

DFT Study of the Six-Membered Heterocyclic $\text{Si}_n\text{N}_{6-n}\text{H}_n$ ($n = 0-6$): Stability and Aromaticity

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One main group of organic chemistry is related to the aromatic compounds. In the present work, we replaced the CH group of benzene by silicon and nitrogen analogues. Then, Density functional theory (DFT) calculations were carried out for six-membered heterocyclic Si-N aromatic rings. Full geometry optimizations were performed in gas-phase, and at B3LYP level using 6-311++G(d,p) and CBSB7 basis sets. Here, the stability and aromatic properties of the molecules were investigated. It was observed that the molecule 1,3,5-triaza-2,4,6-trisilene shows high kinetic stability and low chemical reactivity. Total energies, nucleus-independent chemical shift (NICS) and HOMO-LUMO gap values were calculated to determine the stability, aromaticity and reactivity of azasilenes. NICS calculations denoted high aromatic property for hexasilene and hexazine. We also considered seven different isodesmic reactions for stabilization energy (SE) calculations of molecules. The molecule 1,4,5,6-tetraaza-2,3-disilene showed the greatest aromatic stabilization among all molecules.

Keywords: Azasilene, Aromaticity, Stability, Density functional theory, Theoretical study

INTRODUCTION

Aromatic compounds are important in biochemistry of all living things [1,2]. Aromaticity of a molecule is not a directly measurable or computable quantity [3]. It can be obtained quantitatively by the Nucleus-independent chemical shift (NICS) theoretical method [4]. In 1996, Schleyer proposed the use of absolute magnetic shieldings, computed at ring centers with available quantum mechanics programs, as a new aromaticity/antiaromaticity criterion [5]. To correspond to the familiar NMR chemical shift convention, the signs of the computed values are reversed: Negative NICSs denote aromaticity (-11.5 for benzene, -11.4 for naphthalene); positive NICSs, antiaromaticity (28.8 for cyclobutadiene); small NICSs, non-aromaticity (-2.1 for cyclohexane, -1.1 for adamantane) [6]. The second method is the estimation of aromatic stabilization energies

(ASE) and/or homo-aromatic stabilization energies (HASE) from various isodesmic reactions [7]. The isodesmic reaction is a chemical reaction in which the type of chemical bonds broken in the reactant are the same as the type of bonds formed in the reaction product [8]. The third method for chemical reactivity investigation of a compound is the frontier orbitals (HOMO and LUMO) energies gap [9].

Benzene is a stable organic compound with six carbon atoms that one hydrogen atom attached to each carbon atom. Based on recent studies, replacement of carbon atoms of benzene ring by the isoelectronic groups does not destroy the aromatic and stable structure of unsaturated ring molecules [10]. The silicon analog of benzene (hexasilabenzene) has been also studied theoretically for years [11-13]. The stability of Si_6 was investigated for the first time by Alexander Sax and Rudolf Janoschek in 1986 [14]. Their studies demonstrated that resonance stabilization (RS) of the pi electrons is only 30% smaller for

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hexasilabenzene compared to that for benzene [14]. Unfortunately, other silicon analogues of benzene have been never studied by researchers. In contrast, Jurgen Fabian *et al.* studied the nitrogen analogues of benzene ring, azabenzenes or azines, in 2004 [15].

In the present work, stability and aromatic properties of

all different Si-N six-membered heterocyclic compounds have been investigated theoretically by using quantum chemical treatment. Density functional theory (DFT) has become very popular in recent years [16]. This theory has been developed more recently than other *ab initio* methods [17]. The mentioned properties were investigated at

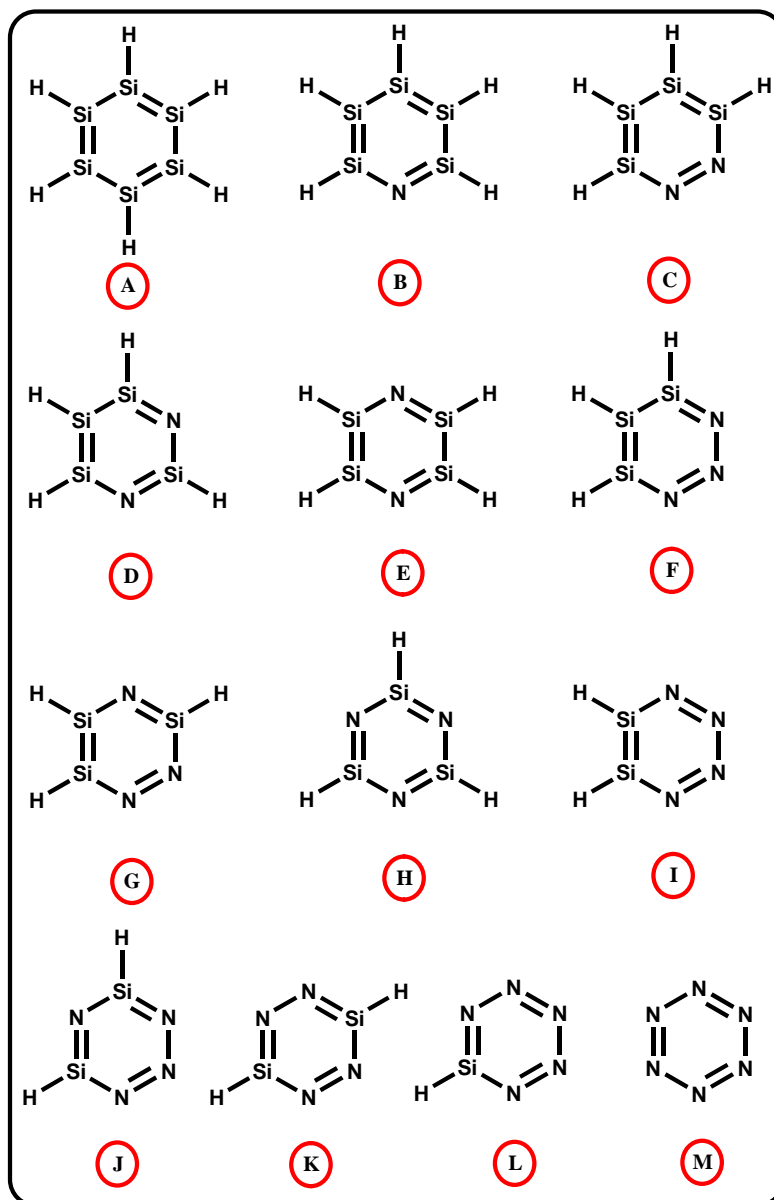


Fig. 1. Structure of all different $\text{Si}_n\text{N}_{6-n}\text{H}_n$ isomers.

B3LYP/6-311++G(d,p) and B3LYP/CBSB7 levels of theory.

COMPUTATIONAL METHODS

Full geometry optimizations were performed for all $\text{Si}_n\text{N}_{6-n}\text{H}_n$ six-membered molecules by DFT method using 6-311++G(d,p) and CBSB7 basis sets. The Becke's hybrid three-parameter exchange functional [18] and the non-local correlation functional of Lee, Yang, and Parr (B3LYP) [19] were used for the geometry optimization. All calculations were carried out without any structural or symmetry restrictions in the gas phase by Gaussian-03 program [20]. The nucleus-independent chemical shifts (NICSs) were computed utilizing the gauge-invariant atomic orbital (GIAO) approach [21].

RESULTS AND DISCUSSION

Relative Energies

Molecular frameworks of the compounds are displayed in Fig. 1. Table 1 shows the computed total energies of the structures at DFT theory (B3LYP) at 6-311++G(d,p) and CBSB7 basis sets, respectively. Total energies are corrected for zero-point vibrational energy (ZPVE). As indicated by data, stability of the compounds decreases when the number of the nitrogen atoms increases. The relative stability order of the compounds in B3LYP/6-311++G(d,p) and B3LYP/CBSB7 basis sets is: for $\text{Si}_2\text{N}_4\text{H}_2$ $I > J > K$; for $\text{Si}_3\text{N}_3\text{H}_3$ $H > G > F$; and for $\text{Si}_4\text{N}_2\text{H}_4$ $D > E > C$.

Stabilization Energies

Here we use the isodesmic reactions (Fig. 2) for determination of the stability of the molecules. An isodesmic reaction is a novel method for estimation of the stabilization energy of compounds [22]. It is the actual or hypothetical reaction in which the types of bonds that are made in forming the products are the same as those which are broken in the reactants [23]. Therefore, we considered seven different isodesmic reactions for our calculations. The calculations were performed at B3LYP/6-311++G(d,p) and

B3LYP/CBSB7 levels of theory. All data from the calculations are listed in Tables 2 and 3. The stabilization energies of the compounds are obtained from $[(E_{\text{Products}} - E_{\text{Reactants}}) \times 627.51]$. As seen from the data, the compound (I) has the greatest aromatic stabilization, while compound (K) has the lowest aromatic stabilization in the Si-N six-membered heterocyclic compounds.

NICS Study of the Compounds

The nucleus-independent chemical shift (NICS) is a theoretical method to compute the absolute magnetic shieldings in a point of interest from above the center of the ring taken with reversed sign [24]. NICS has many different variants [25]. For example, the NICS(0) means that the NICS is obtained on the ring plane of a molecule. In this method negative and positive NICS values indicate aromaticity and antiaromaticity, respectively. The calculations were carried out at B3LYP/6-311++G(d,p) and B3LYP/CBSB7 levels of theory. The NICS values of the molecules are listed in Tables 4 and 5. NICS (0.4-1.2) calculations generally give more reliable results. Therefore, NICS (0.8) was selected for determination of the aromatic character. The NICS order of molecules is: for B3LYP/6-311++G(d,p) basis set $A > \text{Benzene} > M > F > B > E > C > D > G > L > J > H > I > K$; and for B3LYP/CBSB7 basis set $A > \text{Benzene} > M > F > B > C > E > D > G > L > J > H > I > K$. Therefore, the compound (A) has the greatest aromaticity index, while compound (K) has the lowest aromaticity index in the Si-N six-membered heterocyclic compounds. Geometrical optimization of the compounds were performed to prove their aromatic property. The bond length data of the structures are listed in Table 6. Smaller size of the nitrogen atom compared to silicon, and also their electronegativity gap (~1.2 eV) cause that two compounds hexasilene and hexazine show an aromatic character, while other molecules containing both nitrogen and silicon atoms undergo many changes and show low aromaticity.

Frontier Orbital Energies

Energies of the frontier orbitals are important factors in all chemistry fields [26]. The HOMO and LUMO energies

Table 1. Total Energies for all Molecules Computed at B3LYP/6-311++G(d,p) Level of Theory

Structures	Energy (Hartree) B3LYP/6-311++G(d,p)		Energy (Hartree) B3LYP/CBSB7	
	$\text{Si}_n\text{N}_{6-n}\text{H}_{6+n}$	$\text{Si}_n\text{N}_{6-n}\text{H}_n$	$\text{Si}_n\text{N}_{6-n}\text{H}_{6+n}$	$\text{Si}_n\text{N}_{6-n}\text{H}_n$
A	-1744.249058	-1740.575024	-1744.260624	-1740.583297
B	-1508.937314	-1505.275844	-1508.947158	-1505.275844
C	-1273.535500	-1269.852508	-1273.541393	-1269.859508
D	-1273.634740	-1269.966210	-1273.643347	-1269.980151
E	-1273.624511	-1269.938768	-1273.632931	-1269.952625
F	-1038.146895	-1034.495286	-1038.149129	-1034.499869
G	-1038.234122	-1034.540645	-1038.239032	-1034.549870
H	-1038.345638	-1034.674796	-1038.353032	-1034.690328
I	-802.761852	-799.213005	-802.759607	-799.208207
J	-802.856543	-799.189662	-802.857322	-799.195153
K	-802.835211	-799.120624	-802.836257	-799.124490
L	-567.384434	-563.733221	-567.378248	-563.731479
M	-331.941007	-328.339280	-331.928049	-328.331112
Cyclohexane	-235.775410	-235.775410	-235.774497	-235.774497
Cyclohexene	-234.567597	-234.567597	-234.565776	-234.565776
Cyclohexadiene	-233.362180	-233.362180	-233.359490	-233.359490
Benzene	-232.211215	-232.211215	-232.208413	-232.208413

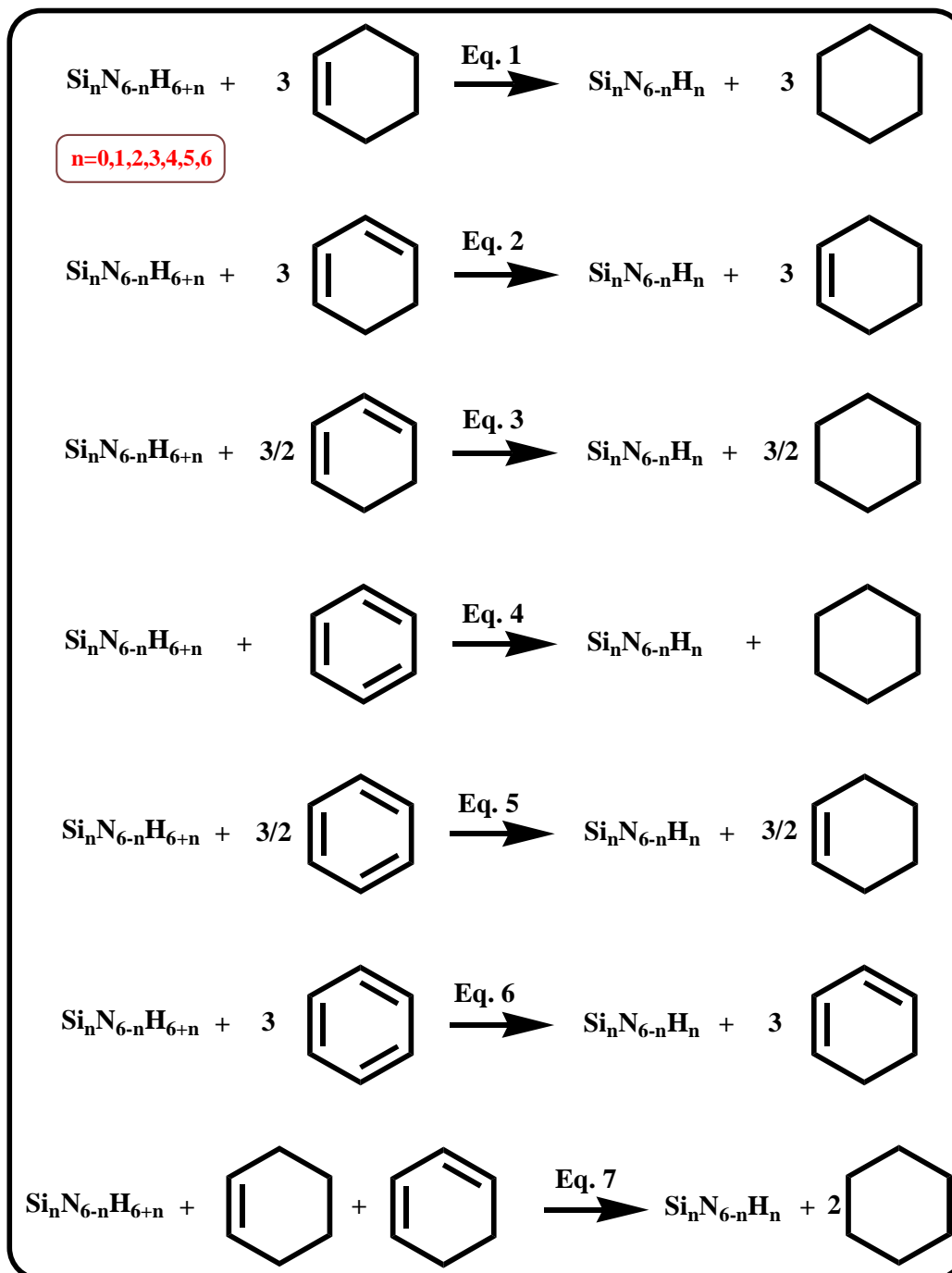


Fig. 2. All different isodesmic formal equations for calculation of the stabilization energies (SE) of the $\text{Si}_n\text{N}_{6-n}\text{H}_n$ isomers.

Table 2. Estimated Stabilization Energies (SE) for all Molecules Calculated Using Different Isodesmic Reactions at B3LYP/6-311++G(d,p) Level of Theory

Structures	Stabilization Energy (kcal mol ⁻¹) B3LYP/6-311++G(d,p)						
	Eq. 1	Eq. 2	Eq. 3	Eq. 4	Eq. 5	Eq. 6	Eq. 7
A	31.75	36.26	34.00	68.93	87.51	138.77	33.25
B	23.86	28.38	26.12	61.04	79.63	130.88	25.37
C	37.37	41.88	39.63	74.55	93.13	144.39	38.87
D	28.30	32.81	30.55	65.47	84.06	135.31	29.80
E	39.10	43.61	41.35	76.27	94.86	146.11	40.60
F	17.68	22.19	19.93	54.85	73.44	124.70	19.18
G	43.95	48.46	46.20	81.13	99.71	150.97	45.45
H	29.75	34.26	32.00	66.92	79.86	136.76	31.25
I	-46.81	-42.30	-44.55	-9.63	8.96	60.21	-45.30
J	27.26	31.77	29.52	64.44	77.38	134.28	28.76
K	57.20	61.71	59.45	94.37	107.31	164.21	58.70
L	17.43	21.94	19.68	54.60	67.55	124.45	18.93
M	-13.62	-9.11	-11.37	23.55	36.49	93.39	-12.12

Table 3. Estimated Stabilization Energies (SE) for all Molecules Calculated Using Different Isodesmic Reactions at B3LYP/CBSB7 Level of Theory

Structures	Stabilization Energy (kcal mol ⁻¹) B3LYP/CBSB7						
	Eq. 1	Eq. 2	Eq. 3	Eq. 4	Eq. 5	Eq. 6	Eq. 7
A	32.13	36.69	34.4	69.81	88.66	140.62	33.63
B	28.36	32.92	30.62	66.03	84.88	136.85	29.86
C	34.95	39.55	37.26	72.67	91.52	143.48	36.49
D	23.22	27.82	25.53	60.94	79.79	131.76	24.77
E	33.95	38.56	36.27	71.68	90.53	142.49	35.50
F	14.50	19.08	16.79	52.19	71.04	123.01	16.02
G	39.53	44.12	41.82	77.23	96.08	148.05	41.06
H	22.90	27.51	25.22	60.63	79.48	131.45	24.46
I	-46.94	-42.33	-44.62	-9.21	9.64	61.60	-45.39
J	22.60	27.18	24.89	60.30	79.15	131.12	24.13
K	53.72	58.30	56.01	91.42	110.27	162.23	55.25
L	12.93	17.51	15.22	50.63	69.48	121.45	14.46
M	-18.34	-13.76	-16.05	19.36	38.21	90.18	-16.81

Table 4. Calculated NICS for all Molecules at B3LYP/6-311++G(d,p) Level of Theory

Structures	NICS(0)	NICS(0.4)	NICS(0.8)	NICS(1.2)	NICS(1.6)	NICS(2)
Benzene	-8.07	-9.40	-10.58	-9.39	-7.05	-4.92
A	-12.13	-11.87	-11.08	-9.81	-8.24	-6.23
B	-10.12	-9.80	-8.91	-7.66	-6.28	-4.94
C	-5.67	-6.43	-7.57	-7.71	-6.79	-5.42
D	-6.99	-6.66	-5.84	-4.85	-3.89	-3.01
E	-8.24	-8.13	-7.68	-6.85	-5.80	-4.68
F	-8.55	-9.02	-9.18	-8.04	-6.27	-4.60
G	-2.88	-3.83	-5.34	-5.88	-5.39	-4.42
H	-3.67	-3.52	-3.14	-2.64	-2.14	-1.68
I	-0.22	-0.18	-0.12	-0.05	0.01	0.06
J	-0.08	-1.40	-3.35	-3.96	-3.52	-2.76
K	7.79	5.04	0.06	-3.06	-3.91	-3.55
L	3.97	0.39	-4.52	-5.93	-5.14	-3.89
M	1.86	-3.56	-9.61	-9.72	-7.39	-5.16

Table 5. Calculated NICS for all Molecules at B3LYP/CBSB7 Level of Theory

Structures	NICS(0)	NICS(0.4)	NICS(0.8)	NICS(1.2)	NICS(1.6)	NICS(2)
Benzene	-8.85	-10.28	-11.54	-10.19	-7.58	-5.19
A	-13.17	-12.85	-11.85	-10.25	-8.34	-6.49
B	-10.33	-9.99	-9.01	-7.57	-5.99	-4.54
C	-5.98	-6.81	-8.00	-8.01	-6.87	-5.35
D	-6.59	-6.27	-5.39	-4.27	-3.21	-2.34
E	-7.30	-7.33	-7.14	-6.43	-5.38	-4.25
F	-8.19	-8.77	-9.07	-7.89	-5.98	-4.20
G	-1.80	-3.00	-4.92	-5.59	-5.05	-4.03
H	-2.32	-2.38	-2.25	-1.74	-1.20	-0.81
I	-0.31	-0.27	-0.21	-0.13	-0.06	0.00
J	1.54	-0.07	-2.49	-3.27	-2.85	-2.14
K	8.65	5.65	0.28	-2.96	-3.74	-3.33
L	5.37	1.54	-3.80	-5.40	-4.68	-3.48
M	2.05	-3.73	-10.14	-10.06	-7.40	-5.02

Table 6. Computed Bond Lengths for all Molecules at B3LYP/6-311++G(d,p) Level of Theory

Structures	Si-Si Bond (Å)	N-N Bond (Å)	Si-N Bond (Å)	Si-H Bond (Å)
A	2.216	-	-	1.481
B	2.220, 2.223	-	1.644	1.479, 1.480, 1.483
C	2.235, 2.223	1.293	1.701	1.473, 1.486
D	2.224, 2.226	-	1.656, 1.649	1.468, 1.478, 1.481
E	2.234	-	1.652	1.479
F	2.215	1.292	1.703	1.476, 1.489
G	2.223	1.305	1.647, 1.661, 1.705, 1.714	1.469, 1.470, 1.485
H	-	-	1.660	1.470
I	2.108	1.096, 7.708	3.555, 6.929	1.493, 1.495
J	-	1.313	1.663, 1.703	1.469
K	-	1.328	1.707	1.464
L	-	1.319, 1.339	1.682	1.465
M	-	1.319	-	-

Table 7. Calculated HOMO-LUMO Gap (kcal mol⁻¹) for all Molecules at B3LYP/6-311++G(d,p) and B3LYP/CBSB7 Levels of Theory

Structures	B3LYP/6-311++G(d,p)			B3LYP/CBSB7		
	HOMO	LUMO	Gap _{L-H}	HOMO	LUMO	Gap _{L-H}
A	-0.20959	-0.08672	77.102	-0.20734	-0.08673	75.684
B	-0.20354	-0.09322	69.227	-0.20089	-0.09153	68.624
C	-0.19546	-0.10121	59.143	-0.19375	-0.09924	59.306
D	-0.21674	-0.08981	79.650	-0.21349	-0.08507	80.585
E	-0.19693	-0.10488	57.762	-0.19372	-0.10063	58.415
F	-0.22983	-0.09874	82.260	-0.22616	-0.09524	82.154
G	-0.20025	-0.10888	57.336	-0.19709	-0.10442	58.151
H	-0.27168	-0.06958	126.820	-0.27048	-0.06248	130.522
I	-0.21103	-0.12915	51.381	-0.20775	-0.12534	51.713
J	-0.23157	-0.11378	73.914	-0.22636	-0.10718	74.787
K	-0.19968	-0.12654	45.896	-0.19631	-0.12321	45.871
L	-0.24205	-0.13843	65.023	-0.23613	-0.13303	64.696
M	-0.32074	-0.17464	91.679	-0.31338	-0.16768	91.428

are related to the ionization potential and the electron affinity, respectively [27]. The word "energy gap" is the difference between frontier orbital energies that is an important parameter for structural stability [28]. Energy gap of the frontier orbitals has been used as a simple indicator of kinetic stability (Table 7) [29]. A large energy gap indicates high kinetic stability and low chemical reactivity [30]. As data indicates, the molecule (H) has the greatest HOMO-LUMO energy separation.

Chemical Hardness

Absolute chemical hardness (η) is used as a measure of kinetic stability or reactivity of the compounds [31]. If $\eta > 0$, the charge transfer process is energetically favorable [32]. The chemical hardness (η) is defined as half of the

magnitude of the energy difference between the frontier orbitals [33]. Table 8 shows the calculated chemical hardness of the structures at DFT theory (B3LYP) at 6-311++G(d,p) and CBSB7 basis sets, respectively. The hardness values indicate that the overall reactivity of the compounds is $K > I > G > E > C > L > B > J > A > D > F > M > H$.

CONCLUSIONS

In this paper, we theoretically studied thirteen isomers of the six-membered azasilane rings. The following conclusions can be drawn from the DFT calculations on the molecules:

-Based on bond length data, it is concluded that compounds

Table 8. Calculated Chemical Hardness (kcal mol^{-1}) for all Molecules at B3LYP/6-311++G(d,p) and B3LYP/CBSB7 Levels of Theory

Structures	Chemical hardness	
	B3LYP/6-311++G(d,p)	B3LYP/CBSB7
A	38.551	37.842
B	34.613	34.312
C	29.572	29.653
D	39.825	40.293
E	28.881	29.208
F	41.130	41.077
G	28.668	29.076
H	63.410	65.261
I	25.691	25.857
J	36.957	37.394
K	22.948	22.936
L	32.512	32.348
M	45.840	45.714

containing both nitrogen and silicon atoms undergo dramatic changes compared to hexasilabenzene and hexazine, because of the difference in size and electronegativity of the atoms.

-Based on total energy values of the compounds, it is concluded that stability of the compounds decreases with increasing the number of nitrogen atoms.

-The compound 1,4,5,6-tetraaza-2,3-disilene has the greatest aromatic stabilization, while compound 1,3,4,6-tetraaza-2,5-disilene has the lowest aromatic stabilization in the Si-N six-membered heterocyclic compounds.

-The compound hexasilabenzene has the greatest aromaticity index, while the compound 1,3,4,6-tetraaza-2,5-disilene has the lowest aromaticity index in the studied compounds.

-The molecule 1,3,5-triaza-2,4,6-trisilene indicates high kinetic stability and low chemical reactivity.

-The hardness values indicate that the compound 1,3,4,6-tetraaza-2,5-disilene is more reactive, while the reactivity of 1,3,5-triaza-2,4,6-trisilene is very low.

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