International Journal of Progressive Sciences and Technologies (IJPSAT)
ISSN: 2509-0119.

http://ijpsat.ijsht-journals.org
Vol. 19 No. 1 February 2020, pp. 100-112

DFT Study on Ground State Electronic Structures of Simple to Complex Molecular Specimens

Anant Babu Marahatta[1, 2]
[1]Department of Chemistry, Amrit Science Campus, Tribhuvan University, Kathmandu, Nepal
[2]Chemistry Subject Committee, Kathford International College of Engineering and Management (Affiliated to Tribhuvan University), Kathmandu, Nepal

Abstract – As the first principles method involves quantum mechanical calculations derived directly from theoretical principles, their inabilities to solve the Schrödinger equation exactly for multi-electron systems make themselves far from fail-safe. To overcome the obstacles of exact computation, a more realistic Density Functional Theory (DFT) method of obtaining an approximate solution to the Schrödinger equation of a many-body system has become very prominent in the recent decades. Present work is aimed at computing ground state electronic structures of very simple to quite complex molecular specimens of the order: Water, Butadiene, Benzene, 1,4-bis (Tri-methylsilyl) Benzene, and Siloxaalkane by using DFT method and further strengthening its existing geometry optimization skills. At first, the isolated molecules of each of these specimens are fully optimized, and measured the dimensions of the particular sets of bond lengths, bond angles, and torsional angles in each ground state geometry. The theoretically computed values are found to be consistent with the concerned experimental values derived from the most advanced instrumentation techniques. It would be a strong evidence to support DFT method for being a very versatile and superb quantum mechanical model especially in computing ground state electronic structures of the complex molecular systems. The significance and novelty of this study lies in providing insight about the DFT predicted structural parameters and geometrical shapes of the aforementioned simple to complex molecular specimens.

Keywords – Water, Butadiene, Benzene, 1,4-bis (Tri-methylsilyl) Benzene, Siloxaalkane.

I. INTRODUCTION

Molecular geometry or molecular structure is the three-dimensional (hereafter, 3D) shape that a molecule occupies in a space [1]. It not only deals with studying how molecular shapes relate to chemical reactivity and physical characteristics such as freezing point, density, polarity, magnetism, phase, color, etc. but also equally associated with predicting biological activity, designing drugs or depicting the function of a molecule. Since the beginning of the field of chemistry, what has been more difficult is to figure out the molecular geometries or the particular arrangement of the atoms in the 3D space. In the recent years, several advanced robust tools such as X-ray crystallography, neutron diffraction, Raman spectroscopy, electron diffraction, electron momentum spectroscopy, and microwave spectroscopy have been employing in experimental research for imaging molecules in the 3D space [2]. However, in theoretical research, a very powerful computational methodology called geometry optimization technique has always become an important part in most quantum chemical calculations for predicting energetically most stable electronic structures. This theoretical technique involves a series of computing processes or repeated mathematical calculations performed on the molecule, and predicts the structure having a minimum electronic energy called ground state electronic structure. While the quantum mechanical computations are on the fly, the wave function and energy are calculated at a starting geometry, then tests various possibilities to see which atomic arrangements and

Corresponding Author: Anant Babu Marahatta

the electrons around the atom will give the lowest energy value, and finally proceeds to search a new geometry of a lower energy [3].

The main part in solving a quantum chemical problem is to solve Schrödinger's wave equation with an electronic molecular Hamiltonian that represents energy of the electrons and nuclei of a molecule. This equation consists of a group of multi-electron wave functions each with an associated energy eigenvalue that would further describe the ground and excited states of the multi-electron atom. While solving it, a series of electronic energy calculations is involved by estimating specific sizes and shapes of the molecules in the 3D space. Unfortunately, as in classical mechanics, an exact solution for this equation cannot be obtained when the system contains three particles or more. Therefore, the electronic structure methods such as *Hartree Fock* (hereafter, HF), Multi-configurational based *ab initio* methods, hybrid methods (quantum mechanics (QM)/molecular mechanics (MM)), and *Density Functional Theory* (hereafter, DFT) methods do attempt to solve the Schrödinger's equation at some level of approximation [4] while implementing geometry optimization technique in electronic structure package *Gaussian*. Unlike HF and other *ab initio* type methods that have unfavorable scaling with the size of the system modeled and largely omit electron correlation, the DFT method emphasizes mostly on the electron density from which energy and properties are calculated. This theory is based on the theorem that the energetically most stable or ground state electronic structures/energies and properties of a system can be uniquely determined by the electron density of a system; regardless of which orbitals (*s*, *p*, *d*, etc.) contribute to it [5], [6]. Thus, this approach rests on pioneering theoretical developments of Kohn and Sham perspectives of mathematical formulation to compute the ground-state energy and electron density of *many* interacting electrons [7], [8], [9]. Despite many more recent improvements, the DFT model still has many notable limitations [10] with the main one being lack of complete mathematical treatment of dispersion in order to account the adverse effect of long-range attraction or Van der Waals type interaction [11], [12], [13], [14], [15]. However, the consequences of formulating and evaluating dispersion type forces in the DFT model can only be appropriate while applying it to the systems that are dominated by dispersion (e.g. interacting noble gas atoms) [16] or where dispersion competes significantly with other effects (e.g. in bimolecular systems) [17]. Otherwise, it is a potential computational methodology in investigating ground state electronic structures of the multi-electron and/or many-body systems [18], [19], [20], [21], [22].

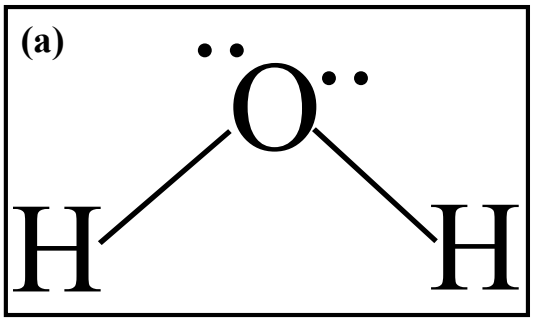
As the local-density approximations (LDA) in the DFT model account for the exchange correlation energy functional, several experimentally relevant physical properties that are based on the 3D molecular structure of the many heteroatomic complex molecular systems can be easily determined to a useful level of accuracy [23]. However, the DFT method is regarded as an inferior to high level *ab initio* method such as HF and almost similar to or even better *than* the second order Møller-Plesset perturbation theory (MP2), the former method always takes less computational time, memory, and disk space than the latter two methods while running the computational calculations. With this in mind, the DFT model is presently applied to very simple to quite complex molecular systems for the purpose of computing their most stable electronic structures and evaluating molecular geometry optimization skills of the DFT. The simple to complex molecular specimens are in the order: Water (H_2O), Butadiene (C_4H_6), Benzene (C_6H_6), 1,4-bis (Tri-methylsilyl) Benzene ($C_6H_4[Si(CH3)_3]_2$), and Siloxaalkane molecule ($C_{54}H_{124}O_3Si_{14}$). The first triatomic molecular specimen with two lone pairs of electrons on the central O atom (chart 1a) is much simple and smaller than almost all other molecules; the second deca-atomic specimen is little complex due to the presence of two unsaturated C=C bonds (chart 1b), the third dodeca-atomic specimen is more complex due to its electronic delocalization above and below the plane of the ring (chart 1c); the fourth (36 atomic species) molecular specimen is further more complex due to its open topology in which tri-methyl end groups are at the periphery of the phenylene ring (chart 1d); and the last (195 atomic species) molecular specimen is the most complex system due to its closed topology (chart 1e) in which significant intra-molecular type interactions exist in between central phenylene unit and surrounding siloxaalkane spokes. The structure of this paper is as follows. The computational methods are outlined in section 2. The results and discussion are presented in section 3. A summary and conclusions are given in section 4.

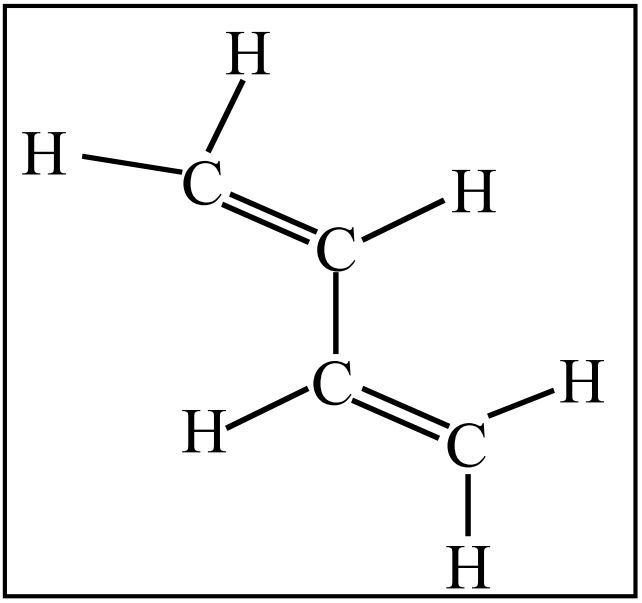
II. Computational Methods

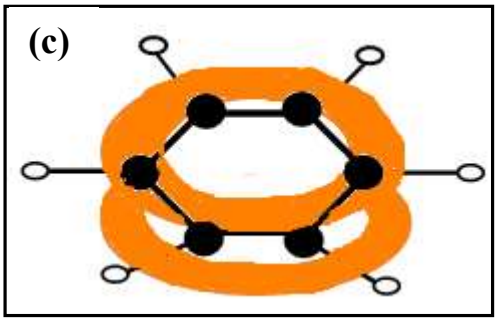
In order to optimize the geometry of each molecular specimen shown in chart 1, the respective initial atomic Cartesian coordinates were used separately as trial structures. The trial structures for water (H2O), butadiene (C4H6), and benzene (C6H6) were built by using GaussView visualization application [24], and those for the

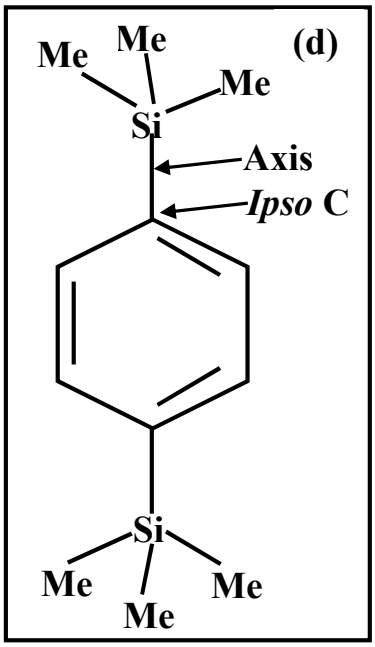
isolated 1,4-bis (tri-methylsilyl) benzene [25], [26] and the most stable configuration of siloxaalkane molecules (out of three) [27] were extracted from the respective X-ray crystallography of their unit cells. The x, y, and z coordinates of each molecular specimen were separately used to prepare Gaussian input files. All the Gaussian keywords and methodologies were selected as instructed in Gaussian 09 manual [28].

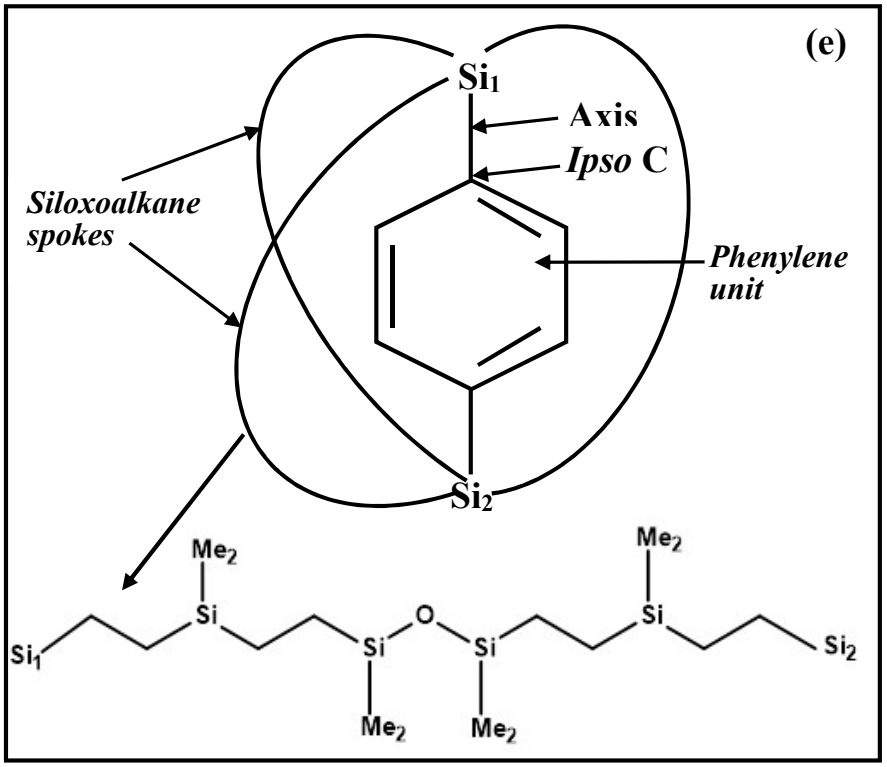
Chart 1.











The hybrid functional based DFT method known as B3LYP was used with the basis set of this type: 6−31G (d, p) i.e. the methodology used was DFT: B3LYP / 6−31G (d, p). For solving the electronic Schrodinger equation iteratively, the self-consistent field (SCF) with both default SCF procedure (SCF=Tight) and Berny algorithm for optimizations to a local minimum were selected in Gaussian 09 [29]. The Gaussian output files such as log, checkpoint (.chk), and formatted checkpoint (.fchk) files of water, butadiene, and benzene were read by using GaussView: the Gaussian graphical interface, and various chemical data displayed in three dimensions were extracted. All the DFT optimized geometries were displayed using Jmol: an open source java viewer for chemical structures in 3D [30]. Then, the optimized ground state electronic structures, optimized parameters such as bond lengths, bond angles, and dihedral angles for each molecule were analyzed thoroughly.

III. Results And Discussion

3.1 DFT optimized geometry of water molecule

In the liquid state, the water molecules are tightly held together by strong intermolecular attractive force, which makes them to be volume-confined. The type of intermolecular attraction is hydrogen bond (hereafter, H−bond) that exists in between neighboring water molecules involving one hydrogen atom (partially positive charged) located between the two oxygen atoms (partially negatively charged). When the surface of the liquid water is exposed to sufficient heat energy, water molecules escape out from the liquid state (evaporation) resulting their isolated form and hence, experience very less or almost no intermolecular force of attraction. In this study, the free or isolated water molecule is realized while optimizing it by DFT method without imposing any sorts of mathematical parameters for addressing intermolecular interactions including H−bond. The optimized geometry of the isolated water molecule visualized by Jmol [30] is shown in Figure 1.

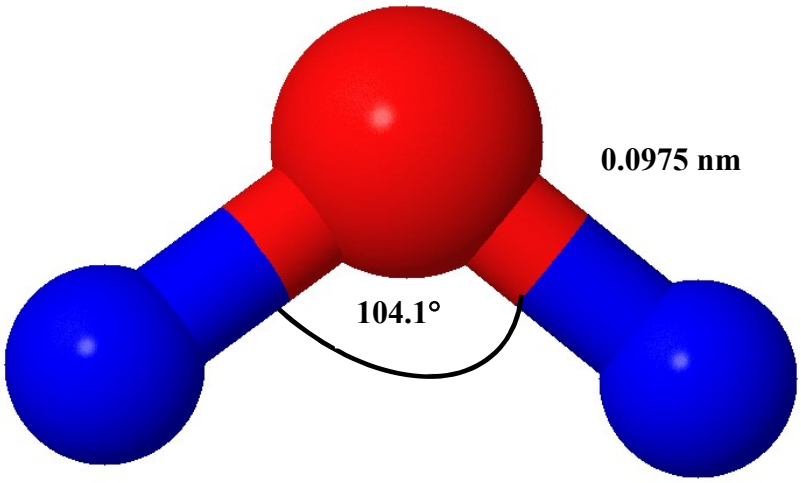


Figure 1. DFT optimized geometry of an isolated water molecule. The red and blue spheroids represent oxygen and hydrogen atoms respectively.

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, the explicitly measured theoretically calculated values of the first two parameters in H2O are presented here. Each O−H covalent bond length is measured as 0.0975 nm and the H−O−H bond angle is 104.1°. 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 H2O molecule, the central oxygen atom has 6 valence electrons and thus needs 2 more electrons from 2 hydrogen atoms to complete its octet. As a result, the oxygen atom has four

electron pairs on the outermost shell, 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. This bent molecular geometry of H2O can also be interpreted by AXN method, where 'A', 'X', and 'N' stand for the central atom, the number of atoms attached to the central atom, and the number of lone pairs present on the central atom respectively. In H2O, 'A' is none other than oxygen and 'X' and 'N' are equal to 2 each. Thus, the outcome is AX2N2, which is a three **atom molecule**, comes with the angular shape.

3.2 DFT optimized geometry of Butadiene molecule

Butadiene, also known as 1, 3-butadiene, is a colorless, non-corrosive gas that condenses to a liquid at −4.5°C and has a mild aromatic odor. It has high volatility and low-water solubility. It is important industrially as a chemical intermediate and as a monomer in the production of polymers such as synthetic rubbers or elastomers [31] [32]. Environmental sources of it include industrial and nonindustrial releases: such as butadiene production industry, automobile exhaust, cigarette smoke and other combustion sources. Being highly volatile, the butadiene molecules remain farther apart to each other and move freely due to very less or almost no intermolecular interactions between themselves. They usually exist in s-trans (both double bonds are on the opposite side of the sigma bond) and s-cis (both double bonds are on the same side of the sigma bond) conformers that are easily interconvertible to each other at room temperature due to free unrestricted rotation about sigma bonds, as shown in Figure 2. It is reported elsewhere [32] that the s-trans conformer is energetically more stable than the s-cis conformer by 2.8kcal/mol. This is the reason why the isolated s-trans conformer is chosen here as a trial structure, and optimized fully by the DFT method without imposing any sorts of intermolecular interactions. The optimized geometry of this conformer visualized by Jmol [30] is shown in Figure 3. The brown and ash-brown spheroids represent C and H atoms respectively. As compared in Table 1, all the DFT predicted structural data (bond lengths and bond angles listed in the 4th column) are quite consistent with the experimentally derived as well as ab initio HF derived data (3rd column). Interestingly, the C=C and C−C bond lengths of the butadiene (double double-bonded compound) are found to be slightly shorter than in ethylene CH2=CH2 (single double-bonded compound: C=C bond length = 0.13305 nm) and ethane CH3−CH3 (electron-localized system: C−C bond length = 0.154 nm) respectively. This is due to the pronounced effect of π-electron delocalization that occurs more in double double-bonded (2π bonds) system than in single double-bonded (1π bond) system as already confirmed by Craig et al. [32]. Similarly, the variation in the bond angles from the original tetrahedral geometry can be explained by the line-bond structure of 1, 3-butadiene, CH2=CH−CH=CH2 where a double bond is in between C1 and C2, a single bond is in between C2 and C3, and another double bond is in between C3 and C4. The terminal carbons C1 and C4 are attached to two H atoms while the central carbons C2 and C3 are attached to an H atom each. The formation of such bonding patterns can only be explained if all the four carbon atoms are in SP2 hybridized state. The terminal carbons C1 and C4 use the three SP2 hybrid orbitals to form three sigma bonds, two with H atoms and one with adjacent C atom while the central carbons C_2 and C_3 use their three SP^2 hybrid orbitals to form one sigma bond with H atom each and two with adjacent C atoms. This type of hybridization involved in the orbitals on each carbon suggests that each bond angle is in the range of 120°.

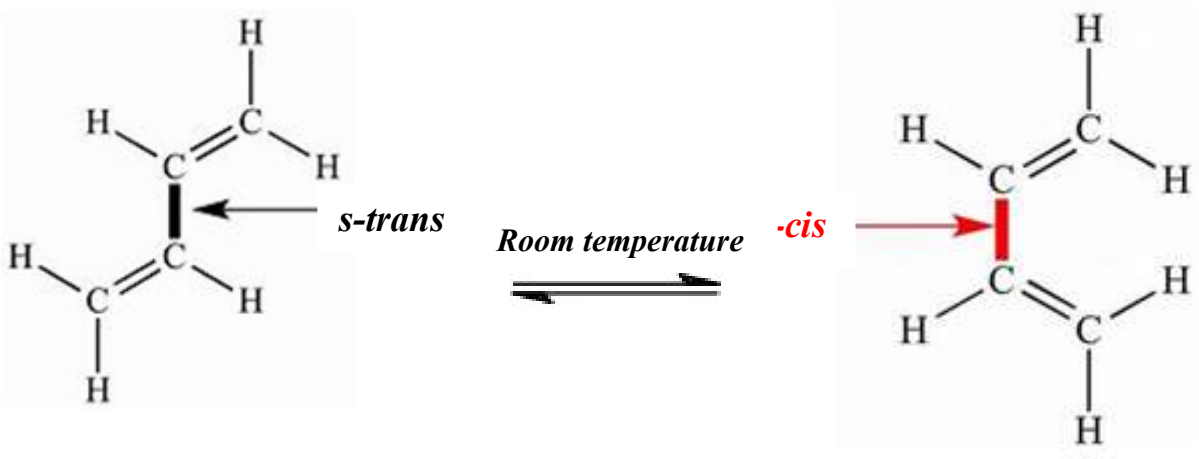


Figure 2. The structural interconversion of *s-trans* and *s-cis* butadiene conformers.

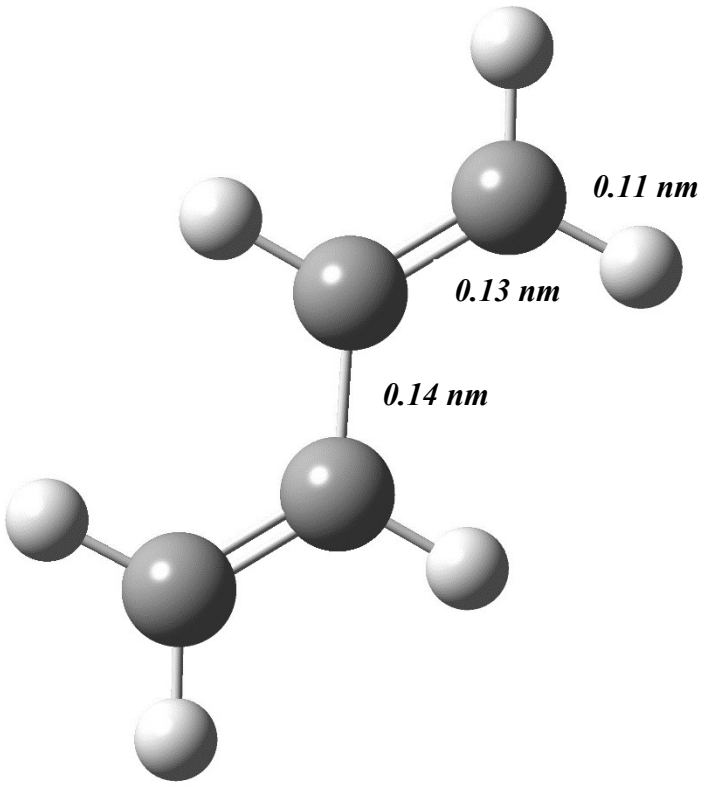


Figure 3. DFT optimized geometry of an isolated *s-trans* butadiene molecule. The brown and ash-brown spheroids represent carbon and hydrogen atoms respectively.

Table 1: Comparison of the structural data for Butadiene

Bond Lengths (nm) / Angles (°)	Experimental Methods		*HF* calc [c]	Present work: *DFT* calc (*B3LYP/6-31G(d, p)*)
	Electron Diffraction [a]	Microwave [b]		
C=C	0.1348	0.1337	0.1322	0.1339
C−C	0.1468	0.1467	0.1467	0.1457
C−H	0.1107	0.1087	0.1077	0.1087
C=C−C	124.3	123.0	124.0	124.299
H−C=C	120.7	121.5	121.5	121.809
H−C−C	–	–	–	118.271
H−C−H	–	–	–	118.722

[a] See Reference 33; [b] Reference 34; and [c] Reference 35.

3.3 DFT optimized geometry of Benzene molecule

Benzene is an aromatic organic compound with the chemical formula C6H6. It is composed of six carbon atoms bonded in a ring structure with one hydrogen atom attached to each. It is a highly flammable colorless liquid with a sweet odor and is comparatively a bigger non-polar aromatic hydrocarbon. It evaporates very quickly when exposed to air, indicating that benzene molecules in the liquid state are bound by very weak Van der Waals type interaction. It further means that large number of benzene molecules evaporate from the liquid state and enter into the surrounding air even at ~ 80°C, 1 atm. pressure, where they remained sink into low-lying areas and move freely due to very less or almost no interactions between themselves. To realize this scenario computationally, a single free benzene molecule is sampled here, and optimized by the DFT method without imposing any sorts of intermolecular interactions. The optimized geometry of such isolated benzene molecule visualized by Jmol [30] is shown in Figure 4. The cyan and blue spheroids represent C and H atoms respectively. This geometry has all six C−C and C−H bond lengths 0.139 nm and 0.109 nm respectively which are consistent with the corresponding X-ray diffraction data: C−C = 0.140 nm and C−H = 0.11nm [33]. 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, the benzene molecule is depicted with a circle inside a hexagonal ring, as shown in Figure 4. The genius of the electrons delocalization model can be understood in detailed by hybridization and valence bond theory concepts as described in many organic textbooks [33]. 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.

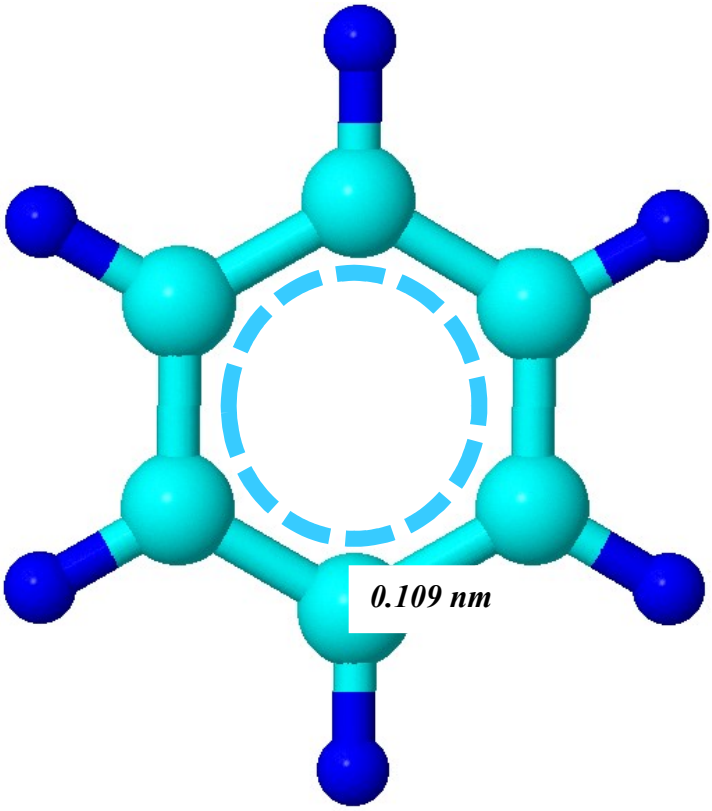


Figure 4. DFT optimized geometry of an isolated benzene molecule. The cyan and blue spheroids represent carbon and hydrogen atoms respectively.

3.4. DFT optimized Geometry of an isolated 1,4-bis (tri-methylsilyl) benzene

The crystalline 1,4-bis(tri-methylsilyl)benzene molecule (molecular formula = C6H4[Si(CH3)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 1e, the phenylene ring of this molecule remains completely open to the surrounding molecules (open topology) as shown in chart 1d. According to the crystallography, it has a monoclinic geometry with two molecules per unit cell [26]. As the DFT method is not suitable to address the intermolecular Van der Waals optimized without imposing any sorts of intermolecular interactions. The experimental and the optimized geometries of the isolated 1,4-bis (tri-methylsilyl) benzene molecule are shown in Figure 5a and Figure 5b. As the molecular geometries are specified mostly in terms of bond lengths, bond angles, and torsional angles, some sets of them that determine atomic orientations more precisely in the 3D space are carefully chosen here. 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 0.10 nm (expt. 0.096 nm) and 0.141 nm (expt. 0.140 nm) respectively; C−H bond length in each CH3 group is 0.101 nm (expt. 0.099nm); C−Si bond length from each ipso carbon of phenylene is 0.189 nm (exp. 0.187 nm); and Si−C bond length to each methyl carbon is 0.191 nm (expt. 0.188 nm). The interior bond angle of the phenylene ring formed by ipso carbon atom is 116.9° (expt. 117.5°) and by rest of the carbon atom is 121.5° (expt. 121.7°) 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−CH3 bond angle is 109.9°(expt. 109°) and H−C−H bond angle in each methyl groups is 107.9° (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 3.3 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. 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 attains 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 5a and Figure 5b, 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.

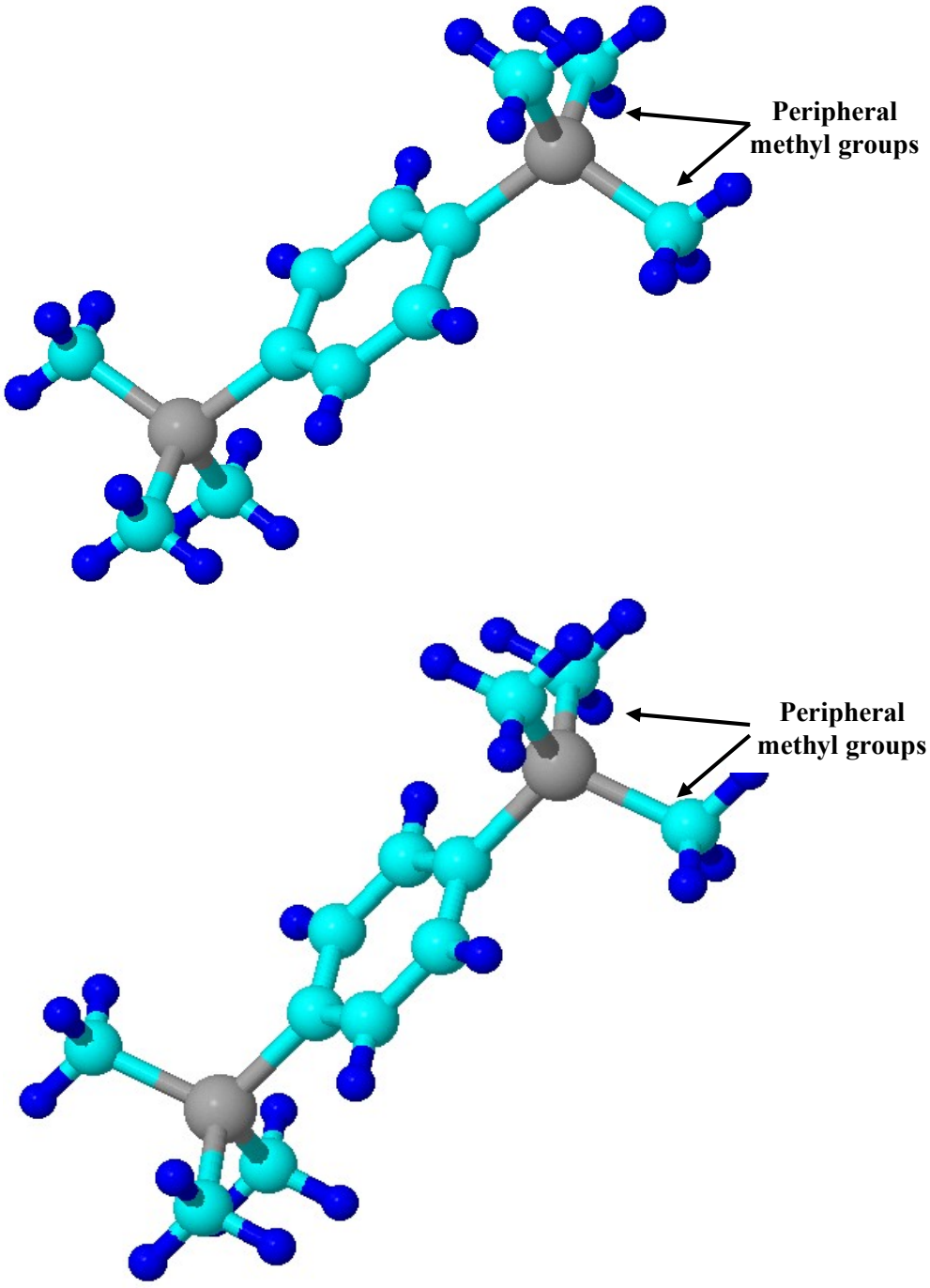


Figure 5. (a) X-ray (b) DFT optimized geometry of an isolated 1,4-bis (tri-methylsilyl) benzene. The cyan, blue, and gray spheroids represent carbon, hydrogen, and silicon atoms respectively.

3.5. DFT optimized geometry of an isolated siloxaalkane molecule

The experimentally synthesized crystalline siloxaalkane molecule (molecular formula = $C_{54}H_{124}O_3Si_{14}$; Molecular weight = 1214.79) has a phenylene ring encased in three long siloxaalkane spokes as shown in chart 1e. 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 ring upon its 1π rotation inside the siloxaalkane spokes has confirmed that there is an enough free space around the central rotating unit of such giant molecular system [34], [35]. Among the three stable structures, the most stable X-ray structure (Figure 6(a)) is chosen here as a trial structure for the DFT optimization. Such molecular structure in isolated form is fully optimized here without imposing any sorts of intermolecular interactions and displayed in Figure 6(b). The proper specification of the molecular geometries can only be drawn up if the structural parameters such as bond lengths, bond angles, and torsional angles are known. Here, some of them that are involved to determine the molecular orientations more precisely in 3D space are carefully chosen. 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 0.111 nm (expt. 0.094 nm) and 0.141 nm (expt. 0.140 nm) respectively; axial C−Si bond length is 0.188 nm (expt. 0.188 nm) and C−C, C−H, C−Si and Si−O bond length in each siloxaalkane arm is 0.152nm (expt. 0.150 nm), 0.109nm (expt. 0.097 nm), 0.180nm (expt. 0.180 nm) and 0.172nm (expt. 0.160 nm) respectively. Similarly, the free space around the phenylene unit is approximated by measuring the distances between the nearest carbon atom of the phenylene ring and the oxygen atom of each siloxaalkane arm (d_{CO}). They are measured as 0.405 nm (expt. 0.390 nm) and 0.525 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 117.4° (expt. 113.5°) and 117.3° (expt. 117.0°) and those by rest of the carbon atoms are121.8° (expt. 123.0°) and 121.6° (expt. 118.5°) while the exterior bond angles formed by the ipso carbon atom of phenylene with each Si atom are measured as 121.7° (expt. 122°), 120.4° (expt. 120°) and 121.7° (expt.123°). Similarly, the phenylene *ipso* C−Si−CH_3 bond angles are 108° (expt. 107.6°), 109.1°(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 −CH_2 group is 106.9° (expt. 107°); each H−C−H bond angle in each −CH_3 group is 108.4° (expt. 109°), and three Si−O−Si bond angles in three different arms are 141.3°(expt. 162.9°), 141.6°(expt. 169.4°), and 147.9°(expt. 172.6°). The major torsional angles of the phenylene with respect to three siloxalkane arms are in one side 69.6° (expt. 64.2°), -49.8°(expt. -55°), -169.6°(expt. -179°) and in opposite side -109.8° (expt.-99°), 11.4° (expt. 21.3°), 131.1° (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 3.3) 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 in the 3D space. 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. 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 DFT optimized structures of the isolated siloxaalkane molecule shown in Figure 6a, Figure 6b, 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. The small discrepancies (though negligible) appeared in the DFT optimized ground state structure are due to the absence of proper mathematical formulation in the DFT model for evaluating the effect of dispersion type force that exists in between central phenylene unit and the siloxaalkane spokes (enclosed by red and black circles respectively in Figure 6). The same author while realizing its unit cell geometry computationally under periodic boundary condition (PBC)

by applying density functional tight binding (DFTB) method produced a comparatively better geometry of the same molecule. See reference [35], [37] for the detailed explanation.

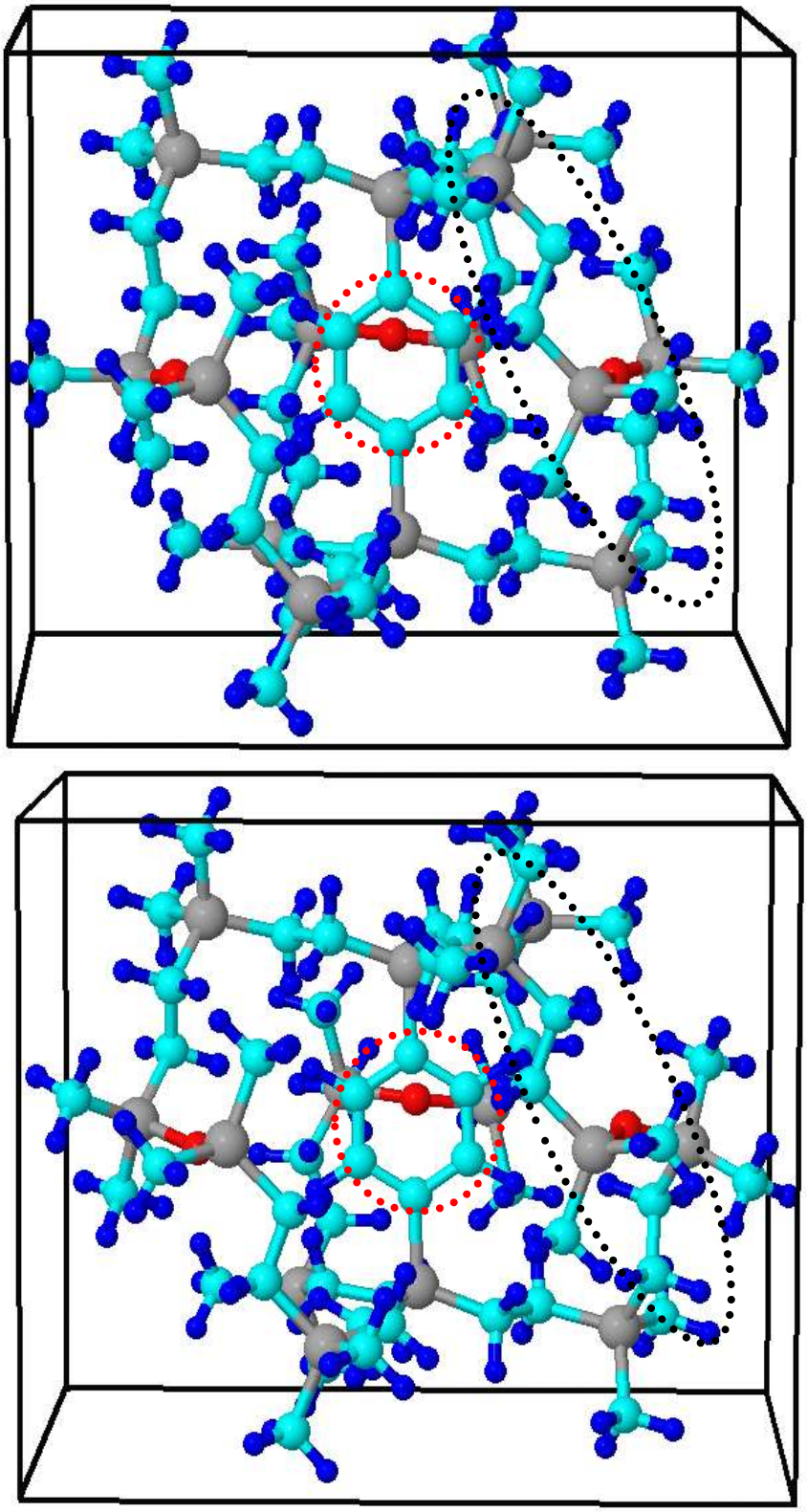


Figure 6. (a) X-ray (b) DFT optimized geometry of an isolated siloxaalkane molecule. The cyan, blue, gray, and red spheroids represent carbon, hydrogen, silicon, and oxygen atoms respectively. The phenylene rings and siloxaalkane arms are enclosed by red and black circles respectively.

IV. Conclusions

As the Density, functional theory (DFT) is a widely used computational method for carrying out quantum calculations in chemistry, materials science, and biology research, its skill to investigate principally the ground state electronic structure of many body systems is awesome. In this contribution, the DFT skill is evaluated while applying it to very simple to quite complex molecular systems of the order: Water; Butadiene; Benzene; 1,4-bis (Tri-methylsilyl) Benzene; and Siloxaalkane. At first, the isolated molecules of each of them are fully optimized under B3LYP/6-31G(d, p) scheme and the DFT predicted dimensions of the structural parameters such as bond lengths, bond angles, and torsional angles in each optimized geometry are compared 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: 104.10°, 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 less simple system such as butadiene is also well converged to its most stable electronic ground state structure whenever each C=C bond is at 0.1339nm, each C−C bond is at 0.1457nm, each C−H bond is at 0.1087nm, and each bond angle is at the range of 120°. For a bigger system like benzene, the theoretically converged most stable structure has all six C−C bonds 0.139 nm, each C−C−C and H−C−C bond angle 120°, and each H−C−C−H torsional angle is 0°. Another more bigger system of 1,4-bis (tri-Methylsilyl) Benzene molecule in isolated form reached to its most stable equilibrium structure even though the phenylene ring is distorted from the planar shape. This distortion is explained on the basis of the steric effects created by the two sets of trimethyl groups bonded at its periphery. The next quite complex molecular specimen of this research work is an isolated siloxaalkane molecule, which is also theoretically converged to the most stable electronic structure. The analyses of its structural parameters suggest that the central phenylene ring is non-planar in shape unlike in benzene due to the steric effects caused by three surrounding siloxaalkane arms and the additional intramolecular type interaction. Except some reasonable inconsistencies in the experimental and theoretical Si-O-Si bond angles of each siloxaalkane arm in the siloxaalkane molecule, the theoretically produced structural parameters and ground state electronic structure of each molecular specimen are found to be resembled quite well with the experimental one.

The above prominent theoretical computations support the extraordinary skills that the DFT method possesses more especially in computing ground state electronic structures for the multi-electronic/many-body systems. Present contribution would be a strong supporting evidence for the DFT method to recommend it for computing molecular geometries of complex systems that have less practically significant intra-molecular type interactions. Even though the author of this article was intended to apply DFT model to crystalline molecular systems of 1,4-bis (Tri-methylsilyl) Benzene and Siloxaalkane separately, it was practically undoable due to the lack of proper mathematical algorithms in DFT scheme for evaluating pronounced effect of dispersion type force existing in the molecular type crystals. However, the same author while applying DFTB method to the same crystalline molecular systems properly addressed the same effect. The theoretically reproduced unit cell geometries are reported elsewhere [35], [37].

Acknowledgement

The Kawashima Shoji Memorial Scholarship Foundation, Japan is acknowledged for the financial support to conduct a small part of this work.

References

[1] F. A. Cotton, G. Wilkinson, C. A. Murillo and M. Bochmann, *Advanced Inorganic Chemistry* (Wiley-Interscience, 1999).

[2] G. L. Miessler and D. A. Tarr, *Inorganic Chemistry* (Prentice-Hall, 1999).

[3] R. Daudel, *Electronic Structure of Molecules* (Elsevier, 1966).

[4] D. A. McQuarrie and J. D. Simon, *Physical Chemistry: Molecular Approach* (Viva Books, 1998).

[5] M. C. Payne, M. P. Teter, D. C. Allan, T. A. Arias, and J. D. Joannopoulos, *Rev. Mod. Phys.* 64, 1045 (1992).

[6] B. B. Yehuda and Y. Avishai, *Quantum Mechanics with Applications to Nanotechnology and Information Science* (ScienceDirect, 2013).

[7] P. Hohenberg and W. Kohn, *Phys. Rev. B*. 136, 864 (1964).

[8] W. Kohn and L. Sham, *Phys. Rev. J.* 140, A1133 (1965).

[9] J. P. Perdew, W. Yang, K. Burke, Z. Yang *et al. PNAS* 114 (11), 2801 (2017).

[10] A. J. Cohen, P. M. Sánchez and W. Yang, *Science* 321, 792 (2008).

[11] A. D. Buckingham, P. W. Fowler and J. M. Hudson, *Chem. Rev.* 88 (6), 963 (1988).

[12] J. Tao, J. P. Perdew and A. Ruzsinszky, *Proc. Natl. Acad. Sci.* U. S. A. 109 (1), 18 (2012).
[13] A. D. Becke, *J. Chem. Phys.* 98, 5648 (1993).
[14] J. P. Perdew, K. Burke and M. Ernzerhof, *Phys. Rev. Lett.* 77, 3865 (1996).
[15] J. Tao, J. P. Perdew, V. N. Staroverov and G. E. Scuseria, *Phys. Rev. Lett.* 91, 146401-1 (2003).
[16] V. Mourik, T. Gdanitz and J. Robert, *J. Chem. Phy.* 116 (22), 9620 (2002).
[17] J. Vondrášek, L. Bendová, and V. Klusák, *J. Am. Chem. Soc.* 127 (8), 2615 (2005).
[18] J. B. Adams, *Encyclopedia of Materials: Science and Technology* (Elsevier, 2001).
[19] A. B. Marahatta, *Int. J. Prog. Sc. Tech.* 16 (1), 51 (2019).
[20] A. B. Marahatta, *Int. J. Prog. Sc. Tech.* 16 (2), 01 (2019).
[21] A. B. Marahatta, *Int. J. Prog. Sc. Tech.* 17 (1), 55 (2019).
[22] A. B. Marahatta, *Int. J. Prog. Sc. Tech.* 18 (2), 43 (2020).
[23] R. O. Jones, *Computational Nanoscience* 31, 45 (2006).
[24] R. D. Dennington, T. A. Keith and J. M. Millam, *GaussView* (Gaussian Inc., 2008).
[25] NIST chemistry webbook, SRD 69. *https://webbook.nist.gov/cgi/cbook.cgi?ID= C1318 3705&Mask=400*
[26] M. Haberecht, H. Lerner and M. Bolte, *Acta. Cryst.* E58, 0436 (2002).
[27] W. Setaka, S. Ohmizu, C. Kabuto and M. Kira, *Chem. Lett.* 36, 1076 (2007).
[28] Gaussian 09 manual. *http://gaussian.com/geom/?tabid=1#GeomkeywordReadOptim izeoption*
[29] M. J. Frisch, G. W. Trucks, H. B. Schlegel, G. E. Scuseria, M. A. Robb, J. R. Cheeseman, G. Scalmani, V. Barone, G. A. Petersson and H. Nakatsuji, *et al. Gaussian 09, Revision C.01*, (Gaussian, Inc. 2004).
[30] Jmol: an open-source Java viewer for chemical structures in 3D. *http://www.jmol.org/*
[31] Butadiene Product Summary, American Chemical Council. *https://www.americanchemistry.com/ProductsTechnology/Olefins/Butadiene-Product-Summarypdf.pdf*
[32] N. C. Craig, P. Groner and D. C. McKean, *J. Phys. Chem. A*, 110(23), 7461(2006).
[33] W. Reusch, *Virtual Textbook of Organic Chemistry* (Michigan State University, 1999).
[34] W. Setaka, S. Ohmizu, C. Kabuto and M. Kira, *Chem. Lett.* 36, 1076 (2007).
[35] A. B. Marahatta and H. Kono, *Int. J. Inn. Res. Adv. Stud.* 6,180 (2019).
[36] G. J. Richard and C. Julian, *Silicon-Containing Polymers: The Science and Technology of Their Synthesis and Applications* (Springer publication, 2000).
[37] A. B. Marahatta and H. Kono, *Int. J. Prog. Sc. Tech.* 15(2), 263(2019).