

Research Article

NMR Studies into the Potential Interactions of Fullerene C₆₀ with Tetraphenylporphyrin and Some of Its Derivatives

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¹H NMR relaxation studies were employed to investigate potential interactions between C₆₀ and tetraphenylporphyrin, H₂[TPP], and parasubstituted tetraphenylporphyrins, H₂[(p-X)₄TPP], where X = CN and OCH₃ in solution. The substituted porphyrins provided a means by which to investigate the role that electronic effects play in the interaction process. A comparison of the relaxation rates, R₁, and correlation times, τ_C, of the pyrrole and phenyl hydrogens in these complexes, without and with the presence of C₆₀, revealed that the introduction of C₆₀ into solution did not have a noticeable effect on R₁ and τ_C of these protons in H₂[TPP], indicating the absence of long-term intermolecular interaction at either of these two sites. A similar analysis of the two protons in the other two substituted tetraphenylporphyrin analogs revealed slower molecular dynamics indicating the presence of intermolecular interactions. Stronger interactions were observed in H₂[(p-OCH₃)₄TPP] indicating that the electron-donating abilities of the -OCH₃ group promote the interaction process. Our results indicate that it is very likely that enhanced selectivity in the chemical purifications of fullerenes and metallofullerenes can be achieved by employing tetraphenylporphyrin-silica stationary phases which have been modified with electron-donating groups.

1. Introduction

Because of their distinctive properties, fullerenes have experienced a tremendous amount of research interest. Pharmaceutically, fullerenes' unique properties have been exploited to develop a variety of applications including being used as conduits for drug delivery, functionalized to serve as antibacterial agents, and tested as HIV inhibitors [1–3]. Porphyrins and fullerenes have been found to spontaneously be attracted to each other [4]. This newly recognized supramolecular recognition element, the attraction of the curved π-surface of the fullerene to the center of the flat π-surface of a porphyrin, is possibly due to π-π and n-π electron interactions. This phenomenon is in contrast to the traditional paradigm which requires the matching of a concave host with a convex guest [5].

During the past few years, the intermolecular interaction of porphyrins and fullerenes has been studied extensively. Due to their potential applications in processes of molecular

recognition [6–11], photosynthesis [12–16], photovoltaics [17–23], energy transfer [24–32], and electron transfer [33–45], 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. Meyerhoff and coworkers have developed columns with selectivity superior to the commercially available “Buckyclutcher” and “Buckyprep” columns [46, 47]. Their work showed that columns packed with (p-carboxyl)triphenylporphyrin-silica gel generated the best fullerene separation. The underlying rationale for the enhanced selectivity is believed to be π-π interactions between tetraphenylporphyrin and the fullerene. 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 [48]. In the crystal structure of this species, C₆₀ was found to be centered over the porphyrin with its electron-rich 6:6 ring-juncture in close

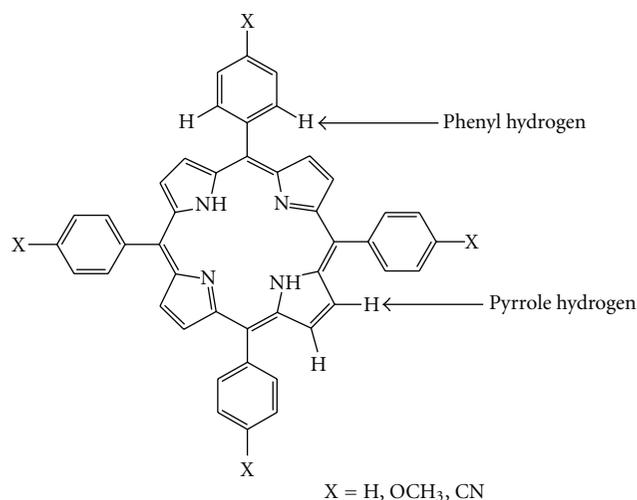


FIGURE 1: Display of parasubstituted tetraphenylporphyrin showing the pyrrole and phenyl hydrogens studied.

proximity to the plane of the porphyrin. The phenyl carbon atoms of the porphyrin were all at distances greater than 4.0 Å from fullerene carbon atoms, indicating that the ortho C-H bonds did not contribute significantly to the association.

In this study, ¹H NMR relaxation studies have been performed to investigate the nature and precise interaction site of fullerene, C₆₀, with tetraphenylporphyrin, H₂[TPP], and parasubstituted tetraphenylporphyrins, H₂[(p-X)₄TPP], where X = CN and OCH₃ in deuterated chlorobenzene-d₅ (CBZ). The porphyrin derivatives were selected to investigate possible interactions changes due to electronic donating or withdrawing capabilities of the substituent group. The pyrrole hydrogen, on the porphyrin ring, and the ortho hydrogen, on the phenyl group, were selected since these hydrogens are strategically located at sites which will allow the determination of the molecular dynamics at the porphyrin and phenyl sites. Relaxation rates of the pyrrole and phenyl hydrogens in the porphyrins, as shown in Figure 1, were determined at several temperatures in the presence and absence of fullerene. In addition, correlation times, τ_C, for these hydrogens were calculated. Possible interaction sites were determined by looking at the difference in relaxation rate, R₁, and correlation time, τ_C, due to the presence and absence of the C₆₀ molecule.

2. Theoretical Background

¹H spin-lattice relaxation in the tetraphenylporphyrin H₂[TPP] system is due primarily to the magnetic dipole-dipole interactions. The relaxation rate, R₁, can be expressed as the sum of intra- and interrelaxation. This relationship is demonstrated below by (1) [49–52]:

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

T₁ is the measured relaxation time and R₁ is simply the inverse of T₁. The intermolecular contribution, R₁^{DD}(inter), can be eliminated experimentally by working with very low mole fractions of a solute and by working in deuterated solvents. These two conditions were met in our measurements: mole fractions of 1.299 × 10⁻⁵ and deuterated chlorobenzene-d₅. In the absence of the intermolecular interaction, (1) reduces to the following [49–52]:

$$R_1 = R_1^{\text{DD}}(\text{intra}) = \left[\left(\frac{2}{3} \right) \frac{\gamma_H^4 \hbar^2}{r_{AB}^6} \right] n_s \tau_c, \quad (2)$$

where γ_H is the hydrogen gyromagnetic ratio, ħ is the h/2π, r_{AB} is the proton-to-proton distance of the interacting nuclei, n_s is the number of interacting nuclei, and τ_c is the rotational correlation time which can be equated to 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, R₁, have been acquired experimentally, the rotational dynamics at a specific molecular site can be determined by solving (2) for τ_c.

3. Experimental Methods

The solvent chlorobenzene-d₅ was selected for these measurements since it provided the best solubility parameters for all tetraphenylporphyrin derivatives and C₆₀. Fullerene C₆₀ and chlorobenzene-d₅ (99.5+ at. %D) were purchased from Acros Organics [53]. Tetraphenylporphyrin H₂[TPP] was purchased from the Aldrich Chemical Company [54]. Para-substituted tetraphenylporphyrin derivatives, H₂[(p-X)₄TPP] (X = CN and OCH₃), of H₂[TPP] were synthesized by adapting and slightly modifying the method reported by Adler et al. [55]. The purity of the H₂[TPP] derivatives was accomplished by several recrystallizations and established by HPLC and NMR methods. Several tetraphenylporphyrin solutions, with decreasing mole fractions, were initially prepared, and relaxation measurements were taken, to establish the solute mole fraction at which porphyrin-porphyrin interactions were absent. Solutions with solute mole fraction of 1.299 × 10⁻⁵ were found to eliminate possible porphyrin-porphyrin interactions as evidence by the constant relaxation rates. This information was used to ensure that subsequent samples were prepared consistently with this solute mole fraction. In solutions containing both host and guest, a 1 : 1 mole ratio in porphyrin : C₆₀ was maintained. Approximately 0.5 mL of the 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.

¹H spin-lattice relaxation times were performed on a Varian 300 MHz instrument by 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 a delay between pulses. Nine delay times were used in the pulse sequence with values, depending on the estimated T₁, ranging from 0.0625 s to 16 s. A delay time (D₁) of approximately 14 s was used between the transients. Each experiment used a minimum of 76 transients resulting in an acquisition time

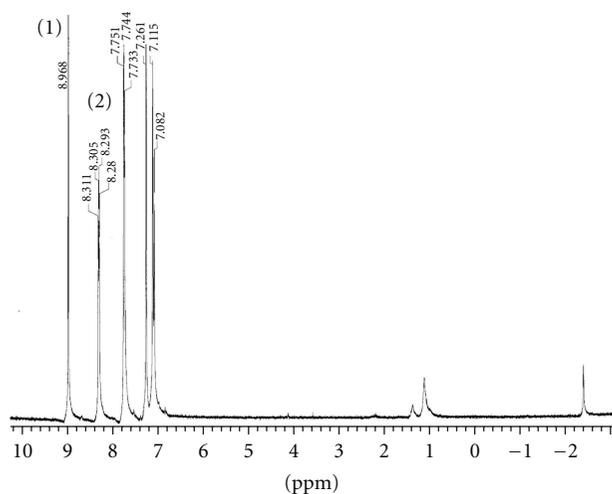


FIGURE 2: ^1H NMR of $\text{H}_2[\text{TPP}]$ in chlorobenzene- d_5 . Peak (1), at about 8.90 ppm, corresponds to the pyrrole hydrogen while the multiplet (2), at about 8.25 ppm, corresponds to the orthohydrogen of the phenyl group.

of approximately 4 hours. Experiments were conducted at five different temperatures. Typical ^1H NMR spectra of the $\text{H}_2[\text{TPP}]$ and some of the derivatives were obtained and are shown in Figures 2, 3, and 4. The disappearance (i.e., broadening) of the N-H proton resonance into the baseline noise, due to the very rapid exchange rate of these porphyrin protons at the higher temperatures, prevented their use in this study. Therefore, the pyrrole and ortho hydrogens of the porphyrin and phenyl ring were utilized to monitor the molecular dynamics of the two molecular sites in these tetraphenylporphyrin complexes.

4. Results and Discussion

4.1. ^1H Relaxation Rates and Correlation Times of the Pyrrole and Phenyl Hydrogens in $\text{H}_2[\text{TPP}]$ with and without C_{60} in Chlorobenzene- d_5 . Shown in columns 2 and 4 of Table 1 are the variable temperature relaxation rates, R_1 , of the pyrrole hydrogen in the absence and presence of C_{60} , respectively. As expected, these rates are seen to decrease with rising temperature indicating a decrease in the effectiveness of the dipolar mechanism. Columns 3 and 5, of the same table, contain the values of the correlation times obtained via the respective relaxation rates and (2). The correlation times, τ_C , are also decreasing with rising temperature indicating faster molecular dynamics with increasing temperature [52].

A comparison of the relaxation rates, without and with the presence of C_{60} , reveals that the introduction of C_{60} to the solution does not affect the relaxation rate of this proton appreciatively. One notices that the change in relaxation rate is within experimental error indicating that the presence of C_{60} does not lead to noticeable intermolecular interaction at the pyrrole site of $\text{H}_2[\text{TPP}]$. This observation is further illustrated graphically in Figure 5. An Arrhenius fit of τ_C versus T^{-1} yielded energies of activation of 7.23 and 6.80 kJ/mole for $\text{H}_2[\text{TPP}]$ without and with C_{60} , respectively,

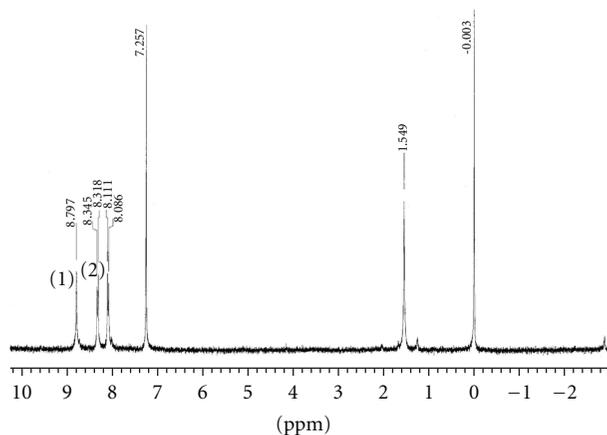


FIGURE 3: ^1H NMR of $\text{H}_2[(\text{p-CN})_4\text{TPP}]$ in chlorobenzene- d_5 . Peak (1), at about 8.90 ppm, corresponds to the pyrrole hydrogen while the multiplet (2), at about 8.28 ppm, corresponds to the orthohydrogen of the phenyl group.

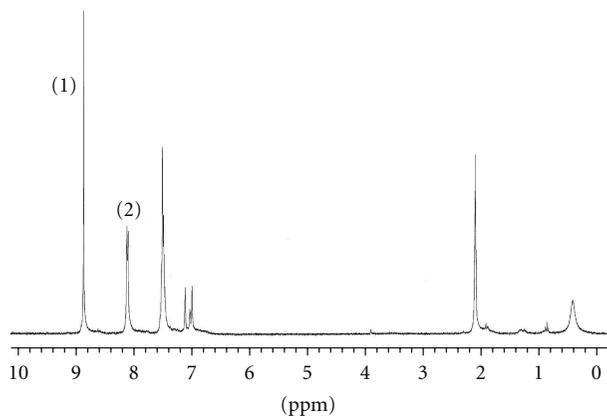


FIGURE 4: ^1H NMR of $\text{H}_2[(-\text{OCH}_3)_4\text{TPP}]$ in chlorobenzene- d_5 . Peak (1), at about 8.90 ppm, corresponds to the pyrrole hydrogen while the multiplet (2), at about 8.28 ppm, corresponds to the orthohydrogen of the phenyl group.

TABLE 1: ^1H relaxation Rates of pyrrole Hydrogen in $\text{H}_2[\text{TPP}]$ with and without C_{60} in chlorobenzene- d_5 .

T (K)	$\text{H}_2[\text{TPP}]$ in CBZ		$\text{H}_2[\text{TPP}]$ with C_{60} in CBZ	
	R_1 (1/s)	τ_C (ps)	R_1 (1/s)	τ_C (ps)
268	0.651 (0.005)	322	0.645 (0.012)	319
283	0.581 (0.006)	288	0.571 (0.013)	283
298	0.496 (0.016)	246	0.515 (0.010)	255
313	0.434 (0.002)	215	0.432 (0.011)	214
328	0.357 (0.002)	177	0.367 (0.012)	182

Values in parentheses represent error limits at the 90% confidence level.

suggesting that the energies of activation for molecular motion in the presence and absence of C_{60} are very similar and within the range of experimental error for these types of measurements.

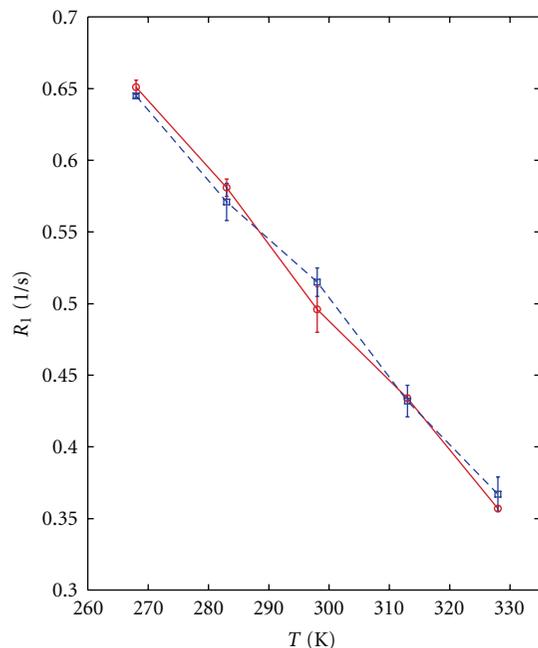


FIGURE 5: Relaxation rates of the pyrrole hydrogen of $H_2[TPP]$ with C_{60} (dash line) and without C_{60} (solid line) in chlorobenzene- d_5 .

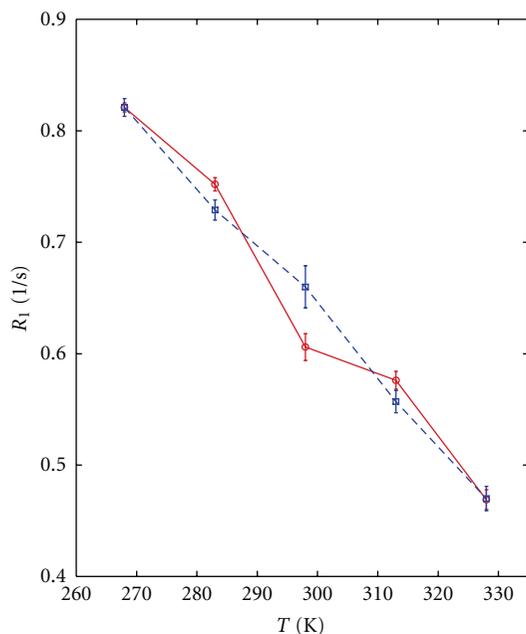


FIGURE 6: Relaxation rates of the pyrrole hydrogen of $H_2[TPP]$ with C_{60} (dash line) and without C_{60} (solid line) in chlorobenzene- d_5 .

Shown in columns 2 and 4 of Table 2 are the relaxation rates of the phenyl hydrogen in the absence and presence of C_{60} . The corresponding correlation times are given in columns 3 and 5. Both R_1 and τ_C for this hydrogen follow the same temperature dependence as was observed for the pyrrole hydrogen indicating the dipolar pathway becoming less efficient with faster molecular motion. As was the case

TABLE 2: 1H relaxation Rates of phenyl Hydrogen in $H_2[TPP]$ with and without C_{60} in chlorobenzene- d_5 .

T (K)	$H_2[TPP]$ in CBZ		$H_2[TPP]$ with C_{60} in CBZ	
	R_1 (1/s)	τ_C (ps)	R_1 (1/s)	τ_C (ps)
268	0.821 (0.004)	232	0.821 (0.008)	232
283	0.752 (0.006)	213	0.729 (0.009)	206
298	0.606 (0.012)	171	0.660 (0.019)	187
313	0.576 (0.008)	163	0.557 (0.010)	158
328	0.469 (0.009)	132	0.470 (0.011)	132

Values in parentheses represent error limits at the 90% confidence level.

TABLE 3: 1H relaxation Rates of Pyrrole Hydrogen in $H_2[(p-CN)_4TPP]$ with and without C_{60} in Chlorobenzene- d_5 .

T (K)	$H_2[(p-CN)_4TPP]$		$H_2[(p-CN)_4TPP]$ with C_{60}	
	R_1 (1/s)	τ_C (ps)	R_1 (1/s)	τ_C (ps)
268	0.825 (0.014)	408	0.921 (0.016)	456
283	0.820 (0.016)	406	0.878 (0.018)	435
298	0.813 (0.024)	402	0.781 (0.009)	397
313	0.809 (0.013)	400	0.765 (0.020)	379
328	0.803 (0.014)	397	0.695 (0.020)	344

Values in parentheses represent error limits at the 90% confidence level.

for the pyrrole hydrogen, a comparison of the relaxation rates of the phenyl hydrogen, with and without C_{60} in the solution, shows that the changes in relaxation rates are within the experimental error indicating that the presence of C_{60} does not lead to noticeable intermolecular interaction at the phenyl site of $H_2[TPP]$. The relaxation rates are also illustrated graphically in Figure 6. The Arrhenius fit of τ_C versus T^{-1} yielded energies of activation of 6.76 and 6.69 kJ/mole for $H_2[TPP]$ without and with C_{60} , respectively. An interesting sidenote is a comparison of the reorientational dynamics at the pyrrole (i.e., overall molecular motion) and phenyl sites. The reorientational motion of the phenyl ring is higher an average of 36% than that at the pyrrole site, indicating significant internal motion being present in this complex.

4.2. 1H Relaxation Rates and Correlation Times of the Pyrrole and Phenyl Hydrogens in $H_2[(p-CN)_4TPP]$ with and without C_{60} in Chlorobenzene- d_5 . The temperature behaviors of the relaxation rates and correlation times of the pyrrole and phenyl hydrogens in $H_2[(p-CN)_4TPP]$, with and without C_{60} , are shown in Tables 3 and 4, respectively. The relaxation rates and correlation times of both hydrogens show the expected temperature behavior, decreasing in magnitude with rising temperature indicating that the molecule is undergoing faster dynamics with an increase in temperature. The temperature behaviors of the relaxation rates for these hydrogens are also illustrated in Figures 7 and 8.

In the absence of C_{60} , the relaxation rate for the pyrrole hydrogen gradually decreases in magnitude with increasing temperature indicating less sensitivity to temperature variations. It is interesting to note that, at both the pyrrole and phenyl hydrogen sites, the relaxation rate is enhanced

TABLE 4: ^1H relaxation Rates of Phenyl Hydrogen in $\text{H}_2[(\text{p-CN})_4\text{TPP}]$ with and without C_{60} in Chlorobenzene- d_5 .

T (K)	$\text{H}_2[(\text{p-CN})_4\text{TPP}]$		$\text{H}_2[(\text{p-CN})_4\text{TPP}]$ with C_{60}	
	R_1 (1/s)	τ_C (ps)	R_1 (1/s)	τ_C (ps)
268	1.01 (0.012)	286	1.04 (0.015)	294
283	0.968 (0.015)	274	0.986 (0.020)	279
298	0.913 (0.015)	258	0.838 (0.020)	237
313	0.879 (0.061)	249	0.832 (0.021)	235
328	0.831 (0.017)	235	0.731 (0.023)	207

Values in parentheses represent error limits at the 90% confidence level.

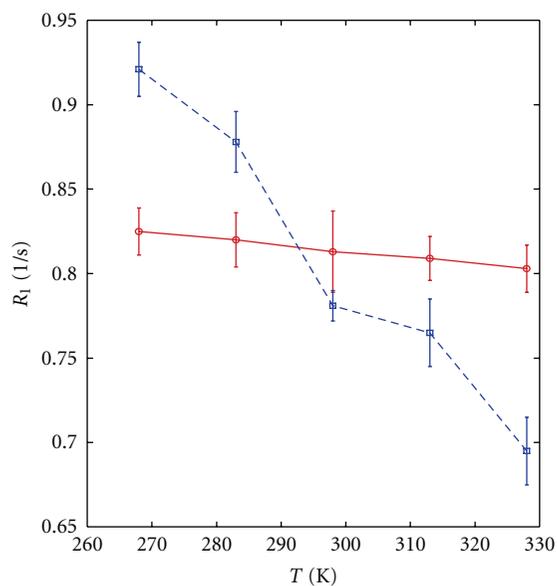


FIGURE 7: Relaxation rates of the pyrrole hydrogen of $\text{H}_2[(\text{p-CN})_4\text{TPP}]$ with C_{60} (dash line) and without C_{60} (solid line) in chlorobenzene- d_5 .

at the two lower temperatures of 268 and 283 K when C_{60} is introduced into the solution. This improved relaxation results in longer correlation times at these two temperatures indicating that the slower rotational motion is enhancing the relaxation mechanism (dipole-dipole) at these temperatures. This observation suggests the presence of noticeable intermolecular interactions of C_{60} at the porphyrin and phenyl sites. While interactions are seen at both sites, a comparison of the data, and also illustrated in Figures 7 and 8, shows a slight interaction preference for the pyrrole site. This observation indicates that electrons withdrawing groups on the phenyl group may enhance intermolecular interactions, at least at reduced temperatures. However, as the temperature rises, the correlation times in the $\text{H}_2[(\text{p-CN})_4\text{TPP}]/\text{C}_{60}$ solution decrease, which has the effect of reducing the efficiency of the relaxation mechanism. This observation indicates that a rise in thermal energy prevents long-lasting $\text{H}_2[(\text{p-CN})_4\text{TPP}]-\text{C}_{60}$ interactions from occurring at both molecular sites. As was the case in the $\text{H}_2[\text{TPP}]$ sample, the reorientational motion of the phenyl ring is much higher than that at the pyrrole site, ranging from 43% at the lower

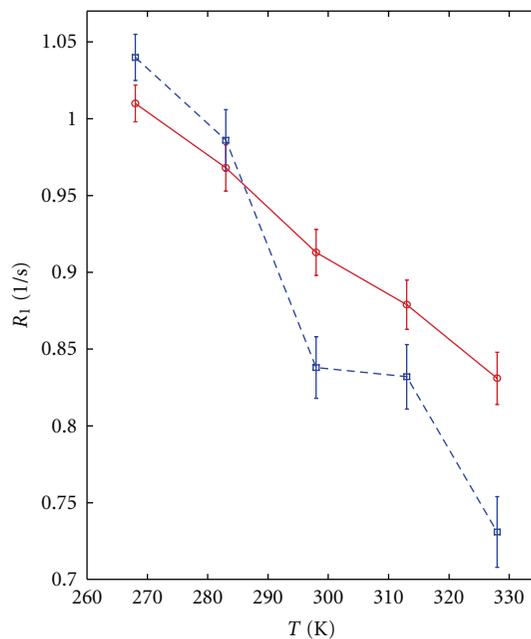


FIGURE 8: Relaxation rates of the phenyl hydrogen of $\text{H}_2[(\text{p-CN})_4\text{TPP}]$ with C_{60} (dash line) and without C_{60} (solid line) in chlorobenzene- d_5 .

TABLE 5: ^1H relaxation rates of phenyl hydrogen in $\text{H}_2[(\text{p-OCN}_3)_4\text{TPP}]$ with and without C_{60} in chlorobenzene- d_5 .

T (K)	$\text{H}_2[(\text{p-OCH}_3)_4\text{TPP}]$ in CBZ		$\text{H}_2[(\text{p-OCH}_3)_4\text{TPP}]$ with C_{60} in CBZ	
	R_1 (1/s)	τ_C (ps)	R_1 (1/s)	τ_C (ps)
268	0.699 (0.012)	346	0.725 (0.009)	359
283	0.660 (0.014)	327	0.688 (0.015)	341
298	0.624 (0.016)	308	0.659 (0.012)	326
313	0.584 (0.015)	289	0.618 (0.018)	306
328	0.547 (0.019)	270	0.585 (0.019)	290

Values in parentheses represent error limits at the 90% confidence level.

temperature and increasing to nearly 66% at the highest temperature indicating the presence of a significant amount of internal motion.

4.3. ^1H Relaxation Rates and Correlation Times of Pyrrole and Phenyl Hydrogens in $\text{H}_2[(\text{p-OCH}_3)_4\text{TPP}]$ with and without C_{60} in Chlorobenzene- d_5 . The data for the pyrrole and phenyl hydrogens for the electron-donating, para- OCH_3 -substituted porphyrin are given in Tables 5 and 6. The temperature behaviors of the relaxation rates are also illustrated in Figures 9 and 10. As was observed previously in $\text{H}_2[\text{TPP}]$ and $\text{H}_2[(\text{p-CN})_4\text{TPP}]$ complexes, both R_1 and τ_C decrease in value with rising temperature indicating the reduced effectiveness of the dipole-dipole mechanism with increased reorientational motion.

A comparison of the pyrrole relaxation rate, as well as τ_C , with and without C_{60} shows that the introduction of C_{60} into solution enhances the relaxation rate of this pyrrole hydrogen

TABLE 6: ^1H relaxation rates of phenyl hydrogen in $\text{H}_2[(\text{p-OCH}_3)_4\text{TPP}]$ with and without C_{60} in chlorobenzene- d_5 .

T (K)	$\text{H}_2[(\text{p-OCH}_3)_4\text{TPP}]$		$\text{H}_2[(\text{p-OCH}_3)_4\text{TPP}]$ with C_{60}	
	R_1 (1/s)	τ_C (ps)	R_1 (1/s)	τ_C (ps)
268	0.857 (0.011)	242	1.00 (0.01)	283
283	0.834 (0.012)	236	0.956 (0.013)	270
298	0.790 (0.016)	223	0.875 (0.015)	247
313	0.778 (0.014)	220	0.847 (0.017)	240
328	0.745 (0.015)	211	0.784 (0.019)	222

Values in parentheses represent error limits at the 90% confidence level.

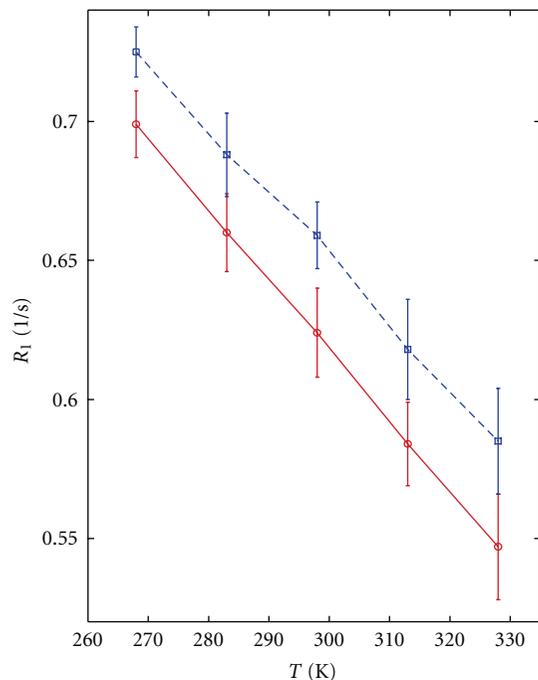


FIGURE 9: Relaxation rates of the pyrrole hydrogen of $\text{H}_2[(\text{p-OCH}_3)_4\text{TPP}]$ with C_{60} (dash line) and without C_{60} (solid line) in chlorobenzene- d_5 .

by slowing the molecular dynamics (i.e., longer τ_C) at this site. This indicates that $\text{H}_2[(\text{p-OCH}_3)_4\text{TPP}]$ is experiencing intermolecular interaction with C_{60} at the pyrrole hydrogen site. This enhanced relaxation is also illustrated in Figure 9. While the error bars in the measurements are somewhat large, the effects of these interactions on the molecular dynamics at this hydrogen site are experimentally observable.

A review of the relaxation rates and correlation times of the phenyl hydrogen, with and without the presence of C_{60} , reveals higher relaxation rates and longer correlation times when C_{60} is present. This observation indicates the presence of phenyl/ C_{60} interactions at this site. A comparison of the pyrrole and phenyl data indicates that, while C_{60} is interacting with $\text{H}_2[(\text{p-OCH}_3)_4\text{TPP}]/\text{C}_{60}$ at both the pyrrole and phenyl sites, there is a noticeable preference for the phenyl site. An illustration of the two types of interactions is given in Figure 11. We attribute this preference to the electron-donating abilities of the $-\text{OCH}_3$ group which

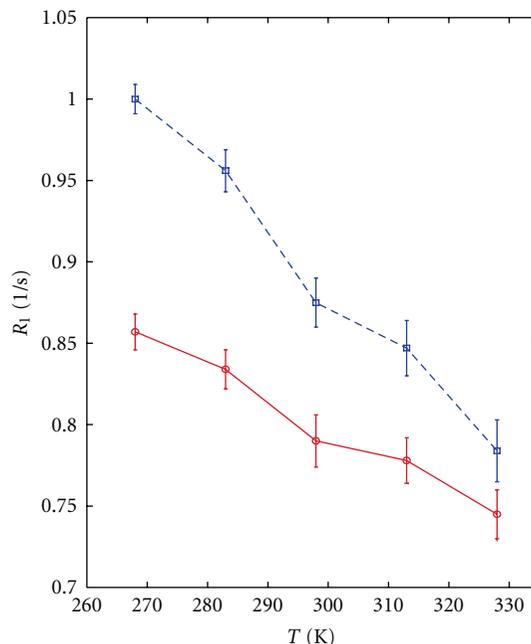


FIGURE 10: Relaxation rates of the phenyl hydrogen of $\text{H}_2[(\text{p-OCH}_3)_4\text{TPP}]$ with C_{60} (dashed line) and without C_{60} (solid line) in chlorobenzene- d_5 .

allows two potential points of interaction with C_{60} . Gung and Amicangelo analyzed the effects of substituents on π - π interactions and found that electron-donating groups increase interaction energies by promoting two types of electronic interactions: the normal π - π parallel stacking and the offset stacking of the substituent group over the guest molecule which can give rise to electrostatic interactions [56]. In some cases, this second type of interaction can lead to charge transfer with significant interaction energies.

5. Conclusion

^1H NMR relaxation studies were employed to investigate potential interactions between C_{60} and tetraphenylporphyrin, $\text{H}_2[\text{TPP}]$, and parasubstituted tetraphenylporphyrins, $\text{H}_2[(\text{p-X})_4\text{TPP}]$, where $\text{X} = \text{CN}$ and OCH_3 in solution. The substituted porphyrins provided a means by which to investigate the role that electronic effects play in the interaction process. A comparison of the relaxation rates, R_1 , and correlation times, τ_C , of the pyrrole and phenyl hydrogens in $\text{H}_2[\text{TPP}]$, without and with the presence of C_{60} , revealed that the introduction of C_{60} into solution did not have a noticeable effect on R_1 and τ_C of these protons indicating the absence of long-term intermolecular interaction at either of these two sites. A similar analysis of the two protons in the electron-withdrawing substituted tetraphenylporphyrin analog, $\text{H}_2[(\text{p-CN})_4\text{TPP}]$, revealed slower molecular dynamics at the two lowest temperatures indicating the presence of intermolecular interactions. However, these interactions were absent at higher temperatures

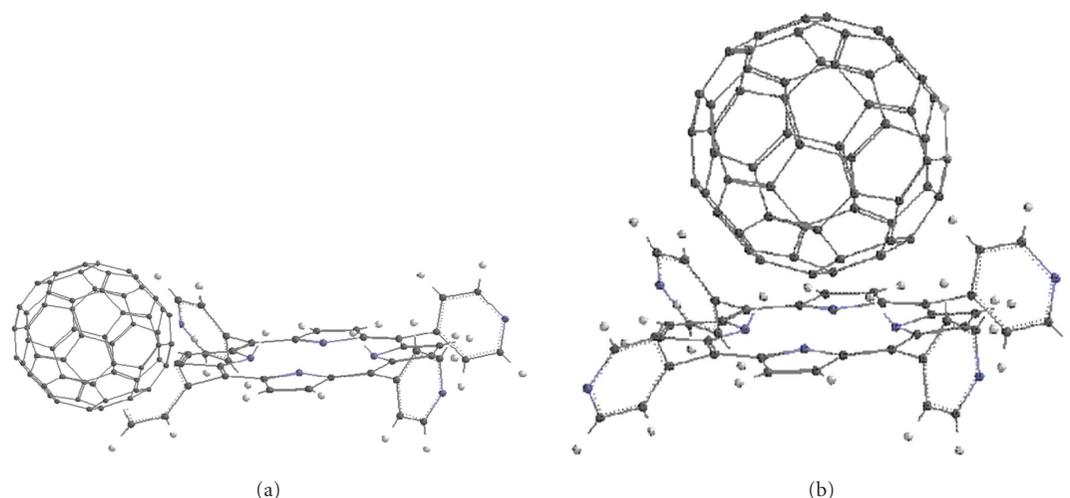


FIGURE 11: Illustration of possible interaction sites of tetraphenylporphyrin with C_{60} .

suggesting that the rise in thermal energy prevents long-lasting interactions from occurring at both molecular sites. A comparison of the pyrrole and phenyl hydrogens data in $H_2[(p-OCH_3)_4TPP]$ indicated that, while C_{60} is interacting at both the pyrrole and phenyl sites, there is a clear preference for the phenyl site. A graphical illustration of these interactions is given in Figure 11. We believe that this preference is due to the electron-donating abilities of the $-OCH_3$ group which allows two potential points of interaction of C_{60} on the phenyl group. This observation is consistent with the results observed by Gung and Amicangelo [56].

Our results indicate that it is very likely that enhanced selectivity in the chemical purifications of fullerenes and metallofullerenes can be achieved by employing tetraphenylporphyrin-silica stationary phases which have been modified with electron-donating groups.

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