

Linewidth Studies in Electron Spin Resonance Spectra: The *Para* and *Ortho* Dinitrobenzene Anions*

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Large variations have been found among the linewidths of the different hyperfine lines in the low-temperature electron spin resonance spectra of the *p*- and *o*-dinitrobenzene anions generated electrolytically in *N,N*-dimethylformamide solutions. The magnitude of the variations in the *para* compound is so great that the spectrum is superficially uninterpretable. Detailed analysis of the spectrum of this radical shows, however, that most of the linewidth differences can be accounted for by modulation through molecular tumbling of the intramolecular anisotropic dipolar and *g*-tensor interactions. There may also be a small contribution from modulation of the isotropic proton hyperfine splittings, the mechanism that accounts for the alternating linewidth phenomenon in a number of radicals, but an alternation of the widths is not observed in the *p*-dinitrobenzene anion spectrum because the contribution from this interaction is small. The sign of the isotropic nitrogen hyperfine splitting a^N has been determined by a new method involving only pure dipolar interactions with the nitrogen nuclei and protons and not depending on any assumptions about the magnitudes of the components of the *g* tensor. A number of features of the relaxation matrix determining the linewidths are discussed, and the problems encountered when the components of a degenerate line have different widths are analyzed. The spectra obtained in dimethylformamide solutions are much better resolved than those previously reported in acetonitrile solutions. Changes of hyperfine splittings with both solvent and temperature are observed.

I. INTRODUCTION

DURING the course of a recent investigation of the phenomenon of alternating linewidths in the electron-spin resonance spectra of substituted dinitrobenzene anion radicals,¹ a study was also made of the three isomeric dinitrobenzene anions. The *meta* isomer was found to have spectra with alternating linewidths,² but the effect was not evident in the *ortho* or *para* compounds. Several interesting linewidth phenomena as well as other spectral properties were observed in these latter two compounds, and, as a result, a detailed quantitative investigation of the *p*-dinitrobenzene anion was undertaken.

The dinitrobenzene anions have been previously studied by Ward, who prepared the radical by alkali-metal reduction in dimethoxyethane,³ and by Maki and Geske using electrolytic reduction in acetonitrile solution.⁴ The alkali-metal-produced radicals exhibited the effects of ion pairing so that the spectra were not truly representative of the nitrobenzene anions, and the resolution of the spectra in acetonitrile was poor. In the present investigation, we have employed *N,N*-dimethylformamide as solvent for the electrolytic generation of the radicals and have obtained very well-resolved spectra down to temperatures just above the freezing point of the solvent.

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¹ J. H. Freed and G. K. Fraenkel, *J. Chem. Phys.* **37**, 1156 (1962).

² J. H. Freed, P. H. Rieger, and G. K. Fraenkel, *J. Chem. Phys.* **37**, 1881 (1962).

³ R. L. Ward, *J. Am. Chem. Soc.* **83**, 1296 (1961).

⁴ A. H. Maki and D. H. Geske, *J. Chem. Phys.* **33**, 825 (1960).

The linewidth variations observed in the *p*-dinitrobenzene anion provide tests of the theory of linewidths in ESR spectra. The theory was originally developed by Kivelson⁵ and has recently been revised and extended by Freed and Fraenkel.⁶ A number of hitherto unexamined effects have been observed in the present work, and a new method is developed for obtaining the relative signs of the isotropic hyperfine splittings.

II. 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.⁷ The potentials during electrolysis were measured between the mercury-pool cathode and a silver-silver perchlorate reference electrode.⁷ Tetra-*N*-propylammonium perchlorate was used as the supporting electrolyte. Its purification, as well as that of the DMF, has been described by Rieger *et al.*⁷ The *p*-dinitrobenzene was obtained from the Eastman Organic Chemicals Division of the Eastman Kodak Company and the *o*-dinitrobenzene from the Aldrich Chemical Company. Both were used without purification.

Cooling of the samples in the ESR spectrometer was accomplished by inserting the sample tube inside a partially silvered Dewar tube in the spectrometer cavity and passing a stream of cold, dry nitrogen through the Dewar tube. Temperatures were monitored with a thermocouple inside the Dewar tube at a point just outside the cavity.

⁵ D. Kivelson, *J. Chem. Phys.* **27**, 1087 (1957); **33**, 1094 (1960).

⁶ J. H. Freed and G. K. Fraenkel, *J. Chem. Phys.* **39**, 326 (1963).

⁷ P. H. Rieger, I. Bernal, W. H. Reinmuth, and G. K. Fraenkel, *J. Am. Chem. Soc.* **85**, 683 (1963).

An X-band super-heterodyne spectrometer was employed^{8,9} with a Varian Model V-4012-3B electromagnet having 12-in. diameter pole caps and a 3-in. air gap. The magnet was provided with a Varian Model V-3506 magnet flux stabilizer and wide-range field-scanning equipment. A frequency-stabilized variable frequency proton-resonance oscillator was used to check the field homogeneity and field-scan linearity, and to calibrate the field during a run. First-derivative spectra were obtained by using 1000-cps field modulation.

Since the direct measurement of the linewidths of the hyperfine components in the ESR spectra from dilute solutions of free radicals is of low precision, we have measured the relative amplitudes of the first derivatives of the hyperfine lines. For lines of a particular shape, the amplitudes of the derivative signal are inversely proportional to the square of the width, and the amplitudes are therefore much more sensitive to linewidth differences among the hyperfine components than the widths themselves. For (unsaturated) Lorentzian lines, the half-width at half-maximum intensity Δ_i of a line of degeneracy D_i can be determined from the peak-to-peak amplitude of the first derivative of the line, A_i , by the relation $\Delta_i = (SD_i/A_i)^{1/2}$, where S is a measure of the sensitivity of the spectrometer. The full width between derivative extrema is given by $\delta_i = (2/\sqrt{3})\Delta_i$, and the transverse relaxation time T_{2i} by $[\gamma_s | T_{2i}]^{-1} = \Delta_i$, where γ_s is the effective magnetogyric ratio of the electron in the free radical and has the value $\gamma_s = -17.61 \times 10^6 \text{ sec}^{-1} \text{ G}^{-1}$ if the spectroscopic splitting factor has the free-electron value of $g = 2.0023$.

The theory of linewidths⁸ shows that, in general, a degenerate hyperfine line is a superposition of Lorentzian shaped lines rather than a single Lorentzian, and there is thus no simple analytical relation between the linewidths and the amplitudes. Nevertheless, departures of observed line shapes from a Lorentzian form, at least in the central portion of the line, are small.⁹⁻¹¹ It is therefore convenient to define an experimental relative-width parameter W_i for the i th hyperfine line with respect to some reference line r (usually the central line of the spectrum) by the relation

$$W_i = [(D_i/A_i)(A_r/D_r)]^{1/2} \quad (2.1)$$

The true relative widths Δ_i/Δ_r or δ_i/δ_r will not be given by W_i unless the departures from Lorentzian shape are small.¹²

⁸ J. M. Hirshon and G. K. Fraenkel, Rev. Sci. Instr. **26**, 34 (1955).

⁹ J. W. H. Schreurs and G. K. Fraenkel, J. Chem. Phys. **34**, 756 (1961).

¹⁰ J. H. Freed, thesis, Columbia University, New York, 1962.

¹¹ J. H. Freed and G. K. Fraenkel (to be published); J. Gendell, J. H. Freed, and G. K. Fraenkel (to be published).

¹² It should be noted that even though experimental studies of line shape usually do not show large departures from Lorentzian form, W_i may still not be a good measure of the relative widths. This problem is discussed fully in Refs. 6 and 11.

The spectra of the *p*-dinitrobenzene anion were recorded at sufficiently low levels of microwave power to eliminate any significant errors from saturation effects,^{9,11} but those for the *o*-dinitrobenzene anion, which was studied less thoroughly than the *para* isomer, were performed at a power about 10 dB higher, and saturation effects may have contributed to the linewidths. The amplitude of the field modulation was about 0.01 G (0.02 G peak-to-peak), which is small enough to ensure that even for the narrowest lines ($2\Delta = 0.08$ to 0.09 G) the amplitude of the derivative signal would be closely proportional to the inverse square of the width.¹³

III. EXPERIMENTAL RESULTS

p-Dinitrobenzene

On electrolysis of DMF solutions of *p*-dinitrobenzene at -1.1 V, a greenish-yellow color is formed immediately and the solution exhibits an ESR spectrum. Reduction at the second polarographic wave gives a yellowish-orange color. The spectra obtained at 12° and -55°C from radicals reduced at the first polarographic wave at room temperatures are shown in Figs. 1 and 2, respectively. The radicals were generated from solutions containing an initial concentration of *p*-dinitrobenzene of $5 \times 10^{-4}M$, and these spectra have narrower linewidths than those obtained when solutions with initial concentration of $0.001M$ or higher were employed. The two spectra are very different from one another: on cursory examination of the -55° spectrum, it is difficult to locate its center, and the low- and high-field lines do not appear to be symmetrically positioned. Comparison of the spectra with the identical stick diagrams in the two figures shows, however, that all the expected lines occur in both recordings. The anomalous appearance of the low-temperature spectrum thus arises from prominent linewidth variations, the lines at high fields being of much lower amplitude, and therefore broader, than those at low fields. In fact, these effects are so marked that it would probably be extremely difficult to analyze the low-temperature spectrum without knowledge of the room-temperature splitting constants.

The resolution of the spectra is much better than found by Maki and Geske⁴ for the *p*-dinitrobenzene anion generated electrolytically in acetonitrile solution, or by Ward³ for the radical formed by alkali-metal reduction in dimethoxyethane solution. The widths of the narrowest lines in Fig. 1 are about 0.1 G, while the smallest widths in Fig. 2 are about 0.05 G. The hyperfine splittings at room temperature in DMF are^{14,15} $|a^N| = 1.48$ G and $|a^H| = 1.12$ G, while those

¹³ H. Wahlquist, J. Chem. Phys. **35**, 1708 (1961).

¹⁴ P. H. Rieger, thesis, Columbia University, New York, 1961.

¹⁵ P. H. Rieger and G. K. Fraenkel, J. Chem. Phys. **39**, 609 (1963).

found by Maki and Geske in acetonitrile⁴ are $|a^N| = 1.74$ G and $|a^H| = 1.12$ G. The field scale of the low-temperature spectrum in DMF was not carefully calibrated, but the ratio of splittings could be determined and was found to have changed from the value $|a^H|/|a^N| = 0.757$ at room temperature to 0.741 at -55° . This change in ratio causes a reversal of the overlapped lines numbered 10 and 11 (and 10' and 11') which is not properly indicated in the stick diagram in Fig. 2.

Examination of the 12° spectrum shows that the amplitudes of the lines on the high-field side are slightly less than on the low-field side, but that otherwise the amplitudes are approximately proportional to the relative statistical weights of the lines. Thus except for this slight increase in width from low to high fields, all the hyperfine components have essentially the same width.

A careful study of the low-temperature spectrum was made by analyzing six spectra, half taken by scanning in each direction of the magnetic field. The reduced amplitudes A_i/D , relative to the reduced amplitude of the central line were computed for each of the six spectra, and the average values are given in Table I. Drift and instability caused primarily by inadequate temperature control caused considerable scatter, and the average standard deviation of the

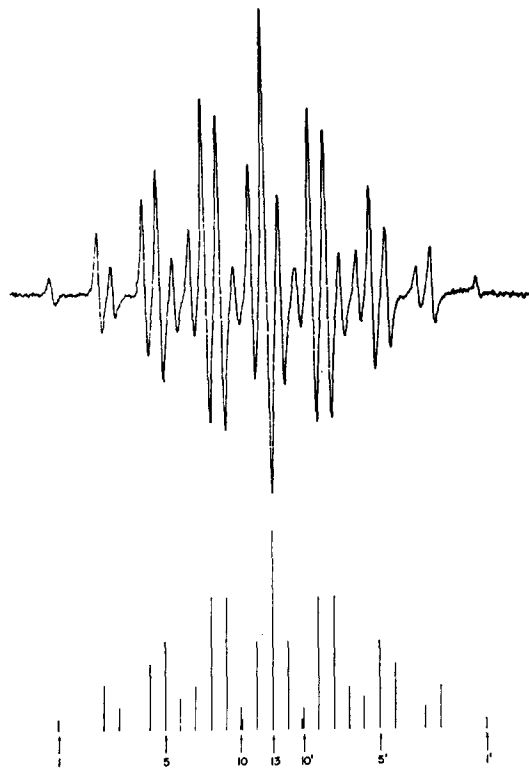


Fig. 1. First derivative of the ESR spectrum of the *p*-dinitrobenzene anion in DMF at 12°C . The magnetic field increases to the right. See Table I.

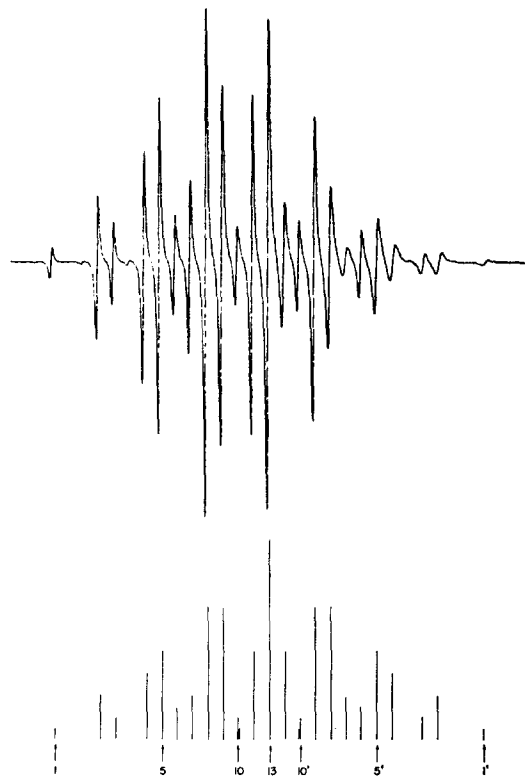


Fig. 2. First derivative of the ESR spectrum of the *p*-dinitrobenzene anion in DMF at -55°C . The magnetic field increases to the right. See Table I. The stick diagram here is drawn to coincide with the 12° spectrum (Fig. 1). The positions of lines numbered 10 and 11 (and 10' and 11') should be interchanged in the stick diagram to correspond properly with the low-temperature spectrum.

relative widths was $\sigma_P = 0.029$. This standard deviation includes all sources of scatter, including drift, and therefore the precision of the average values is undoubtedly somewhat better than indicated because the effects of drift were canceled out to first order by taking an equal number of recordings with both directions of the magnetic-field scan. Lines 10 and 11 (and 10' and 11') were so highly overlapped that they were excluded from the detailed analysis. Slight corrections for overlap of some of the other lines were made, as indicated in the table, by computing theoretical spectra. To make the computations, the lines were assumed to be of Lorentzian shape and relative widths were calculated from the experimental amplitude measurements by using Eq. (2.1). The derivative width of the central line was taken to be $\delta_{13} = 0.05$ G, and the splittings were given the values $|a^N| = 1.51$ G and $|a^H| = 1.12$ G (see below). The spectrum was calculated on an IBM 7090 computer using a program developed by Goodman¹⁶ and the corrected widths obtained by successive approximations.

The isotropic g value was measured at room tem-

¹⁶ S. Goodman, thesis, Columbia University, New York, 1962.

TABLE I. Relative linewidths, *p*-dinitrobenzene anion at -55°C .

Line number ^a	Quantum numbers ^b		Degen- eracy D_i	Experimental results		Calculated relative widths, W_i			
	\tilde{M}_N	\tilde{M}_H		Reduced rel. amplitude ^c	Relative width W_i ^d	Principal nitrogen lines ^e	Principal proton lines ^f	All lines ^g	Deviation $\times 10^3$
1	-2	-2	1	1.148	0.933			0.929	4
2	-2	-1	4	1.287	0.881			0.880	1
3	-1	-2	2	1.512	0.813			0.827	-14
4	-2	0	6	1.428	0.836	0.832		0.831	5
5	-1	-1	8	1.530	0.808			0.828	-20
6	0	-2	3	1.211	0.908 ^h		0.910	0.900	8
7	-2	1	4	1.564	0.800			0.782	18
8	-1	0	12	1.512	0.813	0.827		0.828	-15
9	0	-1	12	1.090	0.958		0.954	0.950	8
{10 ^a	1	-2	2}	Overlapped				1.234	...
{11 ^a	-2	2	1}	Overlapped				0.733	...
12	-1	1	8	1.548	0.803 ^h			0.828	-25
13	0	0	18	1.000	1.000	1.000	1.000	1.000	...
12'	1	-1	8	0.577	1.313 ^h			1.333	-20
{11' ^a	2	-2	1}	Overlapped				1.806	...
{10' ^a	-1	2	2}	Overlapped				0.829	...
9'	0	1	12	0.921	1.042		1.047	1.050	-8
8'	1	0	12	0.494	1.420 ^h	1.441		1.433	-13
7'	2	-1	4	0.277	1.873 ^h			1.955	-82
6'	0	2	3	0.822	1.099 ^h		1.096	1.100	-1
5'	1	1	8	0.420	1.540 ^h			1.533	7
4'	2	0	6	0.231	2.068 ^h	2.061		2.104	-36
3'	1	2	2	0.367	1.639 ^h			1.632	7
2'	2	1	4	0.199	2.233 ^h			2.253	-20
1'	2	2	1	0.191	2.287 ^h			2.402	-115

^a The numbering system is that of Fig. 1, the 12° spectrum. Lines 10 and 11 (and 10' and 11') are reversed in the -55° spectrum, Fig. 2.

^b \tilde{M}_N and \tilde{M}_H are the spectral index numbers for the two nitrogen nuclei and four protons, respectively. They correspond to the total z components of the nitrogen and proton nuclear-spin angular momenta if the hyperfine splittings a^N and a^H are both negative. See text.

^c Ratio of the reduced peak-to-peak amplitude of the first derivative A_i/D_i of Line i to the reduced amplitude for the central line, A_{13}/D_{13} , not corrected for overlap.

^d From Eq. (2.1). Corrected for overlap, see Footnote h and text.

^e From Eq. (5.1).

^f From Eq. (5.2).

^g From Eq. (5.5).

^h Corrected for overlap. The corrections to W_i were less than -0.5% except for the following lines, which had the corrections indicated in parentheses: 7' (-1.4%), 4' (-0.6%), and 3' (-0.7%).

perature in DMF and found to have the value¹⁷ $g_s = 2.00510$.

o-Dinitrobenzene

Electrolysis of a $0.005M$ solution of *o*-dinitrobenzene in DMF at -0.90 V produced an orange-yellow solution which gave an ESR spectrum of only 15 lines. In this spectrum, the linewidth was 0.27 G and the smallest splitting, which arises from a pair of equivalent protons, could not be detected. The linewidth of the room-temperature spectrum was reduced to 0.07 G, and the small splitting resolved, by carrying out the reduction on 0.001 – $0.002M$ solutions.¹⁸ Spectra were

¹⁷ We are indebted to Dr. J. R. Bolton for this measurement of g_s . It is based on measurements of the ESR frequency and of the proton NMR frequency for the field at the central line. Comparison was made with the *p*-benzosemiquinone anion spectrum to correct for systematic errors by using the results of M. S. Blois, Jr., H. W. Braun, and J. E. Maling, Arch. Sci. Geneva **13**, Special Number 243–55 (1960).

¹⁸ The large decrease in linewidth obtained by lowering the concentration of starting material probably resulted from a reduction of the radical-radical intermolecular line broadening effects and of the rate of chemical exchange between the radical and the starting material. Some of the radical generated is probably always destroyed by small residual impurities in the solvent and the electrolysis apparatus, so that the actual radical concentration produced on electrolysis of the dilute solution is likely to be less than that predicted on the basis of the amount of radical obtained from the more concentrated solution.

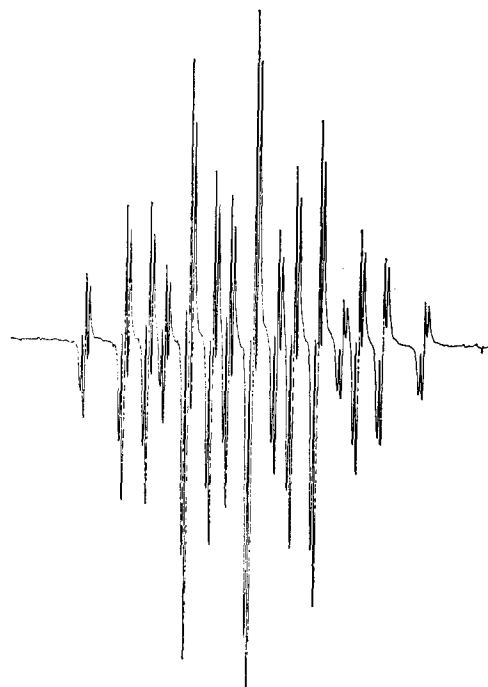


FIG. 3. First derivative of the ESR spectrum of the *o*-dinitrobenzene anion in DMF at -43°C . The magnetic field increases to the right. See Table II.

TABLE II. Relative linewidths, *o*-dinitrobenzene anion.

Line number ^a	Quantum numbers ^b		Degen- eracy D_i	Relative width, W_i			
	\tilde{M}_N	\tilde{M}_H		-45°C		-62°C	
				Experimental ^c	Calculated ^d	Experimental ^e	Calculated ^e
1	-2	-1	1				
2	-2	0	2	0.882	0.867	0.897	0.876
3	-1	-1	2				
4	-2	1	1				
5	-1	0	4	0.875	0.929	0.845	0.911
6	0	-1	3				
7	-1	1	2				
8	0	0	6	1.000	1.000	1.000	1.000
7'	1	-1	2				
6'	0	1	3				
5'	1	0	4	1.017	1.085	1.110	1.169
4'	2	-1	1				
3'	1	1	2				
2'	2	0	2	1.200	1.178	1.408	1.311
1'	2	1	1				

^a The numbering system corresponds to the major groups of lines in Fig. 3.

^b \tilde{M}_N and \tilde{M}_H are the spectral index numbers for the two nitrogen nuclei and the pair of equivalent protons at Positions 4 and 5, respectively. See Footnote b of Table I and text.

^c From experimental amplitudes and Eq. (2.1).

^d From Eq. (5.6).

^e From Eq. (5.7).

also obtained at -43° and -62°C from 0.002*M* solutions electrolyzed at room temperature. The -43° spectrum is presented in Fig. 3.

Again the resolution of the spectra obtained in DMF is considerably better than found by Maki and Geske in acetonitrile.⁴ The hyperfine splittings at room temperature in DMF were found to be, using a numbering system based on 1,2-dinitrobenzene: $|a^N| = 2.66 \pm 0.02$ G, $|a_3^H| = 0.114 \pm 0.005$ G, and $|a_4^H| = 1.72 \pm 0.01$ G. In acetonitrile solution, Maki and Geske⁴ found: $|a^N| = 3.22$ G, $|a_3^H| = 0.42$ G, and $|a_4^H| = 1.63$ G, indicating that there are appreciable solvent effects.^{15,19} The field scales of the low-temperature spectra were not calibrated, but the relative splittings changed from $|a_4^H| : |a_3^H| : |a^N| = 0.646:0.0428:1$ at room temperature to 0.628:0.057:1 at -43° . Although the linewidths in the -43° spectrum are slightly larger than in the room-temperature spectrum (0.08 G as compared to 0.07 G for the central line), the resolution of the low-temperature spectrum is better because of the increase in the magnitude of the smallest splitting.

The complexity and high degree of overlap in the spectrum, as well as possible errors from microwave power saturation, precluded the analysis of any but the lines arising from the nitrogen splitting. The results are presented in Table II.

Effects of Temperature on the Splittings

Although the low-temperature spectra were uncalibrated, the ratios of the magnitudes of the splittings were determined, and each such ratio in DMF at low temperatures had a value that was between the results in DMF and acetonitrile (MeCN) at room tempera-

ture. This observation suggests that the changes of splittings with temperature may be closely related to the changes of splittings with solvent,^{15,19} and perhaps the temperature effects can be represented in terms of the solvent effects by a relation like

$$a_i(\text{DMF}; T_2) = a_i(\text{DMF}; T_1) + \alpha[a_i(\text{MeCN}; T_1) - a_i(\text{DMF}; T_1)], \quad (3.1)$$

where α depends on the radical, solvent pair, and temperature but is independent of the particular splitting a_i in the radical. For the *o*-dinitrobenzene anion, the ratios of splittings at low temperature are $|a_3^H| / |a^N| = 0.057$ and $|a_4^H| / |a^N| = 0.628$ from which α is found to be 0.138 and 0.137, respectively. The agreement here is considerably better than the precision of the experimental data, but is clearly encouraging evidence for the validity of Eq. (3.1). According to this hypothesis, the magnitudes of the low-temperature splittings in the *o*-dinitrobenzene anion in DMF would be 2.73, 0.156, and 1.71 G, respectively, for the nitrogen, and for the protons at Positions 3 and 4. For the *p*-dinitrobenzene anion, the proton splitting is assumed to be unchanged because the room-temperature splittings in DMF and MeCN are identical. From the low-temperature proton splittings, the low-temperature nitrogen splitting is calculated to be 1.51 G, and α is 0.115.

IV. THEORETICAL EXPRESSIONS FOR THE LINEWIDTHS

The linewidths of the hyperfine components in the ESR spectra of solutions of free radicals are determined by the eigenvalues of a relaxation matrix.⁶ The elements of this matrix depend on certain spectral densities which can be calculated if sufficient informa-

¹⁹ J. Gendell, J. H. Freed, and G. K. Fraenkel, *J. Chem. Phys.* **37**, 2832 (1962).

tion is available about the instantaneous molecular conformation and spin-density distribution, and if the molecular motions are known. Although a number of interactions can cause differences in the widths of the different hyperfine lines in a spectrum,^{5,6,9,20} we attempt to account for the linewidth variations described in Sec. III by considering only two types of phenomena. The contributions we include result from the effects of random molecular tumbling on the anisotropic intramolecular interaction of the electron spin with (i) the nuclear spins (dipolar interaction) and (ii) the orbital electronic motions (g tensor interaction). Modulations of the isotropic dipolar interaction⁶ and of the nitrogen quadrupole interaction²¹ are thus neglected (but see Sec. VII), as are any intermolecular effects (such as intermolecular electron²² or quantum-mechanical exchange²³) which affect different hyperfine lines differently. Since the spectra were obtained from very dilute solutions and we are primarily interested in analyzing spectra obtained at low temperatures, the contributions from the intermolecular interactions are certainly unimportant in causing linewidth variations. Nonsecular contributions are also neglected because, for a particular type of interaction, they are smaller than secular and pseudosecular^{5,6} terms by the factor $(1+\omega_0^2\tau^2)^{-1}$, where $\omega_0/2\pi$ is the frequency at which the spectrum is obtained and τ is a correlation time characteristic of the motional modulation of the interaction. This assumption is justified in Sec. VII.

We first calculate the coefficients which determine the anisotropic intramolecular dipolar interaction and then use them to evaluate the spectral densities. Since the relaxation time for molecular tumbling τ_R and the principal values of the g tensor are unknown, these will be treated as parameters to be evaluated by comparison with experiment. Finally, the relaxation matrix will be discussed, and expressions for the linewidths obtained. Most of our considerations are confined to the p -dinitrobenzene anion.

²⁰ M. Stephen and G. K. Fraenkel, *J. Chem. Phys.* **32**, 1435 (1960).

²¹ Estimation of the linewidth contribution from the electric quadrupole interaction of the ¹⁴N nuclei requires detailed evaluation of the molecular electric field gradients at the nucleus. As a crude but reasonable first approximation, we assume the sigma bonds to the nitrogen atom are completely covalent and have sp^2 hybridization so that the only contribution to the field gradient will arise from the deficiency (i.e., deviation from unity) of the electron density in the nitrogen $2p-\pi$ orbital. The relative importance of the quadrupole and dipole terms in affecting the linewidth depends on: (i) the deficiency in the $2p-\pi$ electron density as compared to the $2p-\pi$ spin density; and (ii) the electric quadrupole moment as compared to the nuclear magnetic dipole moment of the ¹⁴N nucleus. The MO calculations¹⁶ indicate that the pi-electron spin density is 1.276. Rough estimates of e^2qQ for an electron in a $2p-\pi$ orbital on ¹⁴N range from about 5.3 to 8.8 Mc/sec. Using the formulas in Ref. 6, the linewidth contributions from quadrupole relaxation are thus estimated to be of the order of 4% or less of the dipole terms.

²² 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).

²³ G. E. Pake and T. R. Tuttle, *Phys. Rev. Letters* **3**, 423 (1959); J. D. Currin, *Phys. Rev.* **126**, 1995 (1962).

a. Coefficients of the Dipolar Interaction, p -Dinitrobenzene Anion

The anisotropic dipolar interaction can be most conveniently expressed in terms of certain coefficients defined in Ref. 6. These can be evaluated from formulas given by McConnell and Strathdee.²⁴ It is also readily shown that the appropriate coefficient for the interaction at a nitrogen nucleus, in the notation of Freed and Fraenkel,⁶ is

$$D_N^{(0)} = (6^3/120) (Z_N/a_0)^3 \rho_N^\pi, \quad (4.1)$$

where ρ_N^π is the pi-electron spin density on the atom containing the nucleus, and a_0 is the Bohr radius. It is assumed in deriving this result that the unpaired electron is in a Slater $2p$ orbital with effective nuclear charge Z_N . The calculation of the dipolar coefficients requires structural parameters and spin densities. We use the x-ray determination of the structure of p -dinitrobenzene,²⁵ which gives the following distances (Å) and angles: C-C:1.38; C₁-N:1.48; N-O:1.21; and \angle O-N-O:124°28'. We also take the C-H bond distance to be 1.084, and use $Z_C=3.25$, $Z_N=3.90$, and $Z_O=4.55$ for the effective nuclear charges in the Slater orbitals of carbon, nitrogen, and oxygen, respectively. For the spin densities, we use the results of Rieger and Fraenkel,¹⁵ $\rho_1^\pi=0.0796$, $\rho_2^\pi=0.0434$, $\rho_N^\pi=0.1042$, and $\rho_O^\pi=0.1148$, where the carbon atoms are numbered according to the scheme for 1,4-dinitrobenzene, and N and O refer to the nitrogen and oxygen atoms. The results are^{26,27}:

$$(1/2\pi) |\gamma_e| \gamma_N \hbar D_N^{(0)} = -0.331\rho_1^\pi - 0.473\rho_2^\pi + 46.674\rho_N^\pi - 2.080\rho_O^\pi = 4.578 \times 10^6 \text{ sec}^{-1} \quad (4.2a)$$

²⁴ H. M. McConnell and J. Strathdee, *Mol. Phys.* **2**, 129 (1959).

²⁵ S. C. Abrahams, *Acta Cryst.* **3**, 194 (1950).

²⁶ Schreurs and Fraenkel⁹ and Stephen and Fraenkel²⁰ used a different notation. The coefficients of the dipolar interaction $D_i^{(m)}$ are related to the coefficients used by these authors by: $D_i^{(0)} = (\frac{2}{3})^{\frac{1}{2}} a_i$, $D_i^{(1)} = (\frac{2}{3})^{\frac{1}{2}} b_i$, $D_i^{(2)} = (\frac{2}{3})^{\frac{1}{2}} c_i$ with $D_i^{(m)} = D_i^{(-m)*}$. Other notation used in the present work is related as follows: $j_{ij}^{(D)}(\omega_0) = \frac{1}{2} K_{ij}$, $j_i^{(DQ)}(\omega_0) B_0 = \frac{1}{4} L_i$, and $j^{(Q)}(\omega_0) B_0^2 = \frac{1}{2} M_j$, where B_0 is the value of the Zeeman field, and we have generalized the results of Stephen and Fraenkel by replacing the expression $[|a|^2 + 2|b|^2 + 2|c|^2]$ of their Eq. (3.5) by $[a_i a_j + b_i b_j + b_i^* b_j + c_i c_j + c_i^* c_j]$. See also Ref. 28.

²⁷ The major contributions to the nitrogen coefficients arise from the pi-electron spin density on the nitrogen atoms and its nearest neighbors, the appropriate formulas being

$$\begin{aligned} (\frac{1}{2}\pi) |\gamma_e| \gamma_N \hbar D_N^{(0)} &= -0.288\rho_1^\pi + 46.692\rho_N^\pi - 2.049\rho_O^\pi, \\ &= 4.607 \times 10^6 \text{ sec}^{-1}, \end{aligned}$$

$$(\frac{1}{2}\pi) |\gamma_e| \gamma_N \hbar D_N^{(2)} = 0.698\rho_1^\pi = -0.090 \times 10^6 \text{ sec}^{-1}.$$

For protons, the contribution of the pi-electron spin density on the adjacent atom does not give a good approximation.⁹ The results, however, are

$$(\frac{1}{2}\pi) |\gamma_e| \gamma_H \hbar D_H^{(0)} = -3.249\rho_2^\pi = -0.141 \times 10^6 \text{ sec}^{-1},$$

$$\begin{aligned} (\frac{1}{2}\pi) |\gamma_e| \gamma_H \hbar D_H^{(2)} &= -(10.520 + 18.220i)\rho_2^\pi, \\ &= -(0.457 + 0.791i) \times 10^6 \text{ sec}^{-1}. \end{aligned}$$

$$(1/2\pi) |\gamma_e | \gamma_N \hbar D_N^{(2)} = 0.752\rho_1^\pi + 0.385\rho_2^\pi + 0.022\rho_N^\pi \\ - 1.239\rho_O^\pi = -0.063 \times 10^6 \text{ sec}^{-1} \quad (4.2b)$$

$$(1/2\pi) |\gamma_e | \gamma_H \hbar D_H^{(0)} = -[4.502\rho_1^\pi + 8.521\rho_2^\pi \\ + 2.624\rho_N^\pi + 3.946\rho_O^\pi] = -1.455 \times 10^6 \text{ sec}^{-1} \quad (4.2c)$$

$$(1/2\pi) |\gamma_e | \gamma_H \hbar D_H^{(2)} = -(4.673 + 0.719i)\rho_1^\pi \\ - (9.301 + 23.485i)\rho_2^\pi - (0.409 + 2.243i)\rho_N^\pi \\ + (2.260 + 2.999i)\rho_O^\pi = -(0.559 + 0.499i) \\ \times 10^6 \text{ sec}^{-1}. \quad (4.2d)$$

The $D_H^{(m)}$ refer to the interactions with the protons at Positions 2 and 5, and these coefficients differ in phase^{6,28,29} from those for Positions 3 and 6. Thus, if we refer to the protons at Positions 2 and 5 as Group 1 and those at Positions 3 and 6 as Group 2, and indicate the groups by subscripts, $D_H^{(0)} = D_{H(1)}^{(0)} = D_{H(2)}^{(0)}$ and $D_H^{(2)} = D_{H(1)}^{(2)} = D_{H(2)}^{(-2)}$. The coefficients for the two nitrogen nuclei are identical. The coefficients $D_i^{(\pm 1)}$ vanish for a planar radical, and $D_i^{(2)} = D_i^{(-2)*}$. The quantities γ_e , γ_H and γ_N are the magnetogyric ratios of the electron, the proton, and the ^{14}N nucleus, respectively. A right-handed molecule-fixed axis system is employed with origin at the center of the molecule, with the z axis perpendicular to the molecular plane, and with the positive x axis passing through the carbon atom at Position 1.

b. Spectral Densities, *p*-Dinitrobenzene Anion

The spectral densities for the dipolar interaction which relate two nuclei i and j are, in the notation of Freed and Fraenkel^{6,26} and with $j_{ij}^{(D)}$ written for $j_{ij}^{(D)}(\omega=0)$,

$$j_{ij}^{(D)}/\tau_R = \frac{1}{5} \hbar^2 \gamma_e^2 \gamma_i \gamma_j \sum_{m=-2}^2 D_i^{(m)} D_j^{(-m)}. \quad (4.3)$$

The g tensor contributes

$$j^{(G_2)}/\tau_R = \frac{1}{20} \beta_e^2 \hbar^{-2} [g_1^2 + g_2^2 + g_3^2 - 3g_s^2], \quad (4.4)$$

where β_e is the Bohr magneton and g_1 , g_2 , and g_3 are the principal values of the g tensor along the molecule-fixed x , y , and z axes, respectively, used above. The isotropic g value g_s is

$$g_s = \frac{1}{3}(g_1 + g_2 + g_3). \quad (4.5)$$

There is also a cross-term between the dipolar and g tensor interactions given by

$$j_i^{(DG_2)}/\tau_R = \frac{1}{10} |\gamma_e | \beta_e \gamma_i \sum_{m=-2}^2 D_i^{(m)} g^{(-m)} \quad (4.6)$$

where

$$g^{(0)} = (1/6^{\frac{1}{2}})(2g_3 - g_1 - g_2) \\ g^{(\pm 1)} = 0 \\ g^{(\pm 2)} = \frac{1}{2}(g_1 - g_2). \quad (4.7)$$

Substituting Eqs. (4.2) into these expressions gives,³⁰ on using $B_0 = 3280$ G for the experimental value of the Zeeman field:

$$j_N^{(D)}/\tau_R = 1.66 \times 10^{14} \text{ sec}^{-2} \quad (4.8a)$$

$$j_H^{(D)}/\tau_R \equiv j_{H(1),H(1)}^{(D)}/\tau_R \equiv j_{H(2),H(2)}^{(D)}/\tau_R \\ = 0.256 \times 10^{14} \text{ sec}^{-2} \quad (4.8b)$$

$$j_{NH}^{(D)}/\tau_R \equiv j_{N,H(1)}^{(D)}/\tau_R \equiv j_{N,H(2)}^{(D)}/\tau_R \\ = -0.520 \times 10^{14} \text{ sec}^{-2} \quad (4.8c)$$

$$j_{H(12)}^{(D)}/\tau_R \equiv j_{H(1),H(2)}^{(D)}/\tau_R = 0.177 \times 10^{14} \text{ sec}^{-2}, \quad (4.8d)$$

$$j_N^{(DG_2)} B_0/\tau_R = [3.388(6^{\frac{1}{2}}g^{(0)}) - 0.0938(6^{\frac{1}{2}}g^{(\pm 2)})] \\ \times 10^{16} \text{ sec}^{-2} \quad (4.8e)$$

$$j_H^{(DG_2)} B_0/\tau_R \equiv j_{H(1)}^{(DG_2)} B_0/\tau_R = j_{H(2)}^{(DG_2)}/\tau_R \\ = -[1.081(6^{\frac{1}{2}}g^{(0)}) + 0.827(6^{\frac{1}{2}}g^{(\pm 2)})] \times 10^{16} \text{ sec}^{-2}. \quad (4.8f)$$

c. Relaxation Matrix and Linewidths, *p*-Dinitrobenzene Anion

The two nitrogen nuclei are equivalent, as are the four protons, but while the two nitrogen nuclei are also completely equivalent,⁶ the protons are not. The protons at Positions 2 and 5 (Group 1) form one completely equivalent subgroup, and those at Positions 3 and 6 (Group 2) form another. Two nuclei are said to be equivalent if the zero-order Hamiltonian is invariant with respect to the interchange of their positions, and they are said to be completely equivalent only if the perturbing Hamiltonian is also invariant.⁶ The zero-order Hamiltonian describes the positions of the lines in the spectrum and the perturbing Hamiltonian causes relaxation and line broadening. The appropriate wavefunction⁶ for the nuclear spin states of the two nitrogen nuclei is thus the coupled representation $|J_N, M_N\rangle$, where M_N is the quantum number for the sum of the z components of the nuclear-spin angular momenta of the two nitrogen nuclei ($M_N = 0, \pm 1, \pm 2$) and J_N is the quantum number for the total nuclear-spin angular momentum of these two nuclei ($J_N = 0, 1, 2$). The protons at Positions 2 and 5 are also most appropriately coupled together, and the wavefunctions are written as $|J_{H(1)}, M_{H(1)}\rangle$, where

³⁰ In Eq. (4.8c), $j_{NH(1)}^{(D)} = j_{NH(2)}^{(D)}$ because the nitrogen atoms lie on a twofold symmetry axis coinciding with a principal axis of the g tensor, and thus $D_N^{(2)}$ is real. In general, however, if b_1 and b_2 refer to nuclei in two different completely equivalent⁶ subgroups of an equivalent group and a refers to nuclei in some different equivalent group, $j_{ab_1}^{(D)} \neq j_{ab_2}^{(D)}$.

²⁸ J. W. H. Schreurs, thesis, Free University of Amsterdam, Amsterdam, 1962; J. W. H. Schreurs and D. Kivelson, *J. Chem. Phys.* **36**, 117 (1962).

²⁹ A. Carrington and H. C. Longuet-Higgins, *Mol. Phys.* **5**, 447 (1962).

TABLE III. Coefficients of dipolar interaction, principal nitrogen lines^a

M_N	J_N	$\frac{[J_N(J_N+1)]}{+(5/3)M_N^2}$	$\frac{\langle J_N(J_N+1) \rangle}{+(5/3)M_N^2}$ ^b
± 2	2	38/3	38/3
± 1	2	23/2	17/3
	1	11/3	
0	2	6	8/3
	1	2	
	0	0	

^a See Eqs. (4.9)ff for notation.

^b $\langle J(J+1) \rangle = D_M^{-1} \sum D_J J(J+1)$, $D_M = \sum D_J$ and the summations are over all values of J consistent with M .

the quantum numbers are defined in a manner analogous to that employed for the two nitrogen nuclei; their possible values are $M_{H(1)} = 0, \pm 1$ and $J_{H(1)} = 0, 1$. A similar wavefunction is used for the protons at Positions 3 and 6, $|J_{H(2)}, M_{H(2)}\rangle$. The total nuclear-spin wavefunction is written as a product over the three completely equivalent subgroups, i.e., $|J_N, M_N\rangle |J_{H(1)}, M_{H(1)}\rangle |J_{H(2)}, M_{H(2)}\rangle$.

In this representation,⁶ the secular part of the relaxation matrix is diagonal, but the pseudosecular part, which is comparable in magnitude to the secular part, contains off-diagonal elements proportional to $j_{H(12)}^{(D)}$. There are also off-diagonal nonsecular contributions which, as mentioned above, we neglect. In order to simplify the discussion, the relaxation matrix for two completely equivalent nitrogen nuclei is treated first and the presence of the protons is neglected. To a first approximation²¹ this analysis will refer to the lines in the spectrum for which $M_H = M_{H(1)} + M_{H(2)} = 0$; these will be called the principal nitrogen lines. The protons will then be considered by neglecting the nitrogen nuclei, and the corresponding lines, called the principal proton lines, will be those for which $M_N = 0$. Finally, the general relaxation matrix will be analyzed.

i. Principal Nitrogen Lines

In the representation chosen, the secular and pseudosecular parts of the relaxation matrix for two completely equivalent nitrogen nuclei contain only diagonal elements. The position of a line in the spectrum is determined by M_N alone, but in general the different components (transitions) which make up a degenerate line arise from states with different values of J_N and the widths of the components are a function of J_N . As mentioned above, each component is of Lorentzian shape with a width given by minus the appropriate

²¹ The error in the approximation involved here is significant only if the lines for $M_H = 0$ must be represented by a superposition of Lorentzian-shaped lines rather than a single Lorentzian, as discussed in the remainder of this section. For the *p*-dinitrobenzene anion the errors introduced by the approximation are negligible.

(diagonal) element of the relaxation matrix, and thus the over-all line for a particular M_N is a superposition of Lorentzian-shaped components.⁶ The width of the component specified by J_N of the line at the position determined by M_N is given by⁶

$$[T_2^{(N)}(M_N; J_N)]^{-1} = j_N^{(D)} [J_N(J_N+1) + \frac{8}{3}M_N^2] + \frac{1}{3}j_N^{(DG_2)}B_0M_N + \frac{8}{3}j^{(G_2)}B_0^2 + X_N'. \quad (4.9)$$

Here only secular and pseudosecular contributions of the anisotropic dipolar and g -tensor interactions are included, and X_N' accounts for other line-broadening mechanisms which presumably do not contribute terms that depend on M_N and J_N . The coefficients of $j_N^{(D)}$ are listed in Table III.

When the spectral densities $j_N^{(D)}$ are small compared to the other terms in Eq. (4.9), the superposition of Lorentzian lines for the different values of J_N can be approximated by a single Lorentzian line with a width determined by an average over the widths of the different components,⁶ in accord with the result originally given by Kivelson.⁵ The average widths are more convenient for a preliminary analysis of the experimental data than the individual component widths given by Eq. (4.9), and as we shall see in Sec. V, they also represent a very good approximation to the data. The averages of the coefficients of $j_N^{(D)}$ are listed in Table III, and from them one readily obtains an expression for the average widths:

$$[T_2^{(N)}(M_N; \langle J_N \rangle_w)]^{-1} = j_N^{(D)} \eta(M_N) + \frac{1}{3}j_N^{(DG_2)}B_0M_N + X, \quad (4.10)$$

where

$$X = \frac{8}{3}j_N^{(D)} + \frac{8}{3}j^{(G_2)}B_0^2 + X_N' \quad (4.11a)$$

and

$$\eta(\pm 2) = 10, \quad \eta(\pm 1) = 3, \quad \eta(0) = 0. \quad (4.11b)$$

Since the sign of the hyperfine splitting a^N cannot be determined from the positions of the lines in the spectrum, the experimental data is expressed in terms of spectral index numbers \tilde{M}_N (and \tilde{M}_H). These are the same as the quantum numbers M_N (M_H) except that they are defined to be positive on the high-field side of the spectrum; the index number \tilde{M}_N (\tilde{M}_H) would be identical to the quantum number M_N (M_H) if the hyperfine splitting constant a^N (a^H) were negative. The signs of the hyperfine splittings are discussed in Sec. VI. For comparison with the experimental data, which is in terms of the widths relative to the central line, we therefore write Eq. (4.10) as

$$W_w(\tilde{M}_N, \tilde{M}_H = 0) = 1 + B_N \tilde{M}_N + C_N \eta(\tilde{M}_N), \quad (4.12)$$

where

$$B_N X = \pm \frac{1}{3}j_N^{(DG_2)}B_0, \quad (4.13a)$$

$$C_N X = j_N^{(D)}, \quad (4.13b)$$

TABLE IV. Coefficients of dipolar interaction, principal proton lines.^a

M_H	$M_{H(1)}$	$M_{H(2)}$	$J_{H(1)}$	$J_{H(2)}$	$j_H^{(D)}(0)$	$j_{H(12)}^{(D)}(0)$	Coefficient of spectral densities	
							$j_H^{(D)}(0)$	$j_{H(12)}^{(D)}(0)$
± 2	± 1	± 1	1	1	22/3	16/3	22/3	16/3
± 1	± 1	0	1	1	17/3	0	14/3	0
	0	± 1	1	1	17/3	0		
	± 1	0	1	0	11/3	0		
	0	± 1	0	1	11/3	0		
0	1	-1	1	1	22/3	-16/3	34/9	-16/9
	-1	1	1	1	22/3	-16/3		
	0	0	1	1	4	0		
	0	0	1	0	2	0		
	0	0	0	1	2	0		
	0	0	0	0	0	0		

^a See Eqs. (4.15)ff. for notation and expressions for coefficients.

and the plus (minus) sign in Eq. (4.13a) applies when a^N is negative (positive).

ii. Principal Proton Lines

As indicated above, the relaxation matrix for the protons contains off-diagonal elements even if the non-secular parts are omitted. These off-diagonal elements result from the incomplete equivalence of the four protons, are pseudosecular in origin, and are proportional to $j_{H(12)}^{(D)}$. If the different eigenvalues of the relaxation matrix contain only small differences arising from the off-diagonal elements, it can be shown that the width is determined by an average over only the diagonal elements of the principal part of the matrix,⁶

$$[T_2^{(H)}(M_H; \langle J_{H(1)}, J_{H(2)} \rangle_{av})]^{-1} = -D_{M_H}^{-1} \sum R_{\alpha\alpha'\alpha\alpha'}, \tag{4.14}$$

where $M_H = M_{H(1)} + M_{H(2)}$, and D_{M_H} is the degeneracy of a proton line with quantum number M_H . The states α and α' have the same nuclear spin quantum numbers but differ in their value of the electron spin quantum number m_s , and the summation is over those matrix elements with values of $J_{H(1)}$, $J_{H(2)}$, $M_{H(1)}$, and $M_{H(2)}$ that can contribute to a state with quantum number M_H (see Table IV). We use this result since, as is seen in Sec. V, the dipolar contributions from the protons are small.

The appropriate diagonal elements of the relaxation matrix are⁶

$$R_{\alpha\alpha'\alpha\alpha'} = - \sum_{u,v=1}^2 j_{H(u),H(v)}^{(D)} \{ M_{H(u)} M_{H(v)} [\frac{8}{3} - \delta_{H(u)H(v)}] + J_{H(u)}(J_{H(v)} + 1) \delta_{H(u)H(v)} \} - \frac{1}{3} \sum_{u=1}^2 j_{H(u)}^{(DG_2)} B_0 M_{H(u)} - \frac{8}{3} j^{(G_2)} B_0^2 - X_H', \tag{4.15}$$

where X_H' is a term analogous to X_N' in Eq. (4.9). The coefficients of $j_H^{(D)}$ and $j_{H(12)}^{(D)}$ from Eq. (4.15), and the average values computed from Eq. (4.14),

are listed in Table IV. The average widths obtained from Eq. (4.14) are thus

$$[T_2^{(H)}(M_H; \langle J_{H(1)}, J_{H(2)} \rangle_{av})]^{-1} = \frac{8}{3} j_H^{(D)} \Gamma_H(12) M_H^2 + \frac{1}{3} j_H^{(DG_2)} B_0 M_H + X, \tag{4.16}$$

where

$$\Gamma_H(12) = \frac{1}{3} [1 + (2j_{H(12)}^{(D)} / j_H^{(D)})], \tag{4.17a}$$

$$X = \frac{8}{3} j_H^{(D)} - \frac{1}{9} j_{H(12)}^{(D)} + \frac{8}{3} j^{(G_2)} B_0^2 + X_H'. \tag{4.17b}$$

From Eqs. (4.8), Γ_H is estimated to be $\Gamma_H(12) = 0.794$. If $j_{H(12)}^{(D)} = j_H^{(D)}$, corresponding to four completely equivalent protons, $\Gamma_H(12) = 1$, and Eqs. (4.16) and (4.17b) reduce to the expression for the average width of the completely coupled states with $J_H = 2$ (1 state), $J_H = 1$ (3 states), and $J_H = 0$ (2 states). The equation for the relative widths, obtained from Eq. (4.16), and analogous to Eq. (4.12), is

$$W_{av}(\tilde{M}_N = 0, \tilde{M}_H) = 1 + B_H \tilde{M}_H + C_H \tilde{M}_H^2, \tag{4.18}$$

where

$$B_H X = \pm \frac{1}{3} j_H^{(DG_2)} B_0, \tag{4.19a}$$

$$C_H X = \frac{8}{3} j_H^{(D)} \Gamma_H(12), \tag{4.19b}$$

and the plus (minus) sign in Eq. (4.19a) applies when a^H is negative (positive).

iii. General Linewidth Expression, All Lines

The secular and pseudosecular part of the general relaxation matrix for the anisotropic dipolar and g -tensor terms contains elements which are just the combination of those for the principal nitrogen and principal proton lines except for the addition of a cross term proportional⁶ to $j_{NH}^{(D)}$. The expression for the average relative width is readily found, by using the above results and methods, to be

$$W_{av}(\tilde{M}_N, \tilde{M}_H) = 1 + B_N \tilde{M}_N + B_H \tilde{M}_H + C_N \eta (\tilde{M}_N) + C_H \tilde{M}_H^2 + E_{NH} \tilde{M}_N \tilde{M}_H, \tag{4.20}$$

where

$$E_{NH}X = \pm \frac{1}{8} j_{NH}^{(D)}, \quad (4.21a)$$

and

$$X = \frac{8}{9} j_N^{(D)} + \frac{34}{9} j_H^{(D)} - \frac{16}{9} j_{H(12)}^{(D)} + \frac{8}{9} j^{(G_2)} B_0^2 + X'. \quad (4.21b)$$

The plus sign in Eq. (4.21a) applies if a^N and a^H have the same sign, the minus sign if they have different signs. The quantity X' represents the contribution from interactions not included in the present calculations.³² The width of the central line is given by

$$[T_{2,A}(\bar{M}_N=0, \bar{M}_H=0)]^{-1} = X. \quad (4.22)$$

d. *o*-Dinitrobenzene anion

Only the principal nitrogen lines in the *o*-dinitrobenzene anion spectra were analyzed, and since these may be in error because of saturation effects, we have not carried out a complete calculation of the dipolar coefficients. The formulas in Footnote 27 give an approximate expression for the $D_N^{(m)}$, and by neglecting $D_N^{(2)}$ in comparison with $D_N^{(0)}$ and using the spin densities given by Rieger and Fraenkel,¹⁵ we find

$$j_N^{(D)}/\tau_R = 1.83 \times 10^{14} \text{ sec}^{-2}. \quad (4.23)$$

The appropriate linewidth expression is given by Eqs. (4.10) and (4.11).

V. FIT TO THEORETICAL EXPRESSIONS FOR THE LINEWIDTH

In this section the parameters in the phenomenological expressions for the linewidths developed in Sec. IV are fitted to the experimental data. The principal nitrogen and proton lines of the *p*-dinitrobenzene anion will be studied first, and the effects resulting from the superposition of several Lorentzian lines of different widths analyzed. A fit will then be made to all the lines of the *p*-dinitrobenzene anion spectrum and to the principal proton lines of the *o*-dinitrobenzene anion spectrum.

Fit to the Principal Nitrogen and Proton Lines, *p*-Dinitrobenzene Anion

The parameters in Eq. (4.12) for the principal nitrogen lines can be determined by fitting this expression to the experimentally determined relative widths for the principal nitrogen lines given in Table I. These lines are numbered 4, 8, 13, 8', and 4'. The least-squares

³² The relations between X' , X_N' , and X_H' are

$$\begin{aligned} X_N' &= X' + (34/9)j_H^{(D)} - (16/9)j_{H(12)}^{(D)} \\ X_H' &= X' + (8/3)j_N^{(D)} \end{aligned}$$

fit gives³³

$$W_A(\bar{M}_N, \bar{M}_H=0) = 1 + 0.3071\bar{M}_N + 0.0447\eta(\bar{M}_N). \quad (5.1)$$

The standard deviation³⁴ estimated from the residual sum of squares of the deviations for the fit is $\sigma_R = 0.019$, while the standard deviations estimated from the six replications used to obtain the experimental data is $\sigma_P = 0.014$. As indicated in Sec. III, σ_P is probably an overestimate of the true precision of the data, and thus σ_R is somewhat larger than the true precision, although not significantly so. The standard deviations of the parameters in Eq. (5.1), using σ_R for the estimate of precision, are $\sigma(B_N) = 0.0059$ (1.9%) and $\sigma(C_N) = 0.0013$ (2.8%). Widths calculated from Eq. (5.1) are listed in Table I.

A similar fit to the principal proton lines (6, 9, 13, 9', 6') gives, using Eq. (4.18),

$$W_A(\bar{M}_N=0, \bar{M}_H) = 1 + 0.0466\bar{M}_H. \quad (5.2)$$

The coefficient of \bar{M}_H^2 has the statistically insignificant value of 0.0008. The standard deviations are $\sigma_R = 0.005$ and $\sigma_P = 0.006$; and using σ_R , the standard deviations of the coefficients are $\sigma(B_H) = 0.002$ (3.5%) and $\sigma(C_H) = 0.001$ (108%). Widths calculated from Eq. (5.2) are given in Table I.

Effects of the Superposition of Lorentzian Lines and of a Nondiagonal Relaxation Matrix

The phenomenological equations for the principal nitrogen and proton lines, Eqs. (4.12) and (4.18), that have been used to fit the experimental data involve two approximations: For both the nitrogen and proton lines, the $M = \pm 1$ and 0 lines are the superposition of Lorentzian-shaped lines of different widths, and Eqs. (4.12) and (4.18) result from averaging the widths of the individual components. The expression for the principal proton lines also involves the neglect of the off-diagonal parts of the relaxation matrix. The statistically insignificant value of C_H , the coefficient of \bar{M}_H^2 , implies that the dipolar interaction for the protons is small, and therefore that the off-diagonal matrix elements, which are determined by the pseudosecular terms in the dipolar interaction, can be neglected. Similarly, since the averaging procedure which leads

³³ The principal nitrogen lines can also be fitted by a quadratic in \bar{M}_N , with the result

$$W_A(\bar{M}_N, \bar{M}_H=0) = 1 + 0.3071\bar{M}_N + 0.1132\bar{M}_N^2$$

and a standard deviation for the fit of $\sigma_R = 0.005$. Thus a quadratic actually gives a somewhat better fit to the data than Eq. (5.1). The standard deviation of the coefficient of the linear term in this expression (using σ_R) is 0.002 (0.6%), while that of the coefficient of the quadratic term is 0.0009 (0.8%). Although the experimental results do not indicate Eq. (4.12) is preferable to a quadratic, there is no theoretical relation between the coefficient of \bar{M}_N^2 above and the spectral densities.

³⁴ The t test was not applied to these data.

TABLE V. Superposition of computed lines: principal nitrogen lines, *p*-dinitrobenzene anion.

\tilde{M}_N	$[T_2^{(N)}(\tilde{M}_N; J_N)]^{-1}$ ^a			$[T_2^{(N)}(\tilde{M}_N; \langle J_N \rangle_{av})]^{-1}$	Computed derivative amplitude ^b			Computed reduced relative amplitudes		
	$J_N=0$	$J_N=1$	$J_N=2$		Superposition of lines	Single line $T_{2,av}$	Difference %	Superposition of lines	Single line $T_{2,av}$	Difference %
-1	...	0.738	...	0.827	3.003	2.924	-2.6	1.461	1.462	0.1
0	0.881	0.970	1.149	1.000	3.084	3.000	-2.7	1.000	1.000	...
1	...	1.352	1.530	1.441	0.971	0.963	-0.9	0.472	0.481	1.9

^a $[T_2^{(N)}(\tilde{M}_N; J_N)]^{-1}$ from Eq. (5.3) with $B_N=0.3071$ and $C_N=0.04467$.

^b Normalized to make the amplitude for the central line of width $[T_2^{(N)}(\tilde{M}_N; \langle J_N \rangle_{av})]^{-1}=1.000$ be 3.000 units.

to Eqs. (4.18) involves only dipolar terms, the procedure is clearly valid for the proton lines. The large value of the parameter C_N in Eq. (5.1), however, indicates that the averaging process may be incorrect for the principal nitrogen lines.

The parameters for the principal nitrogen lines determined in Eq. (5.1) can be used to estimate the validity of replacing Eq. (4.9) by the average result, Eq. (4.10). Using Eq. (4.11a) for X and Eqs. (4.13) for B_N and C_N , Eq. (4.9) can be written

$$[T_2^{(N)}(\tilde{M}_N; J_N)]^{-1} = X \{ 1 + B_N \tilde{M}_N + C_N [J_N(J_N+1) + \frac{5}{3} \tilde{M}_N^2 - \frac{8}{3}] \}. \quad (5.3)$$

The values of T_2^{-1} obtained from this equation, with B_N and C_N from Eq. (5.1), are listed in Table V, and show variations within a particular hyperfine line (particular value of \tilde{M}_N) by as much as 22%. The derivative amplitudes for each value of \tilde{M}_N computed by superimposing Lorentzian-shaped components with the tabulated component widths, together with the amplitudes computed for a single Lorentzian line with a width corresponding to the average over the component widths, are also given in Table V. These results show that despite the large differences between the component widths for a particular line, the amplitudes computed with the average width are only slightly different from the amplitudes obtained in the superposition calculation, and there is an even smaller difference in the reduced relative amplitudes (see the last columns of Table V). Because of the square-root dependence of the widths on the amplitudes, the widths calculated from the relative amplitudes by using Eq. (2.1) are in error by only 0.05% and 1.0%, respectively, for the $\tilde{M}_N = -1$ and $\tilde{M}_N = +1$ lines.

These considerations show that the averaging procedure does not introduce significant errors in the present application. They also illustrate the difficulty of distinguishing between an experimental spectrum that consists of a single Lorentzian-shaped line from one that is composed of a superposition of Lorentzians.

Fit to All Lines, *p*-Dinitrobenzene Anion

One parameter in the expression for the relative widths of all the lines, Eq. (4.20), remains to be evaluated, the intercombination term $E_{NH} = \pm \frac{1}{3} j_{NH}^{(D)} X^{-1}$ which makes a contribution when neither \tilde{M}_N nor \tilde{M}_H are zero. This parameter can be estimated directly from the experimental data by using the relation, based on Eq. (4.20),

$$W^{\text{exp}}(\tilde{M}_N, \tilde{M}_H) - W^{\text{exp}}(\tilde{M}_N, \tilde{M}_H=0) - W^{\text{exp}}(\tilde{M}_N=0, \tilde{M}_H) + 1 = E_{NH} \tilde{M}_N \tilde{M}_H, \quad (5.4)$$

where the W^{exp} are the W_i of Table I. The result is $E_{NH} = 0.0530$ with a standard deviation of 0.005 (8.5%). A least-squares fit of Eq. (4.20) to all the data can also be used to obtain this parameter, as well as slightly revised values for the other parameters. The result is

$$W_{av}(\tilde{M}_N, \tilde{M}_H) = 1 + 0.3024 \tilde{M}_N + 0.0499 \tilde{M}_H + 0.0436 \eta (\tilde{M}_N) + 0.0496 \tilde{M}_N \tilde{M}_H, \quad (5.5)$$

with the coefficient \tilde{M}_H^2 again being statistically insignificant. The standard deviation of the fit is $\sigma_R = 0.040$ as compared with $\sigma_P = 0.028$. Widths calculated from this equation, and the deviations from the experimental data, are listed in the last two columns of Table I. Two lines, numbered 7' and 1', show particularly large deviations (Line 7' is the most highly overlapped of the lines included in the analysis, and Line 1' is the line of lowest amplitude), and if these are excluded from the total sum of squares (but still included in making the fit), one finds $\sigma_R = 0.018$. Taking this smaller value of σ_R , the standard deviations of the parameters in Eq. (5.5) are: $\sigma(B_N) = 0.003$ (1.0%), $\sigma(B_H) = 0.003$ (6.6%), $\sigma(C_N) = 0.007$ (1.6%), and $\sigma(E_{NH}) = 0.003$ (6.0%). All the parameters (except C_H) are thus highly significant. The difference between the estimates for the principal lines and those in Eq. (5.5) are not significant.

o-Dinitrobenzene Anion

The fit of Eq. (4.12) to the principal nitrogen lines of the *o*-dinitrobenzene anion (numbers 2, 5, 8, 5' and 2') using the data in Table II at -45° gives

$$W_{av}(\tilde{M}_N, \tilde{M}_H=0) = 1 + 0.0778\tilde{M}_N + 0.0023\eta(\tilde{M}_N) \quad (5.6)$$

while the data at -62° gives

$$W_{av}(\tilde{M}_N, \tilde{M}_H=0) = 1 + 0.1287\tilde{M}_N + 0.0134\eta(\tilde{M}_N). \quad (5.7)$$

The standard deviations at the two temperatures are, respectively, $\sigma_R=0.064$ and 0.060 . Both fits are thus rather poor. The results calculated from these two equations are given in Table II.

VI. SIGN OF THE NITROGEN HYPERFINE SPLITTING

One of the important questions in the theoretical study of ESR spectra is the sign of the isotropic hyperfine splittings a_i . McConnell has shown on theoretical grounds that the parameter Q_{CH^H} in the relation $a^H = Q_{CH^H}\rho^\pi$ for the proton splitting a^H is negative,^{35,36} and this result has also been experimentally verified.³⁷⁻³⁹ Experimental determination of the sign of a^H can thus be used to give the sign of the spin density ρ^π on the carbon atom bonded to the proton. For nuclei in many-electron atoms such as ^{13}C or ^{14}N , the hyperfine splitting is a function of the spin densities on adjacent atoms as well as on the atom containing the nucleus,^{40,41} and the sign of the splitting is an important prediction of the theory. The positions of the lines in the spectrum of a free radical in solution are, however, independent of the signs of the hyperfine splittings. In this section we therefore review the various methods for obtaining the signs of the isotropic hyperfine splitting, and show that intercombination terms such as E_{NH} in expressions for the linewidths can lead to a determination of the relative signs of these splittings.

There are only a limited number of techniques for establishing the signs of the hyperfine splittings. Studies of a few aliphatic free radicals trapped in a single crystal have yielded the sign of the isotropic splitting

³⁵ H. M. McConnell, *J. Chem. Phys.* **24**, 633, 764 (1956); H. M. McConnell and H. H. Dearman, *ibid.* **28**, 51 (1958).

³⁶ H. M. McConnell and D. B. Chesnut, *J. Chem. Phys.* **28**, 107 (1958) and other papers cited therein.

³⁷ H. M. McConnell, C. Heller, T. Cole, and R. W. Fessenden, *J. Am. Chem. Soc.* **82**, 766 (1960).

³⁸ T. H. Brown, D. H. Anderson, and H. S. Gutowsky, *J. Chem. Phys.* **33**, 720 (1960); H. S. Gutowsky, H. Kusumoto, T. H. Brown, and D. H. Anderson, *ibid.* **30**, 860 (1959).

³⁹ M. E. Anderson, G. E. Pake, and T. R. Tuttle, Jr., *J. Chem. Phys.* **33**, 1581 (1960); M. E. Anderson, P. J. Zandstra, and T. R. Tuttle, Jr., *ibid.* **33**, 1591 (1960).

⁴⁰ M. Karplus and G. K. Fraenkel, *J. Chem. Phys.* **35**, 1312 (1961).

⁴¹ A. D. McLachlan, H. H. Dearman, and R. Lefebvre, *J. Chem. Phys.* **33**, 65 (1960).

by comparison with the known sign of the anisotropic dipolar interaction.³⁷ The signs can also be obtained from NMR studies of concentrated free-radical systems at low temperatures^{36,38,39} but only α, α' -diphenylpicrylhydrazyl and the pyrene anion have been investigated in this way. NMR studies of certain nickel chelates provide analogous but not completely identical information.⁴²

In the ESR spectra of free radicals in solution, any linewidth phenomena which causes appreciable effects that are linear in the quantum number M_i related to the hyperfine splitting a_i can be used to establish the sign of a_i . The most important of these linear terms arises from the cross term between the anisotropic dipolar and g -tensor interactions (spectral density $j_i^{(DG_2)}$), but determination of the sign of a_i requires that the magnitudes of the principal components g_1 , g_2 , and g_3 of the g tensor be estimated. If there are at least two inequivalent groups of nuclei in a radical that have hyperfine splittings of known sign, experimental evaluation of the two spectral densities [Eq. (4.6)] can be used to obtain the components of the g tensor. These can then be employed to determine the signs of the splittings from other nuclei. This procedure, which has not been used, requires an experimental determination of the isotropic g value g_s , calculation of the dipolar coefficients $D_i^{(m)}$, and evaluation, by comparison with experiment, of the spectral density $j_{ii}^{(D)}$ [Eq. (4.3)] and the relaxation time τ_R . Complete information about the magnitudes of the components of the g tensor is not needed for determining the signs of ^{13}C and ^{14}N splittings when the pi-electron spin density on the atom containing the nucleus is not too small compared to the spin densities on neighboring atoms. Terms such as $D_N^{(0)}$ [Eq. (4.2a)] are then much larger than terms such as $D_N^{(2)}$ [Eq. (4.2b)], and thus the sign of $j_i^{(DG_2)}$ is usually independent of $g^{(\pm 2)}$ [see Eqs. (4.6) and (4.7)]. DeBoer and Mackor⁴³ have determined the sign of a ^{13}C splitting in the naphthalene anion in this way by using the theoretical estimate⁴⁴ for planar hydrocarbons that the component of the g tensor perpendicular to the molecular plane, g_3 , is smaller than the mean of the other two components, so that $g^{(0)}$ [Eq. (4.7)] is negative. The sign of the dipolar coefficient $D_i^{(0)}$ must also be known to apply this procedure.

There have always been uncertainties about the relative magnitudes of the components of the g tensors in free radicals containing atoms other than carbon, and thus use of the cross term between the dipolar and g -tensor interactions is not an entirely satisfactory method of obtaining the signs of the isotropic splitting

⁴² W. D. Phillips and R. E. Benson, *J. Chem. Phys.* **33**, 607 (1960); R. E. Benson, D. R. Eaton, A. D. Josey, and W. D. Phillips, *J. Am. Chem. Soc.* **83**, 3714 (1961).

⁴³ E. deBoer and E. L. Mackor, *J. Chem. Phys.* **38**, 1450 (1963).

⁴⁴ H. M. McConnell and R. E. Robertson, *J. Phys. Chem.* **61**, 1018 (1957).

a^N from an ^{14}N nucleus, or of the ^{13}C splittings in a molecule containing hetero atoms. Although a very recent theoretical study⁴⁵ of the g tensor in free radicals may provide the needed information, it seems desirable to explore methods of obtaining the signs of isotropic hyperfine splittings that do not depend on knowledge of the components of the g tensor.

Such a method is provided by analyzing the intercombination effect, with spectral density $j_{rs}^{(D)}$, between two groups of inequivalent nuclei r and s . There is a contribution to the secular part of the linewidth of a term $j_{rs}^{(D)}M_rM_s$ and thus the relative signs of the isotropic hyperfine splittings a_r and a_s can be obtained. In this method, as in the technique based on the dipolar and g -tensor cross term, at least approximate values of the dipolar coefficients must be available.

For the p -dinitrobenzene anion, the analysis of the experimental data in Sec. V shows that E_{NH} is positive, and the calculations of the dipolar coefficients indicate that $j_{\text{NH}}^{(D)}$ is negative [Eq. (4.8c)]. The sign of $j_{\text{NH}}^{(D)}$ can also be arrived at qualitatively by inspection of the form of the dipolar interaction involving the p orbitals making the major contributions.⁴⁶ The sign depends on the assumed positive spin density on the nitrogen atoms and on the carbon atoms bonded to protons. Since E_{NH} and $j_{\text{NH}}^{(D)}$ are of opposite sign, the appropriate sign in Eq. (4.21a) is negative, and therefore a^N and a^H have opposite signs.

As assumed in obtaining the dipolar coefficients, all theoretical estimates of the spin-density distribution in the p -dinitrobenzene anion^{15,47} indicate that the pi-electron spin density is positive at the carbon atoms to which protons are bonded. Since the parameter Q_{CH^H} is negative, the proton splitting a^H is also negative, and therefore the nitrogen splitting a^N is positive. A positive sign for a^N was also chosen by Rieger and Fraenkel on the basis of a semiempirical study of nitrogen splittings in a series of substituted nitrobenzene anions in order to obtain consistency with the sigma-pi interaction theory of the hyperfine-splitting constant parameters.¹⁵ From the positive sign for B_N found in Sec. V, it follows that $j_N^{(DG_2)}$ is negative [see Eq. (4.13a)]. Thus, unless the magnitude of $g^{(\pm 2)}$ is much greater than the magnitude of $g^{(0)}$, it follows from Eq. (4.8d) that $g^{(0)}$ is negative, and consequently $g_3 < \frac{1}{2}(g_1 + g_2)$ in the p -dinitrobenzene anion.

VII. SPECTRAL DENSITIES, g -TENSOR, AND CORRELATION TIME

The evaluation of the parameters in the expressions for the linewidths carried out for the p -dinitrobenzene

⁴⁵ A. J. Stone, Proc. Roy. Soc. (London) **A271**, 424 (1963); Mol. Phys. **5**, 509 (1963).

⁴⁶ Qualitative inspection of the spin densities may, however, be quite misleading in giving the magnitudes and signs of the dipolar interaction for protons. See the discussion of the 2,6-dinitrophenolate dianion in Ref. 11.

⁴⁷ J. C. Schug, T. H. Brown, and M. Karplus, J. Chem. Phys. **37**, 330 (1962).

anion in Sec. V can be used, in principle, with the calculations of the dipolar interaction in Sec. IV to estimate the correlation time τ_R for molecular tumbling and the components of the g tensor. We use Eq. (5.5) and Eqs. (4.13), (4.19), and (4.21), together with the experimentally measured width of the central line. This width is $\delta = 0.050$ G, from which X in Eq. (4.21b) has the value $X = 0.762 \times 10^6 \text{ sec}^{-1}$. The spectral densities are thus found to be (in sec^{-1})

$$\begin{aligned} j_N^{(D)} &= 3.32 \times 10^4, \\ j_H^{(D)} &\gtrsim 0.09 \times 10^4, \\ j_{\text{NH}}^{(D)} &= -0.708 \times 10^4, \\ j_N^{(DG_2)} B_0 &= -4.32 \times 10^4, \\ j_H^{(DG_2)} B_0 &= 0.714 \times 10^4. \end{aligned} \quad (7.1)$$

The signs in the last three expressions have been determined by using the results of Sec. VI. The upper limit on $j_H^{(D)}$ is derived on the assumption that the parameter is less than, or of the order of, $\sigma(\text{C}_H) = 0.0024$ from the fit to Eq. (5.5), and the calculated value of $\Gamma_{\text{H}(12)} = 0.794$ has been inserted into Eq. (4.19b). The first three spectral densities when taken in conjunction with the calculations of the dipolar interaction, Eqs. (4.8), give three estimates for the correlation time. From the N, H, and NH terms, we obtain (in sec) $\tau_R = 2.01 \times 10^{-10}$, $\tau_R \gtrsim 0.35 \times 10^{-10}$, and $\tau_R = 1.36 \times 10^{-10}$, respectively. The agreement between the first and last estimates is reasonably satisfactory when considered in light of all the approximations involved in obtaining the results, but the correlation time implied by the term in $j_H^{(D)}$ is in bad disagreement.

The abnormally low correlation time estimated from $j_H^{(D)}$ is a reflection of the negligibly small value of the coefficient of M_H^2 in the linewidth expressions. This coefficient is much smaller than expected from the linewidth studies on the p -benzosemiquinone ion,⁹ and is qualitatively inconsistent with the magnitude of the cross term between the dipolar and g -tensor interactions for the protons, $j_H^{(DG_2)}$. In fact, if the value $\tau_R = 0.35 \times 10^{-10}$ sec is used with Eqs. (4.8) and (7.1) for the cross terms, unreasonable values are found for the components of the g tensor (see below). This discrepancy requires a re-examination of the assumptions used to obtain theoretical expressions for the linewidths.

Among the least certain factors in the calculations of Sec. IV are the assumed values for the pi-electron spin densities. These are based on the McLachlan modification of the Hückel molecular orbital theory using empirically adjusted parameters to obtain a fit with a large number of nitro-substituted anion radicals,¹⁵ and although good agreement resulted, there is no direct check of the spin densities in the p -dinitrobenzene anion except at the proton-substituted ring

positions. Examination of Eqs. (4.2c) and (4.2d) shows that a reasonable reshuffling of the spin-density distribution cannot remove the large discrepancy for $j_{\text{H}}^{(D)}$ if the spin densities are all positive as predicted by the MO calculations.¹⁵ The valence-bond calculations of Karplus and collaborators,⁴⁷ however, give a negative spin density at Position 1. Estimates of the spectral densities from the valence-bond spin densities is not possible because no calculations of the nitrogen and oxygen spin densities were made, but a negative spin density at Position 1 would be in the right direction to reduce the discrepancy for $j_{\text{H}}^{(D)}$.

Among the other assumptions, we note that nonsecular line-broadening mechanisms have been neglected throughout, and the molecular tumbling has been approximated by an isotropic motion. For a correlation time of $\tau_R = 2 \times 10^{-10}$ sec, the factor $(1 + \omega_0^2 \tau_R^2)^{-1}$, which measures the relative importance of the nonsecular and secular contributions, has the value 0.75% at the frequency of 9.2 kMc/sec used in the experiments. Thus for a reasonable value of the correlation time, the nonsecular contributions can certainly be neglected. The effect of approximating the molecular tumbling as the Brownian motion of an ellipsoid rather than a sphere has recently been studied for NMR spectra,^{48,49} but no applications to the theory of ESR spectra have been carried out.

As a final possibility, we consider the effects of line-broadening mechanisms in addition to the dipolar and g -tensor interactions. The most important of the remaining interactions may well be a modulation of the isotropic hyperfine couplings. When this modulation is the predominant line-broadening mechanism and obeys the proper phase relations, it causes the alternating linewidth phenomenon observed in the dinitro-durene¹ and m -dinitrobenzene² anions. Solvation or rotation of the nitro groups causes a redistribution of spin density¹⁵ which modulates the proton hyperfine splittings, and under reasonable assumptions it can be shown^{6,11} that the protons at Positions 2 and 6 form one completely equivalent subgroup while those at Positions 3 and 5 form another. When the dipolar interactions are included it is apparent that each proton forms a completely equivalent subgroup by itself. Writing $j_{\text{H}(22)}^{(I)}$ and $j_{\text{H}(23)}^{(I)}$ for the (secular) spectral densities describing the isotropic modulation, and with subscripts now referring to proton positions in the radical, the additional averaged contribution⁶⁰ to the linewidth expression for the protons, Eq. (4.16), is^{6,11}

$$\frac{1}{3} [j_{\text{H}(22)}^{(I)} + 2j_{\text{H}(23)}^{(I)}] M_{\text{H}}^2 + \frac{2}{3} [j_{\text{H}(22)}^{(I)} - j_{\text{H}(23)}^{(I)}] \quad (7.2)$$

which reduces to

$$-\frac{1}{3} j_{\text{H}(22)}^{(I)} M_{\text{H}}^2 + \frac{4}{3} j_{\text{H}(22)}^{(I)} \quad (7.3)$$

in the limit $j_{\text{H}(23)}^{(I)} = -j_{\text{H}(22)}^{(I)}$ of complete out-of-

phase correlation of the modulation. The complete coefficient of M_{H}^2 would thus be

$$\frac{1}{3} [8j_{\text{H}(22)}^{(D)} \Gamma_{\text{H}}(1, 2) - j_{\text{H}(22)}^{(I)}] \quad (7.4)$$

and if $j_{\text{H}(22)}^{(I)}$ is sufficiently large, this coefficient can be made negligible, as is needed to remove the discrepancy. The same mechanism, however, also affects the nitrogen lines. Modulation of the hyperfine splittings of the nitrogen nuclei adds the terms⁶ $2[j_{\text{N}(11)}^{(I)} + j_{\text{N}(14)}^{(I)}]$, $j_{\text{N}(11)}^{(I)}$, and $\frac{4}{3}[j_{\text{N}(11)}^{(I)} - j_{\text{N}(14)}^{(I)}]$ for the $M_{\text{N}} = \pm 2, \pm 1$, and 0 lines, respectively, to the average linewidth for the nitrogen lines, Eq. (4.10). Now for small degrees of solvation or rotation of the nitro groups, the changes in the splittings of the two nitrogens are in phase,¹⁵ although for larger effects they are out of phase. In the limit of complete in-phase correlation [$j_{\text{N}(14)}^{(I)} = j_{\text{N}(11)}^{(I)}$], the contribution of the isotropic modulation would be $j_{\text{N}(11)}^{(I)} M_{\text{N}}^2$. Of course complete in-phase correlation is not to be expected even for a small amount of solvation or rotation. The experimental estimate of C_{N} would then be smaller so that the value of τ_R evaluated from C_{N} and $j_{\text{N}}^{(D)}$ would also be smaller. Thus the modulation of the isotropic interaction might well make contributions in the correct direction to reduce some of the discrepancies. There is not sufficient data available from the spectrum of the p -dinitrobenzene anion, however, to analyze these considerations in detail.

If the correlation time for molecular tumbling τ_R were known, the cross terms between the dipolar and g -tensor interactions in Eqs. (7.1) could be used with Eqs. (4.8e) and (4.8f) to evaluate the components of the g tensor. If we assume $\tau_R = 2.01 \times 10^{-10}$ sec, as estimated from the term in $j_{\text{N}}^{(D)}$, and using $g_s = 2.00510$, we find $g_1 = 2.0077$, $g_2 = 2.0046$, and $g_3 = 2.0030$, where Axis 1 passes through the two nitrogen atoms and Axis 3 is perpendicular to the plane of the ring. The quantitative significance of these values is, however, highly questionable because of the uncertainty in the appropriate value of τ_R and in the exact magnitudes of the dipolar coefficients.

The width of the central line, Eq. (4.22), is determined by the quantity X defined in Eq. (4.21b), and several of the terms in this expression have been evaluated. If we assume that there is a contribution from the modulation of the isotropic splittings with complete out-of-phase correlation, the term of unknown magnitude $\frac{4}{3} j_{\text{H}(22)}^{(I)}$ must be added to the right-hand side of Eq. (4.21b). It is still of interest to evaluate the other terms. Using the components of the g tensor calculated above, we find $j^{(G_2)} B_0^2 / \tau_R = 4.79 \times 10^{14} \text{ sec}^{-2}$, or, using $\tau_R = 2.01 \times 10^{-10}$ sec, $\frac{2}{3} j^{(G_2)} B_0^2 = 0.257 \times 10^6 \text{ sec}^{-1}$. For $j_{\text{H}}^{(D)}$ and $j_{\text{H}(12)}^{(D)}$ we use the values calculated from the dipolar interaction [Eqs. (4.8)] with $\tau_R = 2.01 \times 10^{-10}$, and for $j_{\text{N}}^{(D)}$ we use the experimentally determined result. The sum of these terms is

$$\frac{8}{3} j_{\text{N}}^{(D)} + \frac{3}{5} j_{\text{H}}^{(D)} - \frac{1}{9} j_{\text{H}(22)}^{(D)} + \frac{2}{3} j^{(G_2)} B_0^2 = 0.359 \times 10^6 \text{ sec}^{-1}. \quad (7.5)$$

⁴⁸ D. E. Woessner, J. Chem. Phys. **37**, 647 (1962).

⁴⁹ H. Shimizu, J. Chem. Phys. **37**, 765 (1962).

⁶⁰ We neglect the effects of the modulation of the hyperfine splittings and spin-density distribution on the dipolar coefficients. See Refs. 6 and 11.

This is to be compared with the experimental value $X=0.763\times 10^6 \text{ sec}^{-1}$, which indicates that the terms $[\frac{1}{3}j_{\text{H}(22)}^{(T)}+X']$ add up to $0.404\times 10^6 \text{ sec}^{-1}$. The residual line broadening effects represented by X' are thus of the estimated order of magnitude.⁹

VIII. CONCLUSIONS

Large variations have been found among the linewidths of the different hyperfine lines in the low-temperature ESR spectra of the *p*- and *o*-dinitrobenzene anions. The magnitude of these variations in the *para* compound is so great that the spectrum is superficially uninterpretable. The major part of the variations in linewidths in this radical can be represented by terms that are linear in the quantum numbers of the nitrogen nuclei and protons, M_{N} and M_{H} , a term which is an even function of M_{N} , and a term proportional to the product $M_{\text{N}}M_{\text{H}}$. These contributions are interpreted as arising for the most part from modulation by molecular tumbling of the intramolecular anisotropic dipolar and g -tensor interactions. The theory shows that the dipolar relaxation and line broadening effects at the four protons are not identical, and the spectral density $j_{\text{H}(12)}^{(D)}$ introduced by this inequivalence produces about a 20% correction to the pure dipolar interactions with the protons. The term in the expression for the linewidths that is proportional to $M_{\text{N}}M_{\text{H}}$ arises from a cross term involving the pure dipolar interactions with the nitrogen nuclei and protons. The spectral density $j_{\text{NH}}^{(D)}$ associated with this cross term, and the spectral density $j_{\text{H}(12)}^{(D)}$, represent effects not previously studied in detail.

The cross term $j_{\text{NH}}^{(D)}$ between the nitrogen and proton dipolar interactions has been used in a new method to determine the relative signs of the nitrogen and proton hyperfine splittings. In the *p*-dinitrobenzene anion these splittings have been found to be opposite in sign, and since the proton splitting is undoubtedly negative, that of the nitrogen nucleus is positive. This determination of sign is independent of any assumptions about the magnitudes of the principal components of the g tensor, and leads to the conclusion that

the component g_3 perpendicular to the plane of the ring is less than the mean, $\frac{1}{2}(g_1+g_2)$, of the two in-plane components.

The coefficient of M_{H}^2 in the linewidth expression for the *p*-dinitrobenzene anion was found to have a much smaller value than estimated by including only the dipolar interaction. Modulation of the isotropic proton hyperfine splittings may also contribute to the linewidths, and qualitative considerations indicate that under certain conditions this mechanism could remove some of the discrepancies. The occurrence of such a perturbation is not unexpected because modulation of the nitrogen hyperfine splittings causes the alternating linewidth phenomenon in the dinitrobenzene and *m*-dinitrobenzene anions, and modulation of the proton splittings causes the alternating linewidths in the dihydroxybenzene cation. In these radicals the modulation of the isotropic splittings is the predominant line-broadening mechanism, whereas in the *p*-dinitrobenzene anion it makes at most a small contribution.

The theory of linewidths in ESR spectra predicts in general that degenerate lines are the superpositions of Lorentzian-shaped components with different widths. The pure dipolar interaction with the nitrogen nuclei in the *p*-dinitrobenzene anion causes the widths of some of the components within a given line to vary by as much as 22%, but nevertheless numerical analysis shows that the experimentally observed line-shape parameters for this radical are represented within an error of 2% or less by using a Lorentzian line shape with a width equal to the average over the component widths. The correlation time for molecular tumbling was found to be sufficiently long to allow the neglect of nonsecular terms in the relaxation matrix which determines the linewidths. Pseudosecular terms could be satisfactorily approximated by computing average values of the diagonal elements of the matrix, thus ignoring the off-diagonal elements.

The resolution of the spectra in DMF, even at low temperatures, was considerably better than in acetonitrile solutions at room temperature. Large changes in hyperfine splittings with solvent as well as appreciable shifts with temperature were observed.