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FIRST PRINCIPLES INVESTIGATIONS OF ROTATIONAL BARRIER AND HYPERFINE INTERACTIONS OF MUONIUM IN TETRAPHENYLSILANE

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Abstract

In this work, we have used the Density Functional Theory (DFT) method to study the rotational barrier for the muoniated-tetraphenylsilane, SiPh₄-Mu system. Three Muonium (Mu) trapping sites were considered in the investigations, namely ortho, meta, and para positions on one of the phenyl rings. The positions of muonium (Mu) at the three different sites were determined by performing geometry optimization procedures. The geometry optimizations for all the systems were employed to calculate the local energy minima of the system as well as the hyperfine coupling constant for the Mu. The Mu-attached phenyl ring was then rotated about the Si-C bond at the intervals of 10° for a complete 360° rotation. For all three cases, the calculated energy profiles exhibited two barriers. In the case of both meta and para sites, the profiles as well as the location of the barriers were nearly the same. While for the ortho case, the positions of the two barriers differ slightly with the other two cases. The calculated barrier height for the rotation of Mu-attached phenyl ring was less than 0.8 eV. The major part of the total hyperfine coupling constants for the Mu was from isotropic component. The corresponding values vary from 372.40 MHz to 475.65 MHz. On the other hand, a very small value of anisotropic hyperfine coupling constants for the Mu was calculated.

Keywords: Density Functional Theory, Tetraphenylsilane, Muonium, Rotational Barrier

1. Introduction

Group 14 tetraphenyl derivatives XPh₄, where X = C, Si, Ge, and Sn have been widely used as the tetrahedral building blocks for the molecular construction in optoelectronics, liquid crystals, and others. A large number of the experimental and theoretical investigations (Campanelli, *et al.*, 2001; Campanelli, *et al.*, 2011; Chieh, 1972; Claborn, *et al.*, 2002; Hanson, *et al.*, 2010; Knop, *et al.*, 2002; Lin, *et al.*, 2004; Ng, *et al.*, 2005; Pajzderska, *et al.*, 2002; Warner, *et al.*, 2000) have focused on the tetraphenylsilane (SiPh₄) compounds, such as X-ray crystallography, IR, Raman spectroscopy, Muon Spin Rotation/ Relaxation (μ SR) technique, and others. Based on μ SR experimental results (Jayasooriya, *et al.*, 1997; Jayasooriya, 2004; Stride, 1995), three signals corresponding to hyperfine interactions of Mu at three distinct sites were observed. The three possible Mu trapping sites are the *ortho*, *meta*, and *para* positions on one of the phenyl rings. As far as we know there is no computational literature data on muonium addition to tetraphenylsilane. In order to predict the Mu trapping site on SiPh₄, we have carried out the first principle Density Functional Theory (DFT) investigations for the SiPh₄-Mu system. In this investigation, we then examined the rotational barrier of the system and hyperfine parameters of the Mu in the single SiPh₄ molecule. In section 2 we give some details of the computational methodology used. The results and discussion are presented in section 3. Final conclusion is summarized in section 4.

2. Computational Methodology

All molecular calculations were performed with Gaussian 03 software (Frisch, *et al.*, 2004) using the DFT method. In this investigation, the single SiPh₄ molecule was chosen to simulate the tetraphenylsilane host environment. A hydrogen atom was used to represent the Mu and the three Mu trapping sites were considered; namely the *ortho*, *meta*, and *para* positions on one of the phenyl rings. The geometry optimizations for SiPh₄-Mu cluster described above were performed at the B3LYP/6-311G level of theory, allowing the position of the Mu and all the carbon and hydrogen atoms in that particular phenyl ring to relax. In order to predict in detail the rotational barrier of SiPh₄-Mu, the phenyl ring with the Mu attached was rotated about the Si₁-C₂ bond at the intervals of 10° for a complete 360° rotation. For each angle of rotation, the local energy minima of the SiPh₄-Mu cluster were calculated. Next, the isotropic and anisotropic components of the Mu hyperfine coupling constants were evaluated.

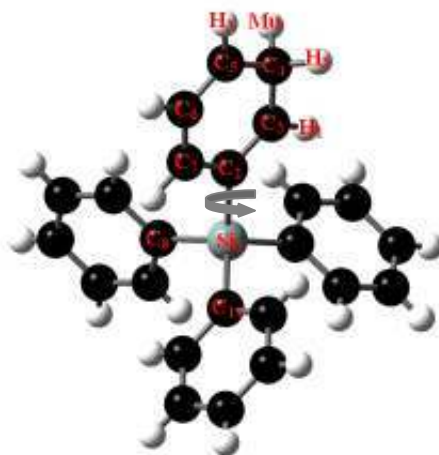


Figure 1: The numbering system used for the SiPh₄-Mu cluster (the Mu trapping at the *meta* position on a phenyl ring of SiPh₄ is shown).

3. Result and Discussion

In view of the SiPh₄-Mu results, the detailed theoretical study of the structural properties, energies, and hyperfine parameters of the Mu are estimated. The variation of Si₁-C₂ bond as a function of the rotation of the Mu-phenyl ring is plotted in Figure 2. From the figure, the corresponding results show the lengthening of Si₁-C₂ bond length is determined to vary from about 1.908 Å to 2.019 Å upon the Mu-attached phenyl ring rotation. For the *ortho* case, the calculated bond length has two maxima; one is located at the angle of about 60° and another at about 260°, respectively. Similarly, for the *meta* and *para* cases, the calculated bond length provides two maxima, which locate at the angles of about 110° and 290°. The analysis shows that the elongation of the Si₁-C₂ bond has a significant effect on the rotation dynamics for the Mu-attached phenyl ring.

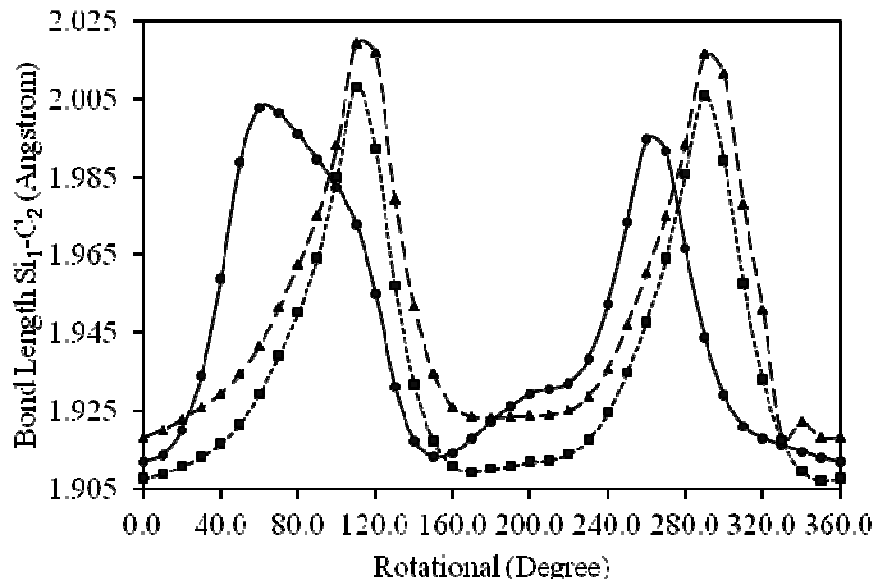


Figure 2: Estimated Si₁-C₂ bond lengths for the three SiPh₄-Mu clusters at the *ortho* (solid line with the round marker), *meta* (dash line with the triangle marker), and *para* (dotted line with the square marker) cases

The relative energies of the SiPh₄-Mu for all three cases are presented in Figure 3. Upon the rotation of the Mu-attached phenyl ring, the energy profile contains two maxima for all three different cases. For the *ortho* case, the height of the first barrier peak at about 60° is determined 0.04 eV lower than that of the second peak at the angle of about 260°. For the *meta* and *para* cases, the shapes of the energy profiles as well as the heights of the barrier peaks are very similar to each other and slightly higher than that of the *ortho* case. Moreover, we can see from the figure, the first barrier peak appears at about 110° has 0.09 eV lower energy than that of the second one at about 290°.

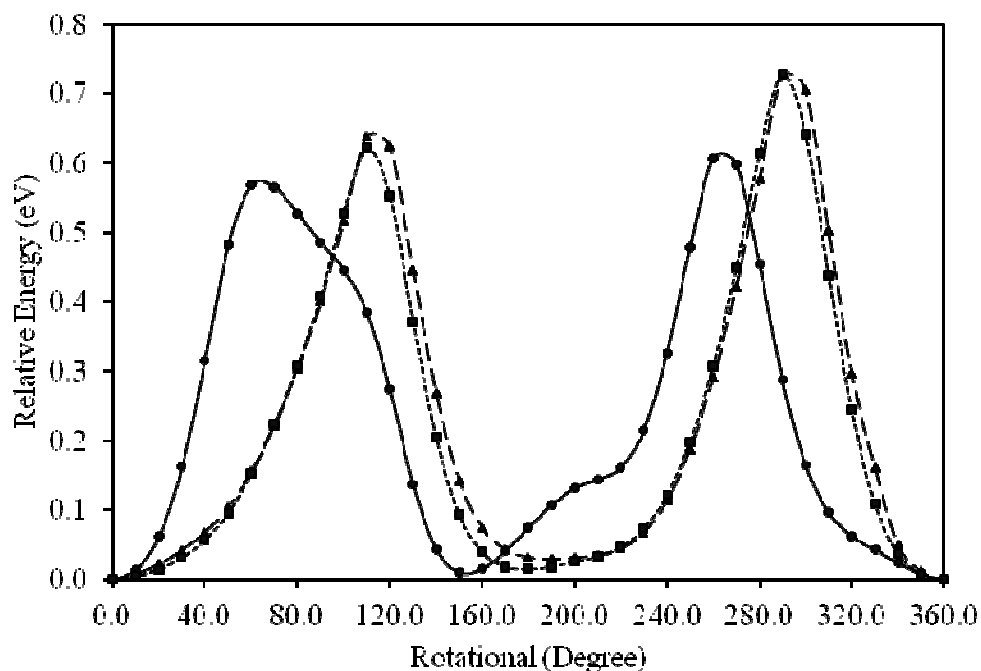


Figure 3: Computed relative energies for the three SiPh₄-Mu clusters at the *ortho* (solid line with the round marker), *meta* (dash line with the triangle marker), and *para* (dotted line with the square marker) cases

The results of hyperfine coupling constants for the Mu calculated at B3LYP/6-311G level of theory are shown in Figures 4 and 5(a)–5(c). The hyperfine coupling constants for the Mu may be divided into the contribution from the isotropic and anisotropic terms. In terms of the isotropic hyperfine coupling constant for the Mu, the corresponding values of 372.40 MHz–475.65 MHz are calculated for the three different trapping sites. For the *ortho* case, the isotropic value varies greatly with a significant drop when the rotational angle appears about 60°, which corresponds to the first barrier peak. Similar to the *meta* case, the corresponding value varies as well as a significant drop when the angle is located about 110°. For the *para* case, the value of isotropic component only shows a very little variation upon the rotational of the Mu–phenyl ring. The largest component for the anisotropic term, B_{aa} only provides very small magnitude and opposite in sign, only 1% to 2% of the corresponding isotropic value. During the rotational of the Mu–phenyl ring, the anisotropic term for the *ortho* case has significant variation if compared with the other two cases. Furthermore, the variation for the *para* case becomes very small with the rotational angle. The total hyperfine coupling constant for the Mu is remained, despite any variation in an anisotropic component.

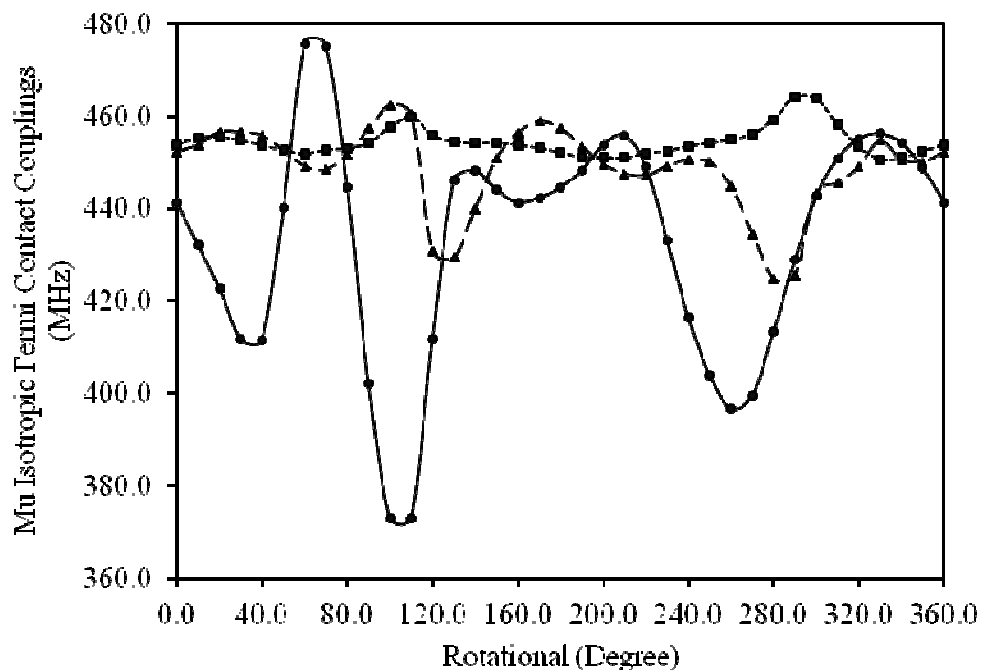
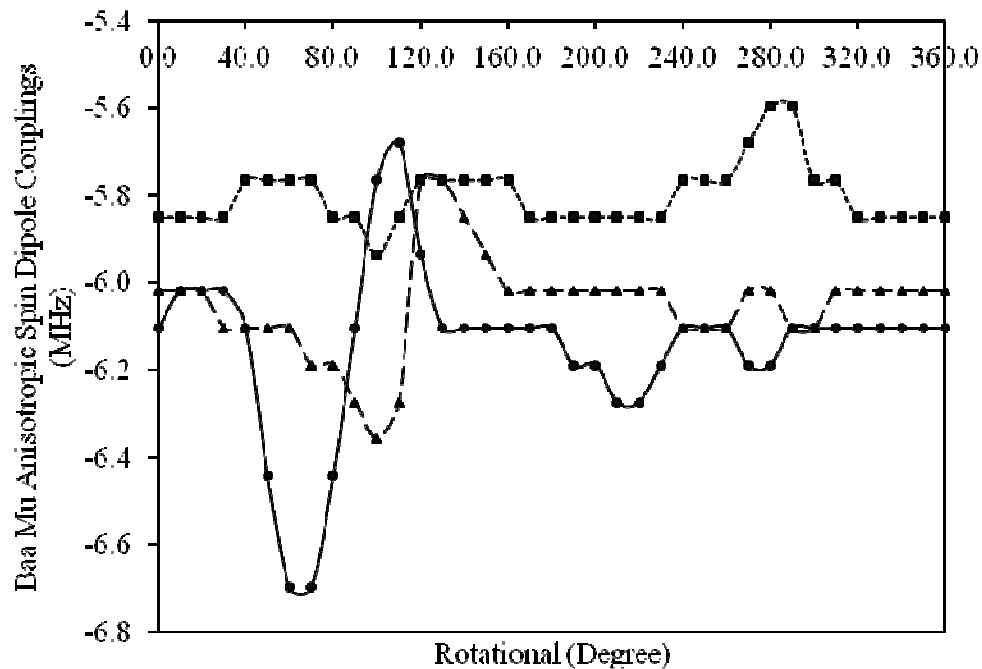
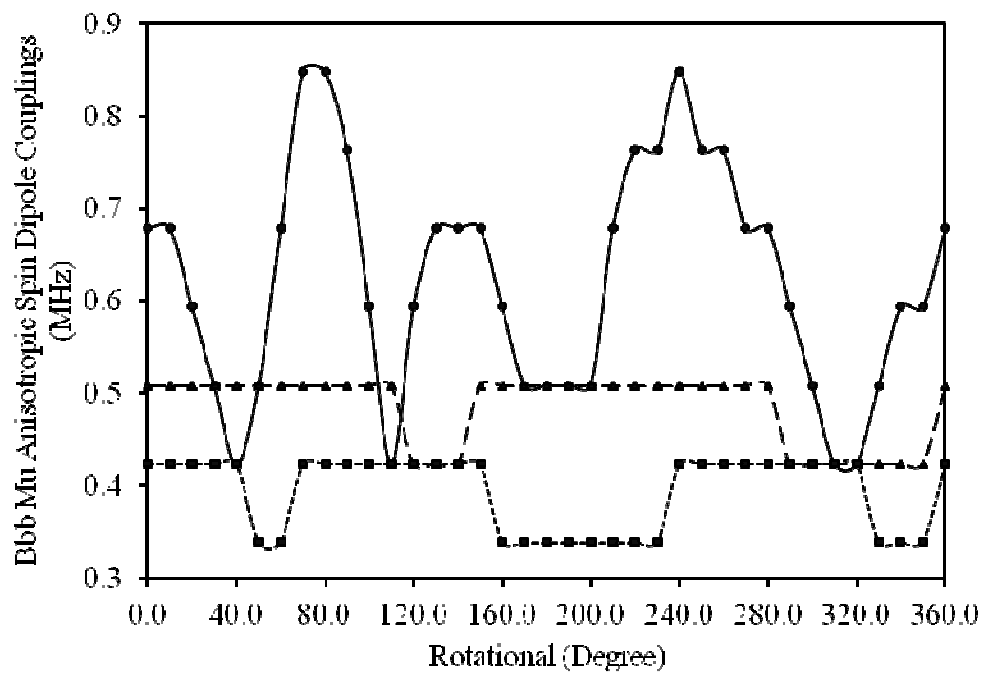


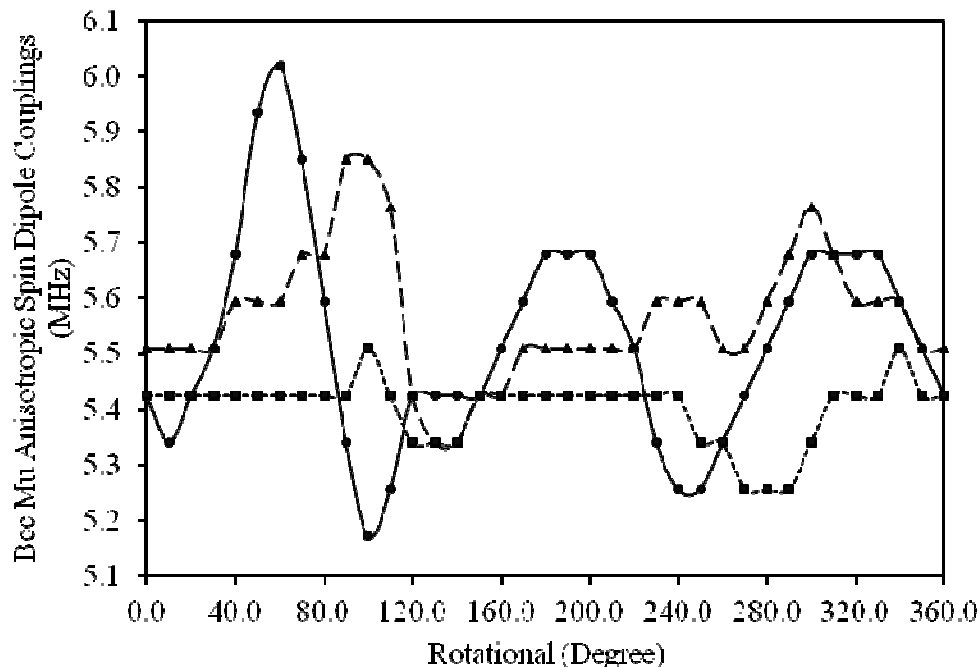
Figure 4: Calculated Mu isotropic hyperfine coupling constants for the three SiPh₄-Mu clusters at the *ortho* (solid line with the round marker), *meta* (dash line with the triangle marker), and *para* (dotted line with the square marker) cases



5(a)



5(b)



5(c)
Figure 5: Predicted (a) Baa, (b) Bbb, and (c) Bcc components of Mu anisotropic hyperfine coupling constants for the three SiPh₄-Mu clusters at the *ortho* (solid line with the round marker), *meta* (dash line with the triangle marker), and *para* (dotted line with the square marker) cases

4. Conclusion

In this study, the calculated Si₁-C₂ bond length was varied in the range of 1.908 Å–2.019 Å with the rotational of the Mu-attached phenyl ring. For all three cases, the energy barrier of the system was calculated for the Mu-attached phenyl ring rotational. Each energy profile shows two barriers. For the *meta* and *para* cases, the shape of the energy profiles, as well as the locations of the barrier peaks were quite similar to each other. The angle for the first peak was found to be about 110° and the second one at about 290°. While the shape of the energy profile for the *ortho* site was slightly different with the peaks were found at about 60° and 260°. The height of energy barrier for the phenyl ring rotation in the SiPh₄-Mu system was found to be less than 0.8 eV. The largest component for the Mu hyperfine coupling constants was contributed from the isotropic term. The corresponding value was varied greatly for the *ortho* and *meta* cases with the completed rotation. Furthermore, a very small and negative of the anisotropic term was available to determine, as well as the value was kept more or less small variation upon the Mu-attached phenyl ring rotation.

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