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FIRST PRINCIPLES INVESTIGATIONS OF ELECTRONIC STRUCTURES AND HYPERFINE INTERACTIONS OF MUONIUM IN TETRAPHENYLSILANE

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Abstract

In this study, the equilibrium structures of muoniated-tetraphenylsilane (SiPh₄-Mu) were stabilized using the first principle investigations employing the Density Functional Theory (DFT) technique. Three Muonium (Mu) trapping sites were considered in the investigations, namely ortho, meta, and para positions on one of phenyl rings. The geometry optimizations for all the systems leading to local energy minima were investigated. The calculated total energy of all the systems were very similar, with the differences of energy being only 0.04 eV lower between the para case and the other two cases. With the DFT procedure, the Mu hyperfine interactions were examined. The major contribution to the Mu hyperfine interactions was from isotropic component with the corresponding values of 441.28 MHz, 452.21 MHz, and 453.78 MHz for the ortho, meta, and para cases, respectively. The anisotropic component was also predicted and it was more and less 6 MHz for all three sites.

Keywords: Density Functional Theory, Tetraphenylsilane, Muonium, Hyperfine Interactions

1. Introduction

In recent years, 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 SiPh₄ compounds, such as X-ray crystallography, IR, Raman spectroscopy, Muon Spin Rotation/Relaxation (μ SR) technique, and others. Since the early stages of the μ SR experimental results (Jayasooriya, *et al.*, 1997; Jayasooriya, 2004; Stride, 1995), three possible positions (*ortho*, *meta*, and *para* positions) of the Muonium (Mu) trapped one of the phenyl rings. In order to study the addition of Mu in the single SiPh₄ molecule, we then examined the electronic structures, energies, and hyperfine parameters of the Mu in the single SiPh₄ molecule. Section 2 describes the computational methodology of this work. The SiPh₄-Mu clusters were studied using the density functional theory (DFT) calculations. The geometries of the SiPh₄-Mu clusters were optimized to calculate their structures, energies, and the Mu hyperfine parameters. The results and discussion were presented in Section 3. Section 4 presents the conclusion of this work.

2. Computational Methodology

The latest crystallographic data from Cambridge crystallographic data centre (CCDC) was chosen in this work. We have utilized the DFT procedure using the Gaussian 03 software package (Frisch, *et al.*, 2004). In this work, we have used a single SiPh₄ molecule to simulate the tetraphenylsilane host environment. A hydrogen atom was used to represent the Mu. Three Mu trapping sites were considered, namely the *ortho*, *meta*, and *para* positions on one of the phenyl rings. Figure 1 present the SiPh₄ cluster model including Mu. Using the SiPh₄-Mu cluster,

the geometry optimization calculations at the B3LYP/6-311G level of theory were performed, allowing the position of the Mu and all the carbon and hydrogen atoms in that particular phenyl ring to relax. Then, the optimized geometries were determined to calculate the local energy minima of the system. As well, the isotropic and anisotropic components of the Mu hyperfine coupling constants were evaluated.

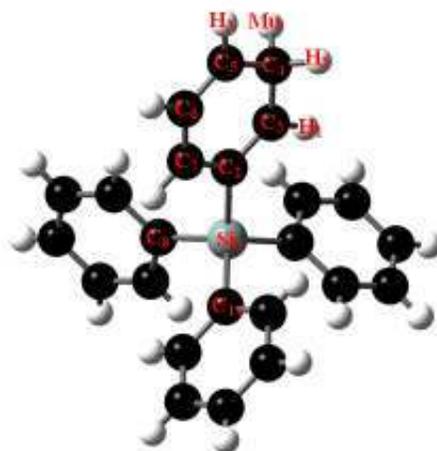


Figure 1: The numbering system used for the SiPh₄-Mu cluster (the Mu trapping at the *meta* position on a phenyl ring of SiPh₄ is shown).

3. Result and Discussion

All molecular calculations have been carried out using the Gaussian 03 package. In Table 1, the results of the geometry calculations for Mu trapped at the three different positions on SiPh₄ are recorded. For the raw SiPh₄ cluster, the Si₁-C₂ bond length is 1.873 Å (Claborn, *et al.*, 2002). As we can be seen from table, the Si₁-C₂ bond lengths are 1.912 Å, 1.918 Å, and 1.908 Å for Mu at the *ortho*, *meta*, and *para* sites, respectively, an increase of 1.9%-2.4% from the raw Si₁-C₂ bond length of SiPh₄. Even though the elongation of the Si₁-C₂ bond length is quite small, it leads to a clear picture that the elongation of the Si₁-C₂ bond length involved in rotating the Mu-attached phenyl ring. The optimized C-Mu bond lengths at the *ortho*, *meta*, and *para* sites are 1.1045 Å, 1.1041 Å, and 1.1042 Å, respectively, which are approximately the same as is seen for the C-H bond length (1.1 Å) in organic compounds. For the Si₁-C₂-C₃ bond angle, the calculated values for the *meta* and *para* sites are 121.84° and 123.12°, quite close to the raw angle in SiPh₄, but the *ortho* site has a significantly lower value. A similar trend for the C₁₄-Si₁-C₂-C₃ dihedral angles but the value for *ortho* site gets much greater.

Table 1: Selected bond parameters in the optimized SiPh₄-Mu clusters

Parameters	<i>ortho</i>	<i>meta</i>	<i>para</i>
Bond Length (Å)			
Si ₁ -C ₂	1.91197	1.91828	1.90766
C ₃ -Mu	1.10448	-	-
C ₄ -Mu	-	1.10414	-
C ₅ -Mu	-	-	1.10416
Bond Angle (°)			
Si ₁ -C ₂ -C ₃	119.15937	121.84285	123.12294
H ₁ -C ₃ -Mu	103.01299	-	-
H ₂ -C ₄ -Mu	-	103.21375	-
H ₃ -C ₅ -Mu	-	-	103.28947
Dihedral Angle (°)			
C ₁₄ -Si ₁ -C ₂ -C ₃	160.82271	129.41932	132.36345

In Table 2, the total energies of calculated structural are presented. The values are between -33100.49 eV and -33100.46 eV, which are determined a little lower than the raw energy value of SiPh₄ system. The zero of energy is chosen as that corresponding to that of the *para* site. The calculated energy difference between the *para* and *meta* sites is about four times as much as that the energy difference between the *ortho* and *para* sites of 0.01 eV. The α - spin HOMO-LUMO energies are also calculated and the values in a range of 3.99 eV-4.115 eV are summarized in Table 2. The energy gaps for the three different positions are very close to each other.

Table 2: Total and frontier molecular orbital energies (eV) of the SiPh₄-Mu clusters

	<i>ortho</i>	<i>meta</i>	<i>para</i>
Total Energies	-33100.486246	-33100.458167	-33100.495119
Relative Energies	0.009	0.037	0.000
α -spin HOMO	-4.549199	-4.516818	-4.591377
α -spin LUMO	-0.558378	-0.471573	-0.476743
α -spin HOMO-LUMO Gaps	3.990822	4.045244	4.114633

In Table 3, the hyperfine coupling constants for the Mu at the three different positions are summarized. As can be seen in the table, for the *meta* and *para* sites, the values of Mu isotropic hyperfine coupling constants are quite similar, which are 452.21 MHz and 453.78 MHz, respectively. For the *ortho* site, the value is 441.28 MHz, which is smaller than those of the other two sites. Additionally, the Baa component of the averaged anisotropic hyperfine coupling constants is also predicted to be -6.10 MHz, -6.02 MHz, and -5.85 MHz for the *ortho*, *meta*, and *para* sites, respectively, which is much smaller than the isotropic component and is opposite in sign.

Table 3: Calculated isotropic and anisotropic hyperfine coupling constants for Mu in the SiPh₄-Mu clusters

Mu Positions	Isotropic Fermi Contact Couplings (MHz)	Anisotropic Spin Dipole Couplings in Principal Axis System (MHz)		
		Baa	Bbb	Bcc
<i>ortho</i>	441.279505	-6.103620	0.678180	5.425440
<i>meta</i>	452.215624	-6.018848	0.508635	5.510213
<i>para</i>	453.777926	-5.849303	0.423863	5.425440

4. Conclusion

In this study, all calculations have been performed using the Gaussian 03 program. We have investigated the three possible trapping sites for Mu in the phenyl ring of the SiPh₄-Mu at the DFT/B3LYP/6-311G level of theory. For the SiPh₄-Mu, the calculated results of the SiPh₄-Mu at B3LYP/6-311G level indicate that the predicted Si₁-C₂ bond lengths for three Mu different positions were slight longer than that of the bond length of the SiPh₄ system. Also, the C-Mu bond length was predicted close to the value of 1.1 Å. For the *para* position, the value of the energy is the lowest if compared with the other two positions. The isotropic hyperfine coupling constants were as well measured in the SiPh₄-Mu system and the values were 441.28 MHz, 452.21 MHz, and 453.78 MHz, which correspond to the *ortho*, *meta*, and *para* sites, respectively. Finally, a very small value of the anisotropic component was also available to be predicted in this study.

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