ESR, $^1$H, and $^2$D Studies of the Radical Anion of 1,3,5-Triphenylbenzene

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(Received 18 September 1970)

MO calculations predict that the monoanion of 1,3,5-triphenylbenzene (Tpb) is in an orbitally degenerate ground state. Nevertheless, the ESR spectrum in liquid NH$_3$ is well resolved; the derivative linewidth is equal to 0.06 Oe only. The $g$ value and the electronic relaxation times $T_1$ and $T_2$ were comparable in magnitude to those of orbitally nondegenerate radicals. It is suggested that twisting of the phenyl rings out of the plane of the molecule, which may lift the orbital degeneracy, is the principal reason of this behavior. $^1$H and $^2$D NMR experiments were performed on a reduced sample of Tpb, containing both normal and perdeutero-Tpb. From the Fermi contact shifts signs and magnitudes of all hyperfine splitting constants have been determined, and they agreed very well with the ESR splitting constants. From the proton linewidths the electronic and dipolar correlation times were inferred. Quadrupole coupling constants for all deuterium nuclei were calculated from the $^2$D linewidths.

I. INTRODUCTION

Some years ago Townsend and Weissman$^1$ reported unusually broad ESR lines exhibited by hydrocarbon aromatic radicals, which are predicted to have orbitally degenerate ground states, because of their high symmetry (e.g., benzene anion). Since then more experimental data$^{2,3}$ have become available, which all confirmed the original observation that orbitally degenerate radicals have unusual relaxation times. In all cases studied these features were accompanied by an anomalous $g$ value. Till now a satisfactory explanation for this behavior is lacking. It has been suggested that both effects are associated with enhanced spin-orbit coupling.\(^2,3\)

We have performed a combined ESR and NMR study of the monoanion of 1,3,5-triphenylbenzene (Tpb\(^-\), see Fig. 1).\(^4\) According to MO calculations this anion belongs to the class of orbitally degenerate radicals.\(^5\) Nevertheless, the hyperfine lines of its ESR spectrum, measured in liquid ammonia, are very narrow and a normal $g$ value is observed. On the other hand, the dianion of Tpb\(^6\) has been shown to occur in a triplet ground state, pointing to orbital degeneracy of the monoanion.

By means of NMR, information has been obtained on the sign of the proton hyperfine splitting constants. The presence of a proton with a small hfsc enabled us to determine from the $^1$H linewidths not only the electronic correlation time ($\tau_e$), but also accurate values for the rotational correlation time ($\tau_r$). This in turn together with the $^2$D linewidths yielded information on the quadrupole coupling constants in the anion of perdeutero-Tpb.

II. EXPERIMENTAL

The ESR experiments have been performed on a Varian 4502 X-band spectrometer, equipped with a variable temperature control. The temperature was measured with a copper-constantan thermocouple. The NMR experiments have been performed on a Varian DP-60-EL spectrometer equipped with a V4331 60-MHz unit for proton resonance and a variable frequency transmitter for deuterium resonance, stabilized at 9.1 MHz by a crystal stabilizer. Frequencies were monitored with a Hewlett-Packard 5245L frequency counter, and magnetic fields were measured with an AEG proton magnetic resonance field meter.

The samples were prepared by standard vacuum line techniques.\(^8\) All samples have been reduced using sodium metal as reducing agent. The NMR experiments have been performed on samples containing 50\% Tpb-H\(_8\) and 50\% Tpb-D\(_8\) using 1,2-dimethoxyethane as solvent. The NMR linewidths have been corrected for modulation broadening\(^2,3\) and broadening by intermolecular dipolar interactions. The latter correction was obtained from the broadening of the proton signals of the solvent.

The electronic relaxation times $T_1$ and $T_2$ have been determined by the continuous saturation method, measuring the linewidths as a function of the microwave power. Recently the same technique was utilized by Kooser et al.\(^2\) in studying some orbitally degenerate free radicals. Since these authors have given an extended description of the method, we refer for further details to their work and to the dissertation of van Broekhoven.\(^11\) Because of overlap of the individual ESR lines, direct measurements of the linewidth as a function of power was impossible. Therefore, the experimental spectra were compared with a series of computer...
simulations, in which the linewidth has been varied from 0.050 to 0.500 Oe in steps of 10 mOe.

III. BASIC EQUATIONS

A. Hyperfine Splitting Constants

Both ESR and NMR techniques can be used to measure hyperfine splitting constants (hfsc) in paramagnetic particles. The ESR hfsc are given by the intervals between the hyperfine lines, and therefore only the absolute value is obtained; the NMR hfsc are derived from the Fermi contact (FC) shift, which is equal to:

$$\delta_0 = - \left( \frac{g\beta_e}{gN\beta_N} \right) A_N \left( \frac{H_p}{4\mu_0 T} \right),$$  \hspace{1cm} (1)

where $\delta_0$ = FC shift expressed in oersted, $H_p$ = resonance field, $A_N$ = hfsc expressed in energy units, $g$ = isotropic g value of the radical, and the other symbols have their usual meaning, so that not only the magnitude but also the sign of the hfsc is obtained. The hfsc provide information on the electron distribution. For proton nuclei in aromatic free radicals, the well-known McConnell-Weissman relation\textsuperscript{12} can be used, which relates the hfsc to the integrated $\pi$ density ($\rho_\pi$)

on the adjacent carbon atoms,

$$a_H = Q \rho_\pi \quad (a_H = A_H / g\beta_e),$$  \hspace{1cm} (2)

where $Q$ is a proportionality factor.

B. Linewidth

Generally the linewidth ($T_2^{-1}$) will depend on intra- and intermolecular interactions. For a nucleus in a paramagnetic molecule the intramolecular interactions are normally by far the most important. In our case the linewidth parameter $T_2$ will be governed by three intramolecular interactions, namely, the Fermi contact (FC), the anisotropic electron spin nuclear spin dipolar ($D$), and the quadrupolar ($Q$) interaction:

$$T_2^{-1} = (T_2^{-1})_F + (T_2^{-1})_D + (T_2^{-1})_Q.$$  \hspace{1cm} (3)

For a radical in solution subjected to rapid Brownian motion, the following expressions can be derived for the relevant relaxation times\textsuperscript{14-16}:

$$(T_2^{-1})_F = \frac{1}{2} (A / \hbar)^2 \left( \Gamma_\pi^* + \tau_\pi / (1 + \omega_\pi^* \tau_\pi^*) \right),$$  \hspace{1cm} (4)

$$(T_2^{-1})_D = \frac{1}{2} (B / \hbar)^2 \left[ 7 \tau_d + \left[ 13 \tau_d / (1 + \omega_\pi \tau_d) \right] \right],$$  \hspace{1cm} (5)

$$(T_2^{-1})_Q = 3/40 (2I + 3) / I^3 (2I - 1) (e^2Qq / \hbar)^2 \times \left[ 1 + (\eta^2 / 3) \right] \tau_e,$$  \hspace{1cm} (6)

where $\omega_\pi$ is the resonance frequency of the electron, $\tau_\pi$, $\tau_d$, and $\tau_e$ are the electron, dipolar, and rotational correlation times, respectively ($\tau_\pi^{-1} = \tau_e^{-1} + \tau_\pi^{-1}$), $e^2Qq / \hbar$ is the quadrupole coupling constant (qcc), and $B^2 = 1/2 (T : T)$, in which $(T : T) = \sum_{\alpha, \beta} T_{\alpha \beta} \omega_\alpha \omega_\beta$, where $T$ is the tensor for the dipolar anisotropic interaction, and $\alpha$, $\beta$ refer to axes of a molecular coordinate system. The other
symbols have their usual meaning. Details of the derivation of Eq. (5) are given in the Appendix.

Under the conditions of our experiments $\omega_S \tau_f^2$ and $\omega_S \tau_f^2 \gg 1$, so that the frequency-dependent terms in Eqs. (4) and (5) can be neglected. In the application of Eq. (6) we will assume an axially symmetric field gradient ($\eta = 0$), which will introduce an error of at most 25% in $q_{cc}$.

IV. RESULTS AND DISCUSSIONS

A. Hyperfine Splitting Constants

Figure 2 shows the ESR spectrum of Tpb~ in liquid ammonia at $-40^\circ$C. The spectrum is very well resolved, and the derivative linewidth is equal to 0.06 Oe. With the hfs values listed in Table I a perfect computer fit was obtained (see Fig. 2).

The spectra in 2-methyltetrahydrofuran (MTHF) (see Fig. 3) and in 1,2-dimethoxyethane (DME) were less resolved, and the derivative linewidths were equal to 0.2 and 0.12 Oe, respectively. These spectra could also be simulated perfectly with the set of hfs in Table I and the above mentioned linewidths (see Fig. 3).

Figure 4 shows the $^1$H and $^2$D NMR spectra. According to Eqs. (4) and (5) the magnetic contributions to the $^2$D linewidth are a factor $(\gamma_H / \gamma_D)^2 = 42.5$ smaller than the corresponding contributions to the $^1$H linewidth. Inasmuch as the magnetic interactions predominate the $^2$D linewidth and the FC shifts are inde-

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**Table I. Hfs and spin densities in Tpb~.**

<table>
<thead>
<tr>
<th>Carbon atom</th>
<th>$\alpha_{\text{ESR}}$ (oersted)</th>
<th>$\alpha_{\text{NMR}}$ (oersted)</th>
<th>$\rho_{\text{ESR}}$</th>
<th>$\rho_{\text{NMR}}$</th>
<th>$\rho_{\text{FCF} + \text{CI}}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>3.58±0.02</td>
<td>-3.57±0.02</td>
<td>0.137</td>
<td>+0.137</td>
<td>+0.047</td>
</tr>
<tr>
<td>2</td>
<td>3.58±0.02</td>
<td>-3.57±0.02</td>
<td>0.137</td>
<td>+0.137</td>
<td>+0.150</td>
</tr>
<tr>
<td>7</td>
<td>0.93±0.02</td>
<td>-0.94±0.01</td>
<td>0.036</td>
<td>+0.036</td>
<td>+0.038</td>
</tr>
<tr>
<td>8</td>
<td>0.93±0.02</td>
<td>-0.94±0.01</td>
<td>0.036</td>
<td>+0.036</td>
<td>+0.032</td>
</tr>
<tr>
<td>9</td>
<td>0.155±0.005</td>
<td>+0.156±0.003</td>
<td>0.006</td>
<td>-0.006</td>
<td>-0.008</td>
</tr>
<tr>
<td>10</td>
<td>1.55±0.02</td>
<td>-1.54±0.01</td>
<td>0.059</td>
<td>+0.059</td>
<td>+0.050</td>
</tr>
</tbody>
</table>

* These values have been calculated by setting $G$ equal to $\Sigma h_i / (\Sigma p_i)_{\text{FCF} + \text{CI}}$, where the summation is over all carbon atoms bearing protons.
dependent of the magnetic moment of the isotope, the resolution in the 2D spectrum will be better than in the ¹H spectrum. In Table I the NMR hfs are also listed; excellent agreement exists with the ESR hfs. The NMR experiments reveal that the spin density on carbon atom 9 is negative.

Column 6 in Table I contains the theoretical z spin densities, calculated with an open-shell Pariser-Parr-Pople SCF MO calculation, including configuration interaction. The agreement with the experimental spin densities, obtained with the aid of Eq. (2) with h = —26 Oe, is very satisfactory. The assignment of the theoretical spin densities is made on the basis of the correspondence with the experimental spin densities.

B. g Value and Electron Relaxation Times

Using the g value of anthracene⁻ in NH₃ as a reference to eliminate systematic errors, the absolute g value of Tpb⁻ in NH₃, corrected for the second-order shift, is equal to 2.00272±4×10⁻⁶. For Tpb⁻ in MTHF a value of 2.002±1×10⁻⁶ was found. Guided by the MO calculations, which predict that the lowest antibonding MO's are degenerate, it was expected that

\[ \Delta g, \text{ the deviation from the free electron } g \text{ value, should not fulfill Stone's semiempirical relation,}^{18,19} \]

\[ \Delta g = \left[ (27.6 \pm 0.8) - (17.2 \pm 2.0) \lambda \right] \times 10^{-5}, \quad (7) \]

which seems to be valid for orbitally nondegenerate radicals. In this equation, λ refers to the Hückel parameter in the energy expression \( E_z = \alpha + \lambda \beta \) for the lowest antibonding MO; for Tpb, \( \lambda = -0.66 \). Substituting this into Eq. (7), one obtains

\[ \Delta g = (39 \pm 1) \times 10^{-5}; \]

the experimental value is

\[ \Delta g = (40.0 \pm 0.4) \times 10^{-5}. \]

Hence, within the limits of error no deviation is found, contrary to the observations for other orbitally degenerate radicals.\(^{18,20,21}\)

The values of the relaxation times \( T_1 \) and \( T_2 \) are collected in Table II. Relaxation times of orbitally degenerate radicals are all of the order of \( 10^{-7} \) sec,\(^{2,3,21,22}\) whereas \( T_1 \) and \( T_2 \) for orbitally nondegenerate radicals are about \( 10^{-6} \) sec. \( T_1 \) and \( T_2 \) of Tpb⁻ in NH₃ closely resemble the values measured for the latter class of radicals.

At this moment a satisfactory explanation for the anomalous g value and relaxation times of orbitally degenerate radicals is still lacking. Most proposed explanations involve an enhanced spin–orbit interaction.\(^{4}\) One may conclude from the normal behavior of Tpb⁻ in this respect that this mechanism is quenched for Tpb⁻. This might be caused by an out-of-plane bending of the phenyl rings, which might lift the orbital degeneracy. The phenyl rings of neutral Tpb in the

<table>
<thead>
<tr>
<th>Solvent</th>
<th>( T ) (°C)</th>
<th>( T_1 \times 10^6 ) (sec)</th>
<th>( T_2 \times 10^6 ) (sec)</th>
</tr>
</thead>
<tbody>
<tr>
<td>MTHF</td>
<td>—79</td>
<td>0.78±0.23</td>
<td>0.32±0.01</td>
</tr>
<tr>
<td>DME</td>
<td>—77</td>
<td>0.47±0.14</td>
<td>0.65±0.02</td>
</tr>
<tr>
<td>NH₃(l)</td>
<td>—51</td>
<td>1.9±0.5</td>
<td>1.3±0.1</td>
</tr>
</tbody>
</table>
solid and in the gaseous state are twisted on the average by about 40°, 2, 3 However, the lifting of the
degeneracy cannot be large since the dianion of Tpb is
in a triplet ground state. 6, 6
The increase of the linewidth of the hyperfine lines
in the ESR spectrum going from NH₃ to less polar
solvents, such as DME and MTHF, is also remarkable.
It was first thought that a small unresolved alkali
splitting or minor changes in the proton hfsc might be
the reason. This can be ruled out, however, because the
NMR hfsc of Tpb⁻, dissolved in DME, are the same as
the ESR hfsc of Tpb⁻, dissolved in NH₃, and the Na
hfsc determined by carrying out ²³Na resonance in a
1M solution at room temperature amounts to +6
mOe only. In addition the T₁ measurements also point
to other mechanisms.
As a possible explanation we suggest the formation of
solvated ion pairs, taking place in the less polar solvents.
The small alkalii hfsc observed by NMR is evidence
for this. The nearby presence of the solvated cation
might induce a more planar structure of the radical,
so that its behavior will more resemble that of orbitally
degenerate radicals. If this is the case, one might also
anticipate an increase of the g value: Degenerate
radicals show deviations from the g value predicted by
Stone's plot of about 10⁻⁴. 2, 3 However, the g value of
Tpb⁻ measured in MTHF is equal to the value meas­
ured in NH₃ within the limits of accuracy. It is possible
that the expected increase of the g value due to the
restored orbital degeneracy will be largely compensated
by the effect of ionic association. Though the g value of
nondegenerate radical anions is lowered only by an
amount of Δg≈10⁻³ upon association with Na⁺, 25–27
we have found evidence that this effect can be much
stronger on orbitally degenerate radicals: The g value of
the planar triphenylene anion, which is orbitally
degenerate, decreases from 2.002839 to 2.00273 (Δg=
11×10⁻⁴) when association with Na⁺ takes place. 11
If it is assumed that this effect is of the same magnitude
in the planar Tpb⁻ anion, then the effect of the orbital
degeneracy upon the g value would be canceled out.

C. NMR Linewidths

The linewidths of the proton and the deuterium NMR
signals, determined at various concentrations, are
collected in Table III. These data can be used to
evaluate correlation times and quadrupole coupling
constants.

1. Correlation Times

The correlation times have been determined from the
¹H linewidths under the experimental conditions that
ωᵢ/istence−¹, so that

\[ T_{1}^{-1}(H) = \frac{1}{2}(A/\hbar)^2 \tau_\alpha + (7/20)(B/\hbar)^2 \tau_\beta. \]  

(8)
The parameter A can be derived from the FC shift,
and the value of B can be calculated using the formulas
of McConnell and Strathdee 28 (see Appendix). For the
latter calculations experimental spin densities are used,
it possible, and otherwise theoretical ones. For the
anisotropic dipolar interaction between the proton and
the electron on the adjacent carbon atom, the experi­
mental values for the C–H fragment in the radical of
malonic acid were used. 29 The numerical values for A
and B are listed in Table IV.

It is clear that two independent equations are re­
quired in order to determine \( \tau_\alpha \) and \( \tau_\beta \). The set of equa­tions arising from linewidth data of protons with large

<table>
<thead>
<tr>
<th>Proton (deuterium) atom</th>
<th>(A/ℏ)²×10⁻¹³</th>
<th>(B/ℏ)²×10⁻¹³</th>
<th>εᵢQ/ℏ (MHz)</th>
</tr>
</thead>
<tbody>
<tr>
<td>2</td>
<td>3974</td>
<td>283</td>
<td>0.64±0.20</td>
</tr>
<tr>
<td>8</td>
<td>268</td>
<td>24.4</td>
<td>0.50±0.06</td>
</tr>
<tr>
<td>9</td>
<td>7.44</td>
<td>10.3</td>
<td>0.46±0.06</td>
</tr>
<tr>
<td>10</td>
<td>745</td>
<td>68</td>
<td>0.65±0.11</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Concentration</th>
<th>τᵢ×10¹¹ (sec)</th>
<th>τ₂×10¹¹ (sec)</th>
<th>τ₋×10¹¹ (sec)</th>
</tr>
</thead>
<tbody>
<tr>
<td>M</td>
<td>τᵢ×10¹¹ (sec)</td>
<td>τ₂×10¹¹ (sec)</td>
<td>τ₋×10¹¹ (sec)</td>
</tr>
<tr>
<td>---------------</td>
<td>--------------</td>
<td>--------------</td>
<td>--------------</td>
</tr>
<tr>
<td>0.42</td>
<td>24 ± 3</td>
<td>0 &lt; τ₋ &lt; 3.4</td>
<td>0 &lt; τ₋ &lt; 3.4</td>
</tr>
<tr>
<td>0.65</td>
<td>11.7±0.5</td>
<td>0.8±0.4</td>
<td>0.9±0.5</td>
</tr>
<tr>
<td>0.82</td>
<td>6.4±0.1</td>
<td>1.7±0.4</td>
<td>2.2±0.6</td>
</tr>
<tr>
<td>1.04</td>
<td>4.0±0.1</td>
<td>1.5±0.3</td>
<td>2.4±0.8</td>
</tr>
<tr>
<td>1.21</td>
<td>2.9±0.1</td>
<td>0.7±0.6</td>
<td>0 &lt; τ₋ &lt; 2.5</td>
</tr>
</tbody>
</table>

Table IV. Linewidth parameters.

Table V. Correlation times.
hfsc will not meet this requirement because both $A$ and $B$ are then proportional to the spin density at the adjacent carbon atom, so that the equations become mutually dependent.

If one of the equations contains significant dipolar contributions from spin densities present on nonadjacent carbon atoms, which is usually the case for protons with small hfsc, the parameter $B$ is not proportional to the spin density at the adjacent carbon atom, and the two equations become independent.

The correlation times in Table V are calculated from the linewidths of protons 8 and 9 because they are the most accurate and can be measured over the entire concentration range studied. Accurate data for $\tau_d$ could only be obtained in the concentration range from $\sim0.8$ to $\sim1.0M$. At lower concentration the dipolar contribution is small with respect to the scalar contribution (10% or less), which renders the determination of $\tau_d$ inaccurate. At higher concentrations the correction for intermolecular broadening is large, especially for $T_{2}^{-1}$ of proton 9, which then restricts the accuracy.

An interesting feature in Table V is the decrease of $\tau_e$ on increasing the radical concentration. According to the model of Pake and Tuttle\textsuperscript{30} $\tau_e$ should be inversely proportional to the concentration of radicals. Figure 5 shows that this is rather well fulfilled.

### 2. Quadrupole Coupling Constants

The quadrupole contribution to the deuterium linewidth can be obtained by subtracting from it the proton linewidth multiplied by $(\gamma_D/\gamma_N)^2$. Substituting the values for $\tau_e$ (Table V) in Eq. (6) with $\eta=0$, the qcc for the four different types of C-D bonds can be calculated. To get meaningful results only the most accurate $\tau_e$ values were used. The qcc in Table IV exceed the value of 0.18 MHz, reported for a C-D bond in a neutral deuterated aromatic molecule,\textsuperscript{31,32} by about a factor 3-4.

For the time being it is not fully clear whether this additional contribution to the qcc is from inter- or intramolecular origin. The calculations of White and Drago\textsuperscript{32} suggest that an intramolecular contribution arising from the presence of the extra electron is perhaps not sufficient to explain this large change in field gradient. If it is intermolecular from origin, arising from the ion pair formation, the field gradient should depend on the structure of the ion pair and hence on the nature of the solvent, counterion, and aromatic molecule.\textsuperscript{6} This is the subject of further investigations.

#### ACKNOWLEDGMENTS

The authors are indebted to J. C. Langendam for assistance in the ESR measurements, and to A.A.K. Klaassen and J. W. M. de Boer for assistance in the NMR experiments. The present investigations have been carried out under the auspices of the Netherlands Foundation of Chemical Research (S.O.N.) and with the aid of the Netherlands Organization for the advancement in Pure Research (Z.W.O.).

#### APPENDIX A: DERIVATION OF THE DIPOLAR LINEWIDTH ($T_{2}^{-1}$)\textsubscript{D}

The Hamiltonian describing the anisotropic dipolar interaction between a nuclear spin and an electron spin in a rapidly tumbling molecule is given by

$$3 \mathcal{C}_D (t) = I \cdot \mathbf{I}(t) \cdot S, \quad (A1)$$

where

$$T_{ij}(t) = g_\alpha g_\beta \gamma_N \alpha N(t) | \{ [I^2(t)(t)] | [I^2(t)] | \psi \}, i, j=x, y, z$$

and $\psi$ is the wavefunction describing the odd electron.

$3 \mathcal{C}_D (t)$ can be rewritten as

$$3 \mathcal{C}_D (t) = (S_x I_x - \frac{1}{2} (S^+ I^- + S^- I^+) \mathbf{F}_0(t) + (S_x I^+ + S^+ I_x) \times \mathbf{F}_1(t) + (S_x I^- + S^- I_x) \mathbf{F}_1^*(t)$$

$$+ S^+ I^+ \mathbf{F}_2(t) + S^- I^- \mathbf{F}_2^*(t), \quad (A2)$$

in which

$$F_0(t) = T_{xx}(t),$$

$$F_1(t) = \frac{i}{2} [T_{xx}(t) - i T_{yy}(t)], \quad (A3)$$

$$F_2(t) = \frac{1}{3} [T_{xx}(t) - T_{yy}(t) - 2 i T_{xy}(t)].$$
Following Solomon, the expression for the \( T^{-1}_d \) becomes
\[
( T^{-1}_d ) = (4\pi^2)^{-1} \left[ \left( \tau_r + \frac{3\tau_r}{1+(\omega_\| - \omega_\perp)^2\tau_r^2} \right) \langle F \tau \rangle + \frac{2\tau_r}{1+\omega_\|^2\tau_r^2} + \frac{4\tau_r}{1+\omega_\perp^2\tau_r^2} \langle | F \rangle \right],
\]
where \( \omega_\| \) and \( \omega_\perp \) are the resonance frequencies of the nuclear spin and the electron spin, respectively, \( \tau_r \) is the rotational correlation time, and the quantities \( \langle F \rangle \) are any of the \( i,j,k,l \) relations holding for the tensor averages. Substituting these values into Eq. (A4), then, under the condition that \( \omega_\perp^2\tau_r^2 \ll 1 \), Eq. (A4) simplifies to
\[
( T^{-1}_d ) = \frac{1}{2} (B/\hbar)^2 \left[ 7\tau_r + \frac{13\tau_r}{(1 + \omega_\perp^2\tau_r^2)} \right],
\]
where \( B^2 = \frac{1}{6} (T:2) \).

When \( S \) is also time dependent the same formula holds, however with \( \tau_r \) replaced by \( \tau_d \), the dipolar correlation time \( \tau_d^{-1} = \tau_r^{-1} + \tau_s^{-1} \).

**APPENDIX B: CALCULATION OF THE DIPOLAR TENSOR ELEMENTS**

The explicit expression for \( T_{\alpha\beta} \) is
\[
T_{\alpha\beta} = -4\beta g_\alpha g_\beta \langle \psi \left[ \langle r^2 \delta_{\alpha\beta} - 3\alpha\beta \rangle / r^6 \right] \rangle \langle \psi \rangle.
\]
Substituting \( \psi = \sum_n \psi_n \phi_n \), where the functions \( \phi_n \) are the 2p AO's of the carbon atom, \( T_{\alpha\beta} \) can be written as
\[
T_{\alpha\beta} = \sum_{m,n} \rho_{nm} T_{mn} = \text{Tr} \{ \rho T \},
\]
with
\[
\rho_{nm} = c_n c_m^*,
\]
\[
T_{mn} = -4\beta g_{\alpha n} g_{\beta m} \langle \psi_n \left[ \langle r^2 \delta_{\alpha\beta} - 3\alpha\beta \rangle / r^6 \right] \rangle \langle \phi_m \rangle.
\]
If the zero overlap approximation is used, only diagonal elements remain, which are calculated with the formulas given by McConnell and Strathdee. 

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4. A preliminary account of this work has been presented at the meeting of the XVI Colloque Ampère at Bucharest, September 1970.