TABLE IX
CHEMICAL SHIFTS AND SPIN–SPIN COUPLINGS IN DIMETHOXYBENZENES

Compound	Group	δ_c, p.p.m.	δ(obsd.) – δ(calcd.), p.p.m.	J, c./s.
1,2-Dimethoxy-	C-1,2	42.4	−4.3	..
benzene	CH-3,6	80.5	3.5	158
	CH-4,5	71.9	1.9	160
	OCH$_3$	137.5		144
1,3-Dimethoxy-	C-1,3	31.7	1.0	..
benzene	CH-2	92.0	−1.0	158
	CH-4,6	86.7	0.7	161
	CH-5	62.8	1.8	160
	OCH$_3$	138.0		145
1,4-Dimethoxy-	C-1,4	38.6	−1.1	..
benzene	CH-2,3,5,6	78.1	1.1	158
	OCH$_3$	137.2		146
1,2-Dimethoxy-4-	C-1 + C-2	43.8		..
methylbenzene	CH-3 + CH-6	80.0		156
	C-4	62.3		..
	CH-5	71.6		158
	OCH$_3$	137.4		142
	CH$_3$	172.2		120

likely that the small differences observed between the different compounds are real. The order anisole, 1,3-dimethoxybenzene, 1,2-dimethoxybenzene (and the 4-methyl derivative), 1,4-dimethoxybenzene is that expected if the interactions take place through the ring and are somewhat altered in the *ortho* compounds.

Spin–Spin Coupling Constants.—All ring CH coupling constants in the phenols and methoxybenzenes are the same as that in benzene (159 c./s.) within the experimental uncertainties, and the CH$_3$ couplings are the same as those in the methylbenzenes.[10] The OCH$_3$ couplings are all within the range 144 ± 2 c./s.

Electron Spin Resonance and Polarographic Investigation of Substituted Nitrobenzene Negative Ions

By August H. Maki and David H. Geske

Electron spin resonance spectra have been obtained for 14 *para* substituted nitrobenzene mononegative ions that were generated in acetonitrile solution by electrochemical reduction within a microwave cavity. Polarographic data were also obtained for these *para* substituents and for 8 *meta* substituents. An excellent linear correlation was found between the half-wave potentials for the *meta* substituents and σ^n and σ^0 values. From gross deviation of p-nitro and p-amino substituents from the *meta* correlation line, *para* resonance energies are estimated. The N^{14} coupling constant of the nitro group is found to decrease as the ease of reducing the parent molecule is increased by the *para* substitution and *vice versa*. Measurement of ring proton coupling constants leads to the conclusion that the total electron spin magnetization in the four central ring π-orbitals is approximately constant. The *para* substituent merely effects a redistribution of the magnetization among these ring positions. Evidence based on hyperfine structure is presented for hindered rotation of the aldehyde group of *para* nitrobenzaldehyde anion, and a maximum rotational frequency of 2.8×10^8 c.p.s. is estimated. Comparison of the F^{19} hyperfine coupling constant of p-fluoronitrobenzene with the *para* proton coupling constant of nitrobenzene leads to the ratio $a_F/a_H = 2.12$; from this ratio is estimated that $Q_F = -47.5$.

Introduction

In recent years numerous electron spin resonance (e.s.r.) studies have been made of organic free radicals, particularly *anion* free radicals prepared by one-electron reduction of the neutral parent molecule.[1] While a variety of anion radicals have been studied, no attempt has been made to examine a related series in which a single substituent is varied. Such a project is of particular interest in view of the possibility of estimates of odd-electron distribution derived from examination of the hyperfine structure of the e.s.r. absorption spectrum.

We have chosen to examine a series of *para* substituted nitrobenzene anion free radicals (·RArNO$_2^-$). The interaction of the odd electron with the nitrogen nucleus is expected to depend on the nature of the substituent, R. The experimental approach is the same as that presented previously[2,3]; the anion radical is generated by electrochemical

reduction of the parent molecule

$$RArNO_2 + e \rightleftarrows \cdot RArNO_2^- \qquad (1)$$
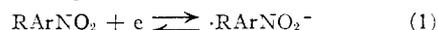
using acetonitrile as the solvent medium. An earlier study,[2] which demonstrated the experimental method, dealt with nitrobenzene anion radical, and a subsequent investigation[3] was concerned with the three dinitrobenzene anion radicals. The experimental simplicity and convenience of the electrogeneration technique have greatly facilitated the present extensive study.

Although a polarographic study of the series of *para* substituted nitrobenzenes was not the primary objective of this study, half-wave potential and current constant data were obtained. Availability of *both* e.s.r. and polarographic data provides an opportunity to relate the two quantitatively.

Experimental

Reagents.—Source and purification of the solvent, acetonitrile and supporting electrolyte, tetra-n-propylammonium perchlorate, were previously given.[2] Unless otherwise noted organic compounds were secured from Distillation Product Industries, Eastman Kodak Co. or K. & K. Laboratories (4-nitrobiphenyl and p-nitroacetophenone). Melting points agreed with literature values. Preparation

(1) (a) J. E. Wertz, *Chem. Revs.*, **55**, 829 (1955); (b) D. J. E. Ingram. "Free Radicals as Studied by Electron Spin Resonance." Academic Press, Inc., New York, N. Y., 1958, pp. 135–169.

(2) D. H. Geske and A. H. Maki, *J. Am. Chem. Soc.*, **82**, 2671 (1960).

(3) A. H. Maki and D. H. Geske, *J. Chem. Phys.*, **33**, 825 (1960).

of p-nitrosonitrobenzene was done according to Bamberger and Hübner.[4] Melting point was 118° (lit. value,[4] 119°). p-Nitrophenylthiocyanate was prepared by the method of Müller[5] with a melting point of 131° (lit. value,[5] 133°). Preparation of methyl p-nitrobenzenesulfonate was carried out according to the procedure of Morgan and Cretcher,[6] starting with p-nitrobenzenesulfonyl chloride obtained from K. & K. Laboratories. The crude product was recrystallized from ligroin–benzene and sublimed under reduced pressure. The white, crystalline sublimate melted at 91° (lit. value,[7] 91–92°).

Polarographic Measurements.—Polarographic data were obtained using the same instrumentation described previously.[2] Measurements of half-wave potential, $E_{1/2}$, and limiting current constant, I_d, were made on approximately 1 mM acetonitrile solutions which were decimolar in tetra-n-propylammonium perchlorate for the supporting electrolyte. An *aqueous* saturated calomel reference electrode (s.c.e.) was used throughout. Drop-weight, m, and drop-time, t, were measured at a potential on the limiting current plateau. Typical values were $m = 1.34$ mg. sec.$^{-1}$ and $t = 4.44$ sec. at -1.1 v. with a mercury column of 50 cm.

Maximum, not average, current values were measured, and thus cell resistances for "iR" correction were determined at maximum drop size. Where multiple waves occurred the tabulated I_d value refers only to current resulting from the new wave, and not to total current as measured from zero.

Free Radical Generation.—The technique of electrochemical generation of anion free radicals in an electrochemical cell placed directly within (*intra muros*) the resonance cavity of an ESR spectrometer has been described earlier.[2,3] The potential for generation of a particular anion radical (ordinarily 0.1 volt more negative than $E_{1/2}$) was chosen on the basis of the polarographic data. An aqueous s.c.e. with an agar bridge was used rather than the soft glass Pyrex Perley seal previously described.[2] Acetonitrile solutions approximately 1 mM in parent molecule and decimolar in tetra-n-propylammonium perchlorate were used in the free radical studies.

E.s.r. Spectrometer.—The e.s.r. spectrometer employed has been described,[2,3] as well as the technique of placing absolute field calibration marks on the e.s.r. spectrum as it is recorded. The sweep was found to be linear within the accuracy of measurement of the field calibration marks.

E.s.r. Results.—In all *para* substituted compounds investigated, except for the p-iodo-, p-nitroso- and p-thio-cyanato-nitrobenzenes, an electro spin resonance was observed when a solution of the compound was electroreduced at the appropriate potential within the microwave cavity. The character of the spectra differs widely. Many spectra exhibit a pronounced three-fold symmetry; that is, the same sub-pattern appears at the center of the resonance and also is displaced by an equal interval toward both high and low fields where it occurs with intensities equal to the central sub-pattern. This interval has been assumed to result from the hyperfine interaction of the electron with the N^{14} nuclear moment of the nitro group (nuclear spin, I, of one). The three-fold symmetry of the hyperfine pattern may be obscured if the nitrogen hyperfine interaction is not dominant. In this case, the nitrogen coupling constant must be derived by fitting the positions and intensities of the observed hyperfine components to a set of coupling constants with all interacting nuclei of the molecule. For this assignment, advantage is taken of the equivalence of nuclei which is a consequence of the symmetry of the parent molecule.

Isotopic substitution was not undertaken in this study. As a result, the assignment of certain coupling constants to particular molecular positions is not unambiguous. From a study of the relative intensities and spacings of the hyperfine pattern, however, the number of equivalent nuclei and the spin of each nucleus associated with a particular coupling constant could be determined in each case. Because of the good resolution and large number of lines observed, it is thought that these assignments are unique. When interaction of the odd-electron with two nuclei of $I = 1$ occurs, the larger coupling constant is identified with the N^{14} of the

(4) E. Bamberger and R. Hübner, *Ber.*, **36**, 3803 (1903).

(5) H. A. Müller, *Chem. Zentr.*, **77**, 1588 (1906).

(6) M. S. Morgan and L. H. Cretcher, *J. Am. Chem. Soc.*, **70**, 375 (1948).

(7) R. Kuhn and H. W. Ruelius, *Chem. Ber.*, **83**, 420 (1950).

nitro group. The coupling constants in Table I were obtained on the basis of this analysis.

E.s.r. spectra in Figs. 1–3 are recorded as the derivative of the absorption, $d\chi''/dH$, $vs.$ magnetic field, H, which increases to the right along the horizontal axis.
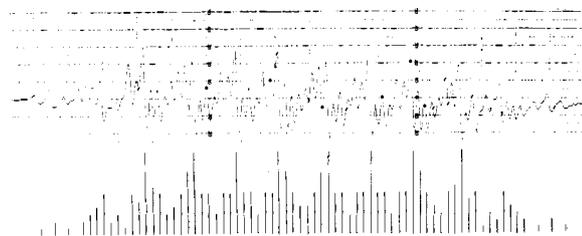
Fig. 1.—E.s.r. spectrum of p-nitrotoluene anion; constructed absorption spectrum calculated from data of Table I. Total width between extreme hyperfine components 41.62 ± 0.05 gauss.
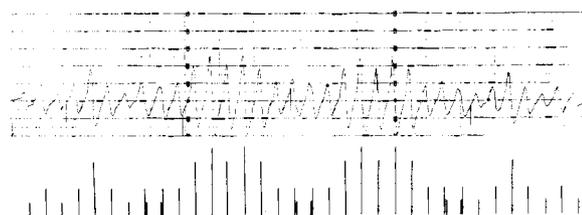
Fig. 2.—E.s.r. spectrum of p-fluoronitrobenzene anion; constructed absorption spectrum calculated from data of Table I. Total width between extreme hyperfine components 39.37 ± 0.05 gauss.
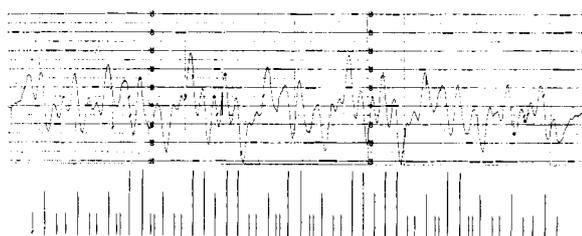
Fig. 3.—E.s.r. spectrum of p-nitrobenzaldehyde anion; constructed absorption spectrum calculated from data of Table I. Total width between extreme hyperfine components 19.24 ± 0.05 gauss.

p-**Aminonitrobenzene.**—The spectrum of the negative ion of p-aminonitrobenzene exhibits three-fold symmetry in the hyperfine structure. This major splitting of 12.18 gauss is assigned to the N^{14} nuclear moment of the nitro group. A very good fit of the observed spectrum is obtained by assuming $a_2 = a_3 = a_4 = 1/3 \, a_1 = 1.12$ gauss where a_1, a_2 and a_3 are each an interaction with two equivalent protons and a_4 is an interaction with one spin of 1 nuclear moment. This assignment predicts multiplets of 13 lines with intensity ratios 1:5:11:16:21:27:30:27:, etc. Observed intensity ratios are 1.4:6.0:11.0:15.4:19.7:26.3:30.0:26.3, etc.

p-**Methoxynitrobenzene.**—The three-fold symmetry in the e.s.r. spectrum of p-methoxynitrobenzene anion again leads to the nitrogen coupling constant which now must refer unequivocally to the nitro group. The spectrum is easily interpreted since the three other coupling constants are sufficiently different in magnitude to be immediately evident upon inspection.

p-**Nitrotoluene.**—The p-nitrotoluene anion exemplifies an e.s.r. spectrum, Fig. 1, lacking the immediately obvious three-fold symmetry. Below the experimental spectrum is an absorption spectrum synthesized from the coupling constants reported in Table I.

p-**Fluoronitrobenzene.**—Fig. 2 shows the spectrum of p-fluoronitrobenzene anion with a synthesized absorption spectrum drawn to scale below. The spectrum was based on

TABLE I

OBSERVED COUPLING CONSTANTS (IN GAUSS) FOR THE NEGATIVE IONS OF VARIOUS *para* SUBSTITUTED NITROBENZENES

Substituent	$a_N{}^a$	Coupling constant (absolute value)			
		a_1	a_2	a_3	a_4
$-NH_2$	12.18	3.36^b	1.12^b	1.12^b	1.12^c
$-OCH_3$	11.57	3.43^b	1.11^b	0.30^d	...
$-CH_3$	10.79	3.98^d	3.39^b	1.11^b	...
$-F$	10.76	8.41^e	3.56^b	1.16^b	...
$-H^f$	10.32	3.97^e	3.39^b	1.09^b	...
$-C_6H_5$	9.84	3.60^b	...	...	...
$-Cl$	9.83	3.46^b	1.17^b	...	...
$-Br$	9.70	3.43^b	1.15^b	...	...
$-CONH_2$	8.37	3.20^b	0.98^b	...	...
$-COOCH_3$	7.73	3.11^b	...	...	...
$-CN$	7.15	3.12^b	0.76^b	0.76^c	...
$-COCH_3$	7.02	2.95^b	0.66^b	0.66^d	...
$-SO_3CH_3$	6.90	3.03^b	0.64^b	...	...
$-CHO$	5.83	3.10^e	2.37^e	1.23^e	0.44^b
$-NO_2{}^g$	1.74	1.12^h	...	...	...

^{a} Nitrogen coupling constant of the nitro group. ^{b} Interaction with two equivalent spins of $I = {}^1/_2$. ^{c} Interaction with one spin of $I = 1$. ^{d} Interaction with three equivalent spins of $I = {}^1/_2$. ^{e} Interaction with one spin of $I = {}^1/_2$. ^{f} Data from ref. 2. ^{g} Data from ref. 3. ^{h} Interaction with four equivalent spins of $I = {}^1/_2$.

the coupling constants given in Table I. Coupling constant a_1 represents an interaction with a single nucleus of spin $^1/_2$ whereas a_2 and a_3 each represent an interaction with two equivalent nuclei of spin $^1/_2$. From symmetry arguments, a_1 must be identified as the hyperfine coupling constant of the F^{19} nucleus.

4-Nitrobiphenyl.—The e.s.r. spectrum of the 4-nitrobiphenyl anion is characterized by the three-fold symmetry which allows the identification of the nitrogen coupling constant and consists of three broad triplets, each with intensity ratios 1:2:1. Further resolution of the spectrum could not be obtained, probably because of the complex hyperfine interaction with the *p*-phenyl ring.

p-**Chloronitrobenzene.**—The three-fold symmetry in the spectrum of the *p*-chloronitrobenzene anion permits identification of the nitrogen coupling constant. An interaction with two pairs of equivalent protons is also evident. No structure resulting from the chlorine nuclear moment is evident, but its presence apparently contributes to the width of the lines.

p-**Bromonitrobenzene.**—The spectrum of the *p*-bromonitrobenzene anion is qualitatively the same as that of the *p*-chloronitrobenzene anion.

p-**Nitrobenzamide.**—The spectrum of the *p*-nitrobenzamide anion reveals a three-fold symmetry which can be attributed to a hyperfine interaction with one of the N^{14} nuclei of the radical. The spectrum is qualitatively similar to that of the *p*-chloronitrobenzene anion except the lines are much broader. The broadness of the lines is possibly caused by unresolved hyperfine interaction with the amide group. The resolved hyperfine interactions are interpreted as arising from the N^{14} nucleus of the nitro group and the four ring protons which, as far as the resolution will allow, seem to be equivalent in pairs.

Methyl *p*-Nitrobenzoate.—Three very broad triplets, each of the intensity ratio 1:2:1, characterize the e.s.r. spectrum of the methyl *p*-nitrobenzoate anion. The nitrogen coupling constant and that of two approximately equivalent ring protons can be identified. It is unlikely that broadening of the lines is caused by the methyl group protons.

p-**Nitrobenzonitrile.**—The large N^{14} coupling constant in the e.s.r. spectrum of *p*-nitrobenzonitrile anion is obtained from the large three-fold splitting. The entire spectrum is well explained by assuming the coupling constants given in Table I. There are two coupling constants, each representing a hyperfine interaction with two equivalent ring protons. The smaller of these is approximately equal to the small N^{14} coupling constant which is assumed to result from the nitrogen atom of the CN group. These latter hyperfine inter-

actions lead to quintets with intensity ratios 1:3:4:3:1 in agreement with the spectral data.

p-**Nitroacetophenone.**—The three-fold pattern in the spectrum of *p*-nitroacetophenone anion leads to the coupling constant of the N^{14} nucleus of the nitro group. The detailed structure is consistent with two more coupling constants, a larger one with two equivalent protons and a smaller one with five equivalent protons. The coupling constant of the methyl group protons, consequently, must be nearly the same as that of one pair of ring protons.

Methyl *p*-Nitrobenzenesulfonate.—The hyperfine structure of the methyl *p*-nitrobenzenesulfonate anion is qualitatively similar to that of the *p*-chloronitrobenzene anion. The coupling constants are given in Table I. The line width is less than that of the *p*-chloronitrobenzene anion. No evidence of hyperfine interaction with the methyl group protons was observed.

p-**Nitrobenzaldehyde.**—The hyperfine structure of the e.s.r. spectrum of the *p*-nitrobenzaldehyde anion which appears in Fig. 3 cannot be explained on the assumption that the ring protons are equivalent in pairs. The synthesized absorption spectrum which appears below the observed spectrum was calculated using the coupling constants given in Table I. The coupling constants a_1, a_2 and a_3 each represent a hyperfine interaction with a single proton, and a_4 represents an interaction with two approximately equivalent protons.

Results of Polarographic Studies.—Polarographic data for substituted nitrobenzenes as given in Tables II and III were obtained for only a single concentration (ca. one mM) for each compound. Thus, this study does not represent the usual systematic investigation in which the dependence of limiting current and half-wave potential on concentration is examined and the dependence of limiting current on height of the mercury column is established. Primary concern was directed toward measurement (under identical conditions) of half-wave potentials (estimated accuracy ± 5 mv.[8]) and limiting current constants for the various one-electron reduction reactions used to generate the anion free radicals. No attempt was made to elucidate electrode reactions occurring at more reducing potentials.

A necessary (but not sufficient) condition for the "polarographic reversibility" of an electrode reaction is that the quantity, $E^{3/4} - E^{1/4}$, has a value of -56 mv. (at 25°) for a one-electron reaction.[9] Values of this quantity for the various reduction waves are given in Table II. Uncertainty of measurement is approximately ± 5mv. With the exception of the iodo- and thiocyanato- compounds (neither of which showed e.s.r.) the first reduction wave for all compounds in Table II shows reasonable agreement with the criterion stated above. Thus, half-wave potentials for these compounds represent thermodynamic standard reduction potentials.[10]

Polarographic behavior of most of the *para* substituted nitrobenzenes was similar to that of nitrobenzene[2] in that the reversible one-electron was followed at more negative potentials by another reduction wave. The latter wave was frequently distorted by a maximum. The second wave of three of the more easily reduced derivatives ($-COCH_3$, $-CHO$ and $-NO_2$) appears to represent a second one-electron reduction.

Although no study of the e.s.r. of *meta* substituted nitrobenzene anion radicals (except for dinitrobenzene[3]) was undertaken at this time, examination of the polarographic behavior of some members of the *meta* series (Table III) seemed desirable. In all of the *meta* compounds examined, a reversible one-electron reduction was found, followed at more negative potentials by further reduction. These data contradict an earlier report[11] that various *meta* substituted nitrobenzenes in acetonitrile undergo a *four*-electron reduction. This mistaken conclusion was based on comparison

(8) For the several cases where replicate determinations of $E^{1/2}$ were made the reproducibility was in fact better than ± 5 mv.

(9) J. Tomes, *Collection Czechoslov. Chem. Commun.*, **9**, 12, 81, 150 (1937).

(10) This statement assumes only that the diffusion coefficients of the oxidized and reduced species are equal and that the half-wave potential is independent of the ionic strength of the solution up to 0.1 M. If the latter assumption is inadequate, then the half-wave potentials represent formal potentials.

(11) L. Holleck, R. Schindler and O. Löhr, *Naturwissenschaften*, **46**, 625 (1959).

TABLE II

POLAROGRAPHIC DATA FOR SUBSTITUTED NITROBENZENES[a]

(0.1 M tetra-n-propylammonium perchlorate supporting electrolyte in acetonitrile at 25.0°)

para Substituents

R	$-E_{1/2}{}^R$	$I_d{}^b$	$E_{1/4} - E_{3/4}{}^c$	σ^n	σ^0	R	$-E_{1/2}{}^R$	$I_d{}^b$	$E_{1/4} - E_{3/4}{}^c$	σ^n	σ^0
-NH₂	1.35₈	3.4	58	-0.172	-0.38	-CONH₂	1.014	3.5	60		
	2.0^d	14					1.6^d	11			
-OCH₃	1.25₀	4.0	60	- .111	- .16	-SCN^e	0.96	4.2	106		
	2.1^d	24					1.3^g	12			
-CH₃	1.20₃	4.0	56	- .129	- .15	-COOCH₃	0.947	4.2	65	0.385	
	2.06	10	112				1.4^d	9			
-H	1.147	4.1	56	0	0	-COCH₃	0.92₅	3.9	60	.502	0.40
	1.9^d	7.5					1.42	4.1	55		
-F	1.12₈	4.3	57	0.056	0.17	-CN	0.87₅	4.0	62	.674	.63
	1.93^d	9.0					1.48^d	9			
-C₆H₅	1.10₃	4.4	63			-CHO	0.86₃	3.7	59	.50	
	1.5^d	12					1.34	3.5	70		
-Cl	1.06₃	4.2	61	.238	.27	-SO₃CH₃	0.847	3.4	58		
	1.8^d	9					1.42	3.8	43		
-Br	1.05₀	4.0	56	.265	.26	-NO₂^h	0.69	5.0	53	.778	.73
	1.49	11					.89	3.6	58		
-I^e	1.05₀	6.2^f	94			-NO^e	.52₅	3.8	60		
	1.8	9					.86	3.5	65		

[a] Half-wave potentials in volts *versus* aqueous saturated calomel electrode. [b] I_d represents the quantity $i_d/m^{2/3}t^{1/6}C$, where m is the drop-weight in mg. sec.$^{-1}$, t is the drop-time in sec., i_d is limiting current in μamp. and C is concentration expressed in millimolar dimensions. [c] Expressed in millivolts; uncertainty of measurement is *ca.* 5 mv. [d] Wave distorted by a maximum. [e] No electron spin resonance observed. [f] Current is not diffusion-controlled. [g] Wave is badly defined and distorted by a maximum. [h] Data from ref. 3. [i] A "primary" σ^n value, ref. 21; unless otherwise indicated, other σ^n values are "secondary" σ^n values.

TABLE III

POLAROGRAPHIC DATA FOR SUBSTITUTED NITROBENZENES[i]

(0.1 M tetra-n-propylammonium perchlorate supporting electrolyte in acetonitrile at 25.0°)

meta-Substituents

R	$-E_{1/2}{}^R$	$I_d{}^b$	$E_{1/4} - E_{3/4}{}^c$	σ^n	σ^0
-NH₂	1.20₈	3.6	58	-0.038^l	-0.14
	1.90	12			
-CH₃	1.18₀	4.0	58	- .069^m	- .07
	1.9^d	11			
-OCH₃	1.147	4.8	61	.076^l	.06
	1.8^g	15			
-COOCH₃	1.044	4.0	58	.321^l	.36
	1.7^d	10			
	2.3	7			
-COCH₃	1.042	3.8	60	.376^m	.34
	1.65^d	10			
	2.06	11			
-CHO	1.016	3.9	59	.381^k	
	1.6^d	6.3			
	1.95	6.0			
CN	0.93₈	4.1	58	.613^l	.62
	1.5^d	11			
-NO₂^h	0.89₈	4.2	61	.710^m	.70
	1.25	3.6	63		
	2.01^g	10			

[i] Footnotes as in Table II. [k] See footnote d, Table IV. [l] Recalculated *meta* σ^n values, see footnote 22. [m] A "primary" σ^n value, ref. 21.

of wave heights with p-benzoquinone. For only one of the seven compounds investigated by both Holleck, *et al.*, and in this study is the agreement of half-wave potentials better than 60 mv. The use of sodium iodide or tetraethylammonium perchlorate as supporting electrolyte[11] by Holleck,

et al., as contrasted to our use of tetra-n-propylammonium perchlorate may be of some significance in comparison of the two sets of data.

Discussion

Polarography.—The polarographic data in Table II can be examined for a possible relation between half-wave potential (for the one-electron reduction) and the nature of the substituent. One such relation is expressed in the Hammett[13] "sigma-rho" equation

$$\log \frac{k}{k^0} = \rho\sigma \qquad (2)$$

where k and k^0 represent rate or equilibrium constants for substituted (*meta* or *para*) and unsubstituted compounds, respectively. ρ is a constant characteristic of the reaction series, and σ is a constant peculiar to the substituent. The correlations of electrochemical data by Brockman and Pearson,[14] Zuman[15] and Fox, *et al.*,[16] are typical of those made using the form

$$\Delta E_{1/2} = E_{1/2}{}^R - E_{1/2}{}^H = \rho\sigma \qquad (3)$$

where $E_{1/2}{}^R$ and $E_{1/2}{}^H$ are the half-wave potentials for the substituted and unsubstituted compounds. Note that in eq. 3, ρ is expressed in volts. The intrinsic difficulties of attempting $E_{1/2} - \sigma$ correlations

(12) Unfortunately the table of half-wave potentials in ref. 11 does not specify to which of the two supporting electrolytes the data refer.

(13) L. P. Hammett, "Physical Organic Chemistry," McGraw–Hill Book Co., Inc., New York, N. Y., 1940, p. 186.

(14) R. W. Brockman and D. E. Pearson, *J. Am. Chem. Soc.*, **74**, 4128 (1952).

(15) P. Zuman, *Chem. Listy*, **47**, 1234 (1953); *Collection Czechoslov. Chem. Commun.*, **19**, 599 (1954).

(16) I. R. Fox, R. W. Taft, Jr., and J. M. Schempf, unpublished results as referred to by R. W. Taft, Jr., and I. C. Lewis, *J. Am. Chem. Soc.*, **81**, 5343 (1959).

when the electrode reactions are irreversible have been stated.[17,18] Unfortunately, many organic reductions and oxidations are irreversible and hence half-wave potentials cannot have thermodynamic significance.

In this context, perusing the data in Table II is somewhat more encouraging. Except for the *para* iodo- and *para* thiocyanato-derivatives all of the electrode reactions for the initial one-electron reduction fulfill to a reasonable extent the previously stated criterion for reversibility. Observation of a free-radical reduction product, furthermore, establishes the course of the reaction beyond question. Since the half-wave potentials for the one-electron reduction are an excellent approximation[10] to the standard reduction potential for the reaction written in eq. 1, they are properly valid data for correlation with σ values.

Examination of a relation between $\Delta E_{1/2}$ and σ may be done graphically merely by linear plotting of one against the other using known σ values.[13,19] Separation of resonance and inductive effects has also been attempted.[16] It seemed most satisfying to us to utilize the recent reëvaluation of the Hammett relation done by van Bekkum, Verkade and Wepster,[20] hereafter referred to as BVW. Inasmuch as the treatment by these workers may not be generally known a recapitulation here seems desirable.

In effect, BVW presented the case for a *continuously variable* scale of *para* σ values in those cases in which the substituent undergoes resonance interaction with the reaction center. Hammett[13] had originally suggested a "duality" of σ constants in certain instances.

BVW designated the normal constant σ values as σ^n and defined a group of ten "primary" σ^n values on the basis of the usual convention that $\rho = 1$ for dissociation of benzoic acids in water at 25°. These primary values,[21] established by precision measurements of acid dissociation constants, were used to calculate new ρ values for the various reaction series in the literature. The recalculated ρ values were obtained with better correlation coefficients and standard deviations than previously attained in the work of Hammett[13] and Jaffe.[19] Using the recalculated ρ values new σ values were then calculated for the other substituents in the various reaction series. Inspection of these data led to the conclusion that there is "little cause to suspect any *meta* substituent of having inconstant σ values".[20,22]

On the other hand, for a given *para* substituent recalculated σ values *extended over rather wide ranges*. BVW then selected those reaction series in which the *para* substituent could not enter into

resonance interaction with the reaction center, and upon finding a relatively narrow range of such σ values, designated the mean σ value as a "secondary σ^n value." Thus the σ^n is intended to represent the substituent constant when no *para* resonance interaction occurs between substituent and reaction center. The extent of change of resonance interaction, $\Delta\Delta F_p$, is given quantitatively[20] as

$$\Delta\Delta F_p = -2.303RT\,\rho\,(\sigma - \sigma^n) \tag{4}$$

where σ is calculated from eq. 3 using the experimental $\Delta E_{1/2}$ and ρ is established by the *meta* substituents.

Essentially the same conclusions regarding inconstancy of *para* sigma values were reached simultaneously by Taft and Lewis.[23] A scale of σ^0 values, which in principle should be identical with the BVW σ^n quantity, was developed[24]; values of σ^0 are included in Tables II and III. The quantitative expression for ΔF_p, eq. 4, was given only by BVW.

Data in Table III for *meta* substituents were used to establish a least-squares correlation between $\Delta E_{1/2}$ and the various sigma values. From the summary of correlations, Table IV, it is clear that there is good correlation between $\Delta E_{1/2}$ values and all three sets of sigma values. The line in Fig. 4 represents the equation

$$\Delta E_{1/2} = 0.376\sigma^n - 0.021 \tag{5}$$

The standard derivation of σ^n as assigned by BVW is shown in Fig. 4 by the length of the horizontal line. Primary σ^n values are plotted as points.

TABLE IV

Least-squares Evaluation of Correlation Equation for *meta* Half-wave Potential and Sigma Values

$$\Delta E_{1/2} = mX - b$$

X	m	b	n^a	r^b	$\pm s^c$
σ^n (BVW)	0.376	0.021	9^d	0.991	0.0137
σ^0 (Taft)	.357	.012	8^e	.997	.0106
σ (Hammett)	.347	.009	9	.991	.0134

^{a} Number of experimental points used. ^{b} Correlation coefficient. ^{c} Standard deviation of a single point, sigma value assumed invariant. ^{d} Recalculated σ^n values for *meta*-aldehyde of 0.464, 0.217, 0.409 and 0.416 are included in Table IX, ref. 20, but a mean value was not included in summary Table III by BVW. Thus we have arbitrarily chosen to employ the older Hammett value[13] of 0.381, which is in fact quite close to the mean of the four values given in the preceding sentence. ^{e} *meta* Aldehyde omitted from correlation.

$\Delta E_{1/2}$-σ^n data for *para* substituents are also plotted in Fig. 4.[25] It is apparent that there are significant deviations of the *para* substituents from the correlation line, eq. 5, at the extremes of the σ^n values. Qualitatively this suggests that there

(17) T. Berzins and P. Delahay. *J. Am. Chem. Soc.*, **75**, 5716 (1953).

(18) W. H. Reinmuth, L. B. Rogers and L. E. I. Hummelstedt, *ibid.*, **81**, 2947 (1959).

(19) H. H. Jaffe. *Chem. Revs.*, **53**, 191 (1953).

(20) H. van Bekkum, P. E. Verkade and B. M. Wepster, *Rev. trav. chim.*, **78**, 815 (1959).

(21) Data for two *para* substituents were included (the remainder being *meta* substituents) and were used in later calculations of ρ only when resonance interaction "could be considered out of the question."

(22) The mean of the recalculated σ values for each *meta* substituent, which was not included in the definitive "primary" group, however, was generally slightly different from the usual value.[13,19]

(23) R. W. Taft, Jr. and I. C. Lewis. *J. Am. Chem. Soc.*, **81**, 5343 (1959).

(24) R. W. Taft, Jr., S. Ehrenson, I. C. Lewis and R. E. Glick, *ibid.*, **81**, 5353 (1959); R. W. Taft, Jr., *J. Phys. Chem.*, **64**, 1805 (1960).

(25) σ^n data are either "primary" (-NO$_2$ and -COCH$_3$) or "secondary" σ^n values from ref. 20. Standard deviations of the latter are shown by the length of the horizontal lines in Fig. 10. The "secondary" σ^n value for fluorine is given in Table IV, ref. 20, with some reservations as to its reliability. The value for -CHO, although not included in the summary Table IV, ref. 20, is estimated later in the paper (p. 838) to have a value of 0.50. For this substituent we have arbitrarily assigned a deviation of ± 0.05 (dashed line in Fig. 10). σ^n data are not available for -C$_6$H$_5$ or -CONH$_2$.

is a loss in *para* resonance interaction (the reduction reaction is "inhibited") when *p*-nitroaniline is reduced. Similarly, the gain in *para* resonance interaction in the reduction of *p*-dinitrobenzene facilitates the reduction reaction.

Evaluation of $\Delta\Delta F_p$ can be accomplished by using eq. 5 to calculate an apparent sigma value for a given $\Delta E_{1/2}$. This apparent sigma value is identified with σ of eq. 4. The values for the two *para* substituents. -NH$_2$ and -NO$_2$, are -0.505 and 1.271, respectively. These quantities, with the σ^n values, -0.172 and 0.778, respectively, permit evaluation of the quantity $(\sigma - \sigma^n)$ in eq. 4. The ρ value is $0.376(F/2.303RT) = 6.35$ at 25°C. Thus the $\Delta\Delta F_p{}^{26}$ values for -NH$_2$ and -NO$_2$ are $+ 2.9$ and $- 4.5$ kcal. mole^{-1}, respectively.

Addition of one electron to *p*-nitroaniline apparently inhibits (perhaps only partially) resonance represented by the limiting structure
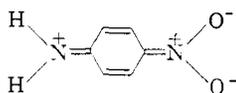
BVW estimated $\Delta\Delta F_p$ for the equilibrium

$$\underset{NO_2}{\underset{\big|}{\overset{NH_3^-}{\overset{\big|}{\bigcirc}}}} \rightleftharpoons \underset{NO_2}{\underset{\big|}{\overset{NH_2}{\overset{\big|}{\bigcirc}}}} - H^- \qquad (7)$$
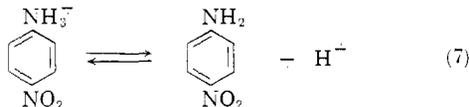
as -1.7 kcal. mole^{-1}. They suggested that since there is no *para* resonance interaction in the anilinium ion, the *para* interaction energy of *p*-nitroaniline is 1.7 kcal. mole^{-1}, which compared with values of 1.7 and 2.0 kcal. mole^{-1} estimated by other means.[27]

Examination of Table II shows that there is a gross difference between the σ^n and σ^0 values -0.172 and -0.38, respectively, for the *para*-NH$_2$ substituent. Taft[28] has suggested that this difference arises because the BVW value is based on the ionization of phenols, whereas the σ^0 is evaluated from reactivities such as the ionization of ArCH$_2$COOH, and thus leveling or "saturation" effects render the BVW value inappropriate. If $\Delta\Delta F_p$ is evaluated by using σ^0 values for the *meta* regression line (Table IV), values of $+ 1.45$ and $- 4.8$ kcal./mole are obtained for *para* -NH$_2$ and -NO$_2$, respectively.

The fact that the $\Delta\Delta F_p$ value of -1.45 kcal./mole for *p*-nitroaniline as evaluated from σ^0 is smaller than the apparent upper limit of 2.0 kcal./mole (rather than larger as is the case for σ^n evaluation) suggests that the Taft σ^0 value for -NH$_2$ is in fact more reliable than σ^n.

It should be pointed out that the electrochemical data, where $\rho = 6$, provide a more strenuous test of eq. 4 than do chemical cases where ρ is ordinarily 2–3.

The large increase in resonance interaction, ~ -4.5 kcal. mole^{-1}, in the reduction of *p*-dinitro-

(26) Positive values of $\Delta\Delta F_p$ signify a decrease in *para* resonance interaction and negative values an increase.

(27) J. Burgers, M. A. Hoefnagel, P. E. Verkade, H. Visser and B. M. Wepster, *Rec. trav. chim.*, **77**, 491, 509 (1958).

(28) R. W. Taft, Jr., private communication.
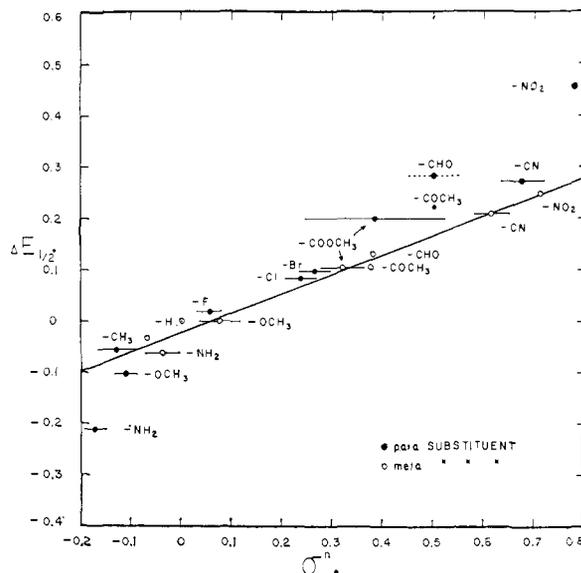
Fig. 4.—$\Delta E_{1/2}$ (volts) *vs.* σ^a; *meta* substituents indicated by open circle, *para* substituents by solid circle.

benzene can be accounted for by the resonance in the anion represented by the limiting structure
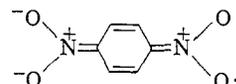
The $\Delta\Delta F_p$ values of most of the other *para* substituents are so small as to have little significance, particularly in view of the magnitude of the standard deviations of σ^n.

Comparison between Values of a_N **and** $E_{1/2}$.—In Fig. 5 the measured values of a_N and $E_{1/2}$ are plotted for the *para* substituted nitrobenzene anions which were measured. The square and triangle points represent the *meta* and *ortho* dinitrobenzene anions, respectively, and are included only for comparison.

We observe that the lower the reduction potential of the parent molecule is, the smaller is the nitrogen coupling constant. A similar comparison of a_N with σ^n or σ^0 values reveals that electron repelling substituents cause an increase in a_N and electron attracting ones cause a decrease. This behavior is reasonable if it is assumed that the effect of the substituent group on the over-all electron distribution is qualitatively reflected in the distribution of the unpaired electron. The nitro group becomes more or less deficient of unpaired electron density as the *para* substituent is made more or less electron attracting. It is also reasonable that as an electrophilic group is substituted into a nitrobenzene molecule, the ease of reduction should increase. The qualitative behavior of a_N vs. $E_{1/2}$ observed in Fig. 5 is consequently seen to be plausible.

Attempts have been made to obtain a simple expression to describe the behavior of a_N vs. $E_{1/2}$. Because of the scattering of the data, however, it is unlikely that any *simple* expression exists between these two quantities. In this connection it should be noted that the estimated experimental
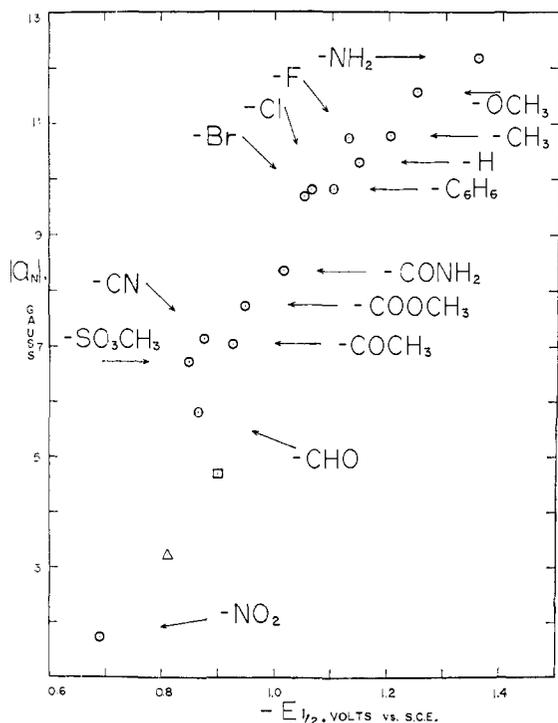
Fig. 5.—Absolute value of nitro group nitrogen coupling constant, $|a_N|$, in gauss $vs.$ half-wave potential (volts $vs.$ aqueous saturated calomel electrode). Square and triangle points represent $meta$ and $ortho$ dinitrobenzene anions, respectively.

accuracy of a point is represented by the size of the circle in Fig. 5. A least-squares fit of the data to a quadratic expression of the form

$$a_N{}^2 = mE_{1/2} + b \qquad (8)$$

yields $m = -226.4$, $b = -151.8$, with a standard deviation, $s = \pm 6.7$ gauss^2, and a correlation coefficient, $r = 0.985$. $E_{1/2}$ is measured $vs.$ the aqueous s.c.e. Attempts to fit the data to a linear relationship yielded a poorer correlation. We do not suggest that there is any theoretical justification to the form of eq. 8; it is merely introduced because it is the simplest form which correlates the data reasonably well.

Ring Proton Coupling Constants.—The theory of isotropic proton hyperfine interactions of aromatic radicals is well understood,[29–31] and recent work has introduced no serious changes.[32,33] The semi-empirical equation that relates the proton coupling constant, a_H to ρ_c, the unpaired spin density on the aromatic carbon atom adjacent to the proton, is

$$a_H = Q\rho_c \doteq -22.5 \, \rho_c \text{ gauss} \qquad (9)$$

The sign of ρ_c may be either positive or negative. It is fairly certain[2] that in the unsubstituted nitrobenzene negative ion, ρ_c is positive for $ortho$ and $para$ carbon atoms and negative for $meta$ carbon atoms.

(29) H. M. McConnell, $J.$ $Chem.$ $Phys.$, **24**, 764 (1956).
(30) R. Bersohn, $ibid.$, **24**, 1066 (1956).
(31) S. I. Weissman, $ibid.$, **25**, 890 (1956).
(32) H. M. McConnell and D. B. Chestnut, $ibid.$, **28**, 107 (1958).
(33) A. D. McLachlan, H. H. Dearman and R. Lefebvre, $ibid.$, **33**, 65 (1960).
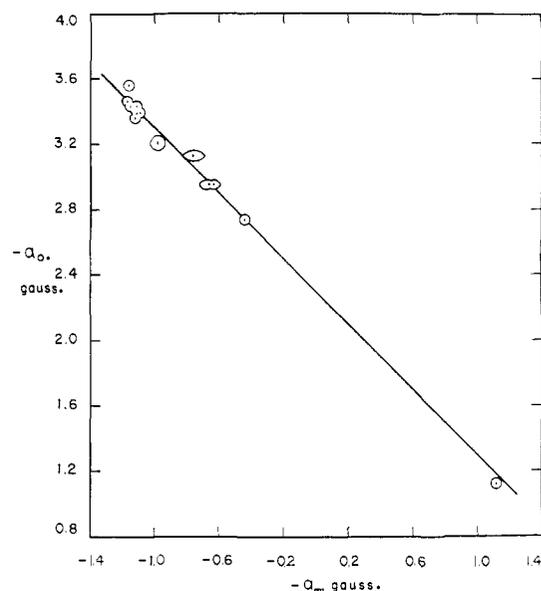
Fig. 6.—Coupling constant of the $ortho$ protons, a_o, $vs.$ that of the $meta$ protons, a_m, for various $para$ substituted nitrobenzenes.

A recent study of isotropic proton magnetic resonance shifts in solid aromatic free radicals[34] has verified the existence of positive and negative spin densities in odd alternant radicals.

In our study, it was possible to assign coupling constants of the ring protons ($ortho$ and $meta$ to the nitro group) for each ion investigated except those of p-nitrodiphenyl and methyl p-nitrobenzoate. For each of the ions studied the larger coupling constant was attributed to the $ortho$ protons and the smaller to the $meta$ protons, by analogy with the unsubstituted nitrobenzene anion.[2] In the p-dinitrobenzene, both positions are equivalent, and the spin density on each of the proton-containing ring carbons must be positive. Fig. 6 shows a plot of the coupling constants assumed for the $ortho$ protons plotted against those of the $meta$ protons. The case of p-nitrobenzaldehyde, in which two $ortho$ proton coupling constants were observed, was introduced into the plot by using the average of the two observed values.

The electron spin density on the $meta$ carbon atoms has been assumed negative in all but the p-dinitrobenzene anion. The line is a plot of the relation

$$a_o + a_m = -2.30 \text{ gauss} \qquad (10)$$

The average deviation of the sum (10) from -2.30 is ± 0.04 gauss, which compares with the average experimental error. Equation 10, when compared with (9), gives the result that the total electron spin magnetization present in the proton-containing ring π-orbitals of the $para$ substituted nitrobenzenes is independent of the substituent. The effect of the substituent on the ring is to cause a redistribution of the magnetization between the $ortho$ and $meta$ positions. From (9) and (10) we find that the total magnetization at these four ring

(34) T. H. Brown, D. H. Anderson and H. S. Gutowsky, $ibid.$, **33**, 720 (1960).

positions is about 0.2 I_e, where I_e is the magnetization of a single π-electron.

It should be stated again that the assignments of the observed coupling constants to the positions *ortho* and *meta* to the nitro group were made by analogy with the known assignment in nitrobenzene negative ion. No isotopic substitution was carried out in the *para* substituted nitro compounds. In each of the compounds represented by points in Fig. 6, however, except the *para*–NH₂, –CONH₂ and –CHO substituted nitrobenzenes, a hyperfine interaction with two pairs of equivalent protons occurred which unambiguously had to be assigned to the four ring protons equivalent in pairs. It could, for instance, be argued that the interaction of 3.36 gauss with two equivalent spins of $^1/_2$ in p-nitroaniline could be assigned to the amine protons, which would lead to the result that all four ring positions interact equally with a coupling constant of 1.12 gauss. We would, however, be led to reject the latter assignment by comparison with the unambiguously assigned ring proton coupling constants of the electronically similar ion, p-methoxynitrobenzene (Table I). The argument for the assignment of the ring proton coupling constants in the –CONH₂ and –CHO compounds are not as strong. The assignment that we have made for these compounds, though, is the only one which brings them into agreement with eq. 10.

A qualitative argument can be made which demonstrates that the data of Fig. 6 are indeed reasonable.

It will be noticed from Fig. 6 that a great number of compounds group in the vicinity of the nitrobenzene negative ion with $a_o \doteq -3.4$, $a_m \doteq +1.1$. These are the *para* substituted compounds in which the *para* substituent cannot undergo extensive resonance interaction with the nitro group *in the negative ion*. The compounds in which a_o and a_m deviate significantly from the values in nitrobenzene negative ion are those in which the *para* substituent may undergo resonance interaction with the nitro group.

Consider first the nitrobenzene negative ion itself. If we go through the process of starring alternant atoms in the π-system[35] (we assume that the nitro group is coplanar with the ring), starring the nitrogen atom first, we get the following diagram
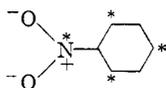
If Ψ is the ground state variational valence bond wave function, then in the approximation that no "long-bonds" are included, the result is obtained that the unpaired spin density in all starred atomic orbitals is positive and is negative in all the unstarred orbitals.[36,37]

Now consider *para*-nitrobenzaldehyde anion as a representative of the group of substituted nitrobenzene anions in which the *para* substituent can

(35) C. A. Coulson and G. S. Rushbrooke, *Proc. Cambridge Phil. Soc.*, **36**, 193 (1940).

(36) P. Brovetto and S. Ferroni, *Nuovo Cimento*, **5**, 142 (1957).

(37) A. D. McLachlan, *Mol. Phys.*, **2**, 223 (1959).

undergo resonance interaction with the nitro group. In this case there is an alternate starring procedure for the negative ion which stars the atoms which were unstarred in the unsubstituted nitrobenzene anion. The two alternate starring procedures are
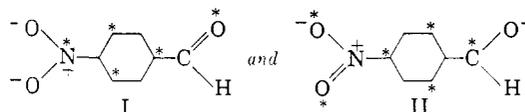
We assume that the aldehyde group is coplanar with the ring. (Evidence for this assumption is presented in the following section.) The ground state variational valence bond wave function must be composed of bond eigenfunctions of both type I and type II. The ground state wave function may then be written as the sum of two parts

$$\Psi = a\psi_I + b\psi_{II}$$

where ψ_I and ψ_{II} are normalized linear combinations of bond eigenfunctions of type I and type II, respectively. If we further assume that they are orthogonal, $|a|^2 + |b|^2 = 1$. It is clear, then, that as $|b|^2$ increases there will be an increase in the contribution of ψ_{II} to Ψ, and negative spin density will be added to the starred orbitals of I and positive spin density to the unstarred orbitals of I. a_N will thus be expected to decrease as $|b|^2$ increases, and a_o and a_m will be expected to approach each other. In the limit of the p-dinitrobenzene negative ion $|a|^2 = |b|^2$ because of the symmetry, and a_o must be equal to a_m. This qualitative behavior is exactly what is observed when the *para* substituent may enter into resonance interaction with the nitro group in the anion.

Hindered Rotation.—If an anion, such as that of p-nitrobenzaldehyde, is constrained to a planar configuration, it has no plane of symmetry except for the molecular plane. In the most general case, the hyperfine coupling constants of the four ring protons will all be different. Consider a pair of protons, H′ and H″, that would be equivalent if the anion had a longitudinal plane of symmetry, for instance the two protons *ortho* to the NO₂ group. Let the hyperfine coupling constants of these protons be a' and a'' (with the same sign for convenience). These values depend upon the electronic wave function of the unpaired electron in the vicinity of each nucleus. If the aldehyde group is allowed to flip by 180°, the effect on the electronic wave function is to interchange the environments of H′ and H″. The switching of the electronic wave function can be treated formally in a manner identical to the exchange of protons H′ and H″, or for the purposes of the analysis of hyperfine structure, an exchange of their spins I′ and I″. If ν_e is the frequency of electron switching, the spin-Hamiltonian for the system, neglecting the Zeeman interaction for brevity, may be written

$$\mathcal{K} = a'\mathbf{s} \cdot \mathbf{I}' + a''\mathbf{s} \cdot \mathbf{I}'' + h\nu_e \mathbf{I}' \cdot \mathbf{I}'' \qquad (11)$$

If $\nu_e = 0$, or is small enough to be ignored, the selection rules for allowed e.s.r. transitions ($\Delta m_s = \pm 1$, $\Delta m_{I'} = \Delta m_{I''} = 0$) lead to four equally intense hyperfine components at energies $\epsilon = \pm \dfrac{(a' - a'')}{2}$, $\pm \dfrac{(a' + a'')}{2}$. For the case that

$h\nu_e$ compares with or exceeds $|a' - a''|$, it is convenient to rewrite (11), recognizing that $I' \cdot I'' = \frac{1}{2}[(I' + I'')^2 - I'^2 - I''^2] = \frac{1}{2}[I(I + 1) - 3/2]$. The last equality follows, since $I' = I'' = \frac{1}{2}$ and we define $I = I' + I''$. The rewritten eq. 11 is

$$\mathcal{K} = \frac{1}{2}(a' + a'')\mathbf{s} \cdot \mathbf{I} + \frac{1}{2}h\nu_e\{I(I + 1) - 3/2\} + \frac{1}{2}(a' - a'')\,\mathbf{s} \cdot (\mathbf{I}' - \mathbf{I}'') \quad (12)$$

Now if $h\nu_e \gg |a' - a''|$ we can neglect the last term of eq. 12 for all electron resonance transitions. (Note that the last term is always zero if $I' = I''$.) Equation 12 thus leads to the following hyperfine energies for the allowed electron resonance transitions

$$\epsilon = 0, 0, \pm \frac{1}{2}(a' + a'')$$

The appearance of the hyperfine structure under the condition $h\nu_e \gg |a' - a''|$ is the same as that of two equivalent protons each with a coupling constant $\frac{1}{2}(a' + a'')$. The effect of increasing $|a' - a''|$ is to cause a mixing of the singlet and triplet components of the state with $m_I = 0$, which breaks down some of the selection rules used in the above treatment. The transition between the two extreme types of hyperfine structure would occur when $|a' - a''| \doteq h\nu_e$.

Observation of three different proton coupling constants, each attributable to the interaction of the electron with a spin of $\frac{1}{2}$ nucleus in p-nitrobenzaldehyde negative ion, is a strong argument for the presence of hindered rotation of the aldehyde group about the carbon-carbon bond. The two largest of these coupling constants, 3.10 gauss and 2.37 gauss, are assigned to the two protons *ortho* to the nitro group and the remaining coupling constant of 1.23 gauss to the aldehyde proton. An upper limit of $(2\beta/h)\Delta H$ can be set on the rotational frequency, ν_e, of the aldehyde group, where ΔH is the separation in gauss of the two *ortho* proton coupling constants. From this we find

$$\nu_e < 2.8 \times 10^6 \text{ c.p.s.}$$

No other clear case of hindered rotation was observed, although the lack of resolution in the spectrum of methyl p-nitrobenzoate anion suggests that a rotational frequency of the order of several megacycles per second may be responsible.

The Fluorine Coupling Constant.—The large hyperfine interaction of 8.41 gauss with a single nucleus of $I = \frac{1}{2}$ must be attributed to the F^{19} nuclear moment of p-fluoronitrobenzene negative ion. If the N^{14} and proton coupling constants of this ion are compared with those of the nitrobenzene anion, it is found that the unpaired electron distribution is not greatly perturbed by the fluorine substitution. Direct comparison of the fluorine coupling constant of p-fluoronitrobenzene with the *para* proton coupling constant of nitrobenzene gives a value of $a_F/a_H = 2.12$. This result differs by only about 20% from the value of 1.75 reported by Anderson, Frank and Gutowsky[38] for fluoro-

semiquinones. Since p-fluoronitrobenzene probably represents a rather extreme example of an aromatic fluorine hyperfine interaction, this result lends support to the suggestion[38] of an expression analogous to eq. 9 to describe aromatic F^{19} hyperfine interaction. On the basis of our result, a Q_F value of about -47.5 is suggested.

Conclusion.—We have prepared 14 *para* substituted nitrobenzene negative ions by controlled potential electrolysis, studied the electron spin resonance of the ions and also obtained polarographic data. Correlation of the reversible polarographic half-wave potentials with σ^n values of van Bekkum, Verkade and Wepster[20] as well as with σ_0 values of Taft and Lewis[23] was made for the 14 *para* substituted nitrobenzenes as well as for 8 *meta* substituted ones. Deviations of the half-wave potentials of p-dinitrobenzene and p-nitroaniline are interpreted as arising from resonance effects and resonance energies are estimated.

From a comparison of the nitrogen coupling constant of the nitro group with the polarographic half-wave potential of the *para* substituted nitrobenzenes, a decrease in the nitrogen coupling constant was found to be concomitant with an increase in the ease of reducing the parent molecule.

The *ortho* and *meta* (to the nitro group) proton coupling constants of the series of *para* substituted nitrobenzenes were found to be correlated by the relationship

$$a_o + a_m = -2.30 \text{ gauss}$$

when certain assumptions regarding the signs and assignment of the coupling constants were made. This relationship implies that the total spin-magnetization in these π-orbitals of *para* substituted nitrobenzenes is independent of the substituent.

Evidence of hindered rotation of the aldehyde group of p-nitrobenzaldehyde anion about the carbon-carbon bond is provided by an analysis of the hyperfine pattern of the resonance. An upper limit to the rotation frequency is 2.8×10^6 c.p.s. Such hindered rotation is also suggested by the lack of resolution in the ESR spectrum of methyl p-nitrobenzoate anion.

Measurement of the F^{19} coupling constant of p-fluoronitrobenzene anion supports the suggestion[38] of a linear relationship between a_F and ρ_c analogous to that describing proton hyperfine interaction.

The g-value reported for the nitrobenzene negative ion in ref. 2 is incorrect. The correct value is $g = 2.0044 \pm 0.0001$.

(38) D. H. Anderson. P. J. Frank and H. S. Gutowsky, *J. Chem. Phys.*, **32**, 196 (1960).