

ESR Relaxation Studies on Orbitally Degenerate Free Radicals. I. Benzene Anion and Tropenyl*

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Careful continuous saturation measurements, which include corrections for nonuniform microwave and modulating fields, have been used to examine, at different temperatures, the ESR linewidths and saturation behavior of the benzene anion in a tetrahydrofuran: dimethoxyethane solvent and the tropenyl radical in molten bitropenyl. It has been found that the ratios of the longitudinal to transverse electron-spin relaxation times (T_1/T_2) for these free radicals in solution are about 1.1 ± 0.1 for the benzene anion below -60°C and for tropenyl at 165°C . Analysis of the results has shown that at 9.1 GHz, g -tensor, anisotropic dipolar, and spin-rotational relaxation mechanisms do not contribute appreciably to the observed times. The anomalously small relaxation times associated with these radicals have been attributed to effects involving the degenerate ground states of these radicals. The spin-relaxation behavior of peroxyamine disulfonate anion in aqueous solution has also been studied.

I. INTRODUCTION

Townsend and Weissman¹ were the first to note the unusually broad ESR linewidths exhibited by hydrocarbon aromatic free radicals which are predicted to have degenerate ground states because of their high symmetry (e.g., benzene anion). Since then, there has been considerable interest in trying to explain this observation.²⁻⁸ Meanwhile, improved techniques for radical generation have resulted in significant decreases in the observed ESR linewidths in many solution spectra largely due to the removal of chemical and Heisenberg spin-exchange effects. Nevertheless, more recent results^{9,10} have confirmed the original observa-

tion that the ESR spectra from highly symmetrical hydrocarbon radicals are indeed significantly broader than those from less symmetrical hydrocarbon radicals.

Another observation of Townsend and Weissman¹ is that the highly symmetrical hydrocarbon radicals are much more difficult to saturate than comparable radicals of lower symmetry. This qualitative observation has now been made in a variety of cases.^{9a,9f,9h,11} Part of the increased difficulty in saturating these lines is clearly due to the increased width (i.e., decreased T_2), but it appears that the longitudinal relaxation time T_1 is also significantly decreased. It would, of course, be valuable to have some quantitative idea of the magnitude of T_1 compared to T_2 in order to determine whether the same anomalous mechanism(s) is effectively contributing to both T_1 and T_2 and whether the relative magnitude of the contributions to T_1 and T_2 could be used to discriminate between various possible mechanisms. We thus undertook to make accurate T_1 measurements for some highly symmetric free radicals.

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¹ M. G. Townsend and S. I. Weissman, *J. Chem. Phys.* **32**, 309 (1960).

² H. M. McConnell and A. D. McLachlan, *J. Chem. Phys.* **34**, 1 (1961). We note that the T_1 mechanism suggested by them is, in fact, an unacceptable one for steady-state saturation behavior; see Ref. 3 (and other referred to therein) for a discussion of the role of nuclear-spin-dependent transition probabilities on saturation behavior.

³ J. H. Freed, *J. Chem. Phys.* **43**, 1427 (1965).

⁴ H. M. McConnell, *J. Chem. Phys.* **34**, 13 (1961).

⁵ A. D. McLachlan and L. C. Snyder, *J. Chem. Phys.* **36**, 1159 (1962).

⁶ D. Kivelson, *J. Chem. Phys.* **45**, 751 (1966).

⁷ (a) J. H. Freed, *J. Chem. Phys.* **49**, 376 (1968). (b) J. H. Freed (unpublished).

⁸ J. H. Freed and R. G. Kooser, *J. Chem. Phys.* **49**, 4715 (1968).

⁹ (a) J. R. Bolton and A. Carrington, *Mol. Phys.* **4**, 271 (1961). (b) R. W. Fessenden and S. Ogawa, *J. Am. Chem. Soc.* **86**, 3591 (1964); (c) R. G. Lawler, J. R. Bolton, G. K. Fraenkel, and T. H. Brown, *ibid.* **86**, 520 (1964). (d) J. R. Bolton, *Mol. Phys.* **6**, 219 (1963). (e) G. Vincow, M. L. Morrell, W. V. Volland, H. J. Dauben, Jr., and F. R. Hunter, *J. Am. Chem. Soc.* **87**, 3527 (1965). (f) M. K. Carter and G. Vincow, *J. Chem. Phys.* **47**, 302 (1967); (g) B. G. Segal, M. Kaplan, and G. K. Fraenkel, *ibid.* **43**, 4191 (1965); (h) M. T. Jones, *ibid.* **42**, 4054 (1965).

¹⁰ (a) J. R. Bolton and G. K. Fraenkel, *J. Chem. Phys.* **40**, 3307 (1964); (b) R. G. Lawler, J. R. Bolton, M. Kaplan, and G. K. Fraenkel, *ibid.* **47**, 2149 (1967); (c) H. W. Brown and R. C. Jones, *ibid.* **36**, 2809 (1962); (d) J. S. Hyde and H. W. Brown, *ibid.* **37**, 368 (1962).

Our initial motivation was indeed based on our belief that such a measurement could distinguish between a spin-orbit pulse mechanism proposed by McConnell⁴ and an Orbach-type process proposed by Kivelson.⁶ While the former was expected to be mainly a line-broadening process,⁴ so that $T_1 > T_2$, the latter was expected to be a nonsecular or "spin-flip-only" process.⁶ Based on the well-known relation for a two-level system,

$$T_2^{-1} = T_2'^{-1} + (2T_1)^{-1}, \quad (1.1)$$

where $T_2'^{-1}$ represents the secular width contributions which are zero in the latter process, we have $T_1 = \frac{1}{2}T_2$ in this case. The applicability of Eq. (1.1) to our multilevel spin systems arising from hyperfine splittings requires only that there not be any important nuclear-

¹¹ (a) H. L. Strauss, T. J. Katz, and G. K. Fraenkel, *J. Am. Chem. Soc.* **85**, 2360 (1963). (b) M. K. Carter and G. Vincow, *J. Chem. Phys.* **47**, 292 (1967).

spin-dependent relaxation processes operative.¹²⁻¹⁴ The absence of any significant variation in widths amongst the hyperfine components for such radicals, as discussed in Secs. IV and V, strongly suggested that this condition should be fulfilled.

Relatively few accurate T_1 or saturation studies at microwave frequencies have been reported for dilute liquid solutions of free radicals.^{9h,10d,15,16} Important experimental considerations were discussed by Schreurs, Blomgren, and Fraenkel,¹⁵ Schreurs and Fraenkel,¹⁶ and Hyde and Brown.^{10d} In our own work, in which it was important to obtain accurate estimates of the ratio T_1/T_2 , we found that a careful re-examination of the experimental factors influencing the progressive saturation method became essential. These are discussed in Sec. II.

Jones has performed an interesting saturation study of the symmetric hexakstrifluoromethyl-benzene anion over a wide range of temperatures.^{9h} This radical is expected to have a degenerate ground state. His measurements showed that T_1 and T_2 were comparable ($T_1/T_2 \cong 1.5$ from -84° – 22°C) with $T_2 = 1.8 \times 10^{-7}$ sec at room temperature. There are two difficulties, however, with utilizing these results: (1) There is the important question of the effects of the presence of fluorine nuclei on the spin relaxation, and (2) a number of important experimental factors discussed in Sec. II were not considered.

In the process of carrying out our saturation studies we also found it advisable to re-examine more carefully the linewidths and line shapes of the unsaturated spectra. Furthermore, it was deemed useful to undertake linewidth studies at 35 GHz to compare with our 9.1-GHz results in order to estimate field-frequency-dependent relaxation effects. These results are also discussed.

We have already given a preliminary account of the results reported in this paper.⁸ In that account, new theoretical results on a variety of spin-relaxation processes, which could be important for free radicals with degenerate ground states, were also presented. It is our purpose in the present paper to give a description of the experimental aspects of the work, while a detailed theoretical treatment will be presented elsewhere.^{7b} Nevertheless, we do discuss in this work (Sec. V) the relevance of our experimental results in distinguishing between various possible relaxation mechanisms. It should be noted in this connection that our main experimental conclusion, that $T_1/T_2 \cong 1.0$ for the hydrocarbon radicals with degenerate ground states, which conflicts with the theoretical proposals of both

McConnell and Kivelson, served as the motivation for our theoretical re-assessment of the relaxation mechanisms.

II. EXPERIMENTAL CONSIDERATIONS FOR SATURATION MEASUREMENTS

The basis of the progressive saturation technique is that for Lorentzian lines one has¹⁵

$$\delta^2 = (4/3\gamma^2)(1/T_2)^2 + (\frac{4}{3})B_1^2(T_1/T_2), \quad (2.1)$$

where δ is the derivative peak-to-peak width, γ is the gyromagnetic ratio of the electron, and B_1 is the circularly polarized magnetic induction at the sample. Thus a linear plot of the experimentally measured δ^2 as a function of B_1^2 yields T_1/T_2 from the slope and T_2 from the intercept. Clearly, the accuracy of the T_1/T_2 determination depends upon an accurate estimate of B_1^2 at the sample. Also it is desirable to have B_1 uniform over that portion of the sample which contributes to the observed signal, or else one must, in general, average over the effects of a nonuniform field distribution.^{15,16} In the work of Hyde and Brown^{10d} and Jones^{9h} no corrections were made for effects of nonuniformity. Schreurs and Fraenkel,¹⁶ however, utilized a special type of sample placement in a TE 102-mode rectangular cavity such that the capillary tube was inserted through small holes in the center of the *broad* face of the cavity. This is expected to yield a nearly constant value of B_1 over the sample length. Since we were concerned with working well below and above room temperatures, initial attempts were made to construct a cavity with wide enough stacks and holes through the broad face to hold a standard variable-temperature Dewar. It was found that this greatly reduced the cavity Q , and the placement of some of our more lossy samples into the Dewar could even destroy the cavity resonance. As a result, in our experiments we chose to utilize a Varian V-4531 multipurpose rectangular cavity with standard sample placement, and to correct for the variation of B_1 across the sample. In this cavity, there is also a nonuniform magnetic-field modulation amplitude B_m across the sample, but its region of maximum strength coincides with that for B_1 . Thus, as long as $\gamma B_m T_2 < 1$ and $\gamma^2 B_1^2 T_1 T_2 \lesssim 1$ only a small central portion of the sample should be making a dominant contribution.

In view of the complications of two nonuniform fields as well as distortions of the microwave modal pattern as discussed below, an experimental correction factor was obtained as follows. The dependence of δ^2 as a function of $\gamma^2 B_1^2 T_1 T_2$ was determined at room temperature in the cavity plus Dewar for a cylindrical or "line" sample of peroxyamine disulfonate as well as a "point" sample (i.e., 3 mm long) of the same material. Every attempt was made to keep the two sets of measurements as nearly identical as possible. Thus both samples were in 1-mm capillary tubes that were

¹² J. H. Freed and G. K. Fraenkel, J. Chem. Phys. **39**, 326 (1963).

¹³ J. H. Freed, J. Chem. Phys. **43**, 2312 (1965).

¹⁴ J. H. Freed, J. Phys. Chem. **71**, 38 (1966).

¹⁵ J. W. H. Schreurs, G. E. Blomgren, and G. K. Fraenkel, J. Chem. Phys. **32**, 1861 (1960).

¹⁶ J. W. H. Schreurs and G. K. Fraenkel, J. Chem. Phys. **34**, 756 (1961).

alternately inserted into a 3-mm-o.d. Pyrex tube to simulate the experimental conditions of the saturation experiments. With capillary tubes $\lesssim 1.0$ mm. o.d. there is not a significant difference in cavity Q between the two types of sample, (about 5% as measured by the methods discussed below), and in fact the Q obtained is quite high (see below). The results are shown in Fig. 1. The scale of the abscissa was adjusted to give a slope of $\frac{4}{3}$ for the point sample and was checked by noting the microwave power required to maximize the derivative amplitude for that sample ($\gamma^2 B_1^2 T_1 T_2 = 0.5$). It is found from Fig. 1 that for fields low enough such that $\gamma^2 B_1^2 T_1 T_2 \leq 1$ the variation of δ^2 with B_1^2 for the "line" sample is very nearly linear but with a slope reduced to 76% of that of the "point" sample. It is thus quite reasonable to introduce a B_1^2 averaged over the "active portion" of the sample: $\langle B_1^2 \rangle = (0.76 \pm 0.09) B_{LM}^2$ into Eq. (2.1). Here B_{LM}^2 is the maximum value of the magnetic induction which is obtained for the center of the cavity as described below. The use of this correction factor necessitated working at microwave powers low enough that $\gamma^2 B_{LM}^2 T_1 T_2 \leq 1$, and should be applicable as long as the microwave field pattern in the cavity is not appreciably altered from that under which the correction factor was measured.

Now B_1^2 may be related to measurable microwave parameters by¹⁷

$$B_1^2 = (\mu Q_0 / 4\pi\nu_0) H_0^2 P_{\text{inc}} (1 - |\Gamma_0|^2) \text{ Wb}^2 / \text{M} \cdot \text{A}. \quad (2.2)$$

In Eq. (2.2), Q_0 is the unloaded cavity Q with the Dewar and sample in place but away from magnetic resonance; ν_0 is the cavity resonance frequency; P_{inc} is the microwave power incident on the cavity; Γ_0 is the power reflection coefficient for the cavity at resonance;

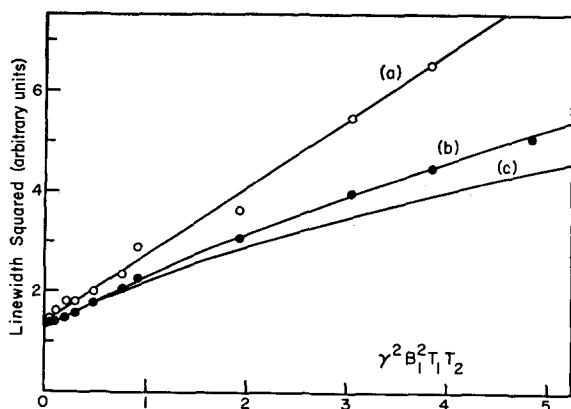


FIG. 1. Saturation behavior of a line versus point sample for type-B filling of a Varian V-4531 rectangular cavity. (a) Point sample; (b) line sample; and (c) line sample, theoretical curve for a uniform modulating field but sinusoidally varying microwave field (cf. Ref. 15). Linewidth squared in units of $(\gamma T_2)^{-2}$.

¹⁷ (a) E. L. Ginzton, *Microwave Measurements* (McGraw-Hill Book Co., New York, 1957). (b) J. H. Freed, D. S. Leniart, and J. S. Hyde, *J. Chem. Phys.* **47**, 2762 (1967).

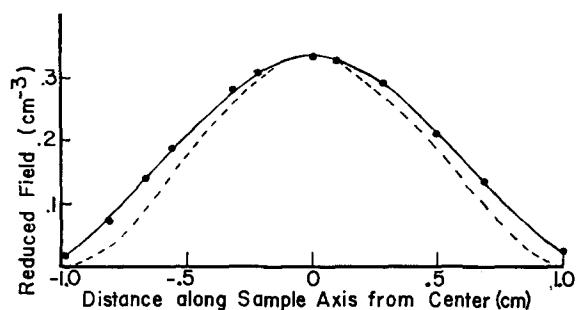


FIG. 2. Variation of the reduced microwave field strength (as determined by the method of perturbing spheres) along the ESR sample axis. Solid line—experimental. Dotted line—distribution for $\sin(\pi x/a)$, where a is the broadside cavity dimension. The theoretical distribution is fitted to the experimentally measured maximum value.

and H_0^2 is the reduced magnetic field strength given by¹⁷

$$H_0^2 = \mu H^2 / 2U, \quad (2.3)$$

where H is the magnitude of the linearly polarized magnetic field and U is the average stored energy in the cavity. It is essentially a geometric factor associated with the microwave field distribution in the cavity. The method of perturbing spheres was used to measure H_0^2 according to¹⁷

$$H_0^2 = [(\nu^2 - \nu_0^2) / \nu_0^2] (1 / 2\pi a^3), \quad (2.4)$$

where ν is the cavity resonance when perturbed by a small metallic sphere of radius a . (Hyde and Brown were the only earlier workers who employed this method in place of using the theoretical value for an empty cavity.) A small steel ball of 1.6 mm diam was located inside the sample tube (3 mm o.d. Pyrex) and the microwave field pattern along the tube was then mapped out yielding the results shown in Fig. 2. It was found that the microwave field inside the Dewar and sample tube varies less along the sample length than expected from the theoretical $\sin(\pi x/a)$ result (here a is the broad-face width of the cavity). In fact it was nonzero at the walls. This is mainly due to the existence of large sample holes at the ends. (The cavity resonance and frequency shifts were measured with a Hewlett-Packard 540B transfer oscillator in conjunction with a 524D counter with appropriate plug-in unit.) This method of perturbing spheres agreed within 10% with the calculated theoretical value for the maximum field ($H_0^2 = 0.188 \text{ cm}^{-3}$) in the empty cavity, but it was considerably higher ($H_0^2 = 0.342 \pm 0.017 \text{ cm}^{-3}$) for Pyrex sample tubes in the benzene anion work ($H_0^2 = 0.308 \pm 0.012 \text{ cm}^{-3}$ for quartz tubes in the trophenyl studies) for the field inside the Dewar and sample tube. This result was expected because of the field compression due to the dielectric material present.

For a perfectly matched cavity, $\Gamma_0 = 0$, and Eq. (2.2) simplifies accordingly. However, it was found that at

the reduced temperatures utilized to study the benzene anion it was not conveniently possible to match the cavity. Thus the following procedure was adopted. The cavity with the Dewar and sample in place was matched as well as possible with the tuning iris; then the parameter $Q_0(1 - |\Gamma_0|^2)$ was determined utilizing the expression¹⁸

$$Q_0 = \left(\frac{|\Gamma|^2 - |\Gamma_0|^2}{|\Gamma_1|^2 - |\Gamma|^2} \right) \frac{\nu_0}{\Delta\nu} \left(\frac{2}{2 \pm |\Gamma_0| - |\Gamma_1|} \right), \quad (2.5)$$

where the upper sign in the denominator is for undercoupling, the lower for overcoupling. In Eq. (2.5) $\Delta\nu$ is the cavity bandwidth usually taken as the full-width at half-power; then Γ , the power reflection coefficient at the half-power point, becomes $\Gamma^2 = 0.5$; Γ_1 is the power reflection coefficient of the cavity away from resonance and was found to be slightly below unity (about 0.9), due to finite cavity losses. The reflection coefficients were determined by first monitoring with a directional coupler the power reflected from the cavity. Then the incident power level was measured by utilizing a shorting plate just in front of the cavity. The cavity bandwidth was measured with the transfer oscillator, etc. The room-temperature value of Q_0 (here $\Gamma_0 = 0$) was checked by utilizing several variations on the basic technique and these yielded values in agreement to within 6% of these obtained by the original technique, although the over-all accuracy of the Q measurements is about $\pm 15\%$. Further details are given elsewhere.¹⁹ A value of $Q_0 = 6400$ ($\Gamma_0 = 0$) was obtained for the peroxyamine disulfonate samples described below. The benzene anion samples showed a *significant decrease* in Q_0 as the temperature was decreased. Thus at 20°C, $Q_0 = 5300$ ($\Gamma_0 = 0$), while in the range -88° to -120° C, $Q_0(1 - |\Gamma_0|^2) = 2500$ with no significant variation over this range. For the bitropenyl-tropenyl solutions, $Q_0 = 7600$ ($\Gamma_0 = 0$) at 165°C and showed no temperature variation. (The incident powers were measured with a Hewlett-Packard 431D power meter and X486A thermistor mount calibrated to have an accuracy of better than 1%.)

Care was taken that the field modulation amplitude at 100 kHz was small enough to avoid line-shape distortions by keeping $\gamma B_m \leq 0.1\delta$. It is still, in general, possible to distort the line shapes as a result of the finite modulation frequencies ω_M . This can lead to errors in both T_1 and T_2 . An analysis of such effects is given in the Appendix, and corrections to T_2 and T_1/T_2 appropriate for $T_1 \approx T_2 = T$ and for small values of $\epsilon \equiv \omega_M T$ are discussed. In the benzene work such corrections were found to be negligible, while for tropenyl and peroxyamine-disulfonate they were never more than 10%.

¹⁸ M. Sucher and J. Fox, *Handbook of Microwave Measurements* (Brooklyn Polytechnic Institute, New York, 1963), Vol. 2.

¹⁹ R. G. Kooser, Ph.D. thesis, Cornell University, Ithaca, N.Y., 1968.

III. EXPERIMENTAL PROCEDURES

A. ESR Spectrometer

The spin resonance experiments were conducted on a Varian V-4502-14 spectrometer system with a 12-in. magnet, and 100-kHz field modulation. (Some final experiments were, however, performed with 15-kHz modulation.) Control of the dc field was achieved with a Varian "Fieldial" utilizing either a Hall-effect probe or a Varian field/frequency lock unit which couples the dc field to the microwave frequency. The latter offers advantages of greater stability when doing low-temperature work since it cancels effects of thermal resonance drifts of the cavity.

A redesigned X-band bridge was used.¹⁹ It includes a four-port circulator as well as a second precision attenuator in the detection arm in order to maintain crystal sensitivity as the microwave power is varied.¹⁶ When it was possible to match the cavity, the detection crystal bias was obtained from a reference arm in the bridge. The temperature was controlled by a Varian variable-temperature unit to within $\pm 1^\circ$ C. The absolute temperature was checked at the geometric center of the cavity with a thermocouple and was found to be accurate to $\pm 2^\circ$ C.

In order to minimize the effects of Zeeman field inhomogeneity, the magnet was shimmed and the field variation was found to be about 5–10 mG over the active sample length (approximately 1 cm) for fields of about 3300 G. Further indications of the magnet homogeneity are shown by the detection of 18-mG linewidths in tetracyanoethylene⁻ in dimethoxyethane solution.

The 35-GHz spectra were obtained with the Varian V-4561 35-GHz bridge, cylindrical cavity, and pole tips. Low temperatures were achieved by immersing the cavity into the Varian 35-GHz liquid-nitrogen Dewar and introducing a controlled flow of chilled nitrogen gas into the Dewar. The temperature was monitored with a thermocouple attached to the cavity body and was stable to $\pm 2^\circ$ C, but was probably accurate to $\pm 5^\circ$ C.

The magnetic field variation at 12 KG with the pole tips in place was found to be about 40 mG at $\frac{1}{4}$ in. from field maximum.²⁰ If we estimate the active sample length at 35 Gc/sec to be about $\frac{1}{2}$ cm, then a 10-mG variation along this length would be expected. Care was always taken to locate the sample and cavity in the magnet gap so as to minimize the observed width.

B. Width and Saturation Measurements at X Band

Absolute linewidth measurements were performed by slowly sweeping through a derivative signal at low-modulation amplitudes as described above. Relative linewidths of the hyperfine components within a single

²⁰ We wish to thank Mr. James Henthorne of Varian Associates for performing the field mapping at 12 kG.

spectrum were studied by comparing the relative peak-to-peak amplitudes of the derivative signal.²¹

In order to insure reproducible and meaningful saturation runs, the power setting which maximized the derivative signal intensity was first determined and a range of powers below that value was used. Furthermore, the order of the power settings that was used was randomized. Reproducibility of the power settings was improved by consistently approaching the attenuator dial setting from the same direction. Usually four sweeps through a line were taken at a given power level and 10 different power settings were used for each saturation run. The sweeps were calibrated with either a Harvey-Wells gaussmeter or by comparison with the known splitting constants of the anthracene anion.^{10a} The resultant data were fitted by least squares to Eq. (2.1). The least-squares fits are reported in Sec. IV and include the sample standard deviation, which just reflects the precision.

C. Width Measurements at 35 GHz

The 35-GHz linewidths required correction for asymmetric lineshapes. These asymmetries are believed to arise from a finite electric field strength at the sample, coupled with a finite conductivity of the sample. This results in a phase variation of the electric and magnetic fields across the sample, so that the true resonant absorption becomes proportional to a mixture of the real and imaginary components of the magnetic susceptibility χ' and χ'' , respectively. Such effects could, in principle, be eliminated by using sample sizes smaller than was practical. These effects are similar to the Dysonian²² line-shape effect in metals, but because the free radical ions diffuse very slowly in liquid solution, the earlier theory of Bloembergen²³ neglecting diffusion is appropriate. From Bloembergen's results on a variety of ideal sample shapes, it is clear that the general case, in the absence of saturation,

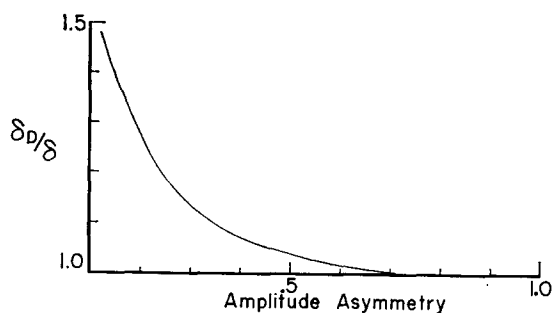


FIG. 3. Correction to the linewidth of the derivative of the absorption for asymmetries induced by microwave electric field gradients over the sample. Here δ_D/δ is the ratio of distorted to correct width. The amplitude asymmetry is defined in the text.

²¹ J. H. Freed and G. K. Fraenkel, *J. Chem. Phys.* **40**, 1815 (1964).

²² F. J. Dyson, *Phys. Rev.* **98**, 349 (1955).

²³ N. Bloembergen, *J. Appl. Phys.* **23**, 1383 (1952).

should be a simple superposition of χ' and χ'' , the relative weightings of which depend on the detailed geometry. In Fig. 3 the results of computer simulations for different weightings of χ' and χ'' are given in a manner to permit correcting the measured linewidth for the asymmetry. The distorted relative linewidth is the measured peak-to-peak derivative width relative to the true derivative width. The amplitude asymmetry A is given by the ratio of the amplitude of the smaller to larger peak, where each is measured from the base line. The linewidth corrections are seen to be negligible for $A > 0.7$. Corrections were generally less than 10%, except for a 14% correction for the naphthalene anion, room-temperature sample.

D. Sample Preparation

The benzene negative ion was made by reducing benzene with Na:K alloy in a degassed solvent mixture consisting of 2:1 by volume of tetrahydrofuran to dimethoxyethane. The reaction was carried out at dry-ice temperatures utilizing procedures similar to those which have been previously outlined.^{10a} The solvents were purified by the methods described by Bolton and Fraenkel,^{10a} and the Na:K alloy was prepared by melting together weighed amounts of the two metals under heptane. Spin concentration measurements on samples 1M and 0.01M in initial C_6H_6 concentration showed that the $C_6H_6^-$ concentrations at equilibrium ranged from about $6-20 \times 10^{-5} M$ and $1-9 \times 10^{-6} M$, respectively, over the temperature range -20° to $-83^\circ C$.²⁴

The tropenyl radical was prepared by means of homolytic thermal cleavage of degassed samples of bitropenyl.^{9e} Solutions of peroxyamine disulfonate dianion (PADS) were prepared by dissolving potassium peroxyamine disulfonate in a 0.05M aqueous solution of K_2CO_3 . Oxygen was removed by bubbling nitrogen through the solution for at least 1 h prior to ESR examination. Naphthalene anion and tetracene cation (in H_2SO_4) were prepared by conventional methods.^{10b,10d}

IV. RESULTS

A. Line Shapes

Since the progressive saturation techniques employed in this study depend crucially on having Lorentzian line shapes, a detailed study of line shapes was carried out. It was found that the radical spectra exhibited nearly Lorentzian character, but tended to decrease somewhat more rapidly in the wings. The experimental

²⁴ These spin-concentration measurements were made by comparison with standard pitch samples (which had been recalibrated). A Varian V4532 dual-sample cavity was used following standard operating techniques, and the first derivative signal was electronically integrated, cf. M.P. Eastman, R. G. Kooser, M. R. Das, and J. H. Freed, *J. Chem. Phys.* (to be published).

TABLE I. Comparison of the line shape of several radicals with a Lorentzian line shape.

Fraction of derivative half-amplitude	Distance from resonance center in units of derivative half-width ^a					
	Lorentzian	C ₆ H ₆ ^{-b} ; -60°	C ₆ H ₆ ^{-b} ; -80°	C ₆ H ₆ ^{-b} ; -100°	Tropenyl; +150°C ^c	PADS ^d —R.T.
0.8	1.65	1.63±0.09 (1.67)	1.59±0.08 (1.67)	1.67±0.10 (1.67)	1.61±0.09 (1.71)	1.64 (1.66)
0.7	1.90	1.83±0.10 (1.89)	1.81±0.10 (1.89)	1.89±0.15 (1.89)	...	
0.6	2.10	2.03±0.10 (2.13)	2.04±0.09 (2.13)	2.11±0.16 (2.13)	2.02±0.11 (2.18)	2.00 (2.13)
0.5	2.41	2.28±0.13 (2.39)	2.27±0.09 (2.39)	2.4±0.2 (2.39)	...	
0.4	2.75	2.58±0.13 (2.70)	2.56±0.13 (2.71)	2.7±0.3 (2.72)	2.55±0.26 (2.76)	2.53 (2.73)
0.3	3.11	2.95±0.13 (3.08)	2.9±0.2 (3.13)	3.1±0.3 (3.14)	...	
0.2	3.80	3.37±0.15 (3.59)	3.3±0.4 (3.71)	3.6±0.4 (3.74)	3.61±0.43 (3.88)	3.39 (3.80)
0.1	5.00	4.0±0.20 (4.40)	3.9±0.3 (4.68)	4.3±0.4 (4.79)	4.67±0.7 (5.12)	4.11 (5.00)

^a Values in parentheses are computer simulations of Lorentzian shapes including isotope-line contributions.

^b For benzene, $a_{\text{H}}=3.78$ G (-100°), 3.76 G (-80°), 3.73 G (-60°), $a_{^{13}\text{C}}=3.73$ G (measured at -100°C but used for all temperatures) (cf. Ref. 9d), $\delta=0.36$ G (-100°), $\delta=0.40$ G (-80°), $\delta=0.52$ G (-60°C). Errors are sample deviations.

^c For tropenyl $a_{\text{H}}=3.67$ G, $a_{^{13}\text{C}}=2.24$ G, $\delta=0.16$ G (cf. Refs. 9e, 34a). Line-shape data from Ref. 34a.

^d For PADS $a_{^{14}\text{N}}=13.0$ G, $a_{^{15}\text{N}}=18.2$ G, $a_{^{33}\text{S}}=1.25$ G [cf. J. J. Windle and A. K. Wierman, *J. Chem. Phys.* **47**, 2462 (1967)]; $\delta=0.168$ G. Line-shape data measured from Ref. 26d.

results are summarized in Table I.²⁵ The line shape for the center component of the benzene anion was found to be temperature independent, within experimental error, over the range -110° to -60°C (cf. Table I). Computer simulations showed that incipient overlap effects from the other proton hyperfine lines were negligible. However, the wings *are* slightly affected by the presence of weak 2.8-G splittings of approximately the same derivative width as the proton lines resulting from ¹³C in natural abundance,^{9d} and computer simulations (summarized in Table I) have shown that at least part of the deviation arises from this source, but the amount depends crucially on the values of a_{H} and $a_{^{13}\text{C}}$ used. Similar corrections to the line shape from isotope splittings were obtained for the central components of the tropenyl and PADS spectra and are compared with the experimental results in Table I. While there is reasonable agreement, it is probably true, especially for PADS, that the lines are decreasing more rapidly than a Lorentzian at about five derivative half-widths. As a result of the good agreement of the line shapes with a Lorentzian line shape to better than two derivative half-widths, no corrections were made in the saturation studies for the isotope splittings or the deviations.

B. PADS—Relaxation

The relaxation times for the center hyperfine component of aqueous solutions of PADS have been measured by several workers under a variety of condi-

tions,^{16,26} but the only previous measurements of T_1 and T_2 at high fields (3200 G) were performed on a $9.8 \times 10^{-4}M$ air-saturated sample by Schreurs and Fraenkel¹⁶ utilizing a cavity filling which avoided nonuniform microwave and modulating fields over the sample length. Furthermore, their work done at room

TABLE II. Measured relaxation times of peroxyamine disulfonate dianion in aqueous solution.^a

A. Degassed solutions ^b				
$T/\eta \times 10^{-2}$ °	2.08(9°C)	3.25(24°C)	3.78(34°C)	
$T_1 \times 10^7$ sec	4.5±0.5	4.1±0.35	3.4±0.3	
$T_2 \times 10^7$ sec	4.7±0.2	4.1±0.2	3.5±0.1	
T_1/T_2	0.95±0.1	0.99±0.1	0.97±0.1	
B. Air-saturated solutions, room temperature				
	$T_1 \times 10^7$ sec	$T_2 \times 10^7$ sec	$[T_1]_{\text{O}_2}$ ^d	$[T_2]_{\text{O}_2}$ ^d
This work ^b	3.4±0.2	2.52±0.09	2.7×10^{-6}	7.2×10^{-7}
Schreurs ^e	3.3	2.5

^a Errors are sample deviations.

^b Corrected for modulation frequency effects. See Appendix.

^c Viscosity values from *Handbook of Chemistry and Physics* (Chemical Rubber Publ. Co., Cleveland, Ohio, 1960), p. 2181.

^d Oxygen interaction components calculated assuming contribution to linewidth and T_1^{-1} is additive and independent of relaxation in absence of oxygen.

^e Reference 16.

²⁵ In other work on TCNE this radical exhibited good Lorentzian behavior to over five derivative widths, M. P. Eastman, R. G. Kooser, M. R. Das and J. H. Freed (unpublished).

²⁶ (a) W. Muller-Warmuth, *Z. Naturforsch.* **15a**, 927 (1960); **18a**, 1001 (1963). (b) J. P. Lloyd and G. E. Pake, *Phys. Rev.* **94**, 579 (1954). (c) A. Landesman, *J. Phys. Radium* **20**, 937 (1959). (d) M. T. Jones, *J. Chem. Phys.* **38**, 2892 (1963).

TABLE III. Variation of the linewidths of the benzene⁻ radical with temperature and initial benzene concentration in THF/DME solution.

Temp (°C)	η^c	$T/\eta \times 10^{-2}^c$	Derivative linewidth (G) ^a		
			0.2M ^b	0.01M ^b	0.001M ^b
-12	0.71	3.7	...	0.85	...
-20	0.79	3.2	0.83±0.04	0.79±0.02	...
-40	1.07	2.2	0.64±0.03	0.63±0.02	...
-60	1.55	1.4	0.51±0.02
-80	2.43	0.80	0.41±0.02
-86	2.79	0.67	...	0.36±0.01	...
-100			0.36±0.01
-105			...	0.32±0.01	0.35±0.01
-115			0.36±0.01	...	0.33±0.01

^a Errors are sample deviations.

^b Initial benzene concentration.

^c Viscosity values (centipoise) taken for solvent mixture as those for

pure THF from Ref. 33. Last two values extrapolated below the THF freezing point by equation given in this reference.

temperature for this stable radical, did not involve the insertion of a high dielectric Dewar into the cavity. In order to compare our technique, with its various correction factors, we measured the spin-relaxation times of an air-saturated $9 \times 10^{-4} M$ solution of PADS. The results are listed in Table II and compared with these of Schreurs and Fraenkel. The two sets of results are well within experimental error, and fortify our belief that the saturation technique utilized in this work should yield absolute values of T_1 with an accuracy of the order of about 20%–30%.

The relaxation times for dilute PADS solutions have also been determined in the absence of oxygen, and the temperature variation was explored. The results are also summarized in Table II. The main points to be made are that $T_1 = T_2$, within experimental error, over this range, and they are both decreasing with increasing temperature. A more detailed study of the T/η dependence of T_2 is given elsewhere.²⁷ For a $1.7 \times 10^{-4} M$ solution of PADS the linewidths were found to be linear in T/η and given by²⁷

$$\delta = 2.54(\pm 0.30) \times 10^{-4}(T/\eta) + 0.097(\pm 0.010) \text{ G.} \quad (4.1)$$

where T/η is in degrees Kelvin per centipoise.

It should be noted that the widths of the three hyperfine components were very nearly the same for the samples studied. However, small width variations, first mentioned by Kivelson and Collins,²⁸ have been confirmed by us in a careful study of the derivative amplitudes of a $6 \times 10^{-4} M$ degassed solution of PADS

at room temperature. The results may be expressed in terms of spectral index number \tilde{M}^{21} as

$$\delta/\delta(\tilde{M}=0) = (1.00 \pm 0.003) + (0.017 \pm 0.002)\tilde{M} + (0.009 \pm 0.004)\tilde{M}^2, \quad (4.2)$$

with $\delta(\tilde{M}=0) = 0.168 \pm 0.006$ G. A study of PADS linewidths in a $6 \times 10^{-4} M$ degassed solution in D₂O showed that the widths were the same as those obtained in H₂O at comparable values of T/η when the data are corrected for the differences in viscosity between D₂O and H₂O²⁹ [e.g., at 21°C or $T/\eta = 2.35 \times 10^2$ °K/cP, $\delta = 159 \pm 8$ mG, which agrees with the value of 157 mG for H₂O solvent calculated from Eq. (4.1)].

C. Benzene Anion

1. Linewidth Studies

Earlier work on the benzene anion^{1,9a,9d,9g,30,31} did not reveal any substantial width variation amongst the hyperfine components. We have carefully studied the relative derivative amplitudes of these components over the temperature range -105° to -40° C and could discern no significant variation from the expected binomial intensity distribution 1:6:15:20:15:6:1. As an example, at -80° C, the relative amplitudes were 1.0:6.2:14.7:20.0:14.8:5.8:1.1 (sample deviation ± 0.1). At temperatures above -40° C the lines begin to overlap slightly and this has a small effect on the relative amplitudes so that the results obtained, while reasonably consistent with the general conclusion, are

²⁷ M. P. Eastman, G. V. Bruno, and J. H. Freed, *J. Chem. Phys.*, (to be published).

²⁸ D. Kivelson and G. Collins, *Proceedings of the 1st International Conference on Magnetic Resonance, Jerusalem, Israel, 1961* (John Wiley & Sons, N.Y., 1962), p. 496.

²⁹ R. C. Hardy and R. L. Cottington, *J. Chem. Phys.* **17**, 509 (1949).

³⁰ G. L. Malinowski and W. H. Bruning, *J. Am. Chem. Soc.* **89**, 3064 (1967).

³¹ M. T. Jones, *J. Am. Chem. Soc.* **88**, 174 (1966).

TABLE IV. Spin-relaxation times for the center component of the benzene anion in solution.

Temperature (°C)	$T_1 \times 10^7$ (sec) ^a	$T_2 \times 10^7$ (sec) ^a
-118	2.56±0.2	1.97±0.03
-115 ^b	1.89±0.2	1.89±0.02
-113	2.01±0.2	2.01±0.02
-104	2.3±0.2	1.90±0.02
-100 ^b	2.0±0.2	1.82±0.02
-93	1.95±0.4	1.95±0.03
-92	2.1±0.3	1.90±0.03
-80 ^b	2.06±0.2	1.58±0.02
-60 ^b	1.58±0.2	1.32±0.02
-60 ^b	1.39±0.2	1.16±0.03
-40 ^b	1.34±0.3	1.03±0.04
-20 ^b	1.40±0.2	0.78±0.02

^a Errors are sample deviations based on least-squares fit of the saturation data.

^b Initial benzene concentration 0.2M. All others $1 \times 10^{-3}M$ or less.

not as accurate. (Such overlap effects will affect the observed T_1 and T_2 in this region, although no such corrections were made in this work.)

On the basis of these results, it was concluded that all further work on linewidths and saturation need only be done on a single hyperfine component, the central line.

The linewidth results were obtained in two ways: (1) by measurement on samples with microwave power levels well below saturation, and (2) from the intercepts of width versus microwave power [cf. Eq. (2.1)] utilized in the saturation studies. The former appear in Table III while the latter are given in Table IV (as T_2). There is generally good agreement between both sets. It is seen from Table III that there is no appreciable dependence of the linewidths on initial benzene concentrations up to 0.2M at temperatures up

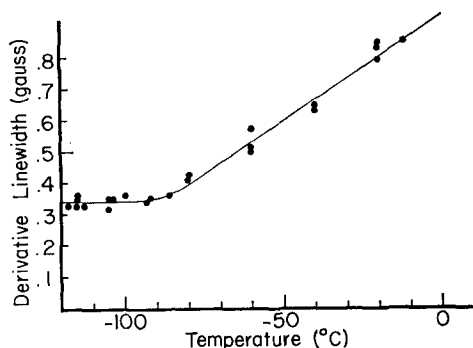


FIG. 4. Derivative linewidth for the benzene anion in 2:1 THF:DME solution as a function of temperature.

to and including -20°C .³² (The linewidths, when an initial benzene concentration of 1.4M was used, were, however, substantially greater.¹⁹) The temperature dependence of all these results considered together is shown in Fig. 4. The linewidth is independent of temperature below about -85°C . However, above -85°C the width increases rapidly with temperature and it may be readily fitted to a linear variation in either T or T/η above -85° given by

$$\delta = -(0.892 \pm 0.073) + (6.68 \pm 0.32) \times 10^{-3} T \text{ G} \quad (4.3a)$$

and

$$\delta = (0.284 \pm 0.017) + (1.631 \pm 0.076) \times 10^{-3} T/\eta \text{ G} \quad (4.3b)$$

Viscosity values for pure THF have been used under the assumption³³ that the solvent mixture will not be radically different than either of the components which have quite similar physical properties.³³ We note that the intercept of the expression in T/η is 0.284 G, which

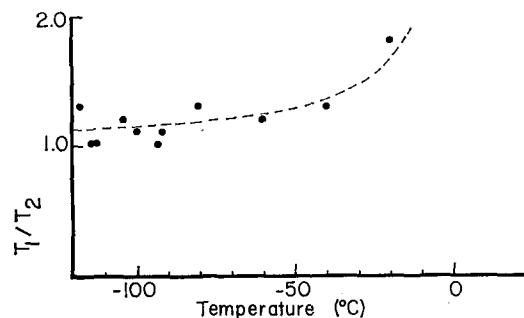


FIG. 5. The T_1/T_2 ratio for the benzene anion in 2:1 THF:DME solution as a function of temperature.

is close to the linewidth in the temperature-independent region.

2. Saturation Studies

The results of the saturation studies performed at two different concentrations and as a function of temperature are summarized in Table IV. It is seen from Fig. 5 that the T_1/T_2 ratio is not significantly temperature dependent below about -60°C , with a mean value in this temperature range of 1.1 ± 0.1 .³⁴ This ratio appears to be increasing at the higher temperatures. As a result, T_1 is reasonably constant below

³² This observation had already been made by Professor R. G. Lawler and co-workers in unpublished work. Their linewidth studies are in good agreement with those reported here. They have also made the additional interesting observation that at temperatures around -20° to -30°C the widths are about the same in the 1:2 THF/DME solvent and in tetraglyme, which is considerably more viscous.

³³ C. Carvajal, K. J. Tolle, J. Smid, and M. Szwarc, J. Am. Chem. Soc. **87**, 5548 (1965).

³⁴ The value at -118°C is higher, but this is the region where the solvent becomes supercooled with anomalously high viscosities (cf. Ref. 31).

-80°C with a mean value of $2.0 \pm 0.2 \times 10^{-7}$ sec and is increasing with temperature above -80°C , but not as rapidly as T_2 .

D. Tropenyl

The saturation studies were conducted at 165°C on the central two components. Earlier work has shown that there is no noticeable linewidth variation amongst the hyperfine components.³⁵ The results of three separate runs are for δ : 0.15 ± 0.01 , 0.13 ± 0.01 , and 0.15 ± 0.02 G with associated T_1/T_2 ratios of 1.00 ± 0.06 , 1.08 ± 0.05 , and 1.06 ± 0.22 . A careful analysis of linewidths as a function of temperature utilizing 15-kHz field modulation in place of 100 kHz (thus requiring no modulation frequency correction, cf. Appendix) demonstrated that the widths remained constant over the range of 135°C ($\delta = 0.16 \pm 0.01$ G) to 200°C ($\delta = 0.15 \pm 0.01$ G). Thus we have $T_2 = (4.4 \pm 0.4) \times 10^{-7}$ sec over this range with $T_1/T_2 = 1.05 \pm 0.11$ at 165°C .

E. 35-GHZ Studies

The linewidths of samples of several radicals were measured at both 9.1- and 35-GHz microwave frequencies. Due to the inherent difficulties of obtaining the radicals in small diameter (1-2-mm-o.d.) capillary tubes, no exhaustive attempt was made to obtain minimum linewidths. The results are given in Table V. The 9.1-GHz widths are all somewhat greater than the minimum reported widths^{9a,9g,10b,10d,16,20d} probably due to some exchange broadening. Since exchange processes are not expected to have any significant field-frequency dependence,^{14,36} this was not deemed as seriously affecting the comparative linewidth study. The minimum 35-GHz linewidths of 130 mG were obtained for the tetracene⁺ and naphthalene⁻ samples. (These

values give an independent upper limit of 60 mG for the dc magnetic field variation over the sample, but this is considerably greater than our estimate of 10 mG from the field contour measurements.) If it is assumed that the linewidths are to a reasonable approximation a sum of a field-frequency-independent and field-frequency-dependent secular g -tensor term, then we may write $\delta = a + bB_0^2$ where bB_0^2 is the g -tensor part. Then for PADS and C_6H_6^- , respectively, we get $bB_0^2 = 12$ and 30 mG for 9.1 GHz. The other values, neglecting field inhomogeneities, appear in Table V.

V. DISCUSSION

A. Peroxylamine Disulfonate

While PADS is not a free radical with enough symmetry to have a degenerate ground state and it was studied primarily as a check on the experimental technique, it is believed that the results, particularly of the degassed samples, are of some interest with respect to an understanding of spin-relaxation processes. Furthermore, since there have been so few careful measurements of T_1 and of field-frequency-dependent widths for free radicals in solution with which to compare the results for the degenerate ground-state radicals, it is of interest to discuss these results.

It has been proposed that the dominant relaxation mechanism in dilute degassed solutions of PADS is a spin-rotational interaction,³⁷ the contributions of which one may approximate as^{37,38}:

$$(T_1^{-1})^{\text{SR}} = (T_2^{-1})^{\text{SR}} = \sum_i (g_i - g_e)^2 / 9\tau_R \quad (5.1)$$

where g_i is the i th component of the g tensor in its principal axis system, g_e is the free-electron g value, and τ_R the rotational correlation time is given in the Stokes-Einstein approximation by:

$$\tau_R = 4\pi\eta a^3 / 3kT, \quad (5.2)$$

where a is the effective radius of the molecule. Thus the relaxation times will be linear in η/T . The other possibilities of g -tensor or anisotropic electron-nuclear dipolar interactions^{12,39} as being the dominant mechanisms were ruled out earlier by experimental work of Landesman.^{26c}

The main features of the results of this study which are relevant to this problem are:

(1) The T_1/T_2 ratio in the absence of O_2 is unity and independent of temperature in agreement with Eq. (5.1) for a spin-rotational mechanism.

(2) The relaxation times are both linear in η/T , as expected for a spin-rotational mechanism, but there

TABLE V. 9.1 vs 35 GHz derivative widths.

Radical/solvent	Temp (°C)	δ_X (G) ^a	δ_R (G) ^a	δ_ρ (G) ^b
Tetracene ⁺ /H ₂ SO ₄	R.T.	0.06	0.13	0.005
PADS/air-saturated H ₂ O	R.T.	0.250	0.41	0.012
Naphthalene ⁻ /DME	R.T.	0.070	0.13	0.004
Naphthalene ⁻ /DME	-60	0.040	0.18	0.010
Benzene ⁻ /DME/THF ^c	-105	0.41	0.82	0.030

^a δ_X and δ_R are the derivative widths at 9.1 and 35 GHz, respectively.

^b δ_ρ is the contribution to the derivative width at 9.1 GHz due to a g -tensor mechanism as calculated from δ_X and δ_R assuming $\delta = a + bB_0^2$ (cf. text).

^c The modulation frequency was 100 kHz. For all other samples it was 15 kHz.

³⁵ (a) W. V. Volland, Ph.D. thesis, University of Washington, Seattle, Wash., 1967. (b) W. V. Volland and G. Vincow, *J. Phys. Chem.* **73**, 1147 (1969).

³⁶ J. H. Freed, *J. Chem. Phys.* **46**, 3452 (1966).

³⁷ P. W. Atkins and D. Kivelson, *J. Chem. Phys.* **44**, 169 (1966).

³⁸ (a) P. S. Hubbard, *Phys. Rev.* **131**, 1155 (1963). (b) P. W. Atkins, *Mol. Phys.* **12**, 133 (1967).

³⁹ D. Kivelson, *J. Chem. Phys.* **27**, 1087 (1957); **33**, 1094 (1960).

appears to be a large (η/T) -independent contribution of about 0.1 G not predicted by Eqs. (5.1) and (5.2).

(3) Anisotropic g -tensor and intramolecular dipolar interactions do not give important contributions to T_2^{-1} at 9.1 GHz, since the g -tensor contribution at 9.1 GHz is no more than 12 mG and there is no substantial width variation amongst the three hyperfine components.^{16,26c,28}

(4) Contributions from intermolecular electron-nuclear dipolar interactions must be negligible since the linewidths are the same for H₂O and D₂O.

We note that the experimental data, in principle, provide a number of independent estimates of τ_R . We first consider the room-temperature linewidth variations given by Eq. (4.2) and compare with the combined effects of g -tensor and intramolecular dipolar interactions given by^{12,39}

$$T_2^{-1} = j^{(D)}(0)M^2[(5/3) - \frac{1}{3}(1 + \omega_0^2\tau_R^2)^{-1}] + j^{(DG_2)}(0)B_0M[(16/3) + 4(1 + \omega_0^2\tau_R^2)^{-1}] + j^D(0)I(I+1)[1 + (7/3)(1 + \omega_0^2\tau_R^2)^{-1}] + j^{G_2}(0)B_0^2[(8/3) + 2(1 + \omega_0^2\tau_R^2)^{-1}] + X, \quad (5.3)$$

where the spectral densities are given by

$$j^{G_2}(0)B_0^2 = \sum_i [(g_i - g_a)^2 \omega_0^2 \tau_R / 80],$$

$$j^D(0) = \frac{1}{5}(\tau_R 4\pi^2) \zeta^2 \sum_{m=-2}^2 |D^{(m)}|^2,$$

and

$$j^{DG_2}(0)B_0 = (\pi/10)\zeta\omega_0\tau_R[D^{(0)}g^{(0)} + (D^{(2)} + D^{(-2)})g^{(2)}],$$

and where

$$\zeta = (1/2\pi) |\gamma_e| \gamma_n \hbar$$

and X is the residual width. The notation of these equations is discussed in several places^{12,13,40,41} and we shall not discuss it further here. Utilizing the data of Weissman and Banfill⁴² on a dilute single crystal, we have for the dipolar terms $\zeta_N D_N^0 \approx 24$ MHz and $D_N^m \approx 0$ for $m \neq 0$. The g -tensor components of PADS have never been measured so we use as an estimate, the g -tensor components measured for di-tertiary-butyl-nitroxide⁴³ (DTBN). We believe this is reasonable because: (1) both compounds should have spin densities mainly localized in the N-O group; (2) most nitroxides measured to date have similar g -tensor components⁴⁴; (3) the DTBN dipolar terms⁴³ are close to those for

PADS; and (4) the isotropic g values of $g_s = 2.0055$ for PADS⁴⁵ and 2.0059 for DTBN⁴³ are very similar.

Our results for room temperature, which include the nonsecular contributions to the linewidth, are $\tau_R = (2.9 \pm 0.5) \times 10^{-12}$ and $(3.7 \pm 1.5) \times 10^{-12}$ sec from the terms linear and quadratic in \tilde{M} , respectively. (Kivelson and Collins'²⁸ earlier estimate is $\tau_R = 5.7 \times 10^{-12}$ sec.) The residual width $X = 2.47 \times 10^6$ sec⁻¹, if attributed entirely to a spin-rotational interaction, [Eq. (5.1)] yields $\tau_R = 2.6 \times 10^{-12}$ sec, which is in surprisingly good agreement with the results obtained from the linewidth variation. If, however, only the (T/η) -dependent part of the width as given by Eqs. (5.1) and (5.2) is used, one has $\tau_R = 6.0 \times 10^{-12}$ sec. Given the considerable uncertainties in the experimental data and their analysis, it is probably not clear which of these two values is closer to being correct. However, the simple Hubbard^{38a} theory for spin-rotational relaxation [Eq. (5.2)] suggests that only the T/η component should be utilized. This raises the question as to whether there is in fact another relaxation process which is closely temperature independent over the small temperature range studied. Such a possibility was strongly suggested by earlier linewidth results of Kivelson and Collins²⁸ on solutions of PADS in glycerine:water mixtures. They found that an increase in τ_R (determined from width variations) by a factor of 42 resulted in X decreasing by a factor of only 1.8.

More recent work by McClung and Kivelson⁴⁶ on solutions of ClO₂ has shown that T_2^{SR-1} is generally monotonic in T/η , but not necessarily linear, due to effects of inertial motion and molecular reorientation which play an increasingly important role as the anisotropic intermolecular potential between radical and solvent molecules becomes weak. One would not expect such effects to become important in the present case of a dinegatively charged radical (PADS) dissolved in highly polar solvents (water and glycerine). Thus, in a study of charged Vanadyl and copper complexes in a variety of solvents, Wilson and Kivelson obtained results for the spin-rotational contribution that is linear in T/η in accordance with Eq. (5.1).⁴⁷ Furthermore the results for PADS in the glycerine:water solvent, wherein such a large change in T/η is brought about, should have caused a much greater decrease in X than was observed, if there were any resemblance with the results for ClO₂. It seems reasonable therefore to conclude that there may well be another, essentially (T/η) -independent, spin-relaxation mechanism. Our saturation work indicates that such a mechanism would

⁴⁰ G. K. Fraenkel, J. Chem. Phys. **42**, 4275 (1965).

⁴¹ G. K. Fraenkel, J. Phys. Chem. **71**, 139 (1967).

⁴² S. I. Weissman and D. Banfill, J. Am. Chem. Soc. **75**, 2534 (1953).

⁴³ O. H. Griffith, D. W. Cornell, and H. M. McConnell, J. Chem. Phys. **43**, 2909 (1965).

⁴⁴ (a) N. Edelstein, A. Kwok, and A. H. Maki, J. Chem. Phys. **41**, 179 (1964). (b) A. van Roggen, L. van Roggen, and W. Gordy, Phys. Rev. **105**, 50 (1957).

⁴⁵ *EPR at Work* (Instrument Div., Varian Assoc., Palo Alto, Calif.), No. 29.

⁴⁶ R. E. D. McClung and D. Kivelson, J. Chem. Phys. **49**, 3380 (1968).

⁴⁷ (a) R. Wilson and D. Kivelson, J. Chem. Phys. **44**, 154, 4440, 4445 (1966). These authors observed some unexplained nonlinearities at low T/η for the vanadyl complex, but unlike our results with PADS, their linear portion extrapolates to zero for $T/\eta \rightarrow 0$. (b) J. H. Freed, *ibid.* **41**, 2077 (1964).

be characterized by $T_1 \approx T_2$, which rules out such possibilities as chemical exchange¹⁴ or any largely secular process.

When one analyzes the field-dependent effects on the linewidth in terms of a g -tensor mechanism, we obtain $\tau_R = 7.1 \times 10^{-11}$ sec. (The estimate of τ_R is reduced slightly if some of the increased width is attributed to field inhomogeneity.) (Here nonsecular contributions to the width are unimportant.) While this result is at least an order of magnitude larger than the estimates already discussed, it is in surprisingly good agreement with the estimate from Eq. (5.2) of 7×10^{-11} sec.³⁹ It is not known why the other estimates are so small, when for charged radicals in polar solvents there is usually reasonably good agreement between τ_R predicted by Eq. (5.2) and experimental estimates.^{21,47} On the other hand, the large disagreement between the estimates of τ_R from linewidth variations at 9.1 GHz and from the field dependence raises the possibility that there could be another field-dependent relaxation term besides the rotational modulation of the g tensor contributing to the linewidth. The only requirement to explain our result is that it not give any cross terms with other mechanisms that depend on \tilde{M} .⁴⁸ (One possibility would be modulation of g_s by solvent or cation interactions, but it would then be necessary that the ¹⁴N isotropic hyperfine interaction not be appreciably affected.¹²) In any event, a field-dependent contribution of form bB_0^2 would only be contributing less than 8% of the total width at 9.1 GHz.

Several workers have noted the effect of oxygen on the high-field ESR linewidths: that the widths increase with increasing oxygen concentration⁴⁹ and the oxygen-dependent component is independent of PADS concentration.^{26d} Our results show that $T_1(\text{O}_2)/T_2(\text{O}_2) > 1$. One would expect the coupling between spins to be either an electron-electron dipolar effect or a scalar coupling, i.e., spin-exchange mechanism.⁵⁰ Our experience with interaction between like free radicals is that spin exchange is the dominant relaxation process in liquids of normal viscosities.⁵¹ However, more detailed experimental studies would be needed before a proper theoretical analysis would be fruitful. But we may note that for either process, if the appropriate correlation time⁵⁰ is short compared to spin transition frequencies involving both PADS and O₂, one would expect $T_1 = T_2$ for PADS. (This assumes rapid independent

relaxation of the O₂.⁵⁰) Our result implies that the correlation time is not so short, i.e., of the order of about 3×10^{-11} sec.

B. Benzene and Tropenyl

We may summarize the most important features of our results as:

(1) In the benzene anion, T_1/T_2 is close to unity from -118° to at least -60°C , while for tropenyl, it is unity at $+165^\circ\text{C}$. The weight of this evidence is that the anomalous relaxation contribution is properly characterized by $T_1/T_2 \approx 1$ in liquids.

(2) Anisotropic g -tensor and intramolecular dipolar interactions do not give major contributions to T_2^{-1} at 9.1 GHz since the g -tensor contribution is no more than 30 mG and there is no measurable width variation amongst the hyperfine components.

(3) The linewidths for benzene anion from -118° to about -85°C and for tropenyl from 135° – 200°C are remarkably temperature independent and for benzene quite insensitive to initial benzene concentration.

(4) The benzene and tropenyl concentration-independent widths ($\delta = 330$ and 160 mG) in the liquid state are anomalously large when compared to those of other hydrocarbons like anthracene and naphthalene anions (15–25 mG).

We note that Results (1) and (3) also rule out exchange-type processes from being the main cause of the anomalous widths.^{14,51} They also rule out mechanisms that are largely secular.^{52a} This leaves us with either an anomalously large spin-rotational con-

⁵² (a) One, largely secular, mechanism which has been proposed for the (T/η) -dependent portion of the width [W. Bruning (private communication)] is residual broadening from unresolved alkali metal (K^+) splittings of magnitude a . The linewidth contribution for ³⁹K with $I = \frac{3}{2}$ would be in the exchange-narrowed region: $T_2^{-1} = (5/4) a^2 [\tau_e + \tau_e / (1 + \omega_0^2 \tau_e^2)]$, where τ_e is the mean lifetime of an ion pair, (cf. Ref. 50). However, one finds that for reasonable values of $(a/\gamma) \sim 0.1$ G [cf. M. C. R. Symons, *J. Phys. Chem.* **71**, 172 (1967)], it is impossible to have a contribution to the derivative width of the order of 0.3 G and still be in the exchange-narrowed region (since $a\tau_e \sim 2.1 > 1$ from the above expression). For unexpectedly large values (for ³⁹K but not for ²³Na) of $a/\gamma \sim 1.0$ G, such widths would result from $\tau_e \sim 1.2 \times 10^{-8}$ sec and $a\tau_e \ll 1$. Here, $\omega_0 \tau_e \gg 1$, so nonsecular terms are negligible compared to secular ones. In either case this mechanism would not contribute significantly to T_1 , so it could not account for the low-temperature experimental results. The possibility that such a mechanism is causing the (T/η) -dependent portion of the width conflicts with (1) the apparent solvent independence of the width (cf. Ref. 32), (2) the expected decrease in τ_e with increasing T/η even though the value of a might be expected to increase with temperature, and also (3) with the fact that for reasonable values of a , as noted, it would probably require (for ³⁹K), $a\tau_e > 1$, so the observed spectral lines are essentially inhomogeneously broadened. This latter condition would lead to lineshapes distorted from the Lorentzian in that they would appear to decay more slowly in the near wings, [cf., Y. S. Lebedev *et al.*, *Atlas of Electron Spin Resonance Spectra*, (Consultants Bureau, New York, 1963)]. Also the distorted shape should be temperature dependent as the relative contribution of this mechanism to the total width and the values of a and τ_e are changing. Both these predictions are contrary to the observations. (b) Anomalous spin-rotational effects arising directly from ground-state degeneracies will be discussed elsewhere (Ref. 7b).

⁴⁸ We note that our estimates for PADS yield $g^{(2)} = 1.4 \times 10^{-3}$ but $D^{(\pm 2)} \approx 0$ so that while $g^{(2)}$ contributes to the g -tensor broadening, it has no cross term with the dipolar interaction. Now anisotropic rotational tumbling in which reorientation about the molecular z axis is relatively slow would cause the $m = \pm 2$ tensor components to relax slower than the $m = 0$ components. This would be qualitatively in the correct direction (cf. Ref. 47b), but quantitatively it yields about a 12% increase in τ_R , not an order of magnitude increase.

⁴⁹ K. Hausser, *Z. Elektrochem.* **65**, 636 (1961).

⁵⁰ A. Abragam, *The Principles of Nuclear Magnetism* (Clarendon Press, Oxford, England, 1961), Chap. 8.

⁵¹ M. P. Eastman, R. G. Kooser, M. R. Das, and J. H. Freed, *J. Chem. Phys.* (to be published).

tribution or else some mechanism based on the ground-state degeneracy of the molecule. We first consider the former, insofar as it may be distinct from the latter.^{52b} The ground-state degeneracy of the benzene anion, tropanyl, and associated radicals has as a necessary condition that these radicals have an axis of threefold or greater symmetry. But this is also a sufficient condition to guarantee that these molecules will be symmetric tops! One may expect that a symmetric-top molecule will rotate more freely about its symmetry axis than if it were asymmetric. According to an extension of the simple spin-rotational theory expressed by Eqs. (5.1) and (5.2) this freer rotation would mean that τ_{Rz} , i.e., the rotational correlation time about the z or symmetry axis, would be substantially reduced. This is equivalent to an increase in τ_{Jz} , the correlation time for rotational angular momentum about the z axis. The proper generalization of Eq. (5.1) (neglecting inertial and reorientational effects) is^{53b,46}

$$T_1^{-1} = T_2^{-1} = \frac{2}{3}kT \sum_i (g_i - g_e)^2 \tau_{J,i} / I_i, \quad (5.4)$$

where

$$\tau_{J,i} / I_i = (8\pi r_0^3 \eta \kappa_i)^{-1},$$

r_0 is the calculated mean radius of the molecule, and $0 \leq \kappa_i \leq 1$ may be thought of as a correction parameter necessitated by the microscopic viscosity being less than the macroscopic value, i.e., it is a measure of the anisotropy of the intermolecular potentials. The point we are making is that one might expect $\kappa_z < \kappa_x = \kappa_y$ for these symmetric tops, thus increasing the contribution from the $i = z$ term to the sum of Eq. (5.4).

Such a mechanism may be criticized on the basis that it would still predict a simple T/η dependence of the anomalous width which has not been seen. Again we note that as κ_z becomes small, inertial and reorientational effects discussed by McClung and Kivelson⁴⁶ begin to be important, yielding a nonlinear variation of $(T_2^{-1})^{SR}$ with T/η . In the case of the charged benzene anion, κ_z would probably not get too small and we would not expect such effects to play a significant role.

Another argument against such a mechanism is that the value of $(g_z - g_e) \sim 6 \times 10^{-5}$ estimated for hydrocarbon radicals by Stone⁵³ is about 5–10 times smaller than $(g_x - g_e) = (g_y - g_e)$ estimated for these radicals.^{9g,53,54} Thus the term in $(g_z - g_e)$ of Eq. (5.4) would

⁵³ A. J. Stone, *Mol. Phys.* **6**, 509 (1963); **7**, 311 (1964).

⁵⁴ An estimate of the order of magnitude of τ_R needed to render the spin-rotational mechanism [as given by Eqs. (5.1) and (5.2)] effective is obtained for $C_6H_6^-$ by first letting $(g_z - g_e) = 6 \times 10^{-5}$, noting $g_x = g_y$ by symmetry, and $g_e = 2.00285$. Then $\sum_i (g_i - g_e)^2 = 1.2 \times 10^{-9}$, so from Eq. (5.1) $\tau_R = 4 \times 10^{-14}$ at $-60^\circ C$ or orders of magnitude shorter than is usual. This would represent a $\kappa \sim 4 \times 10^{-8} - 4 \times 10^{-4}$ sec when compared with usual values of $\tau_R \sim 10^{-10} - 10^{-11}$ sec and $\kappa \sim 0.1 - 1$. One must, however, note that Eqs. (5.1) and (5.4), utilizing g -tensor components, are only approximations to the spin-rotational interaction that Atkins and Kivelson³⁷ introduced, but recent work [W. Buchner and J. H. Freed (unpublished)] has shown that it should be a good approximation, except that the z -component contribution may be even smaller than the above approximations.

make a very small contribution. Stone, however, specifically considered only the radicals with non-degenerate ground states. Segal, Kaplan, and Fraenkel^{9g} found that their average g -value measurements could be well fitted by a semiempirical relationship based on Stone's theory, but the fit to the degenerate ground-state free radicals of Δg_e deviates by about 5×10^{-5} or about 10%.^{9g,11b} While this is a significant deviation, it would appear that rough estimates of the g -tensor components can be made from Stone's theory even for the degenerate ground-state free radicals. This has been borne out by the recent measurement of the g -tensor components of tropanyl by Volland and Vincow,³⁵ who find $(g_z - g_e) = 4 \times 10^{-5}$ and $(g_x - g_e) = 54 \times 10^{-5}$.

We have recently recognized⁵⁵ that there is a simple experimental test of whether to attribute the anomalous relaxation to a mechanism characteristic of a symmetric top versus a degenerate electronic ground state if one is prepared to assume that the same mechanism holds for related radicals. One may compare the widths of the triphenylene (TP) anion radical with that of the neutral perinaphthenyl (PN) radical, both of which have a C_3 symmetry axis, similar shapes and comparable g values.⁵⁵ However, only TP⁻ has a degenerate ground state, while the smaller effective radius and absence of net charge of PN should enhance its relative ability to rotate more freely about its symmetry axis. We have succeeded in obtaining concentration-independent liquid-solution linewidths for these radicals, and have found that for TP, $\delta = 250$ mG and is constant over the range $-100^\circ - -20^\circ C$, while for PN widths as low as 20 mG have been obtained.⁵⁵ There appears to be little question, then, that we can rule out a large spin-rotational contribution, arising solely because these molecules are symmetric tops, as being a major contributor to the anomalous relaxation of these radicals.

This leaves us with the strong likelihood that the explanation does lie with the orbitally degenerate ground states of these free radicals. We have already noted⁸ that a variety of mechanisms involving this degeneracy and its influence on spin-orbit interactions can lead to the prediction $T_1 = T_2$ in accordance with our experimental results. A detailed treatment of these complex mechanisms will be given elsewhere,^{7b} but we note that common necessary requirements for this equality are that as a result of molecular tumbling in an isotropic liquid and decoupling of the axes of quantization of spin and orbital angular momentum, the spin-orbit perturbation itself is independent of a particular choice of laboratory axis. Thus S_x , S_y , and S_z can be relaxed equally by any spin-orbit-induced process provided only the appropriate energy spectrum associated with the particular motional mechanism is the same for relaxation of any of the spin components.

⁵⁵ M. R. Das, S. Wagner, and J. H. Freed (unpublished).

The nature of the energies needed and energy spectra involved are significantly different for the different spin-orbit mechanisms which have been proposed.

We have already noted that field-dependent mechanisms, assumed quadratic in the field, are contributing less than 10% of the 9.1-kMHz linewidth of benzene. Nevertheless, a comparison in Table V with the field dependence of widths of other radicals (even when due consideration is given to the possible contributions from field inhomogeneities) shows that the field-dependent component for the benzene anion is considerably larger than for the others. This might conceivably be due to a g -tensor mechanism enhanced by the electronic degeneracy.⁷ In this connection, we again note that the deviation of the average g values for $C_6H_6^-$ and C_7H_7 are within about 10% of that obtained from Stone's semiempirical equation for nondegenerate hydrocarbon free radicals. Thus, the small deviations of the g values for the degenerate free radicals should be insufficient, in themselves, to account for any anomalously large field-dependent linewidth component.⁵⁶ There exists the possibility that the observed g values are actually a statistical average over those for different, nearly degenerate, vibronic states^{11b,57} and these component g values are very

different, e.g., for the small splitting of the ground doubly degenerate state, one may write a g shift:

$$\Delta g = \Delta g_s \tanh(u),$$

where Δg_s is the large shift for the lower level and $u = \delta/2kT$, where δ is the splitting of the levels.^{8,11b,57} If $u \ll 1$, while δ is significantly greater than the spin-orbit perturbation which couples the two vibronic states, then it is possible to have a small Δg but a large variation in Δg_i (for the i th vibronic state) such that residual broadening arising from the thermal averaging over vibronic levels might yield the desired effect.⁵⁵

We turn now to the dependence of the anomalous relaxation with temperature and solvent viscosity. The emerging pattern appears that the relaxation contribution is remarkably temperature and solvent³² independent. This is true for C_7H_7 , $C_6H_6^-$ below $-85^\circ C$, and recent work on triphenylene and coronene.⁵⁵ Our work on benzene has, however, shown that above $-85^\circ C$ there appears a large temperature- or (T/η) -dependent contribution to T_2^{-1} which does not seem to affect T_1^{-1} quite as strongly. This (T/η) -dependent contribution (as well as the total width) is rather insensitive to initial benzene anion concentration over the range of 10^{-3} – $0.2M$, although the widths are somewhat greater for initial concentrations of $1.4M$.^{19,32} This insensitivity to initial $C_6H_6^-$ concentration appears to rule out broadening by chemical exchange with unreduced C_6H_6 .⁵⁸ On the other hand, the measured spin concentrations of $<10^{-4}M$ indicate that Heisenberg exchange effects should be negligible.⁵¹ One could also postulate an exchange between $C_6H_6^-$ and $C_6H_6^{\cdot-}$ in analogy with the results for $C_8H_8^-$ and $C_8H_8^{\cdot-}$ of Katz *et al.*,^{11a,59} but it would also be expected to be sensitive to initial $C_6H_6^-$ concentration. Nevertheless, it is interesting to note that the observed increasing values of T_2^{-1} as well as T_1/T_2 with temperature for the $0.2M$ samples are consistent with the predictions for an exchange-type process.^{14,19,51} Clearly, further work is needed on this matter.^{52a,60}

⁵⁶ When we use $g_z = 2.00238$ ⁵³ and $g_x = 2.002850$ ⁵⁴ then a 30-mG component for $C_6H_6^-$ would require, according to Eq. (5.3), a value for τ_R of 1.5×10^{-8} sec or at least two orders of magnitude longer than expected. We can obtain an upper limit on τ_R from the fact that there is no experimentally measurable linewidth variation. We note that it is possible for the widths of the outside lines to deviate by a maximum of about 15 mG from that of the center line and still be roughly within experimental error. Now, it is possible to rewrite Eq. (5.3) for the benzene case in terms of average widths for each (multiple) hyperfine line as: [cf. Ref. 41 Eq. (3.50), and subsequent discussion]

$$\langle T_2^{-1}(M) \rangle = (8/15) [jaa^D(0) + 4jab^D(0)] M^2 + (16/3) ja^{(D\sigma)}(0) B_0 M + X',$$

where X' includes all nuclear-spin-independent contributions and we have assumed $\omega_e^2 \tau_R^2 \gg 1$. This equation is for six equivalent protons divided into three completely equivalent pairs, where $jaa^D(0)$ is the dipolar contribution to the spectral density from a single completely equivalent set and $jab^D(0)$ arises from cross terms between different sets. We require only a single $jaa^D(0)$ and $jab^D(0)$ by symmetry. When the values of 1.392 and 1.080 Å are used for the C–C and C–H₂ bond lengths, respectively, with an unpaired carbon spin² density of $\frac{1}{3}$ per atom, and $\langle R_c^{-3} \rangle^{-1} = 1.692 \text{ Å}^{-3}$ with $Z_{eff} = 3.18$ for the Slater orbital, we obtain, using methods discussed elsewhere⁴¹:

$$jaa^D(0) = 3.62 \times 10^{14} \tau_R \text{ sec}^{-1},$$

$$jab^D(0) = -1.33 \times 10^{14} \tau_R \text{ sec}^{-1},$$

$$ja^{(D\sigma)}(0) = 0.910 \times (g_z - g_x) \times 10^{13} \tau_R \text{ sec}^{-1} \cdot G^{-1}.$$

Thus we have

$$\langle T_2^{-1}(M) \rangle = -3.62 \times 10^{14} (M/2)^2 \tau_R + 1.09 \times 10^{14} M \tau_R + X'.$$

Then, using a $\Delta\delta \lesssim 0.015$ G as the linewidth variation, we obtain $\tau_R \lesssim 0.4 \times 10^{-9}$ sec, a very reasonable upper limit.

⁵⁷ H. J. Silverstone, D. E. Wood, and H. M. McConnell, *J. Chem. Phys.* **41**, 2311 (1964). This work also indicates the relevance of low-temperature solid-state studies to the anomalous relaxation problem. We have noted significant differences between spectra of $C_6H_6^-$ in a DME matrix taken at $77^\circ K$ and at $4^\circ K$, cf. Ref. 19. M. T. Jones and co-workers [*Chem. Phys. Letters* **2**, 493 (1968)] have made similar observations.

⁵⁸ The chemical exchange rate between C_6H_6 and $C_6H_6^-$ has been reported by Malinoski and Bruning⁵⁰ for temperatures of $-15^\circ C$ and above. One can extrapolate their results to $-20^\circ C$ and below, in order to estimate the predicted exchange contribution to our linewidths. If we assume that the equilibrium concentrations of C_6H_6 are close to their initial values, (this is not in conflict with the measured spin concentration, cf. Sec. III), then at $-20^\circ C$ one obtains $k = 2.9 \times 10^{17} M^{-1} \cdot \text{sec}^{-1}$, and for initial benzene concentrations of 0.2 and 0.01M one has $\delta x = 0.38$ and 0.019 G, respectively, or a predicted difference of about 0.36 G, while the measured difference is ~ 0.04 G or about an order of magnitude less. Bruning (private communication) has recently informed us that the activation energy for the process has been determined and found to be less than originally stated, so that our results would not be in disagreement with his.

⁵⁹ T. J. Katz, *J. Am. Chem. Soc.* **82**, 3784, 3785 (1960).

⁶⁰ Recent preliminary results by G. Bruno utilizing the ELDOR technique in these laboratories, have indicated that exchange-type processes are not contributing significantly to the relaxation times for $C_6H_6^-$ at $-50^\circ C$ in solutions initially 0.2M or less, but they are for concentrations of 1.0M or greater. The possibility of some other, largely secular relaxation mechanism, is suggested by this result, cf. Ref. 52a.

The possible small deviation of the $C_6H_6^-$ and C_7H_7 line shapes from exact Lorentzian could also be of interest in terms of relaxation processes. In a general theoretical treatment of spin-relaxation,^{7a} one of us has shown that the Lorentzian line-shape characteristic of motionally narrowed spectra, etc., will in general be better approximated by a superposition of two Lorentzians, the main component, and a subsidiary component which is much broader than the first and is subtractive. The relative contribution of the subsidiary component increases as the motional correlation time increases. This effect is probably most important for the effects of secular relaxation terms, wherein the composite line can still be symmetric. Such a composite line decays faster in the wings than a pure Lorentzian. However, more careful line-shape studies than those reported here would be required to justify analyzing these small deviations for such effects.

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APPENDIX: MODULATION FREQUENCY EFFECTS ON A SATURATED SIGNAL

The modulation frequency can significantly distort an ESR line as Hyde and Brown^{10d} have shown. In order to assess the importance of the modulating frequency on the relaxation times determined in this work, the effects of the modulating frequency have been determined to lowest order in the product of the modulation frequency times the relaxation time (ωT). We use a method of expanding the Bloch equations⁶¹ as given by Rowland and Hubbard.⁶² We will follow their notation, modified for negative moments.

The Bloch equations for slow passage can be written in the coordinate frame rotating at the microwave

frequency, ω_1 , as⁶¹

$$(du/dt) + (u/T_2) - \gamma(\Delta\omega + B_m \cos\omega_m t)v = 0, \quad (A1a)$$

$$(dv/dt) + (v/T_2) + \gamma(\Delta\omega + B_m \cos\omega_m t)u - \gamma B_1 M_x = 0, \quad (A1b)$$

$$(dM_z/dt) + (M_z/T_1) + \gamma B_1 v = M_0/T_1, \quad (A1c)$$

where these have been modified to include the modulating field B_m oscillating at ω_m . The parameters in (A1) are: u , dispersion mode ($M_x \cos\omega_1 t + M_y \sin\omega_1 t$); v , absorption mode ($M_x \sin\omega_1 t + M_y \cos\omega_1 t$); M_x , M_y , M_z , and M_0 , the x , y , z and equilibrium magnetizations in the laboratory frame; B_1 , the amplitude of the rotating component of the microwave field; and $\Delta\omega = \omega_0 - \omega_1$, where ω_0 is the Larmor frequency and ω_1 is the microwave frequency. Oscillatory solutions to the equations (A1) are assumed to be of the form

$$u = \sum_{n=-\infty}^{+\infty} u_n(t) \exp(in\omega_m t); \text{ etc.},$$

yielding a set of coupled equations in u_n , v_n , and M_n whose solutions are obtained by taking the leading terms in a power-series expansion in various parameters.

The solution of interest here is obtained under the following assumptions:

- (a) Slow passage through resonance.
- (b) First order in B_m/B_1 .

This involves neglecting the next higher term of the order $(B_m/B_1)^3$ with a coefficient of similar magnitude to B_m/B_1 .⁶² Thus, (B_m/B_1) must be less than unity. [Experimentally it is always possible to choose B_m to meet this condition although it may not always be practical. For $T_1 = T_2$ at maximum derivative signal ($\gamma^2 B_1^2 T_1 T_2 = \frac{1}{2}$), the ratio B_m/B_1 will be about 0.14 if γB_m is about a tenth of T_2^{-1} .]

In usual detection schemes, the absorption component is selected to be oscillating in-phase with the modulating field. From Rowland and Hubbard,⁶² we have for this component

$$v = - \frac{B_m}{B_1} \frac{(1+\rho^2) \Delta\omega \omega_1'^2 T_2^3 M_0 (2A + \sigma B)}{(1+T_2^2 \Delta\omega^2 + \gamma^2 B_1^2 T_1 T_2) (A^2 + B_2)} \quad (A2a)$$

$$\sigma = T_2 \omega_m, \quad \rho = T_1 \omega_m, \quad \omega_1' = \gamma B_1, \quad (A2b)$$

with

$$A = \{1 + T_1 T_2 \omega_1'^2 + T_2^2 \Delta\omega^2 (1 + \rho^2) + \sigma^2 [T_1^2 / (T_2^2 - \rho^2 - 1)] + \rho \sigma \omega_1'^2 T_1 T_2\}, \quad (A2c)$$

$$B = [\sigma \omega_1'^2 T_1 T_2 (1 - T_1/T_2) + 2\sigma (1 + \rho^2)]. \quad (A2d)$$

The equations simplify considerably for $T_1 = T_2 = T$ since Eq. (A2a) becomes

$$v = \frac{-2B_m B_1 M_0 \Delta\omega \omega_1'^2 T^3 (1 + \epsilon^2)}{B_1 [1 + T^2 \Delta\omega^2 + \omega_1'^2 T^2 + \epsilon^2 (T^2 \omega_1'^2 + T^2 \Delta\omega^2) - \epsilon^4] + 4\epsilon^2 (1 + \epsilon^2)^2}, \quad (A3)$$

where $\sigma = \rho = \epsilon$.

⁶¹ F. Bloch, Phys. Rev. **70**, 460 (1946).

⁶² P. S. Hubbard and T. J. Rowland, J. Appl. Phys. **28**, 1275 (1957).

Note that when ϵ approaches zero, Eq. (A3) is equal to the usual derivative of the absorption obtained with field modulation.

We now assume

$$\epsilon = \omega_m T \ll 1. \quad (\text{A4})$$

The linewidth between extrema is obtained by differentiating Eq. (A3) with respect to $\Delta\omega$. When this is done we have to lowest-order terms in $\epsilon(\epsilon^2)$,

$$T^2 \Delta\omega_{\text{exp}}^2 \cong [3(1+\epsilon^2)]^{-1}$$

$$\times (1+\omega_1'^2 T^2 + \epsilon \{ [3/(1+\omega_1'^2 T^2)] + \omega_1'^2 T^2 \}), \quad (\text{A5})$$

where $\Delta\omega_{\text{exp}}$ is the experimentally measured linewidth from the center to one of the derivative extrema. For no saturation, $T^2 \omega_1'^2 \cong 0$, δ becomes

$$\delta \cong 2(1+\epsilon^2)/\sqrt{3}\gamma T = [\delta(\epsilon=0)](1+\epsilon^2). \quad (\text{A6})$$

hence, the line is broadened by the modulation. At moderate saturation, $T^2 \omega_1'^2 = 1$, the width is

$$\delta^2 = [\delta(\epsilon=0)]^2 (1 + \frac{5}{4}\epsilon^2). \quad (\text{A7})$$

Now, when the linewidth is plotted as a function of microwave power in accordance with Eq. (2.1), the slope, from which T_1/T_2 is obtained, will be affected by finite values of ϵ . Thus, if we assume a linear fit is made to the experimental data such that the line passes through the two points given by Eqs. (A6) and (A7), we obtain

$$T_1/T_2 \cong (1 + \frac{5}{2}\epsilon^2) (T_1/T_2)_{\text{measured}}. \quad (\text{A8})$$

Equations (A6) and (A8) have been used to correct the experimental results in this work. When T_1 and T_2 were not quite equal we have used $\epsilon = \omega_m T_2$. One should note that Eq. (A8) gives only a crude estimate of the correction even when $T_1 = T_2$, because the variation of the correction with microwave power is itself nonlinear [cf. Eq. (A5)]. If, instead of Eq. (A7), a second point corresponding to $T^2 \omega_1'^2 < 1$ is used, somewhat larger correction factors are obtained. Equation (A6), however, agrees reasonably well with empirical linewidth comparisons we have made.

Direct Enumeration Study of Self-Avoiding Walks on the Tetrahedral Lattice

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By application of a general procedure devised by Martin, we generated, up to $N=14$, the number of self-avoiding open chains, and determined their mean-square end-to-end distance, their radius of gyration, the number of returns to the origin, and its corresponding mean-square end-to-end distances. The self-avoiding chain results were in excellent agreement with Monte Carlo calculations, and the mean-square radius of gyration of ring systems agreed with our previous Monte Carlo estimates. The number of returns to the origin was used to calculate the order of a phase transition for a tetrahedral model of the helix-to-random-coil system. The higher-order transition found is the same as that previously obtained by Fisher for other three-dimensional model systems.

I. INTRODUCTION

The use of self-avoiding (nonself-intersecting) random walks as a model of a long-chain flexible polymer molecule is well established. Since a real molecule cannot have any of its parts intersect with any of its other parts, the model of the molecule is made self-avoiding. This self-avoidance condition, or the excluded-volume effect, must be its very nature introduce infinitely long correlations in an infinitely long model and thereby destroy the model's Markovian characteristics. Although the model with no excluded volume is Markovian and can be handled rather easily by analytical techniques, the self-avoiding random walk has not yielded to a complete analytical solution since the infinite cor-

relations cannot be handled in closed form. In order to obtain results which may be compared with analytical treatments numerical methods were attempted. These methods fall into two distinct categories: the Monte Carlo techniques and the complete direct enumeration scheme.

Given that there exists a complete set of self-avoiding random walks, the Monte Carlo method generates a subset of the complete set on a specified lattice by high-speed digital-computer techniques and calculates configurational and statistical thermodynamic properties of interest. For example, a linear, flexible molecule confined to the tetrahedral lattice, and neglecting any nonbonded nearest-neighbor interactions, a subset of the self-avoiding walks on the above-mentioned lattice were generated up to 800 steps.¹ The mean-square end-to-end distance $\langle R_N^2 \rangle$

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¹ F. T. Wall and J. J. Erpenbeck, *J. Chem. Phys.* **30**, 634 (1959).