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Line Shapes in Electron Spin Resonance Spectra*

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The theory of the linewidths in the electron spin resonance spectra of free radicals recently developed by Freed and Fraenkel predicts that, in general, composite lines arising from a set of degenerate nuclear spin states should not be Lorentzian in shape, and that the shapes of different lines in the same spectrum should be different. The earlier theory of Kivelson predicted that all the lines should be Lorentzian. To test the differences between the two theories, experimental studies of the line shape in the spectrum of the tetracyanoethylene anion have been made in a solvent consisting of a mixture of absolute ethanol and glycerine. Different lines were found to have different shapes, and the shapes were well represented by a sum of Lorentzian-shaped components, in agreement with the newer theory. Studies of dimethylsulfoxide solutions of the *p*-benzosemiquinone ion were also made. The spectra obtained in this system show only small linewidth variations and, in agreement with the theory, the variations in line shape are negligible. It was also possible to demonstrate that the nitrogen hyperfine splitting a^N in the tetracyanoethylene radical is positive.

I. INTRODUCTION

A GENERAL theory of the linewidths in electron spin resonance (ESR) spectra of dilute solutions of free radicals has been formulated recently by Freed and Fraenkel¹ using the relaxation-matrix theory developed by several authors.²⁻⁴ This new theory differs in a number of important respects from the earlier work of Kivelson,⁵ and in particular predicts that a composite hyperfine line arising from a set of degenerate nuclear spin states should in general consist of a sum of superimposed Lorentzian-shaped components of different widths.⁶ Kivelson's theory, in contrast, predicts that each line in the spectrum should have a Lorentzian shape and that the width of a composite line should be given by an appropriate average over the widths of the individual components. A single Lorentzian line with an averaged width is also a result of the newer theory, but only when the width variations among the different components are small compared to the average width. The object of the present investigation is to obtain an experimental test of these divergent theoretical predictions.

Unfortunately the experimental determination of line shape for lines of Lorentzian or approximately Lorentzian shape is extremely difficult. This can be seen by a simple calculation. We compute, point by point, the

sum of the first derivatives of two Lorentzian curves of equal intensity but with widths differing by a factor of 2. (The first derivative is used because it is the most common form of displaying experimental resonance curves.) A simple Lorentzian-shaped curve can then be chosen so that its derivative has maxima and minima of the same amplitude and at the same positions as the computed curve. A computation of this sort shows that the two-component curve and the single Lorentzian are practically indistinguishable except in the region of the wings farther out than from three to four times the separation of the derivative extrema. In an experimental spectrum, however, the wings are usually obscured by noise and may be distorted in shape either by overlap with other lines or from the presence of ¹³C satellites. The wings can thus not be carefully studied, and so for most spectra each line can be fitted by Lorentzian-shaped curves in the experimentally accessible central region even if the lines depart significantly from a true Lorentzian shape. Such a fit by a Lorentzian curve would, of course, be incorrect if the true lines were not Lorentzian in shape, and would lead to erroneous values for the parameters which describe the line broadening. These parameters are of intrinsic interest because they are related to structural features of the radical and its environment. Some properties of the shape of a line can be obtained, however, by combined measurements of its amplitude and width, and a procedure based on these two quantities is described in Sec. II.

The two linewidth theories differ in another respect. The relaxation-matrix theory is able to account for the recently observed alternating linewidth phenomenon,^{7,8}

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¹ J. H. Freed and G. K. Fraenkel, *J. Chem. Phys.* **39**, 326 (1963).

² A. G. Redfield, *IBM J. Res. Develop.* **1**, 19 (1957).

³ F. Bloch, *Phys. Rev.* **102**, 104 (1956).

⁴ A. Abragam, *The Principles of Nuclear Magnetism* (Oxford University Press, London, 1961).

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

⁶ The curves are, of course, not Lorentzian indefinitely far out in the wings. See R. Kubo and K. Tomita, *J. Phys. Soc. Japan* **9**, 888 (1954) and Ref. 4.

⁷ J. H. Freed and G. K. Fraenkel, *J. Chem. Phys.* **37**, 1156 (1962); J. H. Freed, I. Bernal, and G. K. Fraenkel, *Bull. Am. Phys. Soc.* **7**, 42 (1962); and J. H. Freed, P. H. Rieger, and G. K. Fraenkel, *J. Chem. Phys.* **37**, 1881 (1962).

⁸ J. R. Bolton and A. Carrington, *Mol. Phys.* **5**, 161 (1962). A. Carrington, *ibid.* **5**, 425 (1962); J. R. Bolton, A. Carrington, and P. F. Todd, *ibid.* **6**, 169 (1963).

but the Kivelson theory is not. Under some circumstances,¹ the alternating linewidth effect can also be explained by using the modified Bloch equations.⁸ The phenomenon arises from modulation of the isotropic hyperfine interactions, and the superposition of lines is essential to its theoretical interpretation. Our present interest, however, is concerned with a more subtle aspect of the relaxation-matrix theory: the line-shape effects to be studied arise from the nuclear spin transitions caused by the modulation through molecular tumbling of the intramolecular anisotropic dipolar interaction. These so-called pseudosecular contributions^{1,5} are treated differently in the relaxation-matrix and Kivelson theories. In the recent work of Carrington and Longuet-Higgins,⁹ the pseudosecular terms were neglected, and thus their results are different from both the relaxation-matrix and Kivelson theories. It is clear, however, that the pseudosecular terms are comparable in magnitude to the other parts of the dipolar interaction, and that it is therefore incorrect to neglect them.

We have searched exhaustively for a suitable radical on which to perform line-shape studies. The radical should be stable and should contain a small number of well-resolved lines. There should also be a minimum of interferences from impurities and from satellites like those from the ¹³C nuclei present in natural abundance. It is of course necessary that there be degenerate nuclear-spin states and that the spectra exhibit significant linewidth variations. If possible the end lines of the spectrum should be amenable to study because these lines are predicted to be pure Lorentzians by the relaxation-matrix theory, and the comparison of their shapes with those of the central lines should show the largest effects. Since nuclei with quadrupole moments can cause the theoretical analysis to be quite complicated, it is preferable, although not essential, to study radicals in which none of the nuclei have spins greater than one-half. We were unable to find a radical that meets all these specifications, and were forced to compromise on the tetracyanoethylene (TCNE⁻) anion.^{10,11} The main source of difficulty with TCNE⁻ is the interferences from ¹³C splittings. These prevent the study of the outside pair of lines on each side of the spectrum. Preliminary investigations showed that the linewidth variations are small in solvents of low viscosity, and the solvent chosen was therefore a highly viscous mixture consisting of absolute ethanol and glycerine. It was also desired to check the experimental method by studying a system in which there were no significant variations in line shape. It was found that a dimethylsulfoxide solution of the *p*-benzosemiquinone ion showed small linewidth effects, and it was therefore chosen as a comparison system.

⁹ A. Carrington and H. C. Longuet-Higgins, *Mol. Phys.* **5**, 447 (1962).

¹⁰ P. H. Rieger, I. Bernal, W. H. Reinmuth, and G. K. Fraenkel, *J. Am. Chem. Soc.* **85**, 683 (1963).

¹¹ W. D. Phillips, J. C. Rowell, and S. I. Weissman, *J. Chem. Phys.* **33**, 626 (1960).

II. EXPERIMENTAL METHODS

As indicated in the introduction, it is extremely difficult to detect departures from Lorentzian shape by comparing a computed Lorentzian curve with an experimental curve. We have therefore studied line shapes by using what will be called the line-shape factor S_i . It is defined for the i th line by

$$S_i = (A_i/D_i)^{1/2} \delta_i, \quad (2.1)$$

and is directly measurable in terms of the peak-to-peak amplitude of the derivative of the line A_i and the separation between the derivative extrema δ_i (the derivative width). In this expression, D_i is the degeneracy of the i th line. To determine the properties of the shape factor, let us denote the absorption curve of the i th line by $f_i(B)$, where B is the external magnetic field used in the ESR experiment to split the Zeeman levels. For the usual bell-shaped curve with a single maximum (at B_{0i}), there is always a single parameter, say Δ_i , which describes the breadth of the curve, and all curves of the same shape can be defined in terms of the shape function $g_i(x_i)$, where x_i is the reduced variable $x_i = (B - B_{0i})/\Delta_i$. The function $g_i(x_i)$ will be taken as normalized to unity,

$$\int_{-\infty}^{\infty} g_i(x_i) dx_i = 1. \quad (2.2)$$

It follows that $f_i(x_i) = (I_i/\Delta_i)g_i(x_i)$, where I_i is the intensity of the line, since

$$I_i = \int_0^{\infty} f_i(B) dB$$

and

$$\int_0^{\infty} f_i(B) dB = \Delta_i \int_{-\infty}^{\infty} f_i(x_i) dx_i = \Delta_i \frac{I_i}{\Delta_i} \int_{-\infty}^{\infty} g_i(x_i) dx_i = I_i.$$

We assume, as is customary, that $B_{0i} \gg \Delta_i$. The amplitude A_i is given by (where primes denote derivatives)

$$A_i = f'_i(B)_{\max} - f'_i(B)_{\min} = \Delta_i^{-1} [f'_i(x_i)_{\max} - f'_i(x_i)_{\min}] \\ = (I_i/\Delta_i^2) [g'_i(x_i)_{\max} - g'_i(x_i)_{\min}], \quad (2.3)$$

and therefore the shape factor is

$$S_i = (A_i/D_i)^{1/2} \delta_i \\ = \gamma_i \{ (I_i/D_i) [g'_i(x_i)_{\max} - g'_i(x_i)_{\min}] \}^{1/2}, \quad (2.4)$$

where $\gamma_i = \delta_i/\Delta_i$ is the ratio of the derivative width (separation between derivative extrema) to the parameter Δ_i . Now the reduced intensity I_i/D_i is a constant independent of the shape function for all the lines in a spectrum; and the other quantities on the right-hand side of Eq. (2.4) depend only on the shape, i.e., they are the same for lines of the same shape. Thus the ratio S_i/S_j of shape factors for two lines in the same spectrum is determined only by the shape function; and if all the lines in a spectrum have the same shape,

the ratios of shape factors are all unity. The analysis of the experimental data is carried out in terms of the relative shape factors

$$S_{r_i} = (A_{r_i} D_0 / D_i)^{1/2} \delta_{r_i}, \quad (2.5)$$

where $S_{r_i} = S_i / S_0$, $A_{r_i} = A_i / A_0$, $\delta_{r_i} = \delta_i / \delta_0$, and the subscript zero refers to the central line of the spectrum. For a Lorentzian-shaped line, $S_i = 0.743(I_i / D_i)^{1/2}$. It will be noted that the value of S_i is independent of the particular choice of the parameter Δ_i .

The linewidths were measured in two different ways. The first, and instrumentally the simplest, was to measure the separations between the maximum and minimum of the first derivative of the spectrum on a field-calibrated strip-chart recording. Since the derivative curve is a slowly varying function of the field in the neighborhood of the extrema, the maximum and minimum cannot be located with a high degree of accuracy. In practice it was more difficult to locate the positions of the extrema of the broad components than of the narrow components, and the wide lines were also subject to greater systematic error. The second method involved the use of the second derivative of the spectrum. The width is given by the separation of the zeroes of the second derivative, and since the curve is a rapidly varying function of the magnetic field at the zeroes, it should be possible to determine their location with greater precision and accuracy than is possible for the extrema of the first-derivative curve.

The accurate measurement of linewidths using either method presents no difficulty if the signal-to-noise ratio is sufficiently large, but for the present application the signal strengths were low, and noise became a serious limitation. Weak signals could not be avoided because of three factors which had to be properly minimized: concentration broadening, modulation distortion, and saturation broadening.

Low concentrations are required to prevent radical-radical line-broadening effects from masking out the intramolecular contributions. For the TCNE⁻ studies, the initial concentrations of potassium tetracyanoethylenide were $5 \times 10^{-4} M$ (see below). The radical decayed slowly but the linewidths did not change with time, indicating that radical-radical interactions did not contribute significantly to the linewidths at this low concentration.

The accurate measurement of both the amplitudes and widths requires that the modulation index h_m of the field modulation be small.^{12,13} The modulation index is given by $h_m = (2H_m / \Delta B)$, where $2H_m$ is the peak-to-peak amplitude of the field modulation and ΔB is the half-width of the line at half-maximum intensity. Values of $h_m \lesssim 0.1$ have to be used for both first- and

second-derivative spectra to avoid distortion. In the present work, we have used $h_m = 0.1$ and have experimentally verified that increasing h_m by a factor of 2 doubles the amplitude of the first-derivative signal but does not cause a detectable change in the linewidths. The use of such a low modulation index reduces the signal strength in both the first- and second-derivative spectra, but the latter is more affected than the former. For Lorentzian-shaped lines it is readily shown that the peak-to-peak deflections in the second-derivative spectra are less than those in the first-derivative spectra by the factor $h_m / 2.1$, and thus for $h_m = 0.1$, the second-derivative signal is only about 5% of the first-derivative signal. These results hold for small values of h_m and with the same value of h_m for both the first- and second-derivative spectra. The signal-to-noise level in a distortion-free second-derivative spectrum is thus quite poor, and consequently there is no significant improvement in the precision of width measurements on using second-derivative rather than first-derivative-recording when the signal strength is low.

Microwave power saturation can be particularly troublesome in a careful linewidth study. Even if the lines in a spectrum are all of the same shape, lines of different widths saturate at different rates.¹⁴⁻¹⁷ If the lines are superpositions of Lorentzian-shaped components of different widths it is not at all clear how saturation affects the amplitudes and widths.¹ The power level incident on the cavity was about 0.16 mW, and it was checked that no significant changes in widths occurred when the power was lowered by 5 dB. An increase in power by 15 dB, however, caused appreciable effects. At power levels below 0.16 mW, the signal-to-noise ratio was too low to obtain sufficiently high precision in the width measurements. The cavity Q was not measured, but was probably in the range from 1000 to 1500 (loaded Q , Q_{LE}).¹²

The first-derivative spectra were recorded in the usual way^{15,18} employing a modulation frequency of 1000 cps. The second-derivative spectra were obtained with the same 1000-cps narrow-band amplifier and reference signal for the phase sensitive detector, but a 500-cps voltage was used to power the field-modulation coils. This 500-cps signal was generated by passing the 1000-cps signal through a factor-of-2 frequency divider. Considerable care must be taken to eliminate 1000-cps components in the 500-cps modulation voltage or the second-derivative signal will be distorted by some first-derivative signal. The error from this source is readily estimated. The second derivative $f''(B)$ of a symmetric

¹⁴ J. W. H. Schreurs, G. E. Blomgren, and G. K. Fraenkel, *J. Chem. Phys.* **32**, 1861 (1960).

¹⁵ J. W. H. Schreurs and G. K. Fraenkel, *J. Chem. Phys.* **34**, 756 (1961).

¹⁶ M. J. Stephen and G. K. Fraenkel, *J. Chem. Phys.* **32**, 1435 (1960).

¹⁷ M. J. Stephen, *J. Chem. Phys.* **34**, 484 (1961).

¹⁸ J. M. Hirschon and G. K. Fraenkel, *Rev. Sci. Instr.* **26**, 34 (1955).

¹² G. K. Fraenkel in *Technique of Organic Chemistry*, edited by A. Weissberger (Interscience Publishers, Inc., New York, 1960) 3rd ed. *Physical Methods of Organic Chemistry*, Vol. 1 Part IV, Chap. XLII.

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

TABLE I. Hyperfine splittings in TCNE⁻.

Solvent	Hyperfine splittings (G)				Ratio $a_{\text{CN}}^{13\text{C}}/a^{14\text{N}}$
	$a^{14\text{N}}$	$a^{15\text{N}}$	$a_{\text{CN}}^{13\text{C}^a}$	$a_{\text{C-C}}^{13\text{C}^b}$	
Tetrahydrofuran ^c	1.56		9.4		6.0
<i>N,N</i> -Dimethylformamide ^d	1.574	2.203	9.541		6.062
Absolute ethanol ^e	1.607	2.25	9.466	2.92 ^b	5.890
Water ^e	1.586	2.22	9.34		5.89

^a Carbon-13 splitting from nitrile carbon atom.^b Carbon-13 splitting from ethylenic carbon atom tentatively identified by Rieger *et al.*¹⁰^c From Phillips *et al.*¹¹^d From Rieger *et al.*^{10,21}^e This work.

absorption line $f(B)$ has two maxima of equal amplitude and one minimum. One maximum is on the low-field side of the low-field zero, and the other is on the high-field side of the high-field zero. The presence of a first-derivative signal causes the amplitude of one of these maxima to increase and the other to decrease. Let us designate these amplitudes by a_1 and a_2 , and let α be the ratio of the field-modulation amplitude at frequency 2ν to the modulation amplitude at frequency ν . We define the degree of distortion d by the ratio of the difference in amplitudes divided by the mean amplitude, $d = 2(a_1 - a_2)/(a_1 + a_2)$. If the modulation index at frequency ν [h_m] and α are both small, the distortion of a Lorentzian line can be shown to be

$$d = 4\alpha/h_m. \quad (2.6)$$

Thus with $h_m = 0.1$, a field-modulation amplitude at the second harmonic (2ν) of as little as 0.25% of the modulation amplitude of the fundamental (ν) causes a 10% distortion. Although to first order small distortions do not change the separation of the zeroes of the second derivative, it nevertheless becomes very difficult to locate the zero near the low-amplitude peak if the signal-to-noise ratio is poor, and thus even small distortions can reduce the precision of the width measurements. We therefore employed a multisection filter to reduce the amplitude of the second harmonic to 0.1% of the amplitude of the fundamental.

The X-band superheterodyne spectrometer employed has been described elsewhere.^{15,18} A Varian Model V4012-3B magnet with 12-in.-diam. pole caps and a 3-in. air gap was used. It was equipped with a Varian Model V-3506 magnet flux stabilizer. Without the stabilizer, the field fluctuations were too large to permit accurate line-shape studies. Field scans from a fraction of a gauss to hundreds of gauss, and over a wide range of rates, were made possible by constructing a unit to provide a constant but adjustable voltage to the flux stabilizer at the same time that a saw-tooth voltage of appropriate magnitude was injected into the magnet power supply. The field scans obtained were extremely linear. The magnetic field was calibrated

by placing marks on the strip-chart recording using a controlled-frequency proton-resonance oscillator. The frequency of this oscillator was determined with an electronic counter. The spectrometer was checked for amplitude linearity over the range of signal strengths employed.

The TCNE⁻ samples decayed slowly in intensity and although the rate of decay was not great enough to cause difficulty for the usual ESR investigation, precautions had to be taken in the present study to proceed through the sequence of measurements as rapidly as possible. The speed of recording was adjusted to be slow enough so that no distortion was introduced by the response time of the instrument, and thus a compromise was made between slow response time (and therefore high sensitivity) and rapid recording. Spectra were recorded in both directions of the magnetic-field scan and the results averaged. The decay was small enough so that its effects on the amplitudes were cancelled out by this procedure. It was not necessary to correct the width measurements for radical decay. Systematic errors in the width measurements obtained from the first-derivative spectra were minimized by randomizing the order in which the individual lines were studied.

The potassium tetracyanoethylenide (K-TCNE) was obtained from R. E. Benson of E. I. DuPont de Nemours and Company. The solid radical is stable in the absence of oxygen.¹⁹ It was dissolved in a mixture 1:1 by volume of absolute ethanol and glycerine, and all samples were approximately $5 \times 10^{-4} M$ in K-TCNE. The viscosity of the solvent is 44 cP at room temperature.²⁰ In our work on solutions, traces of oxygen were found to cause both decomposition and broadening of the ESR lines. The sample was prepared as follows: The solution was placed in a reservoir that was connected to a 3-mm-o.d. Pyrex sample tube in the microwave cavity. Nitrogen saturated with solvent was

¹⁹ O. W. Webster, M. Mahler, and R. E. Benson, *J. Org. Chem.* **25**, 1470 (1960).²⁰ J. Timmermans, *The Physico-Chemical Constants of Binary Systems in Concentrated Solutions* (Interscience Publishers, Inc., New York, 1959), Vol. 2, p. 1114.

bubbled through the solution in the reservoir to remove oxygen, and then a portion of the solution was passed into the sample tube. Under these conditions the half-life of the radical was about 8 h. Degassing on a vacuum line was not practical here because of the high viscosity of the solvent.

The *p*-benzosemiquinone was generated by electrolytic reduction of a 0.001*M* solution of the quinone in dimethylsulfoxide at room temperature. The supporting electrolyte was tetra-*n*-propylammonium perchlorate. The techniques employed for electrolytic generation have been described elsewhere.¹⁰

III. RESULTS

Tetracyanoethylene

The spectrum of TCNE⁻ was first reported by Phillips *et al.*¹¹ in tetrahydrofuran and was later studied by Rieger *et al.*^{10,21} in *N,N*-dimethylformamide. We have also obtained the spectrum in absolute ethanol and in water. The hyperfine splittings are listed in Table I. The four nitrogen-14 nuclei give a splitting into a nine-line spectrum with statistical weights 1:4:10:16:19:16:10:4:1. We will identify the lines by the spectral index numbers \tilde{M}_N . The number \tilde{M}_N is identical to the quantum number M_N for the sum of the *z* components of the nuclear spin angular momenta

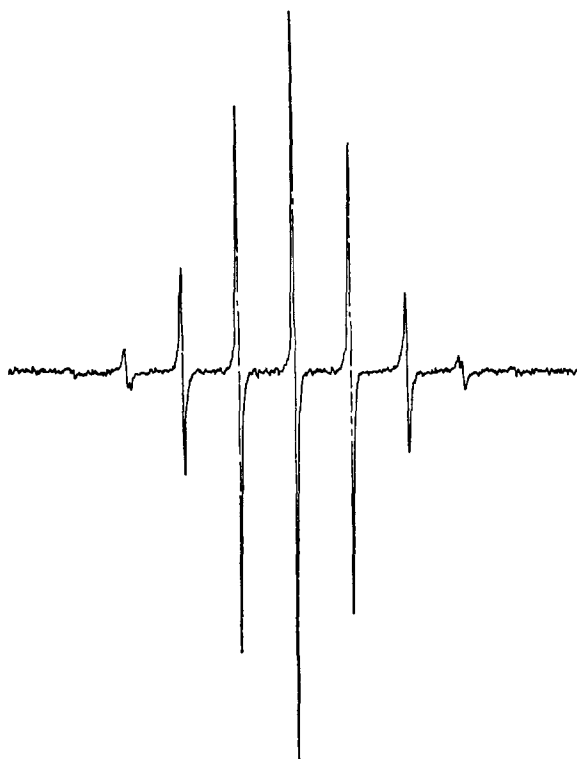


FIG. 1. First derivative of the ESR spectrum of the tetracyanoethylene radical in ethanol-glycerine. The magnetic field increases to the right.

²¹ P. H. Rieger, I. Bernal, and G. K. Fraenkel, *J. Am. Chem. Soc.* **83**, 3918 (1961).

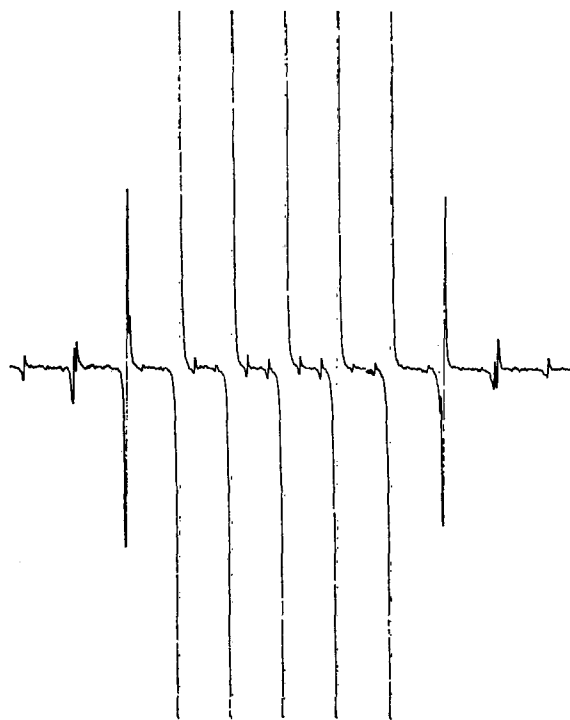


FIG. 2. First derivative of the ESR spectrum of the tetracyanoethylene radical in absolute ethanol. The magnetic field increases to the right.

of the four nitrogen-14 nuclei if the splitting constant a^N is negative, while $\tilde{M}_N = -M_N$ if a^N is positive.²² The possible values of M_N for TCNE⁻ are $\pm 4, \pm 3, \pm 2, \pm 1$, and 0. The spectrum in the ethanol-glycerine mixture is shown in Fig. 1, and in absolute ethanol in Fig. 2. The $M_N = \pm 4$ lines are too weak to be observed in Fig. 1, but they were detected on recordings made at higher sensitivity. The spectrum in Fig. 2 was obtained at high sensitivity in order to show some of the ¹³C splittings from the nitrile carbon atoms, and the central lines are off scale. These ¹³C splittings arise from the natural abundance of the carbon-13 isotope, and produce lines both in the central region and at the ends of the spectrum (see Table IX in the Appendix). They can also be seen on the $M_N = \pm 3$ lines in Fig. 1. The $M_N = \pm 3$ and ± 4 lines had to be excluded from the linewidth study because of the distortion caused by the ¹³C satellites. The effect of these satellites on the remaining lines, and also the linewidth contributions from second-order shifts,²³ were calculated to be much smaller than the experimental errors. These calculations are summarized in the Appendix. The linewidth²⁴ of the central line in Fig. 1 is about 0.040 G, and in Fig. 2 it is about 0.020 G. It will be noted from Table I that there are small but significant solvent effects on the

²² The sign of a^N is not determined by the positions of the lines in the spectrum, but it can be evaluated from the linewidth variations (see Ref. 28).

²³ R. W. Fessenden, *J. Chem. Phys.* **37**, 747 (1962).

²⁴ Linewidths are given as the separation of extrema in the first derivative of the spectrum.

TABLE II. Line-shape data for TCNE⁻.

Method of linewidth measurement	\tilde{M}_N^a	Relative amplitude A_{r_i}	Relative width δ_{r_i}	Line-shape factor $S_{r_i}^b$
First derivative	-2	0.1905 \pm 0.0013 ^c	1.895 \pm 0.020 ^c	1.140 \pm 0.012 ^d
	-1	0.6480 \pm 0.0065	1.210 \pm 0.008	1.062 \pm 0.0088
	0	1.000	1.000 \pm 0.011	1.000 \pm 0.0105
	1	0.5125 \pm 0.0042	1.376 \pm 0.013	1.073 \pm 0.0104
	2	0.1397 \pm 0.0025	2.213 \pm 0.024	1.140 \pm 0.016
Second derivative	-2	0.1980 ^c	1.7795 ^c	1.092
	-1	0.6557	1.1850	1.046
	0	1.000	1.0000	1.000
	1	0.5088	1.3386	1.041
	2	0.1392	2.1023	1.082

^a Spectral index numbers, see text.^b From Eq. (2.5).^c Errors are standard deviations based on four different sets of measurements. The error given for the width measurement of the central line reflects the error in the actual width for the four measurements.^d Errors computed from errors in A_{r_i} and δ_{r_i} .^e Errors estimated to be less than 1% for $\tilde{M}_N = \pm 1$ lines and less than 2% for $\tilde{M}_N = \pm 2$ lines.

splittings,²⁵ and that the ratio of the ¹³C splitting from the nitrile carbon atoms to the ¹⁴N splitting also changes with the solvent.

The results of the line-shape study are given in Table II. The amplitudes A_{r_i} and widths δ_{r_i} are relative values with respect to the central line. The shape factors are defined in Eqs. (2.1) and (2.5). The linewidth results obtained from the first- and second-derivative spectra are listed separately. Four independent measurements were made for the amplitudes and widths using the first-derivative spectra, but only two using the second-derivative spectra. The amplitude measurements were essentially independent of the small amount of radical decay, and the first-derivative width measurements were taken in a randomized order (see Sec. II). The width of the central line in the spectra used for the first-derivative measurements was 0.028 \pm 0.001 G, while in the spectra used for the second-derivative measurements it was 0.034 \pm 0.001 G. These differences in width resulted from uncontrolled factors in the sample preparation, and similar variations for other samples of TCNE⁻ have been found in studies we have made that are not reported on here. The major error in the absolute measurement of the widths resulted from errors in calibration of the magnetic field.

The data indicate that there are significant, though small, variations in the line-shape factor from line to line. There are also small differences in the line-shape factors calculated from the first- and second-derivative measurements of the width which arise from differences in the linewidths for the two sets of measurements (0.028 and 0.034 G, respectively, for the central line). The variations in the line-shape factor for the second-derivative results are somewhat less than those for the first-derivative data because the relative changes within a spectrum caused by linewidth variations of a particular

magnitude are smaller the larger the over-all width contribution common to all lines.

p-Benzosemiquinone

The spectrum of the *p*-benzosemiquinone anion was studied in dimethylsulfoxide solution because preliminary investigation indicated that the linewidth variations were small, and therefore to a first approximation the line-shape factors S_i should be constant. These measurements thus serve as a partial check on the experimental procedure.

The results using the second-derivative method of measuring the widths are given in Table III. Within experimental error, the measured values of the widths and amplitudes of the $\tilde{M}_N = -1$ and -2 lines were the same, respectively, as the values for the $\tilde{M}_N = 1$ and 2 lines, and the results are grouped together in the table. The line-shape factors are essentially constant within the experimental errors. This data therefore supports the procedure used for studying the line-shape variations of TCNE⁻ and confirms that the variations observed for TCNE⁻ are significant.

IV. DISCUSSION

The small but significant variations in the line-shape factor S_i found for the TCNE⁻ radical indicate the

TABLE III. Line-shape data for the *p*-benzosemiquinone ion.

M_H^a	Relative amplitude A_{r_i}	Relative width $\delta_{r_i}^b$	Line-shape factor $S_{r_i}^c$
± 2	0.1231 ^d	1.181 ^d	1.015
± 1	0.5905	1.068	1.005
0	1.0000	1.000	1.000

^a M_H is the sum of the z components of the nuclear spin angular momenta of the four equivalent protons.^b Linewidths were obtained from second-derivative spectra.^c From Eq. (2.5).^d See Note e, Table II.

²⁵ J. Gendell, J. H. Freed, and G. K. Fraenkel, J. Chem. Phys. 37, 2832 (1962).

inadequacy of the Kivelson theory of linewidths.⁵ It is expected that much larger effects would have been observed if it had been possible to study the $M_N = \pm 4$ lines.

The analysis of the width and shape variations in terms of the new linewidth theory¹ requires the specification of the relaxation matrix, and this in turn depends on the nature of the important relaxation and line-broadening mechanisms. It is assumed that the most important contributions are those from the effects of the intramolecular anisotropic dipolar interaction and of the \mathbf{g} tensor. Modulations of the isotropic hyperfine interaction and terms from the quadrupole interaction are thus neglected. There is no evidence to indicate an appreciable modulation of the isotropic interaction in TCNE⁻ or in other nitrile anion radicals; and although the magnitude of the quadrupole interaction is difficult to estimate, it is probably considerably smaller than the anisotropic dipolar contribution.²⁶

The most important contributions to the relaxation matrix are the secular and pseudosecular terms¹; the latter arise from nuclear-spin transitions alone. The nonsecular contributions, which are ones involving electron-spin transitions, can be neglected. They are smaller than the other contributions by the factor $(1 + \omega^2 \tau_R^2)^{-1}$, where $\omega/2\pi$ is (approximately) the frequency of the ESR experiment and τ_R is the correlation time for molecular tumbling. For typical radicals in low viscosity solvents, the nonsecular terms are only a few percent of the others, and because of the high viscosity of the ethanol-glycerine solvent (44 cP) used here, they undoubtedly make a negligible contribution. Both the secular and pseudosecular terms contribute to the diagonal elements of the relaxation matrix, but the latter also give off-diagonal elements. The off-diagonal elements arise because the dipolar interactions for the four nitrogen nuclei are not all identical, and in the terminology of Ref. 1 the nitrogen nuclei are equivalent but not completely equivalent. There are two completely equivalent sets, each made up of the two nuclei that are transformed into each other by a twofold rotation about the symmetry axis perpendicular to the molecular plane.

The dipolar interaction can be calculated from the geometry of the molecule and the spin-density distribution.

²⁶ H. Negita and P. J. Bray [J. Chem. Phys. **33**, 1876 (1960)] have determined the nitrogen-14 quadrupole-coupling constant for benzonitrile to be 3.89 Mc/sec, and this value is probably valid for an order-of-magnitude estimate of the quadrupole-coupling constant in TCNE⁻ since both molecules are planar, conjugated nitriles. The inclusion of a small unpaired electron density in the nitrogen $2p$ orbital (estimated²⁷ to be about 0.0745) would be expected to alter the asymmetry parameter by a small amount. Negita and Bray found it to be 10.7% for benzonitrile. The relative contributions of quadrupolar and dipolar terms is roughly proportional to the square of the ratio of the respective interaction energies, and using the quadrupole coupling constant for benzonitrile and the calculated spin density,²⁷ this is about 0.16.

TABLE IV. Linewidth contributions for TCNE⁻, coefficients of dipolar interaction.

M_N	D_M^a	J_N	D_J^b	$J_N(J_N+1) + (5/3)M_N^2$	$\langle J_N(J_N+1) + (5/3)M_N^2 \rangle_{M^c}$
± 4	1	4	1	140/3	46.667
± 3	4	4 3	1 3	35 27	29.000
± 2	10	4 3 2	1 3 6	80/3 56/3 38/3	15.867
± 1	16	4 3 2 1	1 3 6 6	65/3 41/3 23/3 11/3	8.167
0	19	4 3 2 1 0	1 3 6 6 3	20 12 6 2 0	5.474

^a D_M is the degeneracy with respect to M_N .

^b D_J is the degeneracy with respect to J_N .

^c $\langle J_N(J_N+1) \rangle_{M^c} = D_M^{-1} \sum D_J J_N(J_N+1)$, where $D_M = \sum D_J$ and the summations are over all values of J_N for the particular value of M_N .

bution. The spin densities are estimated to be²⁷: nitrogen atom, 0.0765; nitrile carbon atom, 0.0211; and ethylene carbon atom, 0.3056. Even though the spin density on the carbon atoms is appreciable, the main contribution to the dipolar interaction results from the spin density on the nitrogen nuclei.^{28,29} Because of this, there is only a small departure from complete equivalence between the two sets of completely equivalent nitrogen nuclei, and in the coupled representation for the zero-order Hamiltonian of the spin system,¹ the off-diagonal elements of the relaxation matrix are small. In the coupled representation, the elements of the relaxation matrix are determined by the two quantum numbers M_N and J_N . These quantum numbers refer to the sum of the angular momenta of the four nitrogen nuclei and specify the z component of the sum (eigenvalue M_N) and the square of the total angular momenta of the sum [eigenvalue $J_N(J_N+1)$]. We neglect the off-diagonal elements in order to avoid diagonalizing the relaxation matrix. Even writing down the matrix is a quite formidable task here since there is a matrix for each composite line and its order for a line of degeneracy D_M is D_M^2 [(19)² for the central line]. In effect we are assuming that the four nitrogen nuclei are completely equivalent, so that in the coupled representation the relaxation matrix is diagonal and the linewidths are determined by the diagonal elements of the matrix. For the reasons given above, the errors involved in

²⁷ P. H. Rieger and G. K. Fraenkel, J. Chem. Phys. **37**, 2795 (1962).

²⁸ J. H. Freed and G. K. Fraenkel, J. Chem. Phys. **40**, 1815 (1964).

²⁹ E. DeBoer and E. L. Mackor, J. Chem. Phys. **38**, 1450 (1963).

TABLE V. Computed linewidth and line-shape variations for TCNE⁻.

	\tilde{M}_N	First-derivative width measurements				Second-derivative width measurements	
		Exptl.	Calculated ^a			Exptl.	Calculated ^a
			Ia	Ib	II		II
Relative width $\delta_{r,i}$	-2	1.895	1.899	2.977	1.942	1.780	1.813
	-1	1.210	1.194	1.482	1.215	1.185	1.180
	0	1.000	1.000	1.000	1.000	1.000	1.000
	1	1.376	1.355	1.810	1.385	1.339	1.340
	2	2.213	2.220	3.580	2.265	2.102	2.119
Relative line-shape factor, ^b $S_{r,i}$	-2	1.140	1.000	1.247	1.100	1.092	1.082
	-1	1.062	1.000	1.114	1.037	1.046	1.029
	0	1.000	1.000	1.000	1.000	1.000	1.000
	1	1.073	1.000	1.151	1.055	1.041	1.043
	2	1.140	1.000	1.264	1.110	1.082	1.091

^a Column Ia is obtained by fitting the averaged linewidth expression [Eq. (4.5)] to the width data. Columns Ib and II are based on a superposition of Lorentzian-shaped components using Eq. (4.2) and setting the computed width of the central line equal to unity. In Column Ib, the parameters found in Column Ia were employed. In Columns II, the parameters were fitted (by trial and error) to the width data.

^b From Eq. (2.5).

this assumption are probably small, and they do not affect the general nature of our results.

The possible values of M_N and J_N are given in Table IV. The position of a line in the spectrum is determined by M_N , and except for the end lines of the spectrum ($M_N = \pm 4$), each line is degenerate with respect to M_N (degeneracy D_M) and also with respect to J_N (degeneracy D_J). For a particular line, the D_J transitions that all have the same value of J_N are called a component, and with the approximations we have made, the (diagonal) elements of the relaxation matrix determine the widths of these components. The component J_N contributes a D_J -fold degenerate absorption line of Lorentzian shape and of width $[T_2(M_N, J_N)]^{-1}$ to the total absorption of the D_M -fold degenerate line with quantum number M_N . This width is given by¹

$$[T_2(M_N, J_N)]^{-1} = j^{(D)} [J_N(J_N+1) + \frac{5}{3}M_N^2] + \frac{1}{3}j^{(DG_2)} B_0 M_N + X. \quad (4.1)$$

The spectral densities $j^{(D)}$ and $j^{(DG_2)}$ represent, respectively, the contributions of the intramolecular anisotropic dipolar interaction and of a cross term between this interaction and the \mathbf{g} tensor. The quantity X includes all effects that do not vary from line to line, and B_0 is the value of the external magnetic field. The coefficients of the pure dipolar term $j^{(D)}$ are given in Table IV, and since they vary appreciably from component to component within a given line, the component widths will be quite different from each other if $j^{(D)}$ makes a significant contribution to the linewidth. The coefficients of the cross term $j^{(DG_2)}$ do not depend on J_N so that the width contribution from this term is the same for all the components of a line. For analyzing the experimental data, it is convenient to rewrite Eq. (4.1) in terms of the relative widths of the components (relative to the $M_N=0, J_N=0$ component),

$$\delta_r(\tilde{M}_N, J_N) = 1 + B\tilde{M}_N + C[J_N(J_N+1) + \frac{5}{3}\tilde{M}_N^2], \quad (4.2)$$

where

$$BX = \pm \frac{1}{3}j^{(DG_2)}B_0, \quad (4.3a)$$

$$CX = j^{(D)}, \quad (4.3b)$$

\tilde{M}_N is a spectral index number (see Sec. III), and the upper (lower) sign in Eq. (4.3a) applies if the nitrogen hyperfine splitting a^N is negative (positive).

If $j^{(D)}$ is small compared to the other terms in Eq. (4.1), the width of the line with quantum number M_N can be approximated by an average over the different values of J_N , and the over-all shape is Lorentzian.¹ This limiting result of the relaxation-matrix theory thus coincides with the prediction of the Kivelson theory.⁵ The average values of $[J_N(J_N+1) + \frac{5}{3}\tilde{M}_N^2]$ are given in Table IV. The average width relative to the $M_N=0, J_N=0$ component is thus

$$\delta_r(\tilde{M}_N, \langle J_N \rangle_{av}) = 1 + C \langle J_N(J_N+1) \rangle_{M=0} + B\tilde{M}_N + C\eta(\tilde{M}_N),$$

where

$$\eta(\tilde{M}_N) = \langle J_N(J_N+1) + \frac{5}{3}\tilde{M}_N^2 \rangle_M - \langle J_N(J_N+1) \rangle_{M=0}. \quad (4.4)$$

It is more convenient, when averaging over the component widths of a line, to use the average width relative to the average width of the $M_N=0$ line,

$$\delta_r'(\tilde{M}_N, \langle J_N \rangle_{av}) = 1 + B'\tilde{M}_N + C'\eta(\tilde{M}_N), \quad (4.5)$$

where

$$\delta_r'_{av}/\delta_r'_{av} = B'/B = C'/C = [1 + \langle J_N(J_N+1) \rangle_{M=0}C]^{-1}. \quad (4.6)$$

From Table IV, since $\langle J_N(J_N+1) \rangle_{M=0} = 5.474$, we have $\eta(\pm 4) = 41.193$, $\eta(\pm 3) = 23.526$, $\eta(\pm 2) = 10.393$, $\eta(\pm 1) = 2.693$, and $\eta(0) = 0$. The coefficient of C' is thus approximately, but not exactly, a quadratic function of \tilde{M}_N .

Since the experimental line-shape factors for TCNE⁻ vary from line to line, the averaging procedure cannot be correct. It is convenient, however, to obtain a first approximation to the parameters B and C by using Eqs. (4.4) to (4.6), and it is also of interest to determine whether or not the width data can be fitted by Eq. (4.5). The results of a least-squares fit of the first-derivative data to this equation gives $B'=0.0802$ and $C'=0.102$. The widths calculated from these values and Eq. (4.5) are given in Column Ia of Table V, and they are in good agreement with the experimental results. The calculated shape factors, of course, are all unity and thus disagree with the experimental data. The quality of a fit of typical experimental measurements to an averaged line-shape expression like Eq. (4.5) can therefore not be used as a criterion of whether the lines are Lorentzian or a superposition of Lorentzians.

The determination of the widths and shape factors for the superposition of Lorentzian components requires the numerical computation of the shape functions. The procedure used to do this involved adding together point by point the first derivatives of Lorentzian-shaped components of the proper width and degeneracy by using an IBM-7090 computer.³⁰ Calculated amplitudes and widths were obtained by noting the value and position of the maximum of the computed shape function, and after converting to relative values (with respect to the central line), the relative line-shape factors, Eq. (2.5), were computed. Using $B'=0.0802$ and $C'=0.102$, and solving Eqs. (4.6) for B and C gives $B=0.181$ and $C=0.230$. The calculated widths and shape factors using these parameters in the superposition calculation are given in Column Ib of Table V, and both give a very poor representation of the data. The calculations show, however that for a particular set of linewidth parameters (e.g., B and C) the shapes and widths of a single Lorentzian line computed with an averaged value of the linewidth may be very different from the shapes and widths of a line which is a superposition of Lorentzians. The large deviation from Lorentzian shape found here results because the pure

TABLE VI. Computed linewidth and line-shape variations, p -benzosemiquinone ion.

	M_H	Experimental	Calculated ^a	
			Ia	Ib
Relative width δr_i	± 2	1.181	1.187	1.191
	± 1	1.068	1.047	1.049
	0	1.000	1.000	1.000
Relative line-shape factor, S_{r_i}	± 2	1.015	1.000	1.003
	± 1	1.005	1.000	1.001
	0	1.000	1.000	1.000

^a See Note a, Table V.

³⁰ We are indebted to S. Goodman of these laboratories for developing this program.

TABLE VII. Second-order shifts in TCNE⁻.

M_N	J_N	D_J	Shift, ^a $\Delta B(M_N, J_N)$ (mG)
± 4	4	1	-1.55
± 3	4	1	-4.27
	3	3	-1.16
± 2	4	1	-6.20
	3	3	-3.10
	2	6	-0.78
± 1	4	1	-7.36
	3	3	-4.26
	2	6	-1.94
	1	6	-0.39
0	4	1	-7.75
	3	3	-4.65
	2	6	-2.32
	1	6	-0.78
	0	3	0

^a Computed from Eq. (A.1) with $a^N=1.60$ G, $B_0=3300$ G.

dipolar interaction ($j^{(D)}$) makes an important contribution to the widths.

Since the estimate of B and C from the averaged linewidth expression was so unsatisfactory, a trial-and-error procedure had to be employed. Values of B and C were adjusted using the superposition calculation to give a fit to the width data. The results, shown in the two columns labeled II in Table V, are in quite good agreement with the data for both the linewidths and the shape factors. The parameters obtained were $B=0.095$ and $C=0.114$ for the first-derivative data and $B=0.090$ and $C=0.100$ for the second-derivative data. The shape factors S_0 for the central line were found to be 0.649 and 0.658, respectively, for the two sets of data as compared to 0.743 for a Lorentzian. In computing S , Lorentzians normalized to unity were employed for the component lines. No attempt was made to refine the trial-and-error calculation to give the best possible fit. If the line-shape factors had been used as the criterion of the fit, somewhat different parameters would have been obtained. The differences between the parameters B and C for the two sets of data arise because the spectra employed for the first-derivative measurements were narrower (0.028 G) than the spectra used for the second-derivative measurements (0.034 G). Thus X is smaller, and B and C larger, for the former spectra than for the latter, but since the superposition calculation is not linear in the component widths, the differences are not proportional to the ratios of the widths (X) in the two sets of spectra. As indicated by Eqs. (4.3), the data with the narrower lines (the first-derivative set) should have the larger parameters, in agreement with the values obtained. The relaxation-matrix linewidth theory thus gives an entirely satisfactory description of both the linewidth and line-shape factor variations.

TABLE VIII. Effects of second-order shifts and ^{13}C splittings, TCNE^- .

\tilde{M}_N	D_M	Second-order shift			Carbon-13 ^{a,b}	
		Experimental width $\Delta_i(\text{mG})^c$	Computed width $\delta_i(\text{mG})^d$	Relative line-shape factor, ^e S_{ri}	Computed width $\delta_i(\text{mG})^f$	Relative line-shape factor, ^e S_{ri}
-2	10	46.0	53.34	0.991	52.89	0.995
-1	16	29.4	34.38	0.997	33.94	1.002
0	19	24.3	28.60	1.000	28.00	1.000
1	16	33.4	38.95	0.995	38.55	1.001
2	10	53.7	62.20	0.991	61.54	0.991

^a For method of calculation see text.^b Using $a^N=1.60$ G, $a^C=9.40$ G.^c $\Delta_i=(\sqrt{3}/2)\delta_i$ where δ_i is the experimental derivative width.^d Derivative width computed in second-order shift calculation.^e From Eq. (2.5).^f Derivative width computed in ^{13}C calculation.

The parameters $B=0.095$ and $C=0.114$ which give a good fit to both the width and shape-factor data in the superposition calculation differ by about a factor of 2 from those obtained above from the fit to the widths alone using an averaged linewidth expression ($B=0.181$, $C=0.230$). Although the parameters resulting from the averaged width expression give agreement with the linewidth data, they are actually invalid because the predictions for the shape factor are incorrect. Thus erroneous linewidth parameters are obtained from a fit of the linewidth data alone with an averaged width expression when there are large variations in line shape. Analogous considerations apply to widths computed from amplitude measurements, which is a frequently employed procedure.²⁸

A similar calculation has been carried out for the *p*-benzosemiquinone ion. Now, however, since the linewidth variations are small and the relative line-shape factors are close to unity, it is anticipated that a single

Lorentzian with an average value of the width should be essentially equivalent to a superposition of Lorentzians. The linewidth expressions are identical to Eqs. (4.1) to (4.5), with M_H and J_H replacing M_N and J_N , except that now $\eta(M_H)=\frac{2}{3}M_H^2$ and $\langle J_H(J_H+1) \rangle_{M=0}=2$. The details of this calculation, including certain refinements that we shall not discuss here, are given elsewhere.²⁸ A least-squares fit to the averaged width expression [the modified form of Eq. (4.5)] gives $C'=0.0175$ from which, as above, we find $C=0.0181$. The results of the calculations are given in Table VI, where Column Ia is obtained from the modified form of Eq. (4.4) ($C'=0.0175$), and Column Ib from the superposition calculation ($C=0.0181$). As anticipated, the differences between the two calculations are considerably smaller than the experimental errors. The shape function for the central line was found to be 0.746 as compared to 0.743 for a Lorentzian. In these calculations, B' has been set equal to zero because no

TABLE IX. Carbon-13 satellites in TCNE^- .

Carbon-13 lines					
Nitrogen-14 lines		Nitrile carbon		Ethylene carbon	
Position ^a	Statistical weight ^b	Position ^a	Statistical weight ^b	Position ^a	Statistical weight ^b
		6.95	0.022		
		5.95	0.089		
		4.95	0.224	4.91	0.011
4.00	1	3.95	0.358	3.91	0.045
					0.011
3.00	4	2.95	0.425	3.09	0.112
				2.91	0.045
					0.179
2.00	10	1.95	0.358	2.09	0.112
				1.91	0.213
					0.179
1.00	16	1.05	0.022	1.09	0.179
		0.95	0.224	0.91	0.179
0.00	19	0.05	0.089	0.09	
		-0.05	0.089	-0.09	

^a The splittings are based on the data in absolute ethanol, $a^N=1.607$ G, $a^C=9.466$ G for the nitrile carbon atoms and $a^C=2.92$ G for the ethylenic carbon atoms. Positions are given in units of the nitrogen splitting.

^b The statistical weights of the lines are calculated by taking the natural abundance of ^{13}C to be 1.108% and neglecting molecules with more than one ^{13}C nucleus.

difference was found experimentally for positive and negative values of M_H .

V. CONCLUSIONS

The most important conclusion from the results obtained relates to the test they provide for the theoretical formulations. The Kivelson theory has been shown to be incorrect when there are large intramolecular anisotropic dipolar contributions to the linewidth, and the relaxation-matrix theory gives a completely satisfactory account of the data. It has been shown previously¹ that the Kivelson theory is also unsuitable when there are significant contributions from modulation of the isotropic hyperfine interaction. In general, it is thus necessary to treat degenerate lines as a superposition of Lorentzian components rather than as a single Lorentzian with an averaged width.

It should perhaps be emphasized again that some of the differences between the shape of a single Lorentzian and of a superposition of Lorentzians may be quite subtle. Thus a plot of a Lorentzian fitted to the amplitude and width of an experimental curve is indistinguishable from the latter in the experimentally accessible central region of the line, and the phenomenological expressions for the linewidth derived from the Kivelson theory may fit the width data just as well as those resulting from the relaxation-matrix theory. The parameters resulting from the different interpretations may have quite different values, however, and therefore it is important to use the relaxation-matrix theory if the details of the relaxation and line-broadening mechanisms are to be correctly evaluated. As pointed out above, it is only necessary to use a superposition of Lorentzians when certain contributions to the linewidth variations are large; in other situations the two theories agree. By analyzing the linewidth variations, it is always possible to determine by computation whether the superposition of Lorentzians gives the same results as a single Lorentzian with the appropriately averaged width. Now that the relaxation-matrix theory has been shown to represent the data satisfactorily, linewidth studies provide the needed information and it should not normally be necessary to make line-shape studies. Finally, when effects like the alternating linewidth phenomenon are important, the distinctions between the two theories are no longer subtle: the Kivelson theory does not account for the phenomenon at all.

We also note that the positive value of the coefficient B in the linewidth expression can be interpreted to show that the isotropic nitrogen hyperfine splitting a^N in TCNE⁻ is positive ($\tilde{M}_N = -M_N$). The method of analysis used to obtain this result has been described elsewhere.^{28,29}

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APPENDIX

In this appendix we show that the second-order shifts in the line positions, and the overlapping of unresolved ¹³C splittings with the main lines, do not cause significant effects in the analysis of the widths and shapes of the lines studied.

Straightforward calculation to second order in perturbation theory gives a correction to the expression for the line positions in the high-field approximation which can be written^{23,31}

$$\Delta B(M_N, J_N) = -[(a^N)^2/2B_0][J_N(J_N+1) - M_N^2], \quad (\text{A1})$$

where B_0 is the external magnetic field. The values of the second-order shift for TCNE⁻ are given in Table VII for $a^N = 1.60$ G and $B_0 = 3300$ G. To obtain an approximate idea of the effect of the second-order shifts on the line shape, Lorentzian components of the same width for each line but at the positions and with the degeneracies given in the table were added together and the resulting amplitudes, widths, and shape factors of the computed curves determined, as in Sec. IV. The widths used for each line were the experimentally determined values. Differences in the widths of the different components of a line were thus neglected. The results are shown in Table VIII, and it is clear that the variations are smaller than the experimental errors.

The effect of ¹³C lines was determined in a similar way. Each ¹³C satellite of a main line was given the same width as the main line, and again the widths were taken to be the experimentally determined ones and differences in the widths of the different components were neglected. The positions and intensities of the ¹³C satellites are shown in Table IX. The results in Tables VIII and IX are calculated for $a^N = 1.60$ G and $a^C = 9.40$ G. The contribution of the ¹³C satellites from the ethylenic carbon atoms and of the ¹⁵N satellites were not included. Again it is apparent that the effects are within the experimental error for the lines included in the analysis of the TCNE data. Calculations were also performed with other values of a^C within the range of the experimental data, and although the results were somewhat different, a negligible effect of the satellite was again found.

³¹ B. Bleaney, *Phil. Mag.* **42**, 441 (1951).