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

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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$^2$ 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.$^2$ We have performed a combined ESR and NMR study of the monoanion of 1,3,5-triphenylbenzene (Tpb$^-$, see Fig. 1). 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$^7$ 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-$^1$H and 50% Tpb-$^2$H using 1,2-dimethoxyethane as solvent. The NMR linewidths have been corrected for modulation broadening$^9$ 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...
Fig. 2. ESR spectrum of Tp

\( \text{Na}^+ \text{ in liquid NH}_3 \text{ at } -40^\circ \text{C.} \)

The lower spectrum is a computer simulation.

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

\[
\delta_0 = -\left( \frac{g\beta_e}{gN\beta_N} \right)A_N(H_p/4\hbar T),
\]

where \( \delta_0 = \text{FC shift expressed in oersted}, H_p = \text{resonance field}, A_N = \text{hfsc expressed in energy units}, g = \text{isotropic g value of the radical}, \) 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\(^{13}\) can be used, which relates the hfsc to the integrated \( \pi \) density \( \rho_\pi \) on the adjacent carbon atoms,

\[
\delta_H = Q\rho_\pi \quad (\delta_H = A_N/g\beta_e),
\]

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:

\[
T_2^{-1} = (T_2^{-1})_{FC} + (T_2^{-1})_D + (T_2^{-1})_Q.
\]

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

\[
\begin{align*}
(T_2^{-1})_{FC} &= \frac{1}{2} (A/\hbar)^2 \left[ \tau_e \left[ 1 + \omega_\pi^2 \tau_\pi^2 \right] \right],
\end{align*}
\]

\[
(T_2^{-1})_D = \frac{1}{2} \left( \frac{B}{\hbar} \right)^2 \left[ \frac{7}{\tau_e} + \left[ \frac{13}{\tau_e} + \frac{1}{\omega_\pi \tau_\pi} \right] \right],
\]

\[
(T_2^{-1})_Q = \frac{3}{40} (2I+3)/I^2 (2I-1) (eQq/\hbar)^2 \times [1 + (\eta^2/3)] \tau_e,
\]

where \( \omega_\pi \) is the resonance frequency of the electron, \( \tau_e, \tau_\pi \) and \( \tau_\pi \) are the electron, dipolar, and rotational correlation times, respectively, \( (T_2^{-1})_{FC} + (T_2^{-1})_D = (T_2^{-1})_Q \), \( eQq/\hbar \) is the quadrupole coupling constant (qcc), and \( B^2 = \frac{1}{2} (T/T') \), in which \( (T/T') = \sum_{\alpha,\beta} T_{\alpha\beta} \), where \( T \) is the tensor for the dipolar anisotropic interaction, and \( \alpha, \beta \) refer to axes of a molecular coordinate system. The other
Table I. Hfs and spin densities in Tpb⁻.

<table>
<thead>
<tr>
<th>Carbon atom</th>
<th>$\xi_{ESR}$ (oersted)</th>
<th>$\xi_{NMR}$ (oersted)</th>
<th>$\rho_{ESR}$</th>
<th>$\rho_{NMR}$</th>
<th>$P_{FC+CI}$</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>+0.159</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>0.155±0.005</td>
<td>+0.156±0.003</td>
<td>0.006</td>
<td>-0.006</td>
<td>-0.008</td>
</tr>
<tr>
<td>9</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 $\xi_{ESR}/(\xi_{NMR})_{FC+CI}$, where the summation is over all carbon atoms bearing protons.

symbols have their usual meaning. Details of the derivation of Eq. (5) are given in the Appendix.

Under the conditions of our experiments $\omega_1 T^2$ and $\omega_2 T^2 \gg 1$, 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 $\rho_{ESR}$.

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 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 $^1H$ and $^2D$ NMR spectra. According to Eqs. (4) and (5) the magnetic contributions to the $^2D$ linewidth are a factor $(\gamma_H/\gamma_D)^2 = 42.5$ smaller than the corresponding contributions to the $^1H$ linewidth. Inasmuch as the magnetic interactions predominate the $^2D$ linewidth and the FC shifts are inde-
ESR AND NMR OF ANION OF 1,3,5-TRIPHENYL BENZENE

1991

Fig. 4. 1H and 13C NMR spectrum of normal and perdeutero Tpb (in equal concentrations) in DME completely reduced with Na. As internal deuterium reference about 5 vol% THF-d4 was added. The peculiar shape of the reference signal was caused by saturation effects.

dependent of the magnetic moment of the isotope, the resolution in the 2D spectrum will be better than in the 1H spectrum.7 In Table I the NMR hfsc are also listed; excellent agreement exists with the ESR hfsc. The NMR experiments reveal that the spin density on carbon atom 9 is negative.

Column 6 in Table I contains the theoretical \( \pi \) 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 NH\(_3\) as a reference\(^{18}\) to eliminate systematic errors, the absolute \( g \) value of Tpb\(^-\) in NH\(_3\), corrected for the second-order shift,\(^{18}\) is equal to 2.002722±4×10\(^{-6}\). For Tpb\(^-\) in MTHF a value of 2.0022±1×10\(^{-6}\) was found. Guided by the MO calculations, which predict that the lowest antibonding MO's are degenerate,\(^{6}\) it was expected that \( \Delta g \), the deviation from the free electron \( g \) value, should not fulfill Stone's semiempirical relation,\(^{18,19}\)

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

which seems to be valid for orbitally nondegenerate radicals. In this equation, \( \lambda \) refers to the Hückel parameter in the energy expression \((E_0 = \omega + \lambda \beta)\) for the lowest antibonding MO; for Tpb, \( \lambda = -0.66 \). Substituting this into Eq. (7), one obtains

\[
\Delta g = (39±1) \times 10^{-4};
\]

the experimental value is

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

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\(^{5,3,22}\), whereas \( T_1 \) and \( T_2 \) for orbitally nondegenerate radicals are about 10\(^{-6}\) sec. \( T_1 \) and \( T_2 \) of Tpb\(^-\) in NH\(_3\) 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.\(^2\) 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>NH(_3)(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°.23,24 However, the lifting of the degeneracy cannot be large since the dianion of Tpb is in a triplet groundstate.6,8

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 alkali 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 10−4.21 However, the g value of Tpb− measured in MTHF is equal to the value measured 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 = 10−5 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 = 11×10−9) 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 ωg<<1, so that

\[ T_1^{-1}(H) = \frac{1}{2} (A/\hbar)^2 \tau_+^2 \left( \frac{7}{20} \right) (B/\hbar)^2 \tau_\alpha. \]

The parameter A can be derived from the FC shift, and the value of B can be calculated using the formulas of McConnell and Strathdee28 (see Appendix). For the latter calculations experimental spin densities are used, if possible, and otherwise theoretical ones. For the anisotropic dipolar interaction between the proton and the electron on the adjacent carbon atom, the experimental 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 required in order to determine \( \tau_+ \) and \( \tau_\alpha \). The set of equations arising from linewidth data of protons with large

<p>| Table III. NMR linewidths as function of the concentration. |
|--------------------------|--------------------------|--------------------------|</p>
<table>
<thead>
<tr>
<th>Concentration M</th>
<th>1H linewidth ( T_1^{-1} ) (sec(^{-1} ))</th>
<th>2D linewidth ( T_1^{-1} ) (sec(^{-1} ))</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.42</td>
<td>16 000±2000</td>
<td>490±10</td>
</tr>
<tr>
<td>0.65</td>
<td>7 900±300</td>
<td>247±9</td>
</tr>
<tr>
<td>0.82</td>
<td>4 460±70</td>
<td>180±10</td>
</tr>
<tr>
<td>1.04</td>
<td>2 840±40</td>
<td>130±10</td>
</tr>
<tr>
<td>1.21</td>
<td>26 000±2000</td>
<td>1 190±40</td>
</tr>
</tbody>
</table>

| Table IV. Linewidth parameters. |
|--------------------------|--------------------------|
| Proton (deuterium) atom | \((A/\hbar)^2\times10^{-13}\) (rad/sec)\(^2\) | \((B/\hbar)^2\times10^{-13}\) (rad/sec)\(^2\) | \(\phi qQ/\hbar\) (MHz) |
|-----------------|-----------------|-----------------|
| 2 | 3974 | 283 | 0.64±0.20 |
| 8 | 260 | 24.4 | 0.50±0.06 |
| 9 | 7.44 | 10.3 | 0.46±0.06 |
| 10 | 745 | 68 | 0.65±0.11 |

Concentration M | \(\tau_+ \times 10^{11}\) (sec) | \(\tau_\alpha \times 10^{11}\) (sec) | \(\tau \times 10^{11}\) (sec) |
<table>
<thead>
<tr>
<th></th>
<th></th>
<th></th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>0.42</td>
<td>24</td>
<td>0&lt;(\tau_\alpha&lt;1.0)</td>
<td>0&lt;(\tau_\alpha&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;(\tau_\alpha&lt;2.5)</td>
</tr>
</tbody>
</table>

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 = 11×10−9) 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.

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The parameter A can be derived from the FC shift, and the value of B can be calculated using the formulas of McConnell and Strathdee28 (see Appendix). For the latter calculations experimental spin densities are used, if possible, and otherwise theoretical ones. For the anisotropic dipolar interaction between the proton and the electron on the adjacent carbon atom, the experimental 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 required in order to determine \( \tau_+ \) and \( \tau_\alpha \). The set of equations arising from linewidth data of protons with large
hfs 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 hfs, 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 τ_d could only be obtained in the concentration range from 0.8 to 1.0M. At lower concentration the dipolar contribution is small with respect to the scalar contribution (10% or less), which renders the determination of τ_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 τ_e on increasing the radical concentration. According to the model of Pake and Tuttle the τ_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 (τ_D/τ_e)². Substituting the values for τ_r (Table V) in Eq. (6) with η=0, the qcc for the four different types of C–D bonds can be calculated. To get meaningful results only the most accurate τ_r 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,²¹,²² 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 Drago²³ 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.²⁶ 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}})_{D}

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

\[ 3C_D(t) = I \cdot \tau(t) \cdot S, \] (A1)

where

\[ T_{ij}(t) = g_B \mu_B \beta_B \langle \psi | [\Delta B_{ij} - 3i(t)j(t)]/\tau^4 | \psi \rangle, \]

i, j = x, y, z refer to the laboratory coordinate system, and ψ is the wavefunction describing the odd electron. 3C_D(t) can be rewritten as

\[ 3C_D(t) = \frac{1}{2} (S^+I^- + S^-I^+)F_0(t) + (S_dI^+ + S^+I_d) \]

\[ \times F_1(t) + (S_dI^- + S^-I_d)F_1^*(t) + S^+I^+F_2(t) + S^-I^-F_2^*(t), \] (A2)

in which

\[ F_0(t) = T_{aa}(t), \]

\[ F_1(t) = \frac{1}{3} [T_{aa}(t) - iT_{aa}(t)], \] (A3)

\[ F_2(t) = \frac{1}{2} [T_{aa}(t) - T_{ab}(t) - 2iT_{ab}(t)]. \]
Following Solomon, the expression for the \( (T_{s-1})_D \) becomes
\[
(T_{s-1})_D = (4\pi^2)^{-1} \left[ \left( \tau_r + \frac{1}{4} \tau_r \right) \right] \langle F_s \rangle + \left( \frac{2\tau_r}{1 + \omega_s^2 \tau_r^2} + \frac{4\tau_r}{1 + \omega_s^2 \tau_r^2} \right) \langle F_i \rangle + \left( \frac{4\tau_r}{1 + (\omega_s + \omega_d) \tau_r^2} \right) \langle F_i \rangle, \tag{A4}
\]
where \( \omega_d \) and \( \omega_s \) are the resonance frequencies of the nuclear spin and the electron spin, respectively, \( \tau_r \) is the rotational correlation time, and the quantities \( \langle F_i \rangle \) are any of the tensor averages holding for the tensor averages \( T_{ij}T_{kl} \) where \( i, j, k, l \) are any of the \( x, y, z \) axes.\(^{22}\) It is then found that
\[
\langle F_s \rangle = \frac{2}{3} (T: T),
\]
\[
\langle F_i \rangle = \frac{1}{3} (T: T),
\]
\[
\langle F_i \rangle = \frac{1}{3} (T: T),
\]
with \( (T: T) = \sum_{\alpha \beta} T_{\alpha \beta} \); \( \alpha, \beta \) refer to a molecular coordinate system. Substituting these values into Eq. (A4), then, under the condition that \( \omega_s^2 \tau_r^2 < 1 \), Eq. (A4) simplifies to
\[
(T_{s-1})_D = \frac{2}{3} (B/\hbar)^2 \left[ \tau_r + \left[ 13\tau_r \left( 1 + \omega_s^2 \tau_r^2 \right) \right] \right], \tag{A6}
\]
where
\[
B^2 = \frac{4}{3} (T: T). \tag{A7}
\]
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** \( T_{\alpha \beta} \)

The explicit expression for \( T_{\alpha \beta} \) is
\[
T_{\alpha \beta} = -\frac{\beta}{2} \psi \left[ \left( r^2 \alpha, \beta - 3\alpha \beta \right) / r^2 \right] \psi. \tag{B1}
\]
Substituting \( \psi = \sum_n c_n \phi_n \), where the functions \( \phi_n \) are the \( 2p_s \) AO's of the carbon atom, \( T_{\alpha \beta} \) can be written as
\[
T_{\alpha \beta} = \sum_{m, n} \rho_{mn} T_{mn} = \text{Tr} \left[ \rho T \right], \tag{B2}
\]
with
\[
\rho_{mn} = c_{n}^* c_{m},
\]
\[
T_{mn} = -\frac{\beta}{2} \sum_{n} \psi_n \psi_m \left| \left( r^2 \alpha, \beta - 3\alpha \beta \right) / r^2 \right| \phi_n.
\]
If the zero overlap approximation is used, only diagonal elements remain, which are calculated with the formulas given by McConnell and Strathdee.\(^{28}\)