

Ring Flipping of Seven-membered and Eight-membered Dithienodisila-heterocycles

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Ground state structures and ring flipping transition states of eight- and seven-membered silicon containing heterocyclic compounds such as dithienodisilacyclooctatriene and oxadithienodisilacycloheptadiene derivatives, respectively have theoretically been investigated. Although the bithienylene moiety of the derivatives does not change the ground state structures, they significantly increase the ring flipping barrier by 13–17 kcal/mol in the case of the eight-membered rings (**2**, **3**, and **4**) in comparison with that of silicon containing heterocyclic compound **6**, chosen as a model. The same moiety increases the flipping barrier of seven-membered ring (**5**) is only slightly (3.3 kcal/mol) in comparison with that of model compound **7**. Hence, it has been concluded that not only the existing ring strain of eight-membered ring but also the bithienylene moiety collectively increases the ring flipping barrier so as to prevent such conformational changes explaining anomalous NMR behaviour of dithienodisilacyclooctatriene derivatives (**2–4**). In contrast, the effect of substituents R¹ and R² at the olefinic carbons of the eight-membered ring on the flipping barrier turned out to be mild.

Key Words : Dithienodisilacyclooctatriene, Oxadithienodisilacycloheptadiene, Ring flipping barrier, Twisting angle

Introduction

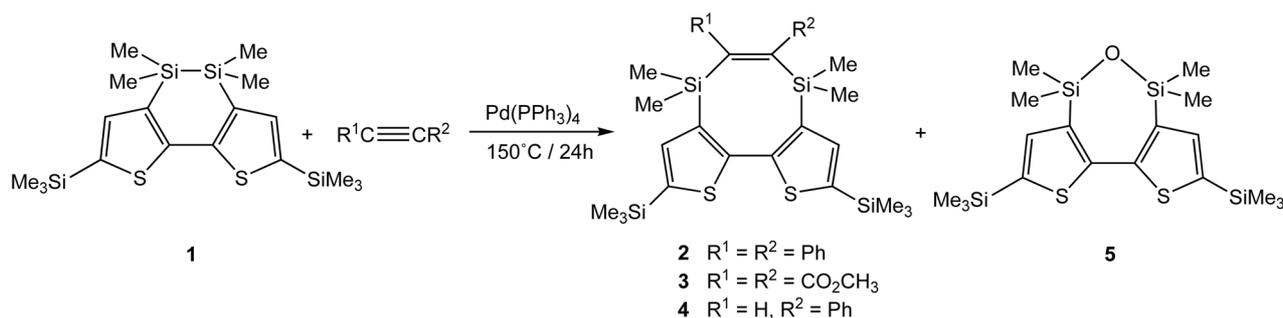
Ring flipping of cyclic systems represents the dynamic behavior of chemical compounds in media. In the investigation of variable-temperature ¹H and ¹³C NMR spectra of 1,3,6-cyclooctatriene¹, no dynamic NMR effect was observed below –180 °C.^{1b} A single resonance attributed to two methylene protons on the respective ring methylene carbon atoms in 1,3,6-cyclooctatriene (eight-membered ring) is due to rapid interconversion through a ring flipping. The conformational energy barrier for the ring inversion of 1,3,6-cyclooctatriene was calculated to be only 4.1 kcal/mol above the ground state.^{1b}

On the other hand, the ¹H and ¹³C NMR spectra of the eight-membered disilacarbycles, 1,1,4,4-tetramethyl-5,6,7,8-tetraphenyl-1,4-disilacycloocta-2,5,7-triene derivatives^{2,3} having phenyl substituents on the ring and 1,1,6,6-tetramethyl-1,6-dihydrotribenzo-[*b,e,g*][1,4]-disilocine⁴ having a biarylene moiety such as a biphenylene, indicated that the two methyl groups on the silicon atom of these eight-membered disilacarbycles were nonequivalent. This nonequivalence of the two methyl groups on the silicon atom in the compounds may be due to the steric repulsions between the methyl substituents on the silicon atom and the phenyl substituents or biphenylene moiety of the eight-membered ring. The ¹H NMR spectrum of the two methyl protons on the silicon atom of the seven-membered ring of 2,2,7,7-tetramethyl-3,4,5,6-tetraphenyl-1-oxo-2,7-disila-3,5-cycloheptadiene⁵ having a flexible Si-O-Si moiety shows magnetically equivalent.

We recently have reported that the palladium-catalyzed reactions of 4,4,5,5-tetramethyl-2,7-bis(trimethylsilyl)dithieno[3,2-*c:c'*:2',3'*e'*]disilacyclohexadiene **1** with alkynes

afforded dithienodisilacyclooctatriene derivatives **2–4** of a eight-membered ring along with a small amount of oxadithienodisilacycloheptadiene derivative **5** of a seven-membered ring (Scheme 1).^{6a} Such insertion reactions of alkynes into the silicon-silicon bond of acyclic and cyclic disilanes in the presence of a transition-metal catalyst have extensively been studied.⁷ The formation of **5** may be due to the oxidation reaction⁸ of the silicon-silicon bond of **1** with a trace of molecular oxygen, which we were unable to remove from the reaction mixture.

We found from the ¹H NMR and ¹³C NMR spectra that the two methyl groups on the respective silicon atoms of the alkyne-insertion products **2–4** containing bithienylene and olefinic moieties are nonequivalent, whereas the two methyl groups on the silicon atom of the oxygen-insertion product **5** containing a Si-O-Si moiety are equivalent. It was suggested that the nonequivalence of the two methyl groups on the silicon atom in compounds **2–4** may be ascribed to the disilacyclooctatriene ring, which is significantly twisted. In fact, the twisting angle of the disilacyclooctatriene ring of **3** is observed as 59.3° by X-ray crystallographic analysis.^{6a} On the other hand, a single resonance attributed to the two methyl groups on the ring silicon atom in compound **5** is presumably due to rapid interconversion through a ring flipping. To our knowledge, little interest have been shown in the examination of the conformational behaviour of seven-membered oxadisilacarbycle and eight-membered disilacarbycle such as oxadithienodisilacycloheptadiene and dithienodisilacyclooctatriene derivatives, respectively. In this paper, we report the ring flipping energy barriers of the alkyne-insertion products **2–4** (eight-membered ring) and the oxygen-insertion product **5** (seven-membered ring) as well as the reactant **1** (six-membered ring). Using computa-



Scheme 1

tional analyses, current investigation attempts to examine the relations between the ring flipping and the anomalous NMR behavior of the $SiMe_2$ groups in the dithienodisilacyclic derivatives **2-5**.

Computational Details

To obtain the conformational energy barriers, electronic structure calculations based on density functional theory were performed using **B3LYP** exchange-correlation functionals. All calculations reported here were performed with the **GAMESS**¹⁰ (general atomic and molecular electronic structure system) electronic structure program. All-electron 6-31+G(d,p)¹¹ basis set was used throughout the investigation. The Hessian matrix (matrix of energy second derivatives) was computed and diagonalized for all stationary points to characterize them. Intrinsic reaction coordinate (IRC) calculations, using the Gonzalez-Schlegel second order method,¹² were conducted to verify that each saddle point connects minima of interest. All the computations were done without imposing symmetry unless otherwise specified.

Results and Discussion

As discussed in the introduction, the 1H and ^{13}C NMR spectra for the alkyne-insertion products **2-4** indicate that the two methyl groups on the silicon atom of the eight-membered disilacyclic derivative containing bithienylene and olefinic moieties are nonequivalent, whereas the two methyl groups on the silicon atom of the seven-membered oxadisilacyclic derivative **5** containing bithienylene and Si-O-Si moieties are equivalent. The 1H NMR spectra of **3** and **5** exhibit two resonances at -0.30 and 0.33 ppm, and a single resonance at 0.27 ppm, respectively which are attributed to the two methyl protons on the silicon atom. In the variable-temperature 1H NMR spectrum for the dithienodisilacyclic derivative **3**, the two nonequivalent methyl protons on the silicon atom did not coalesce up to $60^\circ C$ in $CDCl_3$. However, the two methyl protons on the silicon atom of the oxadisilacyclic derivative **5** were observed as a singlet at $-60^\circ C$ in $CDCl_3$ and even at $-100^\circ C$ in CD_2Cl_2 .

We firstly carried out DFT calculations on the structurally similar compounds **6** and **7**, chosen as models (Chart 1) at the level of B3LYP/6-31+G(d,p) in order to know the overall

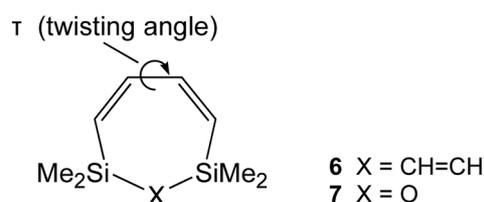


Chart 1. Model Compounds for MO Calculations.

energy changes with the twisting angle (τ).

The relative energy for the model compounds **6** and **7** is plotted as a function of the twisting angles of the butadiene unit of the optimized geometries in Figure 1.

As can be seen in the Figure 1, the flipping barriers were calculated to be 9.7 and 1.2 kcal/mol for disilacyclic derivative **6** (circle) and oxadisilacyclic derivative **7** (triangle), respectively. It clearly shows that the eight-membered ring of **6** has larger relative ring strain than the seven-membered ring of **7** at the ring flipping transition state. However, the difference in the flipping barriers between these two model compounds (8.5 kcal/mol) may not strongly implies the nonequivalence^{6a} of the methyl groups on the ring silicon atom of the compounds **2-4**. The ring flipping barrier can also depend on the biarylene moiety such as a bithienylene in the eight-membered disilacyclic derivatives **2-4** as well as the substituents R^1 and R^2 . In order to investigate such substituent effects on the barrier, transition state calculations were done on the real insertion products **2-4** and **5**, respec-

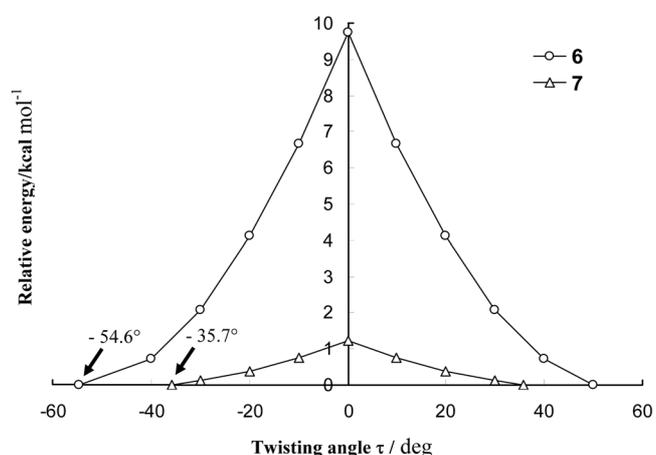


Figure 1. Relative energy derived from MO calculations at the B3LYP/6-31+G(d,p) level for **6** (circle) and **7** (triangle).

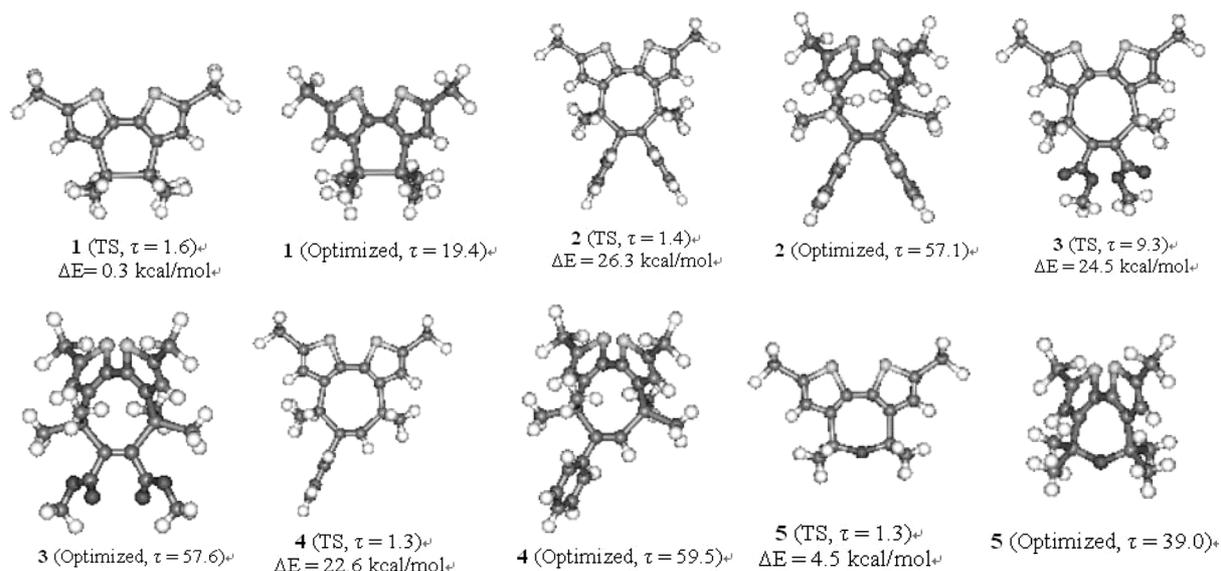


Figure 2. The optimized structures and the corresponding transition states of ring flipping conversions of **1-5**. Optimized and TS stand for optimized structure and transition states, respectively. $\Delta E = E_T$ (transition state) – E_O (optimized structure). τ is the twisting angle of butadiene part of the ring, as depicted in Chart 1.

tively as well as on the initial reactant **1** with the level of B3LYP/6-31+G(d,p). The results are presented in Figure 2.

Full geometry optimization on **1** (six-membered ring) yielded the twisting angle of 19.4° , which is relatively small. The flipping barrier of **1** was calculated to be 0.3 kcal/mol, which is much smaller than those of model compounds **6** and **7** indicating that the ring flipping occurs very easily. It is seen that the bithienylene moiety of the six-membered ring of **1** does not increase the flipping barrier. Table 1 summarizes ring flipping barriers, twisting angles of the optimized structures of **1-7** and observed twisting angles of **2-3** in comparison with that of the reactant **1**.

Full geometry optimizations on the eight-membered disilacarbycles of **2-4** containing bithienylene and olefinic moieties and the seven-membered disilacarbycle of **5** containing bithienylene and Si-O-Si moieties yielded the twisting angles of 57.1° , 57.6° , 59.5° and 39.0° , respectively. When compared to the twisting angle values of the eight-membered disilacarbycle of **6** (54.6°) and of the seven-membered oxadisilacarbycle of **7** (35.7°) which do not have a bithienylene moiety in the ring, the twisting angles of their corresponding real compounds **2-4** and **5** are increased to a negligible extent, implies that the introduction of the bithienylene moiety in the ring does not have significant effects on the ring strain of ground state structures. It is seen that **5** has smaller twisting angle due to the less strained

seven-membered oxadisilacarbycle. The effect of substituents R^1 and R^2 of the olefinic carbons on the twisting angle is mild, since the twisting angles of **2-4** agree within 2° with each other. The twisting angles of the eight-membered disilacarbycles are in good agreements with the available experimental values of 54.28° (**2**) and 59.32° (**3**) by X-ray crystallographic analysis.^{6a} Encouraged by good agreements with experimental twisting angles, the transition states of ring flipping of **2-5** were calculated. The ring flipping barriers, defined as the energy differences between the transition state and the fully optimized structure of **2-5**, were calculated to be 26.3, 24.5, 22.6, 4.5 kcal/mol, respectively. On comparing the flipping barrier value (9.7 kcal/mol) of the model compound **6**, the ring flipping barriers of the real compounds **2-4** are increased significantly, which are may be due to the steric repulsions between the methyl substituents on the silicon atoms and the bithienylene moiety of the eight-membered ring. However, the flipping barrier of **5** is increased only slightly as compared to the model compound **7** indicating that the ring flipping of **5** can still occur easily. It implies that the Si-O-Si unit of the seven-membered ring **5** is very easy to bend for the ring flipping. Since the flipping barriers of **2-4** agree within 4 kcal/mol, the effect of R^1 and R^2 substituents on the flipping barrier is mild. In general, it is seen that the introduction of sterically bulky groups such as phenyl or biarylene groups into the eight-membered ring

Table 1. Ring flipping barriers, twisting angles of the optimized structures of **1-7** and observed twisting angles of **1-3**

	1	2	3	4	5	6	7
ring flipping barriers (kcal/mol)	0.3	26.3	24.5	22.6	4.5	9.7	1.2
twisting angles of optimized structures ($^\circ$)	19.4	57.1	57.6	59.5	39.0	54.6	35.7
observed twisting angles ($^\circ$) ^a	20.2	54.3	59.3				

^a: determined by single-crystal X-ray crystallography (ref. 6)

strongly increases the flipping barriers of transition states and it affects the eight-membered ring compounds **2-4** more significantly than the seven-membered ring compound **5**.

Conclusions

Ground state structures and ring flipping transition states of the initial reactant **1**, the eight-membered disilacarbyclic derivatives **2-4**, and the seven-membered oxadisilacarbyclic derivative **5** as well as their model compounds **6** and **7** were examined to understand the relations between the ring flipping and the anomalous NMR behavior. According to the model compound studies, the flipping barrier of the eight-membered ring is larger than that of the seven-membered ring by 8.5 kcal/mol, which is mostly due to the larger ring strain of the eight-membered ring. Although, the introduction of bithienylene moiety does not affect the twisting angles of the optimized structures to a larger extent, it significantly increases the ring flipping barrier of the eight-membered ring of compound **2-4** by 13-17 kcal/mol in comparison with that of the model compound **6**. However, the same moiety slightly increases the flipping barrier of the seven-membered ring of compound **5** by 3.3 kcal/mol in comparison with that of the model compound **7**. Since the flipping barriers of **2-4** agree within 4 kcal/mol, it is seen that the effect of R¹ and R² substituents at the carbon-carbon double bond of the disilacarbyclics **2-4** is mild. Therefore, it is concluded that not only the existing ring strain of the eight-membered ring but also the bithienylene moiety collectively increases the ring flipping barrier so as to prevent such conformational changes. However, in the case of six- (**1**) and seven-membered rings (**5**), the bithienylene moiety does not affect the ring flipping barrier significantly.

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