

Alternating Linewidths and Related Phenomena in the Electron Spin Resonance Spectra of Nitro-Substituted Benzene Anions*

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Studies of linewidths in the electron spin resonance spectra of a number of nitro-substituted benzene anions are reported. The radicals were generated electrolytically in *N,N*-dimethylformamide solutions, and spectra were obtained over a range from above to below room temperature. Pronounced alternations in the linewidths of the nitrogen lines in many of the spectra were observed. If M_N is the total z component of the nuclear spin angular momentum in compounds containing two equivalent nitrogen nuclei, the alternating linewidth phenomenon causes a broadening of the lines for which $M_N = \pm 1$ and a reduction in the amplitude of the central line. Large alternating linewidths were observed in the room-temperature spectra of the anions of dinitroindurene, dinitromesitylene, and 2,6-dinitro-3,5-dimethyl-4-acetyl-*t*-butylbenzene; and also in a spectrum which shows splittings from two equivalent nitrogen nuclei that was obtained from trinitromesitylene. Slight alternating linewidth effects at room temperature that became more marked at low temperatures were found in the spectra of the 2,6-dinitrotoluene and *m*-dinitrobenzene anions. No linewidth alternations were detectable even at low temperatures in the spectra of the *o*-dinitrobenzene, *p*-dinitrobenzene, and 2,6-dinitrophenolate anions. The 2,6-dinitroaniline anion, which was investigated only at room temperature, showed no evidence of an alternating linewidth effect. None of the spectra of the mononitrobenzene anions examined exhibited any anomalous linewidth phenomena. The experimental observations are in general agreement with the recently developed theory of linewidths. The theory attributes the alternation in widths in these radicals to an out-of-phase correlation of a modulation of the isotropic hyperfine splittings of the two equivalent nitrogen nuclei. This out-of-phase modulation probably arises from either fluctuating solvent complexes with the nitro groups, or from internal rotations of these groups relative to the plane of the benzene ring, and both types of motion may occur simultaneously. Steric hindrance of the nitro groups was found to enhance the magnitude of the alternations in width, as did lowering of the temperature.

I. INTRODUCTION

RECENTLY two independent investigations of electron spin resonance spectra led to the discovery of a new type of linewidth effect: In the dihydroxydurene cation,¹ Bolton and Carrington found that the central line of the spectrum was narrow, but that alternate lines arising from splittings due to the methyl-group protons were broad. Thus, if M_{Me} is the sum of the z components of the nuclear spin angular momenta of the 12 methyl-group protons, lines for which $M_{Me} = 0, \pm 2, \pm 4,$ and ± 6 were sharp, and those for which $M_{Me} = \pm 1, \pm 3,$ and ± 5 were broad. In the dinitroindurene anion,^{2,3} Rieger and Bernal found that the central and outer lines arising from nitrogen splittings were sharp, but that the intermediate lines were broad, or, with M_N being the sum of the z components of the nuclear spin angular momenta of the two ¹⁴N nuclei, lines with $M_N = 0$ and ± 2 were sharp, and those with $M_N = \pm 1$ were broad. These observations were inconsistent with the existing theory of linewidths in the

ESR spectra of radicals in solution,⁴ and thus led us to undertake an intensive program of experimental and theoretical studies. In the present work we report on the experimental investigations of nitro-substituted benzene anions.

The first step in the experimental program was a detailed study of the spectrum of the dinitroindurene anion. Part of the results of these experiments have already been reported,² but a more thorough analysis is given in the following. Since both dihydroxydurene and dinitroindurene are sterically hindered compounds, we also studied other hindered nitro compounds. These include dinitromesitylene, 2,6-dinitrotoluene, 2,6-dinitrophenol, 2,6-dinitro-3,5-dimethyl-4-acetyltertiary-butylbenzene, nitromesitylene, and nitroindurene. The isomeric dinitrobenzene anions were also reexamined. The detailed results on most of these compounds are included in the present work. The nitromesitylenes⁵ and the *o*- and *p*-dinitrobenzene anions⁶ are discussed elsewhere.

II. THEORY OF LINEWIDTH VARIATIONS

The revised theory of linewidths in the ESR spectra of free radicals in solution as developed elsewhere⁷ indicates that an alternating linewidth can arise from mod-

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¹ J. R. Bolton and A. Carrington, *Mol. Phys.* **5**, 161 (1962).

² J. H. Freed and G. K. Fraenkel, *J. Chem. Phys.* **37**, 1156 (1962); J. Freed, I. Bernal, and G. K. Fraenkel, *Bull. Am. Phys. Soc.* **7**, 42 (1962).

³ The alternating linewidth phenomenon in the dinitroindurene anion was first observed by P. H. Rieger and I. Bernal in these laboratories.

⁴ D. Kivelson, *J. Chem. Phys.* **27**, 1087 (1957); **33**, 1094 (1960).

⁵ I. Bernal and G. K. Fraenkel, *J. Am. Chem. Soc.* **86**, 1671 (1964).

⁶ J. H. Freed and G. K. Fraenkel, *J. Chem. Phys.* **40**, 1815 (1964).

⁷ J. H. Freed and G. K. Fraenkel, *J. Chem. Phys.* **39**, 326 (1963).

ulation of the isotropic hyperfine splittings. The results of this theory that are pertinent to the present experimental studies are outlined in this section. We start with a description of the alternation in linewidths for the hyperfine lines from two nitrogen nuclei, and then include the effects of modulation of the isotropic splittings from protons that are either bonded to the aromatic rings or in methyl-group substituents. The effects of the anisotropic intramolecular dipolar and g -tensor interactions are also included in an approximate way.

*Modulation of Hyperfine Splittings,
Two Equivalent ^{14}N Nuclei*

The theory⁷ shows that two parameters determine the linewidth contributions from the modulation of the isotropic hyperfine interactions of two equivalent ^{14}N nuclei. These are the spectral densities $j_{11}^{(i)}(\omega)$ and $j_{12}^{(i)}(\omega)$, where the subscripts refer to the two nuclei. The frequency $\omega/2\pi$ can take on two values, either zero or (approximately) the Larmor frequency of the ESR experiment. Since all the observed linewidth variations can be qualitatively explained by means of the secular terms alone, i.e., those corresponding to $\omega=0$, only these will be retained in the theoretical expressions, and $j_{ij}^{(i)}$ is written as a shorthand notation for $j_{ij}^{(i)}(0)$. The spectrum from two equivalent nitrogen nuclei consists of five lines with intensities in the ratio 1:2:3:2:1 corresponding to $M_N = -2, -1, 0, 1, 2$, where M_N is the sum of the z components of the spin angular momenta of the two nitrogen nuclei. The width contribution from the modulation of the splittings to the $M_N = \pm 2$ lines is⁷ $2(j_{11}^{(i)} + j_{12}^{(i)})$, and that for the $M_N = \pm 1$ lines is $j_{11}^{(i)}$. The $M_N = 0$ (central) line has three components: two have the width contribution $2(j_{11}^{(i)} - j_{12}^{(i)})$, and the third has no width contribution from this mechanism.

The maximum alternating linewidth effect occurs when $j_{12}^{(i)} = -j_{11}^{(i)}$, corresponding to an out-of-phase correlation of the modulations of the splittings of the two nuclei. The width contribution to the $M_N = \pm 2$ lines is then zero, that for the $M_N = \pm 1$ lines is $j_{11}^{(i)}$, while one of the three central components has no width contribution from this mechanism and the other two have a contribution of $4j_{11}^{(i)}$. When $j_{11}^{(i)}$ is large, the outermost lines are narrow, and one component of the central line is also narrow, while the $M_N = \pm 1$ lines are broad and two of the three components of the central line have a width four times that of the $M_N = \pm 1$ lines. In the limit of very large $j_{11}^{(i)}$, the spectrum would appear to consist of only three lines, all of equal amplitude, corresponding to $M_N = -2, 0$, and 2 , as if there were only one nitrogen nucleus causing the hyperfine splitting. In some spectra, however, the modulation of the splittings makes only a small contribution to the total width, and its effect can be satisfactorily represented by averaging over the different component widths of the central line.⁷ The width contribution is then $\frac{4}{3}(j_{11}^{(i)} - j_{12}^{(i)})$, and an alternating linewidth is

not observed. Instead, for out-of-phase correlation this mechanism causes the central line to be the broadest and the outermost lines to be the narrowest.

In Fig. 1, the amplitude of the first derivative of the absorption of the central line, and the width between derivative extrema, are plotted as a function of the ratio $j_{11}^{(i)}/X$ for the case of out-of-phase correlation ($j_{12}^{(i)} = -j_{11}^{(i)}$). The quantity X is the contribution to the width of the central line from mechanisms other than modulation of the isotropic splitting, and it is assumed that each of the three central components has the same contribution from these other mechanisms. The curve was obtained by superimposing Lorentzian-shaped lines of width $T_2^{-1} = X$ with intensity 1 and of width $T_2^{-1} = X + 4j_{11}^{(i)}$ with intensity 2. The derivative of the superimposed curve shows only one maximum and one minimum, and the amplitude of the maximum (normalized to 3.00 for $j_{11}^{(i)}/X = 0$), and the separation between the extrema, are plotted in the figure. Curves are also given for the average width $T_2^{-1} = X + \frac{8}{3}j_{11}^{(i)}$ and the amplitudes computed from this average width. It is seen that for $j_{11}^{(i)}/X$ small, the values computed from the average are good approximations, while for $j_{11}^{(i)}/X \approx 1$, only the component of unit statistical weight with width $T_2^{-1} = X$ makes a significant contribution.

If the modulations of the splittings are correlated so as to be in phase, the spectral densities satisfy the relation $j_{12}^{(i)} = j_{11}^{(i)}$, and the two nuclei are completely equivalent.⁷ The dependence of the width on M_N is then given simply by $j_{11}^{(i)}M_N^2$, and there is no alternation in linewidths.

These results do not depend on the nature of the mechanism causing the modulation of the splittings except insofar as the mechanism determines the values of the two spectral densities. As discussed elsewhere,⁸ a variety of types of modulations can cause an out-of-phase correlation and therefore an alternating linewidth. In the nitrobenzenes, an alternating linewidth can arise if, for example, the two nitro groups have fixed orientations at an angle of 90° relative to each other and undergo free rotational diffusion as a unit.⁸ It can also arise if they oscillate in certain ways either as a unit or relative to each other, or if they undergo jumps between different conformations. For a simple two-jump mechanism, one conformation could consist of an arrangement with one nitro group in the plane of the aromatic ring and the other perpendicular to the plane; in the other conformation, the orientations of the two groups would be interchanged. Interaction of one nitro group at a time with the solvent to form some sort of solvent complex in dynamic equilibrium can also produce an out-of-phase correlation of the spectral densities.

⁸ J. H. Freed and G. K. Fraenkel, "Semi-Classical Theory of the Effects of Internal Motions on the Linewidths in Electron Spin Resonance Spectra" (to be published); "Theory of Line Widths in Electron Spin Resonance Spectra. Motion of Methyl Groups," J. Am. Chem. Soc. (to be published).

The theory developed in Refs. 7 and 8 is restricted to the limit in which the modulation is rapid, but under certain circumstances⁷ when the modulation arises from a jump mechanism this restriction can be removed by using the method of Anderson⁹ or the modified Bloch equations.¹⁰ These latter theories show that for very slow jump rates (in the two-jump case) the spectrum should degenerate into nine lines corresponding to the splittings from two inequivalent nitrogen nuclei.

Modulation of Hyperfine Splittings, Protons

Modulations of the nitrogen hyperfine splittings in nitro groups may arise from mechanisms which redistribute the spin density throughout the molecule,⁸ and thus the hyperfine splittings of ring protons, or of protons in methyl-group substituents, may also be fluctuating functions of time. The magnitude of these fluctuations and their relation to the magnitude of the variations in the nitrogen splittings depend on the details of the modulating mechanism, but certain features can be elucidated just from the dependence of the widths on the spectral densities. We confine our treatment to the *p*-dinitrobenzene and dinitrodurene anions for simplicity. Similar but more complicated treatments can be made for *m*-dinitrobenzenes and for unsymmetrically substituted *para* compounds.

In the 1,4-dinitrobenzene anion, the four equivalent protons split the spectrum into five lines with relative statistical weights 1:4:6:4:1. The protons at Positions 2 and 6 are instantaneously equivalent with respect to any perturbations originating at the nitro groups, and form a subgroup of completely equivalent protons.⁷ The protons at Positions 3 and 5 form another completely equivalent subgroup, and we designate the two groups by 1 and 2, respectively. There are again two spectral densities, $j_{11}^{(I)} (=j_{22}^{(I)})$ and $j_{12}^{(I)} (=j_{21}^{(I)})$ (which are of course different, in general, from the spectral densities for the nitrogen nuclei). Using the methods of Ref. 7, it is readily shown that⁸ the contributions of these spectral densities to the width of the proton lines are identical to the contributions for the modulation of two nitrogen nuclei discussed above except that now two components contribute $2(j_{11}^{(I)} - j_{12}^{(I)})$ to the width of the central line, and four components make no contribution. When the effect of the isotropic modulation of the protons is small, the appropriate average for the central line is $\frac{2}{3}(j_{11}^{(I)} - j_{12}^{(I)})$. A similar analysis can be carried through for the dinitrodurene anion, and here we only quote the result for complete out-of-phase correlation ($j_{12}^{(I)} = -j_{11}^{(I)}$) when this mechanism makes a large contribution to the linewidth ($j_{11}^{(I)}$ large).⁸

⁹ P. W. Anderson, J. Phys. Soc. Japan **9**, 316 (1954).

¹⁰ F. Bloch, Phys. Rev. **70**, 460 (1946); J. A. Pople, W. G. Schneider, and H. J. Bernstein, *High-Resolution Nuclear Magnetic Resonance* (McGraw-Hill Book Company, Inc., New York, 1959); H. S. Gutowsky, D. W. McCall, and C. P. Slichter, J. Chem. Phys. **21**, 279 (1953); and H. M. McConnell, J. Chem. Phys. **28**, 430 (1958).

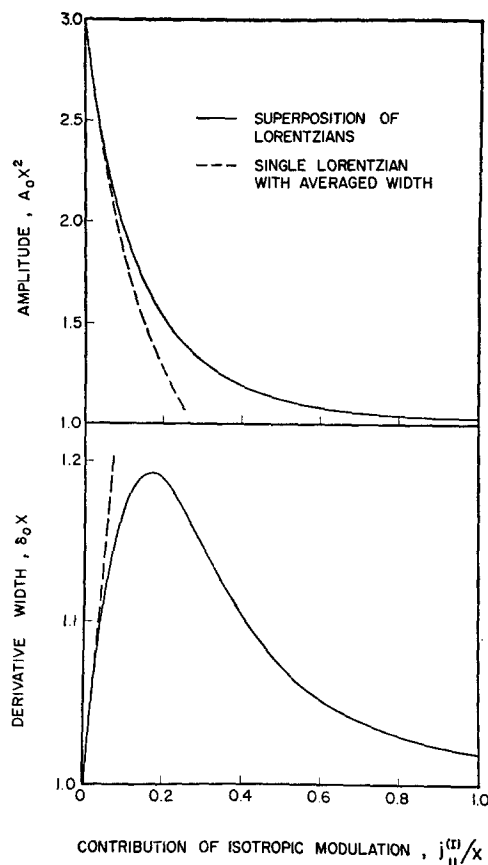


FIG. 1. Computed amplitudes and widths of the central line ($M_N=0$) in the spectrum from two equivalent ^{14}N nuclei as a function of the extent of the out-of-phase modulation of the nitrogen hyperfine splittings. Upper figure: Peak-to-peak derivative amplitude $A_0 X^2$ vs $j^{(I)}/X$, where A_0 is the amplitude, $j^{(I)}$ the contribution of the out-of-phase modulation of the isotropic interaction to the linewidth, and X is the linewidth from other line-broadening effects. Curve normalized so that $A_0 X^2=3$ for $j^{(I)}/X=0$. Lower figure: Separation of derivative extrema, δ_0 , vs $j^{(I)}/X$. Curve normalized so that $\delta_0=1$ for $j^{(I)}/X=0$. The solid curves are computed according to the theory of Freed and Fraenkel as a superposition of Lorentzian-shaped components, and the dashed curves are calculated according to the theory of Kivelson as a single Lorentzian-shaped curve with an appropriately averaged value of the linewidth.

Letting M_{Me} be the sum of the z components of the spin angular momenta of all 12 methyl-group protons, only the lines for which $M_{Me} = \pm 6, \pm 4, \pm 2$, and 0 have narrow components and their statistical weights are 1:36:225:400:225:36:1. In the absence of these linewidth effects, the 13 lines would have relative statistical weights 1:12:66:220:495:792:924:792:...

Methyl-Group Rotation

Rotation of the methyl groups modulates the isotropic hyperfine splittings of the methyl-group protons, and if the rate of rotation is slow enough, linewidth effects should be observable. This problem has been analyzed elsewhere,⁸ and here we only quote a result for the limiting case of a large contribution to the line-

widths from the rotational motion: correlated motion of several methyl groups is predicted to give a spectrum in which every third methyl-proton line is sharp, while the other methyl-proton lines are predicted to be broad.

Dipolar and g -Tensor Contributions

All the lines in a spectrum are also broadened by the modulation, through molecular tumbling, of two anisotropic effects: the anisotropic intramolecular dipolar interaction between the electron spin and the nuclear spins, and the g -tensor interaction. In the few cases that have been investigated in detail,^{6,11} it is permissible, within a particular line, to average over the components that have different widths, and we shall do so here. Off-diagonal elements of the relaxation matrix as well as nonsecular contributions will be neglected.⁷

In most of the radicals investigated in the present work, there are appreciable modulations of the isotropic splittings, and/or the pi-electron spin densities, which modify the magnitudes of the dipolar and perhaps also the g -tensor contributions. Although the extent of these effects can only be estimated from detailed considerations of a particular mechanism, some of the features can be described in a purely phenomenological way. Two equivalent ¹⁴N nuclei in a dinitrobenzene anion, for example, will in general not be completely equivalent⁷ when the spin densities are modulated, and the spectral density $j_{N(11)}^{(D)}$ describing the contribution to the linewidth of the dipolar interactions with one of the nuclei will be different from the spectral density $j_{N(12)}^{(D)}$ governing the cross-term dipolar interactions with both nuclei. The average width from the dipolar and g -tensor interactions can be shown to be⁷

$$[T_{2,N}(M_N)]^{-1} = j_{N(11)}^{(D)}\eta_{11}^{(D)}(M_N) + j_{N(12)}^{(D)}\eta_{12}^{(D)}(M_N) + \frac{1}{3}j_N^{(DG_2)}B_0M_N + X_N, \quad (2.1)$$

where $\eta_{11}^{(D)}(\pm 2) = \frac{1}{9}$, $\eta_{11}^{(D)}(\pm 1) = -\frac{5}{9}$, $\eta_{12}^{(D)}(\pm 2) = \frac{8}{9}$, $\eta_{12}^{(D)}(\pm 1) = \frac{2}{9}$, and $\eta_{11}^{(D)}(0) = \eta_{12}^{(D)}(0) = 0$. The quantity X_N is given by

$$X_N = \frac{1}{3}[56j_{N(11)}^{(D)} - 32j_{N(12)}^{(D)}] + \frac{8}{3}j^{(G_2)}B_0^2 + X_N', \quad (2.2)$$

where X_N' allows for the contributions from other mechanisms which presumably do not depend on M_N . The spectral density $j_N^{(DG_2)}$ arises from a cross term between the dipolar and g -tensor interactions, and $j^{(G_2)}$ results from the g -tensor interaction alone. The external magnetic field which produces the Zeeman splitting is given by B_0 . Equation (2.1) is only applicable to a set of lines for which the sum of the magnetic quantum numbers for nuclei other than the two nitrogens is zero, and must be added to the width contributions arising from modulation of the isotropic splittings. In the limit that the two nitrogen nuclei are completely equivalent,

$j_{N(12)}^{(D)} = j_{N(11)}^{(D)}$, and the coefficient of $j_{N(11)}^{(D)}$ becomes $\eta^{(D)}(M_N)$ where $\eta^{(D)}(\pm 2) = 10$, $\eta^{(D)}(\pm 1) = 3$, and $\eta^{(D)}(0) = 0$. The linewidth variation predicted by Eq. (2.1) has a term which depends linearly on M_N and also a symmetric contribution which is a function of $|M_N|$. The symmetric variation broadens the $M_N = \pm 2$ lines more than the $M_N = \pm 1$ lines and, unless $j_{N(12)}^{(D)} \leq \frac{2}{3}j_{N(11)}^{(D)}$, it also broadens the $M_N = \pm 1$ lines more than the central line. It gives a dependence on M_N which varies approximately, but not exactly, as M_N^2 . The linewidth effects from the dipolar and g -tensor contributions are thus quite different from those arising from an out-of-phase correlation of the modulation of the isotropic splittings. On the other hand, since an in-phase correlation of the isotropic modulation of the nitrogen splittings makes a width contribution proportional to M_N^2 , this type of modulation produces effects that are almost indistinguishable from the pure dipolar interaction.

The contribution of the dipolar and g -tensor interactions to the widths of the proton lines can also be obtained readily. For simplicity, we neglect the effects of modulation of the spin densities, assuming that in the nitrobenzene anions the dipolar interaction with the protons is less affected by this modulation than is the dipolar interaction with the ¹⁴N nuclei. This is a reasonable first approximation because most modulating mechanisms have a larger effect on the nitro groups than on the spin densities of those carbon atoms which contribute significantly to the dipolar terms for the protons. The following expressions, which are readily obtained from the methods of Refs. 6 and 7, are to be added to the contribution from the modulation of the isotropic interactions, and apply when the sum of the magnetic quantum numbers of all other nuclei in the radical is zero. For a single proton,

$$[T_2(m)]^{-1} = \frac{5}{3}j_{11}^{(D)}m^2 + \frac{1}{3}j_1^{(DG_2)}B_0m + X_H, \quad (2.3)$$

where

$$X_H = \frac{3}{4}j_{11}^{(D)} + \frac{8}{3}j_1^{(G_2)}B_0^2 + X_H'. \quad (2.4)$$

For two equivalent, but not completely equivalent, protons (as, for example, the protons at Positions 4 and 6 of 1,3-dinitrobenzene^{7,12})

$$[T_{2,N}(M_H)]^{-1} = \frac{8}{3}j_{12}^{(D)}M_H^2 + \frac{1}{3}j_1^{(DG_2)}B_0M_H + X_H, \quad (2.5)$$

where

$$X_H = \frac{1}{3}[7j_{11}^{(D)} - 4j_{12}^{(D)}] + \frac{8}{3}j^{(G_2)}B_0^2 + X_H'. \quad (2.6)$$

Here $M_H = m_1 + m_2$ and m_i is the z component of spin for the i th proton. The only other case of present interest is that of the four methyl groups in the dinitrobenzene anion. The methyl groups are assumed to be rapidly rotating, and those at Positions 2 and 5 form one completely equivalent subgroup (Group 1) while those at

¹¹ J. W. H. Schreurs and G. K. Fraenkel, *J. Chem. Phys.* **34**, 756 (1961).

¹² J. W. H. Schreurs, thesis, Free University of Amsterdam, Amsterdam, 1962; J. W. H. Schreurs and D. Kivelson, *J. Chem. Phys.* **36**, 117 (1962).

Positions 3 and 6 form another (Group 2).⁶ Using indices on the spectral densities to refer to the subgroups, and letting $M_H = \sum m_i$, one can show that

$$[T_{2,Av}(M_H)]^{-1} = \left[\frac{4}{3} j_{11}^{(D)} + \frac{1}{3} j_{12}^{(D)} \right] M_H^2 + \frac{1}{3} j_1^{(DG_2)} B_0 M_H + X_H, \quad (2.7)$$

where

$$X_H = \frac{2}{11} [57 j_{11}^{(D)} - 24 j_{12}^{(D)}] + \frac{8}{3} j^{(G_2)} B_0^2 + X'_H. \quad (2.8)$$

Each of these averaged expressions for the widths of the proton lines has a term linear in M_H and another that is quadratic in M_H .

Cross Terms

The linewidth formulas also contain cross terms between different groups of equivalent nuclei as, for example, between the nitrogen nuclei and the protons in the *p*-dinitrobenzene anion,⁶ or between the three different types of protons in the *m*-dinitrobenzene anion. This type of cross term involves the product of the quantum numbers of the two different sets of nuclei and can result from either the modulation of the isotropic splittings or from the pure anisotropic dipolar interaction. The only cross term that will be used in the following will be that between the nitrogen nuclei and the proton at Position 4 in the 2,6-dinitrophenolate dianion radical. It is of the form^{6,7}

$$[j_{NH(4)}^{(I)} + \frac{8}{3} j_{NH(4)}^{(D)}] M_N m_4, \quad (2.9)$$

and if the coefficient in brackets is positive (negative) it causes those lines for which M_N and m_4 are of the same sign to be broader (narrower) than those for which M_N and m_4 are of opposite sign. The experimental determination of this cross term will be useful in estimating the relative signs of the hyperfine splittings a^N and a_4^H in the 2,6-dinitrophenolate anion.

III. EXPERIMENTAL PROCEDURES

The radicals were produced by electrolytic reduction in *N,N*-dimethylformamide (DMF) solutions at room temperature using techniques similar to those described previously.¹³ The potentials during electrolysis were measured between the mercury-pool cathode and a silver-silver perchlorate reference electrode.¹³ The procedure for cooling of the samples in the ESR spectrometer, and a description of the spectrometer, are given elsewhere,^{6,11,14} as are the considerations involved in using amplitude measurements of derivative spectra to obtain relative linewidths.^{6,15}

m-Dinitrobenzene and dinitromesitylene were obtained from the Eastman Organic Chemicals Division of the Eastman Kodak Company, and 2,6-dinitrotoluene was obtained from the Aldrich Chemical Company.

¹³ P. H. Rieger, I. Bernal, W. H. Reinmuth, and G. K. Fraenkel, *J. Am. Chem. Soc.* **85**, 683 (1963).

¹⁴ J. M. Hirshon and G. K. Fraenkel, *Rev. Sci. Instr.* **26**, 34 (1955).

¹⁵ J. H. Freed, thesis, Columbia University, New York, 1962.

Nitrodurene and dinitrodurene were synthesized by Bernal,^{5,16} and the other compounds studied were obtained from K & K Laboratories, Inc. The commercially procured materials were used without purification. Tetra-*N*-propylammonium perchlorate was employed as the supporting electrolyte. Its purification, and that of the DMF, have been described by Rieger *et al.*¹³

IV. RESULTS

In this section the results are given separately for each compound studied. The radicals with ESR spectra that exhibited an alternation in linewidths are treated first. Although most of our studies are primarily qualitative in nature, in a few instances semiquantitative interpretations are possible, and before proceeding to the description of the results it is thus necessary to develop techniques for interpreting the linewidth variations in terms of the spectral densities (see Sec. II).

Procedures for evaluating the spectral densities from the amplitudes of the first derivative of the ESR absorption when the contributions from modulations of the isotropic splittings are negligible have been described in detail elsewhere.⁶ These methods can also be employed if the effect of the isotropic interactions is sufficiently small to allow averaging over the widths of the different components. When there is a large contribution from the modulation of the isotropic splittings, however, a different analysis is required. For simplicity we consider only one problem, that of two equivalent nitrogen nuclei with $j_{12}^{(I)} = -j_{11}^{(I)}$ and $j_{12}^{(D)} = j_{11}^{(D)}$.

In the approximation that the contributions of the dipolar and *g*-tensor interactions are small enough to permit an averaging over the different components of a degenerate line, the $M_N = \pm 1$ and ± 2 lines are simple Lorentzian-shaped curves, and the term in $j^{(DG_2)} M_N$ can be evaluated in the usual way.⁶ For the other coefficients, we express the widths of the $M_N = \pm 1$ and $+2$ lines relative to the width of the $M_N = -2$ line by computing the quantity $W_i = (D_i A_{-2} / A_i)^{1/2}$, where A_i is the amplitude and D_i the degeneracy of the *i*th line.⁶ Then the sums S_1 and S_2 ,

$$S_1 = \frac{1}{2}(W_1 + W_{-1}), \quad (4.1)$$

$$S_2 = \frac{1}{2}(W_2 + W_{-2}), \quad (4.2)$$

¹⁶ I. Bernal, thesis, Columbia University, New York, 1963.

¹⁷ The assumption that $j_{12}^{(I)} = -j_{11}^{(I)}$ and, simultaneously, that $j_{12}^{(D)} = j_{11}^{(D)}$, may not be representative of any real molecules. But even when $j_{11}^{(I)}$ is small, there are five parameters which contribute effects that are even functions of M_N ($j_{11}^{(I)}$, $j_{12}^{(I)}$, $j_{11}^{(D)}$, $j_{12}^{(D)}$, and X_N), and one which contributes a function that is linear in M_N ($j^{(DG_2)}$), and there are only five hyperfine lines. Thus, in any case, all the parameters cannot be evaluated without either assumptions like this or a detailed model of the isotropic modulation to interrelate the different spectral densities.

¹⁸ We use a tilde over the quantum number to indicate a spectral index number.⁶ This number is defined to be positive on the high-field side of the spectrum, and the index number \tilde{M}_i is equal to the quantum number M_i if the associated hyperfine splitting is negative, while if the splitting is positive, $\tilde{M}_i = -M_i$.

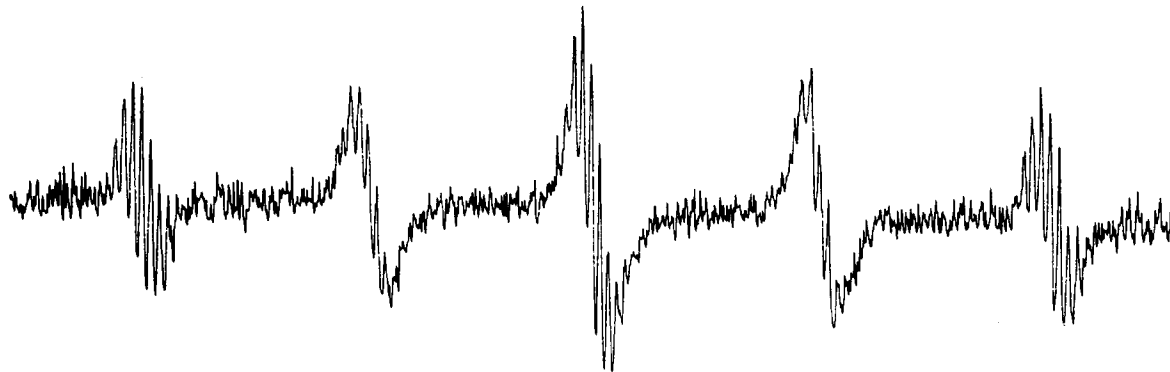


FIG. 2. First derivative of the ESR spectrum of the dinitrodurene anion in DMF at 50°C. The magnetic field increases to the right. The spectrum was scanned from high to low fields (right to left), and the low-field lines are of too low an intensity because of radical decay.

are, from Eq. (2.1) with $j_{N(12)}^{(D)} = j_{N(11)}^{(D)}$,

$$S_1 = \alpha(3j^{(D)} + j^{(I)} + X), \quad (4.3)$$

$$S_2 = \alpha(10j^{(D)} + X), \quad (4.4)$$

where α is a constant determined by the width of the line with $\bar{M}_N = -2$, and $j^{(D)} = j_{N(11)}^{(D)}$, etc. Solving these two equations for $j^{(I)}$ gives

$$j^{(I)}/X = [S_1 - \frac{3}{10}S_2]/(\alpha X) - \frac{7}{10}. \quad (4.5)$$

Proceeding now by trial and error, a value of αX is assumed, and Fig. 1 is used to obtain $A_0 X^2$. Dividing $A_0 X^2$ by the square of the assumed value of αX gives $A_0 \alpha^{-2}$, and it can be shown that $A_0 \alpha^{-2} = (A_0/A_{-2})$, the ratio of the amplitudes of the $M_N = 0$ and $\bar{M}_N = -2$ lines. Comparison of this calculated value of the relative amplitudes with the experimental ratio then allows the proper trial-and-error selection of αX , which, with the experimental value of α , gives X and $j^{(I)}$. The experimental value of α is obtained from the measured width of the $\bar{M}_N = -2$ line. With X and α known, Eq. (4.3) is then solved for $j^{(D)}$.

V. RADICALS WHICH EXHIBIT ALTERNATING LINEWIDTHS

1. Hindered Dinitrobenzenes

The hindered dinitrobenzene anions with spectra that exhibit an alternating linewidth include dinitrodurene, 2,6-dinitrotoluene, dinitromesitylene, and 2,6-dinitro-3,5-dimethyl-4-acetyl-*t*-butylbenzene. The last compound was investigated because it is the most highly hindered dinitrobenzene derivative that was readily available, and it was hoped that spectra corresponding to two different static conformations would be detected at low temperatures (see Sec. II). Such spectra were not found, but the compound did exhibit a pronounced alternating linewidth.

Dinitrodurene (1,4-Dinitro-2,3,5,6-tetramethylbenzene)

Electrolysis at a potential of -1.3 V of DMF solutions containing millimolar concentrations of dinitrodurene produces a radical the room temperature spectrum of which has been reported previously.^{2,16} The spectrum shows a marked alternating linewidth effect.³ Spectra obtained from samples electrolyzed at room temperature were studied in the ESR spectrometer both above and below room temperature. The spectrum obtained at 50° is shown in Fig. 2. Initially the solution obtained on electrolysis was greenish-yellow and only a weak ESR absorption was found; but after appreciable electrolysis it became dark red and gave a strong spectrum. For comparison, we note that the *p*-dinitrobenzene anion spectrum⁶ was obtained from a greenish-yellow solution, but that an orange color was formed upon generating the radical near the second polarographic wave. It is not possible to conclude from our experiments whether the dinitrodurene anion radical is red or greenish-yellow. If the radical is red, it would be necessary to postulate that the greenish-yellow color arises from an impurity, while if the radical is greenish-yellow, the red color would have to be a nonradical by-product of the electrolysis. There is no evidence that more than one stable radical is produced in the electrolysis. Since the alternating linewidth phenomenon is found under a variety of conditions, the uncertainty about some of the nonradical species in the solution does not have a significant bearing on the linewidth observations.

On cooling the red solutions, there was an appreciable decrease in the intensity of the ESR signal. This phenomenon, which was reversible, greatly increased the difficulty of making low-temperature studies.

The room-temperature spectrum of the dinitrodurene anion² is split into five major lines from hyperfine interactions with two equivalent nitrogen nuclei¹⁰ of

¹⁰ Hyperfine splitting constants are arbitrarily given as positive numbers for convenience. When we wish to specify the sign, it is explicitly indicated.

magnitude $a^N = 6.99$ G. These lines correspond to¹⁸ $M_N = -2, -1, 0, 1, 2$, and have predicted relative statistical weights of 1:2:3:2:1. The experimental ratios of the amplitudes of the first derivative, however, are (very approximately) 1:0.67:1.45:0.65:0.73, respectively.²⁰ There is additional splitting in the spectrum from the 12 equivalent methyl-group protons, with splitting constant $a^H \cong 0.25$ G. The most striking indication of the alternating linewidth phenomenon is the poor resolution of the small proton splittings of the $M_N = \pm 1$ lines as compared to the resolution of the $M_N = 0$ and ± 2 lines. Although as a first approximation the linewidth variation could be described as a broadening of the $M_N = \pm 1$ lines, but not of the $M_N = \pm 2$ lines, it is also important to recognize that the amplitude of the central line is significantly less than three times the mean of the amplitudes of the $M_N = \pm 2$ lines. The amplitudes and the widths also vary as an odd function of M_N , the $M_N = +2$ line being broader than the $M_N = -2$ line. An integrated spectrum (i.e., the absorption spectrum) was obtained by Rieger and Bernal,³ who found the relative absorption amplitudes and areas (intensities) of the five principal lines to be in the approximate ratios 1.0:1.5:2.0:1.5:1.0, and 0.38:0.78:1.00:0.71:0.44, respectively. The results for the areas are quite approximate because of a somewhat erratic baseline, particularly for the central line, but the ratios are reasonably consistent with the expected statistical weights. Experiments at increased microwave power did not alter the spectrum to a marked extent, thus indicating that the alternating linewidth phenomenon is not caused by saturation effects.

A spectrum obtained at -30° shows that the $M_N = \pm 1$ lines are broader than at 20° , the dependence on an odd function of M_N is increased, and the symmetric broadening, which has the largest effect on the $M_N = \pm 2$ lines, is enhanced. At $+50^\circ$ (Fig. 2), all these effects are reduced. The low relative intensity of the low-field line in this spectrum arises from radical decay. Thus the extent of the alternating linewidth effect increases with decreasing temperature. At low temperatures the correlation time of the dynamical motion probably increases, and if the mechanism were a two-jump phenomenon, very long correlation times would lead to a spectrum with two different nitrogen splittings (see Sec. II and Ref. 7). To test for this possibility, experiments were conducted at temperatures of -55°C , which is near the freezing point (around -65°C) of the solution. For the very-low-temperature studies, solutions 10mM in dinitrobenzene were employed to overcome in part the decrease of ESR signal intensity at low temperatures. All the linewidth variations increased,

²⁰ The values here indicate the trends of the relative widths for the different lines, but because of the incompletely resolved methyl-proton splittings, the actual numerical results are quite uncertain. Careful fitting of computed curves to the experimental spectra might improve the accuracy somewhat, but this laborious procedure did not seem warranted for a study of the general nature of the line-broadening phenomena.

but no evidence was found for the presence of two inequivalent nitrogen splittings. The linewidths estimated from the derivative spectrum²¹ at -55° were 1.5, 0.88, and 1.6 G, respectively, for the $M_N = -2, 0$, and 2 lines. The $M_N = \pm 1$ lines were so broad and weak that the measured widths of about 2.7 G were extremely uncertain.

An approximate estimate of the spectral densities can be made using the procedure outlined at the beginning of this section based on the curves of Fig. 1. Because of the uncertainties in the experimental data,²⁰ only the over-all trends can be obtained from this analysis. Using the relative amplitudes of the lines, and the approximate widths of the methyl-proton components of the central line at room temperature,²¹ $\delta_0 = 0.1$ G, one finds (in reciprocal seconds) $X_N = 1.5 \times 10^6$, $j_N^{(l)} = 1.45 \times 10^6$, and $j_N^{(D)} = 0.04 \times 10^6$. If the modulation of the isotropic splittings is caused by a two-jump mechanism,⁷ $j_N^{(l)} = \frac{1}{8}\tau_0\gamma^2\Delta a^2$ where τ_0 is the lifetime of each state and Δa is the splitting-constant difference (in gauss) between the two states. Thus, with the experimental value of $j_N^{(l)}$, we have $\tau_0\Delta a^2 = 3.7 \times 10^{-8}$ G²·sec. The two-jump rotational model^{7,8} might lead to a value of Δa of as much as²² 20 G, so that the magnitude of $j_N^{(l)}$ could be accounted for if $\tau_0 \sim 10^{-10}$ sec. Of course Δa might be considerably smaller, with correspondingly larger values of τ_0 , and a two-jump model may not be an adequate representation of the mechanism, so that these numbers only serve to indicate the magnitude of the effects. Nevertheless, the interpretation of the linewidth alternation is entirely consistent with the range of parameters that might be anticipated in a detailed molecular model.

At -55°C , the nitrogen splitting was found to increase by about $3\frac{1}{2}\%$ to 7.25 G. Spectra obtained at room temperature with dimethylsulfoxide as the solvent also showed the alternating linewidth phenomenon, and no significant differences were observed except for an increase of the nitrogen splitting to $a^N = 7.74 \pm 0.03$ G.

The spectra can also be analyzed to obtain information about the variation of the widths of the methyl-proton lines, but since the experiments were not designed to observe these effects, the available data is somewhat scanty. Results are given in Table I for the methyl-proton splittings of the central nitrogen line ($M_N = 0$) at 20° and -30° . One spectrum was used to obtain the data at 20° , and an average of two spectra for the results at -30° (except for the $M_{Me} = \pm 4$ lines). In both spectra the widths²¹ of the methyl-group lines are about 0.1 G. At 20° , the amplitudes of the lines change in an essentially symmetric manner about the center of the spectrum, with a decrease, compared to the predicted statistical weights, as a monotonic function of $|M_{Me}|$. At -30° there is an asymmetric variation of the line-

²¹ Linewidths are given as the full width between derivative extrema.

²² P. H. Rieger and G. K. Fraenkel, J. Chem. Phys. **39**, 609 (1963).

TABLE I. Dinitroreurene anion: amplitudes of methyl-proton lines.

$\tilde{M}_{Me}^{a,b}$	Relative statistical weight	Relative amplitudes ^c	
		20°C	-30°C
-4	0.0715	0.045	0.06
-3	0.238	0.180	0.210
-2	0.535	0.458	0.505
-1	0.858	0.820	0.855
0	1.000	1.000	1.000
1	0.858	0.817	0.832
2	0.535	0.455	0.446
3	0.238	0.185	0.146
4	0.0715	0.030	0.03

^a \tilde{M}_{Me} is the spectral index number¹⁸ for the methyl-proton lines, and is the sum of the \tilde{m}_i 's for the 12 equivalent methyl protons.

^b The $\tilde{M}_{Me} = \pm 5$ and ± 6 lines were too weak to be observed.

^c Amplitudes of the first derivative of the central nitrogen line.

widths which implies the presence of a linewidth contribution that is linear in M_{Me} . It is quite clear that neither spectrum shows a linewidth alternation that depends on M_{Me} , and thus there is no appreciable out-of-phase modulation of the spin densities which affects the methyl-proton splittings nor any significant slowing down of the methyl-group rotations.

The linear term in the variation of the linewidths with respect to M_N [Eq. (2.1)] can be used to estimate^{6,23} the sign of the nitrogen hyperfine splitting a^N if it can be assumed that the component of the g tensor perpendicular to the aromatic ring, g_3 , is less than the mean of the in-plane components,^{24,25} $\frac{1}{2}(g_1 + g_2)$. The results of this analysis show that a^N is positive⁶ (see the discussion of the 2,6-dinitrophenolate anion below).

2,6-Dinitro-3,5-dimethyl-4-acetyl-*t*-butylbenzene (DDTB)

A 3.4mM solution of this compound in DMF was reduced electrolytically at -1.1 V, which is in the vicinity of the first polarographic wave. A yellowish-green solution was obtained which exhibited an ESR spectrum. The radical was quite unstable, and decayed with a half-life of about 3 min. The five lines observed in the spectrum are attributable to hyperfine interactions with two equivalent nitrogen nuclei. The splitting constant is $a^N = 10.6 \pm 0.1$ G. No noticeable fine structure was detectable on the five lines. A particularly pronounced linewidth alternation was observed in which the $M_N = \pm 1$ lines had much smaller amplitudes than the other components, and at -30° the derivative spectra of the $M_N = \pm 1$ lines obtained with the normal field-modulation amplitude⁵ disappeared. No additional lines were observed at temperatures down to -72°, several degrees below the freezing point of the solution, so that even in this highly hindered compound it was

²³ E. deBoer and E. L. Mackor, *J. Chem. Phys.* **38**, 1450 (1963).

²⁴ H. M. McConnell and R. E. Robertson, *J. Phys. Chem.* **61**, 1018 (1957).

²⁵ A. J. Stone, *Proc. Roy. Soc. (London)* **A271**, 424 (1963); *Mol. Phys.* **6**, 509 (1963).

not possible to find inequivalent nitrogen splittings. At -53° the linewidths²¹ were about 1.2 G for the $\tilde{M}_N = -2$ and 0 lines and 1.9 G for the +2 lines, while at -72° they were 2.7 and 5.4 G, respectively. At high reduction potentials an orange-brown solution was obtained which exhibited a three-line spectrum with a splitting of $a^N = 22.6 \pm 0.2$ G. Similar loss of a nitrogen splitting at higher polarographic waves has been observed in the spectra from the polynitromesitylenes and dinitroreurene^{5,16}

2,6-Dinitrotoluene

Electrolysis of a 5mM solution of this compound in DMF at -1.2 V (slightly above the first polarographic wave) produced a bright red solution. A complex spectrum was obtained with linewidths²¹ of about 0.13 G, and the following splittings: ring protons, $a_4^H = 1.14 \pm 0.03$ G and $a_3^H = a_6^H = 4.06 \pm 0.03$ G; methyl protons, $a_{Me}^H = 2.91 \pm 0.03$ G; and nitrogens, $a^N = 4.33 \pm 0.03$ G. The splitting constants are similar to those for the *m*-dinitrobenzene anion (see below), and have been discussed in detail elsewhere.²² The relative amplitudes of the lines in the spectrum predicted using these splitting constants and the appropriate statistical weights are in fairly good agreement with the experimental spectrum, but extensive overlap precluded the possibility of either detailed comparison of amplitudes or a complete analysis of the linewidth variations. There may, however, be a slight alternating linewidth effect.

The spectrum of the 2,6-dinitrotoluene anion obtained at -45° was much simpler than the room-temperature spectrum because of the disappearance of *all* the lines for which $M_N = \pm 1$. There is thus a prominent linewidth alternation at low temperature, and the effect is more marked than for the *m*-dinitrobenzene anion²⁶ (see below). The average linewidth at -45° was about 0.18 G, and there was a significant linear dependence of the linewidths on \tilde{M}_N which broadened the high-field lines.

Examination of several lines arising from methyl-proton splittings showed that there was no appreciable departure of the amplitudes from the relative statistical weights of 1:3:3:1.

Nitromesitylenes

The anion radical produced at the first polarographic wave of dinitromesitylene (2,6-dinitro-1,3,5-trimethylbenzene) has an ESR spectrum with a pronounced alternating linewidth. The room-temperature spectrum, which is reproduced elsewhere,^{5,16} has such broad $M_N = \pm 1$ lines that they are not observable at a field-modulation amplitude sufficiently small to permit detection of the incompletely resolved proton hyperfine structure on the $M_N = 0$ and ± 2 lines. A similar but not identical spectrum is obtained from trinitromesitylene

²⁶ J. H. Freed, P. H. Rieger, and G. K. Fraenkel, *J. Chem. Phys.* **37**, 1881 (1962).

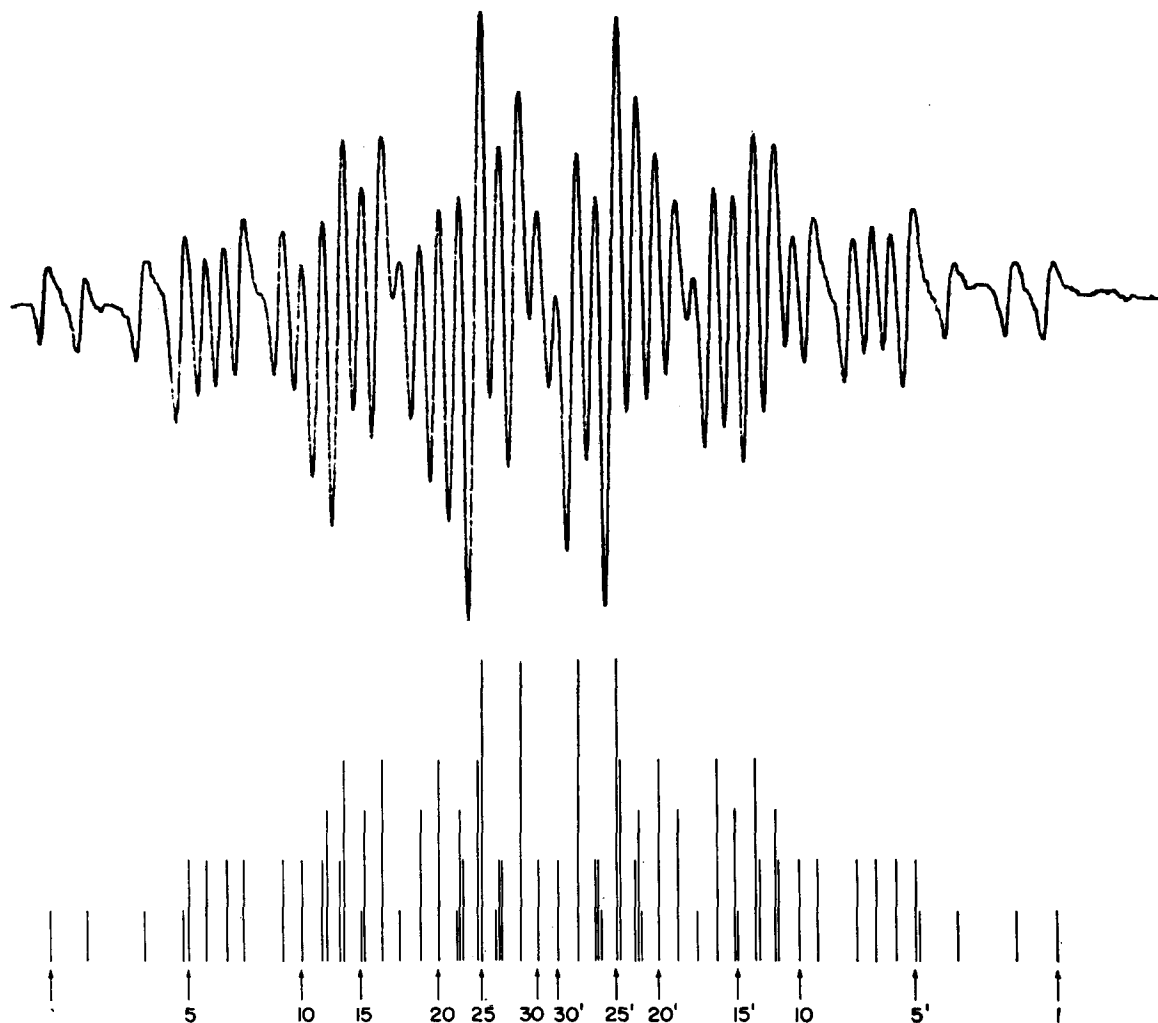


FIG. 3. First derivative of the ESR spectrum of the *m*-dinitrobenzene anion in DMF at 20°C. The magnetic field increases to the right. See Table II.

on reduction at the second polarographic wave. The splittings from only two nitrogen nuclei are observed, and there is a strong alternating linewidth effect.^{5,16} Spectra containing the splittings from only one nitrogen nucleus generated at the third polarographic wave of trinitromesitylene, the second wave of dinitromesitylene, and the first wave of nitromesitylene, do not show alternations in linewidth.^{5,16}

2. Unhindered Dinitrobenzenes

m-Dinitrobenzene

Electrolysis of a 1mM solution of *m*-dinitrobenzene in DMF at -1.1 V yields a bright violet-colored solution immediately after the start of the electrolysis. Spectra obtained at room temperature and at -50° are shown in Figs. 3 and 4, respectively. The spectrum was also studied at -35° and -40° . The linewidths of the room-temperature spectrum are about 0.20–0.25 G, and although we were not able to produce narrower

lines by varying the potential of the electrolysis, more dilute solutions were not investigated. At -50° some of the lines are narrower, the smallest width being about 0.13 G. There are a number of accidental degeneracies in the spectra and the unusual appearance of the low-temperature spectrum arises in part from several linewidth effects which are described in the following. The splitting constants at the two temperatures are slightly different (see below), so that some of the spacings are altered in the two spectra, and certain lines which are completely overlapped at room temperature are resolved at low temperature.

The hyperfine splittings obtained at room temperature are (in gauss): $a^N = 3.97 \pm 0.01$, $a_2^H = 2.77 \pm 0.02$, $a_4^H = a_6^H = 4.49 \pm 0.01$, and $a_5^H = 1.08 \pm 0.02$. These values differ appreciably from those reported by Maki and Geske²⁷ for acetonitrile solutions, namely, $a^N = 4.68$, $a_2^H = 3.11$, $a_4^H = a_6^H = 4.19$, and $a_5^H = 1.08$. This solvent

²⁷ A. H. Maki and D. H. Geske, J. Chem. Phys. **33**, 825 (1960).

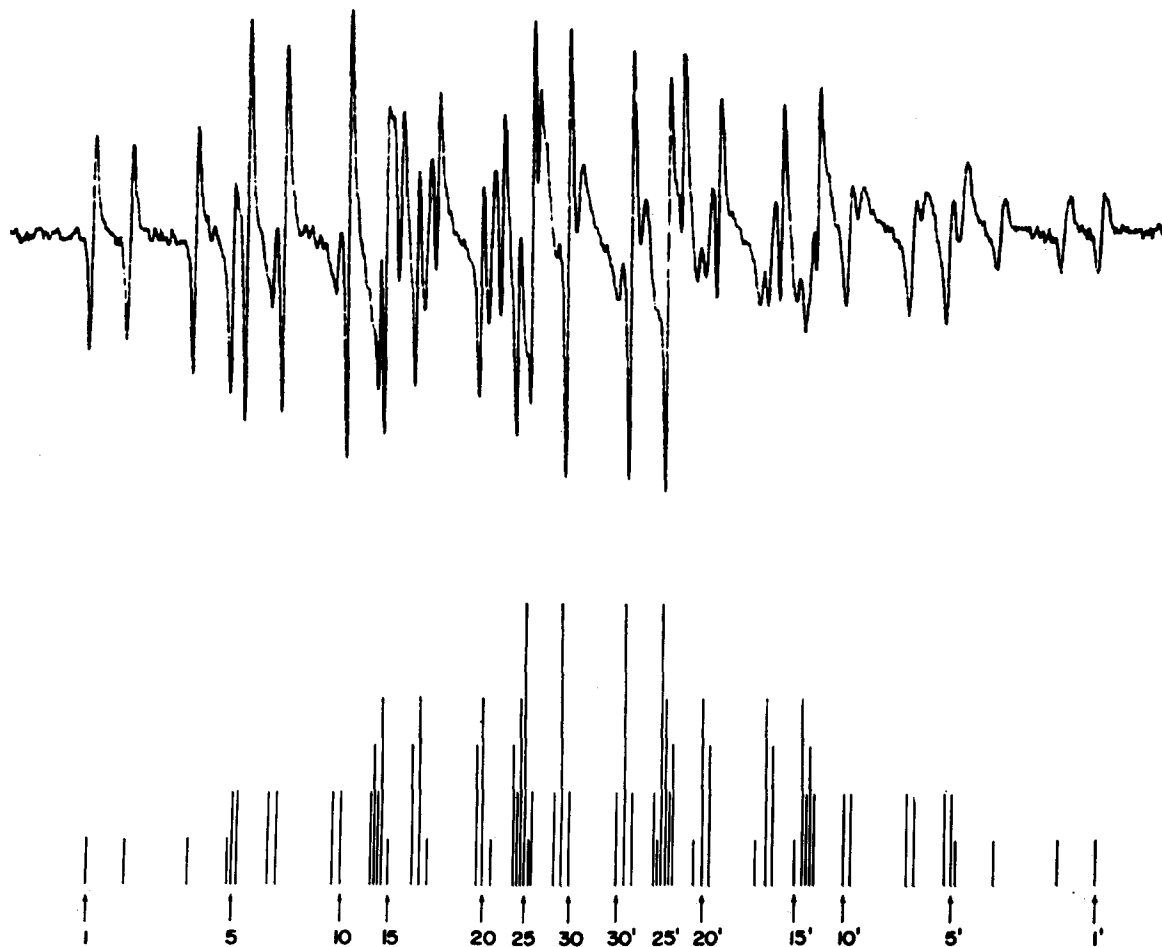


FIG. 4. First derivative of the ESR spectrum of the *m*-dinitrobenzene anion in DMF at -50°C . The magnetic field increases to the right. See Table II.

dependence of the splittings has been discussed elsewhere.²² While the spectra published by Maki and Geske²⁷ for the *p*- and *o*-dinitrobenzene anions are not very well resolved, particularly when compared with the resolution obtained in DMF solutions,⁶ their analysis of these two spectra was quite convincing. The spectrum they reported for the *meta* isomer, on the other hand, was less easily interpreted. It is rather weak and poorly resolved, and the experimental intensities appear to differ from the predicted values. The room-temperature spectrum in DMF, Fig. 3, is much more easily interpreted. It has comparatively good resolution, is quite symmetric, and has relative amplitudes that are in fairly good agreement with the ratios of the statistical weights.

The assignment of spectral index numbers¹⁸ is given in Table II. The lines are numbered to correspond to the scheme in Figs. 3 and 4. The spectral index number \tilde{M}_N applies to the combination of the two nitrogen nuclei; \tilde{M}_4 to the combination of the equivalent protons at Positions 4 and 6; and \tilde{m}_2 and \tilde{m}_5 refer to the protons at Positions 2 and 5, respectively. The numbers included in a bracket to the right are lines which are

overlapped at room temperature, while those included in parentheses to the left are overlapped at -50° .

The table also contains a detailed analysis of the relative amplitudes of the lines in the -50° spectrum obtained from an average of four different spectra. The adjusted relative amplitudes for the unoverlapped lines, given in the last column of the table, are the ratios A_i/D_i divided by $A_{29'}/D_{29'}$, where A_i and D_i are the amplitude and statistical weight, respectively, of the i th line. Inspection of this column indicates that the lines for which $\tilde{M}_N = 2$ are of much lower amplitude (broader) than those for which $\tilde{M}_N = -2$, so that there is an appreciable linear dependence of the linewidths on \tilde{M}_N . Taking into account this linear variation, it is clear that all the unoverlapped lines for which $\tilde{M}_N = \pm 1$ have anomalously low adjusted relative amplitudes. Thus, the amplitudes of the $\tilde{M}_N = -1$ lines are one-sixth or less of the amplitudes of the $\tilde{M}_N = -2$ lines, and one-half to one-third of the values for the $\tilde{M}_N = 0$ lines. Similarly, the $\tilde{M}_N = 1$ lines have amplitudes that are one-third or less of the $\tilde{M}_N = 0$ lines, and for the most part, one-half or less of the $\tilde{M}_N = 2$ lines. All the overlapped lines contain components with $\tilde{M}_N = \pm 1$, and

TABLE II. *m*-Dinitrobenzene anion: spectral index numbers^a and relative amplitudes at -50°C.

Line ^b number	Degen- eracy	\tilde{M}_N^c	\tilde{M}_4^c	$2\tilde{m}_2^c$	$2\tilde{m}_5^c$	Relative amplitude ^d	Standard deviation ^d $\times 10^2$	Adjusted relative amplitude ^e
1	1	-2	-1	-1	-1	0.48	8	0.48
2	1	-2	-1	-1	1	0.46	7	0.46
3	1	-2	-1	1	-1	0.59	3	0.59
(4)	1	-2	-1	1	1	0.49	2	0.49
(5)	2	-1	-1	-1	-1
6	2	-2	0	-1	-1	0.93	3	0.47
7	2	-1	-1	-1	1	0.13	4	0.07
8	2	-2	0	-1	1	0.88	3	0.44
9	2	-1	-1	1	-1	0.11	3	0.06
10	2	-2	0	1	-1	1.06	6	0.53
(11)	2	-1	-1	1	1
(12)	3	0	-1	-1	-1	0.25	4	0.08
(13)	2	-2	0	1	1	0.77	3	0.39
(14)	4	-1	0	-1	-1
15}	1	-2	1	-1	-1	0.40	3	0.40
16}	3	0	-1	-1	1	0.52	5	0.17
17	4	-1	0	-1	1	0.26	8	0.07
18	1	-2	1	-1	1	0.39	3	0.39
19	3	0	-1	1	-1	0.48	3	0.16
20	4	-1	0	1	-1	0.27	7	0.07
21	1	-2	1	1	-1	0.47	1	0.47
(22)	3	0	-1	1	1	0.49	1	0.16
(23)	2	1	-1	-1	-1
(24)	4	-1	0	1	1
(25)	6	0	0	-1	-1	0.87	4	0.15
(26)	1	-2	1	1	1	0.19	1	0.19
(27)	2	-1	1	-1	-1
28}	2	1	-1	-1	1	0.03	1	0.015
29	6	0	0	-1	1	1.09	5	0.18
30	2	-1	1	-1	1	0.13	3	0.065
30'	2	1	-1	1	-1	0.07	2	0.035
29'	6	0	0	1	-1	1.00	0	0.17
28'	2	-1	1	1	-1	0.07	3	0.035
(27')	2	1	-1	1	1
(26')	1	2	-1	-1	-1	0.03	1	0.03
(25')	6	0	0	1	1	1.03	4	0.17
(24')	4	1	0	-1	-1
(23')	2	-1	1	1	1
(22')	3	0	1	-1	-1	0.47	2	0.16
21'	1	2	-1	-1	1	0.09	1	0.09
20'	4	1	0	-1	1	0.19	5	0.05
19'	3	0	1	-1	1	0.51	3	0.17
18'	1	2	-1	1	-1	0.07	1	0.07
17'	4	1	0	1	-1	0.20	6	0.05
16'	3	0	1	1	-1	0.48	3	0.16
15'	1	2	-1	1	1	0.08	3	0.08
(14')	4	1	0	1	-1
(13')	2	2	0	-1	-1	0.09	5	0.045
(12')	3	0	1	1	1	0.49	6	0.16
(11')	2	1	1	-1	-1
10'	2	2	0	-1	1	0.28	4	0.14
9'	2	1	1	-1	1	0.07	4	0.035
8'	2	2	0	1	-1	0.26	3	0.13
7'	2	1	1	1	-1	0.08	4	0.04
6'	2	2	0	1	1	0.27	3	0.14
(5')	2	1	1	1	1
(4')	1	2	1	-1	-1	0.17	4	0.17
3'	1	2	1	-1	1	0.17	1	0.17
2'	1	2	1	1	-1	0.15	2	0.15
1'	1	2	1	1	1	0.15	2	0.15

^a See Ref. 18.^b See Figs. 3 and 4. Lines are numbered from low to high fields. Lines included in a parenthesis, to the left are overlapped at -50°, and those included in a bracket to the right are overlapped at room temperature.^c Spectral index numbers:¹⁸ \tilde{M}_N refers to the sum for the two ¹⁴N nuclei; \tilde{M}_4 to the sum for the two equivalent protons at Positions 4 and 6 ($\tilde{M}_4 = \tilde{m}_4 + \tilde{m}_6$); and \tilde{m}_2 and \tilde{m}_5 to the protons at Positions 2 and 5, respectively. The numbering system used is that for 1,3-dinitrobenzene.^d Based on an average of the amplitudes of the first derivative in four recordings.^e Adjustment of amplitudes is based on the degeneracy. See text.

TABLE III. *m*-dinitrobenzene anion: adjusted relative amplitudes of nitrogen lines as a function of temperature.

\tilde{M}_N^b	Adjusted relative amplitudes ^a			
	20°	-35°	-40°	-50°
-2	1.32	2.55	2.67	2.68
-1	1.20	1.37	1.18	0.38
0	1.00	1.00	1.00	1.00
1	1.09	1.10	0.85	0.35
2	1.16	1.45	1.29	0.92

^a See text for method of computation.

^b Spectral index number.¹⁸

the adjusted relative amplitudes given in the table were obtained by neglecting the $|M_N|=1$ components, i.e., by dividing the relative amplitudes by only the degeneracies of the components for which $|M_N| \neq 1$. Most²⁸ of the relative amplitudes of overlapped lines adjusted in this way agree well with the adjusted amplitudes of the resolved lines with the same value of $M_N (\neq \pm 1)$. This analysis shows that the $M_N = \pm 1$ lines are broad and make a negligible contribution to the overlapped lines. The *m*-dinitrobenzene anion spectrum at -50° thus exhibits the alternating linewidth phenomenon.

A study of the dependence of the linewidths on M_N was made as a function of temperature by using an averaging of the amplitudes of the unoverlapped lines for different values of \tilde{m}_2 and \tilde{m}_5 with $M_4=0$. The data is presented in Table III. There are four lines for each value of \tilde{M}_N with $M_4=0$, but not all of these are resolved. The lines used from Table II are: for $\tilde{M}_N = -2$, numbers 6, 8, and 10; for $\tilde{M}_N = -1$, numbers 17 and 20; and for $M_N=0$, numbers 29 and 29'. The corresponding high-field lines were employed for $\tilde{M}_N = +1$ and $+2$. The amplitude variations of the different proton lines for a single value of M_N were not taken into account, and the data in the table are averages over these differences. The average adjusted amplitudes were obtained by dividing by the appropriate statistical weights, and are tabulated as a ratio to the adjusted amplitude of the

²⁸ There are actually slight departures of the overlapped lines from this description. Thus the overlapped No. 11-12 line is of very low amplitude when corrected for the degeneracy of Component No. 12 (Component 11 corresponds to $\tilde{M}_N = -1$), presumably because of some overlap with the 13-14 line. On the high-field side, the roles of Lines No. 11'-12' and 13'-14' are reversed, i.e., the adjusted amplitude of the 13'-14' line is low when corrected for the statistical weight of Component 13. This difference between the low- and high-field sides of the spectrum arises from the linewidth effects that are linear in M_N , the high-field side being broader than the low-field side. Lines 15', 18', 21', and 26' are weak. They all correspond to $\tilde{M}_N = +2$, $\tilde{M}_4 = -1$, and are broadened by the linear variation with M_N . There also appears to be a significant cross term in the linewidth variations that depends on the product $M_N M_4$ [compare the similar effects for the *p*-dinitrobenzene⁶ and 2,6-dinitrophenolate anion (see below)].

central line.²⁹ The low-temperature spectra show the largest linewidth variations, but examination of the data in the table indicates that there are also significant variations of the amplitudes even at room temperature. The contribution of the term linear in M_N is immediately evident: the lines with $\tilde{M}_N = -2$ are all of higher amplitude than the lines with $\tilde{M}_N = 2$, and the same difference is present to a smaller extent in the $M_N = \pm 1$ lines. The alternating linewidth phenomenon is clearly present in the three low-temperature spectra because the $M_N = \pm 1$ lines are of lower adjusted amplitude than the $M_N = \pm 2$ lines, and the adjusted amplitude of the central line is smaller than all the $M_N = \pm 2$ lines except for the $\tilde{M}_N = 2$ line of the -50° spectrum (and here the linear dependence on M_N predominates). At room temperature there is also an incipient alternating linewidth, but the widths do not actually alternate. The presence of the alternating linewidth effect is evident because the central line has the smallest adjusted amplitude, while if only dipolar and *g*-tensor line-broadening mechanisms were acting, it would have the largest adjusted amplitude.

A semiquantitative evaluation of the different linewidth contributions can be made by using the procedure outlined at the beginning of this section. At 20° , the width of the $\tilde{M}_N = -2$ lines were approximately²¹ $\delta_{-2} = 0.173$ G, while very approximate measurements gave about the same value of $\delta_{-2} = 0.12$ G for the spectra at -35° , -40° , and -50° . The results for the spectral densities at 20° , -35° , -40° , and -50° , respectively, are (in units of 10^6 sec^{-1}): $X_N = 2.2, 1.8, 1.8$, and 1.7 ; $j_N^{(D)} = 0.06, 0.03, 0.04$, and 0.07 ; $j_N^{(I)} = 0.52, 0.72, 1.06$, and 3.0 . The inaccuracies in the width measurements made the differences in the values of X_N at low temperatures uncertain, while the larger value at room temperature may be due to electron exchange with unreduced starting material³⁰ or to quantum-mechanical exchange between radicals.³¹ The large value of $j_N^{(D)}$ at room temperature as compared to the low-temperature results is probably a reflection of the inaccuracies in the calculation and in the assumptions made in deriving the results. The spectral density $j_N^{(I)}$ for the isotropic modulation increases with decreasing temperature quite a bit more rapidly between -40° and -50° than between

²⁹ A test was also made at room temperature to determine the degree of microwave power saturation. At a power 10 dB less than used in the rest of the experiments, the adjusted relative amplitudes of the $\tilde{M}_N = -2, -1, 0, 1$, and 2 lines were found to be, respectively, $1.48 \pm 0.09, 1.27 \pm 0.06, 1.00 \pm 0.04, 1.18 \pm 0.07$, and 1.23 ± 0.1 . These results are to be compared with the first column of data in Table II (for which the errors are $\pm 0.01, \pm 0.03, \pm 0.02, \pm 0.02$, and ± 0.03 , respectively). Saturation thus makes a small but significant contribution to the linewidth variations, but its effects are not sufficient to alter any of the qualitative conclusions.

³⁰ R. L. Ward and S. I. Weissman, *J. Am. Chem. Soc.* **76**, 3612 (1954); **79**, 2086 (1957); P. J. Zandstra and S. I. Weissman, *J. Chem. Phys.* **35**, 757 (1961).

³¹ J. D. Currin, *Phys. Rev.* **126**, 1995 (1962); G. E. Pake and T. R. Tuttle, *Phys. Rev. Letters* **3**, 423 (1959).

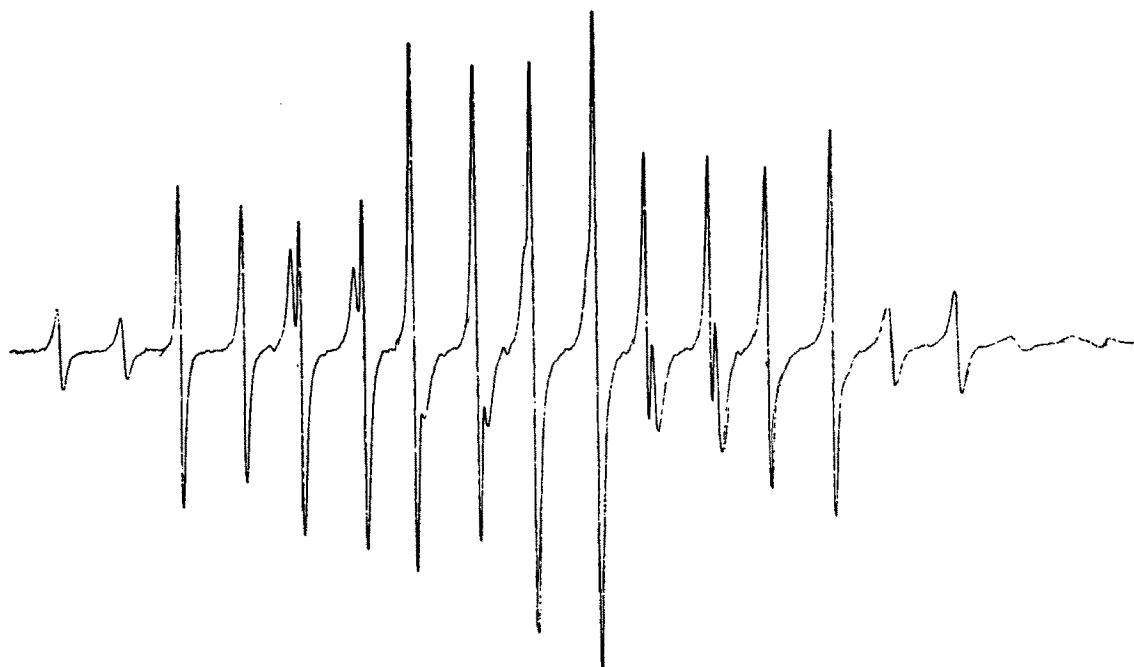


FIG. 5. First derivative of the ESR spectrum of the 2,6-dinitrophenolate anion in DMF at -45°C . The magnetic field increases to the right. See Table IV.

20° and -35° , but it is difficult to attach quantitative significance to the temperature coefficient. The magnitudes of the $j_N^{(i)}$ are consistent with the hypothesis of modulation of the isotropic splittings (see discussion of the dinitroindurene anion above).

The linear variation of the linewidths as a function of M_N leads to the conclusion that the nitrogen hyperfine splitting a^N is positive. This result depends on the same assumptions about the components of the g tensor that were used above for the dinitroindurene anion.³²

The hyperfine splittings at low temperatures were different from those at room temperature, but unfortunately accurately calibrated spectra were not taken at the low temperatures. Reasoning in the same manner as for the *o*- and *p*-dinitrobenzene anions,⁶ we tentatively assume that the splitting-constant change is related to the solvent effect²² and write for the splitting a_i :

$$a_i(\text{DMF}; T_2) = a_i(\text{DMF}; T_1) + \alpha[a_i(\text{MeCN}; T_1) - a_i(\text{DMF}; T_1)],$$

where α depends on the radical, solvent pair, and tem-

³² The cross term in the linewidths that depends on the product $M_N M_i$ cannot be used here to get the relative signs of a^N and a_i^H . This cross term has, however, been employed to obtain relative signs of splittings in the *p*-dinitrobenzene⁶ and 2,6-dinitrophenolate anions (see below). In the *m*-dinitrobenzene anion the difficulty results because the modulation of the isotropic modulation makes an appreciable contribution, and an equation like Eq. (2.9) must be employed to analyze the cross term. The signs of the two spectral densities in this equation can only be determined from detailed considerations of the mechanism of the isotropic modulation.

perature, but is assumed to be approximately independent of the particular splitting a_i . The quantities $a_i(\text{DMF}; T)$ and $a_i(\text{MeCN}; T)$ are the splittings in *N,N*-dimethylformamide and acetonitrile solutions, respectively, at temperature T . Since the splitting at Position 5 is the same in DMF and MeCN at room temperatures, we assume that it is also the same in DMF at the two temperatures, and therefore calculate for the -50° splittings the values (in gauss): $a^N = 4.13 \pm 0.03$, $a_2^H = 2.92 \pm 0.03$, and $a_4^H = a_6^H = 4.38 \pm 0.03$. The values computed for α are, respectively, 0.23 ± 0.06 , 0.44 ± 0.15 , and 0.37 ± 0.17 , where the errors are large because differences are taken between relatively large numbers of comparable magnitude. Maki and Geske²⁷ do not give error estimates for their data, so we have assumed a value of ± 0.03 G. There are thus quite significant changes of splittings in the *m*-dinitrobenzene anion with temperature, and the effects are larger than for the *ortho*- or *para*-dinitrobenzenes.⁶

VI. RADICALS WHICH DO NOT EXHIBIT ALTERNATING LINEWIDTHS

o- and *p*-Dinitrobenzene

The spectra of these two radicals have been discussed in detail elsewhere.⁶ No alternation in linewidths was observed in either of the spectra, but a careful analysis of the spectra of the *para* isomer indicates that it may contain small linewidth variations arising from modulation of the isotropic interaction.

TABLE IV. 2,6-Dinitrophenolate anion: assignment of spectral index numbers.^a

Line number ^b	Degen-eracy	\tilde{M}_N^c	\tilde{M}_s^c	$2\tilde{m}_4$
1	1	-2	-1	-1
2	1	-2	-1	1
3	2	-1	-1	-1
4	2	-1	-1	1
5	2	-2	0	-1
6	3	0	-1	-1
7	2	-2	0	1
8	3	0	-1	1
9	4	-1	0	-1
10	2	1	-1	-1
11	4	-1	0	1
12	2	1	-1	1
13	1	-2	1	-1
14	6	0	0	-1
15	1	2	-1	-1
15'	1	-2	1	1
14'	6	0	0	1
13'	1	2	-1	1
12'	2	-1	1	-1
11'	4	1	0	-1
10'	2	-1	1	1
9'	4	1	0	1
8'	3	0	1	-1
7'	2	2	0	-1
6'	3	0	1	1
5'	2	2	0	1
4'	2	1	1	-1
3'	2	1	1	1
2'	1	2	1	-1
1'	1	2	1	1

^a See Ref. 18.^b See Fig. 5. Lines are numbered from low to high field.^c Spectral index numbers:¹⁸ \tilde{M}_N refers to the sum for the two ¹⁴N nuclei; \tilde{M}_s to the sum for the two equivalent protons at Positions 3 and 5 ($\tilde{M}_s = \tilde{M}_3 + \tilde{m}_5$); and \tilde{m}_4 to the proton at Position 4.

2,6-Dinitrophenol

The first two polarographic waves of this compound in DMF are at -0.8 and -1.4 V. Electrolysis at the first wave gives a yellow solution while at the second the color is dark red. No ESR spectrum was detectable at the first wave, but at -1.5 V the ESR spectrum of an unstable radical was observed. The rate of decay was reduced slightly by cooling the sample tube to 15° . The first polarographic wave probably arises from elimination of the phenolic hydrogen atom, as in similar reactions observed by Rieger *et al.*¹³ The spectrum is readily interpreted as the 2,6-dinitrophenolate dianion radical and gives for the splitting constants (in gauss): $a^N = 3.64 \pm 0.02$, $a_3^H = a_5^H = 6.87 \pm 0.02$, and $a_4^H = 1.89 \pm 0.01$. The linewidths were about 0.06 G, and no difficulty was encountered in obtaining sharp lines. Narrow lines have also been readily produced in the spectra of other anions when a similar chemical reaction takes place at the first polarographic wave.¹³ The spectrum obtained at -45° is shown in Fig. 5. The widths of the sharper lines are about 0.11 G.

The assignment of spectral index numbers¹⁸ to the spectrum is indicated in Table IV, where \tilde{M}_N refers to the two nitrogen nuclei, \tilde{M}_s to the two equivalent protons at Positions 3 and 5, and \tilde{m}_4 to the proton at

Position 4. Linewidth variations are observed at room temperature, but they are more marked in the low-temperature spectra. There are significant contributions from terms linear in \tilde{M}_N and \tilde{m}_4 : the high-field nitrogen lines are broader than the low-field lines, and the low-field lines from proton Number 4 are broader than the high-field lines, as illustrated by lines number 14 and 14'. The symmetric dependence on \tilde{M}_N arising from the pure dipolar interaction with the nitrogen nuclei ($j_N^{(D)}$) is very evident in the low-temperature spectrum, and is also present to a smaller extent at 15° . At -45° , the lines with $\tilde{M}_N = -2$ are quite broad, but many of those with $\tilde{M}_N = 2$ are so broadened by both the linear and symmetric contributions that they are barely visible. In this spectrum the lines with $\tilde{M}_N = 1$ are quite broad, but those with $\tilde{M}_N = -1$ are relatively sharp, so that there is no significant alternating linewidth variation.

There is one other large linewidth variation: lines for which the product $\tilde{M}_N \tilde{m}_4$ is negative are broader than those for which the product is positive. For example, Line No. 1 is of higher amplitude than Line No. 2, and 1' is of higher amplitude than 2'. Lines 9 and 11, 9' and 11', as well as many other sets, indicate the same behavior. A cross term of this type has also been found in the *para*-⁶ and *meta*-dinitrobenzene^{23,32} anion spectra, and in the former was used to obtain the relative signs of the nitrogen and proton hyperfine splittings. The same procedure can be used here by employing Eq. (2.9) and assuming that $j_{NH(4)}^{(D)}$ is smaller than $\frac{8}{3}j_{NH(4)}^{(D)}$, i.e., that the pure dipolar interactions make a larger contribution than the modulation of the isotropic splittings, a result that is consistent with the absence of a significant alternating linewidth effect in the 2,6-dinitrophenolate anion.

To establish the relative signs of a^N and a_4^H only the sign of the spectral density $j_{NH(4)}^{(D)}$ need be known. Because of the large magnitude of the dipolar coefficient^{6,7} $D_N^{(0)}$ for the nitrogen nuclei as compared to $D_N^{(\pm 2)}$, the sign of $j_{NH(4)}^{(D)}$ is determined by the sign of the product $D_N^{(0)}D_{H(4)}^{(0)}$, just as in the case of the *p*-dinitrobenzene anion.⁶ The sign of $D_N^{(0)}$ is determined by, and is the same as, the sign of the pi-electron spin density on the nitrogen atom,⁶ ρ_N^π , and using the analysis in Ref. 6,

$$D_{H(4)}^{(0)} = -\alpha[0.0671\rho_4^\pi + 0.0702(\rho_3^\pi + \rho_5^\pi) + \dots],$$

where α is a positive constant and the remaining terms make smaller contributions than those given explicitly. Using the relation³³ $a_i^H = Q_{CH^H}\rho_i^\pi$ and the experimental splittings, it is clear that the sign of $D_{H(4)}^{(0)}$ is determined by the sign of $\rho_3^\pi = \rho_5^\pi$ and is independent of the sign of ρ_4^π . Thus the sign of $j_{NH(4)}^{(D)}$ is opposite to that of the product $\rho_N^\pi\rho_3^\pi$. As shown in Ref. 6,

³²H. M. McConnell, *J. Chem. Phys.* **24**, 633, 764 (1956); H. M. McConnell and H. H. Dearman, *ibid.* **28**, 51 (1958); H. M. McConnell and D. B. Chesnut, *ibid.* **28**, 107 (1958), and other papers cited therein.

the coefficient $E_{\text{NH}(4)}$ of the product $\bar{M}_N \bar{m}_4$ in the experimental expression for the linewidth variations has the same sign as $j_{\text{NH}(4)}^{(D)}$ if a^{N} and a_4^{H} are of the same sign, and has a sign opposite to that of $j_{\text{NH}(4)}^{(D)}$ if a^{N} and a_4^{H} are of opposite sign. Since lines for which the product $\bar{M}_N \bar{m}_4$ is negative are broader than those for which it is positive, $E_{\text{NH}(4)}$ is negative, and thus the product $\rho_{\text{N}^\pi} \rho_3^\pi$ is positive if a^{N} and a_4^{H} have the same sign and is negative if the two splittings have different signs. Molecular orbital²² as well as valence-bond²⁴ calculations indicate that both ρ_{N^π} and ρ_3^π are positive, and thus a^{N} and a_4^{H} have the same sign. These calculations show in addition that ρ_4^π is negative, so that a_4^{H} is positive, and therefore a^{N} is also positive. Since the high-field nitrogen lines are broader than the low-field lines, a positive value of a^{N} implies⁶ that the component of the g tensor perpendicular to the plane of the molecule, g_3 , is less than the mean of the in-plane components, $\frac{1}{2}(g_1+g_2)$, a result that is in agreement with theoretical estimates of the g -tensor components^{24,25} in aromatic radicals. The positive value of a^{N} is also consistent with the semiempirical study of nitrogen splittings carried out by Rieger and Fraenkel.²² The determination of the sign of the cross-term coefficient $E_{\text{NH}(4)}$ by itself (without using assumptions about the g tensor or estimates of the signs of spin densities from valence-theory calculations) thus does not give an unambiguous result for the relative signs of a^{N} and a_4^{H} , but the over-all analysis clearly lends strong weight to the conclusion that both a^{N} and a_4^{H} are positive.

Since the low-temperature spectrum of the 2,6-dinitrophenolate anion does not show a significant linewidth alternation, it is markedly different from the spectra of the *m*-dinitrobenzene and 2,6-dinitrotoluene anions. In contrast to these other two *meta* dinitrobenzene anions, the splitting constants for the 2,6-dinitrophenolate ion are in good agreement with conventional molecular orbital calculations.²²

2,6-Dinitroaniline

Electrolysis of a 3mM solution of this material in DMF at -0.8 V gives a bright yellow solution which later changed to reddish brown, and although a spectrum was obtained, considerable difficulty was encountered in obtaining narrow lines. Several samples were electrolyzed under slightly different conditions before it was possible to reduce the linewidth even to the comparatively large value of about 0.2 G. The splitting constants were found to be $a_3^{\text{H}} = a_5^{\text{H}} = 7.02 \pm 0.04$ G, $a_4^{\text{H}} = 1.76 \pm 0.03$ G, $a_{\text{NO}_2}^{\text{N}} = 3.72 \pm 0.01$ G, and $a_{\text{NH}_2}^{\text{N}} = a_{\text{NH}_2}^{\text{H}} = 0.41 \pm 0.01$ G. The assignment of the splittings from the two sets of equivalent pairs of protons (at Positions 3 and 5 and in the amino group) was made by comparison with the work of Melchior

and Maki on the *p*-phenylenediamine cation³⁵ and of Maki and Geske on the *p*-nitroaniline anion.³⁶

There are no noticeable linewidth variations in the spectrum, and despite the considerable overlap and complexity, an alternating linewidth effect that broadened the nitro-group $M_N = \pm 1$ lines would be readily detectable. No experiments were performed at low temperatures. As discussed elsewhere,²² both the linewidth variations and molecular orbital calculations for this compound are similar to the 2,6-dinitrophenolate ion but quite different from the *m*-dinitrobenzene and 2,6-dinitrotoluene anions.

Mononitrobenzene

Bernal^{5,16} has observed the spectrum of the mononitrobenzene anion in DMF solution, and Geske and Ragle³⁷ have studied it in acetonitrile solution. Only a splitting into three lines attributable to the single ¹⁴N nucleus was observed, with splittings $a^{\text{N}} = 19.73$ G and 20.4 G for the two solvents, respectively. In the present study it was found that electrolysis of 1mM solutions in DMF leads to the spectrum of Fig. 6 which has partially resolved proton hyperfine splitting. Nineteen minor components are visible with a spacing of about 0.25 G and linewidths of 0.125 G. There is clearly a linear and a symmetric variation of the amplitudes with M_N . At -40° the structure from the proton splittings is so broadened out that it becomes essentially undetectable, and the linewidth variations are enhanced. The widths of the envelopes are about 1.6 G. The relative amplitudes in the -40° spectra, obtained from four different recordings, are 0.887 ± 0.038 , 1.000 ± 0.043 , and 0.655 ± 0.039 , respectively, for the $\bar{M}_N = -1, 0$, and $+1$ lines. The relative linewidth variations fit the quadratic

$$W(M_N) = 1 + 0.088\bar{M}_N + 0.149M_N^2.$$

Unlike the other nitro compounds studied, the pure dipolar term (the coefficient of M_N^2) is larger than the cross term between the dipolar and g -tensor interactions (the coefficient of the linear term). This presumably arises because the pure dipolar term depends approximately on the square of the spin density on the nitrogen atom, and the cross term varies linearly with the spin density. In this radical, the nitrogen splitting is very large, and therefore the spin density on the nitrogen atom is also very large,²² so that the contribution of the pure dipolar term is larger than in the other radicals studied.

³⁵ M. T. Melchior and A. H. Maki, J. Chem. Phys. **34**, 471 (1961).

³⁶ A. H. Maki and D. H. Geske, J. Am. Chem. Soc. **83**, 1853 (1961).

³⁷ D. H. Geske and J. L. Ragle, J. Am. Chem. Soc. **83**, 3532 (1961); D. H. Geske, J. L. Ragle, M. A. Bambenek, and A. L. Balch, J. Am. Chem. Soc. **86**, 987 (1964).

³⁴ J. C. Schug, T. H. Brown, and M. Karplus, J. Chem. Phys. **37**, 330 (1962).

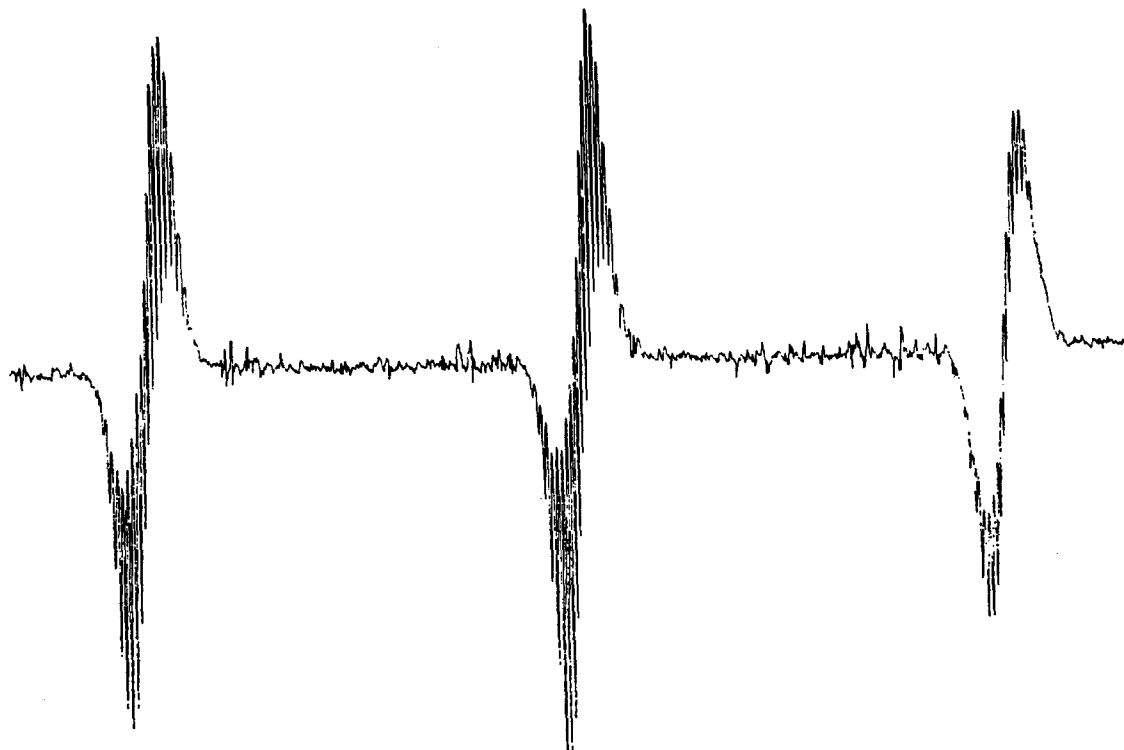


FIG. 6. First derivative of the ESR spectrum of the nitrodurene anion in DMF at 20°C. The magnetic field increases to the right.

VII. DISCUSSION AND CONCLUSIONS

Pronounced alternations in the linewidths of the nitrogen hyperfine lines have been observed in the room-temperature ESR spectra of the anions of dinitrodurene, 2,6-dinitro-3,5-dimethyl-4-acetyl-*t*-butyl-benzene (DDTB), and dinitromesitylene, as well as in the spectrum of the radical showing the splittings from two equivalent nitrogen nuclei that was generated at the second polarographic wave of trinitromesitylene. Slight alternating linewidth effects at room temperature that become more marked at low temperatures have been found in the spectra of the 2,6-dinitrotoluene and *m*-dinitrobenzene anions. No significant linewidth alternations were detectable even at low temperatures in the spectra of the *o*-dinitrobenzene, *p*-dinitrobenzene, and 2,6-dinitrophenolate anions. The 2,6-dinitroaniline anion, which was investigated only at room temperature, showed no evidence of an alternating linewidth effect. None of the spectra of the mononitrobenzene anions examined, including radicals not reported on in the present work, exhibited any anomalous linewidth effects.

The theory developed to explain the alternating linewidth phenomenon^{7,8} attributes the effect to a modulation of the isotropic hyperfine splittings. For two equivalent nuclei, an alternating width is only observed if: (i) this mechanism makes a large contribution as compared to the other line-broadening effects; and (ii) the modulations of the splittings at the two nuclei are correlated in such a way as to have a large

out-of-phase component. Neither in-phase nor small out-of-phase modulations produce an alternating linewidth, but small out-of-phase correlations of the instantaneous splittings broaden the central lines of a spectrum more than the end lines, while the anisotropic intramolecular dipolar interaction broadens the end lines more than those in the center. The classification of radicals with two equivalent nuclei into those which do, or do not, exhibit an alternating linewidth phenomenon is thus frequently more of a quantitative than a qualitative distinction. The observation of an alternation in widths implies an out-of-phase correlation of the instantaneous splittings, but an incipient modulation of this type can only be detected by careful quantitative study of the linewidths. Similarly, since the linewidth dependence on M^2 caused by an in-phase modulation of the splittings is similar to the line broadening that results from the pure dipolar interaction, an in-phase modulation could probably only be detected by quantitative rather than qualitative observations.

The theory⁷ gives phenomenological expressions for the linewidths that are in over-all agreement with the experimental observations. Precise quantitative verification of the phenomenological theory is difficult, however, because most of the spectra which exhibit alternating linewidth variations are quite complicated and contain incompletely resolved hyperfine lines. The theory relates the linewidths to definite functions of

certain spectral densities,^{7,8} and the spectral densities determine the importance of the alternating linewidth effect. The magnitude of the phenomenon is difficult to predict because it depends both on the nature of the modulating mechanism and on detailed molecular parameters relating spin-density fluctuations to internal motions and to interactions between the radical and the solvent. Nevertheless, the semiquantitative experimental results are entirely consistent with reasonable values for the fluctuations in hyperfine splittings and with estimates of the correlation time τ for the molecular motions. Since low temperatures enhance the alternating linewidth phenomenon, the correlation time probably becomes larger with decreasing temperature. The effect might also become larger at low temperatures because of an increase in the magnitude of the fluctuations in splittings as the temperature is lowered.

Steric hindrance of the nitro groups enhances the magnitude of the alternations in linewidth. Thus, among the *para* dinitro compounds, the dinitrodurene anion shows a pronounced alternation in widths while the *p*-dinitrobenzene anion does not. In the room-temperature spectra of the *meta* dinitro radicals, DDTB has a very pronounced alternation, and dinitromesitylene shows a large effect, but *m*-dinitrobenzene shows only an incipient contribution. Steric hindrance is not, however, a necessary condition for the alternating linewidth phenomenon in dinitro compounds since *m*-dinitrobenzene shows a pronounced effect at low temperature. At least part, but not all, of the increase of the alternation in linewidths with steric hindrance may arise from the dependence of the broadening on the splitting-constant differences. In the hindered nitro compounds, the nitro groups are rotated out of the plane of the aromatic ring, and the average nitrogen splitting constant increases with the angle of rotation.^{22,37} Fluctuating motions of the same magnitude in hindered and unhindered compounds may thus cause larger changes of the splittings in the hindered radicals. In the two-jump model, for example, the spectral density which governs the isotropic interaction^{7,8} is proportional to the square of the splitting-constant difference in the two states. Consequently, even if the rate and magnitude of the fluctuating motions are the same for hindered and unhindered radicals, the former may show a larger alternating linewidth contribution. This type of effect might account for part of the difference between the magnitudes of the alternating linewidths in the dinitrodurene ($a^N = 6.99$ G) and *p*-dinitrobenzene ($a^N = 1.48$ G) anions. The larger alternating linewidth effect in the 2,6-dinitrotoluene ($a^N = 4.33$ G) as compared to the *m*-dinitrobenzene anion ($a^N = 3.97$ G), however, probably cannot be attributed to the small difference in average hyperfine splittings.

Two general types of mechanisms have been suggested to account for the out-of-phase modulation of the nitrogen hyperfine splittings.⁸ One is a solvation

mechanism in which a single nitro group interacts instantaneously with either the solvent itself or with the cation.³⁸ Such an interaction would cause the splitting from the ¹⁴N nucleus in one nitro group to change in the opposite direction from the splitting from the nitrogen nucleus in the other group,²² thus giving the required out-of-phase correlation. The other mechanism is a rotation, that is, a change in the orientation of the nitro groups relative to the aromatic ring. The instantaneous reorientation can occur in both groups at once, in each separately, can be a free or hindered internal rotation, can be an oscillation, etc., provided only that there is an appreciable out-of-phase correlation of the splittings from the two nitrogen nuclei. Molecular orbital calculations²² indicate that rotation of a nitro group out of the plane of the aromatic ring does not appreciably alter the sensitivity of the spin densities to solvent interactions,³⁸ but solvation changes the bond orders between the ring and the nitro group and may thus influence the ease of rotation of the nitro groups.²² These calculations also indicate that on the average both nitro groups in the hindered dinitrobenzenes must be rotated out of the plane simultaneously. This conclusion follows because the calculations predict that when only one nitro group is rotated out of the plane the largest average nitrogen splitting in the *p*-dinitrobenzenes is about 4.6 G while in the *meta* compounds it is about 4.2 G. In contrast, when the two nitro groups are rotated out of the plane simultaneously, the splittings go up to slightly over 12 G in both isomers. The calculated values are to be compared with the experimental splittings, for example, of $a^N = 6.99$ G for the dinitrodurene anion and $a^N = 10.6$ G for DDTB. A two-jump rotational model^{7,8} in which each of the two interchanging states have one nitro group in the plane of the ring, and the other perpendicular to the plane, is thus unsuitable. Other rotational models⁸ are not excluded, but although it seems unlikely that the rotational motion itself would involve primarily an out-of-phase correlation, even an *uncorrelated* rotational *motion* causes an out-of-phase component in the fluctuating hyperfine *splittings*.⁸ There is thus no evidence with which to determine the relative contributions of the rotation and solvation mechanisms, but it seems reasonable to assume that the predominant effect in the *m*-dinitrobenzene anion is a fluctuating solvation with perhaps a small contribution from a rotational motion. In the hindered compounds, the rotational mechanism may play a more important role, but solvation effects probably also make a contribution.

All of the *meta* dinitro compounds studied except the 2,6-dinitrophenolate and 2,6-dinitroaniline anions exhibited an alternating linewidth effect. Among radicals showing the alternation, the more hindered the compound the greater the effect; and in those

³⁸ J. Gendell, J. H. Freed, and G. K. Fraenkel, *J. Chem. Phys.* **37**, 2832 (1962).

anions which had sufficiently simple and resolved spectra to permit experimental determination of the ring or methyl-proton splittings, these splittings were in disagreement with the molecular orbital calculations.²² This correlation of an alternating linewidth effect with the inconsistency between experimental and calculated spin densities led, in fact, to the postulate that the instantaneous state of these *meta* dinitro compounds contains two inequivalent nitro groups, and the calculations based on this model are in qualitative agreement with experiment. The 2,6-dinitrophenolate and 2,6-dinitroaniline anions, the latter only examined at room temperature, did not show an alternating linewidth effect, and the experimental spin densities are reproduced by calculations which assume an instantaneous symmetrical equivalence of the two nitro groups. These results suggest that the highly polar groups O⁻ or NH₂ between the two nitro groups prevent an out-of-phase correlation of the solvation and/or rotation of the nitro groups, so that the molecular conformations are always symmetrical and no alternation in linewidths takes place.

Examination of the relative amplitudes of the lines split by the methyl protons in the dinitrodurene and 2,6-dinitrotoluene anions did not reveal any effects due to a slowing down of the methyl-group rotations. Mechanisms which cause modulation of the nitrogen hyperfine splittings also probably modulate the spin densities throughout the radicals,³ but no evidence for large fluctuations in spin density at the positions not substituted with nitro groups was found. Most of the spectra could not be analyzed for any but large effects of this type, but they were clearly absent in the methyl-proton lines of the dinitrodurene anion. There may, however, be a small contribution from modulation of the proton splittings in the *p*-dinitrobenzene anion.⁶ The alternating linewidth phenomenon observed in the dinitro compounds is thus quite different in detail from that observed in the dihydroxydurene cation¹ and in the pyracene anion.³⁹ In these radicals, the lines which exhibit an alternation in width arise from protons in static conformations, and motion at other sites in the molecules causes a spin-density modulation. In the dihydroxydurene, the motion is a switching of the hydroxyl groups from one planar conformation to the other, and in pyracene it is a jumping of a sodium ion between two positions in the molecule. An alternation of linewidths has also been observed in the spectrum of the naphthazarin cation,⁴⁰ but here the predominant

effect is found on lines attributed to the hydrogen-bonded protons. These protons undergo motion between two different positions, and the modulation of their splittings arises directly from the different environments rather than from an over-all fluctuation of the spin-density distribution in the molecule. At low temperatures the spectrum of the naphthazarin radical shows the presence of species with different splittings for the two types of hydrogen-bonded protons, corresponding to the static limit for a jump model. Attempts in the present work to find spectra with two different nitrogen splittings from dinitrobenzene anions which ordinarily have symmetrically equivalent nitrogen nuclei were unsuccessful. A search for such spectra was made carefully for the highly hindered compounds, but as indicated above, the results of the molecular orbital calculations suggest that conformations which would give two inequivalent nitrogen splittings could not account for the large observed splittings and thus such conformations probably do not occur in the hindered compounds studied.

Linewidth studies can sometimes be used to give information about the signs of the isotropic hyperfine splittings.^{6,23} For all the nitro-substituted benzene anions investigated, including radicals not reported on in the present work,^{5,6} the lines from the nitro-group nitrogen nuclei are broader on the high-field side of the spectrum than on the low-field side. By making certain reasonable assumptions about the relative magnitudes of the components of the *g* tensor^{6,23-25} this linewidth effect implies that the nitrogen splitting a^N is positive. The positive sign has been confirmed for the *p*-dinitrobenzene anion without making any assumptions about the components of the *g* tensor,⁶ and thus the uncertainties about these assumptions when applied to radicals containing heteroatoms have been eliminated in this case. The positive sign of a^N in a large series of nitro-substituted benzene anions is also consistent with studies involving semiempirical correlations of hyperfine splittings with molecular orbital calculations.²² In the present investigation, a cross term in the expression for the linewidth variations for the 2,6-dinitrophenolate anion was used to analyze certain relations between the signs of the hyperfine splittings and the spin densities. Using reasonable assumptions, it was confirmed that the signs of a^N and the proton splitting at Position 4, a_4^H , are both positive, and thus that the spin density at Position 4 is negative.

A number of the spectra studied at different temperatures showed significant changes of hyperfine splittings with temperature, and in a few instances, changes of splittings with solvent were also found.

³⁹ E. deBoer and E. L. Mackor, Proc. Chem. Soc. **1963**, 23.

⁴⁰ J. R. Bolton, A. Carrington, and P. F. Todd, Mol. Phys. **6**, 169 (1963).