b	Experi- mental b
Trimethylsemiqui- none	3 p 6 d 5 o	m''+m''+q+2.368=2.278 m''+p''+q+2.368=1.867 m''+m''+q+2.368=1.744	$\left.\right\} \left\{\begin{array}{c} 2.24\\ 1.88\\ 1.77 \end{array}\right\}$
Tolusemiquinone		q+2.368=2.095	2.045

TABLE V.ª

⁸ Since the experiments performed do not indicate how the three methyl proton splitting constants of trimethylsemiquinone are to be assigned, we were guided by the predicted values in making the assignment of the experimental values.

creases. These conclusions might be useful in predicting the course of radical reactions where the density of the unpaired electron at the site of attack would be a controlling factor. No attempt has been made to compare the results of the present investigation with the existing ideas on substituent effects in aromatic systems. It is still not clear whether substituent effects observed in a reaction are inherent in the molecule being attacked or whether the effects are due to polarization caused in the aromatic molecule by the attacking anion or cation. Further, the present investigations are confined to the odd-electron density and may be useful only in complex radical reactions.

Several investigators⁵⁻¹¹ have demonstrated that the interaction between the unpaired electron and the ring protons arises from configuration interaction between π and σ states. McConnell has recently^{8,9} refined his original suggestion (that the ring-proton interaction constants are proportional to the density of the oddelectron at the ring carbon to which the proton is attached) by introducing the concept of the unpaired spin density on the adjacent carbon atom. If the present experimental results are examined with a view to substantiating McConnell's theory, the directive effects of chlorine atoms and methyl groups on ringproton splitting constants seem surprisingly large. For instance, the ring proton splitting constant changes from 2.368 in the unsubstituted semiguinone ion to 1.764 for the proton ortho to the methyl group in

TABLE VI. Hyperfine splitting constants in methyl-substituted semiquinone ions.

Desired a field	Hfs constant of methyl protons (gaus			
semiquinone	Observed	Calculated ^a		
Monomethyl	2.045	2.00		
2,5-Dimethyl	2.248	2.33		
2,6-Dimethyl	2.125	2,00		
2,3-Dimethyl	1.714	1.69		
Trimethyl	(1.77	(1.70		
-	1.88	2.03		
	2.24	2.34		
Tetramethyl	1.897	2.03		

* See reference 5.

tolusemiquinone ion.³¹ This is a change of about 25%relative to the unsubstituted ion and clearly indicates that McConnell's original suggestion cannot be correct. Unfortunately, the more recent theory, which involves a many electron spin-density matrix, is extremely complicated, and in order to state definitely whether or not the theory agrees with the data, long and detailed calculations would be required.

It has been shown by Bersohn⁵ that the interaction between the unpaired electron and methyl group protons can be accounted for by the molecular orbital theory of hyperconjugation.³²⁻³⁴ Using parameters given by Crawford,³⁴ Bersohn calculated the hyperfine splitting constants for a methyl proton in methyl-substituted semiquinones.⁵ Bersohn changed one of Crawford's parameters, namely β_1/β from 0.7 to 0.93, in order to obtain values in agreement with the experi-

TABLE VII. Half of the spectrum of tolusemiquinone ion.

Line	Distance from the center of the spec- trum expressed in terms of the four splitting constants	M	Degen- eracy	Approxi- mate posi- tion (gauss)
(1) (2) (3) (4)	$\begin{array}{c} (a_1/2) - (a_2/2) - (a_3/2) + (b/2) \\ - (a_1/2) + (a_2/2) - (a_3/2) + (b/2) \\ (a_1/2) + (a_2/2) + (a_3/2) - (3b/2) \\ (a_1/2) + (a_2/2) - (a_3/2) - (b/2) \end{array}$	0	3 3 1 3	0.10 0.18 0.31 0.60
(5) (6) (7) (8) (9) (10) (11)	$\begin{array}{l} -\left(a_{1}/2\right)-\left(a_{2}/2\right)+\left(a_{3}/2\right)+\left(3b/2\right)\\ \left(a_{1}/2\right)-\left(a_{2}/2\right)+\left(a_{3}/2\right)+\left(b/2\right)\\ -\left(a_{1}/2\right)+\left(a_{2}/2\right)+\left(a_{3}/2\right)+\left(b/2\right)\\ \left(a_{1}/2\right)-\left(a_{2}/2\right)-\left(a_{3}/2\right)+\left(3b/2\right)\\ -\left(a_{1}/2\right)+\left(a_{2}/2\right)-\left(a_{3}/2\right)+\left(3b/2\right)\\ \left(a_{1}/2\right)+\left(a_{2}/2\right)-\left(a_{3}/2\right)+\left(3b/2\right)\\ \left(a_{1}/2\right)+\left(a_{2}/2\right)-\left(a_{3}/2\right)+\left(b/2\right)\\ \end{array}$	1	1 3 1 1 3 3	1.45 1.87 1.94 2.15 2.22 2.36 2.64
(12) (13) (14) (15)	$\begin{array}{c} (a_1/2)-(a_2/2)+(a_3/2)+(3b/2)\\ -(a_1/2)+(a_2/2)+(a_3/2)+(3b/2)\\ (a_1/2)+(a_2/2)+(a_3/2)+(b/2)\\ (a_1/2)+(a_2/2)-(a_3/2)+(3b/2) \end{array}$	2	1 1 3 1	3.91 3.99 4.40 4.69
(16)	$(a_1/2) + (a_2/2) + (a_3/2) + (3b/2)$	3	1	6.45

mental values, but this change is not highly significant. The good agreement between Bersohn's calculations and the experimental data (Table VI) indicates that the present work is direct experimental evidence for the theory of hyperconjugation.

APPENDIX I. CALCULATION OF OVERLAP CORRECTIONS

For some of the radicals, namely the monochloro, trichloro, tolu, 2,6-dimethyl, and 2,3,5-trimethyl

³¹ If one compares o', m', and p', with o'', m'', and p'', the directive effects of substitution in the ortho position seem strikingly large with respect to the effects of substitution in the meta and arge with respect to the checks of substitution in the maximum and para positions. This suggests a similarity with the "proximity effect" or "ortho effect" [L. P. Hammett, *Physical Organic Chemistry* (McGraw-Hill Book Company, Inc., New York, 1940), first edition, p. 204] in which the substituent constant, σ , is much lower or the substituted compound then for more the substituted to be a more subis much larger for orlho-substituted compounds than for meta- and para- substituted compounds.

³² C. A. Coulson, Valence (Oxford University Press, London, 1953), first edition, p. 307. ³³ V. A. Crawford, Quart. Revs. **3**, 226 (1949).

³⁴ C. A. Coulson and V. A. Crawford, J. Chem. Soc. 1953 2052.

Measured spacings	Obs. val. (kc/sec) ^b	n'	$\sigma(\bar{y}) \times 10^3$ (kc/sec) ^b	Y	Relation to splitting constants	Q	Y'×10 ³
(4, 1)	2.066	7	8	2.091	a_2-b	(2.098)	
(4, 2)	1.787	7	13	1.761	a_1-b	(1.780)	
(4, 3)	1.237	7	13	1.218	$-a_3+b$	(1.196)	-
(4, 5)	3.627	6	10	3.628	$-a_1 - a_2 + a_3 + 2b$	3.634	-6
(4, 6)	5.437	9	6	5,408	$-a_2+a_3+b$	5.414	-6
(4, 7)	5.707	7	10	5.732	$-a_1+a_3+b$	5.732	0
(4, 8)	6.642	8	10	6.617	$-a_2+2b$	6.610	+7
(4, 9)	6.930	6	21	6.940	$-a_1+2b$	(6.928)	
$(\bar{4}, \bar{1}0)$	7 509	8	4	7 512	<i>a</i> 2	7.512	0
(4, 11)	8 703	ğ	ŝ	8 703	h	8 708	-5
(1, 12)	5 446	Ŕ	š	5 418	$-a_2 \pm a_2 \pm b_1$	5 414	⊥ă
(11, 12)	5 711	7	12	5 739	$a_2 + a_3 + b$	5 722	<u>+</u> 6
(11, 13)	7 511	6	12	7 511	$-u_1 + u_3 + v$	7 510	
(11, 14)	7.511	9	3	1.311	a_3	1.512	-1
(11, 15)	8.702	9	9	8.704	0	8.708	-4
(11, 16)	16.222	9	7	16.222	a_3+b	16.220	+2

TABLE VIII. Data for tolusemiquinone ion."

* n' = number of measurements made of spacing; **Y** = observed values corrected for overlap; $\sigma(\bar{y})$ = standard deviation of the average value of the measured spacing; **Q** = calculated values of each spacing using the least squares solution for the splitting constants; **Y**' = **Y**-**Q**.

^b The spacings were measured in terms of the proton resonance and the observed values are therefore given as the proton resonance frequency. The conversion from proton frequency to gauss is given by 0.23479 gauss/(kc/sec).

semiquinone ions, several lines of the spectrum overlapped considerably, and corrections for the overlap were applied to many of the observed spacings.

It was assumed that the line shape is Lorentzian,¹ and that the line width is the same for all lines in a spectrum. The spectrum can then be represented as the sum of Lorentzian components, of appropriate intensity and position, each with the same line width.

The widths of the two lines farthest from the center of the spectrum, which are always nondegenerate lines and, except for the spectrum of the trichlorosemiquinone ion, do not overlap any other lines, were measured on a sample during the course of the measurements of the spacings in the spectrum of the sample. The average value of the measured line widths, and the average value of each of the measured spacings, was used in making the overlap corrections. By trial and error, the positions of the centers of each of the components were adjusted until the separations between the maxima of the spectrum obtained from this theoretical model coincided with the observed spacings.

APPENDIX II.

CALCULATION OF THE SPLITTING CONSTANTS

For the majority of the spectra studied, the splitting constants were overdetermined, i.e., the number of measured spacings was greater than the number of splitting constants for the radical. In such cases, the splitting constants were determined by the method of least squares.

All the spectra were symmetric about the center, and the average values of measurements on both the highfield and low-field sides of a given spectrum were calculated. Where necessary, these averages were corrected for overlap.

A small number of the corrected measured spacings

were not included in the least squares analysis of the data for one of the following reasons: (a) The overlap was very large and therefore the overlap correction was probably quite uncertain. Thus lines which appeared as shoulders in the spectra were not included. (b) The precision with which a particular spacing was determined was very poor compared to that of all the other spacings for that radical.

As an example of the procedure, the details of the calculation for the tolusemiquinone ion will be given. All the lines are expressed in terms of the four splitting constants $(a_1, a_2, \text{ and } a_3 \text{ for the ring protons and } b$ for the three equivalent methyl group protons) by means of the formula[‡]

$m_1a_1 + m_2a_2 + m_3a_3 + (m_4 + m_5 + m_6)b$,

where the m's are the quantum numbers of the individual protons $(m_i = \pm \frac{1}{2})$. The degeneracy of any line is 1 if m_4 , m_5 , and m_6 are all the same, and 3 if one of these methyl group m's is different from the other two. The ordering of the lines is determined by trial and error comparison with the observed spectrum, advantage being taken of the degeneracies. Half of the lines, their degeneracies, and their approximate positions are listed in Table VII. The numbering in the table is from the center towards the high-field side. Also listed is the quantum number $M = \sum_{i} m_{i}$ which determines the position of the center of gravity of each group of lines. (If the protons were equivalent with splitting constant A there would be seven lines at positions determined by MA: 0, $\pm A$, $\pm 2A$, $\pm 3A$ with intensities 20, 15, 6, 1, respectively.) Only half of the M=0 line is listed in Table VII, the other half appearing on the low-field side.

The positions of lines 1 through 11 were measured relative to line 4, and the positions of lines 12 through

A ₄	A ₃	A ₂	A ₁	P4	P ₃	P ₂	\mathbf{P}_1	Y	Measured spacings
-6/43	-4/11	-2/3	-1	2	1	-1	-1	3.628	(4, 5)
-14/43	5/11	1/3	0	1	1	1	0	5.408	(4, 6)
3/43	2/11	1/3	-1	1	1	0	-1	5.732	(4, 7)
34/43	-6/11	-1	0	2	0	-1	0	6.617	(4, 8)
-5/43	1	0	0	0	1	0	0	7.512	(4, 10)
1	0	0	0	1	0	0	0	8.703	(4, 11)
-14/43	5/11	-1	0	1	1	1	0	5.418	(11, 12)
3/43	2/11	1/3	-1	1	1	0	-1	5.738	(11, 13)
-5/43	1	Ō´	ō	ō	1	Ó	Ō	7.511	(11, 14)
1	0	0	0	1	0	0	0	8.704	(11, 15)
38/43	1	Ō	Ō	1	1	0	Ō	16.222	(11, 16)
	5/11 2/11 1 0 1	$ \begin{array}{c} -1 \\ 1/3 \\ 0 \\ 0 \\ 0 \end{array} $		1 1 0 1 1	1 1 1 0 1	$ \begin{array}{c} -1 \\ 0 \\ 0 \\ 0 \\ 0 \end{array} $	0 -1 0 0 0	5.418 5.738 7.511 8.704 16.222	(11, 12) (11, 13) (11, 14) (11, 15) (11, 16)

TABLE IX. Orthogonal vectors for tolusemiquinone ion.

16 were measured relative to line 11. Table VIII shows the experimental data and the relation to the splitting constants. Four of the lines were not used in the least squares calculation: lines 1, 2, and 3 were excluded because there was a large overlap correction; line 9 was excluded because there was a large standard deviation in the measurement of its position.

The least squares solution can be found with a minimum of effort using the method of orthogonal vectors.§ For the tolusemiquinone ion, the 11 corrected observed values are regarded as the components of a vector, Y, and Y is then expressed as a linear combination of four 11-dimensional orthogonal vectors. Four orthogonal vectors are needed because there are four splitting constants to be determined. The computation of the orthogonal vectors proceeds as follows: one first constructs four convenient vectors to represent the relation of each line to the splitting constants. This is illustrated for tolusemiquinone in Table IX. P_1 , for example, represents the dependence on a_1 , i.e., the components of \mathbf{P}_1 are the coefficients of a_1 as determined from column 6 of Table VIII. Y (an therefore be represented as

$$\mathbf{Y} = \sum_{i=1}^{4} a_i \mathbf{P}_i + \mathbf{R}, \qquad (A1)$$

where the a_i are the splitting constants and **R** is the "residual" vector and represents the errors.

From these four vectors, the four orthogonal vectors, Λ_i , are computed using the Schmidt orthogonalization process³⁵ by means of the equation

$$\mathbf{A}_{i} = \mathbf{P}_{i} - \sum_{j=1}^{i-1} [(\mathbf{A}_{j} \cdot \mathbf{P}_{i}) / \mathbf{A}_{j}^{2}] \mathbf{A}_{j}.$$
(A2)

The calculation is started by setting $A_1 = P_1$. Y can now be expressed as a linear combination of the orthogonal vectors

$$\mathbf{Y} = \sum_{i=1}^{4} \beta_i \mathbf{A}_i + \mathbf{E} = \mathbf{Q} + \mathbf{E}, \qquad (A3)$$

and it can be shown that if

$$\beta_i = (\mathbf{Y} \cdot \mathbf{A}_i) / \mathbf{A}_i^2, \qquad (A4)$$

then the square of the error, \mathbf{E}^2 , is a minimum. The vector

$$\mathbf{Q} = \sum_{i=1}^{4} [(\mathbf{Y} \cdot \mathbf{A}_i) / \mathbf{A}_i^2] \mathbf{A}_i,$$

thus represents the least squares fit to the vector \mathbf{Y} . In the present case, evaluation of the coefficients leads to

$$\mathbf{Y} = -5.033\mathbf{A}_1 - 4.745\mathbf{A}_2 + 8.525\mathbf{A}_3 + 8.708\mathbf{A}_4 + \mathbf{E}.$$
 (A5)

The relationship between the A vectors and the P vectors is given by Eq. (A2) and by straightforward substitution one obtains

$$\mathbf{Y} = 10.488\mathbf{P}_1 + 10.806\mathbf{P}_2 + 7.512\mathbf{P}_3 + 8.708\mathbf{P}_4 + \mathbf{E}, \quad (A6)$$

where the coefficients of the **P** vectors are the four splitting constants for tolusemiquinone.

There are two independent methods for estimating σ , the standard deviation for the measurement of the mean of a single spacing (a single component V_i of the vector **Y**). One estimate of σ can be obtained from the calculated value of the square of the error of the least squares fit,

$$\mathbf{E}^{2} = (\mathbf{Y} - \mathbf{Q})^{2} = \sum_{j=1}^{11} (Y'_{j})^{2} = f\sigma^{2},$$

where f is the number of degrees of freedom in the least squares solution. In the present case, since there are 4 splitting constants calculated from 11 observed values, f=7.

An independent estimate of σ can be obtained from the standard deviation of the individual measurements of the spacings, the values listed in the fourth column of Table VIII, by means of the formula

$$\sum_{i=1}^{11} \sigma(\bar{y}_i)^2 = n\sigma^2.$$

 σ was calculated by both of these methods and the F test was applied to determine if the difference between the two estimates for σ was significant. It was found that the difference is not significant within 90% confidence limits.

 [§] We are indebted to Dr. G. E. Kimball for suggesting this method.
 ³⁵ R. Courant and D. Hilbert, Methods of Mathematical Physics

⁽Interscience Publishers, Inc., New York, 1953), Vol. I, p. 4.