



Original Research article

Prediction of the Structural and Spectral Properties and Reactivity of the Silicon Analogs of Cyclobutadiene C₄-nSi_nH₄ (n=0-4) by Density Functional Theory Computations

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ARTICLE INFO

Article history

Submitted: 2023-07-20

Revised: 2023-08-04

Accepted: 2023-09-07

Manuscript ID: CHEMM-1711-1018

Checked for Plagiarism: Yes

Language Editor:

Ermia Aghaie

Editor who approved publication:

Dr. Sami Sajjadifar

DOI: 10.48309/chemm.2023.52049

ABSTRACT

In recent years, it has been noted that the silicon analogs compounds have more pharmaceutical applications due to their excellent lipophilicity properties. The present study evaluated the structural, spectral properties, and reactivity of the silicon analogs of cyclobutadiene compound. This study was conducted based on the quantum-mechanical computations. All the studied compounds were optimized by B3LYP/6-311++G(d,p) basis set of theory. The IR computations showed no imaginary frequency for all molecules, proved the accuracy of the methods. The results revealed that, the silicon analogs have more benefits in terms of the structural and stability properties in comparison with the carbon analog.

KEYWORDS

DFT

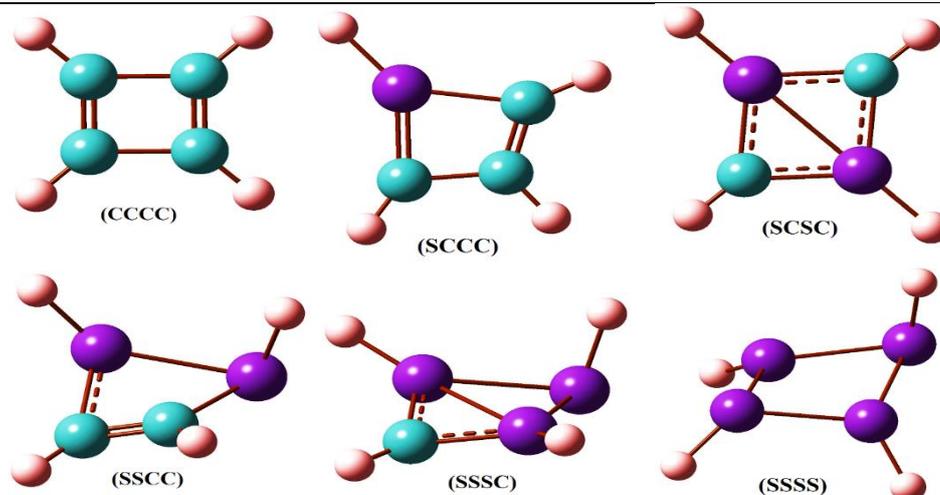
Cyclobutadiene

Silicon analog

NBO analysis

Reactivity

GRAPHICAL ABSTRACT



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Introduction

Cyclobuta-1, 3-diene is the smallest [n]-annulene compounds with the chemical formula C_4H_4 . Firstly, it was prepared by Rowland Pettit et al. in 1965 [1]. This molecule has low stability due to its angle strain factors and antiaromaticity of its molecular structure [2]. Low stability of the cyclobutadiene contributes to its high reactivity and short lifetime [3]. Various sources claimed that the pi electrons of cyclobutadiene system are not conjugated [4]. The energy of this system is higher than that of the 1, 3-butadiene system. So, this molecule is a nonaromatic compound [5]. At high temperatures, two units of this compound react together by Diels-Alder reaction and composed a dimerized molecule [6]. The free cyclobutadiene is a transient intermediate. So, this molecule participates as a ligand in various organometallic compounds such as cyclobutadiene tricarbonyl complexes [7]. As another application of this molecule, it is a part of different medicine structures [8]. In recent years, many scientists had tried to solve the instability and antiaromaticity problems of this annulene by entering silicon atoms in the structure of cyclobutadiene [9, 10]. This comes back to the weakness and high reactivity of silicon pi bonds. The second reason is the high polarity of silicon atoms [10, 11]. So, one can hope that the silicon analogs of this molecule would have had more applications than cyclobutadiene compound. In last decades, various attempts were done for preparation of these analogs [7-11], but its chemistry is very novel and needs more researches to complete the understanding their structures and applications. So, the present study aims at providing some useful information about the structural and spectral properties, reactivity, and natural bond orbital (NBO) population analysis of the cyclobutadiene molecule and its silicon analogs. Our studies are based on density functional theory (DFT) computations. Therefore, I hope this study will be a big window to the world of the silicon analogs of [4]-annulene.

Computational methods

In this study, the quantum mechanical computations [12-18] were used and the molecular structure of the mentioned compounds were optimized using density functional theory (DFT) method (B3LYP functional) with 6-311++G(d,p) basis set of theory by the Gaussian 03W program package [19-22]. Also, the ChemBioDraw Ultra 13.0, GaussView 6.0.16 and GaussSum 3.0 programs were used for drawing molecules, visualizing molecular structures and obtaining spectral graphs, respectively. After optimizing the structures, the vibrational frequencies were computed for all molecules. It had not seen any imaginary frequency for all compounds. So, it proves the accuracy of our computations.

Results and discussion

Structural study of molecules

Scheme 1 indicates the molecular structures of cyclobuta-1, 3-diene (CCCC), silete (SCCC), 1,2-disilete (SSCC), 1,3-disilete (SCSC), trisilete (SSSC) and tetrasilete (SSSS) compounds. The geometry of these molecules were optimized by B3LYP/6-311++G (d,p) basis set of theory. The optimized structures of the mentioned compounds are shown in Figure 1. It's easy to see that changing the carbon atoms by silicon atoms causes the disturbing of the regular molecular structures. As seen in Figure 1, the pi bonds of two compounds CCCC and SCCC are not conjugated. Also, the structure of other molecules is twisted. So, all studied molecule structures cannot be antiaromatic. Table 1 presents the bond lengths data of the studied molecules. It is seen two types of C-C bonds for CCCC molecule with 1.333 and 1.577 Å bond lengths. This shows the non-aromaticity property of this molecule. Other molecules indicate different C-C, C-Si and Si-Si bond lengths too. So, it can be understood that, the pi bonds in our selected molecules are not conjugate. Table 2 similar to Table 1 proves the non-armaticity property of the molecules. We can see the bond order (B.O.) of C-C, C-Si and Si-Si bonds in Table 2. For instance, the C-C bonds of

CCCC molecular structure do not reveals the unique bond order. The Si-Si bond orders of SSSS molecule are 1.012 Å and 1.272 Å. Based on these data (bond lengths and bon orders), the both carbon and silicon analogs of cyclobutadiene molecule have twisted and non-aromatic structures. As can be seen in Table 3, the summation of sigma and pi bond orders of ring is reduced by replacing of silicon atoms with carbon atoms in the studied molecules. This happens because of the electropositive property of silicon atoms. This factor indicates the non-aromaticity property of the molecules too. Another factor for study of aromaticity of unsaturated rings is nucleus independent chemical shift (NICS) character [23-25]. The positive and negative NICSs show the antiaromaticity and aromaticity properties of a compound, respectively. The computed NICS data of all molecules are collected in Table 4. From these data, the CCCC, SCCC and SCSC structures are antiaromatic. In contrast, the SSSC, SSSS and SSSS structures are aromatic compounds. While we saw all compounds are non-aromatic molecules. So, this factor cannot be used for expression of aromaticity property of the selected molecules.

Global and local reactivity of molecules

It is well known that global reactivity indices defined within conceptual DFT is a powerful tool to explain reactivity and the molecular properties. Consequently, global hardness (η), electronic chemical potential (μ), electronegativity (χ), global softness (S), nucleophilicity index (N), and electrophilicity index (ω) for the all compounds were calculated using the following equations [16-25]:

$$\eta \text{ (eV)} = \frac{(\epsilon_{\text{LUMO}} - \epsilon_{\text{HOMO}})}{2}$$

$$\mu \text{ (eV)} = -\frac{(\epsilon_{\text{LUMO}} + \epsilon_{\text{HOMO}})}{2}$$

$$\chi \text{ (eV)} = -\mu$$

$$S \text{ (eV)} = \frac{1}{2\eta}$$

$$N \text{ (eV)} = \epsilon_{\text{HOMO}} - \epsilon_{\text{HOMO(Tetracyanoethylene)}}$$

$$\omega \text{ (eV)} = \frac{\mu^2}{2\eta}$$

The data of global reactivity calculations for all molecules are collected in Tables 5. Stability of molecules is relative to the frontier orbitals (HOMO and LUMO) energies of them. The compounds with high HOMO-LUMO energies gap are more stable than the molecules with low HOMO-LUMO energies gap. From the global hardness data, the stability order of the molecules is: SSCC > CCCC > SSSC > SSSS > SCCC > SCSC. We can see from this order that the SCSC molecular structure has the lowest stability and the highest reactivity among all compounds. Also, the reactivity of SSSS molecule is more than the CCCC compound. On the other hand, the electrophilicity property order of the molecules is: CCCC > SSCC > SSSC > SCCC > SCSC > SSSS. This order indicates the replacing silicon atoms instead of carbon atoms in molecular structure of cyclobutadiene molecule reduced the electrophilicity property of the compound. Figure 2 demonstrates the density of states (DOS) plots of the molecules. As can be seen in the DOS plots; all molecules have more HOMO frontier orbitals than LUMO orbitals. So, all compounds prefer to react with nucleophiles.

Table 6 presents the natural charges data of the atoms of the structures. We see the carbon and silicon atoms show negative and positive charges on themselves. In CCCC molecule, all four carbon atoms show unique negative natural charge. So, only electrophiles can attack to this structure. In contrast, the other molecules can react with both electrophiles and nucleophiles. The electrophiles attack to carbon atoms and nucleophiles show tendency to react with silicon atoms. Also, the four silicon atoms of SSSS molecular structure have not unique reactivity with active nucleophiles and electrophiles.

Spectral study of molecules

There are several spectroscopic techniques which can be used to identify the organic molecules: infrared (IR), mass spectroscopy (MS) UV-Visible spectroscopy (UV-Vis) and nuclear magnetic resonance (NMR) [26]. IR, NMR and UV-Vis spectroscopy are based on observing the

frequencies of electromagnetic radiation absorbed and emitted by molecules.

IR [Harmonic frequencies (cm^{-1}), intensities (KM/Mole)]: CCCC: 535.3079 (0.0009), 587.5747 (152.6736), 600.8853 (0.0017), 702.7518 (9.6274), 886.4584 (0.0001), 1055.1952 (0.5520), 1255.8694 (39.7522), 1617.8887 (0.0029), 1624.4333 (8.3031), 3208.4372 (10.7371), 3230.0171 (18.6088), and 3240.1003 (0.0001). SCCC: 258.9831 (13.0312), 361.8772 (28.3259), 469.7359 (5.7323), 521.2737 (12.7964), 632.4513 (106.4750), 675.5702 (10.7117), 780.2640 (71.3542), 837.7580 (12.7165), 923.6545 (2.6358), 997.5477 (23.5675), 1007.7272 (31.3322), 1127.0949 (31.8691), 1240.9835 (4.6619), 1532.8829 (56.6132), 2212.4929 (103.9822), 3123.3690 (26.7210), 3262.6395 (0.3958), and 3281.5904 (0.1341). SSCC: 295.0648 (1.0762), 315.3322 (1.1790), 390.2509 (22.7673), 478.3536 (3.3505), 540.6453 (1.6743), 601.8483 (25.9051), 629.6918 (12.4267), 742.6100 (17.7836), 756.7392 (122.0962), 813.2838 (78.1008), 930.0689 (2.9339), 973.3476 (1.1806), 1183.1172 (18.7400), 1399.4039 (17.7099), 1994.0995 (267.8572), 2131.6303 (185.9518), 3077.2130 (2.2754), and 3201.4781 (0.6265). SCSC: 132.2318 (35.3830), 439.7340 (0.0001), 475.6387 (110.4807), 552.1272 (0.0001), 569.3793 (110.7612), 703.7180 (0.0431), 756.4359 (57.0555), 950.5451 (162.9173), 953.6606 (0.0010), 1017.2681 (267.1057), 2205.9613 (323.1345), 2215.8670 (0.0015), 3289.7664 (0.4642), and 3290.4896 (12.5230). SSSC: 181.2672 (2.6939), 291.9805 (0.8444), 295.1467 (2.3375), 377.9971 (0.5024), 449.6328 (7.2036), 501.7176 (1.5522), 583.3426 (5.2491), 590.9728 (10.9657), 612.7247 (6.2993), 690.8120 (36.1373), 760.0126 (120.2733), 788.7831 (10.2321), 947.5508 (113.0875), 960.5712 (78.8555), 2019.9376 (223.8703), 2156.1265 (308.4768), 2165.1868 (52.8304), and 3205.7184 (0.3060). SSSS: 115.3881 (26.9009), 235.4028 (32.7654), 257.7249 (21.7626), 329.6320 (0.0386), 355.0223 (1.6252), 412.0029 (4.3798), 424.5655 (19.9269), 488.2611 (4.5187), 501.6938

(1.3771), 537.0069 (1.5171), 586.8543 (13.1764), 600.9626 (1.2903), 653.6382 (0.9910), 731.5103 (28.1948), 2092.3927 (158.1892), 2110.4361 (239.1649), 2155.8095 (192.0354), and 2164.0137 (61.0495). As can be seen, the stretching vibrations of C-H and Si-H appear at frequencies 3000-3300 and 2000-2200 cm^{-1} range, respectively.

UV-Vis [Wavelength (nm), energy (cm^{-1})]: CCCC: 253.919 (39382.712, HOMO to LUMO+2 transition (96%)), 267.534 (37378.410, HOMO to LUMO+1 transition (100%)) and 473.363 (21125.420 HOMO to LUMO transition (77%)). SCCC: 313.350 (31913.160, HOMO to LUMO+2 transition (91%)) and HOMO to LUMO+3 transition (4%)), 353.118 (28319.128, HOMO to LUMO+1 transition (95%)) and 745.989 (13405.027 HOMO to LUMO transition (74%)). SSCC: 283.313 (35296.679, HOMO-1 to LUMO transition (48%)), HOMO to LUMO+2 transition (35%) and HOMO to LUMO+1 transition (6%)), 309.139 (32347.895, HOMO-1 to LUMO transition (15%)), HOMO to LUMO+1 transition (68%) and HOMO-2 to LUMO transition (8%)) and 438.708 (22794.192 HOMO to LUMO transition (90%)) and HOMO to LUMO+1 transition (3%)). SCSC: 335.734 (29785.454, HOMO to LUMO+2 transition (97%)), 391.572 (25538.109, HOMO to LUMO+1 transition (98%)) and 979.099 (10213.469 HOMO to LUMO transition (94%)). SSSC: 313.263 (31922.032, HOMO-1 to LUMO transition (89%)) and HOMO to LUMO+2 transition (4%)), 342.146 (29227.315, HOMO to LUMO+1 transition (73%)), HOMO to LUMO+2 transition (11%), HOMO-1 to LUMO transition (3%) and HOMO-1 to LUMO+3 transition (2%)) and 487.739 (20502.755 HOMO to LUMO transition (97%)). SSSS: 397.446 (25160.639, HOMO-2 to LUMO transition (91%)) and HOMO-1 to LUMO+1 transition (2%)), 470.811 (21239.951, HOMO to LUMO+1 transition (96%)) and 490.518 (20386.611, HOMO-1 to LUMO transition (13%)) and HOMO to LUMO transition (65%)). We can see the HOMO/LUMO electronic transitions of cyclobutadiene and its silicon analogs happen at about 470-490 nm wavelengths.

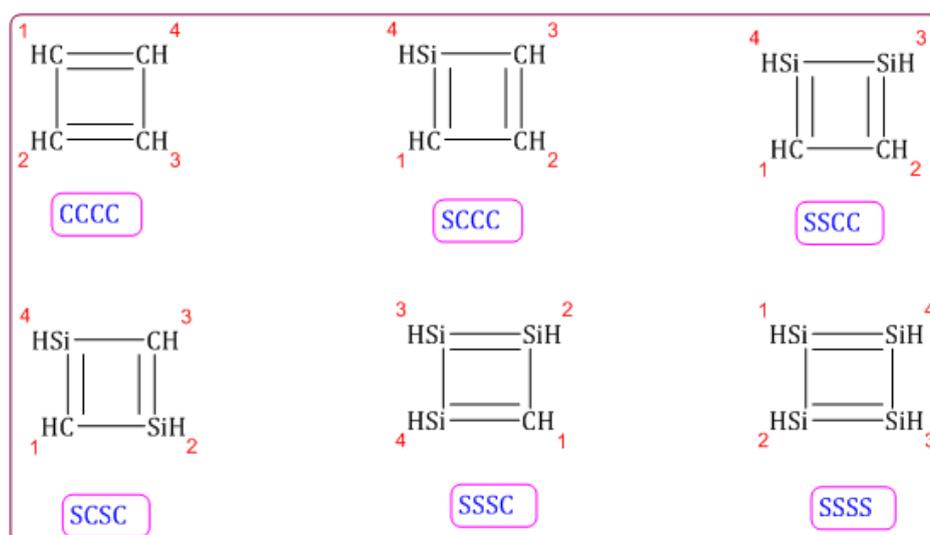
The NMR technique is a good method for identification of the structure of the organic compounds [27]. The ^1H , ^{13}C and ^{29}Si chemical shifts of the studied molecules are listed in Table 7. As can be seen, the chemical shifts of all ^1H and ^{13}C nuclei of cyclobutadiene structure are 5.9 and 147.4, respectively. This is happened because of the planar structure of cyclobutadiene molecule. On the other hand, we see various chemical shifts for these atoms when silicon atom entered instead of carbon atom in the structure. In previous sections, we saw the structure of molecules is twisted by entering silicon atom. So, the atoms feel different magnetic field and because of this reason the various chemical shifts are shown for nuclei. In overall, the nucleus with electron deficiency is seen at high chemical shifts. In contrast, the lowest chemical shifts are belonged to the atomic cores with surplus electron. For example; the chemical shifts of proton and carbon nuclei in SCSC structure are 0.4 and 38.0, respectively. The carbon atoms are connected to two electropositive atoms (silicon atoms) in SCSC molecular structure. Also, the silicon nucleus chemical shift is shown at above 200 Hz.

Natural bond orbital (NBO) study of molecules

In quantum chemistry, a natural bond orbital or NBO is a calculated bonding orbital with

maximum electron density [28-30]. The analysis of natural bond orbitals (NBOs) population of bonds can give us more important information about the structure of unknown molecules. Table 8 has collected the data of the NBO population analysis of the bonds of the selected molecules. It can be seen from the data, in CCCC molecular structure, carbon atoms participate with more p orbitals in C-C bonds than C-H bonds. It happens because of the angular pressure of the cyclobutadiene ring.

By entering the silicon atoms instead of the carbon atoms in molecular structures, low p orbitals of carbon atoms are participated in C-C and C-Si bonds. In these structures the angular pressure of rings reduces because the covalent radius of silicon atom is bigger than the carbon atom. Also, the carbon atoms that are connected to the silicon atoms participate with more p orbitals in C-H bonds than carbon atoms that are connected to other carbon atoms. So, these hydrogen atoms have lower acidity than others. On the other hand, the lowest acidity is related to the hydrogen atoms of Si-H bonds. Another important subject is related to the silicon atoms. These atoms use d orbitals in construction of bonds with other atoms. So, more silicon atoms in one structure cause more twisted structure.



Scheme 1: The molecular structure of the studied silicon analogs of cyclobutadiene

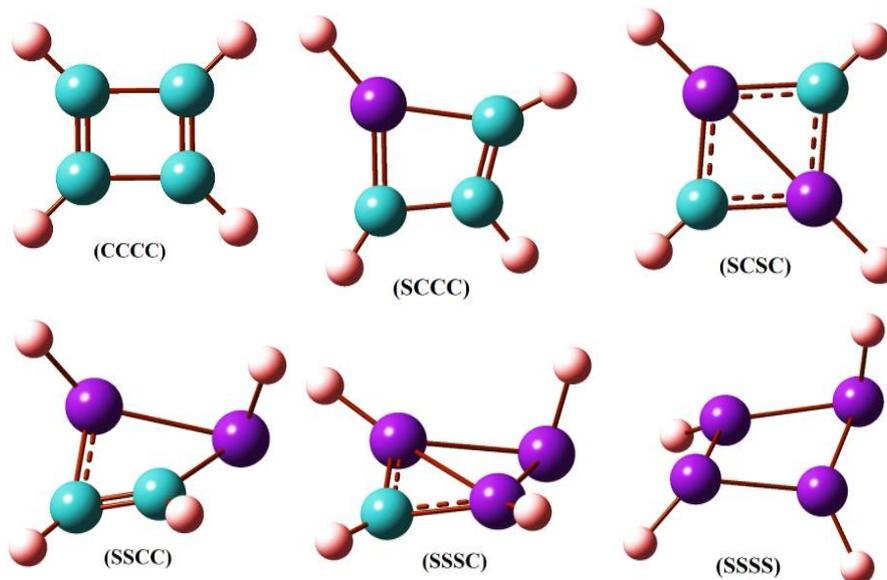


Figure 1: The theoretical geometric structure of the studied molecules

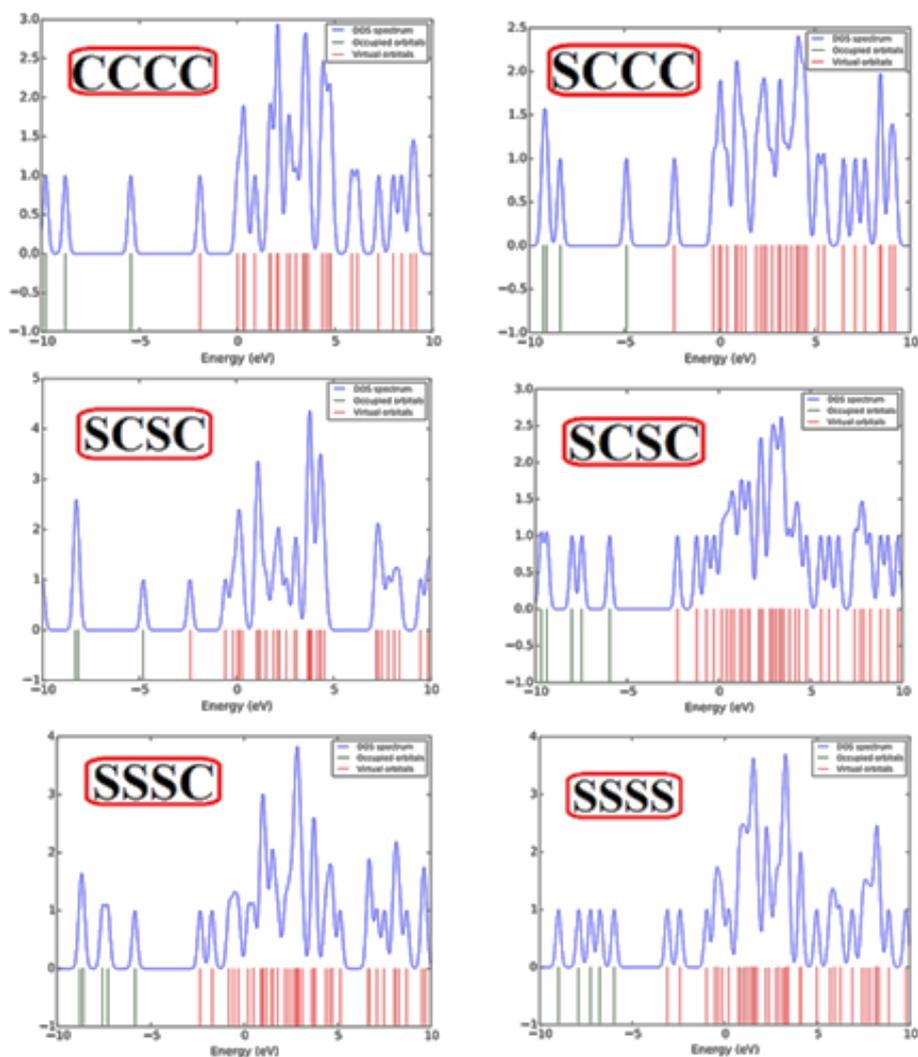


Figure 2: The density of states (DOS) graphs of the studied molecules

Table 1: Bond lengths data of the studied molecules

| Bonds | CCCC | SCCC | S SCC | SCSC | SSSC | SSSS |
|---------|-------|-------|-------|-------|-------|-------|
| C1-C2 | 1.577 | 1.539 | 1.363 | - | - | - |
| C2-C3 | 1.333 | 1.344 | - | - | - | - |
| C3-C4 | 1.577 | - | - | - | - | - |
| C4-C1 | 1.333 | - | - | - | - | - |
| C1-H | 1.081 | 1.076 | 1.082 | 1.075 | 1.082 | - |
| C2-H | 1.081 | 1.089 | 1.093 | - | - | - |
| C3-H | 1.081 | 1.077 | - | 1.075 | - | - |
| C4-H | 1.081 | - | - | - | - | - |
| C3-Si4 | - | 1.918 | - | 1.782 | - | - |
| Si4-C1 | - | 1.709 | 1.806 | 1.782 | 1.778 | - |
| Si4-H | - | 1.486 | 1.502 | 1.487 | 1.496 | 1.509 |
| C2-Si3 | - | - | 2.000 | - | - | - |
| Si3-Si4 | - | - | 2.345 | - | 2.386 | 2.358 |
| Si3-H | - | - | 1.531 | - | 1.524 | 1.497 |
| C1-Si2 | - | - | - | 1.782 | 1.778 | - |
| Si2-C3 | - | - | - | 1.782 | - | - |
| Si2-H | - | - | - | 1.487 | 1.496 | 1.503 |
| Si2-Si3 | - | - | - | - | 2.386 | 2.258 |
| Si1-Si2 | - | - | - | - | - | 2.258 |
| Si4-Si1 | - | - | - | - | - | 2.358 |
| Si1-H | - | - | - | - | - | 1.497 |

Table 2: Bond orders data of the studied molecules

| Bonds | CCCC | SCCC | S SCC | SCSC | SSSC | SSSS |
|---------|-------|-------|-------|-------|-------|-------|
| C1-C2 | 0.978 | 1.033 | 1.722 | - | - | - |
| C2-C3 | 2.004 | 1.930 | - | - | - | - |
| C3-C4 | 0.978 | - | - | - | - | - |
| C4-C1 | 2.004 | - | - | - | - | - |
| C1-H | 0.928 | 0.929 | 0.902 | 0.918 | 0.904 | - |
| C2-H | 0.928 | 0.899 | 0.878 | - | - | - |
| C3-H | 0.928 | 0.924 | - | 0.918 | - | - |
| C4-H | 0.928 | - | - | - | - | - |
| C3-Si4 | - | 0.851 | - | 1.095 | - | - |
| Si4-C1 | - | 1.618 | 0.965 | 1.095 | 1.211 | - |
| Si4-H | - | 0.905 | 0.894 | 0.908 | 0.904 | 0.914 |
| C2-Si3 | - | - | 0.713 | - | - | - |
| Si3-Si4 | - | - | 0.859 | - | 0.957 | 1.012 |
| Si3-H | - | - | 0.894 | - | 0.908 | 0.910 |
| C1-Si2 | - | - | - | 1.095 | 1.210 | - |
| Si2-C3 | - | - | - | 1.095 | - | - |
| Si2-H | - | - | - | 0.908 | 0.904 | 0.907 |
| Si2-Si3 | - | - | - | - | 0.957 | 1.272 |
| Si1-Si2 | - | - | - | - | - | 1.272 |
| Si4-Si1 | - | - | - | - | - | 1.012 |
| Si1-H | - | - | - | - | - | 0.910 |

Table 3: Total bond orders data of the studied molecules

| Compounds | Sum of sigma and pi bond orders of ring |
|-----------|---|
| CCCC | 5.964 |
| SCCC | 5.432 |
| SSCC | 4.259 |
| SCSC | 4.380 |
| SSSC | 4.335 |
| SSSS | 4.568 |

Table 4: NICS(0) data of the studied molecules

| Compounds | NICS(0) |
|-----------|---------|
| CCCC | 26.528 |
| SCCC | 20.413 |
| SSCC | -14.885 |
| SCSC | 12.091 |
| SSSC | -8.403 |
| SSSS | -14.241 |

Table 5: Global reactivity descriptors data of the studied molecules

| Compound | HOMO (eV) | LUMO (eV) | GAP (eV) | χ (eV) | μ (eV) | η (eV) | S (eV) ⁻¹ | ω (eV) |
|----------|-----------|-----------|----------|-------------|------------|-------------|----------------------|---------------|
| CCCC | -5.44 | -1.90 | 3.54 | -3.67 | 3.67 | 1.77 | 0.28 | 3.77 |
| SCCC | -4.89 | -2.37 | 2.52 | -3.63 | 3.63 | 1.26 | 0.40 | 5.27 |
| SSCC | -5.95 | -2.26 | 3.69 | -4.11 | 4.11 | 1.85 | 0.27 | 4.56 |
| SCSC | -4.79 | -2.39 | 2.40 | -3.59 | 3.59 | 1.20 | 0.42 | 5.41 |
| SSSC | -5.86 | -2.36 | 3.50 | -4.11 | 4.11 | 1.75 | 0.29 | 4.90 |
| SSSS | -5.97 | -3.10 | 2.87 | -4.54 | 4.54 | 1.44 | 0.35 | 7.21 |

Table 6: Natural charges data of the atoms of the studied molecules

| Atoms | CCCC | SCCC | SSCC | SCSC | SSSC | SSSS |
|-------|--------|--------|--------|--------|--------|--------|
| H1 | 0.199 | 0.226 | 0.233 | 0.250 | 0.242 | -0.131 |
| H2 | 0.199 | 0.205 | 0.227 | -0.158 | -0.144 | -0.127 |
| H3 | 0.199 | 0.220 | -0.161 | 0.250 | -0.183 | -0.131 |
| H4 | 0.199 | -0.158 | -0.219 | -0.158 | -0.144 | -0.144 |
| C1 | -0.199 | -0.910 | -0.613 | -1.524 | -1.342 | - |
| C2 | -0.199 | -0.146 | -0.624 | - | - | - |
| C3 | -0.199 | -0.662 | - | -1.254 | - | - |
| C4 | -0.199 | - | - | - | - | - |
| Si1 | - | - | - | - | - | 0.238 |
| Si2 | - | - | - | 1.432 | 0.830 | 0.080 |
| Si3 | - | - | 0.823 | - | -0.088 | 0.238 |
| Si4 | - | 1.226 | 0.334 | 1.432 | 0.830 | -0.023 |

Table 7: The chemical shifts data of the atoms of the studied molecules

| Nucleus | CCCC | SCCC | SSCC | SCSC | SSSC | SSSS |
|---------|---------|---------|---------|---------|----------|---------|
| H1 | 5.897 | 4.671 | 8.301 | 0.364 | 7.178 | 8.017 |
| H2 | 5.896 | 6.675 | 9.000 | 8.650 | 8.411 | 9.861 |
| H3 | 5.896 | 3.441 | 5.008 | 0.364 | 3.336 | 8.012 |
| H4 | 5.897 | 8.172 | 6.191 | 8.650 | 8.410 | 4.396 |
| C1 | 147.409 | 134.914 | 171.466 | 38.032 | 163.659 | - |
| C2 | 147.411 | 173.831 | 154.090 | - | - | - |
| C3 | 147.387 | 96.886 | - | 38.033 | - | - |
| C4 | 147.440 | - | - | - | - | - |
| Si1 | - | - | - | - | - | 236.721 |
| Si2 | - | - | - | 204.748 | 208.704 | 238.916 |
| Si3 | - | - | -25.152 | - | -140.006 | 236.486 |
| Si4 | - | 141.311 | 63.788 | 204.749 | 208.479 | -87.229 |

Table 8: The NBO population analysis data of the studied molecules

| Compounds | Bonds | Occupancy | Population/Bond orbital/Hybrids |
|------------------|--------------------|--|---|
| CCCC | σ (C1-C2) | 1.96534 | 50.00% C1 (sp ^{2.71}), 50.00% C2 (sp ^{2.71}) |
| | σ (C2-C3) | 1.99299 | 50.00% C2 (sp), 50.00% C3 (sp) |
| | π (C2-C3) | 1.98364 | 50.00% C2 (sp ^{1.64}), 50.00% C3 (sp ^{1.64}) |
| | σ (C3-C4) | 1.96534 | 50.00% C3 (sp ^{2.71}), 50.00% C4 (sp ^{2.71}) |
| | σ (C1-C4) | 1.99299 | 50.00% C1 (sp), 50.00% C4 (sp) |
| | π (C1-C4) | 1.98363 | 50.00% C1 (sp ^{1.63}), 50.00% C4 (sp ^{1.64}) |
| | σ (C1-H) | 1.99185 | 60.54% C1 (sp ^{1.85}), 39.46% H (s) |
| | σ (C2-H) | 1.99185 | 60.54% C2 (sp ^{1.85}), 39.46% H (s) |
| | σ (C3-H) | 1.99185 | 60.54% C3 (sp ^{1.85}), 39.46% H (s) |
| | σ (C4-H) | 1.99185 | 60.54% C4 (sp ^{1.85}), 39.46% H (s) |
| SCCC | σ (C1-C2) | 1.96435 | 49.29% C1 (sp ^{2.56}), 50.71% C2 (sp ^{2.26}) |
| | σ (C2-C3) | 1.98295 | 50.69% C2 (sp ^{1.62}), 49.31% C3 (sp ^{1.62}) |
| | π (C2-C3) | 1.98724 | 43.50% C2 (sp), 56.50% C3 (sp) |
| | σ (C3-Si4) | 1.94486 | 65.99% C3 (sp ^{3.14}), 34.01% Si4 (sp ^{2.21}) |
| | σ (C1-Si4) | 1.96934 | 68.91% C1 (sp ^{1.94}), 31.09% Si4 (sp ^{1.56d^{0.02}}) |
| | π (C1-Si4) | 1.92046 | 69.40% C1 (sp), 30.60% Si4 (sp ^{d^{0.01}}) |
| | σ (C1-H) | 1.99237 | 61.67% C1 (sp ^{1.65}), 38.33% H (s) |
| | σ (C2-H) | 1.97775 | 60.98% C2 (sp ^{2.21}), 39.02% H (s) |
| | σ (C3-H) | 1.98745 | 61.33% C3 (sp ^{1.66}), 38.67% H (s) |
| σ (Si4-H) | 1.96811 | 42.23% Si4 (sp ^{2.28d^{0.02}}), 57.77% H (s) | |
| SSCC | σ (C1-C2) | 1.98730 | 49.85% C1 (sp ^{1.88d^{0.01}}), 50.15% C2 (sp ^{1.82}) |
| | π (C1-C2) | 1.80071 | 50.74% C1 (sp ^{87.60d^{0.28}}), 49.26% C2 (sp ^{99.99d^{0.19}}) |
| | σ (C2-Si3) | 1.79081 | 77.33% C2 (sp ^{1.89}), 22.67% Si3 (sp ^{8.07d^{0.11}}) |
| | σ (Si3-Si4) | 1.88469 | 31.54% Si3 (sp ^{15.95d^{0.13}}), 68.46% Si4 (sp ^{1.65d^{0.01}}) |
| | σ (C1-Si4) | 1.95685 | 69.46% C1 (sp ^{2.60d^{0.01}}), 30.54% Si4 (sp ^{2.60d^{0.03}}) |
| | σ (C1-H) | 1.98245 | 61.98% C1 (sp ^{1.76}), 38.02% H (s) |
| | σ (C2-H) | 1.96464 | 62.27% C2 (sp ^{2.40}), 37.73% H (s) |
| | σ (Si3-H) | 1.95319 | 38.02% Si3 (sp ^{6.54d^{0.06}}), 61.98% H (s) |
| | σ (Si4-H) | 1.96950 | 42.56% Si4 (sp ^{2.16d^{0.02}}), 57.44% H (s) |
| SCSC | σ (C1-Si2) | 1.95712 | 68.94% C1 (sp ^{2.27}), 31.06% Si2 (sp ^{1.84d^{0.02}}) |
| | σ (Si2-C3) | 1.95712 | 31.06% Si2 (sp ^{1.84d^{0.02}}), 68.94% C3 (sp ^{2.27}) |
| | π (Si2-C3) | 1.74504 | 12.76% Si2 (sp ^{d^{0.04}}), 87.24% C3 (sp) |
| | σ (C3-Si4) | 1.95712 | 68.94% C3 (sp ^{2.27}), 31.06% Si4 (sp ^{1.84d^{0.02}}) |

| | | | |
|------|--------------------------|---------|--|
| | $\sigma(\text{C1-Si4})$ | 1.95712 | 68.94% C1 ($\text{sp}^{2.27}$), 31.06% Si4 ($\text{sp}^{1.84\text{d}^{0.02}}$) |
| | $\pi(\text{C1-Si4})$ | 1.74504 | 87.24% C1 (sp), 12.76% Si4 ($\text{spd}^{0.04}$) |
| | $\sigma(\text{C1-H})$ | 1.99092 | 62.90% C1 ($\text{sp}^{1.58}$), 37.10% H (s) |
| | $\sigma(\text{Si2-H})$ | 1.97456 | 42.54% Si2 ($\text{sp}^{2.32\text{d}^{0.02}}$), 57.46% H (s) |
| | $\sigma(\text{C3-H})$ | 1.99092 | 62.90% C3 ($\text{sp}^{1.58}$), 37.10% H (s) |
| | $\sigma(\text{Si4-H})$ | 1.97456 | 42.54% Si4 ($\text{sp}^{2.32\text{d}^{0.02}}$), 57.46% H (s) |
| SSSC | $\sigma(\text{C1-Si2})$ | 1.96977 | 71.13% C1 ($\text{sp}^{2.17}$), 28.87% Si2 ($\text{sp}^{2.23\text{d}^{0.02}}$) |
| | $\sigma(\text{Si2-Si3})$ | 1.88052 | 62.38% Si2 ($\text{sp}^{1.68\text{d}^{0.01}}$), 37.62% Si3 ($\text{sp}^{11.83\text{d}^{0.09}}$) |
| | $\sigma(\text{Si3-Si4})$ | 1.83645 | 38.29% Si3 ($\text{sp}^{11.83\text{d}^{0.09}}$), 61.71% Si4 ($\text{sp}^{1.59\text{d}^{0.01}}$) |
| | $\sigma(\text{C1-Si4})$ | 1.97033 | 71.13% C1 ($\text{sp}^{2.15}$), 28.87% Si4 ($\text{sp}^{2.23\text{d}^{0.02}}$) |
| | $\pi(\text{C1-Si4})$ | 1.61299 | 74.86% C1 ($\text{sp}^{76.90\text{d}^{0.11}}$), 25.14% Si4 ($\text{sp}^{99.99\text{d}^{38.76}}$) |
| | $\sigma(\text{C1-H})$ | 1.99048 | 62.93% C1 ($\text{sp}^{1.83}$), 37.07% H (s) |
| | $\sigma(\text{Si2-H})$ | 1.97535 | 43.49% Si2 ($\text{sp}^{2.18\text{d}^{0.02}}$), 56.51% H (s) |
| | $\sigma(\text{Si3-H})$ | 1.95381 | 39.91% Si3 ($\text{sp}^{5.96\text{d}^{0.05}}$), 60.09% H (s) |
| | $\sigma(\text{Si4-H})$ | 1.97436 | 43.47% Si4 ($\text{sp}^{2.21\text{d}^{0.02}}$), 56.53% H (s) |
| SSSS | $\sigma(\text{Si1-Si2})$ | 1.93704 | 47.92% Si1 ($\text{sp}^{2.52\text{d}^{0.02}}$), 52.08% Si2 ($\text{sp}^{2.13\text{d}^{0.01}}$) |
| | $\sigma(\text{Si2-Si3})$ | 1.93706 | 52.09% Si2 ($\text{sp}^{2.12\text{d}^{0.01}}$), 47.91% Si3 ($\text{sp}^{2.52\text{d}^{0.02}}$) |
| | $\sigma(\text{Si3-Si4})$ | 1.91704 | 63.16% Si3 ($\text{sp}^{1.70\text{d}^{0.01}}$), 36.84% Si4 ($\text{sp}^{12.08\text{d}^{0.09}}$) |
| | $\sigma(\text{Si1-Si4})$ | 1.91710 | 63.15% Si1 ($\text{sp}^{1.70\text{d}^{0.01}}$), 36.85% Si4 ($\text{sp}^{12.07\text{d}^{0.09}}$) |
| | $\sigma(\text{Si1-H})$ | 1.97935 | 44.28% Si1 ($\text{sp}^{2.12\text{d}^{0.01}}$), 55.72% H (s) |
| | $\sigma(\text{Si2-H})$ | 1.98308 | 45.14% Si2 ($\text{sp}^{1.81\text{d}^{0.01}}$), 54.86% H (s) |
| | $\sigma(\text{Si3-H})$ | 1.97934 | 44.28% Si3 ($\text{sp}^{2.12\text{d}^{0.01}}$), 55.72% H (s) |
| | $\sigma(\text{Si4-H})$ | 1.94188 | 41.54% Si4 ($\text{sp}^{5.68\text{d}^{0.04}}$), 58.46% H (s) |

Conclusions

The main goal of this study is study of the structural and spectral properties and reactivity of the silicon analogs of cyclobutadiene compound. The study was conducted based on the quantum-mechanical computations. All the selected molecules were optimized by B3LYP/6-311++G(d,p) basis set of theory. From the computations and mathematical calculations, the following conclusions were drawn.

1. All studied molecule structures can't be antiaromatic and they are non-aromatic compounds.
2. The SCSC molecular structure has the lowest stability and the highest reactivity among all compounds.
3. The reactivity of SSSS molecule is more than the CCCC compound.
4. The replacing silicon atoms instead of carbon atoms in molecular structure of cyclobutadiene molecule reduce the electrophilicity property of the compound.
5. All compounds prefer to react with nucleophiles.

6. The electrophiles attack to carbon atoms and nucleophiles reveals a significant tendency to react with the silicon atoms.

7. The four silicon atoms of SSSS molecular structure have not unique reactivity with active nucleophiles and electrophiles.

8. The stretching vibrations of C-H and Si-H appear at the frequency range of 3000-3300 and 2000-2200 cm^{-1} , respectively.

9. The HOMO/LUMO electronic transitions of cyclobutadiene and its silicon analogs happen at about 470-490 nm wavelengths.

10. The nucleuses with electron deficiency are seen at high chemical shifts. In contrast, the lowest chemical shifts are belonged to the nucleuses with surplus electron.

11. Carbon atoms participate with more p orbitals in C-C bonds than C-H bonds.

12. Low p orbitals of carbon atoms are participated in C-C and C-Si bonds by entering the silicon atoms instead of the carbon atoms in molecular structures,

13. The lowest acidity is related to the hydrogen atoms of Si-H bonds.

14. The Si-C-H hydrogen atoms have lower acidity than the C-C-H hydrogen atoms.

Conflict of interests

The author declares that there is no conflict of interests regarding the publication of this paper.

Acknowledgments

The author is grateful to Miss. Maliheh-Alsadat Kermanian for her significant contribution.

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HOW TO CITE THIS ARTICLE

Mehdi Nabati*. Prediction of the Structural and Spectral Properties and Reactivity of the Silicon Analogs of Cyclobutadiene C₄-nSi_nH₄ (n=0-4) by Density Functional Theory Computations. *Chem. Methodol.*, 2023, 7(9) 676-687
 DOI: <https://doi.org/10.48309/chemm.2023.52049>
 URL: https://www.chemmethod.com/article_52049.html