1969

Studies of Alpha NitronylNitroxide Radicals and Diradicals Using Electronspin Resonance and Optical Spectroscopic Techniques.

Joseph Albert D'anna Jr
Louisiana State University and Agricultural & Mechanical College

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STUDIES OF ALPHA NITRONYLNITROXIDE RADICALS AND DIRADICALS USING ELECTRON SPIN RESONANCE AND OPTICAL SPECTROSCOPIC TECHNIQUES.

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SPECTROSCOPIC TECHNIQUES

A Dissertation
Submitted to the Graduate Faculty of the
Louisiana State University and
Agricultural and Mechanical College
in partial fulfillment of the
requirements for the degree of
Doctor of Philosophy

in
The Department of Chemistry

by
Joseph A. D'Anna, Jr.
B.S., Southeastern Louisiana College, 1965
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ABSTRACT

This Dissertation is concerned with the study of α-nitronyl-nitrooxide radicals and diradicals by means of electron spin resonance (E.S.R.) and optical spectroscopic techniques. Specifically, the doublet compounds--α-methylnitronylnitrooxide, α-phenylnitronyl-nitrooxide and α-(o-tolyl)nitronylnitrooxide--and the "triplet" molecules--1,2-bis-(α-nitronylnitrooxide)ethane, 1,3-bis-(α-nitronyl-nitrooxide)propane and bis-(α,α'-nitronylnitrooxide) are investigated. The E.S.R. spectra and the electronic absorption spectra have been measured for all compounds. For some of the compounds, these measurements have been made as functions of solvent and temperature.

The electronic spectra indicate that the transitions common to most of the compounds are $\pi \rightarrow \pi^*$ in origin. Solvent studies reveal that the ground state is more polar than the first two excited states. Disproportionately large energy shifts in protic solvents (i.e., ethanol and water) are attributed to hydrogen bonding. No luminescence is observed for any of the compounds.

Solution E.S.R. studies as a function of solvent show changes in the isotropic hyperfine splittings. The effects are quite small, but careful measurement, recalculated line positions, and line width considerations show the effects to be real. There appear to be corresponding changes in the $g$ value, but the limit of random error precludes a definite statement.

From the E.S.R. studies on single crystals, polycrystalline samples, room temperature solutions and 77°K rigid glass solutions,
the symmetry of and spin densities associated with the highest half-filled molecular orbital have been determined. The extent of spin orbit coupling, indicated by the elements of the g tensor, is determined from measurements on single crystals and powder samples. The components of the g tensor are restricted such that $2.004 \leq g \leq 2.010$. From the single crystal E.S.R. spectrum of $\alpha$-methylnitronylnitroxide, it is estimated that the exchange energy between molecules in the crystal is about $0.7 \text{ cm}^{-1}$. This information is valuable in the analysis of the singlet-triplet splitting in the diradical molecules.

Rigid glass solution E.P.R. spectra show that the unpaired electron distribution is essentially the same in all the doublets studied. The unpaired electron occupies a pi-orbital which transforms as $b_1$ with respect to the $C_{2v}$ symmetry of the nitronylnitroxide group itself. The unpaired electron occupies each nitrogen pi-orbital $0.30$ of the time. An "extended Hückel" calculation involving all valence electrons gives results which are in poor agreement with experiment. The discrepancy is attributed to neglect of electron repulsions in the calculations.

Optical and E.S.R. spectra indicate that the compounds, $1,2$-bis-$(\alpha$-nitronylnitroxide)ethane and $1,3$-bis-$(\alpha$-nitronylnitroxide)propane, should be classified as diradicals. Although one observes zero-field splittings in the E.S.R. spectra in rigid matrices, it is inferred--from the E.S.R. powder spectrum--that the singlet and triplet levels of the molecule are nearly degenerate. The chemical
species that one observes in the rigid glass E.S.R. spectra depend upon the nature of the matrix. Pertinent equilibria and chemical species are postulated to interpret the experimental results.

Similar measurements are made for bis-(α,α′-nitronylnitroxide), but the conclusions are uncertain.

Zero-field splittings are calculated for molecular models of 1,2-bis-(α-nitronylnitroxide)ethane and 1,3-bis-(α-nitronyl-nitroxide)propane for selected geometries. The experimental spin-densities, obtained from analysis of the doublet molecules, are used in the calculation. The purpose of the calculations is to associate zero-field splittings with some conformations of the molecules.
INTRODUCTION

A new class of very stable neutral radicals--α-nitronyl-nitroxides (Figure 0.1)--was reported\(^1\) in February 1968. These radicals show sufficient thermal stability and lack of reactivity with oxygen so that the ground state may be characterized. This unusual stability suggested that two nitronylnitroxide groups could be joined by a hydrocarbon bridge to make stable diradicals (Figure 0.2). Such diradicals would have Zeeman energy levels which are dependent upon the mutual orientation of the molecular axes and the magnetic field. The anisotropy of the energy levels could, perhaps, allow these diradicals to be used as sensitive probes in semicrystalline materials (i.e., liquid crystals and micelles). The objective of the research was not to characterize the radical environment, however. The purpose was to characterize the electronic ground state and to select theoretical models to account for observed magnetic interactions. Such knowledge is necessary before the radicals and diradicals can be of use as probes.

Since the compounds were not readily available, it was necessary to prepare many of the desired radicals in these laboratories. The doublet radicals--α-methylnitronylnitroxide (α-MNN), α-phenyl-nitronylnitroxide (α-φNN), α-(o-tolyl)nitronylnitroxide (α-oTNN)--and the diradical, 1,3-bis-(α-nitronylnitroxide)propane (1,3-BNPP) were prepared. 1,2-bis-(α-nitronylnitroxide)ethane (1,2-BNNE) and

**FIGURE 0.1.** $\alpha$-R-nitronyl nitroxide.

**FIGURE 0.2.** Proposed Bis-($\alpha$-nitronyl nitroxide)$R'$ diradicals.
bis-(α,α-nitronylnitroxide)(BNN) were obtained elsewhere. As expected, the diradicals are very stable and amenable to study. As we shall see, solvent and temperature effects are very important to the diradicals. Solvent effects are also important to the parent doublet radicals.

This Dissertation is divided into four chapters. Chapter I, "Theoretical Bases", provides the reader access to the theory used in the interpretation of the experimental results. In Chapter II, the synthesis of the compounds, the purification of the solvents and the details of the experimental measurements are discussed. Chapter III deals with the interpretation of the experimental results of the doublet radicals. Many of the E.S.R. results of the doublet molecules are summarized in Section C of that chapter. Chapter IV is concerned with the experimental results and theoretical models of the diradicals.

Chapters I and II are quite long and detailed. It is hoped that these chapters and the references therein will be helpful to future workers in these laboratories. In an effort to be complete, the writer may have been somewhat verbose. For this, he apologizes.

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2 E.F. Ullman, Research Director of Synvar Research Institute, kindly sent us these compounds.
I. THEORETICAL BASES

(A) Hamiltonians for Doublet Molecules

The magnetic interaction hamiltonian for a single doublet molecule in a static magnetic field is frequently expressed as

\[ \mathcal{H} = g \mathbf{H} \cdot \mathbf{g} \cdot \mathbf{S}_f + \sum_{i=1} \mathbf{S}_f \cdot \mathbf{T}_i \cdot \mathbf{I}_i \]

in which

- \( g = \) Bohr magneton \((\mathbf{0.92731 \times 10^{-20}} \text{ erg/gauss})\)
- \( \mathbf{H} = \) Magnetic Field Vector
- \( \mathbf{g} = \) g tensor
- \( \mathbf{S}_f = \) "ficticious spin vector operator"
- \( \mathbf{T}_i = \) hyperfine tensor \((i)\)
- \( \mathbf{I}_i = \) nuclear \((i)\) spin vector

The nuclear Zeeman energy effects are sufficiently small that they may be neglected in a first order treatment of the electron spin resonance (E.S.R.) spectra encountered in this work.

The g tensor is a mathematical contrivance which includes the effects of spin-orbit coupling, while avoiding explicit inclusion of the orbital angular momentum operator in the hamiltonian. The true form of the first term in equation 1 is \( g_e \mathbf{g} \mathbf{H} \cdot \mathbf{S} + \mathbf{g} \mathbf{H} \cdot \mathbf{L} \) in which \( \mathbf{S} \) is the true spin vector operator, \( \mathbf{L} \) is the angular momentum vector operator and \( g_e \) \((2.002322)\) is the ratio of the magnetic moment to
the spin angular momentum for a free electron.

For molecules that have non-degenerate ground states, the orbital angular momentum is "quenched" (i.e., \(\langle \mathbf{L} \rangle = 0\)). Spin-orbit coupling provides a means by which the "unpaired electron" may acquire orbital angular momentum. In atomic systems this coupling is approximated as \(\zeta \mathbf{L} \cdot \mathbf{S}\) in which \(\zeta\) is a constant for a given orbital on a given atomic center. In the case of molecules made up of several different elements, \(\zeta\) is no longer a constant but is best represented as a function of position. The usual approximations in L.C.A.O. models is to express \(\mathbf{L} \cdot \mathbf{S}\) as \(\sum \zeta_k \mathbf{L}_k \cdot \mathbf{S}\) in which \(\zeta_k\) is the atomic spin-orbit coupling constant. \(\mathbf{L}_k\) is the corresponding atomic orbital (A.O.) orbital angular momentum operator.

Although illustration of the introduction of fictitious spin is not particularly difficult, it is well treated by Carrington and McLachlan\(^2\) and need not be repeated. Suffice it to say that a new set of functions and operators having the operational properties of the true spin wave functions and operators are introduced along with the g tensor. Their introduction eliminates the use of very unwieldy wavefunctions.

The elements of the g tensor expressed in terms of molecular orbitals made up of orthonormal basis functions are given by\(^2\)

\[
\begin{align*}
E_{ij} &= 2.0023 - 2\sum_{n,k,\ell} \frac{\langle \psi_0 | \zeta_k \mathbf{L}_{e_i} \delta_k \mathbf{L}_{e_j} \delta_{\ell} \psi_n \rangle}{E_n - E_0} \ldots 2
\end{align*}
\]


in which ψ₀ is the ground state molecular orbital having energy E₀, and ψₙ are excited state M.O.'s of energy Eₙ.

\[ ψ₀ = \sum_{\alpha k} ϕ_k \]

\[ ψₙ = \sum_{\alpha k} ϕ_k \]

The \( ϕ_k \) are the basis functions.

Since the elements of the g tensor for organic molecules vary only to the extent of a few parts (0-4) per thousand from \( g_e \), the distinction between fictitious spin and true spin is generally neglected. Thus, in further discussions \( S_f \) shall be treated as \( S \).

The second term in equation 1 describes the interaction of the unpaired electron with paramagnetic nuclei. Each of the nuclear interaction terms \( \vec{S} \cdot \vec{T} \cdot \vec{I}_i \) may be expanded. Including the integration of the spatial wavefunctions over all space, one obtains equation 3 in which

\begin{align*}
(1) \quad & \langle \psi | \vec{S} \cdot \vec{T} \cdot \vec{I} | \psi \rangle = \int |\phi(\vec{r})|^2 \frac{8\pi}{3} g_N g_e g_B \vec{I} \cdot \vec{S} \ d\tau \\
(2) \quad & - g_N g_e g_B \int |\psi(\vec{r})|^2 \left[ \frac{\vec{S} \cdot \vec{I}_i}{r_i^3} - \frac{3}{5} \frac{(\vec{S} \cdot \vec{I}_i)(\vec{I} \cdot \vec{r}_i)}{r_i^5} \right] \ d\tau \quad \ldots 3
\end{align*}

\( r_i \) is the distance of the unpaired electron from the \( i \)th nucleus. Part (1) in equation 3 arises from the Fermi interaction and is isotropic. It is generally written as

\[ a \vec{S} \cdot \vec{I} \quad \ldots 3(a) \]
in which \( a = \frac{8\pi}{3} g_\beta g_N N |\psi(o)|^2 \). The "hyperfine splitting constant", \( a \), has units of energy, and \( |\psi_0|^2 \) is the spin density at the nucleus. In terms of hydrogen-like basis functions, only \( s \) orbitals will show hyperfine splitting. One should also realize that \( |\psi(r)|^2 \) is a probability per unit volume; and as such, \( |\psi(o)|^2 \) may be much greater than 1 (i.e., \( |\psi(o)|^2 = 2.148 \times 10^{24} \) electrons/cm\(^3\) for atomic hydrogen). In order for \( |\psi(o)|^2 \) to be a useful quantity in molecular orbital elucidation, an experimental or theoretical nuclear spin density for an A.O. basis function must be available. In a rigorous treatment, one would average over the spins and coordinates of all electrons to obtain the net spin density at the \( i \)th nucleus. It is generally assumed, however, that unpaired electrons in a given M.O. contribute to the spin density at the nucleus \textit{via} the valence A.O.'s on the atom. Thus the percent of the time that an "unpaired electron" occupies a given \( s \) orbital is given by

\[
\text{% occupancy} = \frac{\rho_{\text{observed}}}{\rho_{\text{max}}} \quad \ldots 4
\]

in which \( \rho_{\text{observed}} \) is the electron spin density at the nucleus (calculated using equation 3(a)), and \( \rho_{\text{max}} \) is the spin density assuming that the electron spends all of its time in the space defined by the "s" A.O.

The second term (2) in equation 3 represents the electron-nuclear magnetic dipolar interaction which is anisotropic. In terms
of the principal axes relative to ith nucleus, (2) may be written as

$$H_{\text{dipolar}} = -t'_{xx} S_{xx} - t'_{yy} S_{yy} - t'_{zz} S_{zz} \quad \ldots \ldots 5$$

in which $t'_{xx}$, $t'_{yy}$ and $t'_{zz}$ are diagonal tensor elements. The magnitude of $t_{xx}$, $t_{yy}$ and $t_{zz}$ can provide information about the type of orbital which the unpaired electron occupies. Since a is isotropic, the relation of the diagonal elements to $a$ and $\hat{T}'$ may be expressed

$$t_{xx} = a + t'_{xx} \quad \ldots \ldots 6$$
$$t_{yy} = a + t'_{yy}$$
$$t_{zz} = a + t'_{zz}$$

It may be concluded that a great deal of information regarding the nature of the electronic ground state of a doublet molecule may be obtained from E.S.R. studies. However, it is most often necessary to orient molecules in the magnetic field to obtain that information most completely. Orientation is best achieved by substituting doublet molecules in lattice sites of suitable single crystals. Since suitable host crystals are not necessarily available, it is fortunate that alternate methods are available by which much information may be obtained. Some of these methods are: E.S.R. spectra of single crystals of doublet molecules; the E.S.R. spectra

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in rigid glassy solutions; and the E.S.R. spectra in solutions of low viscosity. The collective use of these methods provides the means by which to elucidate the information that is obtained in studies of oriented dilute crystals.

The hamiltonian for doublet molecules in pure single crystalline form may be written\(^4\) as

\[
\mathcal{H} = g\beta \sum_j S_j^z + \sum_{j<k} \mathcal{A}_{jk} S_j \cdot S_k + g^2 \sum_{j<k} \left\{ \frac{3(r_{jk} \cdot S_j)(r_{jk} \cdot S_k)}{r_{jk}^3} \right\} \ldots 7
\]

in which \(g = 1/3(g_{xx} + g_{yy} + g_{zz})\). The first term represents the Zeeman energies, the second term is the "exchange interaction", and the last term is the magnetic dipolar interaction between unpaired electrons.

In a more general treatment the first term should contain the \(g\) tensor (\(\mathcal{g}_1\)) of the individual molecules.\(^5\) The Van Vleck treatment has been generalized to include \(g\) tensors.\(^6\) In the exchange term, \(\mathcal{A}\) is related to the exchange energy, \(J_{1j}\),

\[
\mathcal{A}_{jk} = 2J_{12} \ldots 8
\]


The exchange term is electrostatic in origin. However, as a result of Fermi statistics, it is directly related to the spin functions and may be conveniently included with the spin hamiltonian. (The origin of the exchange term shall be discussed in greater detail in Section E of this chapter). The electron-electron dipolar coupling terms lead to broadening of the E.S.R. spectrum since it increases the number of possible energy levels for the electrons in the magnetic field. Nuclear-electron dipolar interaction terms have been neglected as they would only contribute to further spectral broadening. Van Vleck\(^4\) has shown by a method of moments that the resonance should show peaking ("exchange narrowing") at \(H = hv/g\beta\) (\(v\) is the microwave frequency) provided the exchange energy is sufficiently large. The exchange energy need not be very large in organic molecules, as it is estimated to be .7 cm\(^{-1}\) in EPPH single crystals and exchange narrowing is observed\(^2\). The half-intensity bandwidth, \(\Delta H_\frac{1}{2}\), is found to vary inversely with a function, \(F(J)\), of the exchange energy. The exact function is determined by the geometry of the crystal, and \(\Delta H_\frac{1}{2}\) decreases as the absolute value of \(J_{ij}\) increases.

In a complete \(g\) tensor treatment, one would expect equivalently oriented molecules to give resonances centered about

\[
H' = hv/g'\beta
\]

in which

\[
g' = (g_1^2\cos^2\theta_1 + g_2^2\cos^2\theta_2 + g_3^2\cos^2\theta_3)^{\frac{1}{2}}
\]
The $\theta_i$ are the angles that the magnetic field makes with the principal axes of the $g$ tensor for the molecule, and the $g_i$ are the diagonal elements of the $g$ tensor. Unless all molecules in the crystal have the same orientation relative to the static magnetic field, the observed spectrum will be a superposition of resonance signals. If the crystal structure is known, then one should be able to determine the $g$ tensor elements in the crystal. Even when the crystal structure is not known, it is often possible to estimate rather accurately the degree of anisotropy of the $g$ tensor.

In summary, the exchange interaction in single crystals results in a narrowed absorption maximum at $H' = hv/g'\beta$, and the hyperfine tensor anisotropy is effectively removed as a broad background.

Since the hyperfine structure is effectively removed from the crystal spectrum, it becomes possible, under the proper conditions, to determine the diagonal $g$ tensor elements from a powder sample E.S.R. spectrum. Poole\textsuperscript{7} has shown that in powder samples of doublet molecules, one should observe intensity maxima in the E.S.R. spectrum at

\begin{align*}
H_1 &= hv/g_{xx}\beta \\
H_2 &= hv/g_{yy}\beta \\
H_3 &= hv/g_{zz}\beta
\end{align*}

\textsuperscript{7}Poole, \textit{op. cit.}, p.830.
The observability of the intensity maxima will depend on the relative sizes of the splittings (i.e., $H_1 - H_2$, etc.) and the line width. Higher microwave frequencies increase the splittings and enhance the probability for success in such measurements. The $g$ tensor elements of DPPH have been determined in this manner and give excellent agreement with measurements from hosted oriented samples.  

The E.S.R. spectra of rigid glassy solutions, showing simple hyperfine splittings, have proved useful in the measurement of the largest anisotropic elements of the hyperfine tensors. The E.S.R. spectra of such solutions show resonances with splittings which correspond to the splittings along the principal axes of the hyperfine tensors. It is the opinion of the writer that these effects could be explained by a treatment similar to that used by Kottis and Lefebvre for triplets in rigid glasses. Such an analysis has not been attempted by the writer since even the simplest case requires a 4 element basis set and a 4th order secular determinant. In addition to the hyperfine effects, the $g$ tensor effects should also be considered.

The tensor formalisms are not important in solutions of low viscosity because the $g$ tensor and hyperfine tensor elements are "averaged" by the motions of the molecule. The tensor elements are

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replaced by scalars which are the average of the diagonal tensor elements. If the trace of a tensor is zero, those terms vanish unless they are very large (i.e., greater than about 30 gauss). Thus the Hamiltonian for a molecule in a dilute solution is

\[ \mathcal{H} = g \mathbf{H} \cdot \mathbf{S} + \gamma a_1 \mathbf{S} \cdot \mathbf{T} \]

...12

g and \( a_1 \) have been previously defined.

The averaging of the tensor elements is a result of "relaxation effects". Relaxation in solution is generally attributed to local perturbations caused by the random motions of solute and solvent molecules; the treatment of relaxation effects is not trivial, however.\(^{11}\) As the gist of this work deals with state functions, only relaxation effects pertinent to this work shall be summarized.

If one treats the bulk properties of a dilute system of particles having a magnetic moment, using the classical Bloch equations, one obtains the following expression\(^{12}\) for absorption of microwaves by the sample in a static magnetic field:

\[ \frac{dE}{dt} = \frac{H^2 \chi_0 \omega_0}{1 + T_2^2 (\omega - \omega_0)^2 + (\frac{2B}{h})^2 H^2 T T^2} \]

...13

Here \( \chi_0 \) is the absolute value of the complex magnetic susceptibility

\(^{11}\)C.P. Slichter, \textit{op. cit.}, 1, Chapter 1, 2, & 5.

\(^{12}\)Carrington and McLachlan, \textit{op. cit.}, 2, p.181.
of the system, $\omega_0 = 2\pi \nu_0$ where $\nu_0$ is the center of resonance, $\omega = 2\pi \nu$ in which $\nu$ is the frequency of $\vec{H}_1$, the magnetic vector of the exciting radiation. $T_1$ and $T_2$ are referred to as the longitudinal and the transverse relaxation times. They are the respective times required for the longitudinal and transverse components of the bulk magnetic moment to return to $1/e$ of the equilibrium value after some perturbation to the system. Since the observed E.S.R. signal is a function of the rate at which energy is absorbed, one would expect equation 13 to be descriptive of such a signal.

For sufficiently small relaxation times and powers, the absorption signal is expected to be Lorentzian in shape. Experimentally, the E.S.R. signals generally have the Gaussian or Lorentizian shapes. The absorption as a function of magnetic field strength for the two cases may be expressed as follows:

$$Y(H) = Y_m \exp[-0.693(H-H_0)^2] \quad \text{(Gaussian)} \quad \ldots 14(a)$$

$$Y(H) = \frac{Y_m}{1 + \left(\frac{H-H_0}{\Delta H_2^o}\right)^2} \quad \text{(Lorentzian)} \quad \ldots 14(b)$$

$Y_m$ is an arbitrary constant and $\Delta H_2^o$ is the half-intensity bandwidth.

Carrington and Longuet-Higgins have shown that the anisotropies of the $\hat{g}$ and $\hat{T}_4$ tensors are largely responsible for

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relaxation of doublet molecules in solution. Dealing with a simple molecule having an anisotropic g tensor and one hyperfine tensor, they have shown that the linewidth varies systematically from one hyperfine line to another according to

$$\frac{1}{T_2} = A + B m_z = C m_z^2,$$

where $m_z$ refers to the z component of the nuclear spin, $B$ is proportional to $\hat{g} \cdot \hat{T}$, and $C$ is proportional to $\hat{T} \cdot \hat{T}$. For more complicated systems, the effects of different nuclei appear to be superimposed.\(^1\)

In more concentrated solutions, electron-electron dipolar interactions become important and the signal is broadened—since $T_2$ is effectively decreased. At very high concentrations, \(1M\), exchange effects become very important and may lead to narrowing of the resonance into a single sharply peaked signal.\(^2\) This is the same exchange effect which causes the narrowing of the resonance signal in single crystals of pure doublets.

(B) E.S.R. of Triplet Molecules

The Hamiltonian which adequately describes the magnetic interaction in most organic triplet molecules is

$$\mathcal{H} = g \beta \hat{H} \cdot (\mathbf{S}_1 + \mathbf{S}_2) + g^2 \beta^2 \left[ \frac{\mathbf{S}_1 \cdot \mathbf{S}_2}{r^3} - \frac{3(\mathbf{S}_1 \cdot \mathbf{r})(\mathbf{S}_2 \cdot \mathbf{r})}{r^5} \right]$$

\(^1\)Conclusion of the writer based on "experience".

in which \( g, \beta, \mathbf{H} \) and \( \mathbf{S} \) have been previously defined. \( |\mathbf{r}| \) is the distance between electrons 1 and 2. \( g \) is used rather than \( \hat{g} \) in view of the relative simplicity, and its use does not lead to serious error in most systems. As the magnetic interaction between the "unpaired electrons" increases, the approximation becomes more nearly correct in the analysis of E.S.R. spectra.

Equation 1 may be rewritten as

\[
\mathbf{3C} = g\beta \mathbf{H} \cdot \mathbf{S} + \mathbf{S} \cdot \hat{D} \cdot \mathbf{S}
\]

in which \( \mathbf{3} = \mathbf{3}^+ + \mathbf{3}^- \) and \( \hat{D} \) is a symmetric, traceless, tensor called the "zero-field tensor". The elements of the zero-field tensor are of the form

\[
D_{\epsilon_i \epsilon_i} = \frac{1}{2} \beta^2 \left( \frac{r^2 - 3\epsilon_i^2}{r^5} \right)
\]

\[
D_{\epsilon_i \epsilon_j} = \frac{1}{2} \beta^2 \left( \frac{-\epsilon_i \epsilon_j}{r^5} \right)
\]

in which \( \epsilon_i \) represents one of the coordinates \( x, y \) or \( z \).

A proper choice of axes or a unitary transformation allows the second part of equation 18 to be written in the still simpler form

\[
\mathbf{S} \cdot \hat{D} \cdot \mathbf{S} = -X S_x^2 - Y S_y^2 - Z S_z^2
\]

in which

\[
X = -D_{xx}, \quad Y = -D_{yy}, \quad Z = -D_{zz}
\]

\[
....19(a)
\]
X, Y and Z are the principal values of the D tensor and are known as the zero-field splittings. The term "zero-field splitting" is especially appropriate since there exists the possibility that three distinct energy levels arise from the dipole interaction—even in the absence of a magnetic field.

The first triplet E.S.R. spectra were measured for photo-excited states of naphthalene oriented in durene single crystals. It is possible, however, to obtain nearly as much information about a triplet molecule by observing the E.S.R. spectrum in rigid glassy matrices. Because of the relative experimental simplicity, rigid glassy matrices are favored for zero-field splitting determinations. Kottis and Lefebre have given a theoretical analysis of the E.S.R. spectra of triplets in rigid glassy solutions.

Kottis and Lefebre have shown that in rigid glassy solution, resonance maxima occur at field positions directly related to the zero-field splittings. The appearance of these maxima relates to the fact that there is a greater probability that the molecule will be oriented with one of its principal axes parallel to the magnetic field and to the fact that the transition probability varies with

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molecular orientation in the field. (There is another resonance, 
$H_{\text{min}}$, which appears at a field strength of $\frac{h\nu}{2g\delta}$). The field strengths 
at which resonance occurs are given by equation 20 for a molecule 
having its $x$ axis parallel to the field. Three additional equations 
for $H_y$ and three for $H_z$ may be obtained by cyclic permutation of 
$x$, $y$ and $z$.

\[
\begin{align*}
H_{\text{min}} &= (2g\delta)^{-1}[\delta^2 + 4(XY+XZ+YZ)]^{\frac{1}{2}} \\
H_{x}^{I} &= (2g\delta)^{-1}[\delta^2 = (Y-Z)^2]^\frac{1}{2} \\
H_{x}^{II} &= (2g\delta)^{-1}[(2\delta-3X)^2 - (Y-Z)^2]^\frac{1}{2} \\
H_{x}^{III} &= (2g\delta)^{-1}[(2\delta+3X)^2 - (Y-Z)^2]^\frac{1}{2}
\end{align*}
\]

in which $\delta = h\nu$.

A maximum of 10 resonances are possible for 1 photon 
transitions. The actual number observed depends upon several factors 
such as the relative values of $\delta$, $X$, $Y$ and $Z$ and the direction of 
polarization of the microwave magnetic vector. The transitions 
corresponding to $H_{x}^{I}$, $H_{x}^{II}$, $H_{x}^{III}$, $H_{y}$, $H_{y}^{II}$, and $H_{z}^{III}$ are polarized 
perpendicular to the direction of the magnetic field and are called 
"$\Delta m_g = 1$" transitions—a apparent analogy with non-interacting spin 
systems. Resonances $H_{x}^{I}$, $H_{y}^{I}$ and $H_{z}^{I}$ are polarized in the direction of 
the magnetic field and are called $\Delta m_g = 2$ transitions. These latter 
transitions are forbidden in the high field limit (large $\delta$), but 
become more allowed as $\delta$ decreases relative to the zero-field splittings.
Van der Waals and deGroot\textsuperscript{17} have shown that the $\Delta m_S = 2$ resonances follow the intensity relationships:

$$
H^I_x \propto \left( \frac{Y-Z}{\delta} \right)^2 \\
H^I_y \propto \left( \frac{X-Y}{\delta} \right)^2 \\
H^I_z \propto \left( \frac{X-Z}{\delta} \right)^2
$$

The $\Delta m_S = 1$ transitions become more "allowed" in the high field limit. $H_{\min}$ arises from $\Delta m_S = 2$ transitions because of their relative isotropy compared to the $\Delta m_S = 1$ transitions. $H_{\min}$ increases in intensity as the zero field splittings increase relative to $\delta$. $H_{\min}$ is not, however, so dependent upon the direction of polarization of the microwave magnetic vector, $H_1$. The latter result is particularly evident for spectrometers in which the microwave magnetic vector is polarized perpendicular to the static magnetic field. In such cases\textsuperscript{18a} $H_{\min}$ is observed while the $\Delta m_S = 2$ transitions are absent. Unfortunately, the spectrometer used in these experiments is of the later design and $H^I_x$, $H^I_y$, and $H^I_z$ could be observed.

It should be noted that for zero-field splittings quite small relative to $\delta$, the $\Delta m_S = 1$ transitions may be more easily observed than $H_{\min}$ (or "cut-off" resonance).

For actual analysis of E.S.R. spectra of rigid glasses, it is more convenient to use the variables $D$ and $E$ in place of $X$, $Y$, $Z$. The relationships among the variables are given in
equation 22.

\[
D = \frac{-3}{2} z
\quad Z = \frac{-2}{3} D
\]

\[
D = \frac{1}{2} (X-Y)
\quad Y = \frac{1}{3} D + E
\]

\[
Z = \frac{1}{3} D - E \quad ....22
\]

Since \( \hat{D} \) is a traceless tensor only two variables are necessary to specify the zero-field splittings. Unless measurements are made at temperatures approaching 0\(^\circ\)K, it is not possible to determine the signs of the zero field splittings. Thus, it shall be assumed that the largest diagonal element (in absolute value) is negative and is along the z axis. It is further taken that \( |z| \geq |y| \geq |x| \).

Using these conventions, the following relationships may be derived from equation 18:

\[
\frac{H_{III}}{z} - \frac{H_{II}}{z} = 2D \text{ (gauss)}
\]

\[
\frac{H_{III}}{y} - \frac{H_{II}}{y} = D + E
\]

\[
\frac{H_{III}}{x} - \frac{H_{II}}{x} = D - 3E \quad ....23
\]

D and E are easily determined. They are customarily reported in units of cm\(^{-1}\) and the conversion factor is

\[
\nu(\text{cm}^{-1}) = \frac{(H_{III} - H_{II})}{\frac{\hbar}{\epsilon}} g\beta
\]

in which \( H_{\text{min}} \) expressed in terms of D and E is given by:

\[
H_{\text{min}} = (g\beta)^{-1} \left[ \frac{1}{4} \frac{1}{\beta^2} - \frac{1}{3} (D^2 + 3E^2) \right]^{\frac{1}{2}} \quad ....25
\]
Using the value of $H_{\text{min}}$ obtained from the E.S.R. spectrum,

$$D^*^2 = (D^2 + 3E_2)^2 = 3\left[\frac{\delta}{2gB}\right]^2 - \frac{H_{\text{min}}^2}{2} \text{ (units of gauss)}$$

The $D^*$ values are useful checks of the zero-field splittings calculated from the $\Delta m_s = 1$ transitions. In some cases $D^*$ is the only parameter that may be determined from experiment.

From the values of $D$ and $E$ one may estimate the average distance between unpaired electrons. Conversely, if one has an estimate of the zero field splittings calculated for a doublet molecule which is part of a diradical, the geometry of the molecule may be approximated with the help of molecular models.

Since the dipole tensor is traceless, one might expect that the resonances of the triplet would be observed in non-viscous solution. Only in the case of very weakly interacting diradicals does the writer know this to be the case. $^{19}$ Bisgalvinoxyl which has $D \approx 110$ gauss does not give an E.S.R. signal in solution. $^{20}$

For further information of the theory of E.S.R. of triplets in rigid glasses, the reader is referred to references 17 and 18 and to a recent review article written by Thomson. $^{21}$


(C) **Solvent Effects**

Molecular solvent effects may be rigorously defined as changes in the energy and wavefunction for an ensemble of interacting molecules relative to the non-interacting gaseous state. In a more practical sense, solvent effects refer to changes in measurable physical properties which accompany a change in the environment of a molecule.

McRae\(^{22}\) has developed a semi-quantitative theory of the effects of electric dipolar interaction on the excitation energies of solute molecules in solvents. His approach in developing the theory is general and is, in principle, applicable to other types of interactions.

In order to treat any arbitrary intermolecular interaction for a large number of molecules, one must use a multi-function basis set.

The wavefunction for an assemblage of stationary non-interacting molecules may be written as a product of the individual unperturbed wavefunctions \(\varphi_i\).

\[
\psi_{v(1),v(2),\ldots,v(n)} = \varphi_0 \varphi_1 \varphi_2 \ldots \varphi_n
\]

The superscripts serve to identify the molecules and the subscripts describe the state of the molecules. If one imagines that the molecules are brought together to some instantaneous configuration,

then equation 27 becomes a zeroth order approximation. The superscript \(v(n)\) is then taken to identify a solute molecule which is surrounded by solvent\((i)\) molecules.

Within the framework of perturbation theory, one may express the perturbing hamiltonian as

\[
H' = \sum_{i=1}^{N} H_{oi} + \frac{1}{2} \sum_{i,j=1}^{N} H_{ij}
\]

\(H_{oi}\) represents the interaction of the solute molecule with the \(ith\) solvent molecule; \(H_{ij}\) represents a solvent-solvent interaction. The order to which the perturbation must be carried depends upon the rapidity—or assumed rapidity—of convergence. Functions like those in equation 25 may be used as the basis functions.

Using second order perturbation theory and several approximations for a dipole interaction, McRae has shown that the change in the electronic excitation energy of a solute molecule in solution relative to the gas phase is given by

\[
\Delta \nu (\text{cm}^{-1}) = A \frac{n_{D}^{-1}}{2n_{D}^{-1}D-1} + B \frac{n_{D}^{-1}}{2n_{D}^{-1}D-1} + C \left[ \frac{D-1}{D+2} - \frac{n_{D}^{-1}}{n_{D}^{-2}+1} \right] + G \left[ \frac{D-1}{D+2} - \frac{n_{D}^{-1}}{n_{D}^{-2}+2} \right] \]

in which \(A\) is a dispersion term and

\[
B = \frac{1}{\hbar c} \left( \frac{M_{\mu\mu}}{M_{\mu\mu}} \right)^2 - \left( \frac{M_{\mu\mu}}{M_{\mu\mu}} \right)^2
\]

\[
C = \frac{2}{\hbar c} \left( \frac{M_{\mu0} - M_{\mu\mu}}{M_{\mu0}} \right)
\]

\[
G = \frac{6}{\hbar c} \left( \frac{M_{\mu0}}{a} \right)^2 \left( \frac{\alpha_{\mu0} - \alpha_{\mu\mu}}{a} \right)
\]
$n_D$ is the refractive index of the solvent at the sodium D line, $D$ is the solvent dielectric constant, $\mu_{\text{oo}}$ is the static dipole moment of the molecule in the ground state, $\mu_{i\text{i}}$ is the dipole moment of the molecule in the $i$th excited state and $a_j$ is the "cavity size" of the molecule. $\alpha_0^H$ is the polarizability of the solute molecule in the ground state, and $\alpha_1^H$ is the polarizability of the solute molecule in the $i$th excited state.

McRae called the last term the quadratic Stark effect as it is proportional to the square of the field induced by the solvent. This term is important only for highly polar solvent molecules.

The first term in equation 3 represents dispersion type forces—i.e., induced dipole—induced dipole types of interactions. $A$ is generally negative, and should thus result in a redshift for all solution spectra. The term is usually small, however, and is unimportant unless both the solvent and solute are non-polar and/or the solvent absorbs in the same region as the solute.

The second term represents the interaction of the solute permanent dipoles and induced solvent dipoles.

The third term arises from interactions between solvent and solute permanent dipoles. It is generally the dominant term when applicable.

Among the approximations of McRae is the assumption of point dipoles. Therefore, solvent molecules which have local dipoles which add to zero behave as polar molecules, and their dielectric...
constants do not effectively describe them. Although the equation is approximate, it should give good qualitative results when used for suitable solvents. Ito, et al.\textsuperscript{23} have applied equation 29 to their study of \( n \rightarrow \pi^* \) transitions in ketones. Those experimenters neglected the dispersion and quadratic Stark effects with apparent success.

In practice, one chooses solvents which may be grouped as non-polar, and polar non-protic and polar protic. Non-polar solvents may be chosen so that the quantity, \( \left( \frac{D-1}{D+2} \right) \), is effectively constant. Thus, a plot of \( \frac{n_{D-1}}{n_{D+2}} \) versus \( \nu \), the excitation energy in cm\(^{-1}\), would ideally yield a straight line if \( A \) and \( G \) are negligible.

The relation of the excited state dipole moment to the ground state dipole moment is inferred from the sign of the slope of the line.

Similarly, polar solvents may be chosen so that a plot of \( \frac{(D-1)/(D+2)}{2n_{D-1}} \) versus \( \nu \) would yield a straight line if \( A \) and \( G \) were negligible. Again the slope determines the relative polarity of the excited state and ground state. If the effects of the polar-protic group are large compared to the polar non-protic group, this is a good indication of hydrogen bonding.

Although McRae's treatment deals with a particular perturbation, any perturbation which changes the energy of a system will alter the wavefunction for an ensemble of solute molecules. Although the ensemble approach is probably more nearly correct, it

is often convenient to think in terms of a wavefunction for a single perturbed molecule. In the case of hydrogen bonding one may also wish to consider the particular solvent functional groups with which the solute is more directly interacting. One of the most direct indications of a change in the wavefunction associated with a solute molecule is a change in the spin density at the nucleus. This data may be obtained for paramagnetic nuclei from the solution E.S.R. hyperfine spectrum since \( a = \frac{8\pi}{3} g_e g_N B_N^2 |\psi(o)|^2 \) (Chapter I, Sect. A, Eq. 3a). Thus, if a molecule is very polar, or if it has the ability to form hydrogen bonds, one would expect the hyperfine splittings to change with the nature of the solvent. This is an effect most easily observed in the ground state.

(D) **Molecular Orbital Calculation**

There are several approaches to molecular orbital calculations ranging from the very rigorous *a priori* calculations to approximate semi-empirical calculations. Clementi\(^{24}\) has recently published a review article in which less exact methods are referenced, and emphasis is placed upon "correct theoretical models". There being no need to repeat such a review, only a resume of Clementi's criteria for a rigorous closed shell model will be summarized.

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A rigorous molecular orbital calculation, according to Clementi, should include the following considerations:

1. All of the electrons should be included considering electron repulsion as well as nuclear interactions.

2. A large basis set should be employed. A linear combination of atomic orbitals (L.C.A.O.) is a special case.

3. The total energy of the system should be minimized (i.e., Hartree-Fock) and the calculation repeated to self-consistency.

4. Configuration interaction should also be included.

5. Relativistic effects should not be neglected.

Calculations of doublet radical molecules involve non-closed shells, and application of the Hartree-Fock theory becomes quite complex. The problem is essentially that which is encountered for non-closed shells in atoms. Two approaches have been taken to the solution of the problem by Löwdin and Pople. Löwdin uses a restricted Hartree-Fock treatment placing two electrons in each spatial orbital, starting with the one of lowest energy, until the unpaired electron is placed in the lowest energy unfilled molecular orbital remaining. Pople and Nesbit contend that there is no a priori reason why each spatial orbital must be doubly occupied by one $\alpha$ and one $\beta$ spin electron. They therefore treat the $\alpha$ and $\beta$ spatial orbitals separately.

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wavefunctions as being orthogonal. Unfortunately, both the approach of Löwdin and of Pople lead to two sets of simultaneous integrodifferential equations which must be solved to self-consistency. Such solutions require much effort and computer time; and the results are not particularly gratifying—even for hydrocarbons.\(^{28}\)

An alternate approach is to employ methods which, while not completely rigorous, have desirable features and which give results which are meaningful and consistent with the research objectives. One such method is the Mulliken-Wolfsberg-Helmholz (M-W-H) or "extended Hückel"-type of calculation\(^{29}\). A special case of such a calculation will be described in the following paragraphs.

The calculation employed in this work utilizes a L.C.A.O. basis set of all valence electrons and semi-empirical evaluation of coulomb (\(H_{ii}\)) and exchange integrals (\(H_{ij}\)). The basis functions are non-orthogonal—except for orbitals centered on a particular atom in the molecule. The basis functions are atomic orbitals which are products of an angular and a radial function. The radial functions are two Slater type functions which give best agreement with the S.C.F. A.O.'s. The primary use of the wavefunctions is in calculating overlap integrals (\(S_{ij}\)).

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The following approximations are utilized in evaluating the
coulomb and exchange integrals\(^{30}\):

\[ H_{ii} = \text{Valence State Ionization Potential (V.S.I.P.)} \]

\[ H_{ij} = (2 - |S_{ij}|)(H_{ii} + H_{jj})S_{ij}/2 \] \(\ldots30\)

V.S.I.P.'s are expressed as functions of the orbital
population (POP) and the net charge (q) on the atom.\(^{31}\)

\[ \text{V.S.I.P.} = A(\text{POP}) + Bq - C \] \(\ldots31\)

The populations are calculated using Mulliken's approximation:\(^{32}\)

\[ (\text{POP}) = (\text{Occ}_k) \sum_k a_{ki} a_{kj} + (\text{Occ}_k)\left(\frac{1}{2}\right) \sum_{k,j,i} a_{ki} a_{kj} \] \(\ldots32\)

\[ a_{ki} \] is the coefficient of the \(i\)th orbital in the \(k\)th M.O., and
\[ \text{Occ}_k \] is the number of electrons \((2,1,\text{or} 0)\) in the \(k\)th M.O.

Orbital populations are postulated for the first computation,
and the orbitals are filled in the order of increasing energy. The
calculation is iterated to self-consistency.

Obviously, this "one-electron" calculation does not include
electron repulsion, yet it does deal with all valence electrons and
it is iterated to self-consistency. To expect exact quantitative
agreement from such a model for large molecules is unrealistic. One


might expect, however, a qualitative model and symmetry orbitals. As shall be seen in the calculated results, the symmetry information is of particular interest.

(E) Composite Molecules

Composite molecules are those systems which are made up of two or more molecular subsystems. The interaction of the subsystems may vary from the extremes of "molecules in molecules" to a "new molecule". Descriptions of composite molecules have been attempted by several methods\(^\text{33}\). This particular research paper deals, for the most part, with molecules whose electronic absorption spectra are indicative of slightly to moderately perturbed subsystems. Since these molecular are doublets or triplets (the singlet and triplet states of the "triplets" are nearly degenerate), a rigorous theoretical description becomes exceedingly complex as was seen in Section D of this chapter. The situation is even more complex if one requires that the molecular wavefunctions also be eigenfunctions of the spin operators $S^2$ and $S^z$ where $\mathbf{S} = \sum_i \mathbf{S}_i$; $N$ is the number of electrons in the molecule. Thus, the quantum mechanical models shall be approximate--serving the purpose of qualitative description.

For simplicity we shall use a one electron hamiltonian acting on wavefunctions which are products of molecular orbitals. The composite hamiltonian is described by equation 31.

$$\mathbf{H} = \mathbf{H}^L + \mathbf{H}^R + \mathbf{H}_{\text{LR}}$$

\(\mathcal{H}^L\) and \(\mathcal{H}^R\) are the hamiltonians for the isolated subsystems and have M.O. eigenfunctions \(\varphi_{Li}\) and \(\varphi_{Rj}\) such that

\[
\mathcal{H}^L \varphi_{Li} = \varepsilon_{Li} \varphi_{Li}
\]

and

\[
\mathcal{H}^R \phi_{Rj} = \varepsilon_{Rj} \phi_{Rj}
\]

The operators and eigenfunctions might well be of the M.W.H. variety described in Section D. \(\mathcal{H}_{LR}\) represents the effective perturbation due to the interaction between subsystems \(L\) and \(R\). For each subsystem the wavefunctions are taken to be the product of 1 electron M.O.'s. The unpaired electron may be placed in the ground M.O. that experiment dictates.

\[
\psi^L_k = \varphi^L_{L1}(\alpha) \varphi^L_{L2}(\beta) \cdots \varphi^L_{LM}(\alpha)
\]

and

\[
\psi^R_{\ell} = \phi^R_{R1}(\alpha) \phi^R_{R2}(\beta) \cdots \phi^R_{RM}(\alpha)
\]

In general, \(\psi^L_k\) and \(\psi^R_{\ell}\) are the eigenfunctions of \(\mathcal{H}^L\) and \(\mathcal{H}^R\), respectively.

If the composite molecule is composed of "unlike" subsystems, the zeroth order wavefunction is written:

\[
\psi^T = \psi^L_k \psi^R_{\ell}
\]

A first order perturbation yields the energy expression:

\[
E^T_{k,\ell} = E^L_k + E^R_{\ell} + B_{k,\ell}
\]
in which

$$B_{k', \ell} = \langle \psi_k^1 \psi_{\ell}^2 | H_{LR} | \psi_k^1 \psi_{\ell}^2 \rangle$$

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Excited configurations (neglecting two electron excitations) shall be described by

$$\psi_{k', \ell}^{12} = \psi_k^1 \psi_{\ell}^2$$

or

$$\psi_{k, \ell'}^{12} = \psi_k^1 \psi_{\ell'}^2$$

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having the corresponding first order energies:

$$E_{k', \ell}^T = E_{k'}^L + E_{\ell}^R + B_{k', \ell}$$

and

$$E_{k, \ell'}^T = E_k^L + E_{\ell'}^R + B_{k, \ell'}$$

......40

The transition moment of a "one electron transition" is approximated as

$$\bar{M} = \langle \psi_{k, \ell}^T | \bar{M} | \psi_{k, \ell}^T \rangle$$

$$= \langle \psi_k^1 | \bar{M} | \psi_k^1 \rangle \langle \psi_{\ell}^2 | \psi_{\ell}^2 \rangle$$

$$= \bar{M}_L$$

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The possibility of charge transfer states in which an electron is totally delocalized from one subsystem to another also exists, i.e.,

$$\psi_{k', L'}^T = \psi_{k, L}(-) \psi_{L'}^k(+)$$

Hence, if the ground state unpaired electron distribution and the electronic transitions are similar to those of the isolated subsystems, it may be said that the "molecules in molecules" approach is a valid description.

A composite molecule having two identical parts shall now be considered—specifically a composite molecule containing two doublet subsystems. Combination of two doublet molecules may lead to singlet or triplet formation. In the case of two doublet pi systems which are connected by a saturated hydrocarbon chain, the correlation of the electrons is quite weak leading to nearly degenerate singlet and triplet levels. As stated earlier, the correct wavefunctions should be eigenfunctions of $S^2$ and $S_z$ and be totally antisymmetrized. Such wavefunctions would be linear combinations of the products of several antisymmetrized wavefunctions. Because of the near degeneracy of the singlet and triplet manifolds of such systems, simple product wavefunctions shall be taken to describe the electronic states. The energy difference between the singlet and triplet state

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shall be given by an operator to be specified.

The singlet-triplet energy difference is expressed in terms of the exchange energy.\(^{35}\) Although the energy arises from the degree of correlation of the "unpaired electrons" and is totally electrostatic in nature, it is intrinsically related to the electron spin and the requirements of Fermi particles. The splitting of the singlet and triplets may then be included in the total hamiltonian by using the operator \(\frac{1}{2} + 2\vec{S}_1 \cdot \vec{S}_2\).\(^{35}\) \(\vec{S}_1\) and \(\vec{S}_2\) are the unpaired electron spin operators and \(J\) is the exchange energy. Operation on "two electron" singlet and triplet wavefunctions with \(\frac{1}{2} + 2\vec{S}_1 \cdot \vec{S}_2\) yields \(J\) and \(-J\), respectively. A positive \(J\) implies that the triplet is the ground state; a negative \(J\) favors a singlet ground state. For \(|J| \approx 0\), the molecule should more appropriately be referred to as a diradical rather than a triplet--since triplet implies correlation. As \(|J|\) decreases in value it becomes more difficult to determine the sign of \(J\), since one must work very near \(0^\circ K\) to appreciably alter the relative populations of the nearly degenerate levels. It is of interest that inclusion of \(\frac{1}{2} + 2\vec{S}_1 \cdot \vec{S}_2\) in the magnetic hamiltonian does not alter the E.S.R. spectra of magnetic triplets having significant zero field splittings. If the zero field splittings and \(J\) are of the same order of magnitude as the hyperfine splittings, inclusion of \(\vec{S}_1 \cdot \vec{S}_2\) in the hamiltonian becomes important.\(^{36}\) This


\(^{36}\)Falle, et al., op. cit.
shall not be the case in this work, however.

Returning to the problem at hand—it shall be assumed that one is dealing with either a singlet or triplet ground state whose zeroth order product wavefunction is approximated by

\[ \psi_{KK,LR}^T = \psi_L^k \psi_R^k \psi_{HC}^k \]

\( \psi_L^k \) and \( \psi_R^k \) are wavefunctions for identical fragments and \( \psi_{HC}^k \) represents a hydrocarbon link between L and R. The Hamiltonian should include interaction between each subsystem. However, we shall simply replace the \( \mathcal{K}^{LR} \) for a two component system by \( \mathcal{K}' \) which includes the pertinent interactions.

Excited states corresponding to the excitation of the left subsystem from state \( k \) to state \( k' \) may be written

\[ \psi_{k',k,\ell}^T = \psi_L^{k'} \psi_R^k \psi_{HC}^\ell \]

This zero-order function is, however, degenerate with \( \psi_{k,k',\ell}^T \) in the zeroth order approximation. Inclusion of \( \mathcal{K}' \) should remove the degeneracy so that the wavefunctions become:

\[ \psi_{12}^{\pm} = \frac{1}{\sqrt{2}}(\psi_{k',k,\ell}^T \pm \psi_{k,k',\ell}^T) \]

with first-order energy

\[ E(\pm) = E_1 + E_2 + E_3 \pm \sqrt{2} B \]

The degeneracy of the excited state is split and the composite molecule electronic spectrum may show a larger number of transitions
than the subsystems. The electronic transition moment for a particular conformation may be approximated by

\[ M(\pm) = \frac{1}{\sqrt{2}} (\vec{M}_1 \pm \vec{M}_2) \]

In the final analysis, the number of transitions seen shall depend upon the degree of interaction among the subsystems and their relative orientation. Thus, comparison of the electronic spectrum of the composite molecule and its subsystems allows one to evaluate the degree of interaction of the subgroups.

If it is found that the interaction between subsystems is small (as for 1,3-BNNE and 1,2-BNNE), a reasonable assumption is that the unpaired electron distributions in the composite molecule may be adequately described by the subsystem wavefunctions. In the specific case of weakly interacting triplet molecules, the zero-field splittings for a particular conformation may be approximated using the doublet unpaired electron distribution. Comparison of calculated and experimental zero field splittings allows one to determine the conformation of the molecule.
II. EXPERIMENTAL METHODS AND MATERIALS

(A) Compounds

The $\alpha$-nitronylnitroxide radicals were prepared by the general method of Osiecki and Ullman. In this method, the desired aldehyde (RCHO) is reacted with 2,3-bis-(hydroxylamino)-2,3-dimethylbutane in appropriate solvents to form the trihydro-$\alpha$-R-nitronylnitroxide. The latter is oxidized in benzene to give the radical. This reaction mixture is filtered through magnesium sulfate to remove the excess lead (IV) dioxide and the lead (II) hydroxide that is formed. The benzene is removed by means of a rotating flask evaporator.

1. 2,3-dinitro-2,3-dimethylbutane: 250 ml. of 6N NaOH were placed into a 2 liter 2 neck flask and cooled with ice to a temperature between 5°C and 0°C. 133.5 grams (1.5 moles) of 2-nitropropane were added to the NaOH via a dropping funnel. The addition was carried out very slowly and the reaction mixture was constantly stirred, so that the temperature was maintained below 10°C. After the addition of the 2-nitropropane was complete, 120 grams of bromine (~75 moles) was added drop by drop while the temperature was maintained below 10°C. The reaction mixture was allowed to

warm to room temperature and 500 ml of 95% ethanol was added. The mixture was gently refluxed for 3 hours. Product usually appeared within an hour. The reaction mixture was transferred to ~800 ml of ice and filtered while cold. Seventy percent or better yields were consistently obtained, while the literature yield was 56%. Our higher yields may be attributable to cooling the mixture during the addition of 2-nitropropane since this was not a part of the literature synthesis. The 2,3-dinitro-2,3-dimethylbutane was used without further purification.

2. 2,3-bis(hydroxylamino)-2,3-dimethylbutane: 2,3-bis-(hydroxylamino)-2,3-dimethylbutane was prepared by reducing 2,3-dinitro-2,3-dimethylbutane with zinc dust in a 50 weight percent ethanol solution which was buffered with ammonium chloride. The 2,3-dinitro-2,3-dimethylbutane (100 grams) was placed in a 3 liter round-bottomed flask with 1150 ml of 50% ethanol. The solution was then stirred constantly with a mechanical stirrer during the course of the reaction. Zinc dust (200 grams) was added over a period of 3 hours while the temperature was maintained below 10°C. The reaction mixture was stirred for 3 additional hours and then allowed to warm and sit overnight at room temperature.

After vigorous stirring, the sludgy mixture was filtered through a Büchner funnel. The zinc sludge was washed twice with 250 ml of water, once with 250 ml of 50% ethanol and twice again with 200 and 175 ml of water, respectively. One could smell the product at
this stage of preparation. The washings were acidified to a pH of 1 or 2 and the solution was evaporated with a rotating flask evaporator at reduced pressure. The rotating flask was heated with a water bath, keeping the temperature below 55°C. When approximately 300 ml of syrupy solution remained in the flask, it was cooled and slowly poured over powdered sodium carbonate. Sufficient sodium carbonate was used to insure that the solid formed was dry. The solid material was extracted with chloroform for about 4 hours in two rather large Soxhlet extractors. Sodium carbonate was used to dry the extract (some of the product would float to the surface where it could be removed). The chloroform was distilled off, leaving the desired product. The residue and previously removed product were recrystallized from ethanol and petroleum ether. The best yield obtained was 30% after recrystallization.

3. \(\alpha\)-methylnitronylnitroxide: 2.7 grams of 2,3-bis-(hydroxylamino)-2,3-dimethylbutane in 25 ml of benzene was reacted with three times the required amount of freshly distilled acetaldehyde. The reaction was allowed to proceed with intermittent stirring for 4 hours. The product, trihydro-\(\alpha\)-methylnitronylnitroxide was recovered by vaporization of the solvent and was recrystallized from ethanol and low boiling (~70°C) petroleum ether. Oxidation of trihydro-\(\alpha\)-methylnitronylnitroxide to the radical was effected with excess PbO\(_2\) in 100 ml of benzene. After filtering the mixture through magnesium sulfate, the benzene was evaporated. The product was
recrystallized from ethanol and petroleum ether yielding red crystals (Melting range 92.5-93.0°C).

α-Methylnitronylnitroxide (α-MNN) single crystals were grown quite by accident. A solution of α-MNN in petroleum ether was left in an erlenmeyer under the exhaust hood for several days. The crystals were found with only a small amount of solution remaining. The remaining solution was poured off, and the crystals were washed with petroleum ether in a Buchner funnel. The crystals appeared to be either rhombohedral or one of the orthorhombic variations.

4. α-phenylnitronylnitroxide: This compound was prepared according to the unpublished method of Osiecki and Ullman⁴. 4.4 grams of 2,3-bis-(hydroxylamino)-2,3-dimethylbutane was added to 150 ml of methanol in which it dissolved (endothermically). To the solution was added 3.5 grams benzaldehyde from a freshly opened bottle. The reaction mixture was stirred 24 hours. Some product crystallized from solution. The remaining solution was evaporated and the product, trihydro-α-phenylnitronylnitroxide, was recrystallized from benzene and petroleum ether (yield 60%). After the standard oxidation procedure α-phenylnitronylnitroxide was recrystallized from ethanol and petroleum ether. (Melting range 87.0-87.2°C). It crystallized as dark blue needles.

5. α-(o-tolyl)nitronylnitroxide: α-(o-tolyl)nitronylnitroxide was prepared by the same method used for α-phenylnitronylnitroxide;

⁴E.F. Ullman, private communication.
the starting aldehyde was o-tolyl-benzaldehyde. Since the reaction rates were much slower, the reaction times had to be doubled. Yields were down to about 47% for the trihydro-α-(o-tolyl)nitronynitroxide. Recrystallization from ethanol and petroleum ether yielded violet crystals which had a melting range of 126.5-127.5°C.

6. **1,3-bis-(α-nitronynitroxide)propane**: Aldrich 40% glutaraldehyde in aqueous solution was reacted directly with an excess of 2,3-bis (dihydroxylaminot)-2,3-dimethylbutane. The product was mixed with a benzene - ethanol mixed solvent and heated to effect solution. Rather than dissolve, the material tended to emulsify. Thus, the product was effectively washed—not truly recrystallized.

1,3-bis-(trihydro α-nitronynitroxide)propane was oxidized in the standard way. The product was recrystallized from a mixed solvent of ethanol and petroleum ether yielding dark red crystals. (Melting range 134-136°C).

7. **1,2-bis-(α-nitronynitroxide)ethane and bis-(α,α'-nitronynitroxide)**: These samples were kindly provided by Dr. E.F. Ullman of Sylvar Research Institute, Palo Alto, California. 1,2-bis-(α-nitronynitroxide)ethane melted sharply at 153°C implying that the sample was very pure.

(B) **Solvents**

1. **Hydrocarbons**: Phillips pure grade 3-methylpentane, n-hexane and isopentane were washed with fuming sulfuric acid for several hours to
remove aromatic impurities. They were washed with water, saturated sodium carbonate solution, and water again. These solvents were normally dried over magnesium sulfate and distilled. Matheson, Coleman and Bell spectroquality cyclohexane was used without further purification—except drying it for E.S.R. and U.V. solvent studies.

2. Ethanol: U.S. Industrial Chemicals Company absolute pure alcohol reagent quality was used without further purification.

3. Ethyl Ether: Mallinckrodt anhydrous analytical reagent grade ethyl ether was used without purification. For solvent studies it was further dried using lithium aluminum hydride.

4. Mixed Solvents:

E.P.A.

E.P.A. is a mixture of isopentane, ethyl ether and ethyl alcohol in a volume ratio of 5:5:2. The preparation of the constituent solvents has been described. Normal procedure in preparing the solvent was to dry the glassware in an oven before preparation. E.P.A. forms a rigid glass at 77°K. The glass should be allowed to thaw slowly; otherwise it will cause delicate absorption cells to crack.

P.M.P.

P.M.P. is a mixture of isopentane and 3-methylpentane in a volume ratio of 8:5. P.M.P. forms a glass at 77°K, but the glass is not so rigid as E.P.A. glasses at 77°K.
5. **Carbon Tetrachloride**: Matheson, Coleman and Bell spectroquality carbon tetrachloride was dried via the $P_2O_5$ method for solvent studies. It was, otherwise, used without further purification.

6. **Chloroform**: Mallinckrodt analytical reagent chloroform was washed with two portions of sulfuric acid, dilute NaOH and finally with $H_2O$ to remove any remaining ethanol or acetone. The chloroform was dried by distilling over $P_2O_5$.

7. **Acetonitrile**: "Baker Analyzed" reagent acetonitrile was dried using the $P_2O_5$ technique.

8. **Methylacetate**: Fisher Scientific Company certified methylacetate was dried using $P_2O_5$.

9. **Isobutylalcohol**: Dried over barium oxide several times.

10. **Drying of Solvents**: Several times in the course of the research, it became necessary to dry the solvents as the purity of the solvent was important. This is especially true for optical solvent effects and for isotropic hyperfine splitting changes of the $\alpha$-nitronyl nitroxide doublets accompanying a solvent change.

    Two drying techniques were used. $n$-hexane and ethyl ether were dried with lithium aluminum hydride. An excess of the hydride was added to the solvent under a nitrogen atmosphere during the hydrogen evolution period. The solvents were distilled from the mixture in an all glass still that was open to air through a $P_2O_5$ drying tube. Benzene, carbon tetrachloride, chloroform,
methyl acetate and acetonitrile were dried with P₂O₅. The solvents were refluxed over P₂O₅ several times until there was little--if any--yellowing of the P₂O₅. The solvents were distilled over sodium carbonate in an all glass apparatus connected to the air through a P₂O₅ drying tube.

(C) **Electronic Spectral Measurements**

The electronic absorption spectra were measured with a Cary 14 spectrophotometer. The measurements were made in a variety of solvents and at several temperatures. The solvents used for this work were purified as previously described. The accuracy of these measurements is estimated to be ±3 angstroms unless otherwise specified. All extinction coefficients (ε) are reported in units of liters per mole centimeter; thus, the units will not be explicitly stated in discussion of maximum intensities.

In the measurement of spectral data designated as room temperature (R.T.), the temperature was not specially controlled but was regulated by the room thermal control. The "room temperature" is about 24°C. Absorption spectra at 77⁰K in rigid glassy solutions were measured by a method previously described by McDonald. For intermediate temperature [77 < T < R.T.], a special temperature controlling device was utilized. The variable temperature device

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5J.R. McDonald, Ph.D. Dissertation, Louisiana State University, 1968.
consisted of an insulated sample compartment\textsuperscript{6} and a cooled nitrogen gas flow system\textsuperscript{7}. The Cary sample compartment was insulated with one-fourth inch asbestos, and the insulating optical windows were one-fourth inch quartz plates. Cooling nitrogen gas was circulated through the Cary sample compartment gas inlets. The cooling nitrogen was obtained by boiling liquid nitrogen from a 15 liter dewar using a variac controlled coiled nichrome wire heater. The cool nitrogen gas was channeled to the sample chamber \textit{via} a heat exchanger. The heat exchanger was a copper coil immersed in liquid nitrogen. Connecting tubing was insulated copper or vacuum rubber tubing. Nitrogen flow rate was controlled by adjusting the heater current. Dry R.T. nitrogen was circulated through the detector, reference and monocromater sections of the Cary 14 to avoid condensation of moisture.

Optical luminescence spectra were measured with the Cary Model 14 spectrophotomater by the method described by Holloway\textsuperscript{8}.

(D) \textbf{E.S.R. Measurements}

E.S.R. measurements were made with a JEOLCO JES-3BX X-band spectrometer. The microwave frequency in these measurements varied between 9200 and 9400 Mc. s\textsuperscript{-1}. A cylindrical cavity, operating in

\textsuperscript{6}The sample compartment was designed by J.H. Wharton and built by A. Maresco.

\textsuperscript{7}The nitrogen flow system was designed and built by Cecil Chopin.

\textsuperscript{8}H. Holloway, Ph.D. Dissertation, Louisiana State University, Baton Rouge, Louisiana, 1967.
the $\text{TE}_{011}$ model was used in all measurements. The largest component of the microwave magnetic field $H_1$ is perpendicular to the "static" magnetic field. (Thus, the $\Delta m_s = 2$ transitions $H_x^I$, $H_y^I$, $H_z^I$ in equation 20 are not observed). The "static" magnetic field is modulated by an 80 cycle/s or a 100Kc/s auxiliary field, and the amplitude of the modulation (i.e., the modulation width) can be varied from 30 gauss to approximately 10 milligauss.

Absolute measurements of the static magnetic field were made with a Magnion Industries Gaussmeter (Model G-502). If one has a precision frequency meter to monitor the proton nuclear magnetic resonance frequencies, it is possible to obtain 6 significant figures in the static magnetic field measurements. The magnetic field is given by:

$$H = (\nu/4256.76) \text{ gauss sec/cycle}$$

in which $\nu$ is the nuclear resonance frequency. Since a frequency counter was not continually available, the gaussmeter frequency meter was calibrated by means of a Hewlett-Packard Model 5245L Electronic Counter\(^9\). The accuracy of the magnetic field, when using the Magnion frequency meter and our calibration table, is approximately $\pm 2$ gauss. The calibrated gaussmeter was used for triplet spectral measurements.

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\(^9\)Thanks is due Dr. R.G. Goodrich of the Louisiana State University Department of Physics and Astronomy for making the counter available.
Small relative changes (a few gauss) in the static magnetic field were measured with the JEOLCO Magnetic Field Calibrator ("N.M.R. marker"). The marker utilizes a variable frequency crystal oscillator, $\nu_V$ and fixed frequency crystal oscillator $\nu_F$. The two oscillators are linearly coupled to give resonances at $\nu_V - \nu_F$, $\nu_V$, and $\nu_V + \nu_F$. These correspond to magnetic field strengths of

$$H_V = \frac{\hbar \nu_F}{g_N S_N}.$$  

The field difference, $\Delta H$, between the resonances centered about $H_V$ is $\frac{2\hbar \nu_A}{g_N S_N}$ (overtone resonances of $\nu_F$ cause extra resonances to appear). $\Delta H$ is approximately 5 gauss and once calibrated it is very stable. The marker was calibrated from E.S.R. spectrum of anthracene cation radical\(^{10}\), and $\Delta H$ was found to be $4.97 \pm 0.02$ gauss. Anthracene cation radical is prepared by dissolving anthracene in 18M sulfuric acid. The solution is placed in a 1 mm capillary tube via "capillary action".

The microwave frequency was measured by means of a tuned frequency meter that is built into the JEOLCO instrument. Frequency meter readings must be converted into frequency by means of a calibration chart. It is estimated that the error in the frequency obtained by this procedure is $\pm 1 \text{ Mc}$.

Certain criteria were followed in measuring the spectra to avoid distortion of the resonance signal\(^{11}\). It was attempted,


whenever possible, to adhere to the following criteria:

(1) The modulation width was kept at less than one fifth the E.S.R. peak to peak derivative extrema, $\Delta H_{pp}$.

(2) The scanning speed and the response time were maintained such that the response time was less than $1/10$ of the time required to scan $\Delta H_{pp}$.

(3) The microwave power was kept below the saturation limit to avoid spectral broadening.

Solutions for R.T. E.S.R. measurement and those frozen for low temperature E.S.R. measurements were degassed thoroughly to remove all oxygen. Each sample underwent four freeze-thaw cycles under vacuum. Since the E.S.R. sample tubes have small diameters, these tubes were connected to a larger tube in order to degass the samples. The apparatus is shown in Figure 2.1. The apparatus also has the advantage that E.S.R. tube concentrations may be diluted by warming the larger tube and cooling the smaller E.S.R. tube. E.S.R. sample tube diameters were varied to fit the nature of the solvent being used. In general, more polar solvents require smaller tubes since the polar solvents absorb in the microwave spectral region. For hydrocarbons or non-polar solvents 5mm O.D. quartz tubes were used. For ethanol, dimethoxyethane and E.P.A. 3MM O.D. pyrex tubes were used; for acetonitrile 2mm O.D. pyrex tubes were used and for water and $\mathrm{H}_2\mathrm{SO}_4$ 1 mm O.D. pyrex capillary tubes were used. No significant impurities were encountered in the pyrex glass tubes, and excellent results were obtained from their use. It is significant that as a solvent "freezes", 
FIGURE 2.1. E.S.R. sample apparatus.
the microwave power loss decreases, and tube size is not so important with regard to dielectric power loss.

For the $77^\circ$K E.S.R. measurements, use was made of a special quartz dewar in which the sample is placed. The dewar is positioned directly in the resonance cavity. Variable temperatures—between R.T. and $-155^\circ$C were achieved with the JEOLCO variable temperature apparatus.

Relative methods of measuring g values were made necessary by the lack of precision measurement equipment. Although relative methods are more time consuming, they do offer some advantages. For example, utilizing absolute methods one does not generally measure the absolute field in the sample, but rather that of the field outside the cavity. If properly executed, the relative method eliminates this systematic error.

The g value of an unknown compound was measured relative to the g value of anthracene cation in sulfuric acid. The E.S.R. spectrum of the anthracene cation radical ($g = g_0$) was measured. The microwave frequency reading and the temperature were measured to determine the microwave frequency ($\nu_0$). The static magnetic field was manually adjusted so that the center line of the anthracene spectrum was in resonance. Having carefully made the latter adjustment, the Magnion Gaussmeter was adjusted until the resonance condition for the N.M.R. proton probe was obtained—as was indicated on the oscilloscope screen of the gaussmeter. Although
the static magnetic field is unknown, it can be precisely reproduced by simply reattaining the resonant condition of the gaussmeter. It is, of course, imperative that the gaussmeter not be adjusted after the critical initial adjustment for the reference compound.

Having completed the adjustment of the gaussmeter, the reference compound in the spectrometer resonance cavity was replaced by the compound having the unknown g value. The E.S.R. spectrum of the unknown was then measured; again, recording the frequency meter reading and temperature from which the microwave frequency \( \nu_1 \) was obtained. The spectrum was scanned very slowly so that the field at which the gaussmeter exhibits resonance could be precisely marked on the spectrum. This latter mark corresponds to the static field \( H_0 \) at which the center line of the anthracene cation radical exhibited resonance. The center of the unknown spectrum corresponds to the "resonant field" \( H_1 \).

From the following relationships,

\[
g_0 \beta H_0 = h \nu_0
\]
\[
g_1 \nu_1 H_1 = h \nu_1
\]
\[
\Delta H = H_0 - H_1
\]

one obtains

\[
g_1 = g_0 \left[ \frac{\nu_1}{\Delta H \frac{g_0 \beta}{h}} \right] \quad \cdots \quad 48
\]

\[
g_1 = g_0 \left[ \frac{\nu_1}{\Delta H \frac{g_0 \beta}{h}} \right] \quad \cdots \quad 49
\]
ΔH was measured by means of the N.M.R. marker (field calibrator). Anthracene was used because the g value of the cation in H₂SO₄ is precisely known ($g_o = 2.00249$)¹², and the radical is easily prepared. Error analysis indicates that the random error in the g value of compounds studied in this research is .0007.

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III. RESULTS AND DISCUSSION OF α-NITRONYLNITROXIDE
DOUBLET RADICALS

(A) α-Methylnitronylnitroxide

1. E.S.R. Data: The room temperature E.S.R. spectrum of α-methylnitronylnitroxide in ethanol is shown in Figure 3.1. The spectrum is consistent with that of a ground state doublet \( g = 2.0064 \pm 0.0007 \) having two magnetically equivalent nitrogens \( |a_N| = 7.6 \) gauss) and three magnetically equivalent hydrogens \( |a_H| = 3.2 \) gauss). The major splittings, giving twenty major bands, are consistent with the \( C_2v \) structure shown in Figure 0.1.

The major bands are composed of several smaller splittings of approximately .2 gauss. These smaller splittings are attributed to the twelve hydrogens associated with the 4 methyl groups which are bonded to the adjacent ring carbon atoms. At best 9 lines are observed that can be associated with the smaller splittings. This is less than the 13 lines predicted on the basis of 12 equivalent protons. The apparent discrepancy may be explained by considering the expected relative intensities for a 12 equivalent hydrogen E.S.R. spectrum.

The coefficients for the expansion \((1+x)^{12}\) give the relative intensity ratios of 1,12,66,220,495,792,924,792,495,220,66,12,1. Based on expected relative intensities and the observed spectrum, the absolute

\[ |a_N| = 7.42 \) gauss and \[ |a_H| = 3.3 \) gauss in benzene.\[1\]b

FIGURE 3.1a. R.T. E.S.R. spectrum of α-MNN in ethanol.
FIGURE 3.1b. R.T. E.S.R. spectrum of α-MNN in benzene.
intensities of the weak outer lines (relative intensities 1 and 12) are predicted to be lower than the noise level of the spectrometer at the required operating conditions. Hence, the four weak lines appear to be missing in the spectrum. The conclusion is that there exist 12 equivalent hydrogens in the molecule which are associated with the four methyl groups as shown in Figure 0.1.

An effort was made to observe the $^{13}\text{C}$ hyperfine splittings in the wings of the "normal E.S.R. spectrum" of $\alpha$-methylnitronyl-nitrooxide using a high gain. The large number of lines in the normal spectrum made it necessary to use a rather high concentration ($\sim 10^{-3}$ M) in order to observe the carbon 13 splittings. The close proximity of the lines made it impossible to detect $^{13}\text{C}$ splittings in the interior of the spectrum. Since $^{13}\text{C}$ has a spin of 1/2, one would expect a normal spectrum line to be split into a doublet by a single $^{13}\text{C}$ atom in a molecule; the intensity of such lines increases as the number of magnetically equivalent carbon atoms increases. Thus, based on the $^{13}\text{C}$ isotopic abundance, and the $^{13}\text{C}$ spin, one would expect a $^{13}\text{C}$ line to be $\sim 1/200$ of the intensity of the "normal spectral" line that it has split.

The E.S.R. spectra at gains of 1 and 100 are shown in Figure 3.2. Two splittings may be identified in the gain 100 scan. One is a shoulder on the now very intense "normal spectrum" end line and the other is barely discernable at a slightly higher field. Based on the expectations stated in the previous paragraph, the
FIGURE 3.2. High gain E.S.R. spectrum of α-MNN in benzene.
shoulder is apparently too intense (by a factor of \( \sim 2 \)) for a single
\( ^{13}C \), while the other line is too weak (by a factor of about 2) to arise
from a single carbon 13. Both lines, however, are much too intense to
arise from two magnetically equivalent carbon 13 atoms on the same
molecule. (This would yield a 3 line spectrum with intensities of
an order of magnitude smaller than that observed).

The logical conclusion is that the actual amplifier gain
does not agree with the instrument panel gain settings. Assuming this
to be the case and considering the relative intensities of the \( ^{13}C \)
resonances, the shoulder (\( |a_{^13C}| = 6 \text{ g} \)) is assigned to the 4 equivalent
methyl carbons. The other \( ^{13}C \) resonance (\( |a_{^13C}| = 12 \text{ g} \)) is considered
to arise from a magnetically unique site in the molecule. The
assignment of the latter hyperfine splitting will not be made at this
point, but shall be deferred to Section C of this chapter.

The spin densities at the various paramagnetic nuclei--from
which splittings have been observed--have been calculated using
equation 3a, Chapter I. The results are given in Table 3.1 along with
the "basis orbital" unpaired electron populations. The unpaired
electron spends approximately 9% of its time in s orbitals of atoms
which give rise to the observed isotropic splittings; this result
is easily obtained from the data in Table 3.1. Of course, these
measurements do not reflect the total s orbital character of the
unpaired electron M.O. The nature abundance of \( ^{17}O \) is only .037% and
### TABLE 3.1

NUCLEAR SPIN DENSITIES AND S ORBITAL SPIN POPULATIONS OF α-MNN

| Atom | $g_N^3$ | $|a|$ (gauss) | $\rho_{\text{max}}$ (a.u.) | Nuclear Spin Density (a.u.) | A.O. Spin Population |
|------|---------|---------------|----------------|--------------------------|----------------------|
| H'   | 5.855   | .2            | .318          | .0001                    | (1S) .0004           |
| H'   | 5.855   | 3.2           | .318          | .0020                    | (1S) .0063           |
| N$^{14}$ | .403   | 7.6           | 4.77          | .067                     | (2S) .014            |
| C$^{13}$ | 1.405  | 6             | 2.77          | .002                     | (2S) .005            |
| C$^{13}$ | 1.405  | 12            | 2.77          | .003                     | (2S) .010            |


precludes observation of the oxygen 17 splittings even at very high gain. The other possible carbon 13 isotropic splittings were, apparently, less than 6 gauss and could not be observed. It should be noted that the nitrogen isotropic hyperfine splitting constant in α-MNN is approximately one-half the value observed for simple nitroxide radicals having a single N-O group. For example, di-t-butyl nitroxide has a measured isotropic hyperfine splitting constant of 15.9 gauss in methanol. This is about 1/2 the magnitude (|a_N| = 7.6 gauss) for α-methylnitronylnitroxide in ethanol. Since α-methylnitronylnitroxide has 2 N-O groups contrasted to one in di-t-butylnitroxide, one would expect the splitting to be about 1/2 as large—if the nature of the unpaired electron M.O. were the same in nitroxide and α-nitronylnitroxides. A premature conclusion (but a helpful hint) is that the two classes of radicals have the same type of unpaired electron M.O. Other comparisons shall be made after more data is examined.

Some further useful properties in determining the ground state of radicals are the g and hyperfine tensor elements. The g value of α-methylnitronylnitroxide in ethanol (see Figure 3.1 for the E.S.R. spectrum) was measured to be 2.0064 ± .0007. The g value is


slightly higher than pure hydrocarbon radicals in which g is generally less than or equal to 2.004. The higher g value is not unexpected since nitrogen and oxygen have greater ability than carbon to induce spin orbit coupling between the ground state and low lying excited states.\(^5\) Considering the moderately low symmetry of the ground state, one would also expect the g tensor to be anisotropic. Knowledge of the degree of anisotropy is especially useful for comparison of theoretical models with experiment.

Qualitative proof of the total anisotropy of the molecule is provided by the broadening of the spectral lines at the high field side of the R.T. E.S.R. spectrum in ethanol (Figure 3.1). The effects are consistent with a relaxation model developed by Carrington and Longuet-Higgins\(^6\) in which the off-diagonal elements of the $\mathbf{g}$ and $\mathbf{T}_1$ tensors for a molecule in a static magnetic field are treated as perturbations acting on the average trace value, g. (See Hamiltonians for Doublet Molecules, Chapter I).

Semiquantitative evidence for the anisotropy of the g tensor was obtained by examination of a small single crystal of $\alpha$-methylnitronylnitrooxide. A small single crystal was placed in a quartz E.S.R. tube and oriented arbitrarily with respect to the static magnetic field. The crystal was rotated in a plane parallel

\(^5\)Note added in Proof: The spin orbit coupling constants for the 2p A,O.'s of C, N, O are 28, 78, 151 cm\(^{-1}\), respectively.\(^5a\)

\(^5a\) A Carrington and A. MacLachlan, op. cit., p.138.

to the magnetic field using the JEOLCO JES-UCR-2X Sample Angular Rotating Device. Resonance spectra were recorded for 30° rotations in the arbitrary crystal plane (see Figure 3.3 and Table 3.2). The position at which the derivative signal crossed the x-axis was taken as the "position" of the resonance; the resonance signal could really be made up of more than one orientation of molecules giving an "effective signal". The signals were symmetrical, but they varied in intensity, and $\Delta H_2^*$ changed with orientation of the crystals. If the signals are assumed to be Lorentzian in shape, $\Delta H_2^*$ varies from 9.4 to 11.2 gauss (see Table 3.2). The measured g value varies from 2.0051 to 2.0091—a difference of about 2 parts per thousand. It is difficult to say if the whole range of g values has been observed, since the E.S.R. spectrum was measured in only one arbitrary plane of the crystal. This question may be answered to some extent by observation of the polycrystalline (powder) E.S.R. spectrum.

The E.S.R. spectrum of a finely ground sample of $\alpha$-MNN was measured. It is shown as the dotted line superimposed on Figure 3.3; the powder sample has $\Delta H_2^* = 15.1$ gauss. Since the powder spectrum just encompasses the superimposed single crystal spectra, the maximum and minimum g tensor values are indicated to be very near (probably within .001) the maximum and minimum values measured for the single crystal. It is also noteworthy that the peaks due to the principal g tensor elements were not observed in the polycrystalline sample. From considerations of the large measured line width in the single crystal and the degree of anisotropy in
TABLE 3.2

FUNCTIONAL DEPENDENCE OF THE E.S.R. FIELD WITH RESPECT TO ORIENTATION OF AN α-MNN SINGLE CRYSTAL

<table>
<thead>
<tr>
<th>Angle* (θ)</th>
<th>( H_0^+ ) (gauss)</th>
<th>( \Delta H_| ) (gauss)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>0.0</td>
<td>10.5</td>
</tr>
<tr>
<td>30</td>
<td>1.9</td>
<td>11.2</td>
</tr>
<tr>
<td>60</td>
<td>0.0</td>
<td></td>
</tr>
<tr>
<td>90</td>
<td>-3.7</td>
<td>10.3</td>
</tr>
<tr>
<td>120</td>
<td>-5.5</td>
<td>9.4</td>
</tr>
<tr>
<td>150</td>
<td>-3.7</td>
<td></td>
</tr>
<tr>
<td>180</td>
<td>0.0</td>
<td></td>
</tr>
<tr>
<td>210</td>
<td>1.9</td>
<td></td>
</tr>
<tr>
<td>240</td>
<td>0.0</td>
<td></td>
</tr>
<tr>
<td>270</td>
<td>-3.7</td>
<td></td>
</tr>
<tr>
<td>300</td>
<td>-5.5</td>
<td></td>
</tr>
<tr>
<td>330</td>
<td>-3.7</td>
<td></td>
</tr>
</tbody>
</table>

*The axis of rotation is perpendicular to \( \mathbf{H} \).

†Relative to \( \theta = 0.\)^°.

‡Lorentzian line shape.
FIGURE 3.3. E.S.R. spectra of α-MNN single crystal and powder sample.
the g tensor, it is concluded that the signals overlap sufficiently
to obscure the structure. The line width in the single crystal is
so large that, in the writer's opinion, splitting in the polycrystalline
E.S.R. spectrum would not be observed—even with K band (~25 K Mc/s)
E.S.R.

Another dividend obtained from the measurement of the single
crystal spectrum is that the exchange energy, \( J_{ij} \), may be estimated;
the \( J_{ij} \) value may be useful in dealing with doublet dimers and ground
state triplets. A rigorous treatment would show that the exchange
energy is a function of the linewidth, the unpaired electron density
in the crystal, and the geometry of the crystal.\(^6\) An approximate
approach will be used because the geometry is unknown, and the amount
of effort required for a more rigorous treatment may not yield more
meaningful results. The approximations will involve the use of
equations for a simple cubic structure (rather than the true geometry)
and the use of the exchange energy and \( \Delta H_{ij} \) of D.P.P.H. as reference
values.

It has been shown\(^7\) that for a simple cubic lattice the
following equations are applicable for extreme exchange narrowing

\[
\begin{align*}
\Delta H_{2} &= (\Delta H_{dd})^2 / H_e \\
H_e &= (1.7 J_{ij} / g\beta) [S(S+1)]^{1/2} \\
H_{dd} &= 2.3(g\beta p) [S(S+1)]^{1/2}
\end{align*}
\]

\(^6\) C.P. Poole, Jr., "Electron Spin Resonance", John Wiley and
Sons, New York, N.Y., 1967; Chapter 20.

\(^7\) P.W. Anderson and P.R. Weiss, Rev. Mod. Phys., 25, 269
(1953).
\( p \) is the unpaired electron density in the crystal. Although these equations are not exact, their qualitative features should be correct. Carrington and McLachlan\(^8\) estimate \( J_{ij} \) to be \( 2 \times 10^{10} \) cycles/second for single crystalline DPPH for which \( \Delta H^2 \) is taken to be 2 gauss.\(^9\) \( \Delta H^2 \) is of the order of 10 gauss for single crystal \( \alpha \)-MNN. The unpaired electron spin density in \( \alpha \)-MNN is estimated to be about 2.5 times as large as in DPPH. Using the above approximations,

\[ J_{\alpha \text{-MNN}} = J_{\text{DPPH}} \quad \text{or surely of the same order of magnitude. In terms of energy,} \quad \frac{17}{1} \text{ cm}^{-1} \quad \text{is not a great deal of energy; thus, the exchange interaction between molecules in the crystal is not appreciable.}

Further information which is useful in characterizing the electronic ground state is an estimate of the \( \hat{T}_{ij} \) anisotropy in the molecule. The information may be inferred from the E.S.R. spectrum of rigid glassy solutions. The E.S.R. spectrum of \( \alpha \)-methyl nitronyl-nitrooxide was measured in rigid glassy solutions of E.P.A. and P.M.P. at 77°K. The doublet spectrum is essentially the same in both glasses. The spectrum in the P.M.P. glass is shown in Figure 3.4. This spectrum is a superposition of the spectra of the molecules in the various orientations relative to the static magnetic field. The first maximum at the low field side of the spectrum to the last maximum going to higher field are separated by 74 gauss. Seventy-four gauss is considerably larger than the 30 gauss spectral width observed in

\(^8\) A. Carrington and McLachlan, \textit{op. cit.}, p.200.
\(^9\) C.P. Poole, Jr., \textit{op. cit.}, p.590.
E.S.R. spectrum (doublet region) of α-MNN in P.M.P. at 77°K.
liquid solution. Since the g tensor anisotropy should not be more than 12 gauss (E.S.R. of the single crystal), there is evidently a great deal of anisotropy associated with the hyperfine splitting. This large anisotropy is not totally unexpected because the simpler nitroxides display a large hyperfine anisotropy. The most likely source of the anisotropy is the nitrogen atoms; this question can be satisfactorily confirmed from analyses of the E.S.R. spectrum of \( \alpha \)-phenynitronylnitroxide and \( \alpha \)-(o-tolyl)nitronylnitroxide which have no \( \alpha \)-methyl hydrogens. As such, an interpretation of the rigid glass spectrum shall be deferred until those doublet molecules have been examined.

The E.P.R. spectrum measured in rigid glassy E.P.A. at 77°K (Figure 3.5) showed a resonance at 1523 gauss when the microwave frequency was 9169 Mc/s. The resonance is in the half-field region and is probably \( H_{\text{min}} \) for a magnetic triplet. Using equation 26, and \( g = 2.006 \), \( D^* \) is calculated to be \( 1.02 \times 10^3 \) gauss \( (.0955 \ \text{cm}^{-1}) \). Although the corresponding \( \Delta m = 1 \) triplet resonances were not observed, it is evident that there is magnetic dimer formation. A half-field triplet resonance was not observed for \( \alpha \)-MNN in the P.M.P. glass. These phenomena will receive further attention in Chapter IV.

Another unusual property of the ground state nitronyl-nitroxide radicals is their tendency to interact strongly with solvent

---

FIGURE 3.5. Half-field resonance of α-MNN in ethanol at 77°K.
molecules. For very strong interactions, it is possible that solvent perturbations may alter the electronic structure sufficiently to change the unpaired electron spin density at the nuclei. The resulting changes in the E.S.R. spectrum are then a measure of the extent and nature of the solvent interaction. As pointed out earlier, there is no noticeable difference in the 77°K doublet spectrum of α-MNN in P.M.P. and ethanol; but those spectra are so broad and structureless, that small changes would be very difficult to detect. The R.T. derivative spectra of α-MNN measured in dilute solutions of benzene and ethanol (Figure 3.1a and 3.1b) are much better resolved. The resonances associated with the major hyperfine splittings are not so resolved in benzene as they are in ethanol. Yet, the minor splittings are better resolved in benzene than in ethanol. This observation suggests differences in the major hyperfine splittings of α-MNN in solutions of the different solvents. Preliminary comparison of the hyperfine splittings of α-MNN in benzene and ethanol indicated the changes were quite small. The splitting changes were so small that very cautious experiments were necessary to show that the splitting changes were, indeed, real.

In order to measure the hyperfine splittings to a high degree of accuracy and precision, the following procedures were followed:

(1) The solutions were diluted until the small hyperfine splittings (0.2 gauss) were resolved in both the benzene and ethanol
solutions. At these concentrations, the paramagnetic molecules are essentially non-interacting.

(2) The middle and low-field E.S.R. splittings were chosen for relative measurements, since these regions of the spectrum show the least anisotropic broadening.

(3) Definite peaks were chosen for measurement. These peaks were labeled 1, 2, 3 and 4 on the spectra measured in the respective solvents. The distances $d_{12}$, $d_{34}$, $d_{13}$ and $d_{24}$ were measured for each scan.

(4) The spectra were measured in sequence making four scans for each solution. In order to keep hysteresis effects to a minimum, the magnetic field setting was not changed. The scan width was reproducible.

(5) The distances $d_{12}$ and $d_{34}$ correspond to the proton splittings while $d_{13}$ and $d_{24}$ correspond to the nitrogen splittings; the very small .2 g splittings were not considered. The distances will not be the same even though they may be associated with the same splittings; this is due to second-order effects which are generally neglected. $^{11}$ Thus, the measurements will not be true splitting constants but good relative measurements. As such, the average for the respective splittings was taken as the "effective splitting constant".

(6) The measure of each distance $d_{ij}$ was taken as the average of several scans, and the random error was $\pm \left(\frac{\sum d^2}{N}\right)^{\frac{1}{2}}$, in

$^{11}$A. Carrington and A. McLachlan, op. cit., p.18.
which $\delta$ is the deviation from the average for a particular measurement. $N$ is the number of measurements. The measurements were taken in arbitrary units and converted to gauss after the averaging process.

The data is shown in Table 3.3. The calculated "effective splitting constants" are $|a_H|_{\text{eff}} = 3.17 \pm 0.01$ gauss and $|a_N|_{\text{eff}} = 7.66 \pm 0.01$ gauss in ethanol and $|a_H|_{\text{eff}} = 3.27 \pm 0.01$ and $|a_N| = 7.44 \pm 0.02$ in benzene. As an internal check of the validity of the measurements, the positions and relative intensities of the low-field half of the E.S.R. spectrum were calculated using the "effective splitting constants". These results and the "calculated" distance between the spectral lines are shown in Table 3.4. From the E.S.R. spectra 3.1 and 3.1a, the linewidths associated with the major bands of $\alpha$-MNN in ethanol and in benzene are measured to be .92 and .98 gauss, respectively---assuming gaussian band shapes. The "calculated" distance between all of the lines in ethanol is greater than .92; thus, their bands should be (and are) resolved in the E.S.R. spectrum. On the other hand several "calculated" lines in benzene are separated by less than .98; additionally the intensity ratios of each pair is at least 2 to 1. Thus, the weaker lines should appear as weak shoulders in the E.S.R. absorption spectrum. Careful inspection of the E.S.R. spectrum in benzene confirms these "calculated predictions". The weaker of two bands separated by less than .98 gauss are "washed-out", or they appear to be several minor splittings rather than a "band". The internal consistency of the "calculated" and measured E.S.R. spectra
TABLE 3.3

MEASUREMENTS AND THE EFFECTIVE VALUE OF THE HYPERFINE SPLITTING CONSTANTS OF α-MNN IN ETHANOL AND BENZENE

<table>
<thead>
<tr>
<th>Spectrum</th>
<th>d_{12}</th>
<th>d_{34}</th>
<th>d_{13}</th>
<th>d_{24}</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>42.6</td>
<td>42.1</td>
<td>102.7</td>
<td>102.0</td>
</tr>
<tr>
<td>2</td>
<td>42.5</td>
<td>41.8</td>
<td>102.5</td>
<td>101.8</td>
</tr>
<tr>
<td>3</td>
<td>42.7</td>
<td>41.9</td>
<td>102.5</td>
<td>101.8</td>
</tr>
<tr>
<td>4</td>
<td>42.8</td>
<td>41.8</td>
<td>102.4</td>
<td>101.2(?)</td>
</tr>
<tr>
<td>Average</td>
<td>42.6±1</td>
<td>41.9±1</td>
<td>102.5±1</td>
<td>101.9±1</td>
</tr>
</tbody>
</table>

\[ |a_H|_{\text{eff}} = 3.17±0.01 \]

<table>
<thead>
<tr>
<th>Spectrum</th>
<th>d_{12}</th>
<th>d_{34}</th>
<th>d_{13}</th>
<th>d_{24}</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>43.8</td>
<td>43.3</td>
<td>99.3</td>
<td>99.0</td>
</tr>
<tr>
<td>2</td>
<td>43.6</td>
<td>43.9</td>
<td>99.3</td>
<td>99.5</td>
</tr>
<tr>
<td>3</td>
<td>44.0</td>
<td>43.2</td>
<td>99.9</td>
<td>99.0</td>
</tr>
<tr>
<td>4</td>
<td>44.8</td>
<td>43.3</td>
<td>99.5</td>
<td>99.1</td>
</tr>
<tr>
<td>Average</td>
<td>43.8±1</td>
<td>43.3±1</td>
<td>99.5±2</td>
<td>99.1±2</td>
</tr>
</tbody>
</table>

\[ |a_N|_{\text{eff}} = 7.44±0.02 \]

*Arbitrary units.

*Conversion factor of .0750 gauss/arbitrary unit.
TABLE 3.4

RECONSTRUCTED LINE SPECTRAL POSITIONS OF \( \alpha \)-MNN USING

THE MEASURED EFFECTIVE HYPERFINE SPLITTINGS

<table>
<thead>
<tr>
<th>Line</th>
<th>Relative Intensity</th>
<th>Ethanol Position(^\dagger)(gauss)</th>
<th>( \Delta )</th>
<th>Benzene Position ( \Delta )</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>1</td>
<td>-20.15</td>
<td>3.18</td>
<td>-19.86 3.28</td>
</tr>
<tr>
<td>2</td>
<td>3</td>
<td>-16.97</td>
<td>3.18</td>
<td>-16.58 3.28</td>
</tr>
<tr>
<td>3</td>
<td>3</td>
<td>-13.79</td>
<td>1.33</td>
<td>-13.30 1.09</td>
</tr>
<tr>
<td>4</td>
<td>2</td>
<td>-12.46</td>
<td>1.85</td>
<td>-12.39 2.37</td>
</tr>
<tr>
<td>5</td>
<td>1</td>
<td>-10.61</td>
<td>1.43</td>
<td>-10.02 .91</td>
</tr>
<tr>
<td>6</td>
<td>6</td>
<td>- 9.28</td>
<td>3.18</td>
<td>- 9.11 3.28</td>
</tr>
<tr>
<td>7</td>
<td>6</td>
<td>- 6.10</td>
<td>1.34</td>
<td>- 5.83 .91</td>
</tr>
<tr>
<td>8</td>
<td>3</td>
<td>- 4.77</td>
<td>1.65</td>
<td>- 4.92 2.37</td>
</tr>
<tr>
<td>9</td>
<td>2</td>
<td>- 3.12</td>
<td>1.53</td>
<td>- 2.55 .91</td>
</tr>
<tr>
<td>10</td>
<td>9</td>
<td>- 1.59</td>
<td></td>
<td>- 1.64</td>
</tr>
</tbody>
</table>

Solvent \( \Delta H_x \) (gaussian)
Ethanol .92 gauss
Benzene 98

\(^\dagger\)Relative to the center of the E.S.R. spectrum.
assure the validity of the hyperfine splitting changes with solvent.

Comparison of the splittings in ethanol and benzene shows that in the more polar solvent, ethanol, there is a migration of the unpaired spin density at the nuclei from the α-methyl hydrogens to the nitrogens. An obvious rationalization of this data is that hydrogen bonding to the non-bonding electrons of the oxygens gives rise to an increase in the spin density in the nitrogen-oxygen region of the molecule at the expense of spin density in the α-methyl region. Supporting this contention is the fact that Osiecki and Ullman have observed protonation of α-phenylnitronylnitrooxide by trifluoroacetic acid in benzene.

In order to see if solvent shifts were due solely to hydrogen bonding, a very polar solvent, acetonitrile, which would not form hydrogen bonds was chosen. The dielectric constants of acetonitrile is 37.5 compared to 24.3 for ethanol. The results, given in Table 3.5, show that the values of $|a_N|$ are almost as large in acetonitrile as they are in ethanol. These results imply that the charge shift is influenced not only by solvents with the ability to hydrogen bond, but also by nonprotic polar solvents. This latter observation suggests that, in general, polar solvents tend to decrease the effective charge on the methyl protons and increase the charge on the nitrogens. Since acetonitrile is more polar than ethanol, one

---

### TABLE 3.5

**MEASUREMENTS AND THE EFFECTIVE VALUE OF THE NITROGEN HYPERFINE SPLITTINGS OF α-MNN₁ IN ACETONITRILE**

<table>
<thead>
<tr>
<th>Spectrum</th>
<th>$d_{12}$</th>
<th>$d_{34}$</th>
<th>$d_{13}$</th>
<th>$d_{24}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>42.8</td>
<td>43.0</td>
<td>101.5</td>
<td>101.9</td>
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<td>2</td>
<td>42.8</td>
<td>24.8</td>
<td>101.5</td>
<td>101.7</td>
</tr>
<tr>
<td>3</td>
<td>42.5</td>
<td>42.2(?)</td>
<td>101.5</td>
<td>101.2</td>
</tr>
<tr>
<td>4</td>
<td>43.0</td>
<td>42.6</td>
<td>101.4</td>
<td>102.0</td>
</tr>
<tr>
<td>5</td>
<td>42.6</td>
<td>43.0</td>
<td>101.4±1</td>
<td>101.5±3</td>
</tr>
<tr>
<td>Average ±</td>
<td>42.7±2</td>
<td>42.7±2</td>
<td>101.5±2</td>
<td></td>
</tr>
</tbody>
</table>

$|a_H|_{\text{eff}} = 3.20±0.02$

$|a_N|_{\text{eff}} = 7.60±0.02$

---

*Arbitrary units.*

*Conversion factor 0.0750 gauss/unit.*
would expect acetonitrile to show the largest changes of the $|a_N|$'s relative to benzene. This is not the case, and thus there is further evidence that the ethanol is hydrogen bonding to the oxygen atoms—which are the most likely positions in the molecule.

From all indications these solvent-solute interactions are very strong and specific interactions—so much so that the interactions might be referred to as complexation. These interactions are discussed further in the discussion of the electronic absorption spectra.

2. Electronic Spectra: The room temperature U.V. absorption spectrum of α-MNN was measured in cyclohexane and ethanol. The spectrum in cyclohexane is shown in Fig. 3.6, and the energies and extinction coefficients of the relative band maxima are shown in Table 3.6. Three distinct electronic transitions are observed in the absorption spectrum. These electronic transitions shall be referred to as transitions 1, 2 and 3 in order of increasing energy, and their absorption bands shall be referred to as bands 1, 2 and 3, respectively.

Band I has two vibrational maxima separated by 1000 cm$^{-1}$. There appear to be two—at least one—shoulders on the high energy side of band I; no such shoulders are indicated on the low energy side of the band. The lowest energy vibrational maximum in band I is observed at 17,560 cm$^{-1}$ and the band is relatively intense. This observation and the absence of a low energy tail, indicative of a forbidden origin, suggests that the potential functions of the equilibrium ground and Franck-Condon excited states are very similar.
FIGURE 3.6. Electronic absorption spectra of α-MNN in cyclohexane and ethanol at R.T.
### TABLE 3.6

**ABSORPTION ENERGIES AND EXTINCTION COEFFICIENTS OF α-MNN IN CYCLOHEXANE AND ETHANOL**

**Cyclohexane Solution**

<table>
<thead>
<tr>
<th>Å</th>
<th>cm⁻¹</th>
<th>ε(1./m.cm.)x10⁻³</th>
</tr>
</thead>
<tbody>
<tr>
<td>5693</td>
<td>17,560</td>
<td>1.74</td>
</tr>
<tr>
<td>5381</td>
<td>18,580</td>
<td>1.67</td>
</tr>
<tr>
<td>3204</td>
<td>31,210</td>
<td>22.1</td>
</tr>
<tr>
<td>3090</td>
<td>32,360</td>
<td>15.6</td>
</tr>
<tr>
<td>~2100</td>
<td>~47,500</td>
<td>~4</td>
</tr>
</tbody>
</table>

**Ethanol Solution**

<table>
<thead>
<tr>
<th>Å</th>
<th>cm⁻¹</th>
<th>ε(1./m.cm.)x10⁻³</th>
</tr>
</thead>
<tbody>
<tr>
<td>5455</td>
<td>18,330</td>
<td>2.32</td>
</tr>
<tr>
<td>3135</td>
<td>31,900</td>
<td>19</td>
</tr>
</tbody>
</table>
As such, the maximum at 17,560 cm$^{-1}$ is the zero-zero (0-0) band. Ground and excited electronic states which have very similar potential energy functions, have correspondingly similar vibrational wavefunctions. Thus, only those transitions between vibrational levels which transform as the same symmetry species are allowed, and the selection rules become $\Delta \nu = 0, \pm 2, \pm 4$, etc. The 0-0 transition is the transition of dominant intensity. The transitions $\Delta \nu = \pm 1, \pm 3, \pm 5$, etc. are allowed, however, if the ground and excited state vibrational modes transform as $a_1$ for the symmetry species $C_{2v}$.

Since the intensity of the second vibrational maximum is not much less intense than the 0-0 band, it is concluded that the vibrational structure is part of a progression ($\Delta \nu = 0, 1, 2, 3, 4$) with an apparent excited state vibrational frequency of 1000 cm$^{-1}$. It is further concluded that the vibrational structure of the 1st electronic transition arises from transitions from the zero-point level of the ground state to an excited state vibrational mode of $a_1$ symmetry and to overtones of that mode.

Band II is very similar in its shape and characteristics to band I. The same type of arguments can be applied to band II as were applied to band I. The excited state vibrational frequency of $a_1$ symmetry is measured to be 1150 cm$^{-1}$ from the spectrum.

---

Band III is not totally resolved, but in very pure n-hexane, it appears that it is truly a structureless band. The excitation energy is about $4.7 \times 10^4$ cm$^{-1}$ and $c_{\text{max}}$ is approximately $4 \times 10^3$.

The electronic absorption spectrum of $\alpha$-MNN measured in ethanol is shown in Figure 3.6. The energies and extinction coefficients are shown in Table 3.6. Bands I and II no longer show two vibrational bands, but show a maximum having a higher energy shoulder. Comparison of the energies of the first maxima of bands 1 and 2 in ethanol to the energies of the zero-zero bands in cyclohexane, shows that the transition energies are blue shifted 770 cm$^{-1}$ and 700 cm$^{-1}$, respectively, in ethanol. Comparison of the half intensity band widths of bands 1 and 2 in ethanol to those in cyclohexane shows them to be slightly narrower in ethanol; yet the vibrational structure is lost in the alcoholic solvent. This loss of vibrational structure and the change in total band contour or width implies that the solvent perturbs the vibrational levels. Such an interpretation would be consistent with hydrogen bonding which persists in the ground and excited states. The proposed hydrogen bonding would increase the reduced mass of the vibrating molecule causing a decrease in the excited state vibrational normal mode frequency, $\nu_0$. The hydrogen bonding effect is statistical in nature and when the distribution over all molecules is taken into consideration, the effect is to broaden each vibrational band to the extent that vibrational structure is lost. These considerations, in turn, would suggest that the
N-O vibrations are quite important to the observed vibrational mode because the oxygen atom is the only logical point for H-bonding. Since it was previously concluded that the pertinent vibration is of \( \alpha_1 \) symmetry, this must involve the symmetrical stretch of each N-O groups as well as other bond length changes.

The differences in the absorption spectra of \( \alpha \)-MNN in cyclohexane and ethanol suggest that an extensive solvent study (Chapter I, Sect.C) is worthwhile. Such a study would tell more about the charge distribution of the excited states relative to the ground state. The E.S.R. solvent effects have already shown that polar solvents cause a shift in the unpaired spin density from the \( \alpha \)-methyl protons to the nitrogens in \( \alpha \)-MNN. The E.S.R. solvent effects do not, however, provide information necessary to a discussion of the polarity or lack of polarity of the ground state. Nine solvents were chosen for the study. The solvents chosen were those used by Ito, et al.\(^{14}\), in their study of \( n \rightarrow \pi^* \) transitions in ketones. The desirable feature of these solvents is that they may be conveniently divided into three classes; nonpolar, polar nonprotic, and polar protic. The distinction of the latter two classes provides a means by which to isolate dipolar effects from combined hydrogen bonding and dipolar effects.

---

The solvents were dried as described in Chapter II, Sect. B. Since a loss of structure is observed in bands I and II in going from non-polar to polar protic solvents, the first band maxima were chosen to locate the "band position" in the solvent study. The solvent, the solvent index of refraction, the solvent dielectric constant, and the measured excitation energies for bands I and II are given in Table 3.7. Values of \((n^2_D-1)/(2n^2_D+1)\) for nonpolar solvents and values for \((D-1)/(D+1)\) for polar nonprotic solvents are listed in Table 3.8. The functional dependence of the excitation energy on \((D-1)/(D+2)\) for bands I and II is shown in Figure 3.7. The functional dependence of the excitation energy on \((n^2_D-1)/(2n^2_D+1)\) is shown for bands I and II in Figure 3.9. Both plots in Figure 3.7 have a positive slope and imply that the ground state is more polar than the first and second excited states. On the other hand, the plots of Figure 3.8 give somewhat contradictory results. Within the limits of random error, the first excited state is confirmed to be less polar than the ground state—since the slope of excitation energy versus \((n^2_D-1)/(2n^2_D-1)\) is positive. For band 2, there is no simple functional dependence of the excitation energy on \((n^2_D-1)/(2n^2_D-1)\). The excitation energies of band I in polar protic solvents (Table 3.7) are greater than in the polar nonprotic solvents. Such a result is consistent with hydrogen bonding in the ground state. The same trend is followed except with respect to chloroform. In chloroform the excitation energy is lower than in any other solvent used. Another chlorine containing compound, carbon tetrachloride, gives
## TABLE 3.7

**ABSORPTION ENERGIES OF α-MNN IN SEVERAL SOLVENTS**

<table>
<thead>
<tr>
<th>Solvent</th>
<th>$n_D$</th>
<th>$D$</th>
<th>Band I (cm$^{-1}$)</th>
<th>Band II (cm$^{-1}$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>n-hexane</td>
<td>1.375</td>
<td>1.89</td>
<td>17,610</td>
<td>31,300</td>
</tr>
<tr>
<td>carbon tetrachloride</td>
<td>1.460</td>
<td>2.238</td>
<td>17,770</td>
<td>30,770</td>
</tr>
<tr>
<td>benzene</td>
<td>1.501</td>
<td>2.284</td>
<td>17,770</td>
<td>31,190</td>
</tr>
<tr>
<td>ethyl ether</td>
<td>1.356</td>
<td>4.335</td>
<td>17,770</td>
<td>31,320</td>
</tr>
<tr>
<td>methylacetate</td>
<td>1.362</td>
<td>6.68</td>
<td>17,890</td>
<td>31,500</td>
</tr>
<tr>
<td>acetonitrile</td>
<td>1.344</td>
<td>37.5</td>
<td>18,030</td>
<td>31,670</td>
</tr>
<tr>
<td>chloroform</td>
<td>1.449</td>
<td>4.806</td>
<td>18,050</td>
<td>30,440</td>
</tr>
<tr>
<td>isobutyl alcohol</td>
<td>1.398</td>
<td>17.7</td>
<td>18,320</td>
<td>31,810</td>
</tr>
<tr>
<td>ethanol</td>
<td>1.361</td>
<td>24.3</td>
<td>18,330</td>
<td>31,900</td>
</tr>
</tbody>
</table>
## TABLE 3.8

**EXCITATION ENERGIES AS FUNCTIONS OF THE ELECTROMAGNETIC PROPERTIES OF SOME SOLVENTS**

### Non-Polar Solvents

<table>
<thead>
<tr>
<th>Solvent</th>
<th>Band I (cm(^{-1}))</th>
<th>Band II (cm(^{-1}))</th>
</tr>
</thead>
<tbody>
<tr>
<td>n-hexane</td>
<td>17,610±10</td>
<td>31,340±40</td>
</tr>
<tr>
<td>Carbon tetrachloride</td>
<td>17,770±10</td>
<td>30,770±40</td>
</tr>
<tr>
<td>Benzene</td>
<td>17,700±10</td>
<td>31,190±40</td>
</tr>
</tbody>
</table>

### Polar Non-Protic Solvents

<table>
<thead>
<tr>
<th>Solvent</th>
<th>Band I (cm(^{-1}))</th>
<th>Band II (cm(^{-1}))</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ethyl ether</td>
<td>17,700±10</td>
<td>31,370±40</td>
</tr>
<tr>
<td>Methylacetate</td>
<td>17,890±10</td>
<td>31,330±40</td>
</tr>
<tr>
<td>Acetonitrile</td>
<td>18,080±10</td>
<td>31,670±40</td>
</tr>
</tbody>
</table>
FIGURE 3.7. Functional dependence of the excitation energies of Bands I and II on $\frac{D-1}{D+1}$.
FIGURE 3.8. Functional dependence of Bands I and II of α-MNN on $\frac{n_{D}^{-1}}{2n_{D}^{2}+1}$. 
an excitation energy lower than other members of its group. Since chlorine is an excellent radical scavenger, and since solutions of \( \alpha \)-MNN are light sensitive, the effects of chloroform and carbon-tetrachloride are disregarded in the solvent study. It is proposed that a loose complex is formed between \( \alpha \)-MNN and chlorine containing compounds. This "complex" has a lower excitation energy in band II. Although the photochemistry of \( \alpha \)-MNN would be an interesting study and might elucidate the nature of the "complex", the topic shall not be pursued in this work.

It is concluded that the ground state of \( \alpha \)-MNN is more polar than the excited state associated with bands I and II. Therefore, the ground state has a permanent dipole moment, or surely local dipoles.

Electronic transitions which blue shift in going to more polar solvents are often assumed to be \( n \rightarrow \pi^* \) transitions.\(^{15}\) Conversely, transitions which are red-shifted in going to more polar solvents are said to be \( \pi \rightarrow \pi^* \).\(^{16}\) Such generalizations are probably true for most molecules, especially if large \( \pi \) dipolar changes are not possible. However, an \( n \rightarrow \pi^* \) transition should also have a low oscillator strength; \( n \rightarrow \pi^* \) transitions normally possess


extinction coefficients of less than 200.\textsuperscript{14} This is surely not the case for α-MNN where the observed bands have extinction coefficients near $2 \times 10^3$. Yet, the electronic transitions in α-MNN show considerable blue shifts in going to more polar solvents. These same effects have been observed in other \(\pi\) type systems in which \(\pi\) electrons contribute to the dipole moments.\textsuperscript{17} In the case of pyridine N-oxide a low intensity transition which also blue shifts has been found in addition to the intense blue shifted transitions. Ito and Hata have attributed the blue shift of the high intensity bands in polar solvents to perturbations which stabilize the ground state. They, therefore, classify the weak transition as \(n \rightarrow \pi^*\) and the high intensity transitions as \(\pi \rightarrow \pi^*\). Considering the structure of the molecule, the writer finds the assignments to be quite reasonable. It is important to recognize that electronic transitions represent the energy difference between states—not just the difference in energy between two orbitals. Thus, dipolar forces or hydrogen bonding perturb the state of the molecules; changes in the molecular orbital scheme undoubtedly accompany such perturbations. The latter as shown by the E.S.R. solvent effects on α-MNN. In view of the observed transition intensities and the similar behavior of the electronic transitions.


absorption spectrum of α-MNN to that of the conjugated N-oxy compounds, bands I and II are assigned as being π → π transitions. There is no evidence for n → π* transitions at lower energy than band I or between bands I and II in the room temperature absorption spectra.

The absorption spectra of α-MNN in E.P.A. and P.M.P. were measured at 77°K. The purpose for the measurements was two-fold. One reason for measuring the 77°K absorption spectra was to see if the vibrational bands could be better resolved at 77°K and to assure that no vibrational modes would be excited in the ground electronic state. The other reason was to check for dimer bands in the E.P.A. spectrum at 77°K. It should be recalled that a dimer triplet was observed in the E.S.R. spectrum of α-MNN in ethanol at 77°K—although at a very low concentration. The R.T. and 77°K absorption spectra in E.P.A. are shown in Figure 3.9 and the relative maxima and their energies are indicated in Table 3.9. The extinction coefficients were not measured. Of course, the E.P.A. at 77°K contracts to about 75% of its room temperature volume. The room temperature absorption spectrum of α-MNN in E.P.A. is very similar in contour to that of α-MNN absolute ethanol. The spectrum is somewhat red-shifted, however. There are probably enough ethanol molecules to hydrogen bond to α-MNN (to give the same band shape as ethanol), but not enough to set up the secondary reaction field as in ethanol. The latter effect leads to the red shift relative to ethanol.

At 77°K the band I and II are better resolved. The first band is only slightly blue shifted; this might be expected since
FIGURE 3.9. Electronic absorption spectra of α-MNN in E.P.A. at R.T. and 77°K.
FIGURE 3.10. Electronic absorption spectra of α-MNN in P.M.P. at R.T. and 77°K.
<table>
<thead>
<tr>
<th></th>
<th>E.P.A.</th>
<th>P.M.P.</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>R.T.</td>
<td>77°K</td>
</tr>
<tr>
<td>Å</td>
<td>cm</td>
<td>Å</td>
</tr>
<tr>
<td>5510</td>
<td>18,150</td>
<td>5476</td>
</tr>
<tr>
<td>5135</td>
<td>19,470</td>
<td>4797</td>
</tr>
<tr>
<td>3154</td>
<td>31,710</td>
<td>3137</td>
</tr>
<tr>
<td>3015</td>
<td>33,170</td>
<td></td>
</tr>
</tbody>
</table>

**TABLE 3.9**

**ABSORPTION ENERGIES OF α-MNN IN E.P.A. AND P.M.P. SOLUTIONS AT R.T. AND 77°K**
the dielectric constant decreases with temperature. The 0-0 band at 18,260 cm\(^{-1}\) is relatively more intense than the other members of the progression. The excited state vibrational frequency is \(\sim 1200\) cm\(^{-1}\).

A new shoulder is found to the low energy side of band II (at 30,300 cm\(^{-1}\)). The shoulder is estimated to have an absorption coefficient of about 200. It is not known if the shoulder arises from a dimer species or from a \(n \rightarrow \pi^*\) transition that was previously obscured by the R.T. band width. Band II, itself, is better resolved and looks much like the R.T. absorption in hydrocarbons. The vibrational frequency is about 1,250 cm\(^{-1}\).

The electronic absorption spectrum of \(\alpha\)-MNN in P.M.P. at R.T. and 77°K are shown in Figure 3.10; the energies are shown in Table 3.9. At 77°K the spectrum is tremendously blue shifted. The zero-zero transitions of bands I and II are blue shifted 1600 cm\(^{-1}\) and 1300 cm\(^{-1}\), respectively. Such an extreme blue shift is unexpected. One can actually see the color of the solution change from a mixture of violet and red (R.T.) to nearly all red at 77°K. The change in color appears to be rather rapid and occurs very near 77°K. This latter statement is based on the observation of the slow thawing of a sample.

Band I is well resolved in P.M.P. and shows two well resolved maxima at 19,440 cm\(^{-1}\) and 20,850 cm\(^{-1}\). There are also shoulders at 22,200, 23,500, and 20,000 cm\(^{-1}\). The absorption at
20,000 cm\(^{-1}\) does not appear in the 77\(^{0}\)K E.P.A. spectrum. Neglecting the "bump" at 20,000 cm\(^{-1}\), one has the following progression of peaks and shoulders: 19,440, 20.850, 22,200 and 23,500 cm\(^{-1}\). These spacings fit rather nicely with an excited state vibrational mode with \(\nu_0 = 1400\) cm\(^{-1}\).

As in E.P.A. a low intensity shoulder appears at the low energy side of band II at 30,300 cm\(^{-1}\). Band II has two clearly resolved maxima at 32,680 and 33,900 cm\(^{-1}\); a shoulder is visible at 35,200 cm\(^{-1}\). These correspond to an excited state vibrational frequency of 1300 cm\(^{-1}\).

The blue shifts of \(\alpha\)-MNN in P.M.P. in going from room temperature to 77\(^{0}\)K are very large. It is possible that water which is soluble at R.T. becomes less soluble at 77\(^{0}\)K and preferentially solvates the \(\alpha\)-MNN molecules. If such were the case, however, one might expect decreased vibrational splittings associated with hydrogen bonding of water molecules to the oxygens on \(\alpha\)-MNN. Such an effect is not observed, however. In fact, the vibrational splittings are larger in P.M.P. than in E.P.A. This is in agreement with the room temperature analyses of the vibrational splittings in cyclohexane and ethanol. The absorption spectrum of \(\alpha\)-MNN in \(\text{H}_2\text{O}\) was measured to compare the blue shift with that observed in P.M.P. at 77\(^{0}\)K. The spectrum is shown in Figure 3.11 and the energies are shown in Table 3.10. Band I is not blue shifted as much in \(\text{H}_2\text{O}\) at R.T. as it is in P.M.P. at 77\(^{0}\)K. Band II has a maximum at about the same
FIGURE 3.11. Electronic absorption spectrum of α-MNN in water at R.T.
TABLE 3.10

ABSORPTION ENERGIES OF α-MNN IN WATER

<table>
<thead>
<tr>
<th>Å</th>
<th>cm⁻¹</th>
</tr>
</thead>
<tbody>
<tr>
<td>5290</td>
<td>18,900</td>
</tr>
<tr>
<td>3050</td>
<td>32,790</td>
</tr>
</tbody>
</table>
energy under both conditions. Similar experimental results shall be encountered for diradical molecules in P.M.P. at 77°K, and shall be further discussed at that time.

Thus, at 77°K the 0-0 bands appears to be more intense relative to R.T., but the same vibrational analysis of the principal bands is applicable at both temperatures. The vibrational splittings of band I are smaller in E.P.A. than in P.M.P., but for band II, the splittings are the same—within experimental error. With regard to the dimer species observed in the E.P.R. spectrum in E.P.A., it is possible that the shoulder at the low energy side of band II arises from the dimer. Nevertheless, the population would be very low; this is in agreement with the prediction from the E.S.R. spectrum.

An attempt was made to measure an emission spectrum of α-MNN in an ethanol glass (95% EtOH) at 77°K. The compound was excited in both the regions of bands I and II; no emission was observed. A search for emission was made at low energy and in the region between bands I and II. It is concluded that α-MNN in solution does not emit.

(B) α-PHENYLNITRONYLNITRROXIDE (α-φNN)

1. E.S.R.: The room temperature E.S.R. spectrum of α-φNN in benzene, as measured in these laboratories (Figure 3.12), consists of five major lines (a_N ≈ 7.5 g) and several smaller hyperfine splittings. These results are in agreement with |a_N| reported
by Osieki and Ullman who assigned the major splittings to two equivalent nitrogens in the molecule. A detailed analysis of the smaller hyperfine splittings, $|a_N| = 0.2 \, g$, has not been attempted. At least twelve lines are visible in a moderately resolved spectrum. This is more than one would expect to resolve for only methyl hydrogens on the nitronylnitroxide ring (see $\alpha$-MNN - E.S.R.). Thus, the phenyl hydrogens are contributing to the spectral splittings. Although the phenyl hydrogens are contributing to the spectral splitting, implying delocalization over the molecule, the net effect is small, and the probability of finding the electron on the phenyl group is probably less than 2%. Interestingly, substitution of a phenyl group in place of a methyl group at the $\alpha$-position affects the splitting constant less than a solvent change from EtOH to benzene.

A high gain E.S.R. spectrum reveals at least one $C^{13}$ splitting, having $|a_{C^{13}}| = 12.0 \, g$ (Figure 3.13; this is the same value as was observed for one of the $C^{13}$'s of $\alpha$-MNN. It is difficult to say, with certainty, whether there is or is not a resonance shoulder on the outer-most principal lines. Based on the previous assignment in $\alpha$-MNN, one would expect such a resonance. The difficulty may be attributed to the increased number of small hyperfine splittings which cause an effective increase in $\Delta H_2$ for the principal five lines.

The measured $g$ value of $2.0075 \pm 0.0007$ is slightly at variance with $g = 2.00651 \pm 0.00003$ reported by Ullman, et al. Since the latter authors did not describe their experimental technique, it
FIGURE 3.13. High gain E.S.R. spectrum of α-ϕNN in benzene.
is not possible to discuss the origin of the discrepancy.

The E.S.R. spectrum of what appeared to be needle-like single crystals of α-ϕNN did not show significant change in the "measured g-value" with orientation. The magnetic field did not shift more than ±2 gauss. The lack of anisotropy, however, does not necessarily mean that g tensor is nearly isotropic. Since crystal geometry is important to the "measured g-value", the observed resonance is probably a superposition of resonances of more than one orientation in the magnetic fields. The E.S.R. spectrum (Figure 3.14) of a powder sample had $\Delta H_{\perp} = 13.4$ gauss.

A rigid glass E.S.R. spectrum of α-ϕNN in ethanol at $77^0K$ (Figure 3.15) is very similar to that observed for α-MNN, except that better resolution is observed in the case of α-ϕNN. The improved resolution results from the absence of the 3.2 g proton splittings present in α-MNN. The similarity of the isotropic splittings and the rigid glass spectrum, which reflects the anisotropic splittings for α-MNN and α-ϕNN, lead the writer to conclude that the unpaired electron undoubtedly occupies the same type of ground state orbital in both compounds. The anisotropic hyperfine splittings are dependent upon the "shape of the orbital"; and, undoubtedly, the "orbital shape" near the paramagnetic nuclei is very similar for α-MNN and α-ϕNN.

The similarity of the rigid glass spectra of α-MNN and α-ϕNN definitely shows that the nitrogen hyperfine tensors are
FIGURE 3.14. E.S.R. spectrum of a powder sample of \( \alpha\)-\( \beta\)NN.
FIGURE 3.15. E.S.R. doublet spectrum of α-ΦNN in ethanol at 77°K.
responsible for the observed anisotropy. Since no other paramagnetic nuclei have considerable isotropic splittings (the \(\alpha\)-methyl group is missing), this is the only logical choice. Further comments shall be reserved until the \(\alpha(o-T)\)NN rigid glassy solution E.S.R. spectrum has been measured.

A triplet resonance was observed in the half-field region for the 77\(^{\circ}\)K ethanol glass of \(\phi\)NN (see Figure 3.16). The corresponding \(\Delta m_s = 1\) triplet resonances were not observed. At a magnetic field of 1524 gauss and a microwave frequency of 9170 Mc/S, D\(^*\) was calculated to be 1.02\(\times10^3\) gauss. This is the same value, that was observed for \(\alpha\)-MNN at 77\(^{\circ}\)K in ethanol. It appears that dimerization may be common to the \(\alpha\)-nitronylnitroxide radicals at 77\(^{\circ}\)K.

The R.T. hyperfine splitting changes of \(\alpha\)-\(\phi\)NN in ethanol and benzene were carefully measured following the procedures previously described for \(\alpha\)-MNN. Because of the different choice of lines, however, the average values are the true splitting constants—not just "effective splitting constants". The distance between each line of relative intensity 2 (giving the lines of lowest intensity a value of 1) and the center line (relative intensity 3) were chosen for the measurements. The measurements and the splitting constants are shown in Table 3.11. As expected, the nitrogen splittings are larger in ethanol solvent than in benzene.
FIGURE 3.16. Half-field E.S.R. spectrum of $\alpha$-NN in ethanol at 77°K.
TABLE 3.11

MEASUREMENTS AND THE EFFECTIVE VALUES OF THE HYPERFINE SPLITTING CONSTANTS OF α-Fe in SOLUTIONS OF ETHANOL AND BENZENE

**Ethanol**

<table>
<thead>
<tr>
<th>Spectrum</th>
<th>(d_{23})</th>
<th>(d_{34})</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>102.6</td>
<td>100.8</td>
</tr>
<tr>
<td>2</td>
<td>103.0</td>
<td>101.5</td>
</tr>
<tr>
<td>3</td>
<td>102.4</td>
<td>101.2</td>
</tr>
<tr>
<td>4</td>
<td>101.9</td>
<td>101.2</td>
</tr>
<tr>
<td>5</td>
<td>102.0</td>
<td>100.9</td>
</tr>
</tbody>
</table>

Average → 102.4±0.4  101.1±0.2

\(|a_N|_{\text{eff}} = 7.63±0.03\)

**Benzene**

<table>
<thead>
<tr>
<th>Spectrum</th>
<th>(d_{23})</th>
<th>(d_{34})</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>100.5</td>
<td>99.0</td>
</tr>
<tr>
<td>2</td>
<td>100.5</td>
<td>99.0</td>
</tr>
<tr>
<td>3</td>
<td>100.5</td>
<td>100.2(?)</td>
</tr>
<tr>
<td>4</td>
<td>99.8</td>
<td>99.5</td>
</tr>
<tr>
<td>5</td>
<td>100.3</td>
<td>98.7</td>
</tr>
</tbody>
</table>

Average → 100.3±0.3  99.7±0.3

\(|a_N|_{\text{eff}} = 7.47±0.03\)

*Arbitrary units.

*Conversion factor of .0750 gauss/unit.
2. **Electronic Absorption Spectra**: The wavelengths of maximum absorption and the corresponding extinction coefficients of $\alpha$-$\phi$NN were reported by Osiecki and Ullman. The absorption spectra have been measured and several transitions have been observed that did not appear in their tables. The absorption spectra of $\alpha$-$\phi$NN in n-hexane and in ethanol are shown in Figure 3.17; the energies, extinction coefficients and vibrational frequencies are given in Table 3.12. The bands originating at $6962\text{\AA} (14,360 \text{ cm}^{-1})$ and at $3628\text{\AA} (27,560 \text{ cm}^{-1})$ are similar to bands I and II of $\alpha$-$\phi$NN, respectively and are again given the labels I and II. The high energy absorptions are designated as absorption region III.

Band I in n-hexane is a broad (5,500 cm$^{-1}$) structured band showing three well resolved vibrational maxima (14,360 cm$^{-1}$; 15,640 cm$^{-1}$; 16,920 cm$^{-1}$) and two shoulders (18,200 cm$^{-1}$; 19,500 cm$^{-1}$). The even spacing between these peaks and shoulders is indicative of a harmonic excited state potential function; the symmetric excited state vibrational frequency is measured to be 1280 cm$^{-1}$. The excited state vibrational interval observed for $\alpha$-$\phi$NN was 1,020 cm$^{-1}$ which compares favorably with 1,280 cm$^{-1}$ for $\alpha$-$\phi$NN. Band I in $\alpha$-$\phi$NN is red shifted 3,200 cm$^{-1}$ from band I in $\alpha$-$\phi$NN and the Franck-Condon contour of the band is slightly altered; band 2 of the vibrational progression is more intense in $\alpha$-$\phi$NN rather than the 0-0 band. Both the red shift and change in band contour are indicative of an increased interaction between the
FIGURE 3.17. Electronic absorption spectra of α-PP in n-hexane and in ethanol.
# Absorption Energies and Extinction Coefficients of α-6NN in n-Hexane and Ethanol Solutions

<p>| | | | |</p>
<table>
<thead>
<tr>
<th></th>
<th></th>
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<th></th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>$\lambda$ (Å)</td>
<td>$\varepsilon$ (cm$^{-1}$)</td>
<td>$\varepsilon_{(1/m \cdot cm)} 	imes 10^{-3}$</td>
</tr>
<tr>
<td><strong>n-Hexane</strong></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>6962</td>
<td>14,360</td>
<td>.212</td>
</tr>
<tr>
<td></td>
<td>6392</td>
<td>15,640</td>
<td>.444</td>
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<td>5909</td>
<td>16,920</td>
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</tr>
<tr>
<td></td>
<td>3628</td>
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<td></td>
<td>2672</td>
<td>37,430</td>
<td>13</td>
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<td></td>
<td>2394</td>
<td>41,780</td>
<td>8.6</td>
</tr>
<tr>
<td></td>
<td>2196</td>
<td>45,540</td>
<td>13</td>
</tr>
<tr>
<td><strong>Ethanol</strong></td>
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<td></td>
</tr>
<tr>
<td></td>
<td>5943</td>
<td>16,820</td>
<td>.632</td>
</tr>
<tr>
<td></td>
<td>3603</td>
<td>27,730</td>
<td>13</td>
</tr>
<tr>
<td></td>
<td>2633</td>
<td>37,970</td>
<td>11</td>
</tr>
<tr>
<td></td>
<td>2387</td>
<td>4,890</td>
<td>8.2</td>
</tr>
</tbody>
</table>
nitronylnitroxide and α-phenyl relative to α-methyl. In alcohol, band I of α-φNN blue shifts 1180 cm\(^{-1}\) and a general loss in structure occurs relative to the spectrum in n-hexane. Both of these effects are analogous to the solvent-induced effects observed for α-MNN.

The marked similarities in energy, vibration interval, absorption intensity, and solvent effect for bands I of α-MNN and α-φNN strongly indicate that the electronic transition responsible for band I is predominately localized in the nitronylnitroxide portion of these molecule.

Band II is very similar in contour to band II of α-MNN. The 0-0 band occurs at 27,560 cm\(^{-1}\), and is at least twice as intense as the other members of the vibrational progression. This suggests that the ground state and Franck-Condon excited state potential functions are very similar. The excited state vibrational frequency is about 1,200 cm\(^{-1}\). The 0-0 band of band II of α-φNN in n-hexane is red shifted 3,65 cm\(^{-1}\) relative to α-MNN. This red shift and the phenyl ring hyperfine splittings definitely imply that the interaction between the nitronylnitroxide and phenyl rings is not negligible. Although there is interaction between the two rings, the energies and/or contours of bands I and II are not so different that they can not be related to the nitronylnitroxide subsystem. In ethanol the vibrational splittings are not so well resolved as in n-hexane and the zero-zero band is blue shifted. For band II of α-φNN in n-hexane, the energy, the Franck-Condon contour and the vibrational splittings
are very similar to band II of α-MNN in cyclohexane. Thus, these similarities establish the "semi-localized" character of the transition. Analogous to band II of α-MNN, band II is assigned as being π → π in nature.

Between bands I and II, a very weak shoulder was observed. The shoulder has a maximum near 4350 Å. It is difficult to separate the absorption since it appears between bands I and II. The molar extinction coefficient is estimated to be about 30. The weak intensity suggests an n-π transition, but no definite assignment shall be attempted. (This band is obscured in ethanol).

Absorption region III is somewhat more complex since it consists of a number of maxima. The bands appear to be "overlapping transitions". The absorption at 37,430 cm⁻¹ and the absorption which is indicated by the rising absorption at 50,000 cm⁻¹ are characteristic of substituted benzenes such as nitrobenzene, benzoic acid and benzaldehyde. In terms of the nomenclature applied to benzene and substituted benzenes by Daub and Vandenbelt, the transitions might easily be associated with the "first primary" and second primary" bands, respectively. These transitions are quite red-shifted relative to benzene and have transition energies similar to nitrobenzene. The maximum at 35,240 cm⁻¹ (really a shoulder) may be related to band III of α-MNN. The absorption maxima at 41,780 cm⁻¹ and 45,540 cm⁻¹ do not appear to belong to the composite systems alone. These transitions might be attributed to interactions

---

between the rings or they may be charge transfer bands in which an electron is transferred from the nitronylnitroxide to the phenyl ring. In going to ethanol, all of the bands in region III are blue shifted relative to the spectrum in n-hexane.

In summary, the phenyl and nitronyl nitroxide ring systems interact—to a limited extent. Bands I and II of \( \alpha-\phi\text{NN} \) are related to bands I and II of \( \alpha-\text{MNN} \). Absorption region III has transitions which are very similar to band III of \( \alpha-\text{MNN} \) and substituted benzenes. On the other hand, there are some transitions which are not related to one subsystem alone. The similarity of the unpaired electron distribution in the ground state of \( \alpha-\text{MNN} \) and \( \alpha-\phi\text{NN} \) should also be recalled (E.S.R., this section). Considering these results, description of \( \alpha-\phi\text{NN} \) as a composite molecule of perturbed subsystems is justified.

3. Other Experiments: Among the experiments reported by Osiecki and Ullman\(^\text{17}\) were the protonation of \( \alpha-\phi\text{NN} \) with trifluoroacetic acid and the synthesis of a compound which they suspected of being the chloride salt of the oxidized \( \alpha-\phi\text{NN} \). There was, however, no electronic absorption data on these compounds. These spectra are important because they should give the "limiting shift" of the electronic absorption bands with protonation and, secondly, the cation spectrum of the radical should be helpful to an assignment of the transitions of the neutral radical.
The protonated species was prepared by dissolving $\alpha$-$\phi$NN in approximately 10% (by volume) trifluoroacetic acid (TFAC) in benzene solution. The E.S.R. spectrum was measured (Figure 3.18). Osiecki and Ullman's interpretation of two inequivalent nitrogens ($|a_N| = 5.7$ gauss, $|a_{N'}| = 4.5$ gauss) and a proton ($|a_H| = 4.7$ gauss) is consistent with experiment. It was found that the E.S.R. spectrum changed with time. The center lines became less intense and two extra lines appeared in the wings of the spectrum; the spectrum appears to be a superposition of the protonated species and some other radical.

The most interesting aspect of the E.S.R. spectrum is the change in the $g$ value of the protonated $\alpha$-$\phi$NN in the trifluoroacetic acid benzene mixture compared to the $g$ value in benzene. The measured $g$ value of 2.0045 is in contrast to 2.0075 in pure benzene. The change in the $g$ value may be attributed to one of—or a combination of—several effects:

(a) A drastic change in the spin density of the orbital with which the unpaired electron is principally associated.

(b) A large change of the energy and/or the symmetry of the orbitals which interact most strongly with the unpaired electron M.O. via spin orbit coupling.

Changes in the isotropic splitting constants—as well as the appearance of a spin density on the added proton—should serve as a measure of the change in the ground state "unpaired electron" M.O. A more rigorous test would be to observe the rigid glass
FIGURE 3.18. E.S.R. spectrum of $\alpha$-NN in solution with TFAC and benzene.
FIGURE 3.19. E.S.R. spectrum of α-6NN in solution with TFAC and benzene (three hours after preparation).
spectrum also. Unfortunately, benzene is not known for its ability to form glasses. It is interesting to note that the splitting at the added proton is 4.7 gauss. Using Equation 3a, the orbital probability is about .01 (i.e., the unpaired electron spends 1% of its time at the additional proton. The observed hyperfine splitting is small, and it is similar to protonated species which are considered to be π systems. As an example, the amino proton splittings in N,N'dihydro-1,4-dipyridinyl cation is 4.2 gauss. Such a comparison indicates that the unpaired electron is in a π orbital.

Although the M.O. model discussed has been restricted to an L.C.A.O. M.O. interpretation, a more rigorous treatment of the electronic structure would include configuration interaction of antisymmetrized wavefunctions. A limited treatment of configuration interaction leads to McConnel's famous relation \( a = Q\rho \), in which \( Q \) is a σ-π parameter and \( \rho \) is the net electron spin density in a carbon π M.O.\(^{20}\). That relationship is used for hydrocarbon aromatic systems. The same type of treatment for an oxygen hydrogen bond should give the correct order of magnitude for the splitting at the proton.\(^{21}\)

If the proton is principally in a π orbital, then the positive \( g \) value contribution would come from interaction of the ground state with excited states in which lower lying σ electrons were excited to the unpaired electron M.O. (see Equation 2). Two important


\[^{21}\text{Opinion of the writer.}\]
questions are: (1) What effect does protonation have on the spin densities at the various atoms in the different M.O.'s?, and (2) What is the effect of protonation on the energies of the σ orbitals relative to the energies of the π orbitals? A qualitative answer to these questions has been expressed by Kawamura, et al., for nitroxide radicals. The protonation has the effect of "delocalizing" the σ electrons to include the proton; thus, the σ electron population is effectively reduced near the oxygen atoms of α-ØNN. These reduced σ charge densities lead to smaller g value contributions of these electrons via spin orbit coupling. The delocalization over the positive proton would have the effect of lowering the σ energy levels more than the π energy levels. This would also decrease spin orbit interaction (see Equation 2, Chapter I, Sect.A). Although Kawamura espoused his argument for hydrogen bonding solvents, the complete protonation is only a special extension of the qualitative argument.

The electronic absorption spectrum of α-ØNN and TFAC in benzene is shown in Figure 3.20. The energies are shown in Table 3.13. The first band maximum occurs at 21,050 cm⁻¹. It is very broad. The transition should be associated with band I observed

---

FIGURE 3.20. Electronic absorption spectrum of α-βNN in solution with TFAC and benzene.
<table>
<thead>
<tr>
<th>( \bar{\lambda} )</th>
<th>cm(^{-1} )</th>
</tr>
</thead>
<tbody>
<tr>
<td>4750±6</td>
<td>21,050±40</td>
</tr>
<tr>
<td>3075±6</td>
<td>32,520±60</td>
</tr>
</tbody>
</table>

**TABLE 3.13**

**ABSORPTION ENERGIES OF \( \alpha - \phi NN \) IN A SOLUTION OF TRIFLUOROACETIC ACID AND BENZENE**
FIGURE 3.21. Absorption spectra of α-ḍNN in benzene upon successive additions of TFAC.
in n-hexane. The assignment is based upon observation of the spectra upon successive additions of one drop of TFAC to a solution of \(\alpha-\phi\text{NN}\) in benzene while in the absorption cell (see Figure 3.21 for spectra). The absorption coefficient increases with the addition of TFAC, and it is estimated to be about 1100 for the protonated species. The value of \(\varepsilon\) at \(\lambda_{\text{max}}\) for band I in ethanol was measured to be 632. Band I has blue shifted 5500 cm\(^{-1}\) relative to its value in ethanol. The second band should be associated with band II in ethanol and n-hexane. Band II has blue shifted 3600 cm\(^{-1}\) relative to its value in ethanol. Unfortunately, the higher energy bands can not be observed as the benzene begins to absorb strongly. The observed blue shifts are very large—even in the light of previous discussion of protonation effects, and are not well understood.

The other spectrum of interest was that of the \(\alpha-\phi\text{NN}\) cation. Osiecki and Ullman produced the cation by oxidizing the radical with chlorine gas. The cation was confirmed by the NMR spectra of the product in \(\text{SO}_2\text{Cl}_2\) which indicated five aromatic hydrogens and a singlet of four methyl groups. Since the compound gave an NMR and no ESR absorptions, there is little doubt that the compound was the cation radical.

In these laboratories, \(\alpha\)-phenyl-1-nitronyl-1-nitroxide, dissolved in carbon tetrachloride, was treated with chlorine gas until the characteristic blue color disappeared. The product was an orange solid which precipitated in carbon tetrachloride. The compound was
very hydroscopic, and would pick up water from the air to give the characteristic blue color of the radical. The compound dissolved in very dry acetonitrile to give a yellow solution. If the acetonitrile was not very dry, the absorption of the unoxidized radical also appeared in the optical absorption spectrum; and the solution gave a strong E.S.R. signal. The solutions were stable for at least twenty-four hours, and addition of water regenerated the radical color. Addition of AgNO₃ to the aqueous solution gave a white precipitate which disappeared and reappeared with successive additions of ammonia and nitric acid—thus, confirming the presence of the chloride ion. Addition of solid sodium bromide to solutions of the orange product in acetonitrile also regenerated the blue radical.

The absorption spectrum in acetonitrile is shown in Figure 3.22, and the energies are shown in Table 3.14. Two broad bands and a rising absorption at 2300 Å (the limit of the absorption range of acetonitrile) were observed. Band I is a broad band with a maximum at 22,340 cm⁻¹. The second band is somewhat sharper occurring at 31,340 cm⁻¹. Comparisons of this spectrum to that observed for the α-ØNN radical are, at least, uncertain. If one associates the first two bands at 22,340 cm⁻¹ and 31,340 cm⁻¹ with bands I and II observed in α-ØNN neutral radical, this implies that the bands are blue shifted from those of the neutral radical by 5,600 cm⁻¹ and 3,600 cm⁻¹, respectively. Although the rising
FIGURE 3.22. Electronic absorption spectrum of \( \alpha \)-NN cation in acetonitrile.
TABLE 3.14

**ABSORPTION ENERGIES OF α-βNN CATION IN ACETONITRILE SOLUTION**

<table>
<thead>
<tr>
<th>λ (Å)</th>
<th>cm⁻¹</th>
<th>ε (1/m.cm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>4477±6</td>
<td>22,340±40</td>
<td>~3.0x10³</td>
</tr>
<tr>
<td>3124±6</td>
<td>31,340±60</td>
<td>~18x10³</td>
</tr>
</tbody>
</table>
absorption at 2300 Å can not be characterized due to solvent absorption, this absorption could presumably be associated with region III observed for the neutral radical. This assignment indicates that the first strong absorption of region III is blue shifted at least 6,000 cm⁻¹ relative to that in the neutral radical. Another possible interpretation is that all or parts of the absorption corresponding to region III for the neutral radical are missing the in the cation spectrum.

In a shell model the Aufbau Principle dictates that the unpaired electron resides in the highest unfilled M.O. The appearance of bands I and II in the spectrum of both the neutral radical and the action indicates that the promotion of the unpaired electron is not responsible for either of bands I and II. The only alternative is that bands I and II in the neutral radical involve the promotion of electrons from lower energy pi M.O.'s to the orbital occupied by the unpaired electron. In the cation bands I and II would then correspond to the promotion of electrons from the lower energy pi M.O.'s to the orbital formerly occupied by the unpaired electron. In the absence of solvent effects and absence of electron correlation between electrons in different M.O.'s, one would expect the cation spectrum to be red shifted relative to that of the neutral radical. The electrons promoted to the completely vacant orbital in α-ΦNN⁺ would experience less repulsion. This expected red shift is not observed, but rather a blue shift. Of course, we are comparing
the spectrum of $\alpha$-$\phi$NN neutral radical in ethanol to that of $\alpha$-$\phi$NN$^+$ in acetonitrile. It is possible that the solvent effects on the cation account for the blue shifts.

If one attempts to associate the first and second bands of the cation with band II and region III of the $\alpha$-$\phi$NN radical, then the red shift (5000 cm$^{-1}$) must be rationalized. In addition, the relative intensities in going from radical to cation would be reversed and each greatly altered in magnitude. The latter discourages this assignment.

Thus, it may be concluded that the first and second bands observed for $\alpha$-$\phi$NN$^+$ correspond to bands I and II, respectively, of $\alpha$-$\phi$NN. In addition, the rising absorption at 2300$\AA$ in the cation spectrum may correspond to region III in the neutral radical spectrum.

(C) $\alpha$-(o-tolyl)Nitronylnitroxide:

1. E.S.R.: The E.S.R. spectra of $\alpha$-oTNN are quite similar to those of $\alpha$-$\phi$NN. The R.T. solution spectrum in ethanol ($g = 2.0064$) is shown in Figure 3.23. Five principal splittings are observed which have $|a_N| = 7.6$ gauss. The presence of smaller hyperfine splittings are indicated by poorly resolved shoulders. Improved resolution could not, however, be obtained in the most dilute solutions. Based on the experimental data, the nitrogens are magnetically equivalent.
FIGURE 3.23. E.S.R. spectrum of α-oTNN in ethanol at R.T.
A high gain R.T. E.S.R. spectrum in benzene (Figure 3.24) reveals a $^{13}\text{C}$ splitting, $|a_{^{13}\text{C}}| = 12.1$ gauss, as was observed for $\alpha$-NN. The presence of a shoulder on the principal resonance is more clearly resolved for $\alpha$-oTNN than for oNN; $|a_{^{13}\text{C}}|$ is estimated to be $6.2 \pm 0.3$ gauss. There is a shoulder at the high field side of the $|a_{^{13}\text{C}}| = 12.1$ gauss resonance. A resonance with such an intensity would be non-reconcilable with known isotopic abundances.

From the collective data (Table 3.15), it may be concluded that the isotropic splittings of $^{14}\text{N}$ and $^{13}\text{C}$ are essentially the same in $\alpha$-MNN, $\alpha$-NN and $\alpha$-oTNN.

E.S.R. spectra of small diamond shaped crystals of $\alpha$-oTNN showed little anisotropy and a powder sample had $\Delta H_2 = 13.5$ gauss. These results are almost identical to those observed for $\alpha$-NN.

The 77\(^\circ\)K rigid glass E.S.R. doublet spectrum (Figure 3.25) is non-distinguishable from that of $\alpha$-NN. Thus, the similarity of the isotropic splittings, the average g values, and the rigid glass spectra give adequate proof of the similar nature of the unpaired electron distribution in the ground state of $\alpha$-MNN, $\alpha$-NN and $\alpha$-oTNN.

A "half-field" triplet resonance (Figure 3.26) was also observed in the 77\(^\circ\)K rigid glass as it was for $\alpha$-MNN and $\alpha$-NN. $D^*$ was calculated to be $1.01 \times 10^3$ gauss (.0945 cm\(^{-1}\)). The associated $\Delta m_s = 1$ resonances were not observed.
FIGURE 3.24. High gain E.S.R. spectrum of α-oTNN in benzene.
FIGURE 3.25. E.S.R. spectrum (doublet region) of α-αTNN in ethanol at 77°K.
TABLE 3.15

COLLECTED VALUES OF THE $^{13}$C AND $^{14}$N ISOTROPIC HYPERFINE SPLITTINGS† OF THE α-NITRONYLNITROXIDES

<table>
<thead>
<tr>
<th></th>
<th>$^{13}$C</th>
<th>$^{13}$C</th>
<th>$^{14}$N</th>
</tr>
</thead>
<tbody>
<tr>
<td>α-MNN</td>
<td>6</td>
<td>12</td>
<td>7.4</td>
</tr>
<tr>
<td>α-δNN</td>
<td></td>
<td>12.0</td>
<td>7.5</td>
</tr>
<tr>
<td>α-ωTNN</td>
<td>6.2±.3</td>
<td>12.1</td>
<td>7.3</td>
</tr>
</tbody>
</table>

† units of gauss
FIGURE 3.26. E.S.R. spectrum (half-field region) of α-oTNN in ethanol at 77°K.
The effects of solvent on the hyperfine splittings and the g values (Table 3.16) follow the trends of α-MNN and α-ρNN. Effective nitrogen splitting constants and g values of α-MNN, α-ρNN and α-oTNN are compiled in Table 3.17. The change in splitting constant with solvent follows the same trend for all of the doublet compounds and increases with increasing solvent polarity.

The g values seem less subject to change except under the extreme condition of protonation—and the anomalously large values for benzene solvent. The bulk magnetic susceptibility of the solvents are not important to the g value and can be neglected. This is easily seen by using the relation

\[ H_{\text{eff}} = H(1 - \frac{2\pi}{3} \chi_v)^{23} \]

which gives the effective "local magnetic field" experienced by molecules in a cylindrical sample. \( \chi_v \) is the volume diamagnetic susceptibility. Some values of \( \chi \) for solvents that were used are shown in Table 3.18. The change will be in the 6th significant figure of the magnetic field. Thus, the change in the g value is undoubtedly due to intermolecular interactions.

Since most of the E.S.R. experimental data on α-nitronyl-nitrooxide doublets has been reviewed, an assignment of the nature of the ground state "unpaired M.O." shall be undertaken.

---


**TABLE 3.16**

**MEASUREMENTS AND EFFECTIVE VALUES OF THE HYPERFINE SPLITTING**

**CONSTANTS OF α-oTNN IN SOLUTIONS OF ETHANOL AND BENZENE**

### Ethanol

<table>
<thead>
<tr>
<th>Spectrum</th>
<th>(d_{12} )</th>
<th>(d_{23} )</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>102.8(?)</td>
<td>100.7</td>
</tr>
<tr>
<td>2</td>
<td>101.5</td>
<td>100.5</td>
</tr>
<tr>
<td>3</td>
<td>101.3</td>
<td>100.1</td>
</tr>
<tr>
<td>4</td>
<td>101.8</td>
<td>100.5</td>
</tr>
<tr>
<td>5</td>
<td>101.5</td>
<td>100.5</td>
</tr>
</tbody>
</table>

Average \( \rightarrow \)

\[ 101.5 \pm 0.1 \]

\[ 101.4 \pm 0.2 \]

\[ 101.0 \pm 0.2 \]

\[ |a_N|_{\text{eff}} = 7.57 \pm 0.02 \]

### Benzene

<table>
<thead>
<tr>
<th>Spectrum</th>
<th>(d_{12} )</th>
<th>(d_{23} )</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>98.2</td>
<td>97.0</td>
</tr>
<tr>
<td>2</td>
<td>98.2</td>
<td>97.1</td>
</tr>
<tr>
<td>3</td>
<td>97.9</td>
<td>97.0</td>
</tr>
<tr>
<td>4</td>
<td>98.0</td>
<td>96.9</td>
</tr>
<tr>
<td>5</td>
<td>98.2</td>
<td>96.6</td>
</tr>
</tbody>
</table>

Average \( \rightarrow \)

\[ 98.1 \pm 1 \]

\[ 96.9 \pm 1 \]

\[ 97.5 \pm 0.1 \]

\[ |a_N|_{\text{eff}} = 7.31 \pm 0.01 \]

*Arbitrary units.*

*Conversion factor of 0.0750 gauss/unit.*
<p>| Solvent   | $|a_N|$ | g   | $|a_N|$ | g   | $|a_N|$ | g   |
|-----------|-------|-----|-------|-----|-------|-----|
| Ethanol   | 7.66±.01 | 2.0064 | 7.62±.03 | 2.0065 | 7.57±.02 | 2.0064 |
| Benzene   | 7.44±.01 | 2.0070 | 7.47±.02 | 2.0075 | 7.31±.01 | 2.0075 |
| Acetonitrile | 7.60±.02 | 2.0063 | .   | .   | .   | .   |
| H$_2$O   | .   | 2.0061 | .   | 2.0063 | .   | 2.0064 |
| Benzene  | .   | .   | .   | .   | 2.0045 |</p>
<table>
<thead>
<tr>
<th>Solvent</th>
<th>$\chi_v \times 10^{24}$ (20°C)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Acetonitrile</td>
<td>.534 unitless</td>
</tr>
<tr>
<td>Benzene</td>
<td>.611</td>
</tr>
<tr>
<td>Ethanol</td>
<td>.575</td>
</tr>
<tr>
<td>3-Methylpentane</td>
<td>.5823</td>
</tr>
</tbody>
</table>

One might expect the unpaired electron to be in a \( \pi \) type orbital since \( \pi \) orbitals are undoubtedly important to the bridging of the N-O groups across the adjoining \( \alpha \)-carbon atom. The size of the observed hyperfine splittings suggests that, indeed, the unpaired electron is in a \( \pi \) type orbital. Additionally, the isotropic hyperfine splittings are about one-half of those observed for simple nitroxides in which the unpaired electron is known to occupy a \( \pi \) orbital.\(^{25}\) Nitroxides, as do the \( \alpha \)-nitronyl nitroxides, exhibit a large anisotropy in rigid glasses, and they have a rather high unpaired electron spin density on nitrogen.

If, by hypothesis, the unpaired electron is principally associated with a \( \pi \) orbital having a significant spin density on the nitrogens, then:

1. The nitrogen hyperfine splittings should be quite anisotropic.

2. The hyperfine tensor components of the nitrogen atoms should be largest in the \( \pi \) direction. These splittings should be observed when the static magnetic field is along the \( \pi \) axis. This assumes that both the isotropic and anisotropic contributions are positive. Indeed, theory also predicts that they are positive for large \( \rho_N \).

3. The \( g \) tensor component should be the smallest in the \( \pi \) direction.

4. The rigid glass spectrum should show splitting to the high field side of the normal R.T. spectrum.

Item 4 follows from items 2 and 3; only 1 and 4 can actually be checked from rigid-glass spectra. A brief discussion of the reasoning which leads to the aforementioned predictions shall be given in the following paragraphs.

The expected anisotropy of the hyperfine splittings may be understood by examining a hypothetical atom in which the unpaired electron occupies a p orbital (Figure 3.27). The diagonal dipolar tensor elements—$t'_{xx}$, $t'_{yy}$ and $t'_{zz}$—are easily found to be $^{26}$:

\[
\begin{align*}
    t'_{xx} &= \frac{2}{5} g_\text{e} g_\text{N} \beta_\text{N} \left( \frac{1}{r^3} \right) \\
    t'_{yy} &= \frac{1}{5} g_\text{e} g_\text{N} \beta_\text{N} \left( \frac{1}{r^3} \right) \\
    t'_{zz} &= \frac{1}{5} g_\text{e} g_\text{N} \beta_\text{N} \left( \frac{1}{r^3} \right)
\end{align*}
\]

in which $r$ is the distance between the unpaired electron and the nucleus. Because of the $r^{-3}$ dependence of $t'_{ee}$, contributions to $t'_{ee}$ decrease very rapidly as $r$ increases. Thus, only spin densities which are near the nucleus are the principal contributors to $t'_{ee}$.

For molecules, good agreement with experiment is obtained by neglecting charge distribution further than a bond length apart. If the spin density on an atomic center is relatively large, spin densities on neighboring atoms may be neglected without serious error. $^{27}$

---

$^{26}$ Carrington and McLachlin, op. cit., p. 111.

$^{27}$ J.R. Morton, op. cit.
FIGURE 3.27. P orbital and its coordinate system.
Hence, a large π orbital population on nitrogen should lead to rather large anisotropy. It also follows that if the isotropic splitting is positive, the hyperfine splitting component in the π direction should be the largest in magnitude.

The g tensor component in the π direction should be smaller than the elements in the y and z direction. This may be ascertained by examining equation 2. The atomic angular momentum operators acting on the $P_x$, $P_y$ and $P_z$ A.O.'s are summarized as follows:

\[
\begin{align*}
\hat{L}_x P_x &= 0 \\
\hat{L}_x P_y &= iP_z \\
\hat{L}_x P_z &= -iP_y \\
\hat{L}_y P_x &= -iP_z \\
\hat{L}_y P_y &= 0 \\
\hat{L}_y P_z &= iP_x \\
\hat{L}_z P_x &= iP_y \\
\hat{L}_z P_y &= -iP_x \\
\hat{L}_z P_z &= 0
\end{align*}
\]

It may be seen that $L_{xk} Y_0 = 0$ when $Y_0$ is a π M.O. in the x direction of a Cartesian coordinate system. It follows that $g_{xx}$ is equal to $g_e$ and that $g_{ex}$ is equal to zero; hence the x axis is a principal axis of the g tensor. It has already been experimentally verified that one component of $\hat{g}$ could be as low as 2.004 and that the other components are larger (see α-MNN, E.S.R., this chapter). Since

\[
H = \frac{\hbar \nu}{g_{xx} \beta}
\]

and $g_{xx} \leq g_{e_i e_i}$ ($e_i \neq x$), H should be a maximum when the static magnetic field is in the x(π) axis of the molecule.
The hyperfine tensors of both nitrogen atoms should each have a principal axis in the x direction (the largest element, at that). Since $g_{xx}$ is a minimum, the rigid glass spectrum should show rather large observable splittings to the high field side of the E.S.R. spectrum. The rigid glass spectrum is a superposition of spectra of many orientations, and the y and z principal axes resonances should be more to the low field side of the spectrum.

The E.S.R. spectra of $\alpha$-NN in ethanol was measured as a function of temperature to follow the spectra through the changes from a random solution, through a viscous solution, and finally to a rigid glass. Spectra at $-90^\circ$C, $-105^\circ$C, $-120^\circ$C, $-145^\circ$C and $-155^\circ$C are shown in Figures 3.28, 3.29 and 3.30. At $-90^\circ$C, the high field hyperfine line began to lose height and broaden as the molecular tumbling rate decreased. Since ethanol forms a glass near $-120^\circ$C, the E.S.R. spectra may be effectively followed through the ethanol phase transition. The two high field lines which emerge at the high field side of the spectrum (Figure 3.30) are interpreted to be two members of the set of lines associated with the large hyperfine splitting, $t_{xx}$. Their peak to peak distance is 18 gauss. Three more lines at lower field increments of 18 gauss were constructed and superimposed on Figure 3.30. As can be seen in Figure 3.30, the constructed low field line coincides with the lowest field resonance maximum—a very encouraging result. The predicted relative intensities
FIGURE 3.28. E.S.R. spectrum of α-βNN in ethanol at -90°C.
FIGURE 3.29. E.S.R. spectra of $\alpha$-phenyl in ethanol at -105, -120, and -145°C.
FIGURE 3.30. E.S.R. spectrum of α-pNN in ethanol at -155°C.
are not quite correct, since the high field resonances are broad and not so well resolved. Such an effect is also observed in the experimental and simulated spectra of nitroxides.\textsuperscript{28} It should be noted that the center of the constructed "x component" spectrum is, indeed, removed to the high field side of the spectrum. The bulk of the resonance is to the low field side of the center line. The "g values" for different positions were not measured as a good reference compound for these temperatures was not available.

Using $t'_{xx} = 18$ gauss and the isotropic splitting constant of 7.6 gauss in ethanol at room temperature, $t'_{xx}$ is estimated to be 10.4 gauss since

$$t'_{xx} = t'_{xx} + a$$

The $t'_{xx}$ may be related to an unpaired electron population in the nitrogen $\pi$ orbital by comparing $t'_{xx}$ with $t'_{xx\text{max}}$, the maximum value of $t'_{xx}$ for total occupation of a nitrogen $\pi$ orbital. Utilizing Roothaan S.C.F. atomic wavefunctions\textsuperscript{29} for a "p" orbital of nitrogen $(^4S, \frac{1}{2})$ was calculated to be 3.099 a.u. Changing to c.g.s. units and substituting into equations 6 and 51, $t'_{xx\text{max}}$ is approximately


equal to 34.2 gauss. Dividing 10.4 by 34.2 gives 0.30 for the
spin population in each nitrogen $2P_x$ orbital. This comparison of
population approach has found wide acceptance for oriented molecules.  
As a further check of the value of .30 for the $\pi$ orbital populations of
nitrogen, we shall utilize a semimprirical method. It is found that
\[ a_N \approx Q_N \rho_N^{31} \]
in which $Q_N$ is an experimental constant and $\rho_N$ is the
$\pi$ molecular orbital spin density in the nitrogen $\pi$ orbital. $Q_N$ has
been found to be about 25 gauss in systems made up of nitrogen,
carbon and hydrogen. The use of this one parameter equation shall
be justified later. Using $|a| = 7.6$ gauss and $Q_N = 25$ gauss$^{31}, \rho$
is calculated to be .30 electrons—exactly the value obtained from
the rigid glass spectra. Such agreement of two independent methods
lends support to our arguments.

If the analysis of the hyperfine tensor elements is applied
to the experimental results of Griffith, McConnel and Cornell for
t-butyl nitroxide$^{32}$, it is estimated that the electron spends $\sim$50% 
of its time in the nitrogen $2P_x$ ($\pi$) orbital. By way of comparison,
the unpaired electron spends a slightly greater portion of its
time on the two nitrogens in the $\alpha$-nitronylnitroxides than on the
one nitrogen in the simple nitroxides.

---

$^{30a}$J.R. Morton, op. cit.

$^{30b}$H. McConnell, C. Heller, T. Cole and R. Fessenden,

$^{31}$Carrington and McLachlin, op. cit., p. 94.

The splittings on the nitrogens may be accounted for by an exchange mechanism which mixes \( \pi \) and \( \sigma \) orbitals. Equation 52 is an expression that may be used to relate the \( \pi \) unpaired spin population to the isotropic splitting constants.

\[
a_N = \left( Q_N \rho_N + Q_0 \rho_0 + Q_{C_1} \rho_{C_1} + Q_{C_2} \rho_{C_2} \right)^{33} \]

Here, \( Q_i \) are sigma-pi parameters which are proportional to the extent of sigma-pi mixing. The \( \rho_i \) represent the unpaired electron pi molecular orbital spin densities on atoms adjacent to the nitrogen. In the case when \( \rho_N \gg \rho_i \) (\( i \neq N \)), equation 51 simplifies to the previously used expression, \( a_N = Q_N \rho_N \).

The \( \alpha \)-methyl hydrogen hyperfine splittings in \( \alpha \)-MNN (\( |a_H| = 3.2 \) gauss in ethanol) may be accounted for by a \( \pi \) M.O. model which includes hyperconjugation of the methyl hydrogens. If group orbitals consisting of linear combinations of the hydrogen 1s orbitals are used for the methyl hydrogens, and the \( \alpha \)-methyl carbon is considered as being sp hybridized, then the methyl group contains pi character of the correct symmetry to overlap with the pi orbitals of the ring. Thus, a pi mechanism of overlap is established between the methyl hydrogens and the \( p_x \) (pi) orbital of the \( \alpha \)-carbon in the ring. Comparison of the magnitude of the \( \alpha \)-methyl hydrogen splitting constants with those of substituted benzenes\(^{34}\) leads to an estimated


unpaired spin density of between .08 and .16 electrons on the 
α-carbon atom in the ring. In like manner the spin densities at 
the other two ring carbons are estimated to be .01 from the small 
(.2 gauss) hydrogen splittings of the 4 equivalent methyl groups. 
Since the sum of the spin densities must add to unity, the oxygen 
spin density on each oxygen $P_x$ orbital must be between .15 and .11 
unpaired electrons. Based on the relatively large spin density at 
the α-carbon atom, it is assumed that the previously unassigned $^{13}$ 
hyperfine splitting originates at the α-carbon.

It must be admitted at least one aspect of the rigid 
glass spectrum is not well understood. The derivative associated 
with peak 2 of Figure 3.30 appears to be a narrowed resonance signal. 
Although such a resonance is expected to occur to the low field side 
of the center line of the "x axis" spectrum, the extent of the shift 
is overly large. Such a difference of position indicates a difference 
of g value of .016 between the maximum and minimum g values. This 
is about twice the variance anticipated on the basis of the single 
crystal spectrum of α-MNN. Although this discrepancy is not 
understood, the consistency of the nitrogen spin density values 
obtained by two approaches and the similarity of the isotropic 
splittings with those of nitroxides lead us to believe that our 
analysis is correct.

2. **Electronic Spectra**: The absorption spectrum of α-oTNN in n-hexane 
is shown in Figure 3.31 and the energies of absorption maxima are
FIGURE 3.31. R.T. electronic spectra of α-oTNN in ethanol and in n-hexane solution.
listed in Table 3.19. The presence of three distinct electronic transitions with intensity maxima at 17,290, 28,260 and 38,730 cm\(^{-1}\) are clearly indicated. There is an absorption which is rising in intensity at the limit of the observable region: 2,050\(\AA\). The transitions are devoid of vibrational structure; this is in sharp contrast to the well resolved spectrum of \(\alpha\)-DNN. The similarity of the two compounds, \(\alpha\)-DNN and \(\alpha\)-oTNN is such that differences in the electronic spectrum should depend upon the relative angles of the phenyl and nitronyl nitroxide rings. The presence of the methyl group in the ortho position in \(\alpha\)-oTNN insures that the ring system is not planar. The possibility of planarity is not excluded for \(\alpha\)-DNN. Thus, the lack of vibrational structure in the room temperature electronic absorption spectrum implies that either KT is large compared to the spacing between torsional oscillation levels or that the solvent plays an important and complex role in the excited state vibrations. Since the latter was not observed in the case of \(\alpha\)-DNN, the lack of structure in the \(\alpha\)-oTNN spectrum is attributed to low frequency torsional oscillations.

Band I corresponds to band I of \(\alpha\)-MNN and \(\alpha\)-DNN. The maximum of band I in \(\alpha\)-oTNN is blue-shifted 1,670 cm\(^{-1}\) with respect to the most intense vibrational maxima in \(\alpha\)-DNN (solvent is n-hexane in both cases). The maximum is red-shifted only 250 cm\(^{-1}\) relative to the 0-0 band of \(\alpha\)-MNN.
<table>
<thead>
<tr>
<th>Å</th>
<th>cm⁻¹</th>
<th>a (1/m·cm)x10⁻³</th>
</tr>
</thead>
<tbody>
<tr>
<td>5776</td>
<td>17,310</td>
<td>.699</td>
</tr>
<tr>
<td>3535</td>
<td>28,290</td>
<td>10.5</td>
</tr>
<tr>
<td>2588</td>
<td>38,640</td>
<td>8.2</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Å</th>
<th>cm⁻¹</th>
<th>a (1/m·cm)x10⁻³</th>
</tr>
</thead>
<tbody>
<tr>
<td>5545</td>
<td>18,030</td>
<td>1.03</td>
</tr>
<tr>
<td>3349</td>
<td>29,860</td>
<td>8.8</td>
</tr>
<tr>
<td>2415</td>
<td>41,410</td>
<td>6.6</td>
</tr>
</tbody>
</table>
Band II corresponds to band II in \(\alpha-\phi\text{NN}\) and \(\alpha\-\text{MNN}\). The maximum of the band is blue-shifted \(730\,\text{cm}^{-1}\) relative to the 0-0 band of \(\alpha-\phi\text{NN}\) and it is red-shifted \(1,930\,\text{cm}^{-1}\) relative to the 0-0 band of \(\alpha\-\text{MNN}\).

Band II stands alone and does not show overlapping transitions as does absorption region III in \(\alpha-\phi\text{NN}\). Region III in \(\alpha-\omega\text{TNN}\) is much simpler than in \(\alpha-\phi\text{NN}\) and more like that of substituted benzenes. The simplicity of the region suggests that there is less interaction between the chromophores in \(\alpha-\omega\text{TNN}\) than in \(\alpha-\phi\text{NN}\). This simplicity and the blue-shift of the electronic transitions in \(\alpha-\omega\text{TNN}\) relative to \(\alpha-\phi\text{NN}\) confirms that the angle between the ring chromophores is important to the absorption spectrum. The angular dependence of the electronic excitation (i.e., \(\alpha-\phi\text{NN}\) and \(\alpha-\omega\text{TNN}\)) energies is further evidence for the existence of \(\pi\) character in the nitronylnitrooxide chromophore.

The R.T. electronic absorption spectrum of \(\alpha-\omega\text{TNN}\) in ethanol is shown in Figure 3.31 and the maxima and their intensities are listed in Table 3.18. The spectrum is essentially the same as in \(n\)-hexane—except that the absorption maxima are blue-shifted.

The absorption of band I was measured in PMP and EPA at \(77^\circ\text{K}\) to determine if lower temperatures would lead to better resolved spectra. The R.T. and \(77^\circ\text{K}\) spectra in PMP and EPA are shown in Figure 3.32. The energies of absorption maxima are shown in Table 3.20. The appearance of vibrational structure at \(77^\circ\text{K}\) may be
FIGURE 3.32. Absorption spectra of band I of α-oTNN in E.P.A. and P.M.P. at R.T. and 77°K.
**TABLE 3.20**

**ABSORPTION ENERGIES OF BAND I OF α-oTNN IN E.P.A. AND P.M.P.**

**AT R.T. AND 77°K**

<table>
<thead>
<tr>
<th></th>
<th>E.P.A.</th>
<th></th>
<th>P.M.P.</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>R.T.</strong></td>
<td><strong>77°K</strong></td>
<td><strong>R.T.</strong></td>
<td><strong>77°K</strong></td>
</tr>
<tr>
<td>Α</td>
<td>cm⁻¹</td>
<td>Α</td>
<td>cm⁻¹</td>
</tr>
<tr>
<td>5605</td>
<td>17,840</td>
<td>5510</td>
<td>18,150</td>
</tr>
<tr>
<td>5800</td>
<td>17,240</td>
<td>5645</td>
<td>17,710</td>
</tr>
</tbody>
</table>
attributed to the smaller number of tortional energy levels accessible at $77^\circ$K. The more narrow distribution of energy levels in the ground state eliminates many of the vibrational sequences that arise upon excitation. It is of interest that there is no extraordinarily large blue-shift in PMP relative to EPA in going from R.T. to $77^\circ$K. This is in contrast to that observed for $\alpha$-MNN.

(D) **M.W.H. Calculation Results:** A.M.W.H. calculation has been carried out for a molecule closely resembling $\alpha$-MNN. The calculation was executed by an I.B.M. 360 digital computer using a program organized by A.T. Armstrong. Only 55 basis orbitals may be used in the program because of computer storage limitations. Hence, the 4 methyl groups bonded to the two equivalent ring carbons were replaced by hydrogens to make the molecule amenable to computer computation. The severity of such an approximation is difficult to assess—especially when the molecule for which the calculation is being performed has not been synthesized.

The input data was based on the structure shown in Figure 3.33. The molecule is assumed to be of $C_{2v}$ symmetry. Thirty-nine basis functions are included in the calculation which, in turn, generates thirty-nine MO's for the forty-five electrons.

---

FIGURE 3.33. Structure of "the molecule" used for the M.W.H. calculation.
The eigenvalues and the Löwdin M.O.'s\textsuperscript{36} are shown in Table 3.21. According to the Aufbau Principle the unpaired electron is associated with MO 23. Molecular orbitals 19, 20, 23 and 24 are \(\pi\) orbitals, while M.O.'s 16, 17, 18, 21, 22, 25 and 26 are \(\sigma\) orbitals. The fact that the unpaired electron is in \(\pi\) orbital is in agreement with experimental data. However, when the magnitudes of the M.O. coefficients and the symmetry of the M.O. are examined, the agreement breaks down.

Molecular orbital 23 transforms as the \(a_2\) representation with respect to the \(C_{2v}\) symmetry operators. Thus, a node is predicted in the \(\pi\) M.O. at the \(\alpha\) carbon. In order to observe a large hyperfine splitting due to the methyl hydrogens in \(\alpha\)-methylnitronylnitroxide there must be \(\pi\) character between the methyl carbon and the \(\alpha\) carbon. The coupling of the \(\pi\) system to the methyl hydrogens is completed via group orbitals for the 3 methyl hydrogens. Unfortunately, the prediction of zero spin density on \(\alpha\) carbon, predicts vanishingly small hyperfine splittings from the three methyl hydrogens which is in conflict with experiment. The pertinent hydrogen group orbitals and the \(p_x\) orbitals of the methyl and \(\alpha\) carbons all transform as the \(b_1\) representation. Examination of the \(\pi\) orbitals shows that, indeed, for all \(b_1\) symmetry M.O.'s, "hyperconjugation" arises

### Table 3.21

SOME EIGENVALUES AND EIGENFUNCTIONS FROM THE M.W.H. CALCULATION

<table>
<thead>
<tr>
<th>M.O. Number</th>
<th>Eigenvalues</th>
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<td>-0.0137</td>
<td>0.0931</td>
<td>0.0702</td>
<td>0.0933</td>
<td>0.2543</td>
<td>0.1085</td>
</tr>
<tr>
<td>S</td>
<td>H 14</td>
<td>0.0138</td>
<td>0.0928</td>
<td>-0.0693</td>
<td>-0.0923</td>
<td>0.2551</td>
<td>0.0280</td>
</tr>
<tr>
<td>S</td>
<td>H 15</td>
<td>0.0044</td>
<td>0.0137</td>
<td>-0.0931</td>
<td>0.0702</td>
<td>-0.0935</td>
<td>0.2543</td>
</tr>
</tbody>
</table>
naturally. From experiment and symmetry considerations, it is concluded that the unpaired electron is a pi orbital of $b_1$ symmetry. It follows that the electronic ground state has $B_1$ symmetry.

In addition to being of the wrong symmetry, the calculated oxygen spin population is 3 times that of nitrogen. This is an exact reversal of that obtained from experiment. This discrepancy might arise from neglect of electron repulsions in the hamiltonian. The effects of the neglect of electron repulsion is apparent for the calculation of eigenvalues of aromatic hydrocarbons in this "extended Hückel" technique. In order to achieve agreement between the experimental and calculated ionization potentials, it is necessary to multiply the V.S.I.P.'s of pi electrons by a correction factor of .8. The .8 is effectively a screening constant for the \( \pi \) electrons. As a result, the pi orbitals are raised in energy relative to the \( \sigma \) electrons. The coefficients and the relative energies of the pi orbitals are maintained. In aromatic hydrocarbons, the "screening factor" works rather well as there is generally not a large charge build-up on a particular site. The effects of electron repulsion are then treated as a small perturbation in subsequent configuration interaction calculations. In polar molecules, the charges are no longer "evenly distributed", and thus each atom must have a proper screening constant. It follows that screening constants should be applied to the \( \sigma \) orbitals also. For a series of small molecules such factors might be obtained; but in this work, the large "size"
of the basic chromophore makes the semiempirical evaluation of such factors impractical.

Although the symmetry and the M.O. basis set coefficients are not in agreement with experiment, the energy relationship of the \( \sigma \) and \( \pi \) orbitals are such that a positive \( g \) value is obtained. The calculated principal values \( g_{yy} \) and \( g_{zz} \) of the \( g \) tensor are higher than experiment dictates with \( g_{yy} \approx 2.020 \) and \( g_{zz} \approx 2.005 \).

In view of the disagreement in the experimental assignment of the unpaired electron M.O. with the calculation, the assignment of electronic transitions becomes very difficult—if not impossible. From symmetry considerations the \( \pi \) M.O.'s transform as either the \( a_2 \) or \( b_1 \) representations under the \( C_{2v} \) symmetry operations. It follows that only \( \pi \rightarrow \pi \) transitions polarized in the plane of the ring are allowed. The possibilities are:

<table>
<thead>
<tr>
<th>Transition</th>
<th>Axis of Polarization</th>
</tr>
</thead>
<tbody>
<tr>
<td>( b_1 \rightarrow b_1 )</td>
<td>( z )</td>
</tr>
<tr>
<td>( a_2 \rightarrow a_2 )</td>
<td>( z )</td>
</tr>
<tr>
<td>( b_1 \rightarrow a_2 )</td>
<td>( y )</td>
</tr>
<tr>
<td>( a_2 \rightarrow b_1 )</td>
<td>( y )</td>
</tr>
</tbody>
</table>

Considering that the first two excited states are less polar than the ground state, the writer finds the calculated M.O.'s to be in over-all poor agreement with experiment. As such, the electronic transitions are not assigned.
In conclusion, the calculation results are in poor agreement with experiment. The poor agreement is attributed to neglect of electron repulsions. Nevertheless, the calculation is helpful from the standpoint of symmetry considerations.
IV. EXPERIMENTAL RESULTS AND DISCUSSION OF DIRADICAL MOLECULES

(A) 1,3-Bis-(Nitronylnitroxide)Propane

1. E.S.R.: The electron spin resonance spectra of 1,3-BNNP were measured in a variety of solvents and at several temperatures. Ethanol, E.P.A., P.M.P. and Duco Cement were the solvents used for the measurements. The large magnetic field difference between the $\Delta m_s = 1$ and the half-field region necessitates the partitioning of the triplet spectrum into two regions—"$\Delta m_s = 1$" and the "half-field" regions.

1,3-BNNP was dissolved in Duco Cement and the glue was allowed to harden. The solid was fragmented and placed in an E.S.R. tube. Measurements of the spectrum were made at several temperatures from room temperature to $-145^\circ$C. Since temperature did not affect the spectrum, only the $\Delta m_s = 1$ spectrum at $-145^\circ$C is shown in Figure 4.1. The centerline is indicative of a doublet, while the outer lines correspond to triplets in which the zero splittings are small ($D \approx 75$ gauss, $E \approx 0$). No half-field resonance was observed in Duco Cement.

E.S.R. spectra of 1,3-BNNP in rigid glassy solutions at $77^\circ$K were measured in E.P.A. (Figures 4.2 and 4.3), ethanol (Figures 4.4 and 4.5), and P.M.P. solvents. The spectra in E.P.A. and ethanol are discussed concurrently because they are very similar. The $\Delta m_s = 2$ regions are identical and will be discussed later.
FIGURE 4.1. E.S.R. spectrum ($\Delta m = 1$ region) of 1,3-BNNP in Duco Cement at $-145^\circ C$. 

$\frac{dI(H)}{dH}$ 

H $\rightarrow$ 

100 gauss
FIGURE 4.2. E.S.R. spectrum ($\Delta m_s = 1$ region) of 1,3-BNNP in E.P.A. at $77^\circ$K.
FIGURE 4.3. E.S.R. spectrum (half-field region) of 1,3-BNNP in E.P.A. at 77°K.
FIGURE 4.4. E.S.R. spectrum ($\Delta m_s=1$ region) of 1,3-BNNP in ethanol at $77^\circ$K.
FIGURE 4.5. E.S.R. spectrum (half-field region) of 1,3-BNNP in ethanol at 77°K.
Although the $\Delta m_s = 1$ spectra measured in E.P.A. and in ethanol are very similar, there are some differences which are important to the interpretation of the spectra. In order to aid in the discussion of the triplet spectra, resonance peaks have been numbered 1 through 8 (Figure 4.2 and 4.4) in the $\Delta m_s = 1$ regions. A doublet resonance (9) is observed in each solvent. The spectrum in E.P.A. is better resolved than that in ethanol and 8 triplet resonances are resolved. The fact that there are more than six resonances suggests that there are at least 2 triplet species in solution. Examination of the E.P.A. and ethanol spectra shows that peaks 1, 2, 3, 6, 7 and 8 maintain essentially the same relative intensity between solvent (with slight variation due, perhaps, to solvation) while peaks 4 and 5 are considerably more intense relative to 1, 2, 3, 6, 7 and 8 in E.P.A. than in ethanol. Thus, peaks 1, 2, 3, 6, 7 and 8 are associated with one triplet species (species 1) and 4 and 5 with another triplet species (species 2). The two different species are attributed to different conformers of the molecules. This conclusion shall be elaborated upon and strengthened in future discussions.

A detailed analysis of the zero-field splittings will be based on the better resolved E.P.A. spectrum. If the peak to peak distance of lines 1 to 8 is taken as 2D for species 1, then $2D_1 \approx 450$ gauss. Having made such a choice, resonances 2 and 7 must be associated with the splitting $D + 3E$ and resonances 3 and 6 with the splitting $D - 3E$. The positions on the bands which were
chosen for the measurements are shown in Figure 4.2, the positions chosen are in accord with standard procedures. It is found from measurement that:

\[
\begin{align*}
2D_1 &= 450 \\
D_1 + 3E_1 &= 148 \\
D_1 - 3E_1 &= 102
\end{align*}
\]

Addition of equations 54 and 55 yields \(2D_1 \approx 250\) gauss, the same value as measured for equation 53. Thus \(D_1\) and \(E_1\) are found to be 225 gauss and 3 gauss, respectively. \(D^*\) is calculated, using equation 26, to be 225 gauss.

Resonances 4 and 5 are, apparently, degenerate or nearly degenerate \(D + 3E\) or \(D - 3E\) resonances of species 2. From the difference in field position of lines 4 and 5, \(D_2\) is estimated to be 93 gauss, while \(E'\) is estimated to be nearly zero. This means that \(D_{2}^* = D_2\) for the second triplet species. This is only slightly larger than the zero-field splittings observed for 1,3-BNNP in the solid Duco Cement. This suggests that the triplet in Duco Cement is the same triplet species 2 in E.P.A. A similar analysis applies to the spectrum in ethanol. Resonances "2 and 3" and "6 and 7" in ethanol are not resolved, so \(D + 3E\) and \(D - 3E\) values cannot be measured. Since \(2D = 250\) gauss in ethanol, the zero-field splitting values from the \(\Delta m_s = 1\) region of 1,3-BNNP in E.P.A. are taken to be

TABLE 4.1

HALF-FIELD TRANSITIONS OF 1,3-BNNP

<table>
<thead>
<tr>
<th>Solvent</th>
<th>H(gauss)</th>
<th>v(Mc/s)</th>
<th>D*(gauss)x10^{-3}</th>
</tr>
</thead>
<tbody>
<tr>
<td>E.P.A.</td>
<td>1524</td>
<td>9170</td>
<td>1.02</td>
</tr>
<tr>
<td>E.P.A.</td>
<td>1628</td>
<td>9170</td>
<td>.221</td>
</tr>
<tr>
<td>Ethanol</td>
<td>1522</td>
<td>9170</td>
<td>1.02</td>
</tr>
<tr>
<td>Ethanol</td>
<td>1625</td>
<td>9170</td>
<td>.250</td>
</tr>
</tbody>
</table>
representative of 1,3-BNNP in ethanol.

The half-field spectra in ethanol and E.P.A. each have two resonances (see Figures 4.3 and 4.5). Two values of $D^*$ may be calculated from the spectral data in each solvent (see Table 4.1). The lowest field resonance in each solvent has a $D^*$ value of $1.02 \times 10^3$ gauss; the higher field $H_{\text{min}}$ has a $D^*$ value of $2.2 \times 10^2$ gauss in EPA and a value of $2.5 \times 10^2$ gauss in ethanol. (The apparent discrepancy is a result of the relatively high "half-field" resonance field. This leads to a small difference of two large numbers in equation 26). The latter values are in excellent agreement with $D^*$ calculated from the $\Delta m = 1$ region; $D^*$ has a value of 226 gauss. The lowest field $H_{\text{min}}$ resonance ($D^* = 1.02 \times 10^3$ gauss) has no counterpart in the $\Delta m = 1$ region. The large value of $D^*$ and the absence of the $\Delta m = 1$ transitions suggest that the concentration of this triplet species is small (refer to Chapter I, Section B for theory and references). Interestingly this resonance is identical in shape and value of $D^*$ with the half-field resonances observed for the $\alpha$-nitronylnitrooxide doublet dimers in ethanol rigid glasses at $77^\circ$K. Thus, we conclude that the triplet dimerizes in such a way to give a triplet species which is magnetically identical to the triplet formed by dimerization of the doublet molecules. It should be noticed that there is no "half-field" resonance which corresponds to the triplet species 2 ($D \approx 93$ gauss, $E \approx 0$) observed in the $\Delta m = 1$ region in ethanol and E.P.A. This is consistent with the
fact that no half-field resonance was observed in Duco Cement.

The $\Delta m_s = 1$ spectra of 1,3-BNNP in ethanol were measured as a function of temperature. Some of the spectra are shown in Figure 4.6; these spectra correspond to temperatures of $-85^\circ C$, $-105^\circ C$ and $-143^\circ C$. Interestingly, the spectrum at $-85^\circ C$ is nearly identical to that in Duco Cement or lines 4 and 5 (triplet species 2) in the $77^\circ K$ ethanol spectrum. As the temperature is lowered, the resonances of triplet species 1 begin to appear. These observations suggest that at lower temperature triplet species 1, which has the larger zero-field splittings, becomes more highly favored. If, indeed, this is an equilibrium process, the absence of triplet species 1 resonances in ethanol at higher temperatures and in the Duco Cement is suspect. This "apparent" discrepancy may be rationalized from considerations of the relative allowedness of the $\Delta m_s = 1$ transitions and relaxation effects. The $\Delta m_s = 1$ transitions become less allowed with increasing zero-field splittings (Chapter I, Sect.B); hence, the intensity of triplet species 1 would be less than that of triplet species 2 if they were at equal populations. In addition, small thermal motions would tend to "relax" the higher zero-field resonances more easily than those of the smaller zero-field splittings. Thus, the larger resonances would tend to be washed out.

The spectrum of 1,3-BNNP in ethanol was measured at $77^\circ K$ for two solutions which were $1.0\times10^{-3} M$ and $4.4\times10^{-3} M$ at R.T. The results showed the intensity of the doublet resonances increased
FIGURE 4.6, E.S.R. spectra ($\Delta m_s = 1$ region) of 1,3-BNPP in ethanol at -85°C, -105°C, and -143°C.
FIGURE 4.7. E.S.R. spectrum ($\Delta m = 1$ region) of 1,3-BNNP in P.M.P. at 77°K.
relative to the $\Delta m = 1$ triplet resonances with increasing concentration. Thus, the doublet species is a function of the 1,3-BNNP concentration. It is believed that the doublets arise from intermolecular interaction which results in the formation of dimer or polymer species. Kosower\(^2\) has suggested a "dangling ends" model such as

\[ \overset{\uparrow}{M} \longrightarrow \overset{\downarrow}{M} \]
\[ M \longrightarrow \overset{\uparrow}{M} \]

in which interacting "ends" of the molecule spin-pair.

The E.S.R. spectrum of 1,3-BNNP in P.M.P. at 77°K (Figure 4.7) is sharply contrasted to those observed in ethanol and E.P.A. There is a very strong doublet signal in the $\Delta m = 1$ region, but no triplet resonances whatsoever. The half-field region is also devoid of resonances. The large doublet signal suggest that the previously discussed intermolecular dimers with dangling ends are a very important chemical species in this system. It should be noted that 1,3-BNNP is quite insoluble in pure hydrocarbon solvents. The solubility is less than $10^{-3}$ moles per liter in n-hexane and P.M.P. On the other hand, 1,3-BNNP is much more soluble in alcoholic solvents.

Collective data of the E.S.R. spectra of 1,3-BNNP in rigid media are summarized in Table 4.2. The sharp contrast of the E.S.R. spectra of 1,3-BNNP with solvent suggests that solvation is very important to the stability of the triplets. Dimerization appears

\[ ^2E.M.\text{ Kosower and Y. Ikegami, J. Am. Chem. Soc., 89, 461 (1967).} \]
TABLE 4.2

COLLECTIVE DATA FROM THE E.S.R. SPECTRA OF 1,3-BNNP
IN RIGID MEDIA

<table>
<thead>
<tr>
<th>Solvent</th>
<th>Doublet Signal</th>
<th>Triplet Species</th>
<th>$D^\dagger$</th>
<th>$E$</th>
<th>$D^*$</th>
<th>$D^{*\prime}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>E.P.A.</td>
<td>weak</td>
<td>1</td>
<td>226</td>
<td>3</td>
<td>225</td>
<td>221</td>
</tr>
<tr>
<td></td>
<td></td>
<td>2</td>
<td>93</td>
<td>N.O.</td>
<td>93</td>
<td>N.O.</td>
</tr>
<tr>
<td></td>
<td></td>
<td>3</td>
<td>N.O.</td>
<td>N.O.</td>
<td>N.O.</td>
<td>1.02x10^3</td>
</tr>
<tr>
<td>Ethanol</td>
<td>weak</td>
<td>1</td>
<td>226</td>
<td>3</td>
<td>225</td>
<td>250</td>
</tr>
<tr>
<td></td>
<td></td>
<td>2</td>
<td>93</td>
<td>0</td>
<td>93</td>
<td>N.O.</td>
</tr>
<tr>
<td></td>
<td></td>
<td>3</td>
<td>N.O.</td>
<td>N.O.</td>
<td>N.O.</td>
<td>1.02x10^3</td>
</tr>
<tr>
<td>P.M.P.</td>
<td>strong</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>N.O.</td>
</tr>
<tr>
<td>Duco Cement</td>
<td>weak</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>N.O.</td>
</tr>
</tbody>
</table>

† In units of gauss

N.O.—Resonances not observed

$D^{*\prime}$—Calculated from $\Delta m = 1$ data

$D^{*\prime\prime}$—Calculated from half-field resonance
to be the chief culprit in complicating the system. The equilibrium scheme in Figure 4.8 "accounts" for the observed phenomena. The proposed conformations have not been verified experimentally and are shown only as examples to clarify the discussions. Triplet species 1 and 2 are simply two conformations of the molecule which have different zero-field splittings. Triplet species 3 represents a "complexation" between 2 ends of separate triplet molecules (species 1 or 2) in close proximity to give the triplet species 3(D* = 1.02x10^3 gauss). Species 4 represents a tight interaction between the ends of two separate molecules in which spin pairing occurs. The separated "dangling ends" are effectively doublets. Although species 3 and species 4 are represented as dimers, the possibility for polymers is not ruled out.

Polar solvents (ethanol and E.P.A.) favor the left hand side of the equilibrium figures in Figure 4.8 at 77°K. There is evidently some species 3; but, as previously mentioned, the concentration is small. There is certainly some spin-pairing to give species 4; the presence of species 4 was indicated by the increasing doublet signal with increasing concentration in ethanol at 77°K. As one goes to less polar solvents, the right hand side of the equation in Figure 4.8 becomes favored as the molecules tend to solvate themselves. This mechanism is supported by the large doublet signal in P.M.P. at 77°K (species 4) and by the inherent insolubility of the compound 1,3-BNNP in non-polar solvents. It is possible that
FIGURE 4.8. Postulated chemical species and equilibria of 1,3-BNPP.
the molecules form microcrystallites or long polymer chains of species 4 in pure hydrocarbon solvent at 77°K. No evidence of microcrystallites was observed with the unaided eye, however. It is believed that these proposed "species" adequately describe the E.S.R. spectra in the rigid media used for the studies.

The solution E.S.R. spectra of 1,3-BNNP in E.P.A. and P.M.P. were measured at room temperature. Both spectra showed some hyperfine splitting, especially the spectra in P.M.P. (Figure 4.9) whose spectrum is indicative of two equivalent hydrogens ($|a_H| = 2.1$ gauss) and two equivalent nitrogens ($|a_N| = 7.4$ gauss). The well resolved hyperfine splittings are undoubtedly caused by impurities or dimer dangling ends such as those postulated as species 4 for the rigid glassy media. "Impurity" is meant to represent molecules that contain only one nitronylnitroxide group and a benzaldehyde or a benzoic acid group on the other end of the chain. (Refer to Chapter II, Sect.1 for synthesis. The types of impurities are readily understood). Nevertheless, the zero-field splittings of 1,3-BNNP appear to be too large for tumbling to narrow the resonances to the extent that hyperfine splitting is observed. At best, one would expect a broad resonance.

The E.S.R. spectrum of a polycrystalline "powder sample" was measured (Figure 4.10). The resonance is characteristic of an exchange narrowed doublet rather than a triplet. Such a result implies that the intermolecular exchange energy among molecules in the crystal is of the same order of magnitude as the intramolecular
FIGURE 4.9. R.T. E.S.R. solution spectrum of 1,3-BNNP in P.M.P.
FIGURE 4.10. E.S.R. spectrum of a polycrystalline sample of 1,3-BNNP.
exchange energy. It is expected that the intermolecular exchange energies are similar to those of the $\alpha$-MNN crystals. This follows since the shapes of the spectra of $\alpha$-MNN and 1,3-BNNP powders are similar and since the unpaired electron spin densities are not changed. (see equation 50 in Chapter III, Sect.A). Thus, the exchange energy in the triplet is of the same order of magnitude as $0.7 \text{ cm}^{-1}$. Hence, the singlet state that accompanies the triplet state of the molecules is predicted to be within $1.5 \text{ cm}^{-1}$ of the triplet. This explains why temperature does not appear to affect the triplet signal in the $77^\circ\text{K}$ range. Further, the description of the diradical molecule as in Chapter I, Section B is justified.

2. **Electronic Spectra**: The R.T. absorption spectra of 1,3-BNNP were measured in cyclohexane and ethanolic (Figure 4.11, Table 4.3). The spectra in P.M.P. and E.P.A. were measured at R.T. and at $77^\circ\text{K}$ (Figures 4.12a and 4.12b and Table 4.4).

The spectra of 1,3-BNNP in the several solvents and at several temperatures are very similar to $\alpha$-MNN. Such a result would be expected and is consistent with weakly coupled composite systems as discussed in Section E of Chapter I. The vibrational splittings are somewhat better resolved for 1,3-BNNP than for $\alpha$-MNN in both hydrocarbon and ethanolic solvents. This is especially true for band I in which the second vibrational splitting is more intense than the zero-zero band in 1,3-BNNP. In $\alpha$-MNN, the second vibrational band in band I is slightly less intense than is the zero-zero band.
**FIGURE 4.11.** R.T. absorption spectra of 1,3-BNNP in solutions of cyclohexane and ethanol.
TABLE 4.3

ABSORPTION ENERGIES AND EXTINCTION COEFFICIENTS
OF 1,3-BNBP IN CYCLOHEXANE AND ETHANOL

<table>
<thead>
<tr>
<th></th>
<th>Cyclohexane</th>
<th></th>
<th>Ethanol</th>
</tr>
</thead>
<tbody>
<tr>
<td>Å</td>
<td>cm⁻¹</td>
<td>Å</td>
<td>cm⁻¹</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Å</td>
<td>cm⁻¹</td>
</tr>
<tr>
<td>5692</td>
<td>17,570</td>
<td>5528</td>
<td>18,090</td>
</tr>
<tr>
<td>5348</td>
<td>18,700</td>
<td>5280</td>
<td>19,130</td>
</tr>
<tr>
<td>3232</td>
<td>30,940</td>
<td>3184</td>
<td>31,410</td>
</tr>
<tr>
<td>3112</td>
<td>32,130</td>
<td></td>
<td></td>
</tr>
<tr>
<td>2160</td>
<td>46,300</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>
FIGURE 4.12a. Absorption spectra of 1,3-BNNP in E.P.A. at R.T. and 77°K.
FIGURE 4.12b. Absorption spectra of 1,3-BNNP in P.M.P. at R.T. and 77°K.
TABLE 4.4

ABSORPTION ENERGIES OF 1,3-BNNP IN E.P.A. AND P.M.P.
AT R.T. AND 77°K

<table>
<thead>
<tr>
<th></th>
<th>E.P.A.</th>
<th></th>
<th>P.M.P.</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>R.T.</td>
<td></td>
<td>R.T.</td>
</tr>
<tr>
<td></td>
<td>Å</td>
<td>cm⁻¹</td>
<td>Å</td>
</tr>
<tr>
<td>5578</td>
<td>17,930</td>
<td></td>
<td>5700</td>
</tr>
<tr>
<td>5313</td>
<td>18,820</td>
<td></td>
<td>5369</td>
</tr>
<tr>
<td>3197</td>
<td>31,280</td>
<td></td>
<td>3222</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>3106</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th></th>
<th>77°K</th>
<th></th>
<th>77°K</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Å</td>
<td>cm⁻¹</td>
<td>Å</td>
</tr>
<tr>
<td>5531</td>
<td>18,080</td>
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<td>5476</td>
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<td>5176</td>
<td>19,320</td>
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<td>5156</td>
</tr>
<tr>
<td>3056</td>
<td>32,720</td>
<td></td>
<td>3173</td>
</tr>
<tr>
<td>3070</td>
<td>32,570</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>
Although there are very subtle changes in band contours and there are small energy shifts of 1,3-BNNP relative to \( \alpha \)-MNN, there do not appear to be any resolved "exciton splittings". As was mentioned previously, the vibrational structure of 1,3-BNNP is somewhat better resolved than in \( \alpha \)-MNN. If exciton splittings of the electronic energy levels were present, the resolution of 1,3-BNNP transitions would be expected to be poorer than those of \( \alpha \)-MNN. Thus, it is concluded that exciton splittings are very weak, if they even exist. The band shapes in \( \alpha \)-MNN and 1,3-BNNP are similar enough so that the extinction coefficients may be taken as a good measure of the relative intensity of the corresponding transitions. The maximum extinction coefficients are larger for bands I and II in 1,3-BNNP than in \( \alpha \)-MNN, and the intensity factors are approximately 1.4 for band I and 1.9 for band II (solvent--ethanol). The simple theory of composite molecules predicts a maximum intensity ratio of 2 when the exciton splitting is very small. It is important that in ethanol at R.T. the intensity of the transitions parallel the concentration to within experimental error. This observation eliminates the possibility of a large dimer concentration in ethanol at room temperature. The absence of exciton effects strongly indicates that the nitronylnitroxide groups interact only weakly. This supports the very small exchange interaction in 1,3-BNNP observed in the analysis of the E.P.R. polycrystalline spectra. Thus, the subsystems are nearly "independent" and interact only to a very limited degree.
The spectra of 1,3-BNNP showed the same trends as α-MNN in
E.P.A. and P.M.P. in going from R.T. to 77°K. At 77°K the spectra
are better resolved than at R.T. and are blue-shifted. The blue-shift
in going to lower temperature in E.P.A. may be attributed to the
increase of the dielectric constant of the solvent with decreasing
temperature. This fact and the use of McRae's equations (Chapter I,
Sect. C) account for the general blue-shift in E.P.A. This does not
account, however, for the anomalously large blue-shift in P.M.P.
It is significant that the magnitude of the blue-shift depends upon
the method by which the solvent is prepared. In P.M.P. solvents
prepared from different bottles, the magnitude of the blue-shift
varies. In solvents that were suspect of being wet--but not wet
enough to cloud the glass--a very large blue-shift of 1300 cm⁻¹
was observed for the 0-0 band of band I in going from R.T. to 77°K.
It, thus, appears that water is the major contributor to the blue-shift
of the electronic transitions of α-MNN and 1,3-BNNP in P.M.P. at
77°K. As the temperature is decreased, H₂O becomes less soluble in
the hydrocarbon (a well known effect to spectroscopists). The water
thus interacts with the best base available--in this case, α-MNN
or 1,3-BNNP. The anomalously large blue-shift does not occur
until very near 77°K. This is ascertained from observations of the
color in the glass as it cools upon immersion in liquid nitrogen.
The blue-shift is indicated by the loss of a violet tinge in the
solution as it changes to purer red. Variable temperature optical
studies have not been undertaken for $\alpha$-MNN and for 1,3-BNNP. The effects of water in hydrocarbon solvents to these polar molecules are also important to other heterocyclic compounds, especially in luminescence studies.

It is also of interest that the well-resolved spectra of $77^\circ K$ do not imply differences in the electronic energies of the conformers of 1,3-BNNP observed in the E.S.R. spectra in E.P.A. at $77^\circ K$. Thus, triplet species 1 and 2 observed in the E.S.R. spectrum are nearly degenerate.

Summarizing, the U.V. absorption spectrum and E.S.R. spectra imply that the two nitronylnitroxide subgroups in 1,3-BNNP are only weakly interacting. No exciton splittings are observed in the electronic spectra; and the exchange energy is estimated from E.S.R. studies to be less than $10 \text{ cm}^{-1}$. The anomalously large blue-shift of $\alpha$-MNN and 1,3-BNNP in going from R.T. to $77^\circ K$ in P.M.P. is attributed to "complexation" with $H_2O$ very near $77^\circ K$.

B. 1,2-Bis($\alpha$-nitronylnitroxide)Ethane(1,2-BNNE)

1. E.S.R.: The rigid glass ($77^\circ K$) E.S.R. spectra for the $\Delta m_s = 1$ regions and $\Delta m_s = 2$ region of 1,2-BNNE in E.P.A. are shown in Figure 4.13 and Figure 4.14, respectively. Those for 1,3-BNNE in P.M.P. are shown in Figure 4.15 and Figure 4.16.

Unlike the case of 1,3-BNNP, only six triplet resonances (peaks 1, 2, 3, 4, 5 & 6) are observed in the $\Delta m_s = 1$ region in both solvents and the spectra of 1,2-BNNE are readily interpreted in terms
FIGURE 4.13. E.S.R. spectrum ($\Delta m=1$ region) of 1,2-BNNE in E.P.A. at $77^\circ$K.
FIGURE 4.14. E.S.R. spectrum (half-field region) of 1,2-BNNE in E.P.A. at 77°K.
FIGURE 4.15. E.S.R. spectrum ($\Delta m_s=1$ region) of 1,2-BNNE in P.M.P. at 77°K.
FIGURE 4.16. E.S.R. spectrum (half-field region) of 1,2-BNNE in P.M.P. at 77°K.
of the zero-field splittings of one triplet conformation. A doublet resonance (7) is observed in both solvents; the relative intensity of the doublet is much greater in PMP than in E.P.A. This solvent effect on the doublet intensity combined with an observed concentration effect indicate that the triplet 1,2-BNNE dimerizes as did 1,3-BNNP to form a doublet species.

Two half-field resonances are observed for 1,2-BNNE in E.P.A. (Figure 4.13). One of these resonances (1) \(D^* = 1.02 \times 10^3 \text{ gauss}\) is identical to those observed for the doublet \(\alpha\)-MNN \(D^* = 1.02 \times 10^3\) and for the triplet 1,2-BNNP \(D^* = 1.02 \times 10^3\) in alcoholic solvents. As in the other cases the corresponding \(\Delta m_s = 1\) transitions are not observed. Undoubtedly, the same chemical change is responsible for this triplet half-field resonance and since both doublet and triplet monomers give the resonance, it is fairly certain that dimerization of the various monomers gives rise to a triplet dimer having rather large zero-field splittings.

The other half-field resonance for 1,2-BNNE in E.P.A.--and the only observed half-field resonance in P.M.P.--are the half-field resonances corresponding to the monomer triplet. The triplet dimer is not observed in P.M.P. for any of the systems studied; but, on the other hand, the doublet dimer is greatly enhanced in P.M.P. for all the systems studied. The room temperature E.S.R. spectrum of 1,2-BNNE in hardened Duco Cement is shown in Figure 4.17. The spectrum is very similar to those in EPA and PMP at 77°K.
FIGURE 4.17. E.S.R. spectrum ($\Delta m_s$ =1 region) of 1,2-BNNE in hardened Duco Cement at R.T.
The zero-field splittings measured and/or calculated are shown in Table 4.5. The values that can be determined independently show rather good internal consistency and hence this adds confidence to our interpretation.

The zero-field splitting for monomer 1,2-BNNE are greater than those observed for 1,3-BNNP. This is consistent with the fact that the two ends are closer by 1 methylene group in the case of 1,2-BNNE. Slight solvent and/or temperature effects are observed in the splittings under different experimental conditions. We have seen that solvent effects alter slightly the spin densities in the doublet portions of the molecule. This combined with the fact that one would not expect the mean conformation of 1,2-BNNE to be identical in the different solvents nor at the different temperatures, accounts for the small changes in the zero-field splittings. Two distinct conformations are not observed.

It should be noted that the P.M.P. glass used for the 77°K E.S.R. spectrum of 1,2-BNNE was somewhat cloudy and was possibly wet. Vigorous shaking was required to dissolve the 1,2-BNNE to about 2x10^-4 moles per liter. Perhaps the solution picks up moisture with continued shaking, and the triplet is stabilized by water. This may be why 1,2-BNNE shows triplet resonances in P.M.P. while 1,3-BNNP does not. An alternate possibility is that the molecules semi-solvate themselves and do not spin-pair.

The room temperature E.S.R. spectra in E.P.A. and P.M.P. are shown in Figure 4.18. In E.P.A. the spectrum is not well
TABLE 4.5

ZERO-FIELD SPLITTINGS FROM 1,2-BNNE IN RIGID MATRICES

<table>
<thead>
<tr>
<th>Solvent</th>
<th>Species</th>
<th>2D</th>
<th>D+3E</th>
<th>D-3E</th>
<th>D'</th>
<th>D''</th>
<th>E</th>
<th>D* '</th>
<th>D*''</th>
</tr>
</thead>
<tbody>
<tr>
<td>E.P.A.</td>
<td>Monomer triplet</td>
<td>448</td>
<td>303</td>
<td>156</td>
<td>224</td>
<td>229</td>
<td>25</td>
<td>228</td>
<td>243</td>
</tr>
<tr>
<td></td>
<td>Dimer triplet</td>
<td>---</td>
<td>---</td>
<td>---</td>
<td>---</td>
<td>---</td>
<td>--</td>
<td>--</td>
<td>1.02x10^3</td>
</tr>
<tr>
<td>P.M.P.</td>
<td>Monomer triplet</td>
<td>448</td>
<td>303</td>
<td>156</td>
<td>224</td>
<td>229</td>
<td>25</td>
<td>228</td>
<td>220</td>
</tr>
<tr>
<td>Duco Cemel</td>
<td>Monomer triplet</td>
<td>414</td>
<td>247</td>
<td>184</td>
<td>207</td>
<td>215</td>
<td>10</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

D'----Calculated from 2D
D''----Calculated from D+3E and D-3E
D* '----Calculated from Am = 1 data
D*''----Calculated from half-field data
FIGURE 4.18. E.S.R. spectrum of 1,2-BNNE in P.M.P. solution at R.T.
resolved, but in P.M.P. hyperfine splittings are resolved. As with 1,3-BNNP, intermolecular dimers are probably present at room temperature. The P.M.P. spectrum shows evidence of 17 lines rather than the expected 15, and the lines are not of the "correct" intensity ratios. A possibility is that some exchange is experienced across the dimer which is causing perturbations.

The R.T. E.S.R. crystal spectrum (Figure 4.19) gives a doublet-species resonance which is quite assymetric. No triplet resonances are observed. Since the shape of the resonance is somewhat different than the polycrystalline samples of the doublet nitronylnitroxides and 1,3-BNNP, it is quite possible that the intramolecular exchange energy is increased. The resonance signal is not drastically changed, however. Thus, it is concluded that the exchange energy is rather small—probably less than 20 cm⁻¹.

2. Electronic Spectra: The R.T. absorption spectra of 1,2-BNNE were measured in n-hexane and ethanol (Figure 4.20). The maxima and their energies are shown in Table 4.6. R.T. and 77ºK spectra of 1,2-BNNE in E.P.A. and P.M.P. (Figures 4.21a and 4.21b) were also measured. Energies of the maxima for the spectra in E.P.A. and P.M.P. are given in Table 4.7.

The contours of the band I of 1,3-BNNP and 1,2-BNNE are very similar, and both are only slightly different than α-MNN. In hydrocarbon solvents, the second vibrational band is more intense
FIGURE 4.19. E.S.R. spectrum of a polycrystalline sample of 1,2-BNNE.
FIGURE 4.20. R.T. absorption spectra of 1,2-BNNE in solutions of n-hexane and ethanol.
TABLE 4.6

ABSORPTION ENERGIES AND COEFFICIENTS OF 1,2-BNNE
IN ETHANOL AND n-HEXANE

<table>
<thead>
<tr>
<th>A (Å)</th>
<th>Ethanol</th>
<th>n-Hexane</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>cm⁻¹</td>
<td></td>
</tr>
<tr>
<td>5500</td>
<td>18,180</td>
<td></td>
</tr>
<tr>
<td>5250</td>
<td>19,050</td>
<td></td>
</tr>
<tr>
<td>3940</td>
<td>25,380</td>
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<td>3186</td>
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<td>5753</td>
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<tr>
<td>5380</td>
<td>18,590</td>
<td></td>
</tr>
<tr>
<td>3525</td>
<td>28,370</td>
<td></td>
</tr>
<tr>
<td>4013±20</td>
<td>24,920±150</td>
<td></td>
</tr>
<tr>
<td>3232</td>
<td>30,940</td>
<td></td>
</tr>
</tbody>
</table>
FIGURE 4.21a. Absorption spectra of 1,2-BNNE in E.P.A. at R.T. and 77°K.
FIGURE 21b. Absorption spectra of 1,2-BNNE in P.M.P. at R.T. and 77°K
<table>
<thead>
<tr>
<th></th>
<th>E.P.A.</th>
<th>P.M.P.</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>R.T.</td>
<td>77°K</td>
</tr>
<tr>
<td></td>
<td>cm⁻¹</td>
<td>cm⁻¹</td>
</tr>
<tr>
<td>5605</td>
<td>17,840</td>
<td>18,050</td>
</tr>
<tr>
<td>5253</td>
<td>19,040</td>
<td>19,280</td>
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<tr>
<td>3950</td>
<td>25,300</td>
<td></td>
</tr>
<tr>
<td>3200±5</td>
<td>31,250</td>
<td>31,650</td>
</tr>
</tbody>
</table>

**TABLE 4.7**

**ABSORPTION ENERGIES OF 1,2-BNNE IN E.P.A. AND P.M.P. AT R.T. AND 77°K**
than the zero-zero band in both 1,2-BNNE and 1,3-BNNP. The zero-zero band is the most intense of the vibrational splittings in the first transition of \( \alpha \)-MNN.

Band II is less resolved in 1,2-BNNE than in 1,3-BNNP or \( \alpha \)-MNN. The absorption spectra of 1,2-BNNE and 1,3-BNNP are most similar in ethanol. However, the extinction coefficients of the band maxima of 1,2-BNNE in ethanol relative to those of \( \alpha \)-MNN are 1.2 for band I and 1.3 for band II, while those of 1,3-BNNE are 1.4 and 1.9 for band I and II, respectively.

In addition to the principal bands, there are weaker transitions at 4010Å and 3520Å in n-hexane. The extinction coefficients are approximately 200 and 1000, respectively. In ethanol, a weak band at about 3950Å is the only secondary band observed. The intensity of the band in ethanol is difficult to estimate since the region between bands I and II shows considerable "base line" absorption which tends to obscure the weak band. The origins of the secondary bands are not known. In any case, they do not appear to be the result of exciton splitting.

The transitions of 1,2-BNNE are blue-shifted in E.P.A. and P.M.P. at 77°K relative to the R.T. spectrum. As with 1,3-BNNP and \( \alpha \)-MNN, the blue-shift in P.M.P at 77°K is exceptionally large. By analogy the blue-shift is attributed to interaction with water at 77°K.

In summary, the electronic spectra of 1,2-BNNE are very similar to those of 1,3-BNNP and \( \alpha \)-MNN. There are additional
transitions whose origins are unknown. They do not appear to be the result of exciton interaction, however. From the E.S.R. spectrum of a polycrystalline sample of 1,2-BNNE, it is concluded that the exchange energy is small. Thus, 1,2-BNNE, although it has only two methylene bridges between subsystems, is essentially a system of only slightly perturbed \( \alpha \)-methynitronylnitroxides.

(C) Bis(\( \alpha,\alpha' \)-NitronylNitroxide)

1. E.S.R.: BNNE is very insoluble in most solvents. In ethanol the solubility is less than \( 10^{-4} \)M; and in hydrocarbon solvent, the solubility is so low that no absorption spectrum is observed from a saturated solution. Only in acetonitrile does the compound dissolve to any appreciable extent (~\( 10^{-3} \)M). Thus, the E.S.R. spectrum was measured in acetonitrile.

The E.S.R. spectrum was measured as a function of temperature in acetonitrile. A doublet resonance was obtained at room temperature (Figure 4.22); there was no structure. The signal was quite weak and the source could possibly be impurity doublets. At about -55\(^\circ\)C the solution solidified, and the cavity quality increased greatly. A very weak half-field resonance was observed (Figure 4.23). \( D^* \) was calculated to be 994 gauss. No corresponding \( \Delta m_s = 1 \) resonances were observed. The value of \( D^* \) is very near the 1.02\( \times 10^3 \) gauss observed for the intermolecular triplet species in 1,2-BNNE, 1,3-BNNP and the \( \alpha \)-nitronylnitroxide radicals in ethanolic matrices at 77\(^\circ\)K.
FIGURE 4.22. E.S.R. spectrum of BNN in acetonitrile at R.T.
FIGURE 4.23. E.S.R. spectrum (half-field region) of BNN in acetonitrile at -55°C.
It is known that a room temperature magnetic susceptibility measurement of BNN reveals that the average magnetic moment per molecule is $\sqrt{4}\mu_B$. This gives 1.24 unpaired electrons using the standard magnetic susceptibility partition functions in which dipole interactions are neglected. Hence, at room temperature some molecules in the solid have unpaired electrons. Based on these results one must assume that the ground state of the molecule is a singlet. The absence of a significant population of triplet molecules in solutions of acetonitrile at -55°C implies that extensive intermolecular polymerization and subsequent spin pairing occur.

2. **Electronic Absorption Spectrum:** The R.T. absorption spectrum of BNN measured in acetonitrile is shown in Figure 4.24. The wavelengths and energies are given in Table 4.8. The concentration and extinction coefficients are unknown. Two principal band systems are observed in the regions of Bands I and II of the other "triplet" molecules. However, the energies and the contours of the bands in those regions are changed to such an extent that the two bands do not derive from the same "type" of transition as Bands I and II of the other compounds. A greater degree of interaction of the subsystems is definitely indicated.

The absorption spectra of region II in E.P.A. at R.T., 223°C and 77°C, are shown in Figure 4.25. Only band II was observable in E.P.A. because of the insolubility of the compound. It should be noted that the first maximum of band II changes in going from
FIGURE 4.25. Absorption spectra of BNN in E.P.A. at R.T., 223 K and 77 K
TABLE 4.8

ABSORPTION ENERGIES OF BNN IN ACETONITRILE AND E.P.A.

**Acetonitrile (R.T.)**

<table>
<thead>
<tr>
<th>Ω Å</th>
<th>cm⁻¹</th>
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<tbody>
<tr>
<td>3520</td>
<td>28,330</td>
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<tr>
<td>3253</td>
<td>30,740</td>
</tr>
<tr>
<td>3127</td>
<td>31,980</td>
</tr>
</tbody>
</table>

**E.P.A.**

**R.T.**

<table>
<thead>
<tr>
<th>Ω Å</th>
<th>cm⁻¹</th>
</tr>
</thead>
<tbody>
<tr>
<td>3265</td>
<td>30,630</td>
</tr>
<tr>
<td>3133</td>
<td>31,920</td>
</tr>
</tbody>
</table>

**77°K**

<table>
<thead>
<tr>
<th>Ω Å</th>
<th>cm⁻¹</th>
</tr>
</thead>
<tbody>
<tr>
<td>3372</td>
<td>29,660</td>
</tr>
<tr>
<td>3275</td>
<td>30,530</td>
</tr>
<tr>
<td>3135±5</td>
<td>31,900</td>
</tr>
<tr>
<td>3010</td>
<td>33,220</td>
</tr>
</tbody>
</table>
acetonitrile to E.P.A. The maximum becomes a shoulder. This appears to be the result of general broadening of the structure and the band causing the subsequent loss of resolution. At 77°C, the spectrum is very sharp and well resolved. The first shoulder of band II—is visible at R.T.—has vanished while the rest of the region is much more intense than at R.T. The R.T. spectrum of band II, except for the low energy shoulder, appears to be made up of the same well resolved bands as observed at 77°C. The spectrum at -50°C shows the sharp bands beginning to be resolved. Thus the loss of the first shoulder of band II at 77°C implies the loss of some chemical species present at room temperature. It is also interesting that the maxima at 3273Å and 3136Å are not blue-shifted very much as is band II of 1,2-BNNE and 1,3-BNNP in going from R.T. to 77°C. This change of character suggests either a change in the nature of the transitions, or a drastic change in solvation properties.

The evidence seems to indicate some sort of equilibrium between two species—possibly singlet and triplet species or triplet and spin paired polymers. The information is inadequate to reach a conclusion, however.

(D) Zero-Field Splittings and Conformers: Several triplet species have been observed in the E.S.R. spectra of the diradicals, 1,2-BNNE and 1,3-BNNP, in rigid matrices. In an effort to associate the zero-field splittings with conformation, the zero-field splittings
for selected conformations of molecular models have been calculated.

The electronic absorption spectra of these diradicals indicate that each of the unpaired electrons is localized in its α-nitronylnitroxide subgroup. This conclusion is supported by the very small exchange interaction between the two unpaired electrons. On the basis of these experimental results, it may be assumed that the unpaired electrons are independent and that the spin densities in the subsystems of the diradicals are the same as observed for the independent doublet subsystems. The elements of the zero-field tensor are given by equation 56 and those generated by permutation of the x, y and z coordinates

\[
D_{xx} = \frac{1}{2} g^2 \beta^2 \sum_{i,j} P_i P'_j \left( \frac{r_{ij}^2 - 3X_{ij}Y_{ij}}{r_{ij}^5} \right)
\]

\[
D_{xy} = \frac{1}{2} g^2 \beta^2 \sum_{i,j} P_i P'_j \left( \frac{-X_{ij}Y_{ij}}{r_{ij}^5} \right)
\]

In these equations, \( \vec{r}_{ij} \) is the vector between the \( i^{th} \) atom of one subgroup and the \( j^{th} \) atom of the other subgroup; \( P_i \) and \( P'_j \) are the probabilities of finding the unpaired electrons on the \( i^{th} \) and \( j^{th} \) atom of their respective subgroups. In general, \( P_i \) and \( P'_j \) may be determined from experiment or from molecular orbital calculations.

The zero-field splittings have been calculated for three conformations of 1,2-BNNE and for one conformation of 1,3-BNNP.
The calculated values of $D$, $E$, and $D^*$ are given in Table 4.9. The differences in the values of $D$ and $E$ for spin density sets I and II illustrate the need for precise spin densities and bondlengths in calculations of $D$ and $E$. From another point of view, one can state that small differences in the conformation of diradicals cannot be determined without an exact knowledge of the electronic structure. The latter is unrealistic in terms of present theoretical methods. In spite of these uncertainties, one can still distinguish between conformers in cases where the differences in structure involve rather large changes in coordinates.

For 1,2-BNNE the experimental zero-field splittings were measured to be $D = 225$, $E = 25$, and $D^* = 228$. Since the zero-field splittings calculated for conformation III can be
FIGURE 4.26. Conformations of 1,2-BNNE and 1,3-BNNP for which zero-field splittings are calculated.
eliminated as the monomer triplet species observed in rigid matrices. This is consistent with the intuitive believe that steric effects between the methyl groups would not favor the "folded-back" conformation. Conformations I and II differ only in the relative orientations of the ring planes (In conformation I the ring planes are parallel and in II they are perpendicular). As such, the calculated values of D are quite similar. However, the calculated values of E are much larger for conformation I than for II. This fact indicates that conformation I agrees most nearly with the experimental data for the triplet species in solution. This conclusion makes one question the fact that the experimental value of D is 25% greater than the larger calculated value for I and the experimental value of E is 100% greater.

Two possibilities exist: (1) The molecule is partially folded--i.e., it is not in any of the extreme conformations for which the calculation has been performed; and (2) that for conformations I and II, small spin densities on the carbon atoms of the methylene bridge have been neglected. In the latter case, small spin densities in the methylene bridge might enhance the calculated values of D and E because of the \( \frac{1}{r^3} \) dependence of the zero-field splittings. This writer does not feel that we are in a position to choose one or the other. Indeed, the correct answer may involve both possibilities.

For 1,3-BNNP the experimental zero-field splittings were: species 1—\( D = 225 \), \( E = 3 \) and \( D^* = 225 \) and for species 2—\( D = 93 \),
E = 0 and D* = 93. The calculated values for conformation I agree quite closely with the experimental values for species 2. However, for 1,3-BNNE there exist numerous conformations that would give calculated zero-field splittings in the range of those for species 1 and 2. Hence it is not claimed that species 2 and conformation 4 are the same, but only that the calculated zero-field splittings for the extended form of the molecule agree with the experimental measurements.

In conformation III of 1,2-BNNE the nitronylnitroxide ring planes were put as close to one another as the methyl groups would permit. The calculated splittings are still considerably smaller than the large splitting (D* = 1.02x10^3 gauss) observed at half-field for the doublets and triplets in ethanolic glasses. Thus, it seems very unlikely that two nitronylnitroxide groups--having their principal symmetry axis in the same direction--could approach one another to the extent that D* would equal 1.02x10^3 gauss. In order to get the ring planes sufficiently close for the calculated value of D* to be as high as 1.02x10^3 gauss, the principal axes of the two nitronylnitroxide groups must be in opposite directions. This analysis is consistent with the triplets observed for the doublet radicals and the "dangling ends" model postulated for the same triplet observed for the diradicals (Section B).

A final conclusion can be made regarding the well resolved doublet spectra observed for the triplets, 1,2-BNNE and
1,3-BNNP, in the room temperature solution spectrum. The magnitudes of the calculated zero-field splittings for the triplets indicate that the monomer diradical spectra should be very broad in the solution spectra. This is true for even the very smallest zero-field splitting expected for any conformation of these monomer diradicals. The fact that well resolved doublet spectra are observed gives strong support to the "dangling ends" model (or a polymer variation) for dimerization of the triplets.
TABLE 4.9

CALCULATED ZERO-FIELD SPLITTINGS† FOR SELECTED CONFORMATIONS OF 1,2-BNNE AND 1,3-BNNP

Spin Densities

<table>
<thead>
<tr>
<th>Atom</th>
<th>Set I</th>
<th>Set II</th>
</tr>
</thead>
<tbody>
<tr>
<td>ring-C</td>
<td>.16</td>
<td>.08</td>
</tr>
<tr>
<td>N</td>
<td>.30</td>
<td>.30</td>
</tr>
<tr>
<td>O</td>
<td>.12</td>
<td>.155</td>
</tr>
</tbody>
</table>

Zero-Field Splittings

<table>
<thead>
<tr>
<th>Conformation</th>
<th>Set I</th>
<th>Set II</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>D</td>
<td>E</td>
</tr>
<tr>
<td>1,2-BNNE</td>
<td></td>
<td></td>
</tr>
<tr>
<td>I</td>
<td>196</td>
<td>11</td>
</tr>
<tr>
<td>II</td>
<td>188</td>
<td>.5</td>
</tr>
<tr>
<td>III</td>
<td>597</td>
<td>60</td>
</tr>
<tr>
<td>1,3-BNNP</td>
<td></td>
<td></td>
</tr>
<tr>
<td>IV</td>
<td>116</td>
<td>5</td>
</tr>
</tbody>
</table>

†Units of gauss.
SUMMARY

The objective of this research was to characterize the electronic ground state of some α-nitroynitroxide radicals and diradicals and to select theoretical models to account for the observed magnetic interactions. Such information would, subsequently, be of use in future applications of the radicals and diradicals. Among the projected applications of the diradicals, is their use as probes in semicrystalline materials such as micelles and liquid crystals.

Since the compounds were not readily available, it was necessary to prepare many of the desired radicals in these laboratories. The doublet radicals—α-methylnitroynitroxide, α-phenylnitroynitroxide, α-(o-tolyl)nitroynitroxide—and the diradical, 1,3-bis-(α-nitroynitroxide)propane, were prepared. 1,2-bis-(α-nitroynitroxide)ethane and bis-(α,α'-nitroynitroxide) were kindly sent to us by Dr. E.F. Ullman, Research Director of Synvar Research Institute.

The ground states of the doublet radicals have been found to have essentially the same unpaired electron distribution in which the unpaired electron is primarily localized on the nitroynitroxide subgroup. The unpaired electron is assigned to a π molecular orbital which transforms as $b_1$ with respect to the $C_{2v}$ symmetry operations of the nitroynitroxide subgroup. From analysis of the E.S.R. spectra of
α-nitronynitroxide doublets in ethanolic glasses and from the isotropic hyperfine splitting constants in solution, the unpaired electron spin density in each nitrogen pi orbital has been found to be .30. The α-carbon pi spin density is estimated to be between .08 and .16.

Solvent studies indicate that the absorption energies and the unpaired electron distribution in the molecules are solvent dependent. Optical absorption studies have shown that the first excited states are less polar than the ground state. Although the excitation energies of these compounds blue shift with increasing solvent polarity, the intensities are moderately high. As a result the transitions are assigned as being $\pi \rightarrow \pi^*$ in origin. The energy shifts and the change of band contour of the moderately intense bands with solvent indicate a potential use of the α-nitronynitroxides as optical probes. A rather common application would be the use of α-nitronynitroxides of aggregation studies of micelles. Attachment of a long hydrocarbon chain at the α position should allow the resulting compound to be incorporated into micelles. A rather trivial application might be in the determination of the critical micelle concentration of solutions from optical absorption studies.

The isotropic hyperfine splitting constants of the α-nitronynitroxides have also been found to be solvent dependent. Unfortunately, the effects are quite small, and the practical application of this particular property appears to be limited.
While the isotropic hyperfine splittings of the doublet molecules have limited utility, the anisotropy of the total hyperfine tensors provide cause for optimism. As a result of the anisotropy, the measured E.S.R. spectra depend upon the orientation of the molecules with respect to the static magnetic field. In solution the spectrum that one observes depends upon the viscosity of the solvent. As the viscosity of the solvent increases, the E.S.R. spectrum tends to broaden and lose structure. In the limit of a rigid matrix, a superposition spectrum is obtained. One may measure spectra from solutions of known viscosity from which estimates of the freedom of the molecule to tumble are obtained. The radical may then be used as a probe. With regard to the previously mentioned studies of micelles, the E.S.R. data could be utilized in conjunction with the optical data. The E.S.R. spectrum of a long chained substituted $\alpha$-nitronyl nitroxide in a micelle could indicate the freedom of the moiety in a micelle. Thus, the optical and E.S.R. measurements would complement one another. Work of this type has been done using simple nitroxides as probes.\(^1\) The investigations deserve further study to eliminate the possibility of specific interactions of the simple nitroxide probes in the systems previously studied.\(^2\)


The compounds, 1,2-bis-(α-nitronylnitroxide)ethane and 1,3-bis-(α-nitronylnitroxide)propane, have been shown to be best classified as diradicals. The E.S.R. spectra of the compounds in rigid matrices have been shown to be highly dependent upon the nature of the matrix. These diradicals also show optical solvent effects which are similar to those of the parent doublet radicals. Of the two diradicals, 1,2-bis-(α-nitronylnitroxide)ethane shows smaller changes in the zero-field splittings with the nature of the matrix. Unlike 1,3-bis-(α-nitronylnitroxide)propane, which shows an equilibrium of two conformations in rigid matrices, 1,2-bis-(α-nitronylnitroxide)ethane shows only one particular conformation per matrix for the monomeric triplets. These properties indicate that 1,2-bis-(α-nitronylnitroxide)ethane would be a better probe in liquid crystals. Since its zero-field splittings would be less sensitive to the type of matrix, it would be a better indicator of the orderliness of a liquid crystal. Mathematical models such as those discussed in Section D of Chapter X V would be of particular value in determining the orientation of the diradicals in the liquid crystals. Of course, one must find a liquid crystal system with which the diradical is compatible and which has the proper geometry for substitution at the "sites" in the liquid crystal phase.

Bis-(α,α'-nitronylnitroxide) was not well characterized in these studies. From the point of view of the pure scientist, the compound deserves further study. With regard to its application to
other systems, its low solubility presents a problem which may hinder its utility. It is, of course, possible that there exist compounds with which it will form excellent solid solutions. In such cases study of the resulting solutions reveal much about the bis-(α,α'-nitronynitroxide) itself.

It is the contention of the author that the general magnetic and optical properties of the α-nitronynitroxides have been well established. Nevertheless, particular applications of these radicals and diradicals will probably require further study under the more specific conditions. For further possible applications of these types of compounds, the reader is referred to reference 2 of this summary.
SELECTED BIBLIOGRAPHY


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VITA

Joseph Albert D'Anna, Jr. was born in New Orleans, Louisiana on July 27, 1943. He was reared in Independence, Louisiana and was educated in the local school system. He graduated from Independence High School in 1961.

In June of 1961, he entered Southeastern Louisiana College from which he received a B.S. in Chemistry in May of 1965.

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