# Study of Steric Effects by Electron Spin Resonance Spectroscopy and Polarography. Substituted Nitrobenzenes and Nitroanilines<sup>1</sup>

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Steric effects in aromatic nitro anion radicals have been studied by polarography and electron spin resonance spectroscopy in acetonitrile solution. In a series of methyl-substituted nitrobenzene compounds the halfwave potential was found to be displaced to more negative potentials as methyl groups were inserted in posiwave potential was found to be displaced to indic negative potentials as including poups were inserted in pos-tions or ho and di-ortho to the nitro group. A larger o-substituent such as the t-butyl group produced an even larger shift in half-wave potential. Although there is no indication from polarographic data of a steric effect on the amino group in substituted p-nitroanilines, evidence of steric perturbations is observed in a series of N,N-dimethyl-p-nitroanilines. Electron spin resonance studies show that as the nitro groups in mononitro and symmetrically substituted dinitro aromatic anion radicals are twisted out of the plane of the benzeering the nitroaniline superfine constants increase significantly while the ring hydrogen coupling constants the nitrogen hyperfine coupling constants increase significantly, while the ring hydrogen coupling constants decrease. In the case of the anion radical of 2,6-dimethyl-1,4-dinitrobenzene, where the 1-nitro group is hindered, a nitrogen coupling constant of 5.7 G. is observed for the 4-nitro group; e.s.r. results for the anion radical of 2.t-butyl-N,N-dimethyl-4-nitroaniline establish that in contrast to the amino group, the dimethylamino group is subject to steric perturbation. Results of the electron spin resonance study are discussed in terms of a charge localization model; illustrative calculations are presented.

#### Introduction

The suggestion of Birtles and Hampson,<sup>2</sup> in 1937, that resonance was subject to steric restriction has had abundant experimental verification in the intervening quarter of a century. The early investigators were concerned primarily with dipole moment measurements of various hindered molecules including substituted nitrobenzenes. Infrared, ultraviolet, and Raman spectroscopy and X-ray crystallography have all been used to advantage.<sup>3</sup> Francel<sup>4</sup> used polarized infrared radiation to establish the twisting of the nitro group from the plane of the ring in several o-substituted nitrobenzenes. Just recently nuclear magnetic resonance studies of carbon-135 and oxygen-176 in substituted nitrobenzenes have been carried out, thus providing an intimate knowledge of  $\pi$ -electron densities in these molecules.

All of the above experimental measurements have been concerned with the properties of various diamagnetic molecules in ground and excited electronic states. Where steric restrictions are pronounced, a significant perturbation in the physical parameter has been observed.

The principle that maximum mesomeric interaction between  $\pi$ -electron systems requires coplanarity of the systems is now fully accepted. It was in this context that the possibility of studying the steric effects on mesomerism in certain *paramagnetic* species in solution was considered. The possibility of 'mapping'' odd-electron spin densities in the free radical species by study of their electron spin resonance (e.s.r.) spectra was particularly attractive.

The early studies of steric hindrance were done by introducing blocking groups into the nitrobenzene molecule. We have chosen the same strategy for an exploration of the e.s.r. of various nitrobenzene and aminonitrobenzene anion radicals for evidences of steric effects on the isotropic hyperfine coupling constants. Inasmuch as the free radicals were generated electrochemically<sup>7,8</sup> in acetonitrile solution by the re-

(1) Presented in part at the Symposium on Electrode Processes, Division of Physical Chemistry, 142nd National Meeting of the American Chemical

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(2) R. H. Birtles and G. C. Hampson, J. Chem. Soc., 10 (1937).
(3) Several of these tools are reviewed by B. M. Wepster in "Progress in Stereochemistry," Vol. 2, ed. by W. Klyne and P. B. D. de la Mare, Butterworths Scientific Publications, London, 1950, pp. 99.

(4) R. J. Francel, J. Am. Chem. Soc., 74, 1265 (1952)

(5) P. C. Lauterbur, J. Chem. Phys., 38, 1432 (1963).

(6) P. Diehl, Abstracts of Papers, 1962 Summer Symposium on High Resolution Nuclear Magnetic Resonance Spectroscopy, Boulder, Colo., July 2-4, 1962, p. 7.

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

(8) A. H. Maki and D. H. Geske, ibid., 83, 1852 (1961).

### action

### $ArNO_2 + e^- \longrightarrow ArNO_2^-$

it was convenient to obtain polarographic data at the same time. Thus two sets of data of a singularly different nature became available-isotropic hyperfine coupling constants which are peculiar to the particular anion radical, and polarographic half-wave potentials which are a property of both the neutral molecule and the anion radical. Some of the e.s.r. results were presented in a previous communication.9

#### Experimental

**Reagents.**—Acetonitrile used for solvent was purified by minor modification of the procedure given by Coetzee, *et al.*<sup>10</sup> The water content was approximately 1 nn*M* as determined by Karl Fischer titration. N,N-Dimethylformamide and dimethyl sulfoxide were purified by distillation of reagent grade material under reduced pressure. Tetra-*n*-propylanimonium perchlorate for use as supporting electrolyte was prepared as previously de-scribed.<sup>7</sup> Unless otherwise stated, nitro compounds were ob-tained from Distillation Products Industries, Aldrich Chemical Co. or K and K I aboratories and were recrustallized (or redis-Co., or K and K Laboratories and were recrystallized (or redistilled) until melting points (boiling points) agreed with literature values. 2,3,5,6-Tetramethylnitrobenzene (nitrodurene) was prepared by the method of Smith and Taylor.<sup>11</sup> Preparation of 2,5dinitro-m-xylene was done by the method of Blanksma.<sup>12</sup> This same compound was labeled with N<sup>16</sup> in the 5-position by the procedure described by Bambenek.<sup>13</sup> Nitration of 1,2,3,4-tetramethylbenzene gave the corresponding dinitro compound (di-nitroprehnitene) which had a melting point of 175–177° com-pared with the literature value<sup>14</sup> of 176°. All *t*-butyl compounds were kindly furnished by Professor B. M. Wepster.

3,6-Dinitro-o-xylene was prepared by oxidation of 2,3-di-

s,6-Dinito-o-xylene was prepared by oxidation of 2,3-di-methyl-4-nitroaniline using the peroxytrifluoroacetic acid method.<sup>15</sup> The observed melting point of 86-88° compared with the value of 89-90° reported by Crossley and Wren.<sup>16</sup> 2,6-Di-*t*-butyl-1,4-dinitrobenzene does not appear to have been described in the chemical literature. Upon oxidation of 2,6-di-*t*-butyl-4-nitroaniline with peroxytrifluoroacetic acid<sup>15</sup> we ob-tained a low yield of crystalline solid, m.p. 80-86°, which we have assumed to be 2.6-di-*t*-butyl-1,4-dinitrobenzene. The infrared assumed to be 2,6-di-t-butyl-1,4-dinitrobenzene. The infrared spectrum of the product was consistent with the assignment. Unfortunately, the quantity of starting material available was so limited that further characterization of the product was not possible.

In several cases it was necessary to examine the e.s.r. of deuterated nitroaniline species in order to assign the coupling constants. The preparative procedure was as follows. Concentrated  $D_2SO_4$  was prepared by repeated evaporations of  $H_2SO_4$  with  $D_2O$  followed by vacuum distillation; 10 mg. of the amine

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(11) L. I. Smith and F. I. Taylor, J. Am. Chem. Soc., 57, 2370, 2468 (1935)

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- (13) M. Bambenek, ibid., 82, 97 (1963).
- (14) K. Auwers and A. Kockritz, Ann., 352, 288 (1907).
- (15) W. D. Emmons, J. Am. Chem. Soc., 76, 3470 (1954) (16) A. W. Crossley and G. H. Wren, J. Chem. Soc., 99, 2341 (1911).

<sup>(9)</sup> D. H. Geske and I. L. Ragle, ibid. 83, 3532 (1961).

was dissolved in several nil. of deuteriosulfuric acid in deuterium oxide. The solution was neutralized with sodium carbonate and the resulting precipitate was filtered and washed carefully with  $D_2O$  and finally dried *in vacuo* over phosphorus pentoxide.

The amine protons in *p*-nitroaniline, 3,5-di-*t*-butyl-*p*-nitroaniline, and 2,5-di-*t*-butyl-*p*-nitroaniline were replaced by this procedure. In all three cases the infrared spectra of the deuterated compound showed new N–D bands at about 4  $\mu$  and a diminution or absence of the N–H stretching bands near 3  $\mu$ .

Synthesis of N,N-dimethylhexadeuterio-4-nitroaniline,  $O_2N-C_6H_4N(CD_3)_2$ , was done by the method of Campbell<sup>17</sup> using  $HN(CD_3)_4$  from Merck Sharp and Dohme.

Polarographic Measurements .--- Polarographic data were obtained at  $25.0^\circ$  using a conventional two-electrode polarograph fabricated from Philbrick operational amplifiers according to a design by Dr. B. Miller, Harvard University. A three-electrode polarograph was also used in certain instances. All polarographic ineasurements were made in acetonitrile solutions 0.1 M in tetran-propylammonium perchlorate. Maximum current values were used in calculating diffusion current constants. Where multiple waves occurred the individual diffusion current constants are tabulated. The observed reproducibility of half-wave potential measurements was  $\pm 5 \text{ mv}$ .<sup>18</sup> All half-wave potentials were measured vs. an aqueous saturated caloniel electrode. Coetzee and Padmanabhan<sup>19</sup> have recently found that when an aqueous saturated caloinel reference electrode with an agar salt bridge is used in acetonitrile solution the potential drifts rather rapidly in the first several minutes but changes very little after 10 to 15 min. The neasurements reported in this and preceding papers<sup>7,8</sup> were made under conditions of "long" immersion. Thus transformation of these potential measurements to the Pleskov<sup>20</sup> silver, silver nitrate scale should be done by the addition of -0.32 v. rather than -0.29 v.

Generation of Free Radicals.—Sample solutions from 0.1 to 1 m M in nitro compound and 0.1 M in tetra-n-propylammonium perchlorate as supporting electrolyte were electrolyzed using the *intra muros* procedure.<sup>7</sup> In several instances it was desirable to carry out a macro controlled potential electrolysis and recirculate the solution through the microwave resonance cavity. The design of Harrinan and Maki<sup>21</sup> proved particularly convenient for this purpose. The potential for electrolysis was ordinarily chosen to be 0.2 v. more negative than the half-wave potential.

It should be noted that a total electrolysis may be desirable from the standpoint of minimizing exchange broadening in instances where the broadening may be particularly prominent.<sup>22</sup> On the other hand, for reasonably stable free radicals the *intra muros* electrolysis<sup>7</sup> after long times is essentially a total electrolysis particularly close to the electrode surface which in turn is ordinarily in the most sensitive region of the microwave cavity. The assumption of diffusion controlled mass transfer is reasonably adequate for the cells we have used. It has been our experience that spectral line widths are frequently narrower after the addition of small amounts of water to the acetonitrile. Results presented in this paper were obtained with ''anhydrous'' acetonitrile.

Electron Spin Resonance Spectrometer.—The X-band spectrometer employed in this study employed a cylindrical cavity operating in the  $TE_{011}$  mode. The field modulation frequency was 100 kc. With the electrolysis cell placed in the cavity in usual operating fashion the loaded Q was  $3.2 \times 10^3$ . The klystron oscillator (Varian V-58) was immersed in a 3-qt. oil bath to minimize frequency drift. The automatic frequency control system locked the klystron frequency to that of the sample cavity by means of small amplitude 6-kc. modulation. A reference arm permitted appropriate crystal bias currents independent of cavity arm balance. Matched crystals were used in a balanced mixer configuration.

The body of the 100-kc. resonance cavity was manufactured from Hysol 6000 EP plastic (Hysol Corporation, Olean, N. V.) according to the design of Maki.<sup>23</sup> A layer of silver was chemically deposited on the plastic to provide a conducting surface for electrodeposition of copper. A 6-in. Varian 4007 magnet and Varian V 2100 A power supply were employed.

Magnet field calibration markers were placed directly on the recorded spectrum by noting the occurrence of proton resonance at a particular oscillator frequency which was then measured with a Hewlett-Packard frequency counter, Model 524D.

(17) T. W. Campbell, J. Am. Chem. Soc., 71, 740 (1949).

(18) Consult ref. 7 for further details of polarographic measurements.
(19) J. F. Coetzee and G. R. Padmanabhan, J. Phys. Chem., 66, 1709 (1962).

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(23) A. H. Maki, personal communication.

### Results

**Polarographic Data**.—Half-wave potentials and diffusion current constants are given in Tables I and II. The shape of polarographic waves is characterized by measurement of the quantity  $E_{3/4} - E_{1/4}$ ; *i.e.*, the difference in potential at one-fourth and three-fourths the limiting current value. The quantity is -56 mv. for a one-electron "reversible" electrode process at  $25^{\circ}$ .

Electron Spin Resonance Data for Substituted Nitrobenzene Anion Radicals.—Coupling constants for the anion radicals of twenty-three substituted nitro- and dinitrobenzenes are given in Table I.

It should be noted from the outset that the assignment of coupling constants to particular molecular positions in the anion radicals is based on the known assignment for nitrobenzene anion radical. Ward<sup>24</sup> and Geske and Maki<sup>7</sup> have examined the electron spin resonance of the 3-deuterionitrobenzene anion radical and have clearly established that the smallest of the hydrogen coupling constants, 1.09 G.,<sup>25</sup> must be assigned to the *m*-protons. Thus, the absolute assignment of coupling constants for nitrobenzene anion radical is that given in Table I. The assignment of coupling constants for twelve *p*-substituted nitrobenzene anions<sup>8</sup> was also based on the fundamental assignment of nitrobenzene anion radical.

Assignment of methyl proton coupling constants in the present series of radicals was facilitated by the fact that substitution of a methyl group for a hydrogen on an aromatic nucleus ordinarily results in three equivalent methyl proton coupling constants which have the same value as that for the displaced hydrogen. This point is well illustrated by the observed<sup>8</sup> equality of the *p*-proton coupling constant in the nitrobenzene anion radical and of the three equivalent methyl proton coupling constants in the p-nitrotoluene anion radical. This result is in substantial agreement with the pre-dicted theoretical relationship.<sup>26</sup> Methyl groups *ortho* to a nitro group are exceptions to this statement. The methyl group does exert a steric effect on the nitro group which results in a smaller hydrogen coupling constant. For the anions of compounds 4, 5, 6, 7, and 8 in Table I where methyl substitution is asymmetric we have resolved no difference in coupling constants between a methyl and ring hydrogen in the same symmetry position.

**Nitrobenzene Anion Radicals**.—It is convenient to discuss the spectra in several broad groups. The radical anions of compounds 2, 3, 4, 5, 6, 7, and 8 in Table I are related by the fact that none of the various methyl substitutions is diortho to the nitro group. Since the nitrogen coupling constant is not significantly larger than in nitrobenzene anion, the e.s.r. spectra of these compounds are similar in appearance to that of nitrobenzene anion except for further splittings due to methyl proton interactions. The spectrum of 3,4dimethylnitrobenzene anion, Fig. 1, is typical of this group of radicals. Line widths<sup>27</sup> were approximately 0.2 G.

Electron spin resonance spectra of anion radicals of compounds 9, 10, and 11, Table I, which all have dio-methyl substitution, are characterized by large nitrogen coupling constants. Consequently, proton multiplet structure does not overlap between the three major nitrogen groups. A preliminary assignment for proton splittings in the 2,6-dimethylnitrobenzene anion was based on the relationship  $a_o = a_m = 0.87$  G.

(24) R. L. Ward, J. Chem. Phys., 30, 852 (1959).

 $(2\delta)$  We employ the abbreviation G. for gauss throughout this paper. Stated values of coupling constants are absolute values throughout.

(26) A. D. McLachlan, Mol. Phys., 1, 233 (1958).
(27) Line widths are given as the full width between derivative extrema.



Fig. 1.—Derivative e.s.r. spectrum of 3,4-dimethylnitrobenzene anion radical from electrolysis of 0.84 mM solution in acetonitrile. Calculated line absorption diagram given in lower half of figure.

Further refinement of the assignment was done by comparison of the experimental spectrum with simulated spectra calculated using the computer program<sup>28</sup> which permits calculation of the magnitude of the derivative at 5-mG. intervals. A line width of 0.18 G. and a Lorenztian line shape were used in the spectrum calculation.

The low field one-sixth of the e.s.r. spectrum for the anion of 2,4,6-trimethylnitrobenzene (nitromesitylene) is shown in Fig. 2. The validity of the assignment of coupling constants is supported by the calculated spectrum shown in the lower part of Fig. 2. For comparison, the calculated spectrum is also shown in the low field region for the case where the two equivalent m-hydrogens do not couple with the unpaired electron. As is expected, the assigned coupling constants are similar to those for the anion radical of 2,6-dimethyl-nitrobenzene.

At high amplification, the spectrum of the anion of 2,3,5,6-tetramethylnitrobenzene (nitrodurene) shows satellite lines as in Fig. 3. The location of the nitrogen-15 (I = 1/2) doublet satellites which can be calculated from the known relationship  $a_N^{15} = 1.402 a_N^{14}$  is indicated on Fig. 3. The natural abundance of nitrogen-15 is 0.365%. Taking the spin value into consideration, each nitrogen-15 line is expected to be 0.547%as intense as the major nitrogen-14 line for radicals where the coupling is with one nitrogen nucleus per molecule. By comparison, the expected intensity relation between the carbon-13 satellite and the parent line is 0.55% for coupling with one carbon atom per molecule. Inspection of Fig. 3 shows that the carbon-13 satellites with a coupling constant of 7.6 G. are more intense than the nitrogen-15 lines; the best resolved carbon-13 line (low field end) is 1.2% as intense as the parent line. This corresponds closely to the calculated value for *two* equivalent carbon atoms per radical which in the nitrodurene anion implies the ring or methyl carbons in the o- or m-positions. The apparent line width observed on electrolysis of a 0.14 mM nitrodurene solution increased from 0.9 to 1.2 G. over the temperature region  $-40^{\circ}$  to  $20^{\circ}$ . The coupling constant increases only to 21.7 G, with as much as 10% water present. This contrasts with the relatively large changes for unhindered nitro aromatic anion radicals.<sup>29</sup> The nitrogen coupling constant anion radical of pentamethylnitrobenzene is 20.5 G.



Fig. 2.—a, Derivative e.s.r. spectrum (low field one-sixth) of 2,4,6-trimethylnitrobenzene anion radical from electrolysis of 0.75 m*M* acetonitrile solution. b, Calculated spectrum using hydrogen coupling constants in Table I and line width of 0.2 G. Dashed line at low field is same calculation except for setting the *m*-hydrogen coupling constant equal to zero.



Fig 3.—Derivative spectrum of nitrodurene anion radical from total electrolysis of 1 mM solution in acetonitrile. Amplification reduced by a factor of 53 to present three major lines. Carbon-13 doublet is indicated for the central line as is the expected position for nitrogen-15 doublet.

Assignment of coupling constants in spectra of anion radicals of the three *t*-butylnitrobenzenes, parent compounds numbers 12, 13, and 14 in Table I, is simplified by the observation that interaction of the unpaired electron with the hydrogens in the *t*-butyl group is almost absent. Nevertheless, in both radicals with mono-o-substitution of the t-butyl group we attribute the abnormally broad line widths of approximately 0.4 G. to small unresolved splittings from the nine equivalent t-butyl hydrogens. In the anion radical of 2-t-butylnitrobenzene the hydrogen multiplet structure consists of seven lines. Assignment of the m-proton coupling constant of 1.1 G. is straightforward. The sum of the o- and p-proton coupling constants is quite accurately established as 5.0 G. from the experimental spectrum, but the breadth of the lines limits the accuracy with which individual values can be assigned to  $\pm 0.1$  G.

The six-line proton hyperfine structure in the spectrum of the 2,5-di-*t*-butylnitrobenzene anion is readily assigned to two equivalent protons with a coupling constant of 2.1 G. and a single proton with a coupling constant of 0.82 G. Assignment to molecular positions given in Table I follows the usual pattern for nitro-

<sup>(28)</sup> E. W. Stone and A. H. Maki, J. Chem. Phys., 38, 1999 (1963).

<sup>(29)</sup> P. Ludwig, T. Layloff, and R. N. Adams, in press.

			-	$(E_{3/4} -$								
	Parent compound	Formula	- E <sub>1/2</sub> , v. vs. s.c.e.	$E_{1/4}$ ), mv.	I <sup>a</sup>	$\Delta E_{\rm S}$ , - mv.	<i>a</i> 1]	nion radical  a2	coupling ( [a3]	constants,*  a <sub>4</sub>	gauss  as	<i>a</i> 6
1.	Nitrobenzene <sup>6</sup>		$\begin{array}{c} 1.147 \\ 1.9 \end{array}$	56	$\begin{array}{c} 4.1 \\ 7.5 \end{array}$		10.32	3.39	1.09	3.97	1.09	3.39
2.	4-Methylnitrobenzene <sup>c</sup>	O <sub>N</sub> O	1.203 1.2	$\frac{56}{112}$	4.0 10		10.79	3.39	1.11	3.98	1.11	3.39
3.	3,5-Dimethylnitrobenzene	o <sub>N</sub> o	1.190 2.0	56	4.0 10		10.6	$3.29^d$	1.08	3.92	1.08 <sup>d</sup>	3.29
4.	3,4-Dimethylnitrobenzene	o <sub>N</sub> o	$\frac{1.233}{2.1}$	55	$\frac{3.2}{3.0}$		10.9	3.35	1.05 <sup>d</sup>	3.95	$1.05^{d}$	3.35
5.	3-Methylnitrobeuzene	o <sub>N</sub> o	1.180 <sup>e</sup>	58	4.0		10.4	3.30	1.07 <sup>d</sup>	3.88	1.07 <sup>d</sup>	3.30
6.	2-Methylnitrobenzene	<sup>6</sup> N <sup>0</sup>	$\frac{1.263}{2.1}$	56	4.6 9.8	60	11.0	$3.12^d$	1.04	3.91	1.04	3.12 <sup>d</sup>
7.	2,3-Dimethylnitrobenzene	° <sub>N</sub> ⁰	$\frac{1.318}{2.1}$	58 200	3.2 8	82	11.7	$2.91^d$	0.99 <sup>d</sup>	3.3	0.99 <sup>d</sup>	2.91 <sup>d</sup>
8.	2,5-Dimethylnitrobenzene	0 <sub>N</sub> 0	1.280	57	4.3	44	11.4	3.25 <sup>d</sup>	$1.02^{d}$	3.88	$1.02^{d}$	3.25 <sup>d</sup>
9.	2,6-Dimethylnitrobenzene	°N <sup>0</sup> ◯	1.402 2.3	58 138	4.3 19	143	17.8	0.85	0.88°	1.41	0.88	0.85
10.	2,4,6-Trimethylnitrobenzene	°No ↓	1.442	56	4.3	127	17.8	0.82	0.82	1.27	0.82	0.82
11.	2,3,5,6-Tetramethylnitro- benzene <sup>7</sup>	o <sub>N</sub> o	1.442 2.6	56	3.8 7.8	117	20.4					
12.	2-t-Butylnitrobenzene	ONO X	1.355 1.98	54 128	$\begin{array}{c} 2.9\\ 8.5\end{array}$	152	14.9	a	1.1	2.5	1.1	2.5
13.	2,5-Di-t-butylnitrobenzene	$\chi \bigcirc^{0_N^0} \chi$	1.360	60	3.5	124	16.6	g	0.82	2.1	a	2.1
14.,	2,4,6-Tri- <i>t</i> -butylnitrobenzene	×	1.500	58	2.8	185	18.8	a	0.85	a	0.85	a
15.	2-Methyl-2-nitropropane		1.70 <sup>k</sup>	Reve	rsible		$26.45^i$					
16.	<i>m</i> -Dinitrobenzene <sup><i>i</i></sup>		0.90 1.25	$\begin{array}{c} 61 \\ 63 \end{array}$	$\frac{4.2}{3.6}$		4.68	3.11	4.68	4.19	1.0	4.19
17.	2,4,6-Trimethyl-1.3-dinitro- benzene		$\begin{array}{c}1.22\\1.47\end{array}$	58 59	3.0 7.6	320 <sup>k</sup>	8.19		8.19			
18.	o-Dinitrobenzene		$\begin{array}{c} 0.81 \\ 1.06 \end{array}$	52 57	4.2 3.20		3.22	3.22	0.42	1.63	1.63	0.42
19.	Tetramethyl-1,2-dinitro- benzene	NO NO	1.13 1.28	57 59	4.5 4.2	$320^{k}$	5.8	5.8	0.56	1.12	1.12	0.56
20.	1,4-Dinitrobenzene	0N <sup>O</sup> $\frac{1}{2}$ 0N <sup>4</sup> O	0.69 0.89	53 58	5.0 3.6		1.74	1.12	1.12	1.74	1.12	1.12

## ELECTRON SPIN RESONANCE OF NITROBENZENES

			Т	able I	(Cont	inued)						
			-	$-(E_{8/4}) -$								
	Parent compound	Formula OrrO	$-E_{1/2}$ , v. vs. s.c.e.	$E_{1/4}$ , mv.	$I^a$	$\Delta E_8, \sim$ mv.	a1	Anion radi	cal couplin	$ a_4 $	s,* gauss—  aş:	146
21.	Tetramethyl-1,4-dinitro benzene		1.216	30	8.0 <sup>1</sup>	530 <sup>d</sup>	8.7			8.7		
22.	2,3-Dimethyl-1,4-dinitro- benzene		0.99	88	$6.5^{l}$	300 <sup>k</sup>	2.14	1.18	1.18	2.14	0.91	0.91
23.	2,6-Dimethyl-1,4-dinitro- benzene	o <sup>N</sup> o	$\begin{array}{c} 0.914 \\ 1.096 \end{array}$	55 55	$\begin{array}{c} 3.2\\ 2.8\end{array}$	$220^{k}$	0.14	0.17	2.49	5.66 <sup>m</sup>	2.49	0.17
24.	2,6-Di-t-butyl-1,4-dinitro- benzene	NO <sub>2</sub> NO <sub>2</sub>					0.72	g	3.14	8.77	3.14	ø

\* Nitrogen coupling constants given here are average of high and low field values. <sup>a</sup> Limiting current constant,  $i_d/m^{2/3}t^{1/6}C$ , where  $i^d$ is expressed in microamperes, *m* in mg. of Hg/sec., *t* in sec., and *C* in mmoles/liter. <sup>b</sup> All data for nitrobenzene were taken from ref. 7-<sup>c</sup> Data from ref. 8. <sup>d</sup> No difference was observed in coupling constant between ring hydrogen and methyl hydrogens in equivalent positions; *i.e.*, four equivalent spin <sup>1</sup>/<sub>2</sub> species were present. <sup>e</sup> The original assignment in ref. 9 incorrectly omitted the coupling due to the *m*-protons. <sup>f</sup> Carbon-13 coupling constant of 7.6 G. observed. <sup>e</sup> No interaction with *t*-butyl hydrogens was observed. <sup>h</sup> Data provided by Dr. W. G. Hodgson, American Cyan amid Co., Stamford, Conn. <sup>c</sup> Data from A. K. Hoffman, W. G. Hodgson, and W. H. Jura, J. Am. Chem. Soc., 83, 4676 (1961). <sup>i</sup> All data for o-, *m*-, and p-dinitrobenzene taken from A. H. Maki and D. H. Geske, J. Chem. Phys., 33, 825 (1960). <sup>k</sup> Value tabulated is  $\Delta E_{1/2}$  with respect to corresponding unsubstituted dinitrobenzene. <sup>l</sup> Two-electron reduction. <sup>m</sup> Examination of anion radical of 1,3-dimethyl-2-nitro-5-nitro<sup>15</sup>-benzene shows interaction with two equivalent nuclei of spin one-half and another single nucleus of spin one-half. The latter coupling constant, 7.94 G., is attributed to the nitrogen-15 nuclei.

			-	$-(E_{3/4} - D_{3/4})$								
	Parent compound	Formula	$-E_{1/2}$ , v.	$E_{1/4}$ .	,	al	Anion	radical c	oupling con	nstants, g	auss — —	
	Tarent compound			1	-	1411	102	14.91	44	44	1461	Jun
1.	4-Nitroaniline <sup>a</sup>	$H_{\mathbf{N}_{1}}H'$	$\frac{1.358}{2.0}$	58	3.4 14	1.12	1.12	3.36	12.18	3.36	1.12	1.12
2.	2-t-Butyl-4-nitroaniline	H <sub>N</sub> H	$\frac{1.393}{2.3}$	54	3.6 12	1.12	ь	3.36	12.2	3.36	1.12	1.12
3.	2,6-Di- <i>t</i> -butyl-4-nitroaniline	ONO HNH X	$\frac{1.40}{2.4^c}$	55	4.2	1.16	ь	3.36	12.2	3.32	ь	1.12
4.	2,5-Di- <i>t</i> -butyl-4-nitroaniline	o <sup>N</sup> o H <sub>N</sub> H V o <sup>N</sup> o	1.46	50	3.1	0.49	ь	1.97	18.7	Ъ	0.70	0.49
5.	3,5-Di- <i>t</i> -butyl-4-nitroaniline	H <sub>N</sub> H	1.553	55	3.5	<0.25 <sup>d</sup>	0.79	ь	19.3	Ъ	0.79	<0.25 <sup>d</sup>
6.	N,N-Dimethyl-4-nitroaniline	${}^{\tilde{\tau}}H_{3}C \underset{\mathfrak{b}}{\overset{C}{\underset{0}}}{\overset{C}{\underset{0}}}H_{3}^{2}$	1.394	57	3.8	1.13	1.10	3.33	11.7	3.33	1.10	0.71
7.	2- <i>t</i> -Butyl-N,N-dimethyl-4- nitroaniline	H <sub>3</sub> C <sub>N</sub> CH <sub>3</sub>	1.117	50	3.6	0.52	b	3.32	10.8	3.32	1.12	0.22
8.	2,5-Di-4-butyl-N,N-dimethyl- 4-nitroaniline	CH <sub>3</sub> CH <sub>3</sub> CH <sub>3</sub> CH <sub>3</sub> CH <sub>3</sub>	$\frac{1.38}{2.2}$	57	4.0 11	e	Ъ	2.2	16.0	Ь	е	e

<sup>a</sup> Data from ref. 8; assignment of coupling constant verified in the present work by deuteration of amino protons. <sup>b</sup> No coupling observed for *t*-butyl group hydrogens. <sup>c</sup> Wave distorted by maximum. <sup>d</sup> Stated upper limits are arbitrarily taken as the peak-to-peak line width. <sup>e</sup> We have not been able to resolve more than six lines in this spectrum. The apparent line width is 1.25 G. It is unlikely that this broadening is simply due to an unresolved *m*-hydrogen doublet which by comparison with the anion radical for compound 4 would be expected to be  $\sim 0.5$  G.; rather, some of the broadening apparently is contributed by unresolved hyperfine structure from small amino nitrogen and methyl hydrogen interactions.

TABLE II



Fig. 4.—Derivative e.s.r. spectrum of tetramethyl-1,2-dinitrobenzene anion radical from electrolysis of 0.5 mM solution in acetonitrile. a, Experimental spectrum under conditions of low field modulation amplitude, 0.16 G. Calculated portion of spectrum at upper left obtained using coupling constants given in Table I and a line width of 0.2 G. b, Same experimental spectrum as a except that high amplitude field modulation, 2.0 G., was used.



Fig. 5.—a, Derivative e.s.r. spectrum (low field one-half) of 2,3dimethyl-1,4-dinitrobenzene anion radical from electrolysis of 0.32 mM solution in acetonitrile. b, Calculated spectrum using coupling constants in Table I and 0.12 G. line width.

benzene radicals. As was the case for the o-t-butylnitrobenzene anion, the line width is ca. 0.4 G.

Electron Spin Resonance Data for Substituted Dinitrobenzene Anion Radicals .- Data for the series of substituted dinitrobenzene anion radicals are given in Table I, parent compound numbers 16-24. The hindered 2,4,6-trimethyl-1,3-dinitrobenzene anion (no. 17, Table I) has previously been studied by Freed and Fraenkel<sup>30</sup> in dimethylformamide solution. These workers attributed the anomalous alternation of line widths to a rotational modulation of the nitrogen coupling constant. We have observed this same alternation of line width for the radical anion in acetonitrile solution. Multiplet structure from interaction with ring and/or methyl protons with a spacing of 1.2 G. occurs only where the magnetic quantum number,  $M_{\rm I}$ , is  $\pm 2$  and 0. Unequivocal assignment of proton coupling constants was not possible.

The tetramethyl-1,2-dinitrobenzene (dinitroprehnitene) anion radical appears to be comparatively unstable. No radicals were observed in a controlled

(30) J. H. Freed and G. K. Fraenkel, J. Chem. Phys., 37, 1156 (1962).



Fig. 6.—a, Derivative e.s.r. spectrum of the 2,6-dimethyl-1,4dinitrobenzene anion radical from electrolysis of 0.3 mM solution in acetonitrile. b, Expanded derivative spectrum (one-half) from a above. c, Calculated spectrum using constants in Table I and line width of 0.15 G.

potential electrolysis at  $20^{\circ}$  using the recirculation cell.<sup>21</sup> However at  $-35^{\circ}$  using the *intra muros* cell, well-resolved spectra (Fig. 4a) were obtained. The spectrum in Fig. 4a was obtained at a field modulation of 0.16 G. The major splitting of 5.8 G. is attributed to coupling with two equivalent nitrogen nuclei. Multiplet structure with a spacing of 0.56 G. is attributed to two sets of six equivalent hydrogens with coupling constants of 0.56 and 1.12 G. This assignment is supported by the calculated spectrum shown above the low field end of the experimental spectrum in Fig. 4a. Assignment of the larger hydrogen coupling constant to the 4- and 5-positions (Table I) is based entirely on analogy with the unsubstituted radical (number 18, Table I). Absence of the expected 1:2: 3:2:1 intensity relationship among the five nitrogen groups is taken as evidence for the occurrence of the alternating line-width effect,<sup>30</sup> apparently the first time the effect has been noted for a substituted odinitrobenzene anion. The spectrum (Fig. 4b) obtained at high field modulation amplitude is shown as a matter of interest.

The anion radical of 2,3,5,6-tetramethyldinitrobenzene (dinitrodurene) has a nitrogen coupling constant of 8.7 G. in acetonitrile solution. The deviation of line intensities from the expected intensity ratio of 1:2:3:2:1 is similar to that reported by Freed and Fraenkel<sup>30</sup> for the same radical in dimethylformamide. These workers attributed the alternation of line width to a rotational modulation of the nitrogen coupling constant. The dinitrodurene anion appears to undergo a slow decomposition in acetonitrile solution since an extraneous radical appears after a period of time. The spectrum of the extraneous radical consists of three equally intense lines with a nitrogen coupling constant of 21.6 G. The line width, 0.7 G., is smaller than we have observed for nitrodurene anion.



Fig. 7.—Derivative e.s.r. spectrum of anion radical of 2,6-di-*t*-butyl-1,4-dinitrobenzene produced by electrolysis of a 0.5 mM acetonitrile solution.

The extraneous radical was not observed in either dimethylformamide or dimethyl sulfoxide solution. Although we have not pursued this problem in detail, the suggestion of formation of the octamethyl-4,4'dinitrobiphenyl anion radical<sup>31</sup> is an interesting one.

The e.s.r. spectrum for the 2,3-dimethyl 1,4dinitrobenzene anion radical, no. 22, is shown in Fig. 5 along with the calculated spectrum obtained using the coupling constants given in Table I and a line width of 0.12 G. The identity of the nitrogen coupling constant,  $a_N$ , was further verified by the observation that when the acetonitrile solution was made 0.32 M in water  $a_N$  increased from 2.14 to 2.38 G. This behavior is consistent with the observed solvent dependence of nitro group nitrogen coupling constants.<sup>29</sup>

The 2,6-dimethyl-1,4-dinitrobenzene anion radical spectrum was readily assigned by assuming interaction of the odd electron with a single nitrogen nucleus,  $a_{\rm N} = 5.66$  G., and a further splitting by two equivalent hydrogens of 2.5 G. In order to make an unequivocal assignment of the nitrogen coupling constant to one of the two nonequivalent positions the radical was labeled with nitrogen-15 in the 4-position, the unhindered nitro group. The e.s.r. spectrum of the corresponding anion radical, Fig. 6a, shows a doublet splitting of 7.94 G. which is attributed to the nitrogen-15 in the nitro group in the 4-position. The line width of 0.15 G. is small enough to permit observation of multiplet structure due to methyl hydrogens and the remaining nitrogen. An expanded spectrum, Fig. 6b, may be compared with the spectrum in Fig. 6c, which was calculated using a methyl proton coupling constant of 0.17 G., a nitrogen interaction of 0.14 G., and a line width of 0.15 G.

The e.s.r. spectrum of the anion of the related *t*butyl compound, 2,6-di-*t*-butyl-1,4-dinitrobenzene, is shown in Fig. 7. The line width is 0.17 G. It is clear from the observation of twenty-seven lines that there is coupling of the odd-electron with both nitro group nitrogens. In analogy with the preceding case we have assigned the larger coupling constant, 8.77 G., to the nitrogen in the unhindered position.

Electron Spin Resonance Data for Substituted Nitroaniline Anion Radicals.—Data are given in Table II for the series of eight anion radicals which were examined. The assignment of coupling constants made previously for the 4-nitroaniline anion radical was verified by deuteration of the amino hydrogens. Spectra of the anion radicals of compounds 2 and 3, Table II, are simplifications of the spectrum for the 4nitroaniline anion since there is no significant coupling



Fig. 8.—a, E.s.r. spectrum (low field one-sixth) of anion radical of 2,5-di-*t*-butyl-4-nitroaniline from electrolysis of 0.63 mM solution. b, Calculated spectrum using coupling constants in Table II and line width of 0.4 G.

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	10	gouss-			* j	*	-0.10		•	1 .

Fig. 9.—Derivative e.s.r. spectrum (low field one-half with center of spectrum on left side) at high gain for anion of 3,5-di-tbutyl-4-nitroaniline produced by electrolysis of 1.1 mM acetonitrile solution. Center of 9.8 G. carbon-13 coupling is indicated as well as the calculated position of nitrogen-15 satellites.

with *t*-butyl hydrogens and the other coupling constants remained essentially unchanged.

By comparison, the coupling constant for the nitro group nitrogen in the anion radical of 2,5-di-*t*-butyl-4-nitroaniline is significantly larger. As was the case for the two nitrobenzene radicals with *o*-*t*-butyl substituents, no. 12 and 13, Table I, the line width for this radical is comparatively large, 0.4 G. This fact limits the accuracy with which the remaining coupling constants may be assigned. The low field one-sixth of the experimental spectrum is shown in Fig. 8 along with the spectrum calculated using the constants given in Table II and a line width of 0.4 G.

The spectrum for the 3,5-di-t-butyl-4-nitroaniline anion shows three widely spaced triplets. Assignment of the small splitting to the 2,6-ring hydrogens is consistent with data for the anion radical of 2,4,6-tri-tbutylnitrobenzene in Table I, compound 14. The spectrum of the radical with amino deuteration showed no change. Under high amplification the spectrum shown in Fig. 9 was obtained. Six of the satellite lines around the main nitro group nitrogen splitting are attributed to a carbon-13 coupling constant of 9.8 G. As indicated in Fig. 9, each of the carbon-13 satellite lines is 1.1% as intense as the corresponding major lines, in agreement with the calculated quantity for coupling with radicals which contain two equivalent carbon sites. As was the case in the nitrodurene spectrum, the carbon-13 and nitrogen-15 satellites overlap. The calculated position of the nitrogen-15 lines is shown in Fig. 9. The remaining satellite lines probably arise from a second carbon-13 constant of

<sup>(31)</sup> Professor A. H. Maki in a private communication has informed us that his preliminary results on the study of this anion establish that the odd electron interacts with only a single  $N^{14}$  nucleus in the molecule.



Fig. 10.—a, Derivative e.s.r. spectrum (low field one-sixth) of anion radical of N,N-dimethyl-4-nitroaniline produced by electrolysis of 1mM acetonitrile solution. b, Calculated spectrum using coupling constants given in Table II and line width of 0.15 G.

3.9 G., apparently also corresponding to two equivalent carbon positions.

In order to obtain a conclusive assignment for the complex spectrum observed for the N,N-dimethyl-4nitroaniline anion we investigated the anion of the corresponding methyl deuterated compound,  $(CD_3)_{2}$ -NC<sub>6</sub>H<sub>4</sub>NO<sub>2</sub>. The nitro group nitrogen coupling constant is immediately obvious from the triplet symmetry of the spectrum. Calculation of line intensities within each of the widely spaced triplets was made under the assumption that the amino nitrogen coupling constant, 1.1 G., equals the 2,6-ring proton coupling constant which in turn is one-third the coupling constant for the 3,5-ring protons. The calculated intensity are 1:3:4:5:7:8:7:5:4:3:1, and the obratios served intensity ratios were 0.92:3.0:3.9:5.0:7.2: 8:7.2:5.0:3.9:3.0:0.92. The good agreement between calculated and observed intensities nominally established all coupling constants except the methyl hydrogen. Hyperfine structure due to deuterium was not resolved. Figure 10 shows the low field one-sixth of the e.s.r. spectrum for the N,Ndimethyl-4-nitroaniline anion. Since the end line region is crucial for assignment of the methyl hydrogen coupling constant, a high-amplification segment, A, is also shown. The calculated spectrum shown below the experimental spectra was obtained using the coupling constants shown in Table II and a line width of 0.15 G. The intensity ratio between lines I and II in segment A is estimated as 0.43 as compared with a calculated ratio of 0.42.

The spectrum for the anion of 2-*t*-butyl-N,N-dimethyl-4-nitroaniline shows threefold symmetry due to a coupling constant of 10.8 G. with the nitro group nitrogen. Within each one-third of the spectrum the coupling constant of 3.32 G. for two hydrogens *ortho* to the nitro group is readily apparent. Remaining multiplet structure is illustrated in Fig. 11a which shows the low field one-twelfth of the spectrum. The validity of coupling constants assigned to the remaining magnetic nuclei, Table II, is supported by the calculated spectrum, Fig. 11b. A line width of 0.15 G. was used in the simulated spectrum.

# Discussion

**Polarographic Data for Nitrobenzene Species.**— Utilization of polarographic data to elucidate steric effects has been made by a number of workers.<sup>32–37</sup> Review articles by Zuman<sup>38</sup> are available.

- (32) B. von Zanten and W. Nauta, Rec. trav. chim., 80, 181 (1961).
- (33) H. Schmidt and L. Holleck, Z. Elektrochem., 59, 531 (1955).
- (34) G. Perret and L. Holleck, *ibid.*, **60**, 463 (1956).



Fig. 11.—a, Derivative e.s.r. spectrum (low field one-twelfth) of anion radical of 2-*t*-butyl-N,N-dimethyl-4-nitroaniline produced from electrolysis of 1.0 mM solution in acetonitrile. b, Calculated spectrum using coupling constants in Table II and line width of 0.15 G.

Polarographic investigation of o-substituted nitrobenzenes in particular was done as early as 1949 by Fields, Valle, and Kane.<sup>39</sup> These authors clearly recognized the possibility that the displacement of the nitro group from planarity by the presence of omethyl groups might be reflected in the half-wave potential of the compound. One procedure for examining such data is to estimate first of all the shift in half-wave potential due to the inductive effect of the substituent methyl groups from known electrochemical data for unhindered m- and p-derivatives. The usual assumption is that the *o*-inductive effect is equal to the *para* effect. The difference between such a "corrected" half-wave potential and the half-wave potential of nitrobenzene,  $\Delta E_{\rm S}$ , is then attributed to steric effects. The polarographic behavior of substituted nitrobenzenes has been correlated in terms of a Hammett  $\rho\sigma$  equation. It is expected that for a given solvent medium  $\Delta E_{\rm S}$  will be independent of the value of  $\rho$ .

Values of  $\Delta E_{\rm S}$  for various degrees of *o*-substitution can be calculated from the data of Fields, et al.<sup>39</sup> Their polarographic study was carried out in semiaqueous media and a dependence of half-wave potential on pH was observed. The pH dependence also extended to values of  $\Delta E_{\rm S}$ , which one would ordinarily expect to be independent of pH. Thus for mono-o-substitution with a methyl group,  $\Delta E_{\rm S}$  was -0.02 and -0.04 v. at pH values of 10 and 7.2, respectively. For o-substitution in nitromesitylene the  $\Delta E_{\rm S}$  values were -0.120 and -0.130 v. at pH 10 and 7.2. In addition to the pH dependence of  $\Delta E_{\rm S}$  there was some ambiguity as to the number of electrons involved in the reduction reaction. The electrode reactions were not "reversible" so that attempts at correlation would depend on assumed constancy of the reduction mechanism and of the transfer coefficient. In summary, one may say that the work of Fields, et al.,39 and later workers40 made clear in a qualitative fashion that the reduction

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(36) G. Hoijtink, Rec. trav. chim., 74, 1525 (1955).

(37) P. Zuman and D. J. Voaden, Tetrahedron, 16, 130 (1961).

(38) (a) P. Zuman, Chem. Listy, **53**, 154 (1959); (b) P. Zuman, Collection Czech. Chem. Commun., **27**, 649 (1962); (c) P. Zuman, "Progress in Polarography," Vol. I, ed. by P. Zuman and I. M. Kolthoff, Interscience Publishers, Inc., New York, N. Y., 1962, pp. 319.

(39) M. Fields, C. Valle, and M. Kane, J. Am. Chem. Soc., **71**, 421 (1949). This work has recently been extended by O. H. Wheeler, Can. J. Chem., **41**, 192 (1963).

(40) C. Prevost, P. Souchay, and C. Malen, Bull. soc. chim. France, 78 (1953).



Fig. 12.—Observed shift in half-wave potential for methylated nitrobenzenes with respect to nitrobenzene vs. calculated shift using three constants defined by black dots. Extent of methylation is indicated for each point as o, m, p for ortho, meta, and para, respectively.

potential is made more negative as the nitro group is twisted out of planarity with the ring; however, reliable quantitative treatment of the data is not possible.

The advantages of a nonaqueous *aprotic* solvent such as acetonitrile for a polarographic study of this type have been discussed in detail.<sup>8</sup> Inasmuch as the reduction reactions are reversible,<sup>41</sup> the measured half-wave potentials are an excellent approximation to thermodynamic standard electrode potentials. Consequently it is possible to draw quantitative conclusions with confidence.

Examining now the polarographic data in Table I it is first of all significant that the over-all effect of methylation of the nitrobenzene half-wave potential can be represented rather closely as an additive function of three constants. A half-wave potential shift,  $\Delta E_{1/2}$ , for o-, m-, and p-substitution is defined as the difference between the half-wave potential for the appropriate nitrotoluene and the half-wave potential for nitrobenzene (-1.147 v. vs. s.c.e.). The values are -116, -33, and -56 mv., respectively, for o-, m-, and p-nitrotoluene. By appropriate combination of these three values, half-wave potentials for seven other methylated nitrobenzenes were calculated. The extent of agreement between calculated and observed values is obvious from inspection of Fig. 12 where the solid line is drawn through the three defined points.

Values of  $\Delta E_{\rm S}$  for the seven methyl-substituted nitrobenzenes are given in Table I. The  $\Delta E_{\rm S}$  value was calculated as described above. We consider it noteworthy that both the experimental values for  $\Delta E_{1/2}$ and  $\Delta E_{\rm S}$  for di-o-methyl substitution are roughly *twice* the value of the corresponding mono-o-methyl substituted compounds. Data for *t*-butyl derivatives are less complete than for the methylnitrobenzenes. If one estimates the inductive effect of *t*-butyl groups to be the same as the methyl groups the values of  $\Delta E_{\rm S}$ are -152 and -185 mv., respectively, for mono- and di-o-butylnitrobenzene; *i.e.*, there is less evidence for



Fig. 13.—Approximate angle of twist for hindered nitrobenzenes in degrees vs. steric effect on half-wave potential shift,  $\Delta E_8$ , volts.

a "doubling" effect than in the methyl system. If one takes polarographic data as evidence for the extent of the steric effect, a single monomethyl substituent in nitrobenzene is actually one-half as effective as two di-*ortho*-groups. This conclusion contrasts with the nitrogen coupling constant (*vide infra*), absorption coefficients,<sup>3</sup> molar refraction,<sup>3</sup> carbon-13 magnetic shielding constants,<sup>5</sup> and dipole moments.<sup>3</sup>

Re-examination of the fundamental definition of  $\Delta E_{1/2}$ , or in our case  $\Delta E_S$ , seems warranted at this point. A standard electrode potential as estimated from a half-wave potential measurement is, of course, proportional to the difference of the standard free energies of formation for reduced and oxidized species.

Consequently  $\Delta E_{\rm S}$  is proportional to  $\Delta \Delta F^{\circ}$ . Thus, the expression for  $\Delta E_{\rm S}$  for a one-electron reduction is

$$\Delta E_{\rm S} \mathfrak{F} = (F_{\rm t} \circ - F_{\rm t} \circ) - (F_{\rm p} \circ - F_{\rm p} \circ)$$

where the subscripts t and p refer to the twisted and planar species and anionic charge is as shown. From this expression it is clear that  $\Delta E_{\rm S}$  is zero only if the absolute energies for anion and neutral molecule change by the *same* amount for the two classes. From the sign of  $\Delta E_{\rm S}$  for a typical case in the present system,  $(F_{\rm T}\circ - F_{\rm t}\circ) > (F_{\rm P}\circ - F_{\rm P}\circ)$ .

Maki and Geske<sup>8</sup> have estimated that the resonance interaction between the two nitro groups in the anion radical of *p*-dinitrobenzene is larger by approximately 4.5 kcal./mole than in the neutral molecule. On this basis it seems likely that the increased energy associated with the twisted anion radical is largely a result of loss of resonance energy between the nitro group and the ring as the nitro group is decoupled from the Unless there is steric hindrance to solvation it ring. seems reasonable that the solvation energy of the twisted anion will be larger than for the planar anion because the effective charge is isolated more completely on the nitro group and consequently in a smaller effective volume. Using the Born charging equation it can be calculated that even a change in effective radius of 5 to 4 Å. represents a free energy change of 8 kcal./ mole. Solvation of the anion radical is thus a facilitating effect; *i.e.*, the half-wave potential is shifted to more positive values. However, this effect must be

<sup>(41)</sup> One condition for reversibility is that  $E_{3/4} - E_{1/4}$  be -56 mv. for a one-electron process. Values for this quantity are given in Tables I and II. See ref. 8 for detailed discussion of relation of  $E_{1/4}$  to  $E^{\circ}$ .

swamped out by the loss of resonance energy on twisting the nitro group.

It is thus expected that the effect of twisting on  $\Delta E_{\rm S}$  will increase as the average twist angle,  $\theta$ , increases. Wepster<sup>3,42</sup> has suggested that the intensity of the visible absorption band in hindered nitrobenzenes is proportional to  $\theta$ . This suggestion correlates rather well with limited crystallographic evidence.<sup>43</sup> Twist angles are available<sup>3</sup> for eight compounds and we see in Fig. 13 that the more highly hindered species exhibit larger  $\Delta E_{\rm S}$  values.

Trotter<sup>44</sup> has estimated the resonance energy between the nitro group and the ring in nitrobenzene as 6.6 kcal. Using this figure and estimating  $\Delta E_{\rm S}$  as -0.15v. for total twisting,<sup>45</sup> the free energy difference between the twisted and planar anions is 10 kcal. The accumulated assumptions make this an extremely crude calculation.

No attempt has been made to estimate  $\Delta E_{\rm S}$  values for the several hindered dinitrobenzenes examined. However, it is apparent from the values of  $\Delta E_{1/2}$ presented in Table I that the behavior is qualitatively similar to the behavior of mononitrobenzenes.

The polarographic behavior of dinitrodurene (1.4dinitrotetramethylbenzene) is particularly interesting. The observed reduction wave is essentially indistinguishable from a two-electron reversible reduction. The value of  $E_{3/4} - E_{1/4}$  is -30 mv. compared with the theoretical value of -28 mv. for a two-electron reaction. There is a variation with solvent, since in N,N-dimethylformamide the two waves are distinguished, the apparent difference between the two halfwave potentials being 50 mv. On the basis of these data we may qualitatively suggest that the decoupling of the two nitro groups is sufficient so that the second electron goes on almost as easily as the first. It is important to note that although the primary electrode reaction may be written as the formation of a dianion, the monoanion can be formed by the equilibrium reaction

 $\mathrm{Ar}(\mathrm{NO}_2)_2{}^{-2} + \mathrm{Ar}(\mathrm{NO}_2)_2 \underbrace{\longrightarrow} 2\mathrm{Ar}(\mathrm{NO}_2)_2{}^{-}$ 

It is expected that the equilibrium constant for this reaction will be at least one.

**Polarographic Data for Nitroaniline Species.**—Among the steric studies of polyfunctional molecules the work on nitroanilines is quite extensive. The geometry of nitroanilines is complicated by the intrinsic tendency of the amino nitrogen to be pyramidal as opposed to the tendency of conjugated systems to be planar for maximum mesomeric interaction. Nevertheless, it seemed that a polarographic study might contribute some further understanding.

Polarographic data for a series of *p*-nitroanilines in acetonitrile solution are given in Table II. Polarographic data for *p*-nitroaniline were obtained in an earlier study.<sup>8</sup> On the basis of a Hammett correlation using the  $\sigma^n$ -values of van Bekkum, Verkade, and Wepster, <sup>46</sup> it was concluded that the reduction potential of *p*-nitroaniline was rendered approximately 0.11 v. more negative because of the loss of *para* interaction between the nitro and amino groups in the anion radical. In other words, addition of an electron to

(43) (a) J. Trotter, Can. J. chem., 37, 1487 (1959); Acta Cryst., 12, 605 (1959); (b) K. J. Watson, Nature, 188, 1102 (1960).

(44) J. Trotter, Can. J. Chem., 37, 905 (1959).

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

p-nitroaniline, one limiting form of which is written below, obliterated mesomeric interaction, at least in



part, in the anion radical.

Evidence for mesomeric interaction in the neutral compound is available from various chemical studies as well as the X-ray crystallographic study of Trueblood, *et al.*<sup>47</sup> The rationalization presented below is based on the premise that the mesomeric interaction between the amino and nitro groups in *p*-nitroaniline is approximately 2 kcal.<sup>8</sup>

Half-wave potentials for compounds 1, 2, and 3 in Table II, where the  $-NH_2$  group is successively hindered, are only slightly different. Hence we conclude that the amino group is too small to be effected by blocking groups, both in the neutral molecule and anion radical, in agreement with earlier observations on the neutral molecule.<sup>48-51</sup>

In compounds 4 and 5 where the nitro group is successively blocked the para interaction energy must be close to zero. Using the  $\rho\sigma$  correlation one would estimate a  $\Delta E_{1/2}$  (with respect to nitrobenzene) of -0.1 v. for a *p*-nitroaniline where the *para* interaction is absent. But of course there is a more negative halfwave potential associated with the twisted nitro group. In fact as a first approximation,  $\Delta E_{1/2}$  values for compounds 4 and 5 with respect to nitrobenzene should be similar to those of 2,5-di-t-butylnitrobenzene and 2,6-dit-butylnitrobenzene. If one subtracts 0.1 v. to account for the residual amino group influence from the  $\Delta E_{1/2}$ values for compounds 4 and 5, the values are -0.20and -0.31 v., in close agreement with the values -0.21and -0.35 v. for the corresponding t-butylnitrobenzenes.52

Substitution of methyl groups for amino hydrogens in the three N,N-dimethyl-4-nitroanilines gives a system which should be more susceptible to steric effects. On the basis of spectrophotometric data<sup>3</sup> for N,N-dimethyl-4-nitroaniline it does seem that significant p-quinoid interaction does occur between the amino and nitro groups. Furthermore the  $\sigma^n$  values<sup>46</sup> and half-wave potentials for N-N-dimethylnitroaniline and p-nitroaniline are nearly identical. Thus in analogy to the reduction of p-nitroaniline we would suggest that there is a loss in mesomeric interaction of approximately 2 kcal. going from N,N-dimethyl-4nitroaniline to the corresponding anion radical. The insertion of a t-butyl group ortho to the N,N-dimethylamino group in 2-t-butyl-N,N-dimethyl-4-nitroaniline decreases the half-wave potential to very near the value for nitrobenzene. This result is the most striking single observation of the entire nitroaniline polarographic series. We attribute the abrupt decrease to the absence of mesomeric interaction in the neutral molecule; consequently the 2-kcal. barrier associated with addition of an electron to the quininoid form as in p-nitroaniline is no longer encountered. The half-wave potential on insertion of a second tbutyl group, this time ortho to the nitro group, 2,5di-t-butyl-4-nitroaniline, is more negative as one would expect for a nonplanar nitro group. In fact,  $E_{1/2}$  is

(47) K. N. Trueblood, E. Goldish, and J. Donohue, Acta Cryst., 14, 1009 (1961).

(48) Reference 3, p. 99.

(49) P. C. Lauterbur, J. Chem. Phys., 38, 1415 (1963).
(50) B. M. Wepster, Rec. trav. chim., 76, 335, 357 (1957)

(51) J. B. Wigers, M. A. Hoefnagel, P. E. Verkade, H. Visser, and B. M.

Wepster, *ibid.*, **77**, 491 (1957). (52)  $\Delta E_{if2}$  for 2,4,6-tri-*i*-butylnitrobenzene,  $-0.35 v_{i,j}$  was used since data for 2,6-di-*i*-butylnitrobenzene are not available.

<sup>(42)</sup> These estimates must be considered as approximate with uncertainties of the order of at least  $\pm 5^\circ.$ 

<sup>(45)</sup> This estimate is based on the fact that in nitrodurene the nitrogen coupling is approximately 0.8 of what appears to be a totally decoupled nitro group, 26 G., in the 2-methylnitropropane abion. Consequently we have taken -0.12 v, to be 0.8 the  $\Delta E_S$  for total decoupling.

 $-1.38~\mathrm{v.}$  compared with  $-1.36~\mathrm{v.}$  for the corresponding nitroben zene.

It thus appears that a reasonable rationalization of the half-wave potentials of the nitroaniline series is possible on the assumption of significant *para* interaction between amino and nitro groups in the neutral unhindered molecules. Half-wave potentials of certain hindered species correlate rather well with values for the corresponding nitrobenzene.

It should be noted that we have made no assertions about the intimate reduction mechanism in the sense of the exact spatial disposition of molecules with respect to the electrode surface. Such comments are not warranted on the basis of these thermodynamic data. Kinetic studies, however, might shed some light on the subject.

Electron Spin Resonance Data for Substituted Nitrobenzene Anion Radicals.--As is well known, hyperfine structure in the e.s.r. spectra of radical species arises from the Fermi contact term in the dipolar interaction between the electronic and nuclear spins, the magnitude of the interaction providing direct information concerning the electronic structure of the radical. However, in  $\pi$ -electron radicals, while the probability of locating a  $\pi$ -electron in association with a particular core can never be less than zero, the local value of the  $\pi$ -electron spin magnetization may in principle either oppose the net molecular spin magnetization or be parallel with it. It has been amply demonstrated<sup>53</sup> that both situations occur experimentally with both signs of spin density often occurring in the same radical. Properly speaking, therefore, there is no relationship between the  $\pi$ -electron spin density obtained from isotropic hyperfine coupling constants and the  $\pi$ -electron charge density which has been the subject of such considerable discussion in the chemical literature. This fact somewhat complicates the interpretation of hyperfine coupling data in terms of intuitive chemical notions concerning inductive and electromeric effects. However, one may adopt the working principle, subject to further experience, that the ring charge and spin densities are similar and behave in a similar fashion on perturbation of the  $\pi$ -electron system under discussion. This supposition is meant to apply to both normal ring positions and those with negative spin density, as the latter positions are generally possessed of small coupling constants, and in general show very low charge densities as well. On the basis of the self-consistent field (s.c.f.) calculations below, this supposition does not appear to be entirely trustworthy for the heteroatoms.

Throughout this study we have supposed that the twisting of the nitro group which is known to occur in neutral aromatic nitro compounds containing bulky groups adjacent to the nitro group also occurs to some extent in the corresponding anion radicals. Experimentally it is observed that steric hindrance of the nitro group results in an increase of the nitrogen hyperfine coupling constant accompanied by a decrease in the hyperfine interactions of ring or methyl hydrogens. On the basis of these observations, we suggested<sup>9</sup> a simple model for the hindered nitro aromatic anions in which the nitro group was sterically decoupled from the benzene ring with a consequent localization of charge on the nitro group. Although, as mentioned above, the spin density distribution is not the same as the  $\pi$ -electron charge distribution, the simultaneous decrease of hyperfine coupling at all ring positions makes it likely that the effect observed is related to a charge transfer from ring to nitro group

(53) T. H. Brown, D. H. Anderson, and H. S. Gutowsky, J. Chem. Phys., **33**, 720 (1960).

rather than a charge redistribution taking place on the nitro group. Such an effect is easily represented in terms of a functional relationship between the steric hindrance and the coupling between the  $\pi$ -electrons on the ring and the nitro group.

The fact that there exists a low-lying spectral transition in *neutral* nitrobenzene which possesses strong *charge transfer* character in the sense ring  $\rightarrow$  nitro group<sup>54a,b</sup> implies that a decrease in the strength of interaction between ring and nitro group in the *anion* will produce transfer of charge in the direction indicated by the behavior of the hyperfine coupling constants. A decrease in the strength of  $\pi$ -system interaction between ring and nitro group on steric hindrance is, of course, just what is expected intuitively and has been a familiar part of organic chemistry for some time.

The problem of obtaining theoretical estimates of spin density in the nitrobenzene anions is examined below by several methods, including the Hückel scheme. The results of these computations are discussed below as a guide toward the interpretation of experimental data and are not to be taken to represent an attempt to compile an exhaustive set of theoretical calculations.

In the usual semiempirical forms of molecular orbital theory, the interaction between ring and nitro group appears only in the resonance integral,  $\beta_{\rm NC}$ , between the nitrogen atoms and its adjacent carbon. If the steric hindrance is represented in terms of a twist angle,  $\theta$ , about the carbon-nitrogen bond axis,  $\beta_{\rm NC}$  takes the form

$$\beta_{\rm NC} = \beta_{\rm NC}^{\circ} \cos \theta \tag{1}$$

Hückel calculations were carried out as the first stage in the approximate unrestricted Hartree–Fock s.c.f. calculations discussed below, with the results shown in Fig. 14 and in Table III for the nitrobenzene anion. Parameters were selected to approximate ring spin densities calculated from a relation of the form below where  $a_{\rm H}$  is the coupling constant for a

$$a_{\rm H} = -23\rho_{\rm C}^{\pi} \tag{2}$$

hydrogen in an o- or p-position, and  $\rho_{\rm C}^{\pi}$  is the  $\pi$ -electron spin density on the contiguous carbon. Table III shows the dependence of the Hückel ring spin den-

#### TABLE III

### INFLUENCE OF HÜCKEL HETEROATOM PARAMETERS ON CALCULATED SPIN DENSITIES OF *o*- and *p*-Positions in Nitrobenzene Anion

Spin density ortho/para	αN	αO	β <sub>NO</sub>	αadj.C
0.147/0.173		Exper	imental	
. 101/ . 124	0.2	0.5	0.7	0.0
.108/ .178	. 2	0.5	1.0	. 0
.117/ .143°	. 5	1.0	1.0	. 2
.097/106	1.0	1.0	1.0	.2
.133/ .178	1.0	1.0	1.3	. 5
.066/ .073	2.0	1.0	1.0	. 2
.067/ .067	2.0	1.0	1.0	. 0
$.106/$ $.127^{b}$	2.2	1.4	1.69	.0

<sup>a</sup> These parameters used in calculation shown in Fig. 14 as "Hückel II" and also in limited configuration interaction of Table IV. <sup>b</sup> These parameters are essentially identical with those used by P. H. Rieger and G. K. Fraenkel, J. Chem. Phys., **39**, 609 (1963), for calculation on nitrobenzene anion in dimethylformamide.

sities on the heteroatom parameters. A very considerable diversity of opinion exists in the literature as to the "proper" value of these parameters: in view of the nature of the Hückel theory no attempt is made

(54) (a) S. Nagakura and J. Tanaka, *ibid.*, **22**, 236 (1954), and later papers of this series; (b) S. Nagakura, *Pure Appl. Chem.*, **7**, 79 (1963).

here to consider the zero angle computation as more than the product of a curve-fitting exercise. Qualitatively, however, the spin densities computed as a function of angle confirm previous expectations as to the appropriateness of the model.

There is also an acceptable degree of consistency between angles of twist estimated from the *ortho-para* coupling constant ratios and from the amount of charge withdrawn from the *p*-position. It is to be noted that  $\pi$ -electron spin and charge densities are identical within the framework of the Hückel scheme.

A principal defect of most naïve forms of molecular orbital calculations is the fact that no account is taken of coulombic correlations between electrons. While partial compensation for this neglect arises from the Fermi correlation between electrons of the same spin, the antisymmetrization of a simple LCAO product function does not correlate electrons with opposite spin. Thus, simple calculations of the Hückel type cannot produce theoretical spin densities which are negative. This situation may be remedied by: (a) the inclusion of configuration interaction among  $\pi$ electrons to some approximation, or (b) the utilization of single LCAO determinantal wave functions composed of different orbitals for different spins, or (c) the use of the valence bond method, which takes a somewhat more detailed view of the molecule's electron structure already in its zeroth order of approximation. By now, many moderately successful calculations at the semiempirical level have been made of spin densities in  $\pi$ -electron radicals using all of the above methods. Calculations related to methods (a) and (b) above are discussed below.

Semiempirical molecular orbital theories of configurational interaction in  $\pi$ -electron species on the basis of the LCAO approximation have been used by Pariser and Parr and others.55 It is well known that use of self-consistent field wave functions in configuration interaction calculations effects a considerable simplification,<sup>56</sup> and accordingly the following computational scheme was first tried. From the experience of Brickstock and Pople,57 Brion, Lefebvre, and Moser,58 and McLachlan,59 the Hückel orbitals for alternant hydrocarbons are known to be excellent approximations to the self-consistent field orbitals, and it is therefore suggested to extrapolate this fact to the present systems. Using the semiempirical electrostatic integrals of Pariser and Parr<sup>60</sup> where relevant, and computing the remaining from the charged sphere method discussed by I'Haya,61 spin densities were calculated for many of the species under discussion with reasonable results. The result of one such calculation is shown in Table IV.

The calculational technique used by Rieger and Fraenkel<sup>62</sup> is closely related to this one. Their results are discussed subsequently.

The validity of the assumption concerning the negligibility of the difference between the Hückel orbitals and the true s.c.f. orbitals is open to test *via* a computation of the full configurational interaction to first order in perturbation theory. Such a computation was undertaken as a check. Unfortunately, the inclusion of the remaining single electron excita-

(55) R. Daudel, R. Lefebvre, and C. Moser, "Quantum Chemistry; Methods and Applications," Interscience Publishers, Inc., New York, N. Y., 1959, p. 499 ff.

- (56) P. O. Lowdin, "Advances in Chemical Physics," Vol. II, Interscience Publishers, 1nc., New York, N. Y., 1959, p. 283.
  - (57) A. Brickstock and J. A. Pople, Trans. Faraday Soc., 50, 901 (1954).
  - (58) H. Brion, R. Lefebvre, and C. Moser, J. chim. phys., 84, 363 (1958).
     (59) A. D. McLachlan, Mol. Phys., 3, 233 (1960).
  - (60) R. A. Pariser and R. G. Parr, J. Chem. Phys., 21, 466, 767 (1963).
  - (61) Y. 1'Haya, J. Am. Chem. Soc., 81, 6120, 6127 (1959).
  - (62) P. H. Rieger and G. K. Fraenkel, J. Chem. Phys. 39, 609 (1963).

TABLE IV

CONFIGURATIONAL INTERACTION CORRECTIONS TO HÜCKEL SPIN DENSITIES IN NITROBENZENE ANION<sup>4</sup>

Molecular position	Hückel	Correction	Total
ortho	0.177	0.039	0.156
meta	. 007	058	051
para	.142	. 083	. 225
Adjacent carbon	.055	083	028
Nitrogen	.283	.018	.301
Oxygen	. 136	. 010	. 146

<sup>a</sup> Only those excited states are considered here which would correct with the ground state to first order in perturbation theory, *assuming* Brillouin's theorem to hold.

tions destroyed any semblance of agreement between theory and experiment. The reason for this is not known, but undoubtedly difficulty arises from at least two sources: First, the use of first-order perturbation theory for the modified wave function is open to some objection on the basis of the magnitude of the corrections obtained. Second, as would be expected, it was found that considerable differences existed between Hückel coefficients which gave a good spin density in the Hückel theory and the Hückel-like core integrals required to produce a reasonable s.c.f. description of the anion (vide infra). For this reason one may suppose that further work on the full configurational interaction approach may be expected to produce more reasonable results: the present configuration interaction calculations were only carried out with two or three sets of parameters. Even though this result is essentially negative, we feel that it is instructive and therefore worth presenting in passing.

Semiempirical s.c.f. calculational schemes based on simple ''nearest-neighbor'' LCAO theory have been developed and utilized in calculation of spin densities in hydrocarbons<sup>59</sup> and hetero molecules.<sup>63</sup> The methods are described in some detail in a series of papers by Pople<sup>57,64-66</sup> and co-workers and will not be the subject of detailed discussion here.

The comments of Löwdin<sup>67</sup> on unrestricted Hartree– Fock theory apply to the present approximate scheme as well. The calculational scheme is based on a model in which the orbitals for electrons of one spin are allowed to be different from those characterizing electrons with the opposite spin. The resultant determinantal wave function is not an eigenfunction of  $S^2$  and hence does not represent a state of definite multiplicity, but projection operator techniques<sup>68</sup> may be used to select pure spin states.

As in any semiempirical theory, one is beset by the problem of choice of parameters. There are two types of parameters which are to be chosen in the present calculation, one set of which may be characterized as Hückel-like parameters describing the interactions of the  $\pi$ -electrons and the partially screened cores, and a second set describing interactions among the electrons. The technique adopted here was to regard the coulomb interactions among electrons as fairly firmly based in theory, and to regard the core integrals as arbitrarily adjustable. Spin densities were then fitted to the untwisted nitrobenzene anion by choosing the latter parameters and using the impure spin state function as generated by the s.c.f. program without annihila-

(63) L. C. Snyder, private communication.
(64) J. A. Pople, Trans. Faraday Soc., 49, 1375 (1953); Proc. Roy. Soc.
(London), A233, 233 (1955).

- (65) J. A. Pople and R. K. Nesbet, J. Chem. Phys., 22, 571 (1955).
- (66) J. A. Pople and P. Schofield, Proc. Roy. Soc. (London), A233, 241 (1955).
- (67) Reference 56, pp. 307-315.

(68) A. T. Amos and G. G. Hall, Proc. Roy. Soc. (London), A263, 483 (1961).



Fig. 14.—Calculation of spin (charge) density for nitroaromatic anion radical as function of twist angle. Left ordinate relative spin density at *p*-position shown in solid lines *vs.* twist angle in degrees. Right ordinate: charge density on nitro group shown in dash-dot-dash lines *vs.* twist angle in degrees. Parameters in calculations: Hückel I,  $\alpha_N = 2.2$ ,  $\alpha_O = 1.4$ ,  $\beta_{NO} = 1.69$ ,  $\beta_{NC} =$  $1.2 \cos \theta$  (these parameters are essentially those used by Rieger and Fraenkel<sup>82</sup>); Hückel II,  $\alpha_N = 0.5$ ,  $\alpha_O = 1.0$ , all  $\beta = 1.0$ except  $\beta_{NC} = \cos \theta$ ,  $\alpha_{adjacent carbon} = 0.2$ ; s.c.f.,  $U_N = 6.0$ ,  $U_O =$ 1.0,  $\beta = 1$  exce = pt  $\beta_{NO} = 0.7$ ,  $\alpha_{adjacent carbon} = 0.5$ .

tion. Several hundred sets of parameters were examined in an attempt to evaluate the uniqueness of fit. The particular parameters used are tabulated below. The only modification necessary to the scheme of Pople and Nesbet<sup>65</sup> is the inclusion of the nonunity core charge of the nitrogen. Structures such as those below show that +2 is an appropriate choice for this core charge.



Simple calculations of this kind are capable of producing negative spin density, and in fact one expects negative spin density on positions contiguous to those bearing excessive amounts of positive spin density. The spin density distribution in nitrobenzene anion shown in Fig. 15 represents the final spin density after 25 iterations of the computation. Bond orders and charge distributions are also shown in Fig. 15. Calculations as a function of twist angle are summarized in Fig. 14.

The negative spin density at the *m*-position is a "result" of the high concentration of  $\pi$ -electron charge at the o- and p-positions in the zeroth order of iteration. The rather low spin density on the nitrogen in turn results from the presence of excessive positive spin density on the oxygen atoms and is to be contrasted with the result that the electronic charge is almost 1.5 units on this site. Snyder<sup>63</sup> has carried out an independent semiempirical s.c.f. investigation of the type reported here, and finds oxygen spin densities lower and the nitrogen spin density higher than reported in Fig. 15. The numerical values of the singleelectron core parameters for the heteroatom part of the molecule were chosen by Snyder to match optical data on nitromethane, and so represent a more satisfying response to the need for empirical input. The differences between these sets of parameters are discussed in more detail in the Appendix, but the principal result emphasizes that a choice of parameters which fits spin densities on ring positions does not necessarily yield information regarding spin densities on the nitro group. Until this point of uncertainty is resolved by further theoretical work, an attempt to



Fig. 15.—S.c.f. calculation for nitrobenzene anion: spin density given at atomic position; charge-density given at atomic position in parentheses; bond order given on left-hand side of figure adjacent to the bond.



Fig. 16.—Experimental data vs. twist angles. Left ordinate: relative para spin densities (see text for definition) vs. twist angle. Experimental point for no. 11 taken from ref. 62. Right ordinate: Nitro group nitrogen coupling constant divided by 26. Numbers on plot refer to position in Table I.

obtain twist angles from nitrogen coupling constants appears to be hazardous.

For purposes of comparison, relative spin densities at the *p*-carbon atom were collected for a number of anions in Table I and are plotted in Fig. 16 (circles) *vs.* twist angles. The relative spin density is defined as the ratio of the *p*-hydrogen coupling constant in the hindered anion to the *p*-hydrogen coupling constant for nitrobenzene anion, 3.97 G. Twist angles as estimated by Wepster<sup>3</sup> for the corresponding neutral molecule are used. The solid line in Fig. 16 does resemble the solid lines in Fig. 14.

The "buttressing" of a single methyl group in the 2position by a second methyl group in the 3-position appears to be a minor effect (compare compounds 6, 7, and 8, and 9, 10, and 11 in Table I). Apparently it is energetically more favorable for the hindrance produced by a single methyl group adjacent to a nitro group to be relieved by a small in-plane deflection of some sort rather than by a twist deformation at the expense of  $\pi$ -electron energy.

Calculations summarized in Fig. 14 suggest that the charge is increasingly localized on the nitro group as the twist angle increases. A direct comparison of these calculations with the experimental nitrogen

coupling constants is not possible for two reasons: (a) we have no unequivocal basis for choosing a particular twist angle, and (b) a detailed understanding of the terms contributing to the nitrogen coupling constant is not available. With these limitations acknowledged, the arbitrary function,  $a_N/26$ , is plotted in Fig. 16 (squares) vs. twist angles which were estimated as described above. The quantity  $a_N/26$  was chosen since it is known that the nitrogen coupling constants in aliphatic nitro anions, such as number 15, Table I, are close to 26 G. In such aliphatic anions the charge is taken to be entirely localized on the nitro group. We do not mean to imply that the ratio  $a_{\rm N}/26$  accurately gives the charge (spin) density on the nitro group of the hindered aromatic anion radicals. Nevertheless, the general shape of the dot-dash-dot curve in Fig. 16 is not entirely dissimilar from the dash-dotdash curves in Fig. 14.

A rationalization of the nitro group nitrogen coupling constant in terms of  $\pi$ -spin densities has recently been developed by Rieger and Fraenkel.<sup>62</sup> Spin densities were calculated using Hückel theory with an approximate configuration interaction correction similar to that discussed above. Coulomb and resonance integrals were adjusted empirically to obtain a best fit of experimental hydrogen coupling constants while at the same time providing a fit to the following equation for the nitrogen coupling constant.

$$a_{\rm N} = 99.0\rho_{\rm N}{}^{\pi} - 71.6\rho_{\rm O}{}^{\pi} \tag{3}$$

In this equation  $\rho_N^{\pi}$  and  $\rho_0^{\pi}$  are the  $\pi$ -spin densities on the nitrogen and oxygen atoms, respectively. Experimental data from more than fifteen substituted nitrobenzene anion radicals were included in the correlation. These authors have extended their calculations to include anion radicals where the nitro group is twisted out of the plane of the ring by expressing the carbon-nitrogen resonance integral as a function of the twist angle

$$\beta_{\rm CN} = 1.2 \cos \theta \tag{4}$$

Calculated nitrogen coupling constants evaluated as a function of  $\theta$  qualitatively agree with the observed coupling constants presented here. Interestingly enough, the calculation for the limiting case of  $\theta$  = 90° gives a value of 24.4 G.<sup>69</sup> This value is similar to the nitrogen coupling constant in several nitroalkane anion radicals.<sup>70</sup>

Examination of experimental data in Table I for dinitrobenzene anions shows that the trend on twisting of the nitro groups is generally the same as for mononitro anion radicals. Twisting *m*-dinitro groups (compound 17) increases the nitrogen coupling constants from 4.68 to 8.19 G. Similarly for the *o*-dinitrobenzene anions we note an increase of the nitrogen coupling constant from 3.2 to 5.8 G. on replacement of ring hydrogens by bulky methyl groups. The sum of the two hydrogen coupling constants decreases from 2.05 to 1.68 G.

The nitrogen coupling constant for the anion of the fully methylated p-dinitrobenzene, 8.7 G., is strikingly larger than for the "flat" anion, 1.74 G. Introduction of only two methyl groups giving the 2,3-dimethyl-1,4-dinitrobenzene radical apparently provides only a minor steric perturbation since the nitrogen coupling constant only increases to 2.14 G.

By placing methyl groups di-*ortho* to one of the nitro groups in *p*-dinitrobenzene, an anion radical anion is obtained which has both a flat nitro group and a twisted nitro group. Qualitatively, one would suppose that the twisted nitro group would be an energetically unfavorable electron site. Experimentally the anion radical of 2,6-dimethyl-1,4-dinitrobenzene shows a nitrogen coupling constant of 5.66 G. for the flat nitro group.<sup>71</sup> The coupling constant for the nitrogen in the 1-nitro group is only 0.14 G. A qualitative rationalization of the hydrogen coupling constants can be done by examining the transition between the limiting cases of *p*-dinitrobenzene anion and the nitrobenzene anion. Thus as the 1-nitro group in the 2,6-dimethyl-1,4dinitrobenzene anion is decoupled from the aromatic system the 1-carbon atom becomes progressively more similar to the p-carbon atom in the nitrobenzene anion. Similarly, the 2,6-ring positions take on the characteristics of the *m*-carbons in nitrobenzene anion. Using eq. 2 and the known proton coupling constants, the spin density on the "meta-like" carbons decreases from 0.049 in p-dinitrobenzene anion to a small negative value in nitrobenzene anion. The observed value in the 2,6-dimethyl-1,4-dinitrobenzene anion is  $\leq 0.007$ . In the same sense the spin density in the 3,5ring positions increases from 0.049 in p-dinitrobenzene anion to 0.148 in the *o*-positions in nitrobenzene anion. The spin density in the present case is 0.108.

The extent to which coupling constants do undergo the changes discussed above will surely depend on the size of the blocking group. Thus in the anion of 2,6di-*t*-butyl-1,4-dinitrobenzene the larger nitrogen coupling constant, 8.8 G., is only 15% smaller than  $a_N$  in nitrobenzene anion. It is expected that there will be some residual inductive effect from the twisted nitro group even if the twist angle is close to 90°. The 3,5-ring hydrogen coupling constant increases to within 10% of the limiting value in nitrobenzene anion.

Remarkably enough the coupling constant for the hindered nitro group nitrogen increases from 0.14 to 0.72 G. with greater blocking. Qualitatively we would expect the spin density on the hindered nitro group to decrease even further as larger blocking groups are introduced. However, the spin density on the 1carbon atom is expected to increase toward the limit of 0.17 as in nitrobenzene anion. We interpret the stated increase of hindered nitrogen coupling constant as evidence for a contribution to the net nitrogen coupling constant from spin density on the contiguous carbon atom. This contribution is only obvious if the spin densities on the nitrogen and oxygen atoms are small as appears to be the case for the 1-nitro group in the 2,6-di-t-butyl-1,4-dinitrobenzene anion. The spin density on the 1-carbon atom may be crudely estimated as 90% of the value of 0.17 for the *p*-carbon in nitrobenzene anion. Thus the interaction constant which describes the contribution made to the nitro group nitrogen coupling constant by the spin density on the adjacent carbon atom in the rationalization of Rieger and Fraenkel,  ${}^{62}Q_{\rm CN}{}^{\rm N}$ , is estimated as  $-5{\rm G}$ .  ${}^{72}$ 

Rieger and Fraenkel<sup>62</sup> have commented that this constant is expected to be small in comparison to the other terms in eq. 3. The calculated nitrogen coupling constants for the case of twisted and untwisted nitro groups in the same anion obtained by Rieger and Fraenkel<sup>62</sup> are in qualitative agreement with results presented above.

Electron Spin Resonance of Substituted Nitroaniline Anion Radicals.—Investigation of the e.s.r. spectra of a series of substituted p-nitroaniline anion radicals was undertaken to elucidate the nature of steric effects on

<sup>(69)</sup> This coupling constant was calculated for dimethylformamide solution. The solvent effect is discussed in ref. 62.

<sup>(70)</sup> L. H. Piette, P. Ludwig, and R. N. Adams, J. Am. Chem. Soc., 83, 3909 (1961); 84, 4212 (1962).

<sup>(71)</sup> Unambiguous assignment to this molecular position was possible on the basis of data for the nitrogen-15 labeled compound.

<sup>(72)</sup> The negative sign is not unambiguously assigned but may be supported by qualitative arguments.

the amino and dimethylamino groups; e.s.r. data for both of these groups are available for cation radicals. Melchior and Maki<sup>73</sup> studied the *p*-phenylenediamine cation radical; the correct assignment for the N,N,N',-N'-tetramethyl-*p*-phenylenediamine (Wurster's Blue) cation has recently been given.<sup>74</sup> However, since both amino and dimethylamino groups are relatively nucleophilic, no studies are available for the aniline and N,N,dimethylaniline anion radicals. In the present case we are using the nitro group as an electron "sink" which has a stabilizing effect on the anion but at the same time spin density is transmitted to the amino group. Utilization of a nitro group to "probe" the behavior of *p*-substitutents is rather generally applicable.

For the anion radicals of compounds 4, 5, and 8 in Table II where the nitro group itself is hindered, the expected increase of the nitro group nitrogen coupling constant is noted. Coupling constants for anion radi-cals of compounds 2 and 3, Table II, are essentially identical with those for the unsubstituted nitroaniline anion, despite the introduction of blocking groups ortho to the amino group. We attribute the absence of any steric perturbation to the fact that the amino group is too small to be affected by the bulky ortho groups. This observation parallels the conclusions of previous investigators for similar neutral molecules. 48-51 It is of interest that the equality of the amino nitrogen coupling constant and the amino hydrogen coupling constant is retained in the anion of compound 4, Table II, even though twisting the nitro group has withdrawn spin density from the ring positions.

In the N,N-dimethylnitroaniline series the crucial test for the occurrence of a steric effect is the data (no. 7, Table II) for the anion radical of 2-t-butyl-N,Ndimethyl-4-nitroaniline. It is known<sup>75</sup> that resonance in the neutral molecule has been perturbed. Hyperfine coupling constants for the anion radical represent strong evidence for a steric effect. The decrease of the nitro group nitrogen coupling constant from 11.7 G. in the N,N-dimethyl-4-nitroaniline anion to 10.7 G., a value only somewhat larger than  $a_N$  for nitrobenzene anion, is taken as evidence for partial decoupling of the N,N-dimethylamino group from the ring. The amino nitrogen coupling constant decreases from 1.1 G. in N,N-dimethyl-4-nitroaniline anion to 0.5 G. in the hindered anion. Similarly, the methyl hydrogen coupling constant decreases from 0.7 to 0.2 G. These observations are consistent with the suggestion that the N,N-dimethylamino group is sufficiently large to be twisted out of the plane of the benzene ring by an adjacent t-butyl group.

**Carbon-13 Coupling Constants.**—In addition to the carbon-13 coupling constants presented in this paper, 7.6 G. for nitrodurene anion and 9.8 G. for 3,5-di-*t*-butyl-4-nitroaniline anion, we have observed a coupling constant of 8.2 G. for two equivalent carbon sites in the anion radical of 2,3,5,6-tetraisopropylnitrobenzene.<sup>76</sup> Observation of coupling with two equivalent carbon sites is a comparatively surprising result since the radicals for which carbon-13 couplings were observed have small ring proton coupling constants. Karplus and Fraenkel<sup>77</sup> have presented a detailed rationalization of carbon-13 hyperfine coupling constants in aromatic hydrocarbon radicals which emphasizes that the coupling constant for a particular ring position is significantly dependent on spin densities on adjacent

(73) M. T. Melchior and A. H. Maki, J. Chem. Phys., **34**, 471 (1961).
(74) J. R. Bolton, A. Catrington, and J. dos Santos-Veiga, Mol. Phys., **5**, 615 (1963).

(75) Reference 3, p. 117.

(77) M. Karplus and G. Fraenkel, J. Chem. Phys., 35, 1312 (1961).

positions. Further data must be obtained before a rationalization for substituted nitrobenzene anions can be attempted.

### Appendix

Discussion of Self-Consistent Field Calculations.— The  $\pi$ -electron systems in nitrobenzene and dinitrobenzene anions were treated using the semiempirical scheme of Pople,<sup>64</sup> discussed in detail in the paper by Pople and Schofield,<sup>66</sup> and modified for radicals according to the prescription of Pople and Nesbet.<sup>65</sup>

Writing the Hamiltonian for the  $\pi$ -electrons as

$$\mathfrak{K} = \Sigma \ \mathfrak{K}; \ \mathrm{core} \ + \sum_{i \ < \ j} r_{ij}^{-1} \tag{A1}$$

and with the usual LCAO orbitals (Greek indices being reserved for core numbering)

$$\phi_i = \sum_{\mu} C_{i\mu} \chi_{\mu} \qquad (A2)$$

one arrives at the following set of equations for electrons of spin  $\alpha$ 

$$\sum_{\nu} F_{\mu} \nu^{\alpha} C_{i\nu}{}^{\alpha} = \epsilon_{i}{}^{\alpha} C_{i}{}^{\alpha}{}_{\mu}$$
(A3)

where

$$F_{\mu\mu}{}^{\alpha} = U_{\mu\mu} + P_{\mu\mu}{}^{\beta}\gamma_{\mu\mu} + \sum_{\sigma \neq \mu} (P_{\sigma\sigma}{}^{\alpha} + P_{\sigma\sigma}{}^{\beta} - Z_{\sigma})\gamma_{\mu\sigma}$$

$$F_{\mu\nu}{}^{\alpha} = U_{\mu\nu} - P_{\mu\nu}{}^{\alpha}\gamma_{\mu\nu}$$

$$P_{\mu\nu}{}^{\alpha} = \Sigma C_{i\mu}{}^{\alpha}C_{i\nu}{}^{\alpha}$$
occupied m.o.'s

and where the core parameters  $U_{\mu\mu}$  represent the energy of an electron on site  $\mu$  (in atomic orbital  $\chi_{\mu}$ ) in the field of its core and the partially-screened cores of the other atoms in the molecule.

 $U_{\mu\nu}$  is taken to be zero for nonbonded atoms. The parameters  $\gamma_{ij}$  are the 1- and 2-center integrals involving coulomb repulsions between electrons which remain after all integrals of the form  $\langle \mu \lambda | r_{12}^{-1} | \gamma \sigma \rangle$  are neglected for which  $\mu \neq \gamma$  and  $\lambda \neq \sigma$ . This is an approximation of uncertain validity<sup>78</sup> for species of the sort described here. The equation A3 is to be solved iteratively until self-consistency is obtained.

A program was written by J. L. R. for carrying out this computational scheme using a Burroughs 220. Matrices were diagonalized using the Jacobi method, and convergence was considered to have been obtained when the total  $\pi$ -electron energy changed by less than one part in 10<sup>6</sup> between adjacent cycles of iteration. As would be expected from the variational principle, the spin densities are changing at this point by a small amount in the *third* figure. The computation was started from the Hückel orbitals, and the total number of iterations necessary to produce self-consistency ran on the average 20 to 25 cycles.

The parameters  $\gamma_{ij}$  utilized in the calculations were taken where possible from the literature Typical electrostatic repulsion parameters utilized for flat nitrobenzene anion are shown in Table AI They are given in units of  $\beta_{CC}$  (equal to -2.39 e.v.).

The oxygen self-energy integral was taken to be either 4.96 (semiempirical value of I Haya<sup>§1</sup> for phenol oxygen) or 5.69 (theoretical value of Hurley<sup>79</sup> for CO<sub>2</sub> oxygen), and its variation between these limits produced only minor effects on the distribution of spin density.

Coulomb repulsion integrals not available in the literature were computed using the uniform charged sphere approximation and the extrapolation technique

(78) See R. McWeeny and T. E. Peacock, Proc. Phys. Soc. (London), A70, 41 (1957).

<sup>(79)</sup> A. C. Hurley, Rev. Mod. Phys., 32, 400 (1960).

TABLE AI COULOMB REPULSION INTEGRALS USED IN SEMIEMPIRICAL S.C.F. CALCULATION (IN UNITS OF -2.39 E.V.)

1	2	3	4	5
-4.4100	-2.0400	-1.1900	-2.2800	-3.1000
-2.0400	-4.4100	-2.4500	-3.1000	-2.2800
1.1900	-2.4500	-5.6900	-2.1100	-1.5700
-2.2800	-3.1000	-2.1100	-4.4100	-3.1000
-3.1000	-2.2800	-1.5700	-3.1000	-4.4100
-1.3000	-3.0900	-3.7000	-2.2800	-1.5100
-1.1900	-2.4500	-2.6700	-1.6400	-1.2400
-2.2800	-3.1000	-1.6400	-2.2800	-2.0400
3.1000	-2.2800	-1.2400	-2.0400	-2.2800
	6	7	8	9
— 1 .	3000 - 1	.1900 - 2	.2800 -3	3.1000
-3.	0900 - 2	-3	.1000 - 2	2.2800
-3.	7000 - 2	-1	.6400 -1	.2400
-2.	2800 - 1	-6400 - 2	.2800 - 2	2.0400
<u> </u>	5100 -1	.2400 - 2	.0400 - 2	2.2800
5.	1400 - 3	-2	.2800 -1	.5100
-3.	7000 —ā	-2	-100 - 1	1.5700
-2.	2800 - 2	-4	.4100 -2	3.1000
-1.	5100 - 1	5700 —3	-4000 - 4	1,4100

discussed in detail by I'Haya.<sup>61</sup> For moderate intercenter distances, this technique gives the same results as the inverse-distance approximation of Pople, which latter technique was accordingly used to estimate *proportional* decreases in ring-nitro group coulomb repulsion integrals on twisting of the nitro group.

repulsion integrals on twisting of the nitro group. The parameters  $U_{\mu\mu}$  and  $U_{\mu\nu}$  for the nitro group and the adjacent carbon were regarded as adjustable and were chosen to fit the experimental spin density on the ring system of flat nitrobenzene anion as closely as possible. It is apparent from the excessive negative spin density at the *m*-position that the electron correlation is somewhat excessive. No combination of parameters was found which reduced this discrepancy while maintaining agreement otherwise. The obvious remedy for a difficulty of this sort lies in the reduction of the various coulomb repulsion integrals involved. A uniform scale reduction of 15 to 25% in the  $\Gamma$ matrix is necessary to produce this effect, but is of such dubious physical significance in view of the approximate nature of the theory that it was not pursued further.

A second symptom of the excessive amount of electronic correlation is the intuitively disturbing small value of spin density of the nitrogen atom. For this reason, and for reasons mentioned above, no attempt was made to obtain an explicit expression for the nitrogen hyperfine coupling in terms of the associated spin densities.

Table AII shows the matrix U used in the final spin density computation for flat nitrobenzene anion. The

large value of the diagonal element for nitrogen reflects the highly electronegative character of the nitrogen core, compared to the oxygen and the carbon. The value of the nitrogen-oxygen resonance integral strongly influences the final spin density. The value finally chosen represents the value obtained if one assumes proportionality between this parameter and overlap integrals. It is to be expected that off-diagonal terms in U in the Pople theory will bear more resemblance to the corresponding Hückel matrix elements than will the diagonal elements.

TABLE AII

Core Integrals Used in Semiempirical S.c.F. Calculation (in Units of -2.39 E.v. and with Zero at  $\alpha_{\rm e}$ ). The Numbering Scheme Is that of Table AI

1	2		3		4	5
0.00000	0.0000	$\overline{0.0}$	00000	$\overline{0.0}$	00000	1.00000
. 00000	. 50000	0.0	00000	1.(	00000	0.0000
. 00000	. 0000	) 1.0	00000	0.0	00000	0.0000
.00000	1.00000	0.0	00000	0.0	00000	1.00000
1.00000	0.0000	).(	00000	1.(	00000	0.0000
0.00000	1.00000	) .:	70000	0.0	00000	. 00000
. 00000	0.0000	).(	00000	. (	00000	. 00000
. 00000	1.0000	) .(	00000	. (	00000	. 00000
1.00000	0.0000	), (	00000	. (	00000	. 00000
	6	7		8		9
0.0	0000	0.00000	0	.00000	1.	00000
1.0	0000	.00000	1	.00000	0.	00000
0.7	0000	.00000	0.	.00000		00000
. 0	0000	.00000		.00000		00000
. 0	0000	.00000		.00000		00000
6.0	0000	.70000		.00000		00000
0.7	0000	L.00000		.00000		00000
. 0	0000 (	).00000		00000	1.	00000
. 0	0000 (	0.00000	1	.00000	0.	00000

The parameters used by Snyder<sup>63</sup> and obtained by reference to spectral properties of nitromethane differ only negligibly from those used here with the exception of the choice of the oxygen core integral,  $U_{0}$ , and the nitrogen–oxygen resonance integral,  $U_{NO}$ . Snyder chose  $U_{0} = 2.0$  and  $U_{NO} = 1.55$ .

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