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Internal rotation of disilane and related molecules: a density functional study

Felipe Valencia ^{a,b}, Aldo H. Romero ^{a,b}, Miguel Kiwi ^{a,*}, Ricardo Ramírez ^a, Alejandro Toro-Labbé ^c

^a Facultad de Física, Pontificia Universidad Católica de Chile, Casilla 306, Santiago 6904411, Chile
 ^b Advanced Materials Department, IPICyT, Apartado Postal 3-74 Tangamanga, 78231 San Luis Potosí, SLP, Mexico
 ^c Facultad de Química, Pontificia Universidad Católica de Chile, Casilla 306, Santiago 6904411, Chile

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Abstract

DFT calculations performed on Si_2H_6 , Si_2F_6 , Si_2Cl_6 and Si_2Br_6 are reported. The evolution of the energy, the chemical potential and the molecular hardness, as a function of torsion angle, is studied. Results at the DFT-B3LYP/6-311++G** level show that the molecules always favor the stable staggered conformations, with low but significant energy barriers that hinder internal rotation. Internal rotation is always accompanied by weakening and lengthening of the central Si–Si bond. In most cases this lengthening seems to be due to an interplay of electrostatic and hyperconjugative interactions. The chemical potential and hardness of Si_2H_6 remains quite constant as the sylil groups rotate around the Si–Si axis, whereas the other systems exhibit different degrees of rearrangement of the electronic density as a function of the torsion angle. A qualitative analysis of the frontier orbitals shows that the effect of torsional motion on electrophilic attack is negligible, whereas this internal rotation may generate different specific mechanisms for nucle-ophilic attack.

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1. Introduction

Recently disilane has attracted attention [1-5] due to its importance in the production of siliconbased semiconductor devices. Its geometry is quite similar to ethane, which is the best known and

*Corresponding author. Fax: +56-2-553-6468.

most widely studied example [6–9] of simple molecules with properties that markedly depend on the rotation of a group of atoms around one or more internal bonds, going through stable and unstable conformations as a full 360° rotation is executed. In particular, the central C–C bond of ethane is a threefold symmetry axis. Thus, as one of the two methyl groups rotates around this axis the molecule goes through (stable) staggered and (unstable) eclipsed conformations (see Fig. 1). The preferred staggered structure is attributed to steric effects [4,6–10], more precisely to increased

E-mail addresses: fvalencia@bethe.fis.puc.cl (F. Valencia), ahromero@puc.cl (A.H. Romero), mkiwi@puc.cl (M. Kiwi), rramirez@puc.cl (R. Ramírez), atola@puc.cl (A. Toro-Labbé).

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Fig. 1. Staggered (left) and eclipsed (right) conformations. The rotation angle is defined as $\alpha = 0^{\circ}$ for the staggered and $\alpha = 60^{\circ}$ for the eclipsed conformations, respectively.

repulsion between electrons in bonds that are drawn closer together [9].

On the other hand, disilane has attracted interest both on its own right [1-4,11-18] and since the fundamental processes in the disilane decomposition on silicon surfaces are relevant to the understanding and optimization of the growth of epitaxial silicon on silicon substrates. The morphological parameters of the eclipsed and staggered ethane and disilane conformations were recently calculated by Pophristic and co-workers [2]. They concluded that the origin of the eclipsed to staggered relaxation of ethane is related to preferential hyperconjugative stabilization [19,20] (meaning energy stabilization through electron excitation to a delocalized state). This charge delocalization changes the electronic properties of the molecule, as a function of the conformation it adopts. Instead, for disilane hyperconjugative stabilization is greatly weakened and does not seem to play a crucial role [2]. It is the Si-Si bond lengthening, induced by electronic repulsion in the eclipsed conformer, which mainly accounts for the barrier height.

When a reaction moves forward along the reaction coordinate, a redistribution of the groundstate electron density takes place, and the resulting energy change can be understood in terms of the response of the system to variations of the total number of electrons N and of the external $v(\vec{r})$ potential [21]. Density functional theory (DFT) [21,22] has been quite successful in providing a theoretical basis for qualitative chemical concepts like chemical potential (μ) and hardness (η), which describe the response of the system when N is varied for a fixed $v(\vec{r})$ [21]. In DFT μ is the Lagrange multiplier associated with the normalization constraint that requires conservation of the number of electrons N. Classical structural chemistry is recovered with the identification of μ as minus the electronegativity ($\mu = -\chi$), a well-known and wellestablished quantity. Definitions of μ and η , two global electronic properties that are implied in the reactivity of molecular systems, were given by Parr et al. [23] and Parr and Pearson [24,25], respectively. One of the aims of this paper is to analyze the internal rotation in terms of μ and η , in order to obtain insights on the origin of the potential barriers that hinder internal rotation, and also to explain the rotation induced lengthening of the central Si–Si bond.

The application of DFT concepts to the analysis of chemical reactions is better appreciated with the help of the principle of maximum hardness (PMH), that asserts that molecular systems reach equilibrium tending towards states with the highest hardness [26–30]. In this context the PMH can also be helpful in identifying transition states where minimum values of η are expected [31].

The main purpose of this contribution is to provide a comparative study of the properties of disilane (Si_2H_6) with the halides Si_2X_6 (X = F, Cl and Br). We thus investigate in detail the geometric and electronic structure of disilane and the family of closely related Si₂X₆ molecules and compare our results with the available literature on the subject [1-4,11-18]. To understand the implications that the geometric and electronic structure has on the properties of this family of molecules we compute the energy profiles, rotational barriers, chemical potentials, chemical hardness and develop an understanding of the reactivity in terms of the LUMO and HOMO densities. We focus our attention on the changes that are induced as the molecular conformation changes periodically from staggered to eclipsed, and back to staggered, through rotation around the Si–Si bond of the SiX₃ group of Si_2X_6 .

This paper is organized as follows: after this introduction we discuss technical aspects of our calculation in Section 2, discuss the molecular geometry in Section 3, the electronic energy profiles and rotational barriers in Section 4 and the chemical potential and the hardness in Section 5. In Section 6 we present a qualitative analysis of the chemical reactivity of silanes and finally, we close the paper in Section 7 drawing conclusions.

2. Computational details

The calculations reported in this paper were performed using the GAUSSIAN 98 [32] package. The results we report were obtained implementing the B3LYP-DFT method and corresponds to the B3LYP/6-311++G** level. A lower level B3LYP/ 6-31G* calculation was tested for comparison purposes. For the staggered and eclipsed conformations, and in order to test the DFT results, MP2/6-311++G** calculations were also carried out to check the quality of the B3LYP results.

3. Geometry

Constrained geometrical optimization was performed varying the dihedral angle α , defined as the rotation angle of the silyl group of Si₂H₆ (or the three X atoms in Si₂X₆), located at one end of the Si–Si bond, relative to the same three atoms at the other end of this bond (see the illustration in Fig. 1). The angle $0 \le \alpha < 60^{\circ}$, with $\alpha = 0$ defined as the staggered conformation and $\alpha = 60^{\circ}$ as the eclipsed one, was varied in steps of 10°.

The structural parameters obtained for the staggered conformation are listed and compared to experimental data – whenever the latter is available – in Table 1. It is apparent that for the lighter molecules (i.e., Si_2H_6 and Si_2F_6) B3LYP/ 6-31G* yields better agreement with experimental values than B3LYP /6-311++G**, while the larger basis set 6-311++G** fares better for Si_2Cl_6 . We expect the same to hold for Si_2Br_6 (a molecule that has not yet been synthesized) since heavier atoms require larger basis sets for a proper description. Thus, in what follows below, our comparisons with experiment are based upon the results of B3LYP/6-311++G**.

Rotation of one sylil group with respect to the staggered conformation is accompanied by a significant change in the Si–Si distance (see Fig. 2) while the Si–X (X = H, F, Cl and Br) distance re-

mains almost unchanged (see Table 1). In fact, Si₂Br₆ displays the largest deformation, which amounts to about 1.59%, while Si_2F_6 undergoes a tiny elongation of only 0.23%. Lengthening of the central bond has already been observed in ethane, disilane and hexafluordisilane [1,2], and has been explained in terms of the delicate balance between electrostatic repulsion and hyperconjugative interactions. Table 1 and Fig. 2 show that elongation of the central bond is even stronger in Si₂Cl₆ and Si₂Br₆. In addition to the above-mentioned electrostatic and hyperconjugative interactions, this enhancement to some extent also has be related to steric hindrance between quite large chemical groups. The angle \angle (SiSiX), between the Si axis and the X-atoms, exhibits a small but systematic increase as a function of α . Again, this change is largest for Si₂Br₆ (approximately 0.66%) and smallest for Si_2F_6 (approximately 0.04%).

4. Energy profiles and rotational barriers

Fig. 3 shows the evolution of the total energy for each molecule studied, measured with respect to the total energy in the staggered configuration. Always the staggered (eclipsed) conformation is of minimum (maximum) energy.

It is also evident from Figs. 2 and 3 that the energy follows the same trend as the Si–Si distance along the torsion angle. Clearly, the torsional potential energy can be understood in terms of the structural changes of the molecule undergoes as α is varied. Si₂F₆ being almost free to rotate, in the sense that it undergoes only minor geometrical changes, presents a rather small rotational barrier of ~0.61 kcal/mol, while Si₂Br₆ has a rotational barrier of ~2.6 kcal/mol, consistent with its larger geometric changes.

The above results suggest that the pairs Si_2Br_6 and Si_2Cl_6 on the one hand, and Si_2H_6 and Si_2F_6 on the other, behave quite differently. In fact, inspection of Fig. 2 indicates that, as α varies by 60°, the former pair undergoes rather large bond stretching (>1%) Instead, for the latter pair the bond stretching is less than 0.5%. The energy changes, illustrated in Fig. 3 are also significantly larger for the Si₂Br₆ and Si₂Cl₆ pair, than for Si₂H₆

Table 1					
Calculated geometries	of Si ₂ H	6, Si ₂ F ₆ ,	$\mathrm{Si}_2\mathrm{Cl}_6$	and	$\mathrm{Si}_{2}\mathrm{Br}_{6}$

Molecule	B3LYP/6-31G*	B3LYP/6-311++G**	Experiment
Si_2H_6 (staggered)			
d(Si–Si)	2.350	2.354	2.331 [1]
d(Si-H)	1.489	1.487	1.492 [1]
∠(SiSiH)	110.4	110.6	110.3 [1]
Si_2H_6 (eclipsed)			
d(Si–Si)	2.360	2.366	
d(Si-H)	1.489	1.487	
∠(SiSiH)	110.8	110.6	
Si ₂ F ₆ (staggered)			
d(Si–Si)	2.319	2.336	2.317 [1]
d(Si–F)	1.593	1.598	1.564 [1]
∠(SiSiF)	110.5	110.7	110.3 [1]
Si_2F_6 (eclipsed)			
d(Si–Si)	2.326	2.341	
d(Si–F)	1.592	1.598	
∠(SiSiF)	110.7	110.7	
Si ₂ Cl ₆ (staggered)			
d(Si–Si)	2.355	2.354	2.320
d(Si–Cl)	2.060	2.056	2.002
∠(SiSiCl)	109.7	109.6	
Si ₂ Cl ₆ (eclipsed)			
d(Si–Si)	2.377	2.378	
d(Si-Cl)	2.059	2.056	
∠(SiSiCl)	110.0	109.9	
Si ₂ Br ₆ (staggered)			
d(Si–Si)	2.335	2.368	
d(Si–Br)	2.211	2.232	
∠(SiSiBr)	108.7	109.2	
Si ₂ Br ₆ (eclipsed)			
d(Si–Si)	2.356	2.405	
d(Si–Br)	2.209	2.232	
∠(SiSiBr)	108.7	110.0	



Fig. 2. Percentage change of the Si–Si distance, relative to the $\alpha = 0$ staggered conformation, for the four molecules studied. The lines are guides to the eye.



Fig. 3. Electronic energy as function of torsion angle $\alpha.$ The lines are guides to the eye.

and Si_2F_6 . In addition, the torsion angle dependence of the energy of Si_2Br_6 (≈ 3 kcal/mol) and Si_2Cl_6 is only slightly smaller than that of ethane [4], while for Si_2H_6 and Si_2F_6 [1,2] it amounts to less than 1 kcal/mol. Similar arguments hold for the bond stretching. It is important to mention that our results, as far as the torsional potential barriers for Si_2H_6 and Si_2F_6 are concerned, are in agreement with previous calculations at different levels of theory [1] and with the experimental data

It is important to remark that at the B3LYP/ $6-31G^*$ level Si₂Br₆ is predicted to be stable in the eclipsed configuration, with a rather significant energy difference of 1.17 kcal/mol relative to the staggered one. MP2/6-31G* also yields a smaller energy for the eclipsed configuration, but with a much smaller difference of only 0.150 kcal/mol. However, the MP2/6-311++G** calculations are in reasonable agreement with the B3LYP/ 6-311++G** results. The former yields 3.37 kcal/ mol, while from the latter the result of 2.592 kcal/ mol, displayed in Table 2, is obtained. Thus, it seems that $6-311++G^{**}$ is the minimum basis set required to properly describe the rotational behavior of Si₂Br₆. In all of these calculations zero point energy was ignored.

available [33].

Table 2 displays the B3LYP/6-311++G** rotational barriers we obtained. Substitution of the hydrogens, by the more electronegative fluor atoms, results in a lowering of the potential barrier. The electronic population is now mainly localized at the SiF₃ groups thus weakening the Si–Si torsional bond. The values for Si₂H₆ and Si₂F₆ compare well with those calculated by Cho et al. [1]. The experimental values for the rotational barrier of Si₂H₆ are ~1 kcal/mol, and for Si₂F₆

Table 2 Calculated rotational barrier at the B3LYP/6-311++ G^{**} level for Si₂H₆, Si₂F₆, Si₂Cl₆ and Si₂Br₆

2 0) 2 0) 2 0 2 0	
Molecule	Rotational barrier (kcal/mol)
${ m Si}_2{ m H}_6 { m Si}_2{ m F}_6$	0.944 0.610
Si_2Cl_6 Si_2Br_6	1.627 2.592

between 0.51 and 0.73 kcal/mol, according to early electron diffraction measurements [33].

On the other hand, substitution of the hydrogens by chlorine and bromine atoms tends to keep the electronic population uniformly distributed, and the observed increase of the potential barrier seems to be related to steric hindrance between quite voluminous chemical groups.

5. Chemical potential and hardness

In DFT the chemical potential of a molecule is defined by the derivative of the energy with respect to the number of electrons N at constant external potential v(r):

$$\mu = \left(\frac{\partial E}{\partial N}\right)_{v(r)},\tag{1}$$

where E is the energy and N the number of particles. For a finite system this extrapolation takes the form [21]

$$\mu \cong \frac{1}{2} [E(N+1) - E(N-1)].$$
(2)

Moreover, following Koopman's theorem [34], the anion energy E(N + 1) can be approximated by $E(N + 1) \approx E(N) + E_{LUMO}$, and the cation energy E(N - 1), by $E(N - 1) \approx E(N) - E_{HOMO}$, where E_{LUMO} and E_{HOMO} are the energies of the Lowest Unoccupied and Highest Occupied Molecular Orbital, respectively. Within this approximation

$$\mu \cong \frac{1}{2} (E_{\text{LUMO}} + E_{\text{HOMO}}). \tag{3}$$

Another relevant characteristic property we want to probe is the chemical hardness η , defined as

$$\eta = \frac{1}{2} \left(\frac{\partial^2 E}{\partial N^2} \right)_{v(r)},\tag{4}$$

which can be approximated by a finite difference as follows:

$$\eta \cong \frac{1}{2} [E(N+1) + E(N-1) - 2E(N)], \tag{5}$$

which in terms of the HOMO-LUMO energies reads

$$\eta \cong \frac{1}{2} [E_{\text{LUMO}} - E_{\text{HOMO}}]. \tag{6}$$

Nevertheless it is important to notice that the actual changes in the torsional energy must include the geometrical changes induced by the removal or addition of electrons. This geometrical relaxation may include symmetry changes, such as the rotations around the Si-Si axis we study in this paper. Thus, the significance of η and μ as calculated above, whether with the HOMO-LUMO approximation or with the unrelaxed (or constraint relaxed) cation and anion energies, is not completely accurate. However, we expect these quantities to be useful to characterize the specific interactions that are responsible for the barrier heights and the geometrical deformations, that are due to internal rotation. In particular, the variation of μ as a function of α implies that charge transfer processes are taking place. These processes, in turn, may favor stabilization through hyperconjugative interactions.

Figs. 4 and 5 display the chemical potential μ and chemical hardness η , respectively, as a function of the torsion angle α , in the HOMO–LUMO approximation. An appreciable difference of the μ values between two reference conformations implies that an electronic rearrangement, with some charge transfer from the higher towards the lower μ conformation, will take place. By inspection of Fig. 4 we observe that the chemical potential versus α profiles for all molecules, except Si₂H₆, display a variation of $\mu \sim 1$ kcal/mol as α varies by 60°, always opposite in sign to the relative to the



Fig. 4. Chemical potential in the HOMO-LUMO approximation.



Fig. 5. Chemical hardness in the HOMO-LUMO approximation.

energy variation displayed in Fig. 5. This is an indication that torsion implies charge transfer, that might originate hyperconjugative interactions which in turn contribute significantly to the elon-gation of the central Si₂X₆ bond. In contrast, for Si₂H₆, the chemical potential remains quite constant over the range $0 \ge \alpha \ge 60^\circ$, with $\Delta \mu \sim 0.10$ kcal/mol, suggesting that for Si₂H₆ the repulsive electrostatic interactions are the cause for the small Si–Si bond lengthening due to internal rotation, as concluded by Pophristic et al. [2].

Further inspection of Fig. 5 reveals that the overall hardness changes are rather small, ranging from ~0.2 kcal/mol for Si_2H_6 to ~1 kcal/mol for Si_2F_6 . Si_2H_6 , Si_2Cl_6 and Si_2Br_6 are chemically hardest in the eclipsed conformation, while Si_2F_6 is hardest in the staggered conformation. It is interesting to mention that the same trends for the chemical hardness are predicted both by the cation–anion energies, at the B3LYP/6-311++G** level, and by the HOMO–LUMO approximation at MP2/6-311++G** level, as seen in Table 3, where the numerical values of the hardness in the staggered and eclipsed conformations are listed.

It is important to notice that the PMH is verified only for Si_2F_6 , while Si_2H_6 , Si_2Cl_6 and Si_2Br_6 exhibit hardness profiles obeying the same trend as their energy profiles. Obeying the PMH, the η value of Si_2F_6 displays a maximum at the stable staggered conformation and a minimum at the unstable eclipsed conformation. Moreover, we

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Molecule	HOMO–LUMO, B3LYP	Anion and cation, B3LYP	HOMO-LUMO, MP2
Si ₂ H ₆	0.185	0.308	0.52
Si_2F_6	-0.995	-0.856	-0.90
Si ₂ Cl ₆	0.473	0.634	
Si_2Br_6	0.738	1.071	1.39

Table 3 Change in chemical hardness $\Delta \eta = \eta_e - \eta_s$ in kcal/mol

want to remark on the complementary behavior of energy and hardness: whereas for Si_2F_6 the almost free internal rotation does not allow to distinguish the energetically most favorable α value, the hardness profile allows this characterization. In fact, for Si_2F_6 the hardest and less reactive isomer is the staggered conformation but, the more reactive eclipsed conformation, lies only a few tenths kcal/mol apart. In contrast, the hindered rotation in Si_2X_6 (X = H, Cl, Br) yields energetically distinguishable conformations, but they cannot be characterized by the hardness profiles, since all conformations display a similar η versus α dependence.

6. Reactivity of silanes

The reactivity of these systems, induced by the internal rotation, cannot be rationalized in terms of the profiles of μ and η alone, due to their almost constant behavior as a function of α . However, a different perspective of the electronic structure and reactivity is provided by the LUMO and HOMO densities. In Fig. 6 the HOMO of the Si₂H₆ molecule is shown and we observe very similar orbitals to the other Si₂X₆ molecules we have considered. The majority of the orbital charge accumulates on



Fig. 6. HOMO for Si_2H_6 . Left panel: staggered configuration. Right panel: eclipsed configuration.

the Si–Si bond with some contribution on the hydrogens, and with a bond of clear π -character. Moreover, there is little difference between the HOMO staggered and eclipsed charge distributions, indicating that the effect of the torsional motion on an electrophilic attack is negligible.

The LUMO electronic structure, as illustrated in Fig. 7, is completely different. For Si_2H_6 , in the lowest energy (staggered) configuration, the charge density is delocalized on the sylil groups. On the contrary, in the eclipsed conformation the charge is delocalized on the Si–Si bond, with a π -antibond character. This, and the low torsion barrier, indicates that a nucleophilic attack on Si₂H₆ may present different specific mechanisms for different adducts. Inspection of Figs. 6 and 7 shows that the largest overlap between HOMO and LUMO orbitals occurs for Si_2F_6 , which suggests that in the staggered configuration this molecule might exhibit some degree of hyperconjugative effects [4]. In the Si_2F_6 staggered configuration the delocalization process is different: the charge is delocalized on the Si-Si bond, with antibond character, and is symmetric around the Si-Si bond, but with an asymmetry in the direction of the sylil groups. Instead, in the eclipsed conformation, the charge is again delocalized on the Si-Si bond with antibond character, but with some preferential charge on the sylil side when viewed in a plane with four hydrogen atoms. In addition, the delocalization volume is larger in the staggered conformation. The preceding analysis of the shape of the LUMO density, plus the rather free internal rotation of Si₂F₆, suggests that there is no specific mechanism for a nucleophilic attack.

Finally, we consider the Si₂Cl₆ molecule (Si₂Br₆ behaves similarly), which in its staggered configuration has the charge localized on the Si atoms, with a very clear σ -character, but with some



Fig. 7. LUMO's for the different molecules considered. Left panel: staggered configuration. Right panel: eclipsed configuration. From top to bottom, Si_2H_6 , Si_2F_6 and Si_2Cl_6 (the LUMO's for Si_2Br_6 are quite similar to Si_2Cl_6).

asymmetry in the sylil group directions. This is similar to the eclipsed configuration, where the charge distributes in much the same way, except in that it is completely symmetric around the Si–Si bond. The above results suggest that the low, but significant, barriers that hinder internal rotation may induce the formation of adducts of different symmetry during a nucleophilic attack.

7. Concluding remarks

We have performed DFT calculations on Si_2H_6 , Si_2F_6 , Si_2Cl_6 and Si_2Br_6 of the evolution of geometrical parameters, torsional potential energy, chemical potential and molecular hardness as a function of torsion angle. For all these molecules at the DFT-B3LYP/6-311++G** level, the staggered conformation is predicted to be the most stable one. Moreover, except for Si_2F_6 , it is softer than the eclipsed configuration due to a different charge delocalization at the LUMO orbital. Low, but significant, energy barriers hinder internal rotation. For Si_2H_6 the chemical potential and the hardness remain quite constant during the torsion process, while the other molecules show different degrees of electronic density rearrangement as a function of the torsion angle. In particular Si_2F_6 shows a large variation of hardness, which peaks at the staggered configuration, in agreement with the PMH. Although it was not possible to fully characterize the reactivity just on the basis of the chemical potential and hardness profiles, they proved useful to identify specific interactions that explain the Si–Si bond lengthening and the nature of the torsion energy barriers.

Qualitatively the Si_2X_6 family can roughly be grouped into two pairs: Si_2H_6 and Si_2F_6 on the one hand, and Si_2Cl_6 and Si_2Br_6 on the other. The latter have large bond stretching and large energy barriers for torsional motion, which are of the same order of magnitude as for ethane [1,2].

The qualitative analysis of the frontier orbitals shows that for the Si_2X_6 series there is little difference between the HOMO staggered and eclipsed charge distributions. This indicates that the effect of the torsional motion on an electrophilic attack is negligible. In contrast, the low but significant barriers that hinder internal rotation may induce different nucleophilic attack mechanisms.

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