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Stabilization of Square Planar Silicon: A New Building Block for Conjugated Si-Containing Systems

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The feasibility of square planar silicon as a building block for conjugated systems was investigated by ab initio calculations. A five-membered ring model system was used to map electronic and steric substituent effects that might help in the stabilization of the planar structure. A π push−pull arrangement around the silicon was found to prefer planarity. Aromaticity was proven to play an important role in stabilization as well. With the help of steric constraints, a new structure was proposed as a synthetic target containing square planar silicon. The kinetic stability of this structure was also investigated.

Introduction

The synthesis of planar tetracoordinated carbon-containing molecules has received considerable attention over the past decades.[1] Planar tetracoordinated silicon, however, has received much less interest, although, according to early quantum chemical calculations, it is inherently easier to achieve than its carbon counterpart.[2] The preparation of a compound featuring square planar silicon **1a** (Figure 1) was reported in 1979.[3] The quality of the recorded X-ray crystallographic data did not make the determination of the exact atomic positions possible; nevertheless, on the basis of the unit cell symmetry, a planar structure has been assumed. The validity of this reasoning was later questioned,[4] and the crystal structure of the related bis(tetramethylethylenedioxy)silane has been proved to be a distorted tetrahedron.[5] Furthermore, calculations at the MNDO level[6] resulted in a tetrahedral gas phase structure **1b**. Some considerations, however, still support the feasibility of the planar geometry: in the solid phase, the complexing effect of the oxygen atoms in the adjacent molecules can stabilize the planar structure **1c**. Calculating the complexation of water molecules above and below the silicon atom of the model structure bis(ethylenedioxy)silane at the MNDO level gave complexation energies large enough to overcome the energy difference of the planar and tetrahedral forms.[6]

On the basis of HF/3-21G* calculations, tetraazafenestrane **2a** (Figure 2) was also considered as a candidate for the square planar structure;[7] subsequent attempts to synthesize this type of compounds, however, were unsuccessful.[8]

Planar tetracoordinated silicon has already been found embedded in inorganic frameworks. High-level calculations predicted the thermodynamical stability of the square planar $Si(CO)_4$ complex,[9] and the nonsquare planar $SiCAl_4$[10] and B_4H_2Si[11] molecules.

Recently, conjugated systems have received widespread attention because of their possible role as conducting polymers or organic light-emitting diode (OLED) materials. Square planar silicon (SpSi) could provide a novel building block for such systems. The aim of this work was

- to reinvestigate structure **1a** both in the gaseous and the crystalline phase that was previously suggested to contain SpSi;
- to conduct a systematic study of the electronic and steric factors that might influence the stability of SpSi; and
- use the gained information to find possible synthetic goals containing this unusual bond structure.

Computational Methods. Quantum chemical calculations on single molecules were carried out with the help of the Gaussian 03 program package.[12] All geometry optimizations (with the exception of dimerization reaction pathways) were carried out at the MP2/6−31+G* level of theory. Second derivative calculations were applied at this level to establish the nature of the stationary point on the potential enegy surface (PES). The eligibility of this approach was tested on the planar-tetrahedral energy differences of selected cases of **3** substituted at the R_1 and R_2 positions. Increasing the basis set to 6-311+G** did not change the relative energies by more than 1.8 kcal/mol (Table 1). Dimerization pathways were investigated using density functional theory (DFT) calculations with the B3LYP functional and 6-31+G* basis set. The last row of Table 1 shows that, although the B3LYP functional slightly overestimates the stability of the planar form, the results are quite close to the MP2 ones (largest difference is 3.4 kcal/mol), and the trends on substitution are conserved. For the modeling of condensed phases, the VASP code[13] was applied. Gamma-point calculations were carried out using hard projector augmented wave (PAW) pseudopotentials provided with the VASP package and the PW91 exchange-correlation functional. Additionally, 875 eV was used as the cutoff energy for the plane wave basis set (prec = high).

Results and Discussion

Early quantum chemical calculations already established that the gas phase structure of bis(o-phenylenedioxy)silane **1a** is nonplanar, and the energy difference is 32.9 kcal/mol at the MNDO level of theory in favor of the tetrahedral form.[6] Our calculations at the MP2/6-31+G* level also favor the tetrahedral

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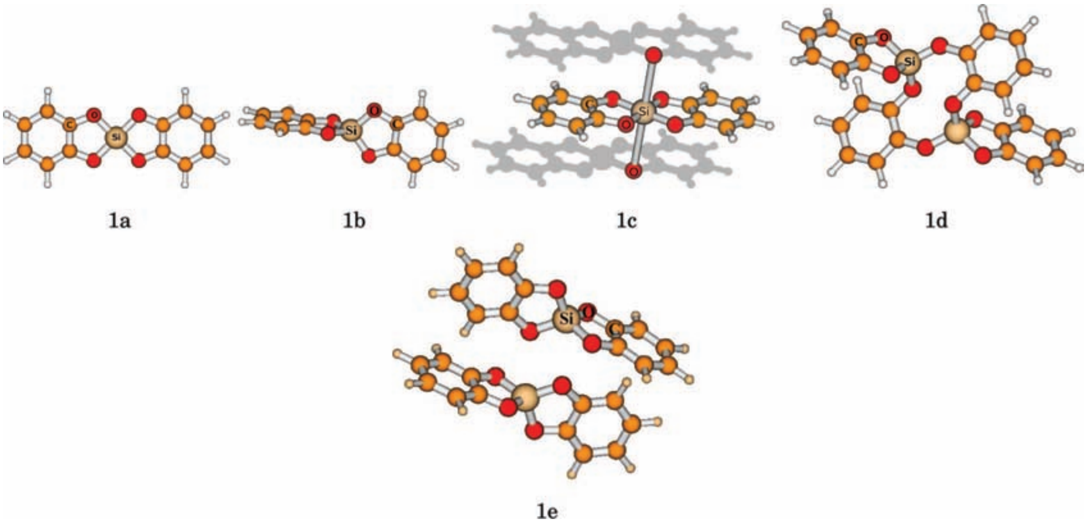

Figure 1

TABLE 1: Basis Set Dependence of the Energy Differences (kcal/mol) of the Planar and Tetrahedral Forms of 3 and 1a-1b

R_1	3				
	O	N	N	N	
R_2	H	H	CH_3	NO_2	**1a-1b**
MP2/6-31+G*	37.5	20.8	26.4	14.1	29.1
MP2/6-311+G**	39.3	21.4	26.3	15.4	30.5
MP2/6-311++G**	39.3	21.5	26.4	15.5	30.7
MP2/aug-cc-pvdz	34.9	18.5	20.9	10.7	27.2
MP2/aug-cc-pvtz	38.7	20.6	24.9	14.1	29.8
B3LYP/6-31+G*	34.1	20.3	25.4	12.2	28.5

structure by 29.1 kcal/mol, describing the planar structure as a first-order saddle point on the PES. One of the strongest arguments supporting the planarity of this molecule was the supposed stabilizing effect of the nearby oxygen atoms in the solid phase.[3] To test the validity of this argument, periodic plane wave DFT geometry optimizations were carried out from various initial intermolecular distances. Using the cell parameters from the X-ray study[3] ($P2_1/c$, $a = 10.56$, $b = 5.60$, $c = 10.96$ Å, $\beta = 122°$) and planar starting geometries (optimized in the gas phase with planarity constraints) for the individual molecules in the unit cell (intermolecular distance was 2.6 Å), the optimization gave the dimerized structure **1d** containing two tetrahedral silicon centers. Geometry optimization started from a larger intermolecular distance (3.0 Å) resulted in a tetrahedral structure resembling the gas phase minimum **1e**. No geometry corresponding to the planar structure **1a** could be found.

2a, calculated to be planar at the HF/3-21G* level[7] is also proved to be nonplanar by our MP2/6-31+G* calculations, although the planar saddle point is only 1.1 kcal/mol higher than the nonplanar minimum. Interestingly this molecule does not adopt a tetrahedral arrangement: its preferred structure is a tetragonal pyramid with a N−Si−N angle of 156° **2b**. A possible explanation to this finding is provided at the end of this paper.

Contrary to carbon, SpSi has a σ-type highest occupied molecular orbital (HOMO) and a vacant p-orbital, thus favoring electronegative, π-donor substituents.[6] Since planar geometry allows SpSi to be incorporated into and possibly stabilized by π-conjugation, it is likely that five-membered 6π electron rings stabilize the SpSi structure. Five-membered rings have the additional advantage of easily accommodating the reduced bond angles of the planar arrangement. Considering these advantages, we chose the silacyclopentene **3** (Figure 3) as the model system for our study.

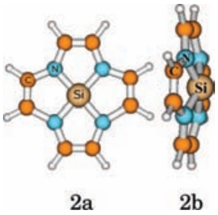

Figure 2

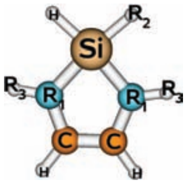

Figure 3. Structure of compound **3**.

Calculating the energy difference between the planar and tetrahedral Si forms of **3** with various R groups allows us to estimate the stabilizing effect of different substituents on SpSi. π-donor, σ-acceptor substituents at the R_1 position stabilize the planar bond arrangement around the Si atom over the tetrahedral one (Table 2). In the case of R_1 = O, N, S, or P, the possibility of a 6π electron delocalization arises, which might contribute to the stabilizing effect. Since the ring containing a nitrogen atom on each side of the central silicon showed the largest stabilization, further substitution (R_2 and R_3 positions) was carried out on this ring. Substitution on the Si atom (R_2 position) showed significant (>2 kcal/mol) stabilization of the planar form in the case of the $-NO_2$, $-CF_3$, −CHO, −CN, and −COOH groups. These groups (unlike the preferentially π-donor R_1 substituents) are π acceptors, indicating that a π push−pull arrangement around the silicon is preferred for the planar structure. This consideration is fully supported by the structure **4a** (Figure 4), exhibiting a second, nonaromatic ring and showing a planar-tetrahedral energy difference of 5.6 kcal/mol. Varying the same substituents around the silicon atom in a way that neither ring has 6π electrons (**4b**) raised the difference to 27.5 kcal/mol. Substitution on the R_3 position of **3** could not achieve considerable energy gain; however, π-withdrawing groups destabilize the planar form, confirming the importance of the π donation of the N atoms toward the silicon. Variation

TABLE 2: Energy Differences (kcal/mol) of the Planar and Tetrahedral Forms of 3

	$R_2 = R_3 = \mathrm{H}$						
R_1	O	N	S	C	C=O	B	P
ΔE	37.5	20.8	38.7	81.1	76.7	[a]	22.5

	$R_1 = \mathrm{N},\ R_3 = \mathrm{H}$											
R_2	CH_3	Cl	F	NH_2	NO_2	OH	Ph	CF_3	CHO	BH_2	CN	NC	COOH
ΔE	26.4	22.5	23.0	23.0	14.1	21.5	24.1	18.3	17.9	20.5	18.2	19.4	16.1

	$R_1 = \mathrm{N},\ R_2 = \mathrm{H}$									
R_3	CH_3	Cl	F	OH	Ph	CF_3	CHO	BH_2	CN	COOH
ΔE	18.1	23.9	27.8	18.7	24.0	38.6	50.1	42.9	30.3	50.4

[a] Instead of a five-membered ring, boron produces a bridged structure.

TABLE 3: Relative Energies, Bonding, and Conjugation Descriptors of 3

structure	R1	R2	ΔE_{p-t} [kcal/mol]	q_{Si}	Si−R_1 [Å]	ε_{Si-R1}	$\rho_{Si\text{-}R1}$	NICS(2)
planar	N	−H		1.560	1.791	0.232	0.105	−3.0
tetrahedral	N	−H	20.8	1.713	1.753	0.141	0.117	−0.3
planar	O	−H		1.892	1.743	0.114	0.115	−1.9
tetrahedral	O	−H	37.5	1.863	1.702	0.078	0.117	−0.4
planar	S	−H		1.023	2.181	0.113	0.088	−4.3
tetrahedral	S	−H	38.7	1.003	2.146	0.051	0.098	−1.2
planar	N	$-NO_2$		1.778	1.749			−3.3
tetrahedral	N	$-NO_2$	14.1	1.999	1.722	0.179	0.126	
planar	N	$-CH_3$		1.817	1.794	0.229	0.106	−2.8
tetrahedral	N	$-CH_3$	26.4	1.938	1.757	0.137	0.117	
planar	N	−F		2.039	1.755	0.247	0.111	−2.8
tetrahedral	N	−F	23.0	2.161	1.731	0.152	0.123	
planar	N	−CN		1.707	1.772	0.246	0.108	−3.1
tetrahedral	N	−CN	18.2	1.880	1.734	0.160	0.123	
planar	N	−NC		1.915	1.755	0.257	0.111	−3.0
tetrahedral	N	−NC	19.4	2.062	1.749	0.158	0.125	
planar	N	−COOH		1.638	1.777	0.236	0.105	−3.2
tetrahedral	N	−COOH	16.1	1.854	1.739	0.156	0.121	
planar	N	$-CF_3$		1.712	1.769	0.256	0.109	−3.2
tetrahedral	N	$-CF_3$	18.3	1.871	1.732	0.169	0.123	
planar	N	−CHO		1.663	1.786	0.229	0.106	−3.2
tetrahedral	N	−CHO	17.9	1.836	1.728	0.156	0.119	

of the substituents on the ring carbons did not produce significant changes in the relative stability. No substituent combinations were able to produce a planar energy minimum purely by electronic effects; all planar structures were first-order saddle points on the PES, with the imaginary mode moving the substituents around the Si atom toward the tetrahedral structure.

In order to gain a deeper understanding of how the different substituents achieve the stabilization of SpSi, natural population analysis (NPA) charges on the Si atom as well as bond lengths and atoms-in-molecules (AIM)-derived bond descriptors (ellipticities: ε, and electron densities at bond critical points: ρ) were calculated (Table 3) for the Si- R_1 bonds of both the planar and tetrahedral forms of **3** substituted at the R_1 and R_2 positions. Examining the correlation between these parameters and the energy difference of the two forms (ΔE_{p-t}) we can observe that NPA charges of the Si atom of the planar structures do not show any dependence on ΔE_{p-t}. The difference of charges between the planar and tetrahedral structures, however, gives a clear correlation (Figure 5). With the exception of the R_1 = O and S cases, the planar form is less positive than the tetrahedral form. The larger difference in the charges corresponds to the larger relative stability of the planar form. Since the main difference between the planar and tetrahedral structures is the possibility of interactions in the π-system of the former, we can conclude that the stability of the planar form is strongly influenced by π-conjugative effects. Similarly, differences of ρ show an increasing trend with the increasing stability of the planar form

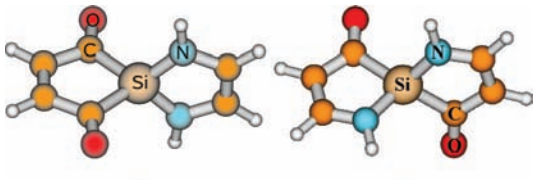

Figure 4. Structures of compounds **4a** and **4b**.

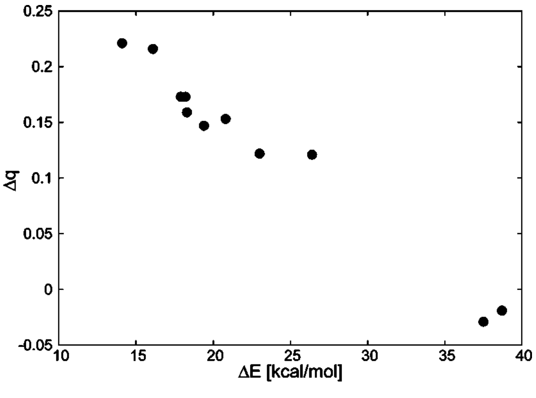

Figure 5. Differences of NPA-derived charges plotted against ΔE_{p-t}.

TABLE 4: Energy Differences of the Planar and Tetrahedral C−C Saturated Forms of 3

R_1	O	N	S	C
ΔE_{unsat}	37.5	20.8	38.7	81.1
ΔE_{sat}	46.5	37.5	51.0	79.4

(Figure 6) with the exception of the R_1 = S case. Ellipticities of the Si−R_1 bond, however, do not display any correlation with $\Delta E_{\text{p-t}}$. Geometrical parameters, such as Si−R_1 distances are also insensitive to the conjugative stabilization of the planar structure.

In order to investigate the possible contribution of aromaticity to the stability of SpSi species, $\Delta E_{\text{p-t}}$ values were computed for some saturated analogues of **3** (Figure 7), thus making aromatic conjugation impossible. The energy differences increased significantly (9−17 kcal/mol) in the case of the π-donor O, NH, and S R_1 groups in favor of the tetrahedral form, indicating the importance of conjugation in the five-membered ring (Table 4). NICS(2) values[15] were also computed as a measure of aromaticity (Table 3) for the R_1- and R_2-substituted cases of **3**, showing correlation with the energy differences (Figure 8). The NICS(2) value of, for example, the R_1 = N, R_2 = H molecule is −3.0, indicating some aromaticity (the corresponding value for pyrrol is −4.2 at the same level of theory). The R_1 = S case again produced an extremely high value, not fitting into the correlation, similarly to the ρ values.

A further planarizing effect can be the placement of the Si atom in a bridgehead position between fused rings. This, besides introducing a further steric hindrance toward tetragonalization, can increase the planarizing contribution of the aromatic conjugation as well. A similar phenomenon was described in the case of the planarization of the inherently pyramidal tricoordinate phosphorus.[14] Indeed, **6** (Figure 9), the ring-fused derivative of **3** proved to be a planar minimum on the PES. No corresponding tetrahedral minimum could be located. The NICS(2) values of the fused rings are −3.3, showing a similar although slightly larger value than the single ring.

The kinetic stability of **6** was also investigated by mapping the reaction route toward dimerization (Figure 10). Since dimerization over the Si−N bond is expected to be energetically favorable, a suitably high kinetic barrier is an imperative factor in the chemical stability of these compounds. The Gibbs free energy barrier toward dimerization of the central Si−N bond of **6** is calculated to be 17.4 kcal/mol. This value, however, can be increased by the inclusion of groups that favor the planar structure in the R_2 position (see Table 2). Substitution of the remaining hydrogen of the silicon atom in **6** to a −CHO group gives 23.5 kcal/mol, while $-CF_3$ gives 23.8 kcal/mol. Steric hindrance provided by bulky substituent groups (e.g., *tert*-butyl trimethylsilyl) is expected to raise the barrier further. Interestingly, the product of dimerization, lying on the PES 4.1 kcal/mol lower than the monomer, is not completely tetrahedral: it adopts a silatrane-like structure with the original central Si−N bond remaining semiclosed (Si−N distance is 2.25Å). Although further opening of this bond results a tetrahedral structure as well, that minimum lies higher on the PES than the semipentavalent one. In the case of the $-CF_3$ substituent, this minimum disappears from the PES, due to the electron-withdrawing effect of the susbstituent group that favors the pentavalent structure.[16] The dimerization of the peripheral Si−N bonds and the mixed central-peripheral dimerization of **6** was also calculated with R_1 = −H (see Figure 11). The barrier lies very close to that of the central bonds (18.0 and 17.9 kcal/mol respectively), indicating the similar reactivity of these bonds. An intriguing question is that, if **6** is planar, why does the tetraazafenestrane **2a** (that contains four fused five-membered rings and this can be concieved as an extension of the steric stabilization method used at the buildup of **6**) adopt a nonplanar geometry? The answer probably lies in the preferred Si−N bond lengths in the planar tetragonal structure. While in **6**, the Si−N distances are 1.788Å, the completely closed outer ring in the planar form of **2** confines the Si−N bond to 1.752Å, causing an energetically adverse strain. The nonplanarity caused by the confinement of the Si−N bonds can also be observed in the computed geometry of **7** (Figure 12), the molecule containing three fused rings. This effect, however, is smaller than in the case of the completely confined **2a**: at the MP2/6-31+G* level of theory, the nonplanar minimum was only 0.1 kcal/mol lower than the planar saddle point showing an extremely flat potential surface.

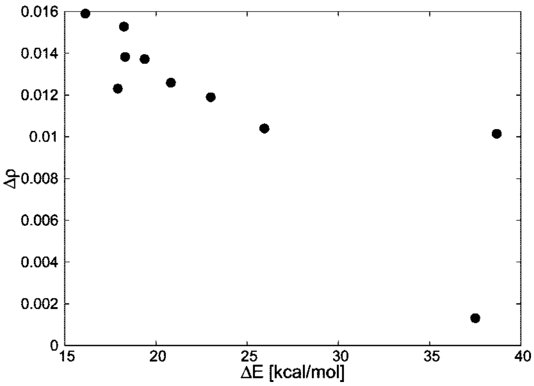

Figure 6. Differences of electron densities at the Si−R_1 bond critical point plotted against $\Delta E_{\text{p-t}}$.

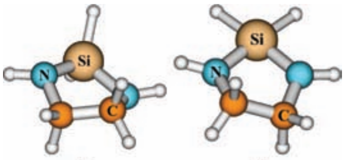

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Figure 7. C−C saturated derivatives of **3**.

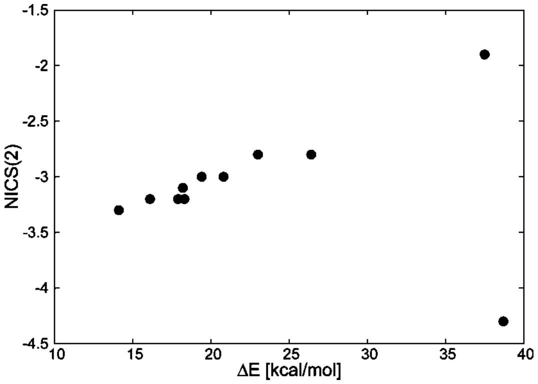

Figure 8. NICS(2) values plotted against $\Delta E_{\text{p-t}}$

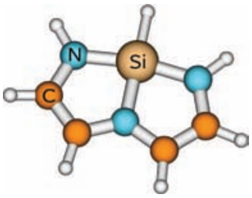

Figure 9. Compound **6**: a structure exhibiting planar tetracoordinated silicon.

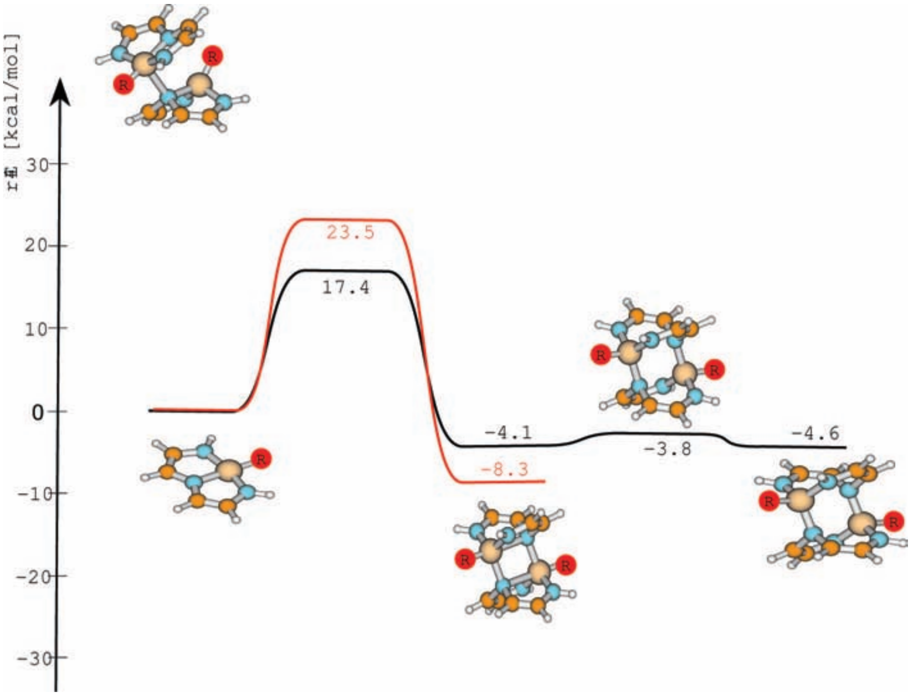

Figure 10. Reaction path for dimerization over the central Si−N bond of **6**. Black line denotes R = H, red line denotes R = −CHO.

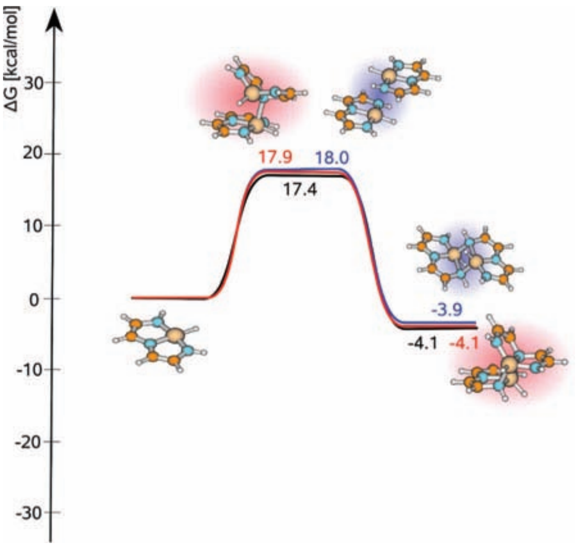

Figure 11. Reaction path for dimerization over different Si−N bonds of **6**. Black line denotes the reaction profile of the central bonds, blue is the peripheral, and red is the central-peripheral arrangement.

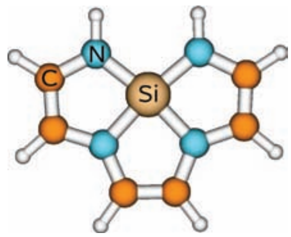

Figure 12. Structure of compound **7**.

Conclusions

Electronic factors governing the stability of SpSi were studied in a five-membered ring system. While in the ring, π-donor, σ-acceptor neighbors provide the largest stabilization, the preferred substituent groups in exo position on the silicon atom possess π-acceptor properties, resulting a π push−pull arrangement. Investigation of NPA-derived charges indicate the importance of π-conjugative effects in the stabilization of the planar form. NICS values show considerable aromaticity for the most stable planar species. No susbstituent combinations were able to produce a planar minimum. Introduction of steric hindrance via a second fused ring produces **6**, a minimum on the PES without a tetrahedral counterpart. Calculating reaction pathways toward dimerization of **6** establishes the kinetic stability of this species.

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