NMR Studies into the Potential Interactions of Fullerene C\(_{60}\), with Tetraphenylporphyrin and Some of its Derivatives

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ABSTRACT

The curved \(\pi\) surface of fullerene, C\(_{60}\), shows a tendency to interact with other molecules, making it an interesting target for building supramolecular arrays. The interaction can be relative strong and may even exist in solutions, often leading to stable complexes. An important class of the macrocycles that interacts with fullerenes is the porphyrins. In our study, \(^1\)H NMR spectrometric studies have been done to gain information on the nature and the precise interaction site of fullerene 1, with tetraphenylporphyrin, H\(_2\)[TPP] \(\text{2, and para-substituted tetraphenylporphyrins, } H_2[(p-X)\_4\text{TPP}], \text{where } X= \text{CN and OCH}_3 \text{ in deuterated chlorobenzene-d}_5 (\text{CBZ}) \text{ and toluene-d}_8. \text{ The porphyrin derivatives have been used to investigate any correlation in the interaction site due to changes in substituent. Relaxation rates of the pyrrole and phenyl hydrogen in the porphyrins were determined at temperatures of 288, 298 and 313 K for all the complexes in the presence and in the absence of fullerene, C\(_{60}\). To study solvent effects on interactions, Toluene-d\(_8\) and chlorobenzene-d\(_5\) solvents were used. Overall, our data indicated}
that C₆₀ interacted with H₂[TPP] at both the pyrrole and phenyl hydrogen sites however, these intermolecular interaction are not long-lasting in chlorobenzene-d₅.

The porphyrin derivatives showed that the substituents have an effect on which site is preferred for interaction. For the case of H₂[(p-OCH₃)₄TPP], that has an electron–donating group, both phenyl and pyrrole hydrogen sites interacted with C₆₀, but preferably at the pyrrole hydrogen at all the three temperatures (283, 298, and 313 K). In the case of H₂[(p-CN)₄TPP] with an electron-withdrawing group CN, our data indicates that at lower temperature there is a noticeable, but slight preference for the interaction of C₆₀ at pyrrole site but is quickly destroyed with an increase in temperature.
NMR Studies into the Potential Interactions of Fullerene C$_{60}$, with Tetraphenylporphyrin, H$_2$[TPP] and some of its Derivatives.

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<th>Description</th>
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<tr>
<td>NMR</td>
<td>Nuclear magnetic resonance</td>
</tr>
<tr>
<td>CBZ</td>
<td>Chlorobenzene</td>
</tr>
<tr>
<td>H₂[TPP]</td>
<td>Tetraphenylporphyrin</td>
</tr>
<tr>
<td>Sfrq</td>
<td>Spectrometer frequency</td>
</tr>
<tr>
<td>AT</td>
<td>Acquisition time</td>
</tr>
<tr>
<td>Sw</td>
<td>Spectral window</td>
</tr>
<tr>
<td>Tpwr</td>
<td>Transmittance power</td>
</tr>
<tr>
<td>Pw</td>
<td>90° pulse width</td>
</tr>
<tr>
<td>p1</td>
<td>180° pulse width</td>
</tr>
<tr>
<td>d1</td>
<td>Delay time</td>
</tr>
</tbody>
</table>
CHAPTER I

INTRODUCTION

Porphyrians and fullerenes have been found to spontaneously be attracted to each other.\(^1\) This newly recognized supramolecular recognition element, the attraction of the curved $\pi$-surface of the fullerene to the center of the flat $\pi$-surface of a porphyrin, is possibly due to $\pi$-$\pi$ and $n$-$\pi$ electron interactions. This phenomenon is in contrast to the traditional paradigm which requires the matching of a concave host with a convex guest.\(^2\)

During the past few decades, the intermolecular interaction of porphyrians and fullerenes has been studied extensively. Due to their potential applications in processes of molecular recognition,\(^3\)-\(^8\) photosynthesis,\(^9\)-\(^13\) photovoltaics,\(^14\)-\(^20\) energy transfer,\(^21\)-\(^29\) and electron transfer\(^30\)-\(^40\) porphyrin-fullerene complexes have attracted a great deal of attention. Of particular interest is the development of tetraphenylporphyrin-appended silica stationary phases for the chromatographic separation of fullerenes as illustrated below in Figure 5(a). With columns of these materials, Meyerhoff has reported that their selectivity is superior to the commonly used “Buckyclutcher”\(^41\) and “Buckyprep” columns \(^42\)-\(^43\) shown below in Figure 1(b). The basis of the separation is proposed to be $\pi$-$\pi$ interaction between zinc tetraphenylporphyrin and the fullerene.\(^44\)
The $\pi$-$\pi$ interactions are non-covalent interaction between organic compounds containing aromatic moieties often dependent on one being more electron rich and the other electron poor. The arrangement of the five- and the six-member rings in $C_{60}$ leads to its spherical shape. As illustrated below in Figure 2(a), the five-member rings are attached to the sides of six-member rings, each carrying three alternate $\pi$-bonds in such a way that none of the $\pi$-bonds are in the 6,6-
ring junctions and not in 5,6-ring junction. This kind of structure is energy-minimized and the surface is curved. The $\pi$-bonds are bent on the curved exterior surface of $C_{60}$ as shown in Figure 2 (b).

![Figure 2](image)

**Figure 2.** (a) Three-dimensional structure of $C_{60}$ (b) bent $\pi$-bonds on the surface of $C_{60}$

As shown in Figure 2 (a) above the double bonds are exocyclic to the 5-membered rings. This means that all the 5,6-ring junctions are single bonds, since a double bond on a 5-membered ring is energetically unfavorable. Thus, all the 6-membered rings have three double bonds each and delocalization is unfavorable. On the other hand, each 5-member ring has to contend with 5-electrons each, one short of aromatization and hence these rings are highly electron–deficient.

![Figure 3](image)

**Figure 3.** Addition of an electron brings in aromaticity to a pentagonal ring
Overall, the strong electron-deficient character coupled with the three-dimensional symmetrical shape of the C<sub>60</sub> sphere favors π-π and π-n interactions with electron-rich molecules such as porphyrins, pthalocyanines, etc.

The close association of a fullerene and a porphyrin was first recognized in the molecular packing of a crystal structure of porphyrin-fullerene assembly containing a covalent fullerene-porphyrin conjugate as shown in Figure 4 below.<sup>4</sup>

---

**Figure 4.** (a) Stereoview of packing diagram for H<sub>2</sub>[TPP].C<sub>60</sub>.3 toluene, (b) A fragment of porphyrin/C<sub>60</sub> chain.<sup>4</sup>
In the crystal structure of this species, C_{60} was found to be centered over the porphyrin with electron-rich 6:6 ring-juncture C-C bonds in close approach to the plane of the porphyrin core at an average distance of 2.75 Å, shorter than separations of familiar π-π interactions. The closest atom-to-atom contacts were from the two 6:6 fullerene carbon atoms to the porphyrin N atoms. They ranged from 3.09 to 4.74 Å. The phenyl carbon atoms of the porphyrin were all at distances >4.0 Å from fullerene carbon atoms, indicating that the ortho C-H bonds do not participate significantly to the association. The angle between the porphyrin planes is 45.2°. The remaining exposed surface of C_{60} was solvated by the methyl groups of lattice toluene, the methyl carbon to fullerene carbon distances lying in the range 3.39-3.59 Å. The closest carbon-to-carbon atom distance between fullerenes in adjacent chains is 3.37 Å. The interaction that is shown to exist in solid state is also shown to extend to solutions, often leading to stable complexes.

In our study, ^1^H NMR relaxation studies have been done to gain information on the nature and the precise interaction site of fullerene 1, with tetraphenylporphyrin, H_2[TPP]_2, and para-substituted tetraphenylporphyrins, H_2[(p-X)_4TPP], where X= CN and OCH_3 in deuterated chlorobenzene-d_5(CBZ) and toluene-d_8. The porphyrin derivatives have been used to investigate possible interactions with C_{60}, to investigate any correlation in the interaction site due to changes in substituent, and to probe potential solvent effects on intermolecular interactions. Relaxation rates of the pyrrole and phenyl hydrogen in the porphyrins, as shown in Figure 5(a) were determined at temperatures 288, 298 and 313 K for all the complexes in the presence and in the absence of fullerene. In addition, correlation times, τ_c, for these hydrogen were calculated. Possible interaction sites were determined by looking at the difference in relaxation rate, R_1, and correlation time, τ_c, due to the presence and absence of the C_{60} molecule.
Figure 5. (a) Structure of H$_2$[TPP], and Para-substituted tetraphenylporphyrins, H$_2$[(p-X)$_4$TPP], (b) Possible interaction sites of H$_2$[(p-X)$_4$TPP] and C$_{60}$
Objectives of the study

To employ dynamic NMR measurements to study potential interaction sites of fullerene $C_{60}$ with tetraphenylporphyrin, $H_2[TPP]$, and para-substituted tetraphenylporphyrins, $H_2[(p-X)_4TPP]$, where $X = \text{CN}$ and $\text{OCH}_3$ in deuterated chlorobenzene-$d_5$(CBZ) and toluene-$d_8$.

A second objective was to determine if there is a preferred site of interaction on the porphyrin based on substituent effects of an electron donating ($X = \text{OCH}_3$) or electron withdrawing group ($X = \text{CN}$). A third objective was to determine the energy of activation of the interactions between $C_{60}$ and the various tetraphenylporphyrins. A fourth objective was to probe whether solvent molecules affect the interaction between $C_{60}$ and the tetraphenylporphyrin, $H_2[TPP]$, and para-substituted tetraphenylporphyrins, $H_2[(p-X)_4TPP]$. 
CHAPTER II

THEORY

2.1 Basic NMR theory

Nuclear magnetic resonance (NMR) spectroscopy involves the magnetic energy of nuclei when placed in a magnetic field. Fields of appropriate strength cause transitions between nuclear energy levels occur. These fields have a frequency in the radiofrequency (RF) region of the spectrum. The nuclear spin quantum number (I), which may take values of 0, 1/2, 1, 3/2, etc., in units of $\hbar/2\pi$, is the nuclear property that is responsible for the NMR phenomenon and its value for a given nucleus is dependent on its mass and atomic numbers.

Nuclei of certain natural isotopes of the majority of the elements possess intrinsic spin or angular momentum. A fundamental postulate of modern physics is that the total angular momentum, $P$, of an isolated nucleus has total magnitude that takes only discrete values:

\[ P = \hbar[ I ( I + 1)]^{1/2} \]  \hspace{1cm} (1)

where $\hbar$ is the reduced Planck's constant, $\hbar/2\pi$, I is the nuclear spin quantum number, which takes the value of 1/2, 1, 3/2, and so on. For $^1$H, I the value is 1/2. Angular momentum exhibits a vector characteristic, therefore, its full description takes into account its magnitude and direction. The directional properties of $P$ are given by the magnetic spin quantum number $m_I$.

According to the principles of quantum mechanics, a nucleus having a spin quantum number of I will have $2I + 1$ orientations ranging in values from: $+I$, $-I-1$, $-I$, $-I-2$, $..., 0, -I$. 

Since angular momentum of the nucleus, \( P \), is quantized its energy is also quantized. In the absence of an external magnetic field, all the energy levels are degenerate. In the presence of a uniform magnetic field, \( B_0 \) the spinning nucleus will produce a magnetic dipole moment which is also quantized and the energy levels lose their degeneracy. The magnitude of the nuclear magnetic dipole moment is given by

\[
\mu = \hbar g_N \mu_N P
\]  

(2)

where \( \mu_N \) is nuclear magneton, its value is \( 5.05095 \times 10^{-27} \, \text{J T}^{-1} \), \( g_N \) is the nuclear g-factor, which is a constant for a given type of isotope. For \(^1\text{H} \), \( g_N \) is 5.585. Usually the magnitude of the spin magnetic moment is expressed in terms of the magnetogyric ratio, \( \gamma \).

\[
\mu = \gamma P
\]  

(3)

Substituting \( P \), as given by equation (1) into equation (3), gives the following equation:

\[
\mu = \frac{\hbar}{2\pi} \gamma [ I (I + 1)]^{1/2}
\]  

(4)

Equation (4) shows that the magnitude of the spin magnetic moment is quantized. Its directional properties (orientations) are also quantized and are given by the quantum number, \( m_I \). A nucleus with spin quantum number \( I \) may lie in \((2I+1)\) different orientations relative to the nuclear axis. Its spin state will split into \((2I+1)\) energy levels. For \(^1\text{H} \), with \( I = \frac{1}{2} \), there will be two spin states which are assigned \( m_I \) values of \( \frac{1}{2} \) and \( -\frac{1}{2} \).

When \(^1\text{H} \) nuclei are placed in an external magnetic field, the nucleus’s own magnetic field, caused by nuclear spin, can align either with or against the external field. When the nuclear spin generates a local field in the same direction as the external field, then this spin state
is assigned a magnetic spin quantum number, \( m_1 \) (+1/2), and the spin is said to be "aligned".

When the nucleus creates a local field in the opposite direction of the external field, the nucleus magnetic spin quantum number \( m_1 \) is assigned a value of -1/2; and the spin is said to be “opposing” the field. The nuclei with aligned spin are of lower energy than the nuclei with opposing spin. This identifies the energy difference between the separate spin states as shown in Figure 6 below.

![Figure 6: Energy difference, \( \Delta E \) between \(^1\text{H}\) spin states in magnetic field \( B_0 \).](image)

When the applied magnetic field is assigned the z direction, the projection of the magnetic moment on this z axis will be given by equation (5):

\[
\mu_z = \frac{\hbar}{2\pi} \gamma m_1
\]  

(5)

Its energy is then given by:

\[
E = - \mu_z B_0 = - \frac{\hbar}{2\pi} \gamma m_1 B_0
\]  

(6)
Transitions between the energy levels will occur when $|\Delta m|$ satisfies the condition of ±1. Therefore, the energy change upon a transition is given by:

$$\Delta E = \frac{\hbar}{2\pi} \gamma B_0$$

(7)

The frequency, $\nu_0$ of radiation that can induce a transition between adjacent levels is given by

$$\nu_0 = \frac{\Delta E}{h} = \frac{\gamma B_0}{2\pi}$$

(8)

or

$$\omega_0 = 2\pi \nu_0 = \gamma B_0 \text{ (rad sec}^{-1})$$

(9)

where $\omega_0$ is known as angular frequency.

At equilibrium, the nuclei maintain a Boltzmann distribution among the spin states, hence one expects more nuclei to reside in the lowest energy states. For a system of spin -1/2 nuclei a Boltzmann distribution would give:

$$\frac{N_u}{N_l} = e^{-\Delta E/kT}$$

(10)

Where $N_u$ and $N_l$ are the numbers of nuclei in the upper and lower energy states respectively, $\Delta E$ is the energy separation, $k$ is the Boltzmann constant, and $T$ is the absolute temperature.

After the disruption of this distribution by absorption of radio frequency energy, the nuclear spin system will revert back to equilibrium with the "lattice" (its surroundings) by a first-order relaxation process characterized by a time $T_1$, called the spin-lattice relaxation time.\(^{47}\)
2.1.1 Spin-lattice relaxation

It has been shown that a torque exerted on a magnetic moment by an applied magnetic field will cause the magnetic moment to precess about the direction of the field with a frequency given by

\[ \omega_0 = \frac{\gamma B_0}{2\pi} \quad \text{or} \quad \omega_0 = \gamma B_0 \text{ (rad sec}^{-1}) \]  

(11)

The precession of the magnetic moment of a nucleus is shown in Figure 7(a). Energy will be absorbed only when the radio frequency \( (\nu_{rf}) \) of the second magnetic field (B₁), which is perpendicular to B₀ (i.e., in the xy plane) as depicted in Figure 7(a) are equal i.e. \( \nu_{rf} = \nu_0 \). This absorption is called "resonance". On absorption of energy from B₁, the magnetic moment will tip to a different angle \( \theta \), but its precession frequency will remain the same.

The discussion above is for a single nuclear magnetic moment, but we typically study a large collection of identical nuclei referred as an ensemble. Figure 7(b) illustrates the precession of moments of nuclei with \( I = \frac{1}{2} \) and all moments precesses at the same frequency. There is a directional reference along the magnetic field B₀ which has been traditionally assigned the z direction. Based on Boltzmann distribution, at equilibrium more nuclei will be aligned in the direction of B₀ than opposing it. Consequently, when an ensemble of nuclei are placed in a magnetic field, this will result in a net magnetization M oriented along the field direction given by:

\[ M = \frac{N\gamma^2h^2I(I+1)B_0}{8\pi^2kT} \]  

(12)

where N is the nuclei number density.
When \( M \) is perturbed from its equilibrium value \((M_0)\) by applying a second magnetic field \((B_1)\) perpendicular to \( B_0 \), the equation of motion of this non-equilibrium magnetization, after \( B_1 \) has been turned off and in the absence of interactions between spins or with the surrounding, is simply given by

\[
\frac{dM}{dt} = \gamma (M \times B_o)
\]  

(13)

From the above equation states, \( M \) will precess about the field direction with a frequency given by \( \omega_0 = \gamma B_0 \) (Larmor equation). In NMR, it is a common practice to view \( M \) from a reference frame rotating at the Larmor frequency which simplifies the characterization of its motion. In the rotating frame, the magnetization appears to be a static vector with components both parallel \((M_z)\) and perpendicular \((M_x, M_y)\) to the applied field.

![Figure 7](image)

**Figure 7.** (a) Precession of \( \mu \) about \( B_0 \); (b) Precession of an ensemble of nuclei with \( I=1/2 \)

The situation described above represents a non-equilibrium population of energy states. At equilibrium, components \( M_x \) and \( M_y \) of \( M \) are equal to zero. Because of the natural processes that cause nuclei to exchange energy with each other and their environment, their environment is considered to be a constant temperature reservoir (lattice) having infinite heat capacity. The coupling of spins to the lattice permits the exchange of energy, allowing an
approach back to an equilibrium population of energy states, and therefore returning $M_Z$ to its equilibrium value, $M_0$. Bloch showed that this could be treated as a first order rate process and is expressed by the following equation:\textsuperscript{50}

$$\frac{dM_Z}{dt} = -\frac{1}{T_1} (M_Z - M_0) \quad (14)$$

where $T_1$ is called the spin-lattice relaxation time. The integration of equation (14) gives:

$$M_Z(\tau) - M_0 = (M_Z(0) - M_0) e^{\tau/T_1} \quad (15)$$

where $M_Z(\tau)$ is the value $M_Z$ at different delay times of $\tau$, $M_0$ is the value $M_Z$ at equilibrium.

The explanation for the relaxation of the $M_Z$ component of the magnetization $M$ is as follows. In mobile liquids, the microscopic environment of a spin is exposed to rapid changes due to the translational and orientation motions of molecules in the sample which lead to random fluctuations of the magnetic fields experienced at the nucleus. In these rapid fluctuations, there will be Fourier components at the Larmor frequency which will couple different energy states and thus, allow the relaxation of $M_Z$ to its equilibrium value.

There are various independent mechanisms which couple the spins to the lattice and thus promote spin-lattice relaxation. The relaxation rate for a particular nucleus in a specific chemical environment will depend upon which mechanisms are operating in this environment. In later sections of this chapter, a brief review of the more important mechanisms present of the hydrogen being studied in tetraphenylporphyrin, ($H_2[TPP]$) will be discussed.
2.2 Relaxation mechanisms

Spin-lattice relaxation, as discussed in the previous section, will only occur if there is a physical coupling between the resonant nuclei and the lattice by which energy exchange can take place. The following types of interactions are known to couple the nuclei to the lattice:

(a) Quadrupole interaction

(b) Chemical shift anisotropy

(c) Scalar coupling

(d) Spin rotation

(e) Magnetic dipole-dipole

Each of the above mechanisms contributes to a different degree to the overall relaxation process. However, in the tetraphenylporphyrin H$_2$[TPP] system only the magnetic dipole-dipole interactions are operative. Due to the very high value of the hydrogen gyromagnetic ratio, g, the dipole-dipole interactions will dominate the relaxation process.$^{45}$ A brief description of the above mentioned relaxation mechanism is given below.

2.2.1 Quadrupole interaction mechanism

Nuclei with spin $I > \frac{1}{2}$ have an electrical quadrupole moment, which is caused by the non-spherical charge distribution inside the nucleus. The coupling between this electric field and the electric field gradient generated by the molecular environment in which the nucleus is situated provides an effective way towards relaxation of this type of nucleus. The rate of quadrupole relaxation, $R^Q_1$, assumes extreme narrow conditions and is given by the expression: $^{51}$

$$R^Q_1 = \left(\frac{1}{\tau_1}\right) = \frac{3}{40} \left[\frac{(2I+3)}{I(I-1)}\right] \left[\frac{e^2Q}{\hbar h}\right]^2 \tau_0$$  \hspace{1cm} (16)
Where $I$ is the spin of the quadrupole nucleus, $(e^2Qq/h)$ is the quadrupole coupling constant (in rad.sec$^{-1}$) and $\tau_0$ is the rotational correlation time. It is worth noting that in the current study the nuclei of interest (C and H) have spin values of $\frac{1}{2}$ hence quadrupole relaxation mechanism pathway is non-existent.

### 2.2.2 Chemical shift anisotropy

The local electromagnetic field experienced by the nucleus is given by

$$H_{\text{loc}} = H_0 - \sigma H_0 = H_0(1 - \sigma) \quad (17)$$

where $\sigma$ and $H_0$ are the shielding factor and static field respectively. If a molecule is anisotropic, $\sigma$ will vary in direction and different chemical shifts will be observed along different molecular axes. Since motions in non-viscous liquids are rapid, one only sees an average shield, $\frac{2\sigma_\perp + \sigma_\parallel}{3}$. However, anisotropy in $\sigma$ will result in an orientation dependence of the instantaneous local magnetic field at the nucleus and modulation of coupling between $H_{\text{loc}}$ and the relaxing nucleus by molecular rotation will furnish a pathway for relaxation. The expression characterizing the relaxation rate is:

$$R_1^{\text{CSA}} = \left(\frac{1}{T_1}\right)^{\text{CSA}} = \frac{2}{15} y^2 H_0^2 (\sigma_\parallel - \sigma_\perp) \tau_\theta \quad (18)$$

Where $\sigma_\parallel$ and $\sigma_\perp$ are components of the shielding tensor parallel and perpendicular to the axis of symmetry and $\tau_\theta$ is the correlation time for tumbling motion. It has been found that, in the presence of other relaxation mechanisms and at moderate field strengths, the CSA contribution to the overall relaxation rate is very small and can be neglected.$^{51}$
2.2.3 Scalar coupling

The scalar (spin-spin) coupling mechanism is similar to the dipolar process. The effect of scalar coupling relaxation on $T_1$ is significant only if the two interacting nuclei have very close frequency. It’s very rare for that this condition to be met. It takes place for instance for Br-79 (75.29 MHz with $B_1=7.06$ T and) Carbon-13 (75.56 MHz with $B_1=7.06$ T) which are very close in frequency. Scalar relaxation is more important for the $T_2$ relaxation as with this mechanism the quadrupolar nuclei can broaden lines significantly on nuclei that are coupled to it.

2.2.4 Spin-rotation mechanism

Spin rotation is known in some cases to significantly contribute to nuclear relaxation. The molecular rotation in a medium generates a magnetic field at the nucleus of interest. The magnitude of which depends on the angular velocity (or alternatively on the angular momentum, $J$). Collisions of the molecule with its neighbors will cause a change in the field at the nucleus. The randomly fluctuating magnetic field due to the collisions will cause relaxation of the nuclear spin system. The Magnitude of this interaction is characterized by the spin-rotation coupling constant ($\tau_1$) and the rate of relaxation for a spherical molecule is given by: \(^{49}\)

$$R^{SR} = \left(\frac{1}{\tau_1}\right)^{SR} = \frac{2kT}{\hbar^2} C^2 \tau_j$$

(19)

Where $C$ equals ($2C_\perp + C_\parallel$), $I$ is the molecule moment of inertia and $\tau_j$ is the correlation time, decay time of the angular momentum correlation function (17). The above mechanism is not applicable to the system of interest in this study as the concentration of molecules is very dilute precluding interaction.
2.2.5 Magnetic dipole-dipole relaxation

Proton, $^1$H, spin-lattice relaxation can be expressed as the sum of intra and inter-relaxation. This relationship is demonstrated below by equation (20).\(^{52}\)

$$\frac{1}{T_1} = R_1 = R_1^{DD} \text{(intra)} + R_1^{DD} \text{(inter)} \quad (20)$$

$T_1$ is measured by NMR and $R_1$ is simply the inverse of $T_1$. In cases where the mole fraction of a solute is as small as $1.299 \times 10^{-5}$ and when working in deuterated solvents, the inter-relaxation becomes negligible. When dipole-dipole relaxation is due to hydrogen-hydrogen interaction the above equation can be reduced and rewritten as

$$R_1 = R_1^{DD} \text{(intra)} = \left(\frac{\mu_0}{4\pi}\right)^2 \left(\frac{\gamma}{3}\right) \frac{\gamma H^4 \mu_0^2}{r_{AB}^6} \eta \tau_c \quad (21)$$

where $\gamma_H = 2.6752 \times 10^4 \text{ rad G}^{-1}\text{s}^{-1}$ gyromagnetic ratio, $r_{AB}$ is the proton-to-proton distance of the interacting nuclei, $n_s$ is the number of interacting nuclei, $\mu_0$ is the vacuum permeability constant ($12.57 \times 10^{-6}$ j.s/C$^2$.m) and $\tau_c$ is rotational correlation time. The rotational correlation time is the period of time necessary for a specific nuclear site to undergo reorientation (i.e. movement) to a new position which is different by about 54°.

Once relaxation rates have been determined, the rotational dynamics at a specific molecular site can be analyzed since the correlation time can be expressed by equation (22).

$$\tau_c = \left(\frac{\mu_0}{4\pi}\right)^2 \left(\frac{2}{3}\right) \left(\frac{\gamma H^4}{\hbar^2 \gamma_H^4}\right) R_1^{DD} \text{(intra)} \eta^{-1} \quad (22)$$
Once relaxation rates have been determined, the rotational dynamics at a specific molecular site can be analyzed since the correlation time can be expressed by equation 22. A straightforward method of analyzing possible complexation at a site is by determining the variation of the relaxation rate of the host in the presence and absence of a guest molecule. The changes in $R_1$ (i.e. $\Delta R_1$) can also be used to determine the site of complexation. The first step in determining $\Delta R_1$ is measuring the relaxation rate of particular nuclei in the host in CBZ (deuturated chlorobenzene), $R_1(A)$, followed by measuring the relaxation rate of the same nuclei after the introduction of a guest, $R_1(B)$. The difference in measurements can then be used to acquire the necessary information.

$$\Delta R_1 = R_1(A) - R_1(B)$$  \hspace{1cm} (23)

$R_1(A)$ is the value obtained when only host is present in the solution while $R_1(B)$ is the relaxation rate obtained for the host in the presence of the guest solute. Since the relaxation rates are obtained with equivalent mole fractions and in the same solvent environment, the observed difference in the relaxation rates, $\Delta R_1$ can be correlated to dynamical changes due to intermolecular complexations. The energy can be calculated once the rotational correlation times have been obtained at several temperatures.

### 2.3 Arrhenius fit of correlation times

Once the correlation times $\tau_c$ is determined from the dipole-dipole relaxation rates, as shown in equation 22, correlation times were related to activation energy, $E_a$, using equation (24);

$$\tau_c = \tau_0 e^{-\frac{E_a}{RT}}$$ \hspace{1cm} (24)
where $\tau_c$ is correlation time, $\tau_o$ is the inertial or ‘free rotor’ correlation time, is an experimentally obtained parameter which is often associated with the rotational motion in pure ‘slip’ limit. The activation energy, $E_a$, is the amount of energy necessary for the portion of the molecule, containing the hydrogen in question, to undergo rotation to a new position that is approximately $54^\circ$ different from a previous location. Equation 24 can be modified to become equation 25 by taking natural log of both sides.

$$\ln(\tau_c) = \ln(\tau_o) - \frac{E_a}{RT}$$

(25)

A plot of $\ln(\tau_c)$ versus $T^{-1}$ (K) will generate a line with a slope equal to $-E_a/R$. Once $E_a$ is determined for every studied proton, the energy of complexation at each site can be determined. Both change in relaxation rates, $\Delta R$ and activation energy, $E_a$ for every studied proton provides information regarding complexation at a site. Both are important since each provides a slightly different type of information. $E_a$ give the energy requirements for rotational motion (low values indicate low energy barrier for rotation and vice versa) and $\tau_c$ gives a “raw” indication of which hydrogen site is moving faster. The $\tau_c$ values can range from 0.1 ps in methyl groups to 15 ps in larger molecules such as C$_{60}$.

2.4 Experimental measurement of the spin-lattice relaxation Rate

The measurement of spin-lattice relaxation time can be done by using the standard inversion-recovery pulse sequence (i.e. $D_1-\pi-\tau-\pi/2$) where $\pi$ is a 180° pulse, $\pi/2$ is a 90° pulse, $\tau$ is a delay which is under the control of the operator. This method is illustrated in Figure 3. In Figure 2, $M_0$ is the Boltzmann equilibrium value of magnetization $M$. The magnetization is initially aligned along the $z$ axis and is inverted to -$z$ by the $\pi$ pulse. After a short delay, the
magnetization will not have recovered to any significant extent and the $\pi/2$ pulse will rotate it to the $-y$ axis. Since the instrument detector is phase sensitive and configured to detect along the $y$ axis, the signal, after Fourier transformation, will appear inverted compared to a signal generated by a $\pi/2$ pulse of the equilibrium magnetization. If, in a separate experiment, we wait a little longer before applying the $\pi/2$ pulse, the magnetization would recover to a point just below the origin. Now a $\pi/2$ pulse will move the magnetization to the $-y$ axis, producing a smaller but still negative signal. If we wait longer periods of time, the magnetization will pass through the origin, and the $\pi/2$ pulse will generate $+y$ magnetization and a positive signal will be produced. If we wait long enough between the pulses, the magnetization will eventually recover to its equilibrium value of $M_0$.

The $z$ component of magnetization as a function of $\tau$ is given by the following equation

$$M_z(\tau) - M_0 = (M_z(0) - M_0) \exp(-\tau/T_1)$$

(26)

where $M_z(\tau)$ is the signal intensity at various $\tau$ values, $M_0$ is the signal equilibrium value, and $M_z(0)$ is the signal intensity immediately after the $180^\circ$ pulse (i.e., no delay time before the $180$ and $90$ pulse). At $\tau = 0$, $M_z(0) = -M_0$. Substitution of this relation into equation (26), followed by rearrangement, gives equation (27):

$$\ln(M_0 - M_z(\tau)) = \ln2 + \ln(M_0) - \tau/T_1$$

(27)

The experimental relaxation rate, $R_1 (1/T_1)$ is obtained from a linear fit of $\ln(M_0 - M_z)$ versus $\tau$. 
Figure 8. Vector diagram of the inversion–recovery pulse sequence
CHAPTER III

EXPERIMENTAL

3.1 Chemical and materials

Fullerene C_{60}, chlorobenzene-d_5 (99.5+ at.% D) and toluene-d_8 were purchased from Acros Organics.\textsuperscript{53} Tetraphenylporphyrin H_2[TPP] was purchased from the Aldrich Chemical Company.\textsuperscript{54} The derivatives of para- substituted tetraphenylporphyrin derivatives H_2[(p-X)_4TPP](X = CN and OCH_3) H_2[TPP] were synthesized as described below.

3.2 Synthesis of para- substituted tetraphenylporphyrin derivatives H_2[(p-X)_4TPP](X = CN and OCH_3)

The synthesis of the porphyrins was done by a previous student in our research group and the method used was adapted from the synthesis as reported by Adler et al.\textsuperscript{55}

The appropriate benzaldehyde was refluxed with pyrrole in propionic acid in a round-bottom flask fitted with a water condenser. After refluxing, the reaction mixture was cooled to room temperature and cold methanol is added. The flask was then chilled in an ice bath while stirring, and crystallization was induced by scratching the sides of the flask with a glass stirring rod. The deep-purple crystals were filtered by vacuum filtration with a Buchner funnel. The flask and crystals are washed with three 0.5-mL portions of cold methanol followed by three 0.5-mL portions of boiling distilled water. The crystals were air-dried on the Buchner funnel. For H_2[(p-CN)_4TPP], 4-cyanobenzaldehyde was used and for H_2[(p-OCH_3)_4TPP], 4-methoxybenzaldehyde was used.
3.3 Solvent and sample preparations

Chlorobenzene-d$_5$ and Toluene-d$_8$ were received prepackaged in scored glass ampoules and were used as received. Host and guest amounts were initially introduced into toluene-d$_8$ according to the amounts given below follows:

a. (i) 7.99 mg (0.1299 µmoles) of H$_2$TPP was dissolved in 1.50 ml of solvent.
   (ii) 7.99 mg (0.1299 µmoles) of H$_2$TPP and 9.35 mg (0.1299 µmoles) of C$_{60}$ were dissolved in 1.50 mL of solvent.

The solute and solvent amounts produced solution with a mole fraction of 0.1299 µmoles.

After preparing these toluene-d$_8$ solutions, sample precipitation was noticed occurring in H$_2$[(p-OCH$_3$)$_4$TPP] and H$_2$[(p-CN)$_4$TPP] solutions. Therefore, a second more appropriate solvent was sought. After investigating various solvents, chlorobenzene-d$_5$ was determined to be applicable with all the samples. Solutions of H$_2$[TPP] and other derivatives were prepared according to the following amounts:

a. (i) 3.87 mg (6.29 µmoles) of H$_2$TPP was dissolved in 1.0mL of solvent.
   (ii) 3.87 mg (6.29 µmoles) of H$_2$TPP and 4.53 mg (6.29 µmoles) of C$_{60}$ were dissolved in 1.0 mL of solvent.

b. (i) 4.63 mg (6.29 µmoles) of H$_2$[(p-OCH$_3$)$_4$TPP] was dissolved in 1.0 mL of the solvent
   (ii) 4.63 mg (6.29 µmoles) of H$_2$[(p-OCH$_3$)$_4$TPP] and 4.53 mg (6.29 µmoles) of C$_{60}$ were dissolved in 1.0 mL of the solvent.

c. (i) 4.50 mg (6.29 µmoles) of H$_2$[(p-CN)$_4$TPP] was dissolved in 1.0 mL of solvent.
(ii) 4.50 mg (6.29 µmoles) of H₂[(p-CN)₄TPP] and 4.53 mg (6.29 µmoles) of C₆₀ were dissolved in 1.0 mL of the solvent.

Approximately 0.5 mL of each sample was transferred into a 5-mm NMR tube, connected to a vacuum line and thoroughly degassed by several freeze–pump–thaw cycles to eliminate molecular oxygen. The tubes were then sealed under vacuum.

### 3.4 Instrumental

¹H spin-lattice relaxation measurements were made on Varian 300 NMR with field strength of 7.0 tesla. Experiments were conducted at three different temperatures (283, 298, and 313 K). Typical acquisition parameters are listed below:

**Table 1. Instrumental parameters for T₁ measurements**

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>Sfrq</td>
<td>299.935 MHz</td>
</tr>
<tr>
<td>AT</td>
<td>3.7 db</td>
</tr>
<tr>
<td>Sw</td>
<td>4000 Hz</td>
</tr>
<tr>
<td>Tpwr</td>
<td>60 db</td>
</tr>
<tr>
<td>Pw</td>
<td>27 µs</td>
</tr>
<tr>
<td>p1</td>
<td>54µs</td>
</tr>
<tr>
<td>d1</td>
<td>14s</td>
</tr>
<tr>
<td>Nt</td>
<td>76</td>
</tr>
</tbody>
</table>
3.5 Calibration of 90° and 180° degree pulses

Acetone-d₆ chemical reagent was chosen a standard for this calibration of the NMR. Standard regular proton NMR spectrum for the standard was taken and the pulse width (pw) 90 ° pulses in microseconds were determined from a well phased spectrum. The pulse width (pw) was varied and peak intensity was measured. Starting with the pw value obtained and a properly phased spectrum, pw was adjusted such that a series of spectra that started in positive, pass through a null at 180°, became negative. The peak heights were measured to ascertain they were of the same intensity.

3.6 Measurement of relaxation time

All relaxation measurements for the pyrrole and phenyl protons of tetraphenylporphyrin, H₂[TPP], and para-substituted tetraphenylporphyrins, H₂[(p-X)₄TPP] were done on Varian instrument operating at 7.0 tesla. Typical ¹H NMR spectra of the H₂[TPP], H₂[(p-OCH₃)TPP], and H₂[(p-CN)₄TPP] were obtained as shown in Figure 9, Figure 10, and Figure 11 respectively. The spectra values agreed with those reported by Adler et al.⁵⁵ thus we were able to differentiate the pyrrole and phenyl protons.

The relaxation studies were carried out at three different temperatures (283, 298, and 313 K) for each solvent chosen within the melting and boiling points of each solvent. For each proton of interest at the three temperatures, relaxation time measurement was done in triplicate.

All relaxation times were obtained using the standard inversion-recovery pulse sequence (i.e. D₁-π-τ-π/2), where π is a 180° pulse, π/2 is a 90° pulse and τ is the delay time.
Nine delay times were used in the inversion-recovery pulse sequence and the values ranged from 0.0625 s to 16 s times depending on the estimated \( T_1 \). A delay time \( (d_1) \) of approximately 14 s was used between the transients. Each experiment used 76 transients resulting in an acquisition time of approximately 4 hours.

**Figure 9.** \(^1\)H NMR of \( \text{H}_2[\text{TPP}] \) in chlorobenzene-d\(_5\). The peaks at 8.95, 8.31 and -2.5 ppm corresponds to the pyrrole, ortho phenyl and N-H proton respectively.
Figure 10. $^1$H NMR of H$_2$[(p-OCH$_3$)TPP] in chlorobenzene-d$_5$. Peak 1, at about 8.87 ppm, corresponds to the pyrrole hydrogen while peak 2, about 8.11 ppm, corresponds to the ortho hydrogen of the phenyl group.

Figure 11. $^1$H NMR of H$_2$[(p-CN)$_4$TPP] in chlorobenzene-d$_5$. Peak 1, about 8.80 ppm, corresponds to the pyrrole hydrogen while peak 2, at about 8.32 ppm, corresponds to the ortho hydrogen of the phenyl group.
3.7 Statistical Analysis of Data

Ninety percent (90%) confidence limits for relaxation times, $R_1$ values was determined using equation 27 below. This was especially important because these values provide the basis for telling if the porphyrin and $C_{60}$ are interacting. Confidence limits are calculated according to the equation:

$$\lambda = \frac{t (90\%) \sigma}{\sqrt{N}}$$

(27)

where $t(90\%)$ is the statistical “Student t-factor” of 2.353, $\sigma$ is the standard deviation of the relaxation rates, and $N$ is the number of experiments performed in the set. A value of 0.01 for $\lambda$, at the 90% confidence limit, would be interpreted as; “there is a 90% probability that the real or true value is +/- 0.01 of the reported value.”
CHAPTER IV

RESULTS AND DISCUSSION

1.1 $^1$H Relaxation rates and correlation time of pyrrole hydrogen in H$_2$[TPP] with and without C$_{60}$ in chlorobenzene-d$_5$

Shown below in column 2 of Table 2 is the relaxation rate, $R_1$ of the pyrrole hydrogen in the absence of C$_{60}$ for H$_2$[TPP]. The rate is seen to decrease with increasing temperature. This trend is also illustrated in Figure 12 below and indicates that the dipole-dipole relaxation pathway is becoming less efficient or less effective in relaxing this hydrogen as the temperature increases. The effectiveness of the dipole-dipole pathway is inversely proportional to how fast the dynamic motion is at that molecular site. This is further shown in the correlation time, $\tau_c$. The correlation time is decreasing with increasing temperature indicating that the molecule is undergoing faster dynamics with rising temperature. As the temperature increases, Brownian motion increases and the correlation time decreases.\textsuperscript{49}

The fourth column of Table 2 contains the relaxation rate of the same pyrrole proton, but now in the presence of C$_{60}$. The relaxation rate is also seen to decrease with rising temperature. This also suggests that the pathway is becoming less efficient at relaxing this hydrogen with rising temperature. We also see that the correlation time, $\tau_c$ decreasing with rising temperature which again indicates faster molecular motion.

The introduction of C$_{60}$ to the solution does not affect the relaxation rate of this proton appreciatively. One notices from the values that the change in relaxation rate, $\Delta R$ are within the experimental error. This indicates that the presence of C$_{60}$ does not lead to noticeable intermolecular interaction at the pyrrole site of H$_2$[TPP].
The variation of the relaxation rate and correlation time with temperature for this proton is also further illustrated graphically in Figures 12 and 13 respectively. The graphs were obtained through joining the points.

Table 2. $^1$H Relaxation rates of pyrrole hydrogen in H$_2$[TPP] with and without C$_{60}$ in chlorobenzene-d$_5$(CBZ).

<table>
<thead>
<tr>
<th>T (K)</th>
<th>H$_2$[TPP] in CBZ</th>
<th>H$<em>2$[TPP] with C$</em>{60}$ in CBZ</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>$R_1$ (1/s)</td>
<td>$\tau_C$ (ps)</td>
</tr>
<tr>
<td>283</td>
<td>0.581</td>
<td>288</td>
</tr>
<tr>
<td></td>
<td>(0.006)</td>
<td></td>
</tr>
<tr>
<td>298</td>
<td>0.496</td>
<td>246</td>
</tr>
<tr>
<td></td>
<td>(0.016)</td>
<td></td>
</tr>
<tr>
<td>313</td>
<td>0.434</td>
<td>215</td>
</tr>
<tr>
<td></td>
<td>(0.002)</td>
<td></td>
</tr>
</tbody>
</table>

Values in parenthesis are error limits at the 90% confidence levels. Each relaxation time, $R_1$ is an average of three measurements.
Figure 12. Relaxation rates of pyrrole hydrogen in H$_2$[TPP] with C$_{60}$, R$_1$ (dashed line) and without C$_{60}$, R$_1$C$_{60}$(Solid line) in Chlorobenzene-d$_5$. The lines on the graph represent connected dots.
Figure 13. Experimental Correlation times of pyrrole hydrogen in H$_2$[TPP] with C$_{60}$, R$_1$ (dashed line) and without C$_{60}$, R$_1$C$_{60}$ (Solid line) in Chlorobenzene-d$_5$. The lines on the graph represent connected dots.

An Arrhenius fit of $\ln(\tau_c)$ versus $T^{-1}$ (K) as shown in figure 14 generated activation energy, $E_a$, values of 7.2 and 6.80 kJ/mole for H$_2$[TPP] without and with C$_{60}$ respectively.
Figure 14. Linear fit of experimental correlation times of the pyrrole protons of H$_2$[TPP] in neat chlorobenzene-d$_5$ to obtain activation energy of complexation at the site of interaction.

1.2 $^1$H Relaxation rates and correlation time of phenyl hydrogen in H$_2$[TPP] with and without C$_{60}$ in chlorobenzene-d$_5$

As seen in column 2 of Table 3, the relaxation rate of the phenyl hydrogen in the absence of C$_{60}$, is seen to decrease with rising temperature indicating that the relaxation pathway is becoming less efficient or less effective. This is further shown in the correlation time, $\tau_c$. One sees that the correlation time decrease with increasing temperature indicated that the molecule is undergoing faster dynamics at this site. Column 4 of the same table contains the relaxation rate
of the same hydrogen upon the introduction of C\textsubscript{60} into solution. The relaxation rate is seen to
decrease with rising temperature. This also suggests that the pathway is becoming less efficient
at relaxing this hydrogen. We also see that as the temperature rises, the correlation time
decreases, an indication of faster molecular motion.

Again as seen in column 6 of Table 3, the introduction of C\textsubscript{60} to the solution does not
affect the relaxation rate of this proton appreciatively. The values of the change in relaxation rate
\(\Delta R\) are within the experimental error an indication that the presence of C\textsubscript{60} does not lead to
noticeable intermolecular interaction at the pyrrole site of H\textsubscript{2}[TPP].

The above trends of relaxation rates and correlation times of this proton with respect to
temperature are further illustrated in Figures 15 and 16 respectively.

An Arrhenius fit of Ln \(\tau_c\) versus \(1/T\) illustrated in figure 17 gave values of 6.76 and 6.69
kJ/mole for H\textsubscript{2}[TPP] and H\textsubscript{2}[TPP] with C\textsubscript{60}, respectively, suggesting that the energy difference of
activation for molecular motion with and without C\textsubscript{60} are very similar.

Table 3. \(^1\)H Relaxation rates of phenyl hydrogen in H\textsubscript{2}[TTP] with and without C\textsubscript{60} in chlorobenzene-d\textsubscript{5} (CBZ)

<table>
<thead>
<tr>
<th>T (K)</th>
<th>H\textsubscript{2}[TTP] in CBZ</th>
<th>H\textsubscript{2}[TTP] with C\textsubscript{60} in CBZ</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>(R_1) (1/s)</td>
<td>(\tau_C) (ps)</td>
</tr>
<tr>
<td>283</td>
<td>0.752 (0.032)</td>
<td>106</td>
</tr>
<tr>
<td>298</td>
<td>0.606 (0.012)</td>
<td>86</td>
</tr>
<tr>
<td>313</td>
<td>0.576 (0.008)</td>
<td>81</td>
</tr>
</tbody>
</table>

Values in parenthesis are error limits at the 90\% confidence limits. Each relaxation time,\(R_1\) is an
average of three measurements.
Figure 15. Relaxation rates of phenyl hydrogen in H$_2$[TPP] with C$_{60}$, R$_1$ (dashed line) and without C$_{60}$, R$_1$C$_{60}$(Solid line) in chlorobenzene-d$_5$. The lines on the graph represent connected dots.
Figure 16. Experimental Correlation times of phenyl hydrogen in H$_2$[TPP] with C$_{60}$, R$_1$ (dashed line) and without C$_{60}$, R$_1$C$_{60}$(Solid line) in chlorobenzene-d$_5$. The lines on the graph represent connected dots.
Figure 17. Linear fit of experimental correlation times of the phenyl protons of H$_2$[TPP] with C$_{60}$ in neat chlorobenzene-d$_5$ to obtain activation energy of complexation at the site of interaction.

Overall, our data indicates that there no long-lasting intermolecular interaction between H$_2$[TPP] and C$_{60}$ in chlorobenzene-d$_5$ at the pyrrole site where as at the phenyl hydrogen site the results are within the experimental error an indication that the presence of C$_{60}$ does not lead to noticeable intermolecular interaction at the pyrrole site of H$_2$[TPP].
2.1 $^1$H Relaxation rates and correlation time of pyrrole hydrogen in $\text{H}_2[(\text{p-OCH}_3)_4\text{TPP}]$

with and without $\text{C}_{60}$ in chlorobenzene-$d_5$

In column 2 of Table 4, the relaxation rate of the pyrrole hydrogen $\text{H}_2[(\text{p-OCH}_3)_4\text{TPP}]$ in the absence of $\text{C}_{60}$ is given. One sees that the relaxation rate decreases with increasing temperature suggesting that the relaxation pathway is becoming less efficient or less effective as the temperature increases. The effectiveness from the dipole-dipole pathway is inversely proportional to how fast the dynamic motion is at that molecular site. This further illustrated in the correlation time, $\tau_c$. One sees that the correlation time decrease with increasing temperature indicating that the molecule is undergoing faster dynamics with rising temperature.

Column 4 of the same table shows the relaxation rate of the same proton with the introduction of $\text{C}_{60}$ into solution. One sees that the relaxation rate is decreasing with rising temperature. This also suggests that the pathway is becoming less efficient at relaxing this hydrogen. We also see that the correlation time decrease with rising temperature which again indicate faster molecular motion.

Interestingly, the introduction of $\text{C}_{60}$ to the solution enhances the relaxation rate of this proton as seen in positive values of $\Delta R$. These positive values indicate that the relaxation mechanism (dipole-dipole) is more efficient with the presence of $\text{C}_{60}$. The effectiveness is enhanced because of the slowing down of the dynamic motion of the $\text{H}_2[(\text{p-OCH}_3)_4\text{TPP}]$ at this site. This indicates that $\text{H}_2[(\text{p-OCH}_3)_4\text{TPP}]$ is undergoing intermolecular interaction with $\text{C}_{60}$ at this site. The temperature behavior of the relaxation rates and correlation times of pyrrole proton with and without $\text{C}_{60}$ is illustrated in Figures 18 and 19 respectively.

An Arrhenius fit of $\tau_c$ versus $1/T$ gave values of 2.99 and 2.33 kJ/mole for $\text{H}_2[(\text{p-OCH}_3)_4\text{TPP}]$ and $\text{H}_2[(\text{p-OCH}_3)_4\text{TPP}]$ with $\text{C}_{60}$, respectively.
Table 4. $^1$H Relaxation rates of pyrrole hydrogen in $\text{H}_2[(p\text{-OCH}_3)_4\text{TPP}]$ with and without $\text{C}_{60}$ in chlorobenzene-d$_5$ (CBZ).

<table>
<thead>
<tr>
<th>T (K)</th>
<th>$\text{H}_2[(p\text{-OCH}_3)_4\text{TPP}]$ in CBZ</th>
<th>$\text{H}_2[(p\text{-OCH}_3)<em>4\text{TPP}]$ with $\text{C}</em>{60}$ in CBZ</th>
<th>$\Delta R_1$ (1/s)</th>
<th>$\Delta \tau_C$ (ps)</th>
</tr>
</thead>
<tbody>
<tr>
<td>283</td>
<td>$R_1$ (1/s) $= 0.660$ (0.04)  $	au_C$ (ps) $= 334$</td>
<td>$R_1$ (1/s) $= 0.688$ (0.035)  $	au_C$ (ps) $= 344$</td>
<td>$0.028$</td>
<td>$10$</td>
</tr>
<tr>
<td>298</td>
<td>$R_1$ (1/s) $= 0.624$ (0.045)  $	au_C$ (ps) $= 316$</td>
<td>$R_1$ (1/s) $= 0.659$ (0.062)  $	au_C$ (ps) $= 333$</td>
<td>$0.035$</td>
<td>$17$</td>
</tr>
<tr>
<td>313</td>
<td>$R_1$ (1/s) $= 0.584$ (0.015)  $	au_C$ (ps) $= 295$</td>
<td>$R_1$ (1/s) $= 0.618$ (0.293)  $	au_C$ (ps) $= 313$</td>
<td>$0.034$</td>
<td>$18$</td>
</tr>
</tbody>
</table>

Values in parenthesis are error limits at the 90% confidence limits. Each relaxation time is an average of three measurements.
Figure 18. Relaxation rates of pyrrole hydrogen in H$_2$[(p-OCH$_3$)$_4$TPP] with C$_{60}$, R$_1$ (dashed line) and without C$_{60}$, R$_1$C$_{60}$ (Solid line) in chlorobenzene-d$_5$. The lines on the graph represent connected dots.
Figure 19. Experimental Correlation times of pyrrole hydrogen in H$_2$[(p-OCH$_3$)$_4$TPP] with C$_{60}$, R$_1$ (dashed line) and without C$_{60}$, R$_1$C$_{60}$(Solid line) in chlorobenzene-d$_5$. The lines on the graph represent connected dots.
2.2 $^1$H Relaxation rates and correlation Time of phenyl hydrogen in H$_2$[(p-OCH$_3$)$_4$TPP] with and without C$_{60}$ in chlorobenzene-d$_5$

In column 2 of Table 5, the relaxation rate of the phenyl hydrogen in the absence of C$_{60}$, is shown. The relaxation rate also is seen to decrease with rising temperature indicating that the dipole-dipole relaxation pathway is becoming less efficient or less effective. As noted earlier the effectiveness from the dipole-dipole pathway is inversely proportional to how fast the dynamic motion is at that molecular site. Further this is shown in the correlation time, $\tau_c$ where the correlation time is seen to decrease with increasing temperature indicating that the molecule is undergoing faster dynamics.

In column 4 of the same table shows the relaxation rate of the same hydrogen in the presence of C$_{60}$. The relaxation rate of this hydrogen is seen to decrease with rising temperature. We also see that the correlation time decrease with rising temperature which again indicates faster molecular motion.

It is noted that the introduction of C$_{60}$ to the solution enhances the relaxation rate of this proton as seen in positive values of $\Delta R$. These positive values indicate that the dipole-dipole relaxation mechanism is more efficient with the presence of C$_{60}$. The effectiveness is enhanced because of the slowing down of the dynamic motion of the H$_2$[(p-OCH$_3$)$_4$TPP] as a result of undergoing simultaneous face-to face and face-to-edge $\pi-\pi$ interactions between the phenyl moiety and C$_{60}$. Figure 20 and 21 illustrates the how relaxation rates and correlation times of the phenyl hydrogen varies with the temperature in the presence or absence of C$_{60}$ respectively.

An Arrhenius fit of $\tau_c$ versus 1/T gave values of 1.72 and 1.80 kJ/mole for H$_2$[(p-OCH$_3$)$_4$TPP] and H$_2$[(p-OCH$_3$)$_4$TPP] with C$_{60}$, respectively.
Table 5. $^1$H Relaxation rates of phenyl hydrogen in H$_2$[(P-OCH$_3$)$_4$TPP] with and without C$_{60}$ in chlorobenzene-d$_5$ (CBZ).

<table>
<thead>
<tr>
<th>T (K)</th>
<th>H$_2$[(P-OCH$_3$)$_4$TPP] in CBZ</th>
<th>H$_2$[(P-OCH$_3$)$<em>4$TPP] with C$</em>{60}$ in CBZ</th>
<th>$\Delta R_1$ (1/s)</th>
<th>$\Delta \tau_C$ (ps)</th>
</tr>
</thead>
<tbody>
<tr>
<td>283</td>
<td>0.660 (0.04)</td>
<td>0.688 (0.035)</td>
<td>0.028</td>
<td>10</td>
</tr>
<tr>
<td>298</td>
<td>0.624 (0.045)</td>
<td>0.659 (0.062)</td>
<td>0.035</td>
<td>17</td>
</tr>
<tr>
<td>313</td>
<td>0.584 (0.015)</td>
<td>0.618 (0.293)</td>
<td>0.034</td>
<td>18</td>
</tr>
</tbody>
</table>

Values in parenthesis are error limits at the 90% confidence limits. Each relaxation time is an average of three measurements.

Figure 20. Relaxation rates of phenyl hydrogen in H$_2$[(p-OCH$_3$)$_4$TPP] with C$_{60}$, $R_1$ (dashed line) and without C$_{60}$, $R_1$C$_{60}$ (Solid line) in chlorobenzene-d$_5$. The lines on the graph represent connected dots.
Figure 21. Experimental Correlation times of phenyl hydrogen in $\text{H}_2[(\text{p-OCH}_3)_4\text{TPP}]$ with $\text{C}_{60}$, $R_1$ (dashed line) and without $\text{C}_{60}$, $R_1\text{C}_{60}$ (Solid line) in chlorobenzene-$d_5$. The lines on the graph represent connected dots.

Our data indicates that $\text{C}_{60}$ interacts at both the pyrrole and phenyl hydrogen site of $\text{H}_2[(\text{p-OCH}_3)_4\text{TPP}]$. The values indicate a slight preference for the pyrrole hydrogen site. This is shown in Table 5 where the change in $\Delta R$ and $\Delta \tau_c$ at the pyrrole site are more positive or larger than at the phenyl site.
3.1 $^1$H Relaxation rates and correlation Time of pyrrole hydrogen in $\text{H}_2[(\text{p-CN})_4\text{TPP}]$ with and without $\text{C}_{60}$ in chlorobenzene-$d_5$

The temperature behavior of relaxation rates and correlation times of the pyrrole hydrogen in $\text{H}_2[(\text{p-CN})_4\text{TPP}]$ with and without $\text{C}_{60}$ is illustrated in Figures 22 and 23 respectively. Column 2 of Table 6 shows that as the temperature increases the relaxation rate of the pyrrole hydrogen in the absence of $\text{C}_{60}$, is seen to decrease. This implies that the dipole-dipole relaxation pathway is becoming less efficient or less effective as the temperature increases. The effectiveness of the relaxation from the dipole-dipole pathway is inversely proportional to how fast the dynamic motion at that molecular site. The correlation time, $\tau_c$ is seen to decrease with increasing temperature indicating the molecule is undergoing faster dynamics with rising temperature.

Column 4 of the same table contains the relaxation rate of the pyrrole hydrogen with $\text{C}_{60}$ into solution. One sees that the relaxation rate of the pyrrole hydrogen is decreasing with rising temperature. This also implies that the pathway is becoming less efficient at relaxing this hydrogen. We also see that the correlation time decreasing with rising temperature which again indicates faster molecular motion.

It is worth noticing that, with the introduction of $\text{C}_{60}$ to the solution the relaxation rate is enhanced as seen in positive value of $\Delta R$ only at the temperature $283^\circ\text{C}$. This positive value indicates that the relaxation mechanism (dipole-dipole) is more efficient with the presence of $\text{C}_{60}$ at this temperature. As the temperature rises, there is no noticeable interaction indicating that a rise in thermal energy overcomes any long-lasing interactions at this site. An Arrhenius fit of $\tau_c$ versus $1/T$ gave values of 2.99 and 2.33 kJ/mole for $\text{H}_2[(\text{p-CN})_4\text{TPP}]$ and $\text{H}_2[(\text{p-CN})_4\text{TPP}]$ with $\text{C}_{60}$, respectively.
Table 6. $^1$H Relaxation rates of pyrrole hydrogen in H$_2$[(p-CN)$_4$TPP] with and without C$_{60}$ in chlorobenzene-d$_5$ (CBZ).

<table>
<thead>
<tr>
<th>T (K)</th>
<th>H$_2$ [(p-CN)$_4$TPP]</th>
<th>H$_2$[(p-CN)$<em>4$TPP] with C$</em>{60}$</th>
<th>ΔR$_1$</th>
<th>Δτ$_C$</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>R$_1$ (1/s) τ$_C$ (ps)</td>
<td>R$_1$ (1/s) τ$_C$ (ps)</td>
<td></td>
<td></td>
</tr>
<tr>
<td>283</td>
<td>0.820 (0.0625) 415</td>
<td>0.878 (0.147) 444</td>
<td>0.058</td>
<td>29</td>
</tr>
<tr>
<td>298</td>
<td>0.813 (0.094) 418</td>
<td>0.781 (0.021) 395</td>
<td>-0.032</td>
<td>-23</td>
</tr>
<tr>
<td>313</td>
<td>0.809 (0.050) 455</td>
<td>0.765 (0.090) 403</td>
<td>-0.044</td>
<td>-52</td>
</tr>
</tbody>
</table>

Values in parenthesis are error limits at the 90% confidence limits. Each relaxation time is an average of three measurements.

Figure 22. Relaxation rates of pyrrole hydrogen in H$_2$[(p-CN)$_4$TPP] with C$_{60}$, R$_1$ (dashed line) and without C$_{60}$, R$_1$C$_{60}$ (Solid line) in chlorobenzene-d$_5$. The lines on the graph represent connected dots.
Figure 23. Experimental correlation times of pyrrole hydrogen in H$_2$[(p-CN)$_4$TPP] with C$_{60}$, R$_1$ (dashed line) and without C$_{60}$, R$_1$C$_{60}$ (solid line) in chlorobenzene-d$_5$. The lines on the graph represent connected dots.
3.2 $^1$H Relaxation rates and correlation Time of phenyl hydrogen in H$_2$[(p-CN)$_4$TPP] with and without C$_{60}$ in chlorobenzene-d$_5$

The relaxation rate of the phenyl hydrogen of H$_2$[(p-CN)$_4$TPP] in the absence of C$_{60}$ shown in column 2 of Table 7. As seen in this table, the relaxation rate decreases with rising temperature suggesting that the relaxation pathway is becoming less efficient or less effective. This is further shown in the correlation time, $\tau_c$. Correlation time is decreasing with increasing temperature indicated that the molecule is undergoing faster dynamics with rising temperature. These observations are also illustrated in Figure 24.

Column 4 of the same table contains the relaxation rate of the same proton in presence of C$_{60}$ in solution. One sees that the relaxation rate decreases with rising temperature suggesting that the pathway is becoming less efficient at relaxing this hydrogen. We also see that the correlation time decrease with rising temperature which again indicate faster molecular motion.

The relaxation rate of this proton is seen to be enhanced with the introduction of C$_{60}$ to the solution as reflected in the positive values of $\Delta R$ at the temperature 283 K. This positive value indicates that the relaxation mechanism (dipole-dipole) is more efficient with the presence of C$_{60}$. As the temperature rises there is no noticeable interaction indicating that rise in thermal energy overcomes any long lasting interaction at this site.

An Arrhenius fit of $\tau_c$ versus 1/T gave values of 2.40 and 2.30 kJ/mole for H$_2$[(p-CN)$_4$TPP] and H$_2$[(p-CN)$_4$TPP] with C$_{60}$, respectively.
Table 7. \(^1\)H Relaxation rates of phenyl hydrogen in H\(_2\)[(p-CN)\(_4\)TPP] with and without C\(_{60}\) in chlorobenzene-d\(_5\) (CBZ).

<table>
<thead>
<tr>
<th>T (K)</th>
<th>H(_2)[(p-CN)(_4)TPP]</th>
<th>H(_2)[(P-CN)(<em>4)TPP] with C(</em>{60})</th>
<th>(\Delta R_1) (1/s)</th>
<th>(\Delta \tau_C) (ps)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>(R_1) (1/s)</td>
<td>(\tau_C) (ps)</td>
<td>(R_1) (1/s)</td>
<td>(\tau_C) (ps)</td>
</tr>
<tr>
<td>283</td>
<td>0.968 (0.152)</td>
<td>136</td>
<td>0.986 (0.236)</td>
<td>139</td>
</tr>
<tr>
<td>298</td>
<td>0.913 (0.260)</td>
<td>128</td>
<td>0.838 (0.037)</td>
<td>118</td>
</tr>
<tr>
<td>313</td>
<td>0.879 (0.161)</td>
<td>185</td>
<td>0.832 (0.129)</td>
<td>131</td>
</tr>
</tbody>
</table>

Values in parenthesis are error limits at the 90% confidence limits. Each relaxation time is an average of three measurements. The lines on the graph represent connected dots.
**Figure 24.** Experimental correlation times of phenyl hydrogen in H$_2$[(p-CN)$_4$TPP] with C$_{60}$, R$_1$ (dashed line) and without C$_{60}$, R$_1$C$_{60}$ (Solid line) in toluene-d$_8$. The lines on the graph represent connected dots.

In H$_2$[(p-CN)$_4$TPP] porhyrin derivative, our data indicates that at lower temperature (283 K) there is a slight preference for interaction of C$_{60}$ at the pyrrole site but is quickly destroyed with increase in temperature.
4.1 $^1$H Relaxation rates and correlation Time of pyrrole hydrogen in H$_2$[TPP] with and without C$_{60}$ in toluene-d$_8$

In order to investigate the possible role that a solvent can play on interaction, the relaxation rates of the pyrrole and phenyl hydrogen were done in toluene-d$_8$. In Table 8, column 2 and 4 shows the relaxation rates of the pyrrole hydrogen of H$_2$[TPP] without and with C$_{60}$ respectively. One sees a small increase in the relaxation rates at all the temperatures. Increasing relaxation rates indicates slower dynamical motion at that site which is also reflected in the longer correlation times, $\tau_C$, that is observed when C$_{60}$ is added to the solution. Figure 25 and 26 also illustrates the temperature behavior of relaxation rates and correlation times with and without C$_{60}$ being in solution respectively. These changes are indicating that C$_{60}$ may be interacting at this site.

<table>
<thead>
<tr>
<th>T (K)</th>
<th>H$_2$ [TPP] in Toluene</th>
<th>H$<em>2$[TPP] with C$</em>{60}$ in Toluene</th>
<th>$\Delta R_1$ (1/s)</th>
<th>$\Delta \tau_C$ (ps)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>$R_1$ (1/s) $\tau_C$ (ps)</td>
<td>$R_1$ (1/s) $\tau_C$ (ps)</td>
<td></td>
<td></td>
</tr>
<tr>
<td>283</td>
<td>0.518 256</td>
<td>0.523 259</td>
<td>0.005 3</td>
<td></td>
</tr>
<tr>
<td></td>
<td>(0.005)</td>
<td>(0.002)</td>
<td></td>
<td></td>
</tr>
<tr>
<td>298</td>
<td>0.432 214</td>
<td>0.444 220</td>
<td>0.012 6</td>
<td></td>
</tr>
<tr>
<td></td>
<td>(0.010)</td>
<td>(0.002)</td>
<td></td>
<td></td>
</tr>
<tr>
<td>313</td>
<td>0.363 180</td>
<td>0.374 185</td>
<td>0.011 5</td>
<td></td>
</tr>
<tr>
<td></td>
<td>(0.001)</td>
<td>(0.003)</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

Values in parenthesis are error limits at the 90% confidence limits. Each relaxation time is an average of three measurements.
Figure 25. Relaxation rates of pyrrole hydrogen in H₂TPP with C₆₀, R₁ (dashed line) and without C₆₀, R₁C₆₀ (Solid line) in toluene-d₈. The lines on the graph represent connected dots.
4.2 $^1$H Relaxation rates and correlation Time of phenyl hydrogen in H$_2$[TPP] with and without C$_{60}$ in toluene-d$_8$

In column 2 of Table 9 contains the relaxation rate of the phenyl hydrogen in the absence of C$_{60}$. The relaxation rate are seen to decrease with rising temperature indicating that the relaxation pathway is becoming less efficient or less effective. The correlation time is seen to decrease with increasing temperature indicating that the molecule is undergoing faster dynamics with rising temperature. An illustration showing the variation of relaxation rate and correlation times of the phenyl hydrogen with temperature in absence and presence of C$_{60}$ is shown in Figures 27 and 28.

Figure 26. Experimental correlation times of pyrrole hydrogen in H$_2$[TPP] with C$_{60}$, R$_1$ (dashed line) and without C$_{60}$, R$_1$C$_{60}$ (Solid line) in toluene-d$_8$. The lines on the graph represent connected dots.
Column 4 shows the relaxation rates of the same hydrogen with the introduction of C$_{60}$ into solution. It is shown that the relaxation rate decreases with rising temperature. We also see that the correlation time decreases with rising temperature which again indicate faster molecular motion.

**Table 9.** $^1$H Relaxation rates of phenyl hydrogen in H$_2$[TPP] with and without C$_{60}$ in toluene-d$_8$.

<table>
<thead>
<tr>
<th>T (K)</th>
<th>$^{1}$H[TPP] in Toluene</th>
<th>$^{1}$H[TPP] with C$_{60}$ in Toluene</th>
<th>$\Delta R_1$ (1/s)</th>
<th>$\Delta \tau_C$ (ps)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>$R_1$ (1/s)</td>
<td>$\tau_C$ (ps)</td>
<td>$R_1$ (1/s)</td>
<td>$\tau_C$ (ps)</td>
</tr>
<tr>
<td>283</td>
<td>0.674 (0.009)</td>
<td>95</td>
<td>0.677 (0.005)</td>
<td>96</td>
</tr>
<tr>
<td>298</td>
<td>0.578 (0.017)</td>
<td>82</td>
<td>0.574 (0.003)</td>
<td>-4</td>
</tr>
<tr>
<td>313</td>
<td>0.469 (0.013)</td>
<td>66</td>
<td>0.483 (0.004)</td>
<td>68</td>
</tr>
</tbody>
</table>

Values in parenthesis are error limits at the 90% confidence limits. Each relaxation time is an average of three measurements.
Figure 27. Relaxation rates of phenyl hydrogen in H$_2$[TPP] with C$_{60}$, R$_1$ (dashed line) and without C$_{60}$, R$_1$C$_{60}$ (Solid line) in toluene-d$_8$. The lines on the graph represent connected dots.
Figure 28. Experimental correlation times of phenyl hydrogen in H$_2$[TPP] with C$_{60}$, R$_1$ (dashed line) and without C$_{60}$, R$_1$C$_{60}$ (Solid line) in toluene-d$_8$. The lines on the graph represent connected dots.

Although the introduction of C$_{60}$ to the solution enhances the relaxation rate of this proton, as seen in positive values of $\Delta R$, the relaxation rates for this hydrogen are within experimental error and are inconclusive suggesting that there is little or no intermolecular interaction at this site.
CONCLUSIONS

1. Our data indicates that the introduction of C\textsubscript{60} in solution of H\textsubscript{2}[TPP] does not lead to noticeable intermolecular interaction at both the pyrrole and phenyl hydrogen sites of H\textsubscript{2}[TPP] since the interactions are not long-lasting in chlorobenzene-d\textsubscript{5}.

2. Our data indicates that C\textsubscript{60} interacts at both the pyrrole and phenyl hydrogen site of H\textsubscript{2}[(P-OCH\textsubscript{3})\textsubscript{4}TPP], with a slight preference for the pyrrole hydrogen site.

3. For the complex H\textsubscript{2}[(P-CN)\textsubscript{4}TPP], our data indicates that at lower temperature there is a noticeable but slight preference for the interaction of C\textsubscript{60} at pyrrole site at lower temperature(283 K), but is quickly destroyed with an increase in temperature.

4. The porphyrin derivatives show that the substituents have an effect on interaction site due to a change in substituent. For the case of H\textsubscript{2}[(p-OCH\textsubscript{3})\textsubscript{4}TPP], that has an electron – donating group, OCH\textsubscript{3} both phenyl and pyrrole hydrogen sites are seen to interact with C\textsubscript{60}, with a slight preference at the pyrrole hydrogen at all the three temperatures(283, 298, and 313\textdegree C). In the case of H\textsubscript{2}[(p-CN)\textsubscript{4}TPP] with an electron-withdrawing group CN, only at lower temperature(283 K) does the pyrrole hydrogen site interact with C\textsubscript{60}.
REFERENCES


(54) Aldrich Chemical, P. O. Box 14508, Saint Louis, MO 63178, USA, http://www.sigmaaldrich.com/, 800-325-3010.