

Reactivity and aromaticity of hexasilene derivatives Si_6XH_5 (X = H, F, Cl, Br, COOH, NO_2 , NH_2 , CH_3 and tBu)

Mehdi Nabati*

Synthesis and Molecular Simulation Laboratory, Chemistry Department, Pars Isotope Company, P.O. Box: 1437663181, Tehran, Iran

Received February 2018; Accepted March 2018

ABSTRACT

During recent years, the silicon organic-inorganic compounds play the key role in medicinal chemistry and pharmaceutical industry. This is because of their similar chemical properties with carbon compounds. The second reason is related to their easy transfer from the cell membranes. So, molecular simulation and study the properties of novel organosilicon compounds can be more important. From this sight of view, we designed and investigated silicon analogs of benzene ring before. Here, the various derivatives of hexasilene molecule will be discussed in the following. Our investigations are based on the density functional theory (DFT) computations. The present research work was focused on investigation of the structural and spectral properties and reactivity of hexasilene using B3LYP/cc-pVDZ level of theory. The Fukui indices (local reactivity) showed that the electrophilic attacks happen on the Si4 atoms of the molecules. On the other hand, the molecules containing electron-donating and electron-withdrawing substituents prefer do nucleophilic reactions on their Si4 and Si3 positions, respectively.

Keywords: Density functional theory; Hexasilene; Reactivity; Benzene silicon analogs; Structural properties.

INTRODUCTION

Silicon (Si, atomic number 14) is a hard blue-grey crystalline solid and a member of group 14 in the periodic table. It is below carbon and above germanium, tin and lead elements. From the mass point of view, it is the eighth most common atom in the world. The silicon element is composed of three stable isotopes, ^{28}Si (92.23%), ^{29}Si (4.67%) and ^{30}Si (3.10%). The ^{29}Si isotope is used in nuclear magnetic resonance (NMR) spectroscopy [1]. The silicon atom is found out in the earth's crust as stone, silica sand and clays. The silicate compounds are used in the

structure of mortar, cement and stucco materials [2]. Also, it has various uses in high-strength ceramics components [3]. In inorganic chemistry field, it is used in various forms such as silicon dioxide, silanes, hexafluorosilicates, silanols, silicides, hyperbranched aminosilicas, polysilazanes, silazanes, silenes, silicon oxynitride and silicates [4]. One important part of silicon compounds is related to the organosilicon compounds. These compounds comprise bis(trimethylsilyl) amides, carbosilanes, organosilicon polymers, silicon heterocycles and siloxanes [5]. Other main silicon

*Corresponding author: mnabati@ymail.com

molecules are halo-organosilicon molecules such as trimethylsilylchloride (TMS-Cl), triethylsilylchloride (TES-Cl) and tert-butyldimethylsilylchloride (tBuDM-Cl). These chemical agents give the molecules chemoselectivity in a multistep organic reaction as a protective group by protection of a functional group [6].

In recent decade, silicon compounds play the key role in medicinal chemistry [7]. This is because of their similar chemical properties with carbon compounds. The second reason is related to their easy transfer from the cell membranes [7]. So, simulation and preparation of silicon analogs of carbon compounds is more important in novel medicinal fields. To access this, we simulated and discussed the nitrogen and silicon analogs of benzene ring recently [8]. We saw the hexasilabenzene compound is an aromatic molecule with NICS(0) -12.13 and -13.17 in B3LYP/6-311++G(d,p) and B3LYP/CBSB7 levels of theory, respectively. It was concluded that the hexasilene compound has more aromaticity than benzene ring. So, during the present research work we want to discuss the reactivity and stability of various derivatives of hexasilene.

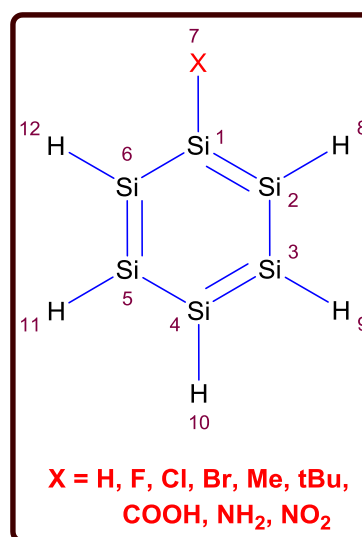
COMPUTATIONAL METHOD

The geometry optimizations and single point calculations of the compounds in gas phase have been carried out using the density functional theory (DFT) method [9] with Becke, 3-parameter, Lee-Yang-Parr (B3LYP) exchange correlation corrected functional [10] and the cc-pVDZ basis set using the GAUSSIAN 03 program [11]. The imaginary frequencies were not shown in frequency computation analysis of the optimized molecules. The energies of the molecules were computed with a self-consistent field (SCF)

convergence of 10^{-8} a.u. for the density matrix.

RESULTS AND DISCUSSION

During the present research work, the various derivatives of hexasilene molecule are discussed theoretically. The studied structures are given in Scheme 1. All considered compounds are presented in the Table 1.



Scheme 1. The studied structures with atomic numbering.

OPTIMIZED STRUCTURES

Table 1 indicates the bond lengths data of the optimized structures (Figure 1) of the studied molecules. From the Figure 1, we can see the hexasilene derivatives containing NH_2 , F, Cl and Br substituents retain the original geometry structure of hexasilene molecule. In contrast, the hexasilene derivatives containing NO_2 , COOH, CH_3 and tert-butyl (tBu) substituents exhibit a disruption to the geometry structure of hexasilene compound. The bond lengths data of these molecules are collected in Table 1. From the data of the Table 1, the Si-Si bond lengths of F, Cl and Br derivatives of hexasilene are same as Si-Si bond length of hexasilene molecule. In contrast, the Si-Si

bond lengths of the hexasilene derivatives containing NH_2 , NO_2 , COOH , CH_3 and tert-butyl (tBu) substituents are longer than the ones of hexasilene molecule. Also, the Si-H bond lengths of all molecules are similar (1.5 Angstrom). Table 2 collects the bond orders (B.O.) data of all studied compounds. We can see the Si1-Si2 bond order of all derivative are smaller than the one in hexasilene molecule. The Si2-Si3 and Si3-Si4 bond orders of hexasilene derivatives containing NO_2 , COOH , CH_3 and tert-butyl (tBu) substituents are small to the ones in molecules containing F, Cl and Br substituents. These data shows that

all derivatives are not aromatic compounds. One important parameter to recognize the aromaticity property of molecules is nuclear independent chemical shift (NICS) factor. The negative and positive NICS parameters show aromatic and antiaromatic ring compounds, respectively [12]. From the NICS(0) data of the molecules (Table 3), all derivatives are aromatic compounds but we saw the Si-Si bond orders of each molecule are not equal together. So, it can be concluded that the NICS(0) parameter cannot indicates the aromaticity property of hexasilene derivatives.

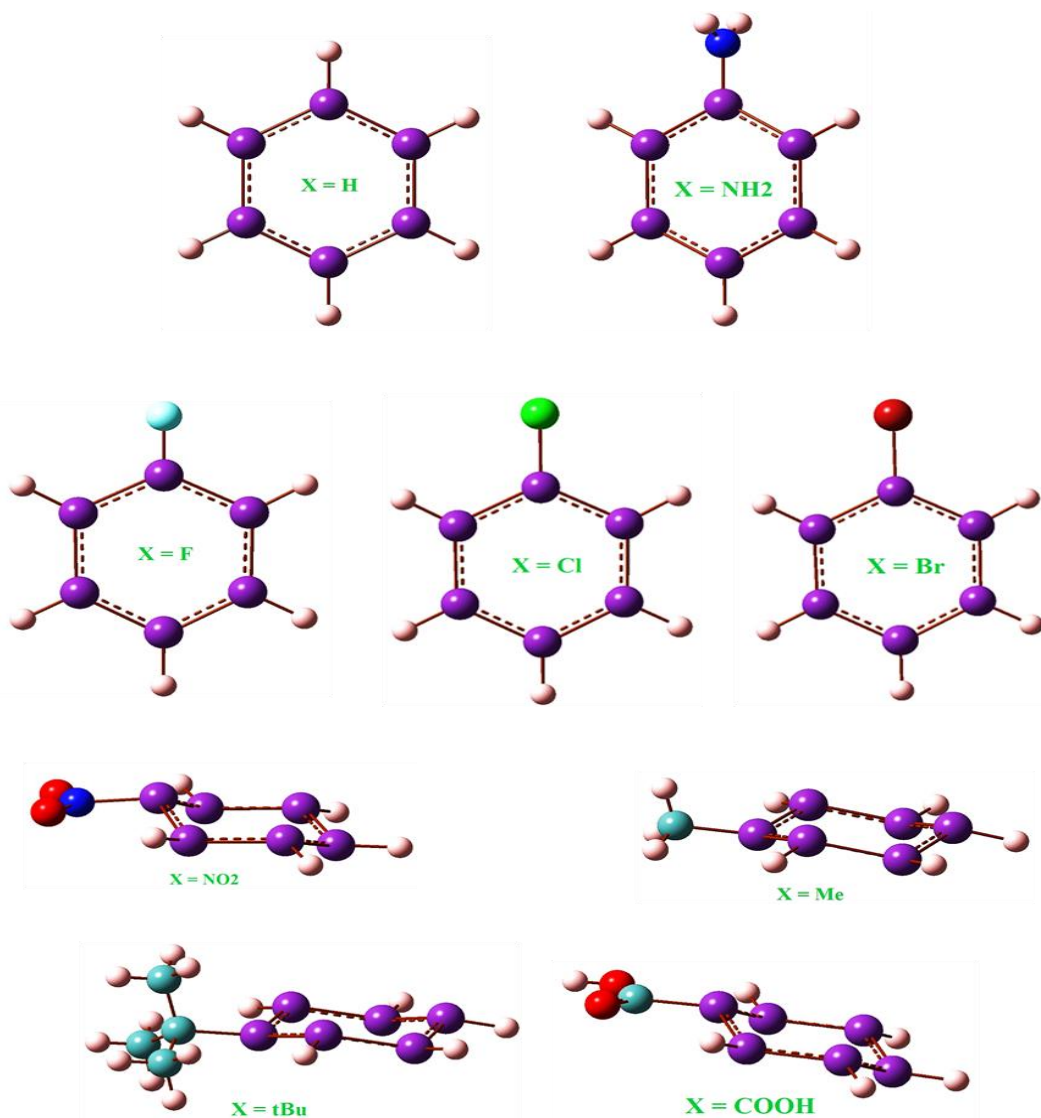


Fig. 1. The optimized structures of the studied molecules.

Table 1. The bond lengths of the studied structures

X	Si1-Si2	Si2-Si3	Si3-Si4	Si1-X	Si2-H8	Si3-H9	Si4-H10
H	2.221	2.221	2.221	1.492	1.492	1.492	1.492
F	2.219	2.222	2.220	1.656	1.489	1.491	1.490
Cl	2.222	2.222	2.221	2.097	1.489	1.491	1.490
Br	2.224	2.222	2.221	2.255	1.489	1.491	1.490
COOH	2.250	2.248	2.249	1.937	1.496	1.498	1.498
Me	2.252	2.250	2.251	1.906	1.500	1.499	1.499
tBu	2.256	2.249	2.249	1.953	1.500	1.499	1.499
NH ₂	2.229	2.225	2.221	1.737	1.493	1.492	1.492
NO ₂	2.262	2.252	2.251	1.917	1.495	1.497	1.497

Table 2. The bond orders (B.O.) of the studied structures

X	Si1-Si2	Si2-Si3	Si3-Si4	Si1-X	Si2-H8	Si3-H9	Si4-H10
H	1.421	1.421	1.421	0.962	0.962	0.962	0.962
F	1.361	1.415	1.423	0.601	0.966	0.962	0.964
Cl	1.367	1.416	1.421	0.900	0.966	0.962	0.963
Br	1.366	1.416	1.421	0.969	0.965	0.962	0.963
COOH	1.350	1.385	1.385	0.847	0.958	0.956	0.956
Me	1.365	1.386	1.382	0.874	0.956	0.955	0.956
tBu	1.373	1.387	1.383	0.772	0.956	0.955	0.956
NH ₂	1.365	1.413	1.423	0.773	0.962	0.961	0.962
NO ₂	1.312	1.380	1.380	0.595	0.958	0.956	0.957

Table 3. The NICS(0) data of the studied structures

X	NICS(0)
H	-13.234
F	-14.717
Cl	-14.021
Br	-13.794
COOH	-11.208
Me	-10.630
tBu	-11.191
NH ₂	-14.096
NO ₂	-11.403

REACTIVITY AND STABILITY

In organic chemistry, frontier molecular orbitals (FMOs) give us more information about molecular structures and their reactivity and stability [13-15]. Table 4 collects the frontier molecular orbitals (HOMO and LUMO) energies, electronegativity (χ), ionization potential (μ), hardness (η), softness (S) and electrophilicity (ω) of all studied hexasilene derivatives. From the data, the ionization potential and hardness factor of nitro derivative of hexasilene are 4.74 eV

and 1.64 eV, respectively. These data show this molecule is the most unstable derivative of hexasilene molecule. On the other hand, we saw the stability of hexasilene is more than its derivatives. The electrophilicity index order of compounds is $\text{NO}_2 > \text{COOH} > \text{Me} > \text{tBu} > \text{Cl} > \text{F} > \text{Br} > \text{H} > \text{NH}_2$. So, the molecules containing mesomeric electron-withdrawing groups show more tendencies to electrophilic reactions. This is proven by the density of states (DOS) graphs of the molecules (Figure 2). It can be seen from the graphs

that the virtual orbitals density of all hexasilene derivatives is more than the occupied orbitals density. The local reactivities of silicon atoms of the molecules are computed by Fukui indices and collected in Table 5. From these data the following orders are obtained.

For nucleophilic attacks on the molecules:

F and Cl derivatives: Si3 > Si4 > Si2

Br and COOH derivatives: Si2 > Si3 > Si4

Me and tBu derivatives: Si4 > Si2 > Si3

NH₂ derivative: Si4 > Si3 > Si2

NO₂ derivative: Si3 > Si2 > Si4

For electrophilic attacks on the molecules:

F, Cl, Br, Me and tBu derivatives: Si4 > Si2 > Si3

COOH derivative: Si2 > Si3 = Si4

NH₂ and NO₂ derivatives: Si4 > Si3 > Si2

For radical attacks on the molecules:

F and Cl derivatives: Si2 > Si4 > Si3

Br derivative: Si4 > Si2 > Si3

COOH and NO₂ derivatives: Si4 > Si3 > Si2

Me derivative: Si3 > Si4 > Si2

tBu derivative: Si3 > Si2 > Si4

NH₂ derivative: Si2 > Si3 > Si4

So, it can be concluded all molecules accept the electrophilic attacks on their Si4 atoms. On the other hand, the molecules containing electron-donating and electron-withdrawing substituents prefer do nucleophilic reactions on their Si4 and Si3 positions, respectively.

Table 4. The global reactivity data of the studied structures

X	HOMO (eV)	LUMO (eV)	GAP (eV)	χ (eV)	μ (eV)	η (eV)	S (eV) ⁻¹	ω (eV)
H	-5.60	-2.26	3.34	-3.93	3.93	1.67	0.30	4.63
F	-5.61	-2.43	3.18	-4.02	4.02	1.59	0.31	5.01
Cl	-5.62	-2.43	3.19	-4.03	4.03	1.60	0.31	5.03
Br	-5.60	-2.41	3.19	-4.01	4.01	1.60	0.31	4.98
COOH	-5.84	-2.82	3.02	-4.33	4.33	1.51	0.33	6.19
Me	-5.55	-2.46	3.09	-4.01	4.01	1.55	0.32	5.15
tBu	-5.52	-2.42	3.10	-3.97	3.97	1.55	0.32	5.04
NH ₂	-5.36	-2.07	3.29	-3.72	3.72	1.65	0.30	4.15
NO ₂	-6.20	-3.28	2.92	-4.74	4.74	1.46	0.34	7.64

Table 5. The local reactivity data of the studied structures

X	Nucleophilic attack			Electrophilic attack			Radical attack		
	Si2	Si3	Si4	Si2	Si3	Si4	Si2	Si3	Si4
H	-0.048	-0.048	-0.048	-0.079	-0.079	-0.079	-0.064	-0.064	-0.064
F	-0.167	-0.052	-0.062	-0.102	-0.069	-0.126	-0.135	-0.062	-0.094
Cl	-0.170	-0.041	-0.063	-0.088	-0.070	-0.121	-0.129	0.041	-0.092
Br	-0.039	-0.043	-0.102	-0.088	-0.071	-0.126	-0.064	-0.057	-0.119
COOH	-0.049	-0.052	-0.130	-0.001	0.000	0.000	-0.025	-0.026	-0.065
Me	-0.073	-0.134	-0.049	-0.083	-0.061	-0.123	-0.078	-0.098	-0.082
tBu	-0.062	-0.132	-0.050	-0.107	-0.046	-0.113	-0.087	-0.089	-0.082
NH ₂	-0.204	-0.075	-0.054	-0.059	-0.088	-0.099	-0.132	-0.082	-0.077
NO ₂	-0.058	-0.049	-0.114	-0.065	-0.082	-0.111	-0.062	-0.066	-0.113

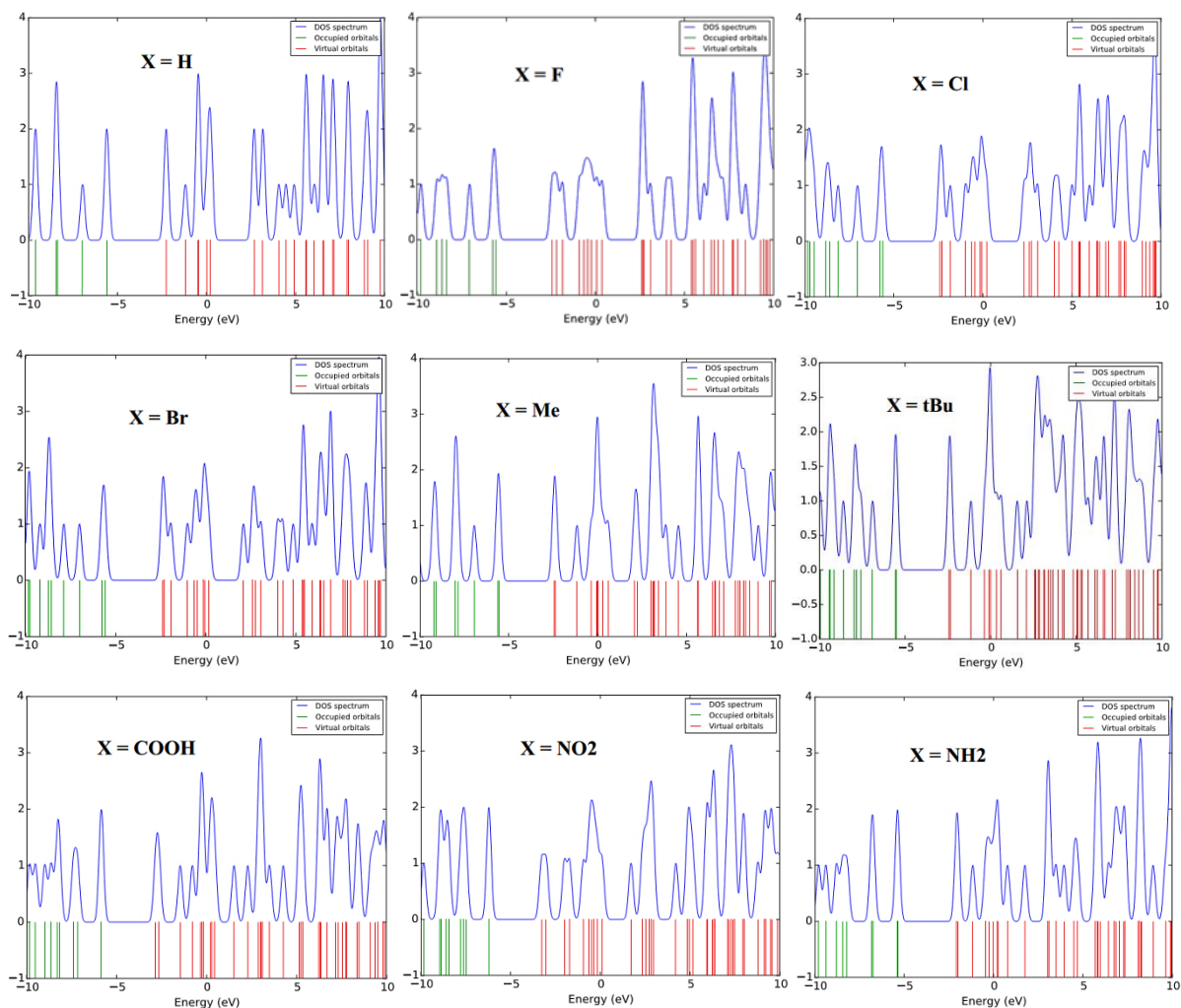


Fig. 2. The density of states (DOS) graphs of the studied molecules.

SPECTRAL STUDIES

In chemistry, the identification of chemical molecules is done by spectroscopy methods [16-19]. Here, the various spectral properties of the studied molecules are investigated and discussed. Figure 3 indicates the IR spectrum of the studied molecules.

Hexasilene: IR [Harmonic frequencies (cm^{-1}), intensities (KM/Mole)]: 339.7737 (0.0058), 344.4791 (0.0090), 348.1608 (0.0184), 445.1424 (3.1511), 445.3403 (3.1217), 555.3685 (0.0001), 555.6540 (0.0002), 593.1493 (0.0016), 711.8076 (0.0006), 712.5492 (0.0019), 721.1679 (43.4075), 722.4463 (43.5271), 2203.1527

(19.9751), 2205.4785 (0.0004), 2210.4069 (0.0042), 2212.7786 (181.0130), 2217.2279 (188.6967), and 2220.3993 (0.0045).

F derivative of Hexasilene: IR [Harmonic frequencies (cm^{-1}), intensities (KM/Mole)]: 40.9076 (0.0146), 135.5383 (2.1169), 143.7783 (1.0041), 148.1071 (0.2267), 187.2728 (2.5089), 269.1547 (0.5160), 297.9904 (0.0471), 342.9634 (0.2059), 363.4710 (0.0816), 404.8073 (0.2538), 430.2901 (1.2195), 459.2660 (0.7704), 547.8929 (0.6109), 552.0538 (0.0658), 569.7709 (0.6585), 589.3791 (0.7984), 661.0473 (15.2792), 686.9686 (21.9527), 707.2217 (16.3572), 720.4158

(31.5207), 868.4113 (131.8059), 2211.9349 (4.6054), 2214.5897 (48.0103), 2222.6172 (105.9226), 2225.8716 (108.5934), and 2227.4623 (0.0018).

Cl derivative of Hexasilene: IR [Harmonic frequencies (cm^{-1}), intensities (KM/Mole)]: 44.8659 (0.0342), 89.3264 (0.2182), 110.4226 (0.7763), 137.5457 (0.0217), 163.2943 (0.0891), 257.7900 (0.6415), 309.3748 (0.0336), 342.3453 (0.0793), 343.4777 (5.4041), 404.1600 (0.1049), 419.4766 (0.5783), 456.6532 (1.6547), 541.4452 (38.3636), 546.4629 (0.2524), 566.6064 (0.2153), 573.4260 (115.5561), 592.7991 (0.3899), 655.3396 (9.2363), 704.3312 (2.7375), 709.1590 (18.1063), 718.8177 (31.8309), 2210.8233 (5.1731), 2213.6091 (44.6402), 2221.0861 (105.8429), 2223.9162 (115.9741), and 2225.5741 (2.4296).

Br derivative of Hexasilene: IR [Harmonic frequencies (cm^{-1}), intensities (KM/Mole)]: 43.8506 (0.0249), 74.5414 (0.0167), 88.5839 (0.2919), 120.5500 (0.0618), 160.7970 (0.0128), 239.7012 (2.3485), 312.8777 (0.0255), 320.8468 (11.0528), 321.0398 (0.0078), 342.1879 (0.0523), 403.9995 (0.0690), 409.6525 (3.1972), 455.4789 (1.9304), 497.4360 (83.1357), 545.8093 (0.1922), 555.4339 (12.7205), 565.3416 (0.1377), 594.5150 (0.3112), 653.1928 (7.5975), 703.3618 (0.3304), 709.8825 (18.4335), 718.1448 (41.2968), 2210.1696 (5.9449), 2212.9325 (45.3019), 2220.5195 (105.8017), 2223.2942 (116.9914), and 2224.9205 (3.9998).

CH_3 derivative of Hexasilene: IR [Harmonic frequencies (cm^{-1}), intensities (KM/Mole)]: 50.0414 (0.0621), 76.0739 (0.8206), 101.0009 (1.1586), 124.7376 (1.8430), 127.7880 (0.0276), 141.2201 (0.7351), 147.7542 (0.3665), 166.9839 (0.0098), 199.4836 (2.5408), 330.4889 (0.1329), 356.6652 (3.2145), 373.1912 (6.4145), 379.6545 (1.9707), 398.3190 (1.3110), 427.4387 (2.9283), 449.5702

(7.7010), 478.8715 (3.0204), 522.1436 (0.0008), 525.0224 (0.0028), 530.5310 (0.5549), 595.7525 (0.3777), 646.2749 (5.8946), 667.7832 (50.9165), 714.3051 (24.2612), 714.9605 (43.6750), 734.0491 (2.1186), 765.1842 (21.4996), 810.3865 (13.1594), 1254.0007 (0.3758), 1427.2169 (5.4757), 1428.1071 (3.2218), 2168.7531 (35.2876), 2168.9984 (45.7333), 2172.8624 (80.5048), 2177.5200 (245.9401), 2182.6448 (76.6968), 3036.7810 (4.1039), 3123.9090 (2.3771), and 3128.1727 (1.3688).

tBu derivative of Hexasilene: IR [Harmonic frequencies (cm^{-1}), intensities (KM/Mole)]: 5.5923 (0.0002), 52.0606 (0.2138), 87.1817 (0.0262), 100.7270 (1.0051), 104.4943 (1.6928), 124.3441 (0.2474), 137.7949 (0.1748), 153.0821 (0.0716), 188.4571 (1.7708), 223.7555 (0.0369), 242.1646 (0.0004), 250.4096 (0.0893), 276.7093 (3.3369), 277.4202 (0.0027), 290.2826 (2.0165), 357.9133 (3.4762), 370.0919 (3.1564), 374.3986 (0.6134), 375.8960 (0.2197), 380.0351 (0.3582), 388.6767 (5.3453), 409.5286 (3.1273), 438.8028 (13.0096), 452.9113 (5.3396), 478.0333 (3.3994), 524.7062 (0.0062), 526.3972 (0.0120), 539.6383 (0.8692), 582.7612 (16.3028), 602.2801 (0.4135), 653.8721 (8.4800), 708.9638 (10.7377), 716.9655 (24.0804), 734.9954 (59.9028), 816.6398 (13.1115), 941.1934 (0.6773), 944.9706 (0.7977), 952.8539 (0.0013), 1021.8517 (2.1453), 1024.4515 (1.7238), 1191.0885 (64.6484), 1206.7403 (1.7599), 1211.1817 (0.0949), 1383.0305 (6.3571), 1383.7214 (5.1827), 1412.8037 (0.1734), 1447.1252 (0.0749), 1451.6994 (0.2496), 1454.4417 (0.0295), 1471.2208 (13.3850), 1474.0179 (8.3903), 1483.0801 (9.9458), 2169.0033 (35.7727), 2169.3634 (25.2241), 2173.7535 (72.5945), 2176.9195 (257.6220), 2182.5760 (96.2100), 3001.1490 (34.7957), 3007.6753 (17.5263), 3012.2580 (91.6710), 3076.9565 (2.8063), 3077.0623

(6.0775), 3081.2050 (74.0917), 3101.2276 (2.5610), 3103.3093 (26.2343), and 3107.2635 (16.0397).

COOH derivative of Hexasilene: IR [Harmonic frequencies (cm^{-1}), intensities (KM/Mole)]: 42.0591 (1.1751), 56.1628 (0.1633), 68.8155 (0.8818), 102.6373 (1.3921), 105.1703 (1.0151), 125.0659 (0.0946), 140.4977 (0.1661), 149.7714 (0.1430), 195.4755 (1.6185), 265.5506 (3.4710), 301.6134 (4.2530), 364.1246 (3.1301), 374.7900 (0.7578), 379.3572 (9.6632), 392.5950 (0.4011), 421.7969 (0.3432), 455.1348 (5.5493), 465.3429 (3.1945), 478.6081 (42.6340), 492.9345 (28.5435), 525.5346 (0.3307), 528.0424 (4.1652), 550.2094 (0.8898), 591.6588 (1.0004), 652.4238 (10.4676), 678.4171 (38.9471), 690.3865 (82.2276), 708.8870 (11.0882), 715.6972 (28.0115), 725.5741 (68.6955), 1119.0671 (415.9090), 1305.4226 (39.0910), 1775.6328 (268.9692), 2178.3335 (1.6242), 2181.9542 (80.2942), 2187.5945 (169.1455), 2194.0353 (99.0212), 2199.1307 (51.4312), and 3633.2857 (56.7026).

NH_2 derivative of Hexasilene: IR [Harmonic frequencies (cm^{-1}), intensities (KM/Mole)]: 62.8407 (0.1967), 116.5561 (1.6382), 139.1868 (0.3652), 149.5243 (0.0594), 190.7201 (1.2346), 273.0214 (0.0302), 335.7204 (0.0053), 348.0489 (0.0014), 360.5826 (0.0212), 414.9040 (0.0028), 432.4059 (1.6418), 451.7846 (0.9593), 541.2799 (0.3606), 550.2523 (0.1225), 557.4514 (0.8970), 594.8140 (0.1128), 654.5365 (8.7789), 698.0237 (22.1312), 714.7060 (18.1916), 718.9615 (49.5127), 763.0720 (9.7811), 863.4835 (123.7226), 1519.4710 (19.0614), 2201.2989 (30.9320), 2202.4358 (7.2146), 2207.9548 (42.5528), 2208.6503 (214.1670), 2216.1930 (71.1013), 3572.2267 (78.5430), and 3673.4702 (49.7520).

NO_2 derivative of Hexasilene: IR [Harmonic frequencies (cm^{-1}), intensities (KM/Mole)]: 45.6659 (0.0221), 56.4021 (0.7715), 77.9024 (0.8303), 101.3247 (0.8071), 108.3408 (1.1807), 123.8598 (0.6961), 142.7579 (0.2524), 149.3147 (0.1980), 191.8326 (2.6590), 255.8382 (0.1198), 300.8877 (5.5490), 361.5903 (2.9543), 364.8529 (4.0310), 383.7159 (4.4992), 393.4791 (0.1176), 425.3394 (0.5683), 455.2491 (8.0907), 456.1254 (11.2703), 472.6827 (16.5099), 516.7098 (2.3270), 523.5734 (0.1886), 540.3187 (20.0794), 541.6198 (0.3720), 584.3264 (0.9745), 649.5332 (5.3006), 684.7800 (0.7177), 712.2523 (25.9026), 720.5032 (42.3615), 834.0049 (63.9671), 1373.0426 (334.8402), 1579.4879 (146.5575), 2181.5260 (3.3841), 2183.9858 (85.0942), 2191.7864 (142.2046), 2200.9300 (109.1087), and 2202.0425 (4.6437).

The UV-Vis spectrum is one of the most important methods in determining the chemical properties of organic-inorganic compounds [20-22]. Here, the electronic transitions of the studied molecules are discussed.

Hexasilene: UV-Vis [wavelength of electronic transition (nm), energies (cm^{-1}), electronic transitions]: It is not observed any electronic transition for this molecule.

F derivative of Hexasilene: UV-Vis [wavelength of electronic transition (nm), energies (cm^{-1}), electronic transitions]:

a. 478.091 nm (20916.520 cm^{-1}), HOMO-1 to LUMO+1 (38%) and HOMO to LUMO (63%)

b. 438.646 nm (22797.418 cm^{-1}), HOMO to LUMO+2 (96%)

Cl derivative of Hexasilene: UV-Vis [wavelength of electronic transition (nm), energies (cm^{-1}), electronic transitions]:

a. 487.783 nm (20627.772 cm^{-1}), HOMO-1 to LUMO+1 (41%) and HOMO to LUMO (60%)

b. 431.502 nm (23174.888 cm^{-1}), HOMO to LUMO+2 (96%)

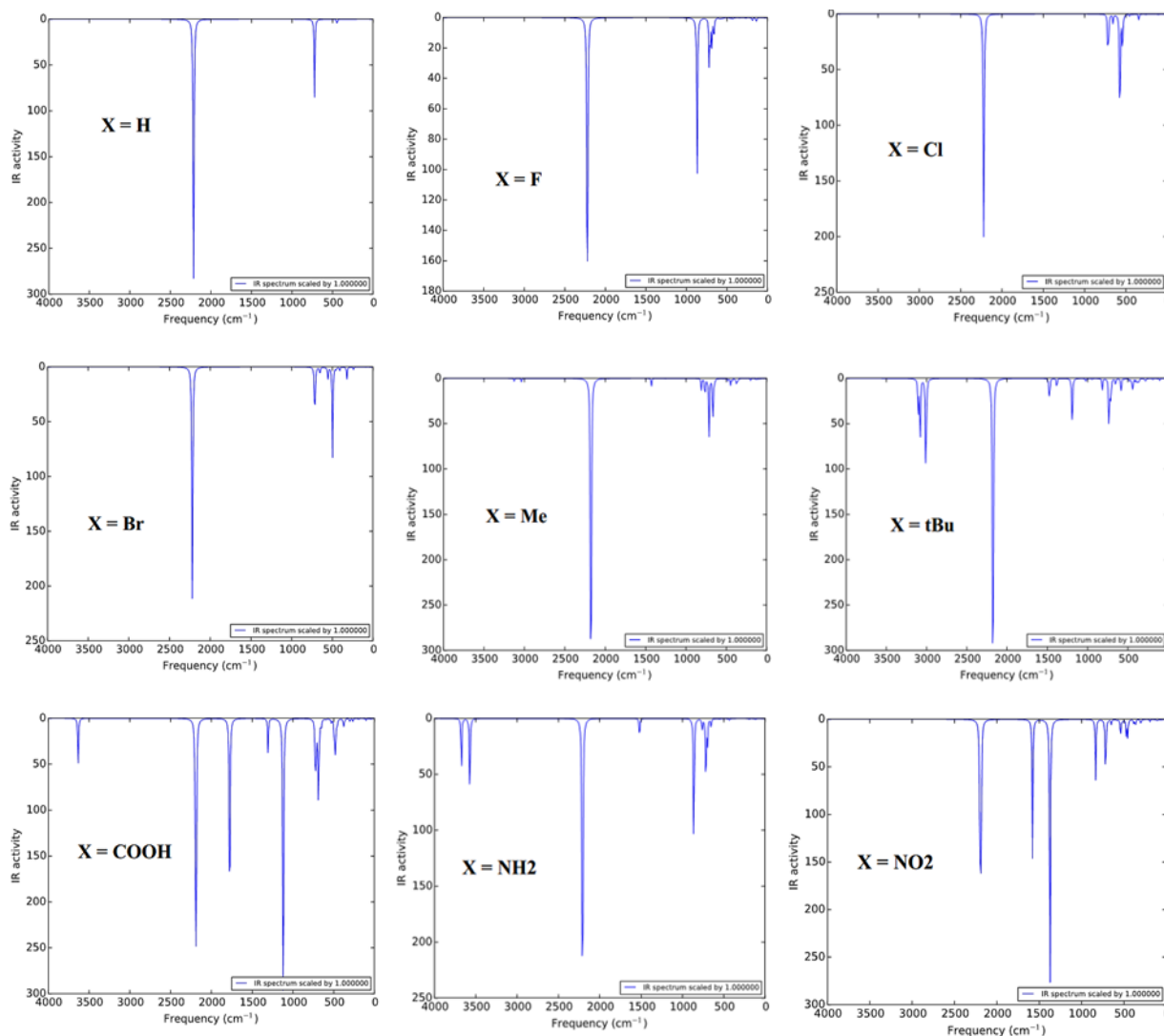


Fig. 3. The IR spectra of the studied molecules.

Br derivative of Hexasilene: UV-Vis [wavelength of electronic transition (nm), energies (cm^{-1}), electronic transitions]:

a. 487.413 nm ($20516.467 \text{ cm}^{-1}$), HOMO-1 to LUMO+1 (42%) and HOMO to LUMO (60%)

b. 446.433 nm ($22399.784 \text{ cm}^{-1}$), HOMO to LUMO+2 (95%)

CH_3 derivative of Hexasilene: UV-Vis [wavelength of electronic transition (nm), energies (cm^{-1}), electronic transitions]:

a. 516.490 nm ($19361.473 \text{ cm}^{-1}$), HOMO-1 to LUMO+1 (47%) and HOMO to LUMO (55%)

b. 445.119 nm ($22465.922 \text{ cm}^{-1}$), HOMO-1 to LUMO (44%) and HOMO to LUMO+1 (43%)

c. 371.630 nm ($26908.458 \text{ cm}^{-1}$), HOMO-1 to LUMO (31%), HOMO-3 to LUMO+6 (3%) and HOMO to LUMO+1 (33%)

tBu derivative of Hexasilene: UV-Vis [wavelength of electronic transition (nm), energies (cm^{-1}), electronic transitions]:

a. 517.265 nm ($19332.437 \text{ cm}^{-1}$), HOMO-1 to LUMO+1 (48%) and HOMO to LUMO (54%)

b. 446.562 nm (22393.332 cm^{-1}), HOMO-1 to LUMO (43%) and HOMO to LUMO+1 (44%)

c. 374.018 nm (26736.657 cm^{-1}), HOMO-1 to LUMO (32%), HOMO-4 to LUMO+5 (3%) and HOMO to LUMO+1 (32%)

COOH derivative of Hexasilene: UV-Vis [wavelength of electronic transition (nm), energies (cm^{-1}), electronic transitions]:

a. 527.678 nm (18950.934 cm^{-1}), HOMO-1 to LUMO+1 (42%), HOMO to LUMO (55%) and HOMO-1 to LUMO (3%)

b. 453.919 nm (22030.380 cm^{-1}), HOMO-1 to LUMO (52%), HOMO to LUMO+1 (30%) and HOMO to LUMO (2%)

c. 380.282 nm (26296.276 cm^{-1}), HOMO-1 to LUMO+1 (36%), HOMO to LUMO (23%), HOMO-4 to LUMO+4 (2%), HOMO-1 to LUMO (2%) and HOMO to LUMO+1 (3%)

NH₂ derivative of Hexasilene: UV-Vis [wavelength of electronic transition (nm), energies (cm^{-1}), electronic transitions]:

a. 482.013 nm (20746.336 cm^{-1}), HOMO-1 to LUMO+1 (49%) and HOMO to LUMO (54%)

b. 377.136 nm (26515.660 cm^{-1}), HOMO to LUMO+2 (96%)

NO₂ derivative of Hexasilene: UV-Vis [wavelength of electronic transition (nm), energies (cm^{-1}), electronic transitions]:

a. 540.680 nm (18495.227 cm^{-1}), HOMO-1 to LUMO+1 (39%) and HOMO to LUMO (62%)

b. 470.061 nm (21273.827 cm^{-1}), HOMO-1 to LUMO (62%) and HOMO to LUMO+1 (22%)

c. 393.223 nm (25430.837 cm^{-1}), HOMO-2 to LUMO (11%), HOMO to LUMO+1 (42%), HOMO-3 to LUMO (3%), HOMO-2 to LUMO+3 (3%), HOMO-1 to LUMO (8%) and HOMO-1 to LUMO+2 (8%)

CONCLUSIONS

In summary the present research work was focused on investigation of the structural and spectral properties and reactivity of hexasilene using B3LYP/cc-pVDZ level of theory. The main goal of this work was discussion about the structural properties (bond lengths, bond angles, dihedral angles and bond orders), aromaticity, reactivity (local and global reactivity) and spectral analysis (UV-Vis and IR spectroscopy techniques) of the studied molecular structures. In first step, the molecules were optimized at mentioned computational level of theory. Then, the other computations were done on the structures. The structural properties of the molecular structures indicated that all derivatives are not aromatic compounds. On the other hand, the reactivity of the molecules was analyzed by the global reactivity indices. These indices and the DOS graphs show that the virtual orbitals density of all hexasilene derivatives is more than the occupied orbitals density. Also, the Fukui indices indicated that the electrophilic attacks happen on the Si₄ atoms of the molecules. On the other hand, the molecules containing electron-donating and electron-withdrawing substituents prefer do nucleophilic reactions on their Si₄ and Si₃ positions, respectively.

CONFLICT OF INTERESTS

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

ACKNOWLEDGMENTS

The corresponding author is grateful to Mr. Hossein Abbasi for providing valuable suggestions.

REFERENCES

- [1] D. Fu, J. Chung, Q. Liu, R. Raziq, J. S. Kee, M. K. Park, S. Valiyaveetil and

- P. Lee, *Sens. Actuators B.* 257 (2018) 136.
- [2] H. Fujii, B. Waters, K. Hara, N. Ikematsu, M. Takayama, A. Matsusue, M. Kashiwagi and S. Kubo, *Forensic Toxicol.* 36 (2018) 225.
- [3] F. Hindelang, Y. Roggo and R. Zurbach, *J. Pharm. Biomed. Anal.* 148 (2018) 334.
- [4] G. T. Vladislavljevic, E. E. Ekanem, Z. Zhang, N. Khalid, I. Kobayashi and M. Nakajima, *Chem. Eng.* 333 (2018) 380.
- [5] M. Nabati and M. Mahkam, *Iran. J. Org. Chem.* 5 (2013) 1157.
- [6] M. Nabati and M. Mahkam, *Silicon*, 8 (2016) 461.
- [7] M. Nabati and M. Mahkam, *Iran. Chem. Commun.* 2 (2014) 129.
- [8] M. Nabati and M. Mahkam, *Org. Chem. Res.* 2 (2016) 70.
- [9] S. H. Vosko, L. Wilk and M. Nusair, *Can. J. Phys.* 58 (1980) 1200.
- [10] C. Lee, W. Yang and R. G. Parr, *Phys. Rev. B.* 37, (1988) 785.
- [11] M. J. Frisch, G. W. Trucks, H. B. Schlegel, G. E. Scuseria, M. A. Robb, J. R. Cheeseman, J. A. Montgomery Jr., T. Vreven, K. N. Kudin, J. C. Burant, J. M. Millam, S. S. Iyengar, J. Tomasi, V. Barone, B. Mennucci, M. Cossi, G. Scalmani, N. Rega, G. A. Petersson, H. Nakatsuji, M. Hada, M. Ehara, K. Toyota, R. Fukuda, J. Hasegawa, M. Ishida, T. Nakajima, Y. Honda, O. Kitao, H. Nakai, M. Klene, X. Li, J. E. Knox, H. P. Hratchian, J. B. Cross, C. Adamo, J. Jaramillo, R. Gomperts, R. E. Stratmann, O. Yazyev, A. J. Austin, R. Cammi, C. Pomelli, J. W. Ochterski, P. Y. Ayala, K. Morokuma, G.A. Voth, P. Salvador, J. J. Dannenberg, V. G. Zakrzewski, S. Dapprich, A. D. Daniels, M. C. Strain, O. Farkas, D. K. Malick, A. D. Rabuck, K. Raghavachari, J. B. Foresman, J. V. Ortiz, Q. Cui, A. G. Baboul, S. Clifford, J. Cioslowski, B. B. Stefanov, G. Liu, A. Liashenko, P. Piskorz, I. Komaromi, R. L. Martin, D. J. Fox, T. Keith, M. A. Al-Laham, C. Y. Peng, A. Nanayakkara, M. Challacombe, P. M. W. Gill, B. Johnson, W. Chen, M. W. Wong, C. Gonzalez and J. A. Pople, *Gaussian 03. Revision B.01.* Gaussian Inc. Wallingford. CT. 2004.
- [12] M. Nabati, *J. Phys. Theor. Chem. IAU Iran*, 12 (2015) 325.
- [13] M. Nabati, *J. Phys. Theor. Chem. IAU Iran*, 13 (2016) 133.
- [14] M. Nabati, M. Mahkam and Y. G. Atani, *J. Phys. Theor. Chem. IAU Iran*, 13 (2016) 35.
- [15] M. Nabati and M. Mahkam, *J. Phys. Theor. Chem. IAU Iran*, 12 (2015) 121.
- [16] M. Nabati and M. Mahkam, *J. Phys. Theor. Chem. IAU Iran*, 12 (2015) 33.
- [17] M. Nabati, *J. Phys. Theor. Chem. IAU Iran*, 14 (2017) 49.
- [18] M. Nabati, *Chem. Method.* 2 (2017) 128.
- [19] M. Nabati, M. Kermanian, H. Mohammadnejad-Mehrabani, H. R. Kafshboran, M. Mehmannaavaz and S. Sarshar, *Chem. Method.* 3 (2018) 85.
- [20] M. Nabati and M. Mahkam, *Inorg. Chem. Res.* 1 (2016) 131.
- [21] M. Nabati, M. H. Mofrad, M. Kermanian and S. Sarshar, *Iran. J. Org. Chem.* 9 (2017) 1981.
- [22] M. Nabati, M. Kermanian, A. Maghsoudloo-Mahalli and S. Sarshar, *Iran. J. Org. Chem.* 9 (2017) 2067.