ELECTRON SPIN RESONANCE ABSORPTION IN BENZOPHENONE

PHENYLHYDRAZONE NEGATIVE ION

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[Signatures]

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ELECTRON SPIN RESONANCE ABSORPTION IN BENZOPHENONE

PHENYLHYDRAZONE NEGATIVE ION

THESIS

Presented to the Graduate Council of the North Texas State University in Partial Fulfillment of the Requirements

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By

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CHAPTER I

INTRODUCTION

Paramagnetism occurs whenever a system of charges has a resultant angular momentum. If this angular momentum is of electronic origin, one speaks of electronic paramagnetism. Such paramagnetism is found in all atoms having an odd number of electrons, in ions having partly-filled inner electron shells, in molecules having an odd number of electrons, in a small number of molecules with an even number of electrons but having a resultant angular momentum (as in $O_2$), in free radicals, and in metals and semi-conductors.

If any such paramagnetic system is placed in a magnetic field, the energy levels of the system are split into sets of multiplets (the Zeeman levels) by the interaction of the magnetic moments with the field. Transitions between some of these Zeeman levels may be induced by an external radiation field, provided the frequency of the radiation satisfies the well-known Bohr condition

$$\Delta E = h\nu$$

where $\Delta E$ is the energy separation between the two Zeeman levels, $h$ is Planck's constant, and $\nu$ is the frequency of the radiation field. The process whereby energy is absorbed
in such transitions is called Electron Paramagnetic Resonance Absorption (EPR). If the magnetic moment of the absorption system is due to spin-only angular momentum, the process is sometimes called Electron Spin Resonance Absorption (ESR).

The first experimental observations of laboratory-induced transitions between the Zeeman levels of electrons were by Zaviosky\textsuperscript{2} in 1945 in the U.S.S.R. and subsequently by Cummerow and Halliday\textsuperscript{3} in the U.S.A. At about the same time Bloch, Hansen and Packard\textsuperscript{4} and Purcell, Torrey and Pound\textsuperscript{5} observed Nuclear Paramagnetic Resonance Absorption. Shortly thereafter Penrose\textsuperscript{6} observed a hyperfine structure in EPR due to the magnetic interaction between nuclei and electrons.

During the last two decades magnetic resonance techniques have been developed as highly sophisticated procedures for probing the magnetic environment of electrons and nuclei in bulk matter. This thesis reports an ESR study of the hyperfine interaction between nuclei and a single "nearly-free" electron in dilute solutions of the benzophenone phenylhydrazone free radical $\left((C_6H_5)_2C:NNH:C_6H_5\right)$ in tetrahydrofuran.
REFERENCES


CHAPTER II

THEORETICAL BACKGROUND

The interaction Hamiltonian for an isolated electron with magnetic moment $\vec{\mu}_e$ and angular momentum $\vec{S}$ with a static magnetic field $\vec{H}_0$ is given by\(^1\)

$$\mathcal{H} = -\vec{\mu}_e \cdot \vec{H}_0 = \gamma_e \hbar \vec{S} \cdot \vec{H}_0,$$

where $\gamma_e = (2.80/2\pi) \times 10^6$ Hz/gauss is the gyromagnetic ratio for the electron. If $\vec{H}_0$ is taken along the z direction, the interaction becomes

$$\mathcal{H} = \gamma_e \hbar S_z H_0$$  \hspace{1cm} (1)

with eigenvalues

$$E = \gamma_e \hbar S_z m_S,$$  \hspace{1cm} (2)

where $m_S = \pm \frac{1}{2}$ is either eigenvalue of the $S_z$ operator. Since the two states given by Eq. (2) are separated in energy by

$$\Delta E = \gamma_e \hbar H_0,$$  \hspace{1cm} (3)

radiation of angular frequency $\omega$ applied to the system may stimulate transitions between the states (with a corresponding absorption or emission of energy) if

$$\hbar \omega = \Delta E.$$  \hspace{1cm} (4)
Equations (3) and (4) show that the required radiation frequency is exactly the classical Larmor precession frequency for a spin in a magnetic field,

$$\omega = \kappa g H_0.$$  \hspace{1cm} (5)

Pake\textsuperscript{2} and Slichter\textsuperscript{3} have discussed the "spin resonance problem" in great detail from this classical point of view.

The idealized model of an isolated electron in a magnetic field is well approximated by many s-state paramagnetic ions in dilute solution, since the dilution assures negligible interaction between ions. The presence of magnetic nuclei within the ion, however, presents an added complication. The $m_s = \pm \frac{1}{2}$ levels of Eq. (2) are split into multiplets by the interaction of electron and nuclei. This interaction, which by analogy with a similar optical phenomenon is called a "hyperfine interaction", may be visualized as arising from the additional magnetic field contributed by the presence of the nuclei. One may then think of a nuclear hyperfine field as the source of the multiplet structure.

The general theory of the hyperfine interaction as it affects the ESR of paramagnetic species has been given by Abragam and Pryce\textsuperscript{4} in the form of a hyperfine Hamiltonian which, for the interaction of a single electron with a single nucleus, takes the form

$$\mathcal{H}_{hf} = -\kappa \gamma_n \hbar^2 \left[ \frac{\mathbf{r} \cdot \mathbf{S}}{r^3} - \frac{3(r \cdot \mathbf{r})(r \cdot \mathbf{S})}{r^5} - \frac{\mathbf{B}_{rf}}{5} \mathbf{I} \cdot \mathbf{S} \delta(r) \right], \hspace{1cm} (6)$$
where $\gamma_n$ is the nuclear gyromagnetic ratio, $\hat{r}$ is the nuclear spin operator, $\vec{r}$ is the position vector of the electron relative to the nucleus, and $\delta(\vec{r})$ is the three-dimensional delta function for the electron-nucleus separation.

The first two terms of Eq. (6) constitute the ordinary classical dipole-dipole interaction,\(^5\) the potential energy of a dipole of moment $-\gamma_e \vec{S}$ at distance $\vec{r}$ in the field of another dipole of moment $\gamma_n \vec{I}$. The contribution of this classical dipolar interaction vanishes whenever the electron cloud has spherical symmetry, and Weissman\(^6\) has shown that the rapid tumbling of ions in solution averages this interaction to zero in all cases.

The delta function term in Eq. (6) is related to the probability of finding the electron at the nucleus and it is, for this reason, sometimes called the "contact interaction."\(^7\)

This interaction was first derived by Fermi,\(^8\) proceeding from the Dirac equation, but much simplified semi-classical developments have more recently been made.\(^9-14\)

The appropriate Hamiltonian for an interacting nucleus with the unpaired electron on an ion in dilute solution is written

$$\hat{\mathcal{H}} = \gamma_e \vec{S} \cdot \vec{H}_0 - \gamma_n \vec{I} \cdot \vec{H}_0 + a \vec{I} \cdot \vec{S},$$

where the first term is the Zeeman interaction of the electron with the external field [Eq. (1)], the second term is likewise the Zeeman interaction of the nucleus with the external field, and the third term is the non-vanishing portion of Eq. (6),
where the short-hand definition

$$\alpha = \frac{\hbar}{3} \gamma_n \frac{\hbar^2}{\gamma_n} \delta(\vec{r})$$

(8)

has been made. In ESR spectroscopy the nuclear Zeeman term plays no essential role (it merely adds a constant to each energy level) so the Hamiltonian of interest reduces to

$$\hat{H} = \gamma_n \vec{S} \cdot \vec{H}_0 + \alpha \vec{I} \cdot \vec{S}.$$  

(9)

If $H_0$ is sufficiently large, the Zeeman term in Eq. (9) will be much larger than the hyperfine term, and the eigenvalues of the Hamiltonian operator can be found from first-order perturbation theory to be

$$E(m_L, m_s) = \gamma_n \hbar^2 \vec{H}_0 m_s + \alpha m_I m_s,$$

(10)

where $m_I$ is any one of the eigenvalues $[I, I-1, I-2, \ldots, -(I-1), -I]$ of the $z$ component of the nuclear angular momentum operator. Carrington and McLachlan detail this problem and also carry it to the second order.

From Eqs. (2) and (10) it is seen that the contact interaction splits each electronic Zeeman level into a $2I + 1$ multiplet with successive level spacings equal to $\Delta m_s = \hbar a$. The ESR selection rules $m_s = \pm 1, m_I = 0$ permit transitions such that

$$\Delta E = \gamma_n \hbar^2 \vec{H}_0 + \alpha m_I$$

(11)
The single Zeeman transition of Eq. (3) is thus split into $2I + 1$ allowable transitions by the hyperfine field and, in fixed $H_o$, transitions may be excited at any one of a set of $2I + 1$ equally-spaced Larmor frequencies

$$\omega = \gamma_e H_o + \alpha m_I / \gamma_n .$$

Conversely, for a fixed operating frequency $\omega$, transitions will occur at any one of a set of $2I + 1$ external fields given by

$$H_o = \omega / \gamma_e - \alpha m_Z / \gamma_n .$$

The number of observed hyperfine components fixes the spin of the interacting nucleus, and the separation between adjacent hyperfine spectrum components measures the hyperfine constant $\alpha$ [Eq. (8)].

Equations (9) - (13) may easily be generalized to account for the interaction of a single electron with $n$ nuclei. The Hamiltonian becomes, following Eq. (9),

$$\mathcal{H} = \gamma_e \vec{S} \cdot \vec{H}_o + \sum_{i=1}^{n} \alpha_i \vec{I}_i \cdot \vec{S}$$

with eigenvalues

$$E = \left[ \gamma_e \vec{S} \cdot \vec{H}_o + \sum_i (\alpha m_i) \right] m_s$$

and allowed ESR transitions

$$\Delta E = \gamma_e \vec{S} \cdot \vec{H}_o + \sum_i (\alpha m_i) .$$
Thus, for example, a nucleus with \( I = \frac{1}{2} \) (such as \(^1\text{H}\) or \(^{19}\text{F}\)) would split the ESR spectrum into two equally intense lines. A nucleus with \( I = 1 \) (such as \(^2\text{D}\) or \(^{14}\text{N}\)) would split the ESR spectrum into three equally intense lines. Two nuclei with \( I = \frac{1}{2} \) would produce a four-line spectrum, two nuclei with \( I = 1 \) would produce a nine-line spectrum, and one nucleus with \( I = \frac{1}{2} \) and one with \( I = 1 \) would produce a six-line spectrum. Generally, the number of hyperfine lines is given by

\[
N = \sum_{i=1}^{n} (2I_i + 1),
\]

where \( n \) is the number of nuclei coupled to a single electron, and \( I_i \) is the spin number for the \( i^{th} \) nucleus.

If any two \( \alpha_i \) in Eq. (16) are identical, as will frequently occur in symmetric molecules, then the number of discrete hyperfine levels [Eq. (15)] is reduced and the intensities of the transitions between degenerate levels correspondingly increased. It can be shown\(^\text{17}\) that \( n \) equivalent nuclei (same \( \alpha_i \)) give rise to \( 2nI + 1 \) lines with relative intensities which are proportional to the coefficients of the binomial expansion \((1 + x)^n\). The complexity of the spectra of molecular ions thus increases rapidly with the number of magnetic nuclei, and analysis can be next to impossible unless there are such simplifications as large numbers of equivalent nuclei or widely differing values for the \( \alpha_i \).
Since the atomic wave functions for hydrogen are well known, the hyperfine field can be calculated directly to be 506.8 gauss.\textsuperscript{18} The hyperfine fields at protons in complex molecular ions, however, are always much smaller because the unpaired electron is distributed over many atoms. Thus, for example, one could explain an observed five-oersted proton splitting in a complex molecule either by saying that a highly mobile unpaired electron spends about one percent of its time in the 1s orbital of that particular hydrogen atom or by saying that the spins of the electrons bound to that nucleus are slightly unpaired, with a net magnetic moment equal to one percent of that of a free electron. This latter viewpoint is particularly fruitful in explaining the observed proton hyperfine splittings in aromatic free radicals where the probability for finding the unpaired electron (\pi-orbital) at a proton site is zero. One simply assumes that the presence of the magnetic unpaired electron of a neighboring carbon atom polarizes the adjacent electron cloud about a bonded proton. McConnell\textsuperscript{19-23} has, in fact, shown that this polarization is directly proportional to the probability of finding the unpaired \pi-electron on an adjacent carbon atom, and the resulting polarization of the proton-electron cloud has been analyzed in detail in terms of a superposition of atomic electron configurations.\textsuperscript{19,20,24-26} The theory provides for both positive and negative spin polarizations,\textsuperscript{27,28} a difference to which the ESR experiment is essentially insensitive [\textit{i.e.}, the set specified by Eq. (1)]
is independent of the sign of the hyperfine constant. The existence of both positive and negative polarizations within the same molecular ion has been demonstrated unambiguously from low-temperature nuclear magnetic resonance data.\textsuperscript{29,30}

An essentially endless number of paramagnetic species in solution may be prepared by reacting (in sulfuric acid, for example) hydrocarbons, or their derivatives, to form position ions or by reducing the same substances with sodium or potassium in a good charge-transfer solvent to form negative ions. The work reported here is a study of the hyperfine interaction observed in the negative benzophenone phenylhydrazine ion in dilute solution.
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CHAPTER III

EXPERIMENTAL APPARATUS

A block diagram for the X-band ESR spectrometer constructed for this investigation is shown in Fig. 1. The apparatus was modelled after conventional designs, utilizing a hybrid tee in a microwave bridge with video detection.¹

The microwave source was a Varian Associates Model X-13 reflex klystron powered by a Hewlett-Packard Model 716B regulated power supply and decoupled from the rest of the microwave apparatus by a 20 dB ferrite isolator. The klystron was thermally lagged in approximately three quarts of transformer oil, and the filaments were powered from a regulated dc source. These precautions were sufficient to insure the required degree of source stability for this investigation without the necessity for electronic frequency stabilization.

The attenuator following the isolator, a Hewlett-Packard X382A, was used to reduce the nominal klystron output of a few hundred milliwatts to a convenient operating level, usually between one and ten milliwatts. The operating frequency of the klystron was determined with a direct-reading cavity wavemeter, a Waveline Model 698DR.

The heart of the microwave system shown in Fig. 1 is the hybrid tee. The essential feature of this device is that power
Figure 1--Block diagram of spectrometer.
fed into any one of the four arms is divided equally between the two adjacent arms, and no power is transferred to the opposite arm if the two adjacent arms are terminated in equal impedances. If the two terminating impedances are not equal, then there is a transfer of power to the opposite arm, the transfer being proportional to the mis-match. This four-terminal network thus has the properties of a bridge circuit. In a microwave spectrometer the experimental sample forms part of the terminating impedance for one of the side arms. Resonance absorption modifies this impedance and thus unbalances (or changes the initial unbalance of) the bridge. Detailed analyses of hybrid-tee impedance bridges may be found elsewhere.

The experimental sample in a microwave ESR spectrometer is usually placed in a resonant cavity, preferably in a region of high microwave magnetic field to enhance the magnetic dipole transition probability and in a region of low microwave electric field to minimize dielectric heating losses. It has been shown that the resonant absorption of power from a material specimen in a microwave cavity reduces the $Q$ of the cavity and simultaneously shifts the frequency of the cavity. If the experimental sample in a cavity terminates one arm of a microwave bridge (as in Fig. 1), the small changes in $Q$ and in cavity frequency affect the equivalent impedance of the cavity in such a way that $\Delta Q$ changes only the amplitude of the signal reflected from the cavity and $\Delta \omega_c$ changes only the phase of the signal reflected from the cavity.
The $\text{TE}_{102}$ cavity$^6$ employed in the spectrometer described here was constructed from a short length of standard copper X-band waveguide. The cavity is shown schematically in Fig. 2. The inside dimensions were 0.40 x 0.90 x 1.85 inches. A 4-40 teflon screw was centered in the end of the cavity for fine tuning. The nominal frequency was 8.90 GHz. The cavity was not silvered and had a $Q$ of about 3000. The cavity was coupled to the waveguide system through a circular iris 0.286 inches in diameter in a five-mil brass sheet forming one end of the cavity. This iris geometry was chosen experimentally to provide critical coupling for the cavity (i.e., perfect impedance match and no reflection of incident power) at the operating frequency.

The bridge arm opposite the cavity was terminated in a matched resistive load so as to balance the bridge. The slide-screw tuner$^7$ shown in series with the matched load was included so that deliberate mis-matches could be introduced into the bridge. The particular microwave detector elements (1N23-series silicon diodes) employed in this spectrometer were more sensitive when biased with a quiescent operating current of about 100 microamperes,$^8$ and deliberate bridge unbalance was used to provide this biasing. Furthermore, the bridge could be made insensitive to one or the other of the cavity changes $\Delta Q$ or $\Delta \omega_b$ by careful adjustment of the phase of the deliberate mis-match.$^9,10$ In this particular study the bridge was always adjusted to be insensitive to small changes in the cavity resonant frequency. This choice was made to simplify the interpretation of the observed
Figure 2—Schematic diagram of TE$_{102}$ cavity.
spectra since it has been shown\textsuperscript{11} that $\Delta Q$ is proportional to the power absorbed by the sample at magnetic resonance.

The magnetic field $H_0$ of approximately 3200 gauss was provided by a Varian Associates Model 3600 electromagnet with Model V-FR2503 field-regulated power supply. The twelve-inch magnet poles were tapered to nine inches at the 2.25-inch air gap, and the field was homogeneous to three parts in $10^5$ over a 2.75-inch circle at the center of the gap. This homogeneity far exceeded the requirements of this experiment. The magnet power supply included a motorized drive unit which was used to sweep $H_0$ linearly with time for signal-recording purposes. The field could be swept as slowly as $2.5 \times 10^{-3}$ gauss/min and (over a limited range) as rapidly as $8 \times 10^4$ gauss/min.

In order that ac detection techniques could be used, the magnetic field was sinusoidally modulated at 400 Hz. This modulation was effected by passing a small alternating current through a set of series-connected single-layer pancake coils cemented to the face of each magnet pole cap. These modulation coils were calibrated with a pickup coil of known area and number of turns connected to an ac voltmeter. At 400 Hz the modulation coils produced 4.52 gauss peak-to-peak for each volt rms of applied driving signal.

The 400 Hz resonance absorption signals were detected with a 1N23-series silicon diode in one arm of the microwave bridge, processed with a Tektronix Model 122 pre-amplifier and Electronics, Missiles and Communications, Inc., Model RJB lock-in
amplifier, and displayed on a Beckman Model 1005 strip-chart recorder. The 400 Hz field modulation signal and the lock-in amplifier reference signal were derived from a Hewlett-Packard Model 200D audio oscillator.

Before the benzophenone phenylhydrazone experiments were begun, the entire ESR apparatus was tested against several samples with known ESR spectra. Figure 3 shows the first derivative of the absorption spectrum of the peroxylamine disulfonate anion radical \( \text{ON}(\text{SO}_3)_2^- \) in \( 10^{-2} \text{ M} \) aqueous solution. The ion has an odd number of electrons and so might be expected to exhibit the paramagnetic properties of a single-electron system (with all remaining electron spins paired off). The only magnetic nucleus in the ion is \( ^{14}\text{N} \), a particle with \( S = 1 \), so a hyperfine spectrum of three lines of equal intensity would be expected. The thirteen-gauss separation between hyperfine components shown in Fig. 3 is in agreement with the work of Pake et al. \(^{13}\) and of Powels and Moseley. \(^{14}\)

Figure 4 shows the first derivative of the absorption spectrum of a small speck of the solid free radical DPPH (Diphenyl picrylhydrazyl). \(^{15}\) The line width of 3.2 gauss between maximum and minimum slopes is in agreement with that reported by Goldsborough et al. \(^{16}\) Because of the very strong single-line spectrum obtained from this substance it is very frequently used as a standard for adjusting spectrometers and comparing their sensitivities.
Figure 3—First-derivative absorption spectrum of peroxylamine disulfonate anion radical in $10^{-2}$M aqueous solution.
Figure 4—First-derivative absorption spectrum of solid DPPH.
If DPPH is prepared in dilute solution so that intermolecular magnetic interactions are negligible, then a hyperfine structure appears. Figure 5 shows the five-line hyperfine spectrum obtained from a $0.49 \times 10^{-3}$ M solution of DPPH in benzene. This spectrum has been explained by postulating that the single unpaired electron on each radical is equally coupled to two nitrogen nuclei and negligibly coupled to the remaining magnetic nuclei in the molecule. Such a model gives a five-line spectrum with relative intensities in the ratio $1:2:3:2:1$. A computer analysis of the spectrum of Fig. 5 yields relative intensities of $1:2:4:2:1$. The extra contribution to the central line could easily be due either to a small amount of undissolved DPPH in the sample or to simple paramagnetic impurities in the material.

The concentration of the sample used to obtain Fig. 5 was successively reduced until the resonance signal vanished in the noise. In this way it was determined that the absolute detection sensitivity of the apparatus was roughly $10^{16}$ spins for this 50-gauss-wide spectrum. If all of the intensity of the signal of Fig. 5 were in the central component of the spectrum rather than distributed among five (which arise from nine different transitions), the central amplitude would be nine times greater and the minimum number of detectable spins would be approximately $10^{15}$. Spectrometer sensitivities, however, are usually compared for hypothetical lines of one-gauss width. Since the intensity of an absorption line is proportional to the amplitude and to the square
Figure 5: First-derivative absorption spectrum of DPPH in 4.9 x 10^-4 M benzene solution.
of the width of the derivative display\textsuperscript{18} whereas the signal-to-noise ratio depends only on the amplitude, the measured sensitivity may be reduced to that for a one-gauss line by dividing by the square of the width of one of the components in the spectrum of Fig. 5. An estimated component width of five gauss then yields an absolute spectrometer sensitivity of $4 \times 10^{-13}$ spins in a one-gauss line. This compares favorably with the best sensitivities reported.\textsuperscript{19}
REFERENCES


2. Ibid., Ch. 5.


6. Poole, op. cit., p. 264.

7. Ibid., p. 239.

8. Ibid., p. 436.


The literature on DPPH is tremendous. Poole, op. cit., pp. 863-867, gives a bibliography with 69 entries.

Poole, op. cit., p. 551.

Feher, op. cit.
The negative ion radical of benzophenone phenylhydrazone (BPPH) \[ \left[ \left( \text{C}_6\text{H}_5 \right)_2\text{C:NNH}_6\text{H}_5 \right] \] was prepared in solution in the following manner. A pyrex sample tube 10 cm in length by 0.30 cm i.d. was filled with tetrahydrofuran, and a small lump of metallic potassium was added to the solvent. The contents of the sample tube were then allowed to boil (in a hot water bath) for five or six minutes to drive off any dissolved oxygen in the solvent. This process also melted the potassium, removing oxidation products from the surface and depositing them as an insoluble residue in the bottom of the sample tube. The hydrazone was then added to the sample tube and the tube and contents were placed in a 0°C ice bath. Ten to twelve minutes later the colorless diamagnetic solution turned to a dark red. The sample was immediately transferred to the cavity of the microwave spectrometer, and electron spin-resonance absorption was observed.

At an ion concentration of approximately \( 10^{-1} \text{M} \) the resonance signal consisted of a single line at a field corresponding closely to \( g = 2.00 \), indicating the practical absence of any orbital contribution to the electronic angular momentum and the effective "free spin" character of the elementary paramagnets. Figure 6 shows the spectrum from a \( 2 \times 10^{-3} \text{ M} \) solution, with at
Figure 6—First-derivative absorption spectrum of benzophenone phenylhydrazone negative ion in 2 x 10⁻²M tetrahydrofuran solution.
least five hyperfine components clearly visible. Further dilution produced no improvement in the resolution of the spectrum. The samples decomposed slowly, on the time scale of a few hours, with the color of the solution and the intensity of the ESR signal vanishing simultaneously.

The radical ion may be considered as simply the BPPH molecule with an extra added electron in a highly delocalized orbital spreading over a large portion of the molecule. If this delocalized and unpaired electron were to interact with every magnetic nucleus in the molecule (two $^{14}\text{N}$ with $I = 1$ and sixteen $^{1}\text{H}$ with $I = 1/2$), each Zeeman level would be split into 589,824 hyperfine components. Table I shows the various possibilities if no two nuclei are equally coupled to the electron. The fact that the observed number of lines in Fig. 6 is a small number which does not appear in Table I indicates that there may be approximately equal couplings to two or more nuclei, and/or there is significant localization of the electron orbital, and/or the recorded figure is just an average of a much more complicated unresolved spectrum. Some combination of all three is probably.

The five-line spectrum of Fig. 6 suggests in analogy with DPPH (cf. Fig. 5) the possibility of equal interaction of the electron with the two central $^{14}\text{N}$ nuclei in the molecule and negligible interaction with any others. This possibility was investigated by means of a computer curve fitting to Fig. 6 with fifteen free parameters. The spectrum was assumed to consist of five Lorentzian-shaped lines with the locations, half widths and
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<td>12,288</td>
<td>36,864</td>
</tr>
<tr>
<td>13</td>
<td>8,192</td>
<td>24,576</td>
<td>73,728</td>
</tr>
<tr>
<td>14</td>
<td>16,384</td>
<td>49,152</td>
<td>147,456</td>
</tr>
<tr>
<td>15</td>
<td>32,768</td>
<td>98,304</td>
<td>294,912</td>
</tr>
<tr>
<td>16</td>
<td>65,536</td>
<td>196,608</td>
<td>589,824</td>
</tr>
</tbody>
</table>
amplitudes of each unspecified. Figure 7 shows the best fit superimposed on recorded data points. Table II gives the computer values for the parameters of each constituent line. The curve fit to the data is obviously excellent, but whether the details of Table II represent real physical information is uncertain. The intensity ratios for the five lines (proportional to $ab^{-1}$ in Table II) stand approximately as 1:5:12:5:1, whereas the required ratios for equal coupling to two nuclei with $I = 1$ is 1:2:3:2:1. Figure 6 is therefore not a "two-nitrogen" hyperfine spectrum unless it is perhaps superimposed on some broad single-line unknown background with large absorption amplitude at the center of the spectrum.

One may approach the analysis in a different way by taking the 1:5:12:5:1 intensity ratios as given and trying to construct any sort of consistent spectrum. A 1:5:12:5:1 intensity pattern, for example, suggests that each Zeeman level might actually consist of twenty-four $(1 + 5 + 12 + 5 + 1)$ separate levels falling more or less into five distinguishable groups. From Table I one sees that twenty-four lines is a possibility, provided the principal coupling of the unpaired electron is with one nitrogen nucleus and three protons. Further examination shows, however, that there is no way to produce the required spectrum from the specified components.

The data in Table II, showing that the best-fit computer spectrum consists of unequally spaced lines (column c) of unequal
Figure 7—Computer simulation of BPPH spectrum.
### TABLE II

**COMPUTER ANALYSIS DATA FOR THE BPPH SPECTRUM**

<table>
<thead>
<tr>
<th>Line</th>
<th>a</th>
<th>b</th>
<th>c</th>
<th>$ab^{-\frac{1}{2}}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>24.3767</td>
<td>0.102927</td>
<td>-12.8244</td>
<td>75.94</td>
</tr>
<tr>
<td>2</td>
<td>83.6970</td>
<td>0.043578</td>
<td>-6.68989</td>
<td>402.4</td>
</tr>
<tr>
<td>3</td>
<td>161.234</td>
<td>0.027939</td>
<td>-0.03272</td>
<td>971.3</td>
</tr>
<tr>
<td>4</td>
<td>84.5871</td>
<td>0.042679</td>
<td>6.66943</td>
<td>410.6</td>
</tr>
<tr>
<td>5</td>
<td>23.9777</td>
<td>0.104839</td>
<td>12.8339</td>
<td>74.00</td>
</tr>
</tbody>
</table>

$$y = \frac{a}{1 + b(x - c)^2}$$
widths (column b^{-k}) suggest that a more ambitious program might be in order. Since the widths decrease with distance from the center of the spectrum, one might consider a nine-line spectrum grouped in clusters like 1:2:3:2:1. This pattern is what one would expect from coupling to two nitrogen nuclei with slightly differing coupling coefficients. One might be able (with a larger computer) to construct a good fit to the spectrum with nine such lines having some regularity in the spacing and half-widths. The intensity problem would seem to remain, however. It is difficult to visualize any way in which a spectrum could be constructed so as to fall anywhere near a 1:5:12:5:1 pattern without some mixture of different paramagnetic species.

There remains the possibility that the 1:5:12:5:1 requirement is artificial even though specified by the computer best fit. The best-fit program is not inherently intensity-conserving. Thus, if one were to construct an artificial spectrum by superimposing two equal Lorentzian lines and then determine the best-fit approximation of a single Lorentzian line to this composite, one might reasonably inquire about the relationship between the intensity (area under the curve) of the real spectrum and its simpler approximation. The relationship will clearly be one-to-one as the spacing goes to zero, but for large spacings this is not at all apparent. If, in fact, this relationship is very sensitive to spacing at small separations, then the 1:5:12:5:1
sequence may really be without useful meaning. This rather simple mathematical problem would seem to merit independent investigation.

One may also suggest that the spectrum of Fig. 6 might be better resolved by alternate experimental techniques. If the appropriate relaxation mechanisms, as well as sufficient microwave power, are available, then the ENDOR double-resonance approach might be fruitful. If the ion can be prepared in sufficiently high concentration, then low-temperature NMR may also be helpful. Either approach should simplify both the experimental spectrum and its analysis, since proton and nitrogen contributions to the hyperfine structure would be completely separated.
REFERENCES


3. The IBM-1620 curve-fitting procedure was programmed by Prof. H. J. Mackey.


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