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Electron-Spin Resonance of Electrochemically Generated Free Radicals. Isomeric Dinitrobenzene Mononegative Ions*

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The mononegative ions of *meta-*, *ortho-* and *para*-dinitrobenzene have been prepared in acetonitrile by controlled potential electrolysis within a microwave cavity and their electron spin resonance observed. The radical spectra exhibit hyperfine structure due to the isotropic magnetic interaction of the unpaired electron with the nitrogen and ring proton nuclear moments. Coupling constants were obtained with the aid of deuterium substitutions in the parent molecule. The nitrogen hyperfine coupling constants for the isomeric meta, ortho, and para anions were found to be 4.68, 3.22, and 1.74 gauss, respectively, and were identical for each of the two nitrogen nuclei of a given radical. Proton coupling constants range between 0.42 gauss and 4.19 gauss. The larger total hyperfine width of the *meta*-dinitrobenzene anion compared with the ortho and para isomers is ascribed to the existence of negative spin density in the π system of the first-mentioned radical and to the possibility of quinonoid resonance in the others which places considerable unpaired spin density in the oxygen nonbonding orbitals.

INTRODUCTION

(a) Electron-Spin Resonance of Free Radicals

THE study of nitrobenzene derivatives by electron-spin resonance (ESR) has been introduced by a report on the nitrobenzene mononegative ion.[1] This initial work, to be referred to as I, forms the basis for a second study of the three isomeric dinitrobenzene mononegative ions. These ions have been prepared by controlled potential reduction at a mercury pool electrode within a microwave cavity. The generated radicals are sufficiently stable that the ESR can be detected in the solution near the electrode surface.

ESR studies of solutions of aromatic free radicals[2] and singly charged ions[3] are already numerous. In general, dilute solutions of these free radicals exhibit complicated hyperfine structure; analysis of these structures leads to isotropic hyperfine coupling constants[4] of the unpaired electron with the various magnetic nuclei of the molecule. The hyperfine structure exhibited by aromatic hydrocarbon radicals must be assigned to protons, and since the interaction is not averaged out by molecular tumbling it must arise from the *s* character of the unpaired electron at the proton positions.[5]

A theoretical treatment of the problem by McConnell and Chestnut[6] has shown that a π-σ exchange interaction on aromatic carbon atoms causes a penetration of unpaired electron density into the σ system of the hydrocarbon. The magnitude of the coupling constant for a given proton, furthermore, is approximately proportional to the unpaired electron density in the π orbital of the contiguous carbon atom. For this reason proton hyperfine coupling constants are useful in "mapping" the unpaired electron distribution in the π system of the aromatic hydrocarbon radicals.

On the basis of this theory it is predicted that C^{13} and heteroatoms such as N^{14} and N^{15} should also give rise to isotropic hyperfine structure. This prediction has been substantiated by experiment.[1,7,8] Consequently, the measurement of the hyperfine coupling constants of heteroatom nuclei in aromatic radicals is also useful in a study of the unpaired electron distribution. For an sp^2 hybridized atom, the hyperfine interaction might be expected to be roughly proportional to the unpaired electron density in the π atomic orbital of that atom. An atom which is not sp^2 hybridized, but which none the less overlaps the π system of the radical, would be expected to exhibit isotropic hyperfine structure because of the zero order *s* character in the interacting atomic orbital. No first-order π-σ configuration interaction is necessary to account for the isotropic hyperfine interaction in this case. An example of this type of atom is the nitrogen atom of a nitro group that is sterically hindered from assuming a coplanar configuration with the π system.

The three dinitrobenzene mononegative ions form a

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

[2] C. A. Hutchison, Jr., R. C. Pastor, and A. Kowalsky, J. Chem. Phys. **20**, 534 (1952); H. S. Jarrett and C. J. Sloan, *ibid.* **22**, 1783 (1954); P. Sogo, M. Nakazaki, and M. Calvin, *ibid.* **26**, 1343 (1957); E. Müller, K. Ley, K. Schleffer, and K. Mayer, Chem. Ber. **91**, 2682 (1958).

[3] B. Venkataraman and G. K. Fraenkel, J. Am. Chem. Soc. **77**, 2797 (1955); J. Chem. Phys. **23**, 588 (1955); B. Venkataraman, B. G. Segal, and G. K. Fraenkel, *ibid.* **30**, 1006 (1959); D. Lipkin, D. E. Paul, J. Townsend, and S. I. Weissman, Science **117**, 534 (1953); D. E. Paul, D. Lipkin, and S. I. Weisman, J. Am. Chem. Soc. **78**, 116 (1956); E. de Boer and S. I. Weissman, *ibid.* **80** 4549 (1958); M. Adams, M. S. Blois, Jr., and R. H. Sands, J. Chem. Phys. **28**, 774 (1958).

[4] E. Fermi, Z. Physik **60**, 320 (1930).

[5] S. I. Weissman, J. Chem. Phys. **22**, 1378 (1954).

[6] H. M. McConnell and D. Chestnut, J. Chem. Phys. **28**, 107 (1958).

[7] T. R. Tuttle and S. I. Weissman, J. Chem. Phys. **25**, 189 (1956).

[8] R. L. Ward and M. P. Klein, J. Chem. Phys. **28**, 518 (1958); **29**, 678 (1958); R. L. Ward, *ibid.* **30**, 852 (1959).

natural series for study by ESR for the following reasons:

(i) They are all stable enough to be studied by the electrolytic method within the microwave cavity.[1,9]

(ii) Resonance theory[10] predicts widely different electronic structures for them and ESR hyperfine structure should reflect these differences.

(iii) They form a complete, isomeric set.

(b) Polarography and Free Radicals

The first paper on the subject of polarography was published in 1922.[11] Since then, chemical transformations occurring at the surface of a microelectrode have been the subject of extensive research. A potential is applied between a microelectrode and a large *reference electrode* and the resulting current through the cell is measured. A current-potential plot of this type is called a polarogram. An inert electrolyte, such as potassium nitrate, is also present to increase the conductivity of the solution and is called a *supporting electrolyte*. A less rudimentary description of this method is beyond the scope of this paper; the reader is referred to a standard text, such as Kolthoff and Lingane.[12]

The substance being investigated is dissolved in a suitable solvent, frequently water. Recent work with organic solvents substituted for water has greatly extended the usefulness of polarography in the study of organic systems. Work by Hoijtink *et al.*[13] has shown that in 96% dioxane the reduction of anthracene and other hydrocarbons at a mercury drop is represented by the sequence:

$$R+e^- \rightleftharpoons \cdot R^- \tag{1}$$

$$\cdot R^- + e^- \rightleftharpoons R^{--}. \tag{2}$$

Both reactions are reversible and (2) occurs at a more negative potential than (1). Addition of a proton donor such as water or hydrogen iodide to the solvent causes the substitution of the following irreversible sequence, which takes place at the potential of (1):

$$R+e^- \rightleftharpoons \cdot R^- \xrightarrow{H^+} \cdot RH \xrightarrow{e^-} :RH^- \xrightarrow{H^+} RH_2. \tag{3}$$

Austin *et al.*[14] have used ESR to confirm the existence of free radicals in the controlled potential reduction of anthracene, benzophenone, and anthraquinone, using the aprotic solvent *N*,*N*-dimethylformamide. Samples were removed during electrolysis and frozen. The ESR was detected at liquid oxygen temperature.

Thus, it becomes apparent that, if controlled potential reduction were carried out at a potential at which (1) occurred but (2) did not occur, and in an aprotic solvent so that the sequence (3) were suppressed, the mononegative ions could be generated and their ESR observed. This is the basis of the method that is used here to generate the free radical ions. The electrode at a controlled potential is a versatile, selective reducing agent.

Preliminary polarography of a solution of R (which need not be a hydrocarbon) is done to verify that one-electron reduction occurs and is polarographically reversible. Subject to the condition that the mononegative ions is sufficiently stable, its study by ESR is possible.

Acetonitrile (CH_3CN) was chosen as the solvent in this study and tetra-*n*-propylammonium perchlorate as the supporting electrolyte. As in I, a small mercury pool was used as the polarizable electrode. The part of the electrolytic cell containing the mercury pool was placed inside the microwave cavity of the ESR spectrometer so that the portion of the solution immediately above the microelectrode was in the region of maximum rf magnetic field. Radicals were then generated by applying a previously determined potential between the mercury pool and a saturated calomel reference electrode. As the negative ions were formed at the surface and diffused into the solution they were directly detected by the ESR spectrometer. Since the radicals were present in solution, the resonances were characterized by well-resolved hyperfine structure.

The advantages of this method of free radical generation in comparison with the conventional alkali metal reduction are threefold. Since these have been elaborated in I, they will only be outlined here.

(i) Alkali metal ions are eliminated from the solution of the radical anion.

(ii) Complicating effects of ion association are minimized by use of a relatively high dielectric constant solvent along with a bulky (tetra-*n*-propyl-ammonium) counter ion.

(iii) Since the potential of the microelectrode is controlled during electrolysis, we have reasonable assurance that no reaction other than the reversible one-electron transfer (indicated by polarographic criteria for reversibility) is taking place at the electrode.

It is necessary to mention a limitation in this method of radical study. Free radicals, as they are produced at the surface of the mercury pool, are in a region of relatively low filling factor and must diffuse upwards away from the metallic surface before they enter a region of reasonable sensitivity. Also, the electrolysis current is limited by the rate of diffusion of the parent molecules to the electrode surface. Both of these conditions limit the technique described in this paper to the study of relatively long-lived radicals. With our spectrometer we have found that radicals with lifetimes of five minutes could be conveniently studied by this method.

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[9] A. H. Maki and D. H. Geske, J. Chem. Phys. **30**, 1356 (1959).

[10] L. Pauling, *The Nature of the Chemical Bond* (Cornell University Press, Ithaca, New York, 1960), 3rd ed.

[11] J. Heyrovsky, Chem. Listy **16**, 256 (1922).

[12] I. M. Kolthoff and J. J. Lingane, *Polarography* (Interscience Publishers, New York, 1952), 2nd ed.

[13] G. J. Hoijtink, J. van Schooten, E. deBoer, and W. J. J. Aalbersberg, Rec. trav. chim. **73**, 355 (1954).

[14] D. E. G. Austin, P. H. Given, D. J. E. Ingram, and M. F. Peover, Nature **182**, 1784 (1958).

We have made some preliminary investigations of electrolytic reduction of hydrocarbons including naphthalene, anthracene, acenapthene, diphenylene, triphenylene, and coronene within the microwave cavity. Preliminary polarography indicated that in each case the electrode reaction in acetronitrile was a reversible one-electron transfer. ESR has been observed in each case. All but the triphenylene and coronene negative ions exhibited a well-resolved hyperfine structure. Triphenylene and coronene negative ions gave broad resonances with little resolution. This result is in agreement with the findings of Townsend and Weissman,[15] who attribute this lack of resolution to a Jahn-Teller effect.

EXPERIMENTAL

(a) ESR Spectrometer

The ESR spectrometer is of conventional design and employs a cylindrical microwave reflection cavity operated in the TE_{011} mode. The resonant frequency of the cavity containing the electrolysis cell is about 9200 Mc. A proton resonance spectrometer locked to a BC–221 frequencymeter is used to monitor the magnetic field, which is modulated at 280 cps and slowly swept through the ESR spectrum of the sample. The amplitude of the modulation is kept smaller than the line width of the resonances to obtain maximum resolution. The Varian, Inc. X–13 klystron is immersed in a bath of mineral oil for cooling and thermal stabilization. In addition, it is locked to the sample cavity frequency by a modified Pound stabilization circuit that operates at 100 kc.

(b) Electrolysis Cell

The electrolysis cell consists of a 3-mm o.d. Pyrex tube sealed over a platinum wire at the lower end. The microelectrode is a small mercury pool at the bottom of this tube and makes electrical contact with the platinum. The tube extends into the center of the cylindrical microwave cavity and is attached at the upper end to the main compartment of the cell; the whole is filled with the solution to be electrolyzed. The upper compartment contains a fritted tube through which prepurified nitrogen is bubbled to exclude atmospheric oxygen from the solution. A subcompartment is separated from the main compartment by a sintered disk. The solution in this compartment is connected by means of a salt bridge to the reference electrode, which is a large aqueous saturated calomel electrode (SCE). A potential is applied between the SCE and the mercury microelectrode by means of a simple potentiometer circuit. A microammeter is used to monitor the current through the cell.

TABLE I. Polarographic data. 0.1 M tetra-n-propylammonium perchlorate supporting electrolyte in acetonitrile at 25.0°.

	$-E_{1/2}$,v vs SCE	$-(E_{3/4}-E_{1/4})$ mv	I_d[e]
meta-Dinitrobenzene[a]	0.90	61	4.19
	1.25	63	3.61
	2.01	d	10.24
ortho-Dinitrobenzene	0.81	52	4.17
	1.06	57	3.20
	2.54	d	19.3
para-Dinitrobenzene	0.69	53	4.99
	0.89	58	3.56
	ca 2.5	d	f
Nitrobenzene[b]	1.15	56	4.07
	1.9[c]	...	7.5

[a] These data contradict the report of L. Holleck, R. Schindler, and O. Löhr, Naturwissenschaften **46**, 625 (1959) that *meta*-dinitrobenzene has an irreversible wave at −1.200 v in acetonitrile.

[b] Data from I.

[c] Wave distorted by maximum.

[d] Wave was irreversibly drawn out.

[e] I_d represents the quantity $i_d/m^{2/3}t^{1/6}C$, where i_d is the maximum diffusion current in microamperes, m the drop-weight in mg sec^{-1}, t is the drop time in seconds, and C is the millimolar concentration of electroactive material. I_d is given for individual waves.

[f] Drawn-out wave did not have a diffusion current plateau.

(c) Electrolytic Radical Generation

In the case of each isomer the electrolysis within the microwave cavity was carried out at a potential just on the plateau of the first reduction wave, or at a potential about 100 mv more negative than the half-wave potential. The current-time behavior of the system was similar to that described for nitrobenzene in I. Good spectra were obtained after about fifteen minutes of electrolysis; after this the number of radicals in the cavity appeared to have become approximately constant. Successive tracings of spectra over the period of one to two hours showed no significant differences. During one run with a solution of *para*-dinitrobenzene, the electrolysis current was discontinued while the most prominent hyperfine component in the spectrum was observed. The ESR signal was observed to decay with a time constant of about five minutes. This is a much shorter time than would be required for a significant fraction of the radicals to diffuse out of the microwave cavity and is attributed to the decay of the radical. Since no new lines were observed in the spectrum, the decay must be products which do not exhibit ESR, probably diamagnetic products. This time interval (five minutes) is about the same as that associated with a color change from greenish yellow to red, which may be observed if the electrolysis is carried out outside of the cavity.

(d) Synthesis of Deuterium Substituted Compounds

1,3-Dinitrobenzene-5-d_1

3,5-Dinitroaniline, prepared according to the pro-

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[15] M. G. Townsend and S. I. Weissman, J. Chem. Phys. **32**, 309 (1960).

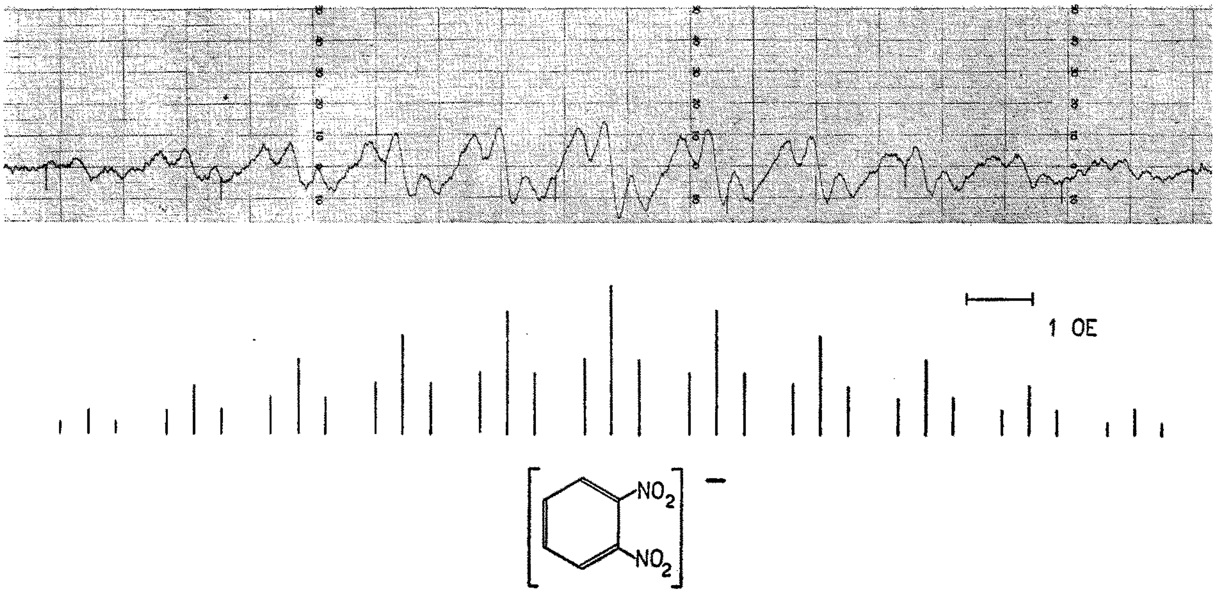

FIG. 1. Derivative of electron-spin resonance absorption spectrum vs magnetic field strength for *o*-dinitrobenzene anion in acetonitrile (upper portion); spectrum calculated using coupling constants of Table II shown to scale (lower portion).

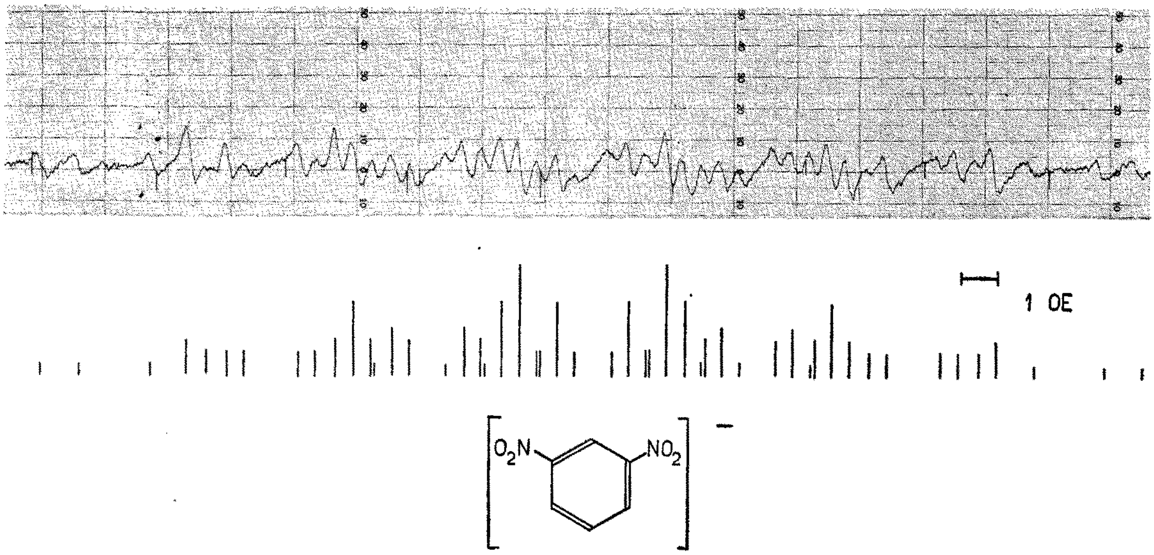

FIG. 2. Derivative of electron-spin resonance absorption spectrum vs magnetic field strength for *m*-dinitrobenzene anion in acetonitrile (upper portion); spectrum calculated using coupling constants of Table II shown to scale (lower portion).

cedure of Blanksma and Verberg,[16] was diazotized by dissolution in *deutero*nitrosylsulfuric acid[17] at 0°. *Deutero*hypophosphorous acid was added to reduce the diazonium compound to the dinitrobenzene. The reduction reaction was accelerated by diluting the reaction mixture with deuterium oxide. The solid material which precipitated had a melting point of 90.0° after one recrystallization from water. Mass spectral analysis showed 83% monodeuteration.

1,3-Dinitrobenzene-d_4

Benzene-d_6 (99.5% isotopic purity) obtained from Merck Company, Ltd., Montreal, Canada, was nitrated with potassium nitrate in concentrated *deutero*sulfuric acid. After recrystallization from an ethanol-water mixture the 1,3-dinitrobenzene-d_4 had a melting point of 90.0°.

1,2-Dinitrobenzene-3,5-d_2

2-Nitro-3-aminosulfonic acid was hydrolyzed to 2-

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[16] J. J. Blanksma and G. Verberg, Rec. trav. chim. **53**, 988 (1934).

[17] L. Welsh, J. Am. Chem. Soc. **63**, 3276 (1941).

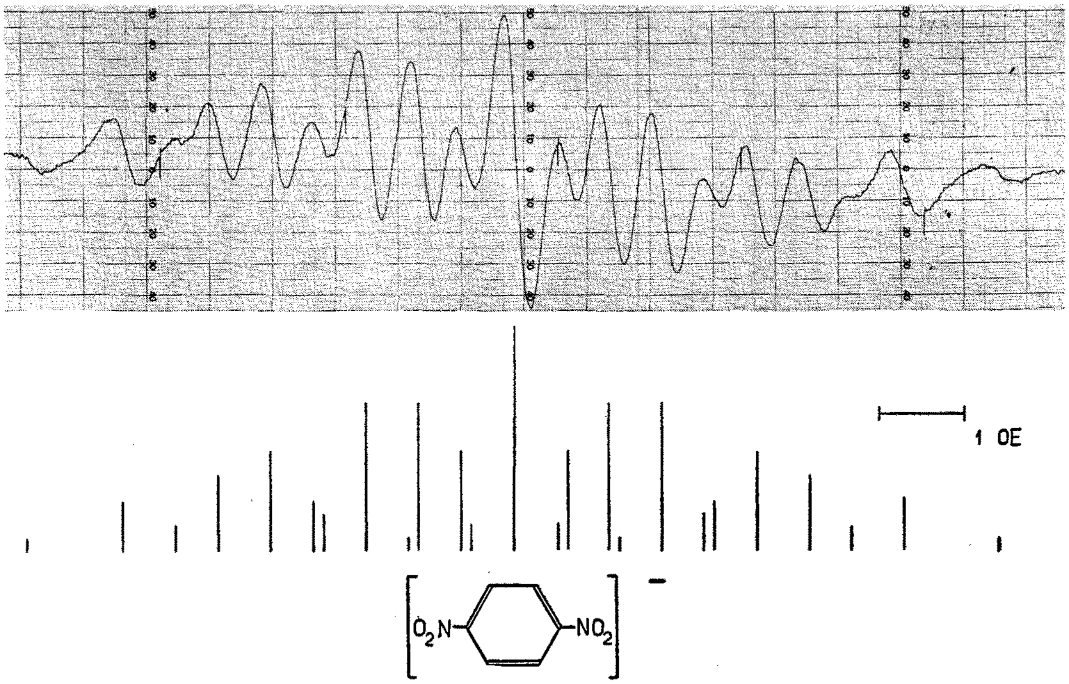

FIG. 3. Derivative of electron-spin resonance absorption spectrum vs magnetic field strength for *p*-dinitrobenzene anion in acetonitrile (upper portion); spectrum calculated using coupling constants of Table II shown to scale (lower portion).

nitroaniline-3, 5-d_2[18] by refluxing for 30 min in 56% *deutero*sulfuric acid in deuterium oxide. The nitroaniline was oxidized to 1,2-dinitrobenzene-3,5-d_2 (mp 115°) with trifluoroperoxyacetic acid.[19] Mass spectrometric analysis showed 94.9% dideuteration and 4.5% monodeuteration.

1,2-Dinitrobenzene-3-d_1

2,3-Dinitroaniline was prepared by nitration of *m*-nitroacetanilide[20] followed by hydrolysis in concentrated sulfuric acid.[20] The amine was diazotized with *deutero*nitrosylsulfuric acid in the presence of *deutero*phosphoric acid.[17] The reduction with *deutero*hypophosphorous acid was accelerated by dilution of the reaction mixture with deuterium oxide. After two recrystallizations from water the melting point was 116°. Mass spectrometric analysis showed 87.5% monodeuteration.

RESULTS

(a) Polarography

The polarography of the dinitrobenzenes has been studied in various ethanol-water mixtures.[21–23] Two reduction waves were observed for each isomer. The half-wave potentials are all dependent on the *p*H of the media. Pearson reports that the first wave represents the four-electron reduction of the dinitrobenzene to the corresponding monohydroxylamine. Polarographic data have also been obtained in concentrated sulfuric acid[24] and glacial acetic acid.[25] While a systematic polarographic study of reduction of the dinitrobenzenes in acetonitrile was beyond the scope of the present project, preliminary data (Table I) were obtained for a single concentration (*ca* one millimolar) of each isomer. For each isomer three waves were observed, the first two being approximately equal in magnitude and the third being significantly larger.[26]

One criterion for a reversible wave is that $E_{3/4}-E_{1/4}=-56$ mv for a one-electron reaction at 25°. Since this criterion is approximately fulfilled for both the first and second waves (Table I) the $E_{\frac{1}{2}}$ values are essentially equal to the standard reduction potential for the corre-

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[18] While assignment of one deuterium to the 3-position is unequivocal because of the hydrolysis of the sulfonic acid group, the assignment of the second deuterium to the 5-position is based on assumed ring-activation of the 5-position. The electron spin resonance spectrum of the corresponding anion radical is consistent with this formulation.

[19] W. D. Emmons, J. Am. Chem. Soc. 76, 3470 (1954).

[20] K. H. Pausacker and J. G. Scroggie, J. Chem. Soc. **1955**, 1897.

[21] J. Pearson, Trans. Faraday Soc. **44**, 683 (1948).

[22] S. F. Dennis, A. S. Powell, and M. J. Astle, J. Am. Chem. Soc. **71**, 1484 (1949).

[23] E. Gergely and T. Iredale, J. Chem. Soc. **1953**, 3226.

[24] J. C. James, Trans. Faraday Soc. **47**, 1240 (1951).

[25] I. Bergman and J. C. James, Trans. Faraday Soc. **48**, 956 (1952).

[26] The quantity I_d in Table I is approximately proportional to the number of electrons involved in the reactions. The fact that the I_d value for the second wave is somewhat smaller than the first remains unexplained. Similar behavior has been observed by S. Wawzonek, R. Berkey, E. W. Blaha, and M. E. Runner, J. Electrochem. Soc. **103**, 456 (1956), in the reduction of quinones in acetonitrile.

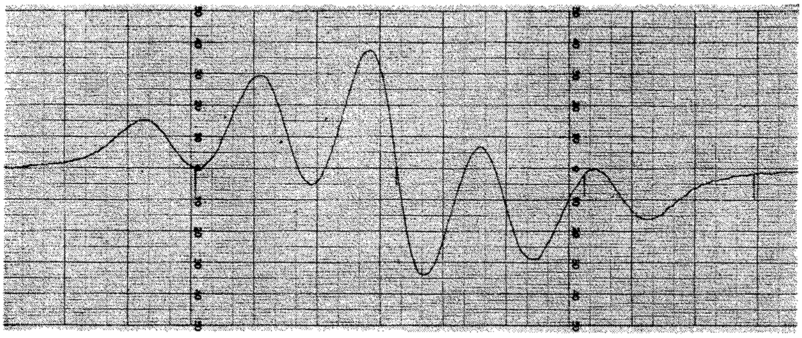

FIG. 4. Derivative of electron-spin resonance absorption spectrum vs magnetic field strength for 1,3-dinitrobenzene-d_4 anion in acetonitrile.

sponding redox couple. These data should thus be indicative of the energy necessary to place the first and then the second electron into the lowest unoccupied molecular orbital of the dinitrobenzene. The order, *meta*>*ortho*>*para*, for the quantity $-E_{\frac{1}{2}}$ of the first wave in acetonitrile is the same as in ethanol-water media where a four-electron reaction is involved.

The fact that the wave for the addition of the second electron also approximates reversibility is rather surprising. The implication is that the dianion does not rapidly undergo irreversible protonation. Also of interest is the observation that the difference between the half-wave potentials for the first and second waves varies for the three isomers. This probably reflects the difference in coulomb repulsion energy of two electrons in the lowest unoccupied molecular orbital of the three isomers, since it may be argued that the solvation energies of the ions are comparable.

(b) ESR

Derivatives of the ESR absorption spectra of the three isomeric dinitrobenzenes are displayed in Figs. 1–3. Directly below each spectrum is the calculated absorption spectrum based upon the coupling constants given in Table II. Only in the case of *p*-dinitrobenzene negative ion is the assignment of coupling constants to specific nuclei of the radical possible without isotopic substitution, and this is done on the basis of relative intensity considerations. In the other cases deuterium substituted molecules were prepared and the negative ions investigated.

The line widths are about 0.35 gauss between points of maximum slope for each of the undeuterated ions. Spectra of the deuterium substituted ions have broader lines when the deuterium hyperfine structure is not resolved and therefore contributes to the line width. In each case, the observed spectrum was compared with spectra calculated on the basis of the several possible coupling constants for the substituted proton(s). There was only one obvious assignment in each case. Spectra of the negative ion of 1,3-dinitrobenzene-5-d_1 were consistent with the assumption that the substituted proton has a coupling constant of 1.08 gauss and not 3.11 gauss The spectrum of the negative ion of 1,3-dinitrobenzene-d_4 is shown in Fig. 4. This ion was studied to verify the magnitude of the nitrogen coupling constant in the *meta*-dinitrobenzene negative ion. The five lines are separated by the nitrogen coupling constant and are in the approximate intensity ratios 1:2:3:2:1, indicating an equal hyperfine interaction with both nitrogen nuclei. From spectra of the negative ion of 1,2-dinitrobenzene-3,5-d_2 one proton with a coupling constant of 1.63 gauss was found to have been substituted with a deuteron. This demonstrated that the large proton coupling constant is 1.63 gauss and not 3.22 gauss. The ESR spectrum of the 1,2-dinitrobenzene-3-d_1 identified the substituted proton as one of the pair with the small 0.42 gauss coupling constant. In this case the doublet structure resulting from the remaining proton with 0.42 gauss coupling constant is clearly evident, since the deuterium nuclear moment produces no significant line broadening. The derivative spectrum of 1,2-dinitrobenzene-3-d_1 negative ion is shown in Fig. 5.

DISCUSSION OF RESULTS

The electron-spin resonance spectra presented in the last section are all consistent with the full molecular symmetry of the parent dinitrobenzene isomer. Protons and nitrogen nuclei that are interchanged by covering operations of the molecule are characterized by the same hyperfine coupling constant. Our results on the *meta*-dinitrobenzene negative ion are thus in disagreement with results recently reported by Ward,[27] who finds one dominant nitrogen coupling constant of 9.0 gauss in solutions of *meta*-dinitrobenzene in 1,2-dimethoxyethane which has been reduced with metallic potassium. We do not understand this result on the basis of a simple *meta*-dinitrobenzene negative ion. Possibly, ion pairing between metal and radical ions in 1,2-dimethoxyethane might sufficiently perturb the symmetry of the electron distribution of radicals to give the observed result, but it is also possible that reduction reaction might have proceeded beyond a simple electron transfer, in which case the identity of the radical remains to be determined. The large value of the single nitrogen coupling constant is characteristic of negative ions of aromatics containing but one nitro

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[27] R. L. Ward, J. Chem. Phys. **32**, 410 (1960).

group in the ring.[28] One would expect a smaller value of the coupling constant if more than one nitro group were involved as an electron acceptor.

The three isomeric dinitrobenzene negative ions generated electrochemically exhibit widely divergent hyperfine structure. This behavior indicates that the unpaired electron distribution among the atoms comprising the π system depends strongly on the relative positions of the two nitro groups in the ring. One of the most striking aspects of the spectra is the large range of the total width of the hyperfine structure. This total width between extreme hyperfine components is 11.44 gauss for the para isomer, 17.00 gauss for the ortho isomer and 31.28 for the meta isomer. These results may be compared with the value of the total splitting in the nitrobenzene anion, which is 33.60 gauss.[1] The ions can be roughly divided into two groups: those having a small hyperfine width (the *ortho*- and *para*-dinitrobenzenes) and those having a large hyperfine width (the meta isomer and nitrobenzene itself).

If we make the reasonable assumption that the anions are planar (although this is not exactly true for the ortho isomer for steric reasons), we can go through the process of starring alternant atoms of the π system,[29] regardless of whether they are carbon atoms or heteroatoms. We do this in such a way that at least one nitrogen atom is starred. The nitrobenzene negative ion under the starring process is analogous to an odd alternant hydrocarbon radical. The *meta*-dinitrobenzene anion is similarly analogous even though it has an even number of atoms, because no covering operation of the molecule interchanges starred and unstarred atoms. It is then possible that negative spin density occurs in the p_z orbitals of the unstarred atoms of these two radicals. This is a result which is already familiar for hydrocarbon radicals[6,30] and which has recently been rigorously proved.[31] Clearly it is not possible to have alternation in the signs of spin densities in the isomeric para and ortho anions, for in these cases a covering operation of the molecule exists which interchanges starred and unstarred atoms; they are analogous to even alternant hydrocarbon mononegative and monopositive ion radicals. From this argument it is not surprising that the total hyperfine widths of the ions that are analogous to odd alternant hydrocarbon radicals are greater than the widths of those analogous to even alternant hydrocarbon ions. No attempt is made to make this argument on as quantitative a basis as it has been made for hydrocarbons. We lack knowledge of the spin densities on the oxygen atoms and do not have quantitative relationship between the spin distribution in the π system vicinal to the nitrogen atom and its hyperfine coupling constant.

TABLE II. Absolute values of nitrogen and proton hyperfine coupling constants.

	Hyperfine coupling constants (gauss)					
Anion	$\lvert A_N \rvert$	$\lvert A_2 \rvert$[c]	$\lvert A_3 \rvert$	$\lvert A_4 \rvert$	$\lvert A_5 \rvert$	$\lvert A_6 \rvert$
1,2-Dinitrobenzene	3.22[b]	...[d]	0.42	1.63	...	...
1,3-Dinitrobenzene	4.68[b]	3.11	...	4.19	1.08	...
1,4-Dinitrobenzene	1.74[b]	1.12	...	...	...	...
1-Nitrobenzene[a]	10.32	3.39	1.09	3.97	...	...

[a] Values from I.

[b] Both nitrogen nuclei interact equally.

[c] The proton which interacts with $\lvert A_i \rvert$ is the one bonded to the ith ring carbon atom. Carbon atoms are numbered cyclically.

[d] A position without an entry is either occupied by the second nitrogen atom, or the coupling constant is given by the position(s) related to it by the covering operation(s) of the ion.

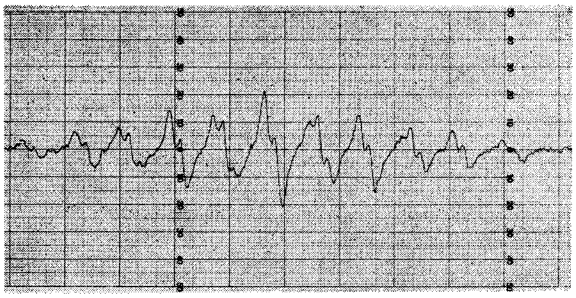

FIG. 5. Derivative of electron-spin resonance absorption spectrum vs magnetic field strength for 1,2-dinitrobenzene-3-d_1 anion in acetonitrile.

It is noteworthy that the ring proton coupling constants of both the nitrobenzene and *meta*-dinitrobenzene anions suggest the alternation of positive and negative spin densities since the proton interaction on unstarred carbon atoms is about $\frac{1}{3}$ to $\frac{1}{4}$ that on starred carbon atoms. For instance, this result may be compared with the perinapthenyl radical[32] for which this ratio is 0.30.

The nitrogen coupling constants might be expected to be about the same in the ortho and para anions. The larger nitrogen coupling constant in the ortho isomer can be explained on the basis of a steric effect. The nitro groups cannot be coplanar with the ring and consequently some s character is expected to occur in the π orbitals of the nitrogen atoms.[33]

Another effect which undoubtedly contributes to the smaller total hyperfine width of the *para* and *ortho* isomers is the possibility of quinonoid type resonance,[10] which would be expected to result in considerable unpaired electron density in the oxygen nonbonding orbitals of these isomers. The pertinent bond eigen-

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[28] A. H. Maki and D. H. Geske, unpublished work on negative ions of various substituted nitrobenzenes.

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

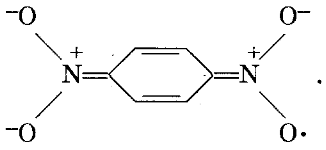
[30] P. Brovetto and S. Ferroni, Nuovo cimento **5**, 142 (1957).

[31] A. D. McLachlan, Mol. Phys. **2,** 223 (1959).

[32] P. B. Sogo, M. Nakazaki, and M. Calvin, J. Chem. Phys. **26,** 1343 (1957).

[33] S. I. Weissman, J. Chem. Phys. **25,** 890 (1956).

functions are of the type:



This kind of quinonoid resonance is not possible in the meta isomer or in the nitrobenzene negative ion.

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Diamagnetism as a Test of Wave Functions for Some Simple Molecules

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A theoretical study is made of the diamagnetism of some simple molecules in a gaseous form, attention being mainly devoted to the "neon-like" series Ne, H_2O, NH_3, and CH_4. In this way an attempt is made to gain insight into the way in which the radial electron density distribution within the molecules is influenced, firstly, by the allowance of exchange effects and secondly, by the inclusion of angular terms which must be accounted for in any "physically real" description of the electron density.

In general, it is found that exchange effects cause the radial density distribution to contract, while the inclusion of angular terms results in the subsequent radial electron density becoming more diffuse.

INTRODUCTION

IT has been demonstrated recently[1] that by adopting central-field wave functions it was possible to provide a very satisfactory theoretical interpretation of the x-ray scattering to be observed from the series of "neon-like" molecules Ne, H_2O, NH_3, and CH_4, all in gaseous form. Such an approach was amply justified by a detailed study of the water molecule.[2] Here it was shown that, for such a series, angular terms when included in the density made an almost negligible contribution to the resulting x-ray scattering factor, the major contribution arising from the radial or spherically symmetrical density term. Thus it was seen that, for this series of molecules, the use of central-field analytical wave functions of determinantal form does tend to provide a radial distribution of electrons which is a good first approximation to the true electron density within the molecule when averaged over angles.

Nevertheless, while the over-all radial density distribution may be accounted for quite satisfactorily by using a central-field method, it is only to be expected that the averaged density in the outer regions of the molecule may not be very adequately described in detail by such an approach. A physical quantity which is comparatively sensitive to the radial distribution of the outer electrons is the diamagnetic susceptibility. Recently Weltner[3] has provided, for this series of molecules, values for the subsidiary paramagnetic contribution to this quantity based on other experimental observations, thus rendering the determination of the total susceptibility a more tractable problem. The major contribution, or purely diamagnetic part, of the total susceptibility may then be determined from the electron density after averaging over angles.

Such calculations were performed using various approximate results for the electron density. Hence, by comparing the theoretical susceptibility with the observed value it is hoped to demonstrate how the radial density distribution (i.e., the electron density within the molecule when averaged over angles) is influenced not only by including exchange effects but also by making allowance for angular terms which must be accounted for in any realistic description of the density within polyatomic molecules.

CALCULATION OF THE DIAMAGNETIC SUSCEPTIBILITY

Van Vleck[4] has shown that the diamagnetic susceptibility χ for a molecule may be expressed as

$$\chi=\chi_r+\chi_{hf}, \tag{1}$$

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[1] K. E. Banyard and N. H. March, Acta Cryst. **9**, 385 (1956).

[2] K. E. Banyard and N. H. March, J. Chem. Phys. **26**, 1416 (1957).

[3] W. Weltner, J. Chem. Phys. **28**, 478 (1958).

[4] J. H. Van Vleck, *Theory of Electric and Magnetic Susceptibilities* (Oxford University Press, London, 1932).