

Geometry Optimization Skills of DFTB: Simple to Complex Molecular Systems

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Abstract - As the Density-functional theory (DFT) is an exact theory in principle for computing ground state electronic structures of the multi-electron and many-body systems, its approximate variants currently being used are far from fail-safe. One of the very fundamental problem that has become apparent is its inability to account the substantial effect of van der Waals (vdW) type interactions exist in large molecular assemblies. To overcome such problem, a density functional tight binding (DFTB) theory whose fundamental formulation is based on the DFT but implements Slater–Kirkwood model and Slater–Koster files with a focus on solid state systems having vdW interactions as a binding force has been widely used recently. Its self-consistent charge (SCC) approach is more promising theoretical model due to introducing self-consistent calculation of Mulliken charges. Present work is aimed at evaluating the geometry optimization skills of such DFTB method while applying to very simple to quite complex molecular systems of the order: water, benzene, crystalline 1,4-bis (tri-methylsilyl) benzene, and crystalline siloxane. We fully optimized the isolated molecules of each of them as well as the unit cell geometries of the last two specimens and measured the dimensions of the particular sets of bond lengths, bond angles, and torsional angles in each optimized geometry. These values are found to be in an excellent agreement with the concerned experimental values. It makes the DFTB method very versatile and superb quantum mechanical model for computing ground state electronic structures.

Keywords - DFTB, Self-Consistent Charge (SCC), Geometry Optimization, Molecular Geometry, Crystalline Molecular Systems.

I. INTRODUCTION

Molecular geometry or molecular structure is the three-dimensional (hereafter, 3D) arrangement of atoms within a molecule [1]. It is not only used to determine many of the properties of a substance such as polarity, magnetism, phase, color, and chemical reactivity but also equally used to predict biological activity, to design drugs or depict the function of a molecule. Since, the molecular and structural formulae of the compounds cannot represent the orientation of the atoms bonded each other by covalent bonds, imaging the actual atomic orientations in the 3D space is very essential. There are several experimental methods such as x-ray crystallography, neutron diffraction, infrared spectroscopy, Raman spectroscopy, electron diffraction, and microwave spectroscopy can be used to image molecular structure in the 3D space [2]. In theoretical/ computational

research, the ground state molecular structure that is referred to the structure having a minimum electronic energy can be produced by a series of computing process or repeated mathematical calculations performed on the molecule. Such procedure calculates the wave function and energy at a starting geometry and then proceeds to search a new geometry of a lower energy. This repeated computational process that tests various possibilities to see which atomic arrangements and the electrons around the atom will give the lowest energy value is called geometry optimization [3].

The Schrodinger's wave equation that associates a molecular Hamiltonian in terms of a Hamiltonian operator representing the energy of the electrons and nuclei in a molecule is the main part of the wave mechanical model [4]. The exact computational solution for this equation involves a series of electronic energy calculations by estimating

specific sizes and shapes of the molecules. Unfortunately, an exact solution for this equation cannot be obtained for multi-electron atomic or molecular systems and therefore, many approximations have been used to develop different types of theoretical models. One of them is Density-functional theory (hereafter, DFT) [5]. Even though it is widely used especially in investigating ground state electronic structures of the multi-electron and many-body systems [5], [6], [7], [8], it has many notable limitations [9] with the main one being lack of proper mathematical formulations to account the pronounced effect of long-range attraction or van der Waals (hereafter, vdW) interaction [10], [11], [12], [13], [14]. Thus, the quantum mechanical geometry optimization calculations of DFT may not produce global minimum structure for the complex crystalline molecular systems.

More recently, the Density-Functional based Tight-Binding approximation (hereafter, DFTB) [7], [15], [16], [17], [18], [19] whose fundamental formulation is based on the DFT but being one or two orders of magnitude faster has been implemented in the DFTB+ quantum mechanical package for calculating electronic structures. It not only allows to perform calculations for large and complex molecular systems over long timescales even on a desktop computer but also relatively computes more accurate results typical of standard time-dependent DFT at a low computational cost. Mathematically, it is an approximate Kohn-Sham density functional theory (KS-DFT) scheme with an LCAO representation of the KS orbitals:

$$\Psi_n(r) = \sum_{i\alpha} c_{i\alpha}^{(n)} \varphi_{i\alpha}(r) \quad (1)$$

Where, Ψ_n = Kohn-Sham wave function; i = Index of an atom; α = Index of an orbital; c = superposition of the valence orbitals; $\varphi_{i\alpha}$ = atomic-like wave functions centered at the atomic sites r (atom centered).

The tight binding (TB) secular equation is:

$$\sum_{j\beta} (H_{i\alpha,j\beta} - E_n S_{i\alpha,j\beta}) c_{j\beta}^{(n)} = 0 \quad (2)$$

Where, $H_{i\alpha,j\beta}$ = TB Hamiltonian Matrix;

$S_{i\alpha,j\beta}$ = Overlap matrix; and E_n = Eigen value

Here,

$$H_{i\alpha,j\beta} = \langle \varphi_{i\alpha} | \hat{h} | \varphi_{j\beta} \rangle \text{ and } S_{i\alpha,j\beta} = \langle \varphi_{i\alpha} | \varphi_{j\beta} \rangle \quad (3)$$

Where, $\hat{h} = [-\frac{1}{2}\nabla^2 + V_{eff}(r)]$ and $V_{eff}(r) = \sum_i V_0^i(r)$.

In the DFTB Hamiltonian, the matrix elements are approximated as:

$$H_{i\alpha,j\beta} = \begin{cases} E_{i\alpha}^{neutral\ freeatom} & i\alpha = j\beta \\ \langle \varphi_{i\alpha} | -\frac{1}{2}\nabla^2 + V_0^i + V_0^j | \varphi_{j\beta} \rangle & i \neq j \\ 0 & \text{otherwise} \end{cases} \quad (4)$$

Since the indices i and j in equation 4 indicate the atoms on which the wave-functions and potentials are centered, only two-center Hamiltonian matrix elements are treated and explicitly evaluated in combination with the two-center overlap matrix elements [16]. The total energy approximated is equivalent to the zeroth-order expansion of the Kohn-Sham total energy in DFT with respect to charge density fluctuations and is commonly called “non-self-consistent-charge DFTB” (NCC-DFTB) approach [17], [18]. On the other hand, the second-order approach is equivalent to a “self-consistent-charge DFTB” (hereafter, SCC-DFTB) [20], [21] in which the charge distribution in a molecule, represented by point charges, is obtained in an iterative self-consistent manner by taking into account charge interactions between atoms. Both DFTB approaches implement Slater–Kirkwood model [22] and Slater–Koster files (hereafter, SK-files) [23], [24] with a focus on solid state systems having vdW interactions. That is why, they become very useful theoretical methods for investigating the electronic structures and dynamics of the complex crystalline molecular systems [25].

As the self-consistent calculation of Mulliken charges is introduced in the SCC procedure and corresponding nuclear forces are derived, the SCC-DFTB method enables one to cope with many heteroatomic complex molecular systems [26], [27] where charge balance between atoms is crucial. Presently, we selected such method for computing the most stable electronic structures of the very simple to quite complex crystalline molecular systems. The simple to complex molecular specimens of our choice are in the order: water (H_2O) molecule, benzene (C_6H_6) molecule, crystalline 1,4-bis (tri-methylsilyl) benzene molecule ($C_6H_4[Si(CH_3)_3]_2$), and crystalline siloxaalkane molecule ($C_{54}H_{124}O_3Si_{14}$). The first triatomic molecular specimen with two lone pairs of electrons on the O atom (chart 1a), is much simple and smaller than almost all other molecules; the second dodeca-atomic specimen is little complex due to its electronic delocalization above and below the plane of the ring (chart 1b); the third (36 atoms/molecule, 2 molecules/per unit cell) molecular specimen is more complex due to its crystalline geometry and tri-methyl end groups at the periphery of the phenylene ring (chart 1c); and the last (195 atoms/molecule, 2 molecules/unit cell)

molecular specimen is the most complex system due to its crystalline geometry with closed topology (chart 1d) in which significant intra- and inter- molecular vdW type interactions exist. This research work is mainly aimed at investigating the most stable electronic structures of the very simple to complex molecular specimens by employing computationally cheap yet decent SCC-DFTB method and unveiling its geometry optimization skills. The structure of this paper is as follows. The computational methods we employed are outlined in section 2. The results and discussion are presented in section 3. A summary and conclusions are given in section 4.

II. COMPUTATIONAL METHODS

In order to optimize the geometry of the molecular specimens shown in chart 1, we used the initial atomic Cartesian coordinates of them as trial structures. The trial structures for H_2O and C_6H_6 were built by using GaussView visualization application [28], and those for the crystalline 1,4-bis (tri-methylsilyl) benzene [29], [30] and siloxaalkane molecules [31] were obtained from the respective x-ray crystallography. While optimizing the isolated molecule of all the specimens, we set the DFTB keyword "Periodic = No" [32] and the trial structure was specified explicitly by using the general format (DFTB keyword: "GenFormat") method. The conjugate gradient algorithm was selected as a driver to change the geometry of the input structure while the calculations were on the fly. The force component for controlling the optimization process was set to an *ab initio* level i.e. $1\text{e-}6$ as its maximal absolute value. No any geometry constraints were specified i.e. all the atoms were allowed to move freely. While optimizing the unit cell geometries of crystalline 1,4-bis (tri-methylsilyl) benzene and siloxaalkane molecules separately, more additional DFTB keywords and parameters were set as: "Periodic = Yes" followed by proper specification of the respective lattice vectors; the recommended force component maximal absolute value $1\text{e-}4$ for being these optimizations computationally expensive; the dispersion energy parameter sets available elsewhere [25], [32] for addressing vdW interactions; and the k-points and weights data sets available elsewhere [32] for the Brillouin-zone integration. The respective lattice vectors used are $a = 6.541, 0.000, 0.000$; $b = 0.000, 10.545, 0.000$; $c = -1.092, 0.000, 10.338$; and $a = 11.84, 0.000, 0.000$; $b = 0.000, 14.619, 0.000$; $c = -3.884, 0.000, 23.874$. In both type of optimizations, we set the keywords "Hamiltonian = DFTB" and "SCC=Yes" for forcing the DFTB script to implement DFTB Hamiltonian and SCC calculations. The SCC tolerance was set to $1\text{e-}5$ as its stopping criteria and the Slater-Koster files of mio-1-1

set were explicitly used for every pairwise permutation atomic types [32].

III. RESULTS AND DISCUSSION

3.1 SCC-DFTB optimized geometry of water molecule

In the liquid state, the water molecules are confined to some volume by strong intermolecular attraction between them. The type of intermolecular attraction is hydrogen bond that is usually formed between the partially negatively charged O atom of one H_2O molecule and the partially positive charged H atom of nearby molecules. With enough heat energy, water molecules escape out from the liquid state by overcoming this binding force also known as evaporation which makes the water molecules more isolated and experience very less or almost no intermolecular force of attraction. Here, we have realized the free water molecule while optimizing it by SCC-DFTB without imposing any sorts of intermolecular interactions. The optimized geometry of the isolated water molecule visualized by Jmol [33] is shown in Figure 1. The red and blue spheroids represent O and H atoms respectively. As the molecular geometries can be specified mostly in terms of three parameters namely bond length: an average distance between the nuclei of two atoms bonded together in any given molecule; bond angle: angle formed between three atoms across the two bonds; and torsional angle: angle between the plane formed by the first three atoms and the plane formed by the last three atoms, we explicitly measured the theoretically calculated values of first two parameters in H_2O and presented here. Each O-H covalent bond length is measured as 0.0975 nm and the H-O-H bond angle is 103.2° . These theoretically calculated values are as close as the experimentally (spectroscopic and diffraction methods) determined values: O-H bond length = 0.09584 nm and H-O-H bond angle = 104.45° . In a H_2O molecule, there are four electron pairs on the outermost shell of central O atom, out of which two pairs are in between O and H atoms and involved in covalent bond formation called bond pairs and the remaining two pairs are free non-bonding electron pairs called lone pairs. These electron pairs form electron cloud around the water molecule that spreads out approximately tetrahedrally around the central oxygen atom and repel each other. The magnitude of the repulsion is according to valence shell electron pair repulsion (VSEPR) theory: the repulsion between lone pair-lone pair > lone pair-bond pair > bond pair-bond pair. While the lone pairs repel themselves, they push the two O-H bond pairs more closely. As a result, the H-O-H bond angle is distorted from the tetrahedral

geometry resulting "V-shaped" structure as shown in Figure 1.

3.2 SCC-DFTB optimized geometry of Benzene molecule

Benzene is composed of six carbon atoms joined in a ring with one hydrogen atom attached to each. Being a bigger hydrocarbon and a non-polar in nature, benzene molecules in liquid state are bound by weak vdW type interaction. It belongs to a class of volatile organic compounds due to having high vapor pressure (12.7 kPa at 25 °C) and low boiling point (80.1°C at 1 atm. pressure). That is why, large number of benzene molecules evaporate from the liquid state and enter into the surrounding air where they remain farther apart to each other and move freely due to very less or almost no interactions between themselves. With this, we realized a single free benzene molecule and optimized by SCC-DFTB without imposing any sorts of intermolecular interactions. The optimized geometry of such isolated benzene molecule visualized by Jmol [34] is shown in Figure 2. The cyan and blue spheroids represent C and H atoms respectively. This geometry has all six C-C bond lengths 0.139 nm which is consistent with the value determined by X-ray diffraction as 0.140 nm. This C-C bond length is intermediate if we compare it with the lengths of a double bond (bond length = 0.135 nm) and a single bond (bond length = 0.147 nm). It indicates that benzene has partial double bond characters, in which the electrons are not associated with any single atom or single covalent bond but are likely to be found equally anywhere along the chemical bonds. Such dynamic behavior of electrons inside the ring is called electrons delocalization. In order to accurately reflect the nature of bonding and electrons delocalization, we have depicted the benzene molecule with a circle inside a hexagonal ring, as shown in Figure 2. The genius of the electrons delocalization model can be understood in detailed by hybridization and valence bond theory concepts [35]. Moreover, each C-C-C (interior angle) and H-C-C (exterior) bond angle in an optimized geometry of benzene is measured as 120°, which is exactly equal to C-C-C bond angle but unequal to H-C-C bond angle of the corresponding cyclic alkane (cyclohexane). This dissimilarity is because of the angular strain in the cyclohexane molecule. Similarly, each H-C-C-H, H-C-C-C, and C-C-C-C torsional angle is measured as 0°, 180°, and 0° respectively. All these bond angles and torsional angles of benzene suggest that the six carbon atoms form a perfectly regular hexagon with no angular strain at all giving exactly a planar hexagonal shape unlike that of cyclohexane.

3.3. SCC-DFTB optimized Geometry of 1,4-bis (tri-methylsilyl) benzene

The crystalline 1,4-bis(tri-methylsilyl)benzene molecule (molecular formula = $C_6H_4[Si(CH_3)_3]_2$; Molecular weight = 222.47) has a phenylene ring and two sets of peripheral tri-methyl end groups. Unlike in the molecule shown in chart 1d, the phenylene ring of this molecule remains completely open to the surrounding molecules as shown in chart 1c. According to the crystallography, it has a monoclinic geometry with two molecules per unit cell [30]. In our DFTB optimization calculations, we at first optimized its isolated molecule without imposing any sorts of intermolecular interactions, and then optimized its unit cell under periodic boundary condition (hereafter, PBC) with dispersion energy parameters.

3.3.1 Isolated 1,4-bis (tri-methylsilyl) benzene molecule

The optimized and the experimental geometries of the isolated 1,4-bis (tri-methylsilyl) benzene molecule are shown in Figure 3a and Figure 3b. As the molecular geometries are specified mostly in terms of the parameters: bond lengths, bond angles, and torsional angles, we have carefully chosen some sets of them that determine atomic orientations more precisely in 3D space. The concerned experimental (hereafter, expt.) values are given in the parenthesis after each theoretical value. All the values given here are in average. The bond lengths are measured as: C-H and C-C bond lengths in the phenylene ring are 0.109 nm (expt. 0.095 nm) and 0.141 nm (expt. 0.140 nm) respectively; C-H bond length in each CH_3 group is 0.11 nm (expt. 0.098nm); C-Si bond length from each ipso carbon of phenylene is 0.189 nm (exp. 0.188 nm); and Si-C bond length to each methyl carbon is 0.19 nm (expt. 0.186 nm). The interior bond angle of the phenylene ring formed by ipso carbon atom is 116.8° (expt. 117.3°) and by rest of the carbon atom is 121.5° (expt. 121.8°) while the exterior bond angle formed by the ipso carbon atoms with the Si atoms are measured as 122.4° (expt. 123°) and 120.8 (expt. 120.2°). Similarly, the ipso C-Si- CH_3 bond angle is 109.9°(expt. 109°) and H-C-H bond angle in each methyl groups is 107.7° (expt. 109.4°). The major torsional angles we measured here includes each ipso carbon and each Si atom along with phenylene H and C atoms, are 0.3°(expt. 0.5°) and -179.8° (expt. -179.5°) respectively.

The analysis of these parameters suggest that the electrons undergo delocalization in the central phenylene ring as explained in subsection 3.2 and the phenylene ring interacts with the two sets of trimethyl groups bonded at the

periphery. This interaction is most commonly called steric effects of the alkyl groups that always influences the shape or conformation of the molecules [35]. Such steric hindrance creates constraints on the phenylene and directly affects its torsional angles. As a result, it is forced to adjust particular conformation and becomes distorted hexagonal shape. That is why, the bond angles and torsional angles measured in the optimized geometry are found to be deviated compare to original benzene ring. Moreover, by comparing the experimental and theoretical structures shown in Figure 3a and Figure 3b, one can reconfirm the above mentioned features for the optimized structure that the orientations of the phenylene ring and the two axial C-Si bonds are well reproduced. Besides that the orientation and conformation of the six peripheral methyl groups attached to two Si atoms are also not noticeably different.

3.3.2 Crystalline 1,4-bis (tri-methylsilyl) benzene molecule

In contrary to the isolated 1,4-bis (tri-methylsilyl) benzene molecule where the central phenylene ring experiences steric effects caused by the peripheral methyl groups, the additional intermolecular interactions in crystalline form force the molecules present in the unit cell to adjust in different conformations. As a result, more distortions especially in the bond angles and torsional angles are expected in the crystalline form. Since, there are several sets of bond lengths, bond angles, and torsional angles in two differently aligned molecules present in the unit cell as shown in Figure 4a, we listed here the average values of few sets of them that are mostly involved to affect the orientations of the phenylene rings and the unit cell molecules. The concerned experimental (hereafter, expt.) values are listed in the parenthesis. The bond lengths are measured as: C-H, C-C bond lengths in each phenylene ring are 0.11 nm (expt. 0.095nm), 0.141 nm (expt. 0.140 nm) and C-H bond length of CH₃ and C-Si bond length in each molecule is 0.11 nm (expt. 0.098 nm) and 0.187 nm (exp. 0.188 nm) respectively. The interior bond angle of each phenylene ring formed by the ipso carbon atoms is 117.7° (expt. 116.8°) and by rest of the carbon atoms is 121.1° (expt. 121.6°) while the exterior bond angle formed by each ipso carbon atom with each Si atom is measured as 121.3° (expt. 120.2°). Similarly, the ipso C-Si-CH₃ bond angle and the H-C-H bond angle in each CH₃ group is measured as 108.6°(expt. 109°) and 108.3° (expt. 109.4°) respectively. The major torsional angles we measured here includes each ipso carbon and each Si atom along with phenylene H and C

atoms, are 0.9°(expt. 0.5°) and -179.3° (expt. -179.5°) respectively.

The analysis of these values for the two unit cell molecules suggest that the central phenylene rings are nonplanar and have electrons delocalization inside the rings as in isolated molecule (subsection 3.3.1). The steric hindrance generated by the six peripheral methyl groups of each molecule along with the additional intermolecular non-bonding interactions creates more constraints on each phenylene ring as well as on peripheral methyl groups resulting more distorted conformations of them in compare to isolated 1,4-bis (tri-methylsilyl) benzene. In addition to this, the experimental and theoretical structures of the unit cell shown in Figure 4a and Figure 4b are found to be resembled well. It reconfirms the above mentioned features for the optimized structure that the orientations of the phenylene rings and the alignment of the two molecules in the unit cell are almost reproduced well. Besides that the orientation and conformation of the six peripheral methyl groups present in each unit cell molecule are also not significantly different.

3.4. SCC-DFTB optimized geometry of siloxaalkane molecule

The experimentally synthesized crystalline siloxaalkane molecule (molecular formula = C₅₄H₁₂₄O₃Si₁₄; Molecular weight = 1214.79) has a phenylene ring encased in three long siloxaalkane spokes as shown in chart 1d. In this molecular system, both intra-molecular interactions (between the phenylene ring and surrounding framework) and intermolecular interactions exist in the crystal. According to the crystallography, it has a monoclinic geometry with two molecules per unit cell. The experimentally observed three stable positions of the phenylene upon 1 π rotation confirmed three stable structures of the siloxaalkane molecule [25], [31]. Among them, we have chosen the most stable structure as a trial structure for SCC-DFTB optimization. At first, we fully optimized its isolated molecule without imposing any sorts of intermolecular interactions and then optimized its unit cell under PBC with dispersion energy corrections parameters.

3.4.1 Isolated siloxaalkane molecule

The proper specification of the molecular geometries can only be drawn up if the values of the parameters such as bond lengths, bond angles, and torsional angles are known. Here, we have carefully chosen some of them that are involved to determine the molecular orientations more

precisely in 3D space. The theoretically estimated values of these parameters are given in average followed by the concerned experimental (hereafter, expt.) values in the parenthesis. The bond lengths are measured as: C-H and C-C bond lengths in the phenylene ring are 0.110 nm (expt. 0.094 nm) and 0.141 nm (expt. 0.140 nm) respectively; axial C-Si bond length is 0.187 nm (expt. 0.188 nm) and C-C, C-H, C-Si and Si-O bond length in each siloxaalkane arm is 0.153 nm (expt. 0.150 nm), 0.110 nm (expt. 0.097 nm), 0.180 nm (expt. 0.180 nm) and 0.174 nm (expt. 0.160 nm) respectively. Similarly, the free space around the phenylene unit is approximated by measuring the distance between the nearest carbon atom of the phenylene ring and the oxygen atom of each siloxaalkane arm (d_{CO}). They are measured as 0.407 nm (expt. 0.390 nm) and 0.523 nm (expt. 0.550 nm) for the two closest arms and one farthest arm respectively. The interior bond angles of the phenylene ring formed by the ipso carbon atoms are 117.6° (expt. 113.5°) and 117.6° (expt. 117.0°) and those by rest of the carbon atoms are 121.2° (expt. 123.0°) and 121.2° (expt. 118.5°) while the exterior bond angles formed by the ipso carbon atom of phenylene with each Si atom are measured as 121.9° (expt. 122°), 120.4° (expt. 120°) and 121.9° (expt. 123°). Similarly, the phenylene ipso C-Si-CH₃ bond angles are 107° (expt. 107.6°), 109.3° (expt. 108.3°), and 107° (expt. 108.2°); all the C-Si-C bond angles in each siloxaalkane arm are in between max. 113° (expt. 113.6°) and min. 108.6° (expt. 106°); each H-C-H bond angle in each -CH₂ group is 106.9° (expt. 107°); each H-C-H bond angle in each -CH₃ group is 108.4° (expt. 109°), and three Si-O-Si bond angles in three different arms are 141.1° (expt. 162.9°), 141.1° (expt. 169.4°), and 147.4° (expt. 172.6°). The major torsional angles of the phenylene with respect to three siloxaalkane arms are: in one side 69.5° (expt. 64.2°), -49.7° (expt. -55°), -169.3° (expt. -179°) and in opposite side -109.6° (expt. -99°), 11.6° (expt. 21.3°), 131.2° (expt. 138.1°).

The analysis of these parameters suggest that the central phenylene ring has some degree of electrons delocalization as explained in benzene (subsection 3.2) and is nonplanar in shape due to the nonbonding interactions with the three surrounding siloxaalkane arms. This interaction is most commonly called steric effects. As explained earlier in subsection 3.3, the steric hindrance creates constraints and imposes the phenylene ring to adjust particular conformation. That is why, the interior and exterior bond angles and the torsional angles of the central phenylene ring are found to be distorted from the original values measured in benzene (subsection 3.2). The d_{CO} values confirm that the

phenylene ring is found to occupy enough space inside the siloxaalkane spokes as observed experimentally. The main discrepancies are found in experimental and theoretical Si-O-Si bond angles. However, this is also in good agreement if we consider the flexibility of the Si-O-Si linkage. The partial ionic and double bond characters of this linkage not only governs its strength but also contributes to exceptional conformational flexibility of the $-(Si-O)_x-$ chains and their segments [36]. Additionally, one can compare the experimental and SCC-DFTB optimized structures of the isolated siloxaalkane molecule shown in Figure 5a and Figure 5b and reconfirm the above mentioned features for the optimized structure that the orientation of the phenylene ring and the conformations of the siloxaalkane spokes around it are well reproduced. Besides that the orientation and conformation of the methyl groups attached to three siloxaalkane arms are also not noticeably different.

3.4.2 Crystalline siloxaalkane molecule

In contrary to the isolated siloxaalkane molecule where surrounding siloxaalkane arms are involved to interact significantly with the central phenylene ring (intra-molecular interactions), the additional intermolecular interactions in crystalline form force the molecules present in the unit cell to adjust in different conformations. As a result, more distortions especially in the bond angles and torsional angles are expected. As there are several sets of bond lengths, bond angles, and torsional angles in two differently aligned molecules in a unit cell, we have chosen here few sets of them that directly affect the orientations of the central phenylene ring and the conformations of the siloxaalkane spokes. The concerned theoretical and experimental (hereafter, expt.) values are listed here in average. The bond lengths are measured as: C-H and C-C bond lengths in each phenylene ring are 0.110 nm (expt. 0.094 nm) and 0.141 nm (expt. 0.138 nm) respectively; axial C-Si bond length in each phenylene ring is 0.187 nm (expt. 0.188 nm); Si-C, Si-O and C-H bond length in each arm of each molecule are 0.188 nm (expt. 0.180 nm), 0.174 nm (expt. 0.16 nm), and 0.11 nm (expt. 0.098 nm) respectively. Similarly, the interior bond angle of each phenylene ring formed by the ipso carbon atoms is 117.6° (expt. 117° and 113.5°) and by rest of the carbon atoms is 121.2° (expt. 123.0°) while the exterior bond angles formed by the ipso carbon atoms of each phenylene with the Si atom are measured as 109.3° (expt. 109°), 108.1° (expt. 110°), and 107.1° (expt. 107°). The six Si-O-Si bond angles present in six siloxaalkane arms of two unit cell molecules are 141.1° (expt. 162.9°), 141.1° (expt. 169.4°), and 147.4° (expt.

172.6°). For the first molecule, the major torsional angles of the phenylene ring with respect to three siloxalkane arms: in one side -69.5° (expt. -81.9°), 49.7°(expt. 40.5°), 169.3°(expt. 157.3°) and in opposite side 109.6° (expt.116°), -11.6 ° (expt. -7.5°), -131.2° (expt.-124.2°) and for the second molecule: in one side -109.6° (expt.-99.0), 11.6 ° (expt. 21.3), 131.2° (expt.138.1) and in opposite side 69.5° (expt. 81.9°), -49.7°(expt.-40.5°), -169.3°(expt. -157.3°).

As explained earlier in subsection 3.4.1, the steric hindrance generated by the three surrounding arms creates constraints and affects the torsional bond angles of the phenylene directly. Additionally, the same effect is experienced by the surrounding arms from the same type of the arms present in nearby molecule of a same unit cell. As a result, more angular distortions in the phenylene ring and the siloxalkane arms are found to occur compare to isolated siloxalkane molecule. The reasons behind the major discrepancies observed in experimental and theoretical Si-O-Si bond angles are already explained in subsection 3.4.1. If we compare the experimental and SCC-DFTB optimized unit cell geometries shown in Figure 6a and Figure 6b, we can reconfirm the above mentioned features for the optimized structure that the orientation of the molecules and the arrangement of the three siloxalkane spokes in each molecule are well reproduced. Besides that the orientation and conformation of the methyl groups attached to three siloxalkane arms of each molecule are also not noticeably different. As a rule, the DFTB script constructs a super cell by periodic repetition of the unit cells while optimizing unit cell geometry under PBC with the appropriate lattice vectors. Figure 7 depicts the beautifully arranged assembly of siloxalkane molecules in the newly formed super cell. Such skill of DFTB is very essential in computational research especially while realizing the crystalline molecular systems. It allows us to handle very complex crystalline molecular systems even at low computational cost and hence, makes the DFTB method very versatile and superb quantum mechanical model for investigating ground state electronic structures and dynamics of large and complex molecular assemblies.

IV. CONCLUSIONS

As the DFTB method is not new to theoretical chemists/physicists for investigating the electronic structures and dynamics of the different types of molecular systems in different physical states, we presently employed its self-consistent charge (SCC) approach to compute ground state electronic structures of the very simple to more complex molecular systems of the order: water; benzene;

crystalline 1,4-bis (tri-methylsilyl) benzene; and crystalline siloxalkane. In this work, we fully optimized the isolated molecules of each of them as well as the unit cell geometries of last two molecular specimens under SCC conditions. While optimizing unit cell geometries, we used dispersion energy correction parameters with specific lattice vectors under periodic boundary condition (PBC) and transformed the unit cells to super cell. We measured the dimensions of bond lengths, bond angles, and torsional angles in all the optimized geometries and compared them with the concerned experimental values.

In the case of very simple system such as water, the theoretically converged equilibrium structure has each O-H covalent bond length: 0.0975 nm and the H-O-H bond angle: 103.2°, which are as close as the experimentally determined O-H bond length: 0.09584 nm and H-O-H bond angle: 104.45°. The comparatively bigger system such as benzene is also converged theoretically to the most stable structure whenever all six C-C bonds are at 0.139 nm, each C-C-C and H-C-C bond angle is at 120°, and each H-C-C-H torsional angle is at 0°. The computed C-C bond length is as equal as the experimental C-C bond length: 0.140 nm. Another more bigger system of 1,4-bis (tri-methylsilyl) benzene molecule in isolated as well as in crystalline form reached to the most stable equilibrium structures even though the phenylene rings of them are distorted from the planar shape. We explained such distortion is because of the steric effects created by the two sets of trimethyl groups bonded at its periphery. The more complex system of isolated siloxalkane molecule is also theoretically converged to the most stable electronic structure. The analysis of its bond lengths, bond angles, and torsional angles suggested that the central phenylene ring is non-planar in shape unlike in benzene due to the steric effects caused by three surrounding siloxalkane arms. The most complex and computationally expensive system of siloxalkane molecule in crystalline state is also theoretically converged to the most stable electronic structure. This time, additional interaction between the molecules present in the unit cell adds an extra strength to the siloxalkane steric effects experienced by the central phenylene ring. Thus, more deviations in the bond angles and dihedral angles of both phenylene ring as well as surrounding siloxalkane spokes are observed. Except some reasonable inconsistencies in the experimental and theoretical Si-O-Si bond angles of each siloxalkane arm, the theoretically produced unit cell geometry is found to be resembled quite well with the experimental one.

The above notable theoretical findings unveiled the extraordinary skill of the DFTB method in computing energetically most stable electronic structures for the very simple to giant molecular systems. It would be a strong supporting evidence for the DFTB method to recommend it for computing molecular geometries of different types of crystalline substances. In particular, the DFTB method with dispersion energy corrections under PBC and self-charge consistency puts considerable demands on the accuracy of the computational/theoretical methods for investigating electronic structures of the wide varieties of molecular systems.

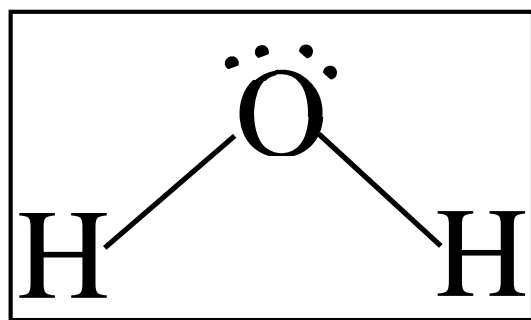
ACKNOWLEDGEMENT

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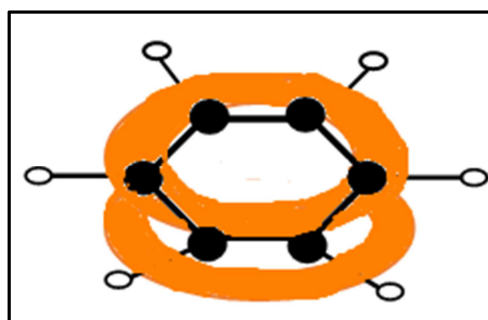
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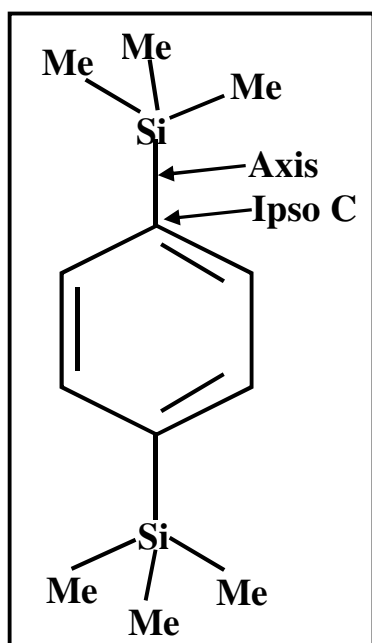
Chart 1



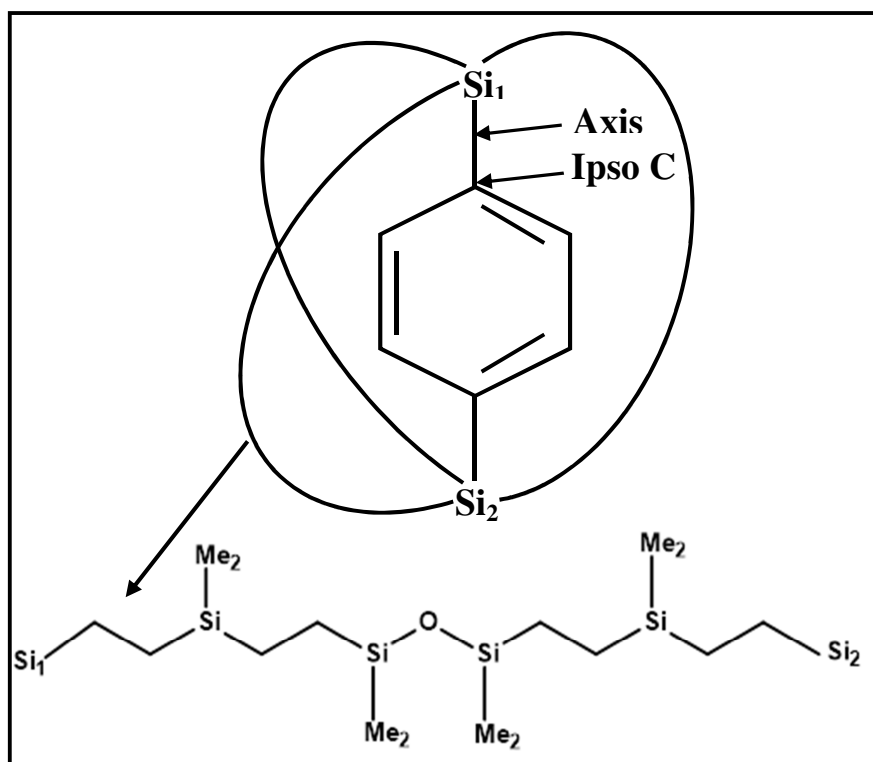
(a)



(b)



(c)



(d)

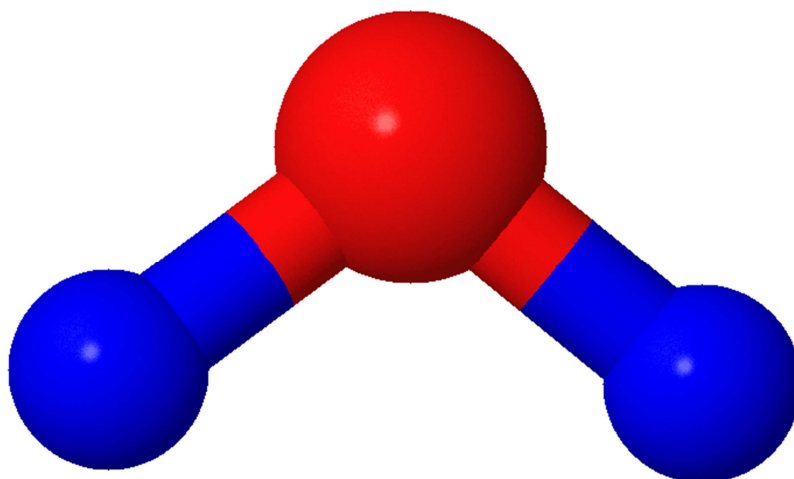


Figure 1. SCC-DFTB optimized geometry of an isolated water molecule. The red and blue spheroids represent oxygen and hydrogen atoms respectively.

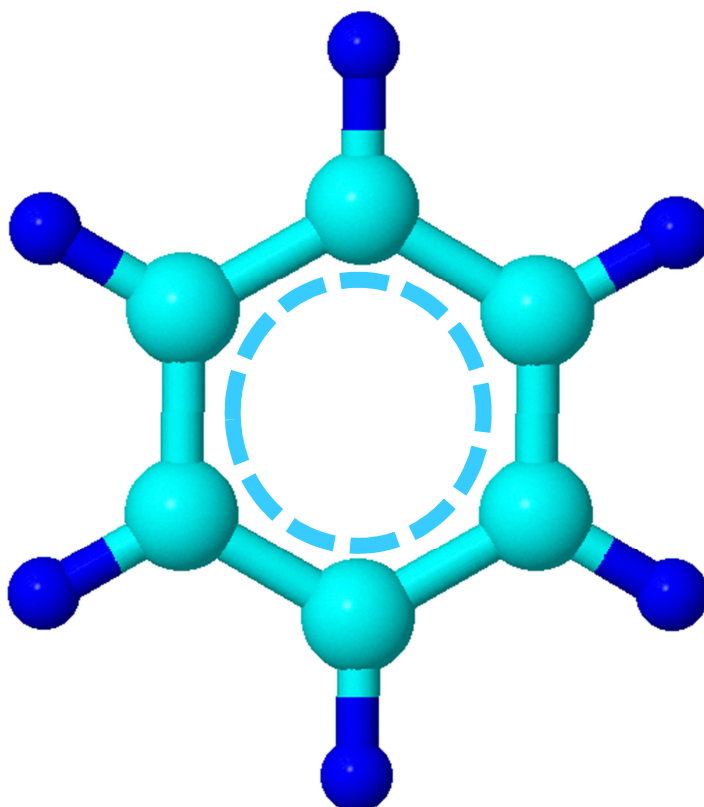


Figure 2. SCC-DFTB optimized geometry of an isolated benzene molecule. The cyan and blue spheroids represent carbon and hydrogen atoms respectively.

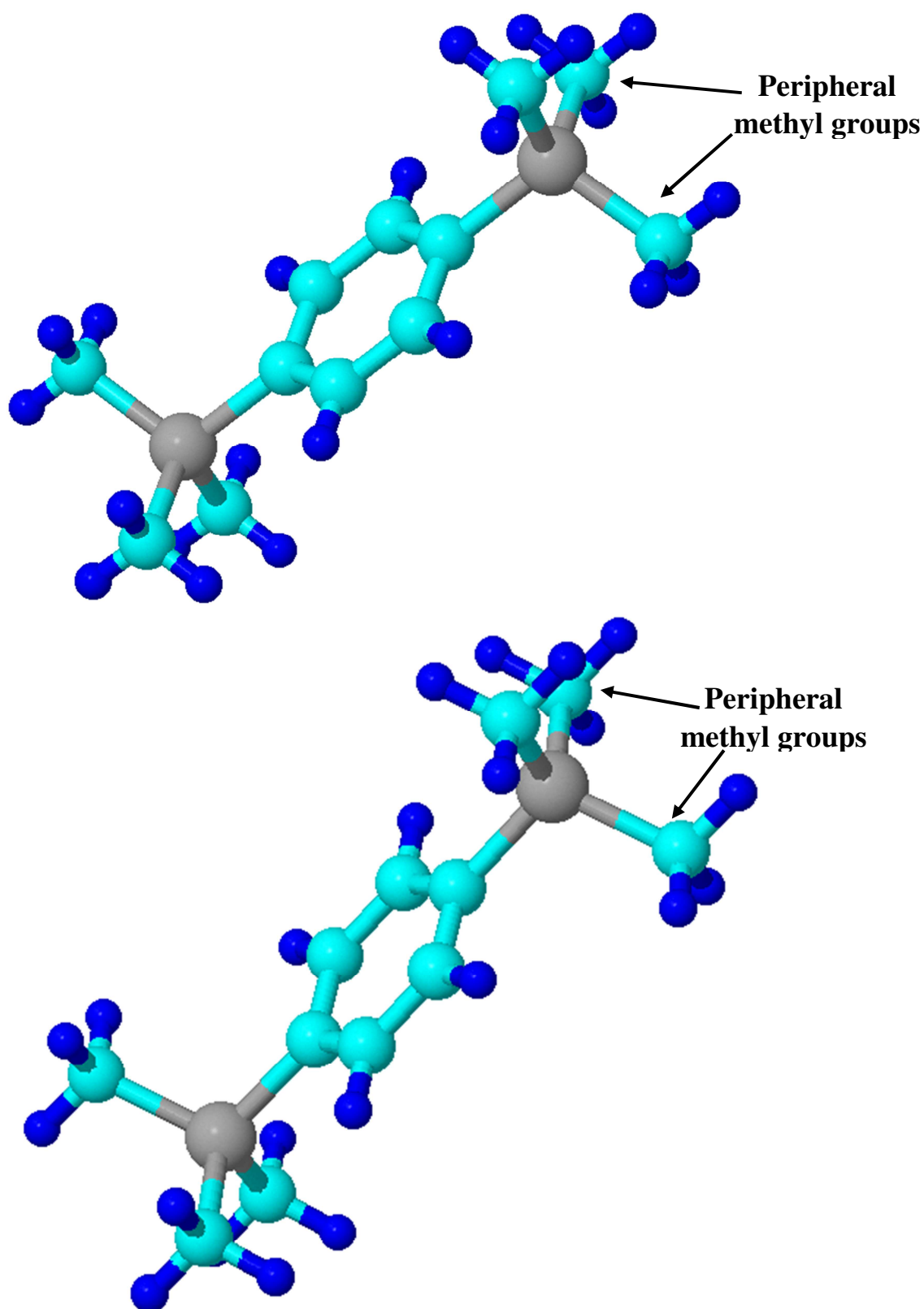


Figure 3. (a) X-ray (b) SCC-DFTB optimized geometry of an isolated 1,4-bis (tri-methylsilyl) benzene. The cyan, blue, and gray spheroids represent carbon, hydrogen, and silicon atoms respectively.

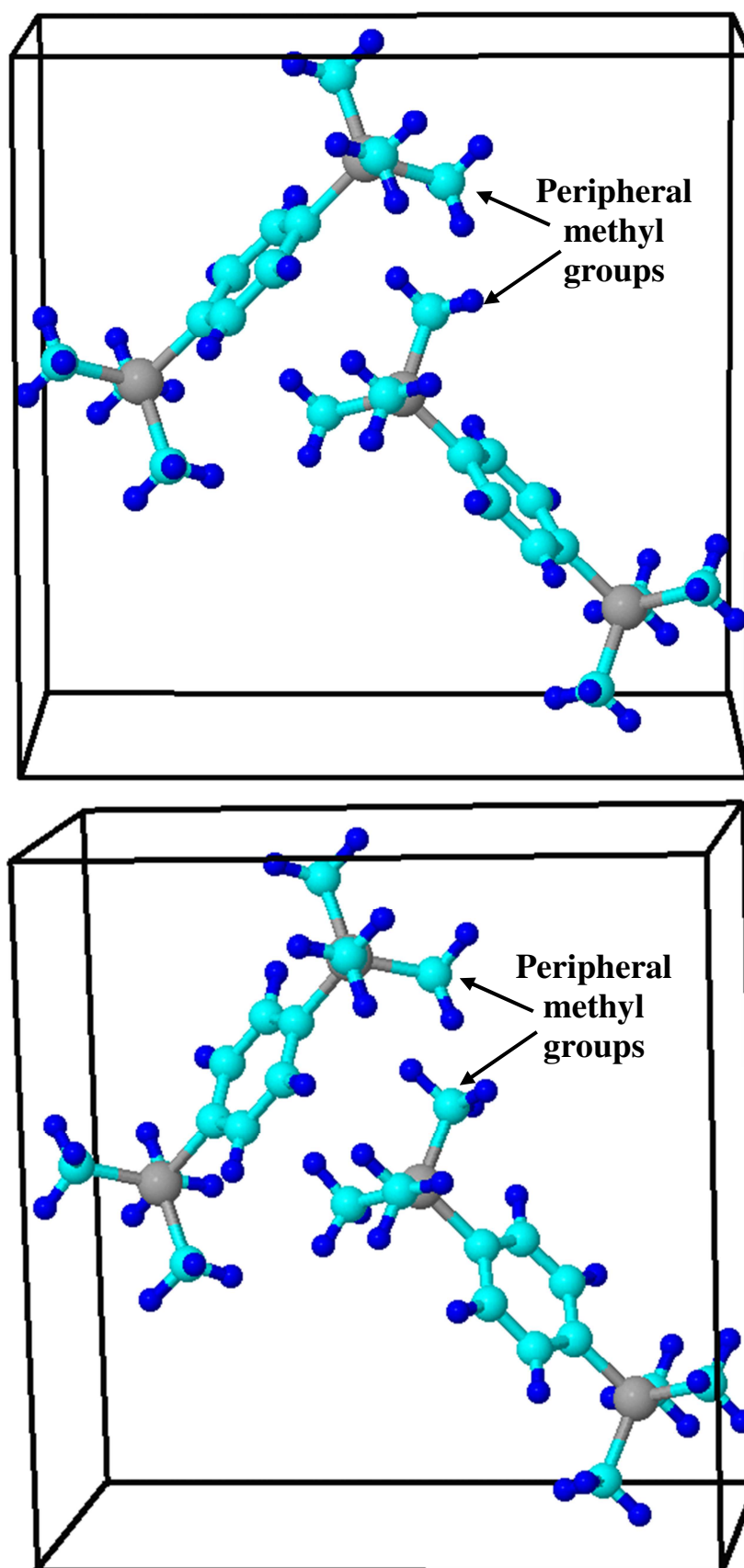


Figure 4. (a) X-ray (b) SCC-DFTB optimized unit cell geometry of 1,4-bis (tri-methylsilyl) benzene. The cyan, blue, and gray spheroids represent carbon, hydrogen, and silicon atoms respectively.

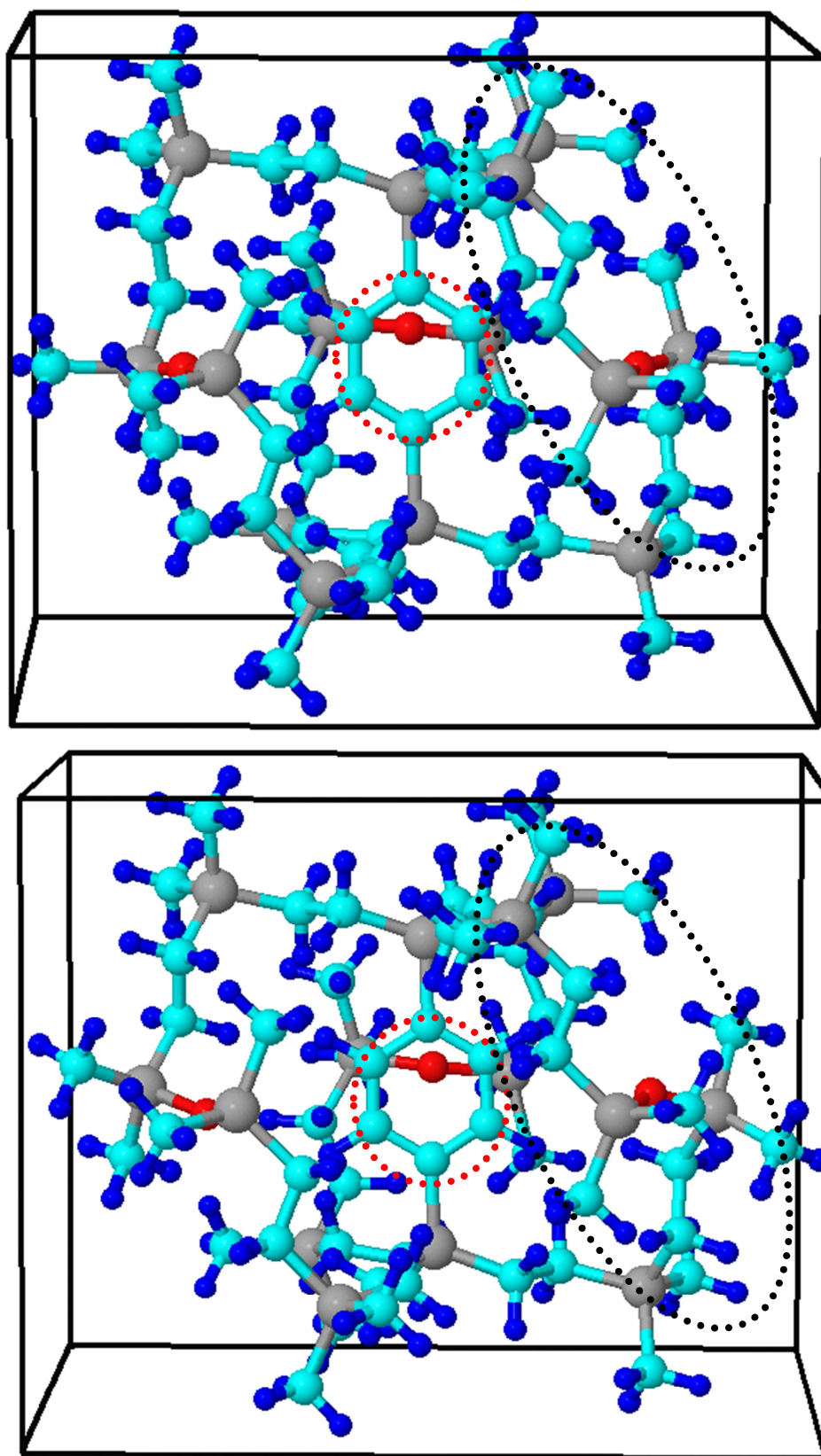


Figure 5. (a) X-ray (b) SCC-DFTB optimized geometry of an isolated siloxaalkane molecule. The cyan, blue, gray, and red spheroids represent carbon, hydrogen, silicon, and oxygen atoms respectively. The phenylene rings and siloxaalkane arms are enclosed by red and black circles respectively.

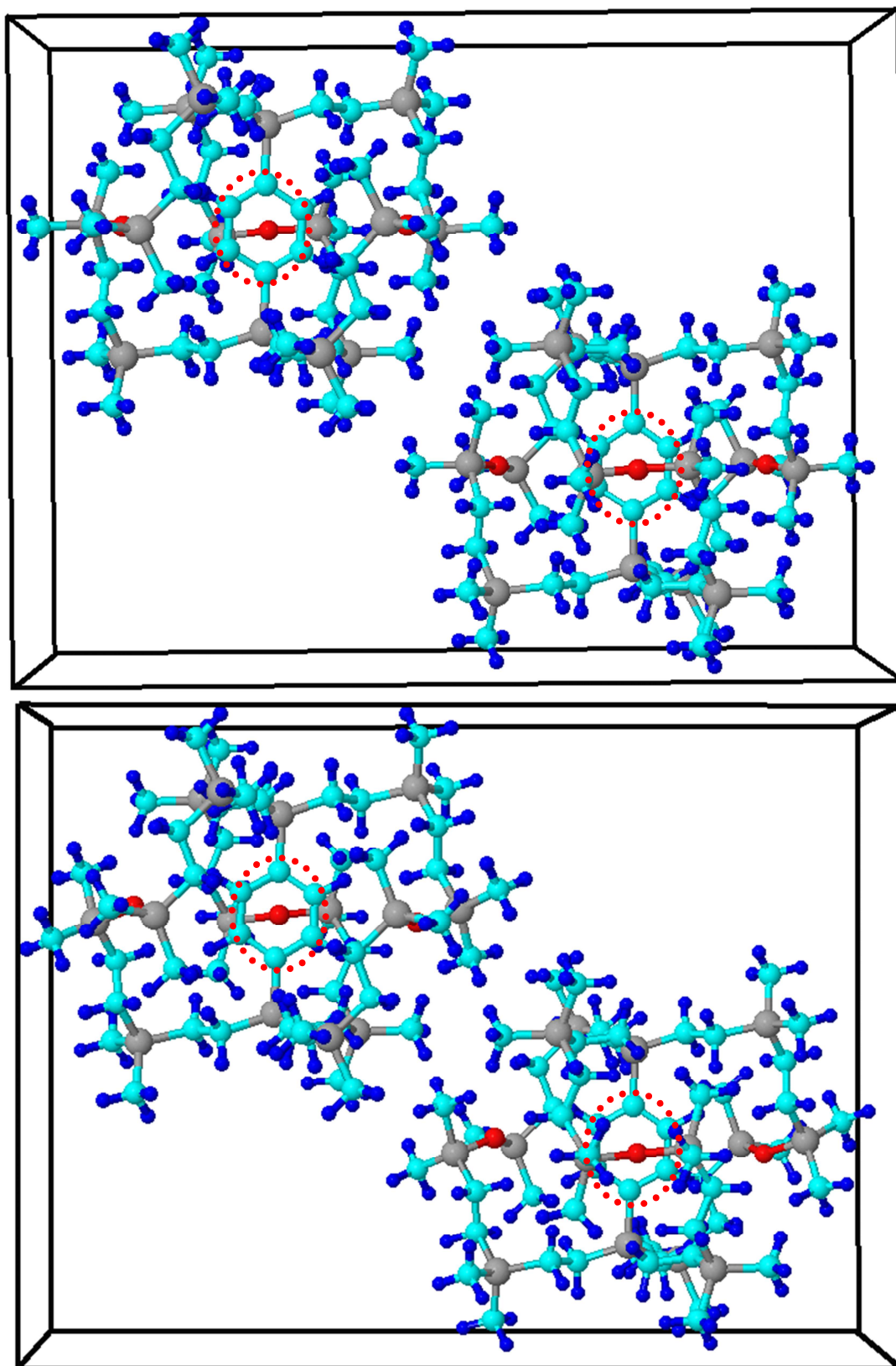


Figure 6. (a) X-ray (b) SCC-DFTB optimized unit cell geometry of siloxalkane molecule. The cyan, blue, gray, and red spheroids represent carbon, hydrogen, silicon, and oxygen atoms respectively. The phenylene rings are encircled

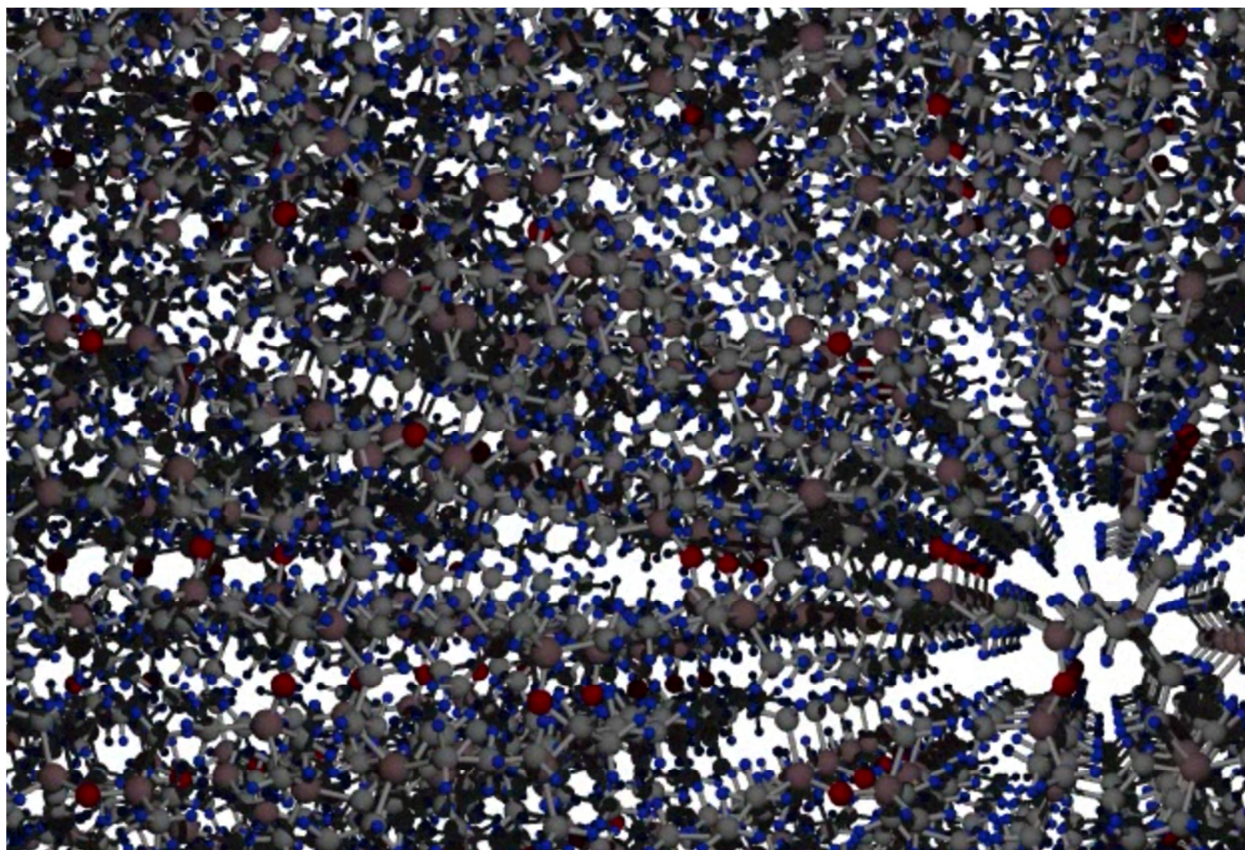


Figure 7. A snapshot of the super cell with siloxalkane molecular assembly. The periodic boundary condition with the lattice vectors $\mathbf{a} = 11.84, 0.000, 0.000$; $\mathbf{b} = 0.000, 14.619, 0.000$; and $\mathbf{c} = -3.884, 0.000, 23.874$ are used to transform unit cell to super cell.