

## Computational studies of silanediimine rings



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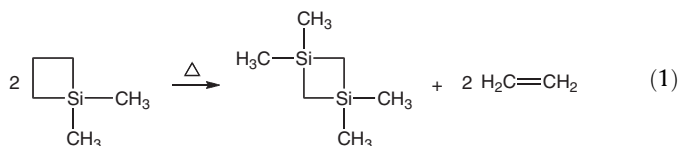
### ABSTRACT

Computational studies of alicyclic silanediimines ( $\text{RN}=\text{Si}=\text{NR}$ ) (rings five through twelve), mainly at the MP2/6-31G(d,p)//MP2/6-31G(d,p) level of theory, were conducted to (1) attempt to locate the transition states between silanediimines isomers, (2) follow their torsional IRC paths to either enantiomeric or diastereomeric pairs, and (3) compare silanediimine results with recently published, related studies of alicyclic carbodiimides ( $\text{RN}=\text{C}=\text{NR}$ ). Transition states for rings six, seven, eight, nine, eleven, and twelve have been found. The  $\text{RN}=\text{Si}=\text{NR}$  dihedral angle is  $\sim 0^\circ$  for the even-numbered ring transition states, but deviates from  $0^\circ$  for rings seven and nine. The eleven-ring transition state that has been located is quite different from its carbodiimide analog. The even- and odd-numbered ring transition states have different symmetry point groups with the  $\text{C}_s$  transition states (even rings) having an imaginary frequency mode that transforms as the asymmetric irreducible representation of the group and the  $\text{C}_2$  transition state (odd ring) having a mode transforming as the totally symmetric representation. Intrinsic reaction coordinate (IRC) analyses followed by energy minimization along the antisymmetric pathways lead to enantiomeric pairs. The symmetric pathways give diastereomers. No five-membered ring silanediimine was obtained; instead ring opening to a silylene species occurred. A twelve-membered ring transition state ( $\text{C}_s$ ) that was located could be found only by applying a different computational approach. Molecular mechanics were used to obtain structures to search for a ten-membered transition state without success. Barriers to the transition states are too low to expect the silanediimine species studied to be optically resolvable.

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### 1. Introduction

Multiple bonding to silicon has a long and fascinating history largely resulting from questions concerning the similarities and differences between silicon multiple bonding and that of its congener carbon. The earliest instances of multiple bonding between silicon and carbon did not involve isolable examples [1–6]. Thermolysis of 1,1-dimethylsilacyclobutane to afford 1,1,3,3-tetramethyl-1,3-disilacyclobutane and ethene (Eq. (1)) strongly indicated the intermediacy of the silene,  $(\text{CH}_3)_2\text{Si}=\text{CH}_2$ . Not



surprisingly, the quest for stable silenes and for other multiply bonded silicon species, isolable and not, has become an active research field and resulted in many interesting accomplishments [7–19] with interest not abating [20–25]. Studying multiple bonds to silicon has naturally included those to nitrogen [7–9,26–32].

Our recent computational studies of a series of alicyclic carbodiimides ( $\text{RN}=\text{C}=\text{NR}$ ) transition states of various rings sizes demonstrated that, depending on ring size and the symmetry of the transition states, the preferred mechanism of stereoisomerization is torsional affording either enantiomeric (for  $\text{C}_s$  transition states) or diastereomeric (for  $\text{C}_2$  transition states) isomers [33]. The barriers that were found typically were not sufficiently high to indicate that enantiomers of these carbodiimide rings could be resolved. This extension of the carbodiimide work focuses on alicyclic silicon analogs of these carbodiimides, namely the silanediimines ( $\text{RN}=\text{Si}=\text{NR}$ ). Silanediimines were first prepared in the late 1980's by West, Michl, and coworkers by matrix isolation trapping and characterized by spectroscopic studies [34,35]. No additional experimental work on discrete silanediimines has been reported since, although computational studies of the parent molecule have [36,37].

### 2. Computational methods

Geometry optimizations based on previously described protocols [38,39] were carried out for alicyclic silanediimines of ring sizes five through twelve without symmetry constraints ( $\text{C}_1$ ). An MP2/6-31G(d,p)//MP2/6-31G(d,p) [40–43] protocol was employed

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almost entirely throughout, although a restricted Hartree–Fock correlation consistent polarized valence triple zeta basis (RHF/cc-pVTZ) [44] protocol helped to characterize the twelve-membered ring as described later. When examination of a  $C_1$  optimized structures suggested higher symmetry, further computations were conducted using appropriate symmetry constraints. Harmonic frequency calculations were carried out using standard techniques on the optimized structures [45]. All reported species are local minima (no imaginary frequency) or transition states (TS) (one imaginary frequency) as indicated. The energies reported or referred to are ZPE-corrected. The transition states found were connected to their corresponding minima by following the reaction coordinate partway in both directions using intrinsic reaction coordinate (IRC) methodology [46–49]. Typically fifteen points in each direction were calculated with a small step size. Minima were computed subsequently by taking the IRC structures obtained after fifteen points and performing full geometry optimizations. All computations were carried out using the GAMESS suite of programs (1 May 2012 and 1 May 2013) [50] with MacMolPlot [51] visualization of the molecular structures. The convergence tolerance in GAMESS typically was increased 10-fold beyond the default (to OPTTOL =  $10^{-5}$ ) for the reported species. Two different dihedral angles are discussed subsequently. One is simply called the dihedral angle generally and represents the bold, underlined atoms (**C–N–Si–N–C**). The other is generally called the vicinal dihedral angle and is meant to represent **H–C–C–H**.

Molecular mechanics (MM) studies of the ten-membered ring were carried out to explore its potential energy surface more widely. Beginning from the  $C_1$  ten-membered silanediimine ring structure with a dihedral angle of  $0^\circ$ , the Merck Molecular Force Field (MMFF94) [52] was employed to study the ten-membered ring system in detail. Various structures found were subsequently submitted to geometry optimization. Details are presented in the following section describing the ten-membered ring.

### 3. Results and discussion

In focusing on locating a series of cis alicyclic silanediimine transition states (TS)<sup>1</sup> and studying their fates along the intrinsic reaction coordinate (IRC), this computational study compares the results found for such silanediimines with their corresponding carbon analogs, the carbodiimides [33]. The carbodiimide studies provide a guide in evaluating silanediimine behavior under similar study conditions. Many similarities are shown to exist between the silicon and carbon analogs.

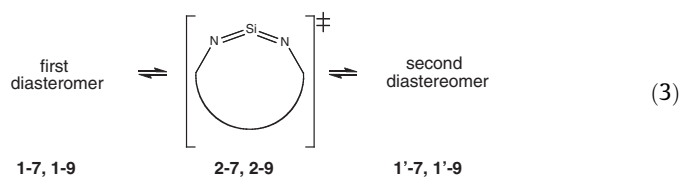
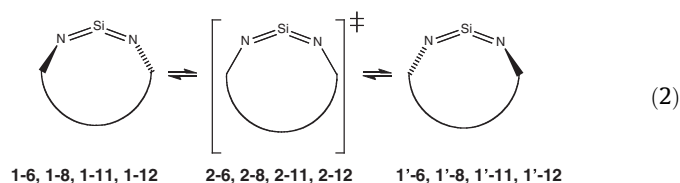
A regular pattern from ring size six through eleven in the alicyclic carbodiimides revealed that the transition states of the even rings had  $C_s$  symmetry and consequently transformed along the IRC pathways to enantiomeric pairs, whereas the odd size rings were  $C_2$  and transformed to diastereomeric pairs [33]. Ring size twelve did not extend this pattern; only a  $C_1$  transition state could be located. Thus, carbodiimide rings six, eight, and ten led to enantiomeric products, while rings seven, nine and eleven gave diastereomeric products. The barriers computed from the enantiomers to their corresponding transition states made it clear that optical isomers would not be stable under ordinary conditions.

<sup>1</sup> The six ( $C_s$ ), seven ( $C_2$ ), eight ( $C_s$ ), and nine ( $C_1$ ) transition states and their resulting minima are typically used in comparisons because their properties most closely resemble their carbodiimide counterparts in structure and symmetry terms. Ring size eleven is quite different as mentioned in the text and has not been used in comparisons. In general, the studies on ring size twelve, being slightly convoluted by the dependence on the electronic structure method used as discussed in the text, are not used in comparisons.

Similar patterns are manifested in the silanediimines with the transition states of the six, seven, eight, and twelve silanediimine rings following the carbodiimide patterns (even rings,  $C_s$ : odd ring,  $C_2$ ). The nine-ring silanediimine, although only found as its  $C_1$  transition structure, has similar characteristics to the  $C_2$  nine-membered carbodiimide. The ten and eleven silanediimine rings differ from the alicyclic carbodiimide structures found. No transition state could be located for the ten-ring despite considerable searching efforts. Only a  $C_s$  transition state was found for the eleven-ring, but it is incompatible with barrier expectations for silanediimine structures discussed below and with the structural features of the eleven-ring carbodiimide transition state.

The silanediimines  $C_s$  transition state structures exhibit an imaginary normal mode that transforms as the antisymmetric irreducible representation ( $A''$ ) of the symmetry point group (shown for ring-eight later), while the  $C_2$  structure exhibits an imaginary normal mode of motion that preserves the symmetry of the molecule or, in other words, transforms in the totally symmetric irreducible representation ( $A$ ) of the group (shown for ring-seven later). Thus, those silanediimine transition states exhibiting an antisymmetric normal mode ( $A''$ ) follow IRC torsional motions in opposing directions to enantiomeric products. The barriers in these cases are low suggesting that optical resolutions of enantiomers in such systems is impossible. The transition state with a totally symmetric normal mode ( $A$ ) leads to a diastereomeric pair along opposing IRC paths.

In what follows, all enantiomeric and diastereomeric products are designated as either **1-X** or **1'-X** with X referring to the ring size and the prime simply distinguishing the second isomer found along opposing IRC paths in each case. The transition states are designated as **2-X** in a similar way (Eqs. (2) and (3)). When higher energy structures are discussed, an asterisk is used (e.g. **1-X\***, **1'-X\***, or **2-X\***). Details are considered in the following sections organized by ring size. Separate sections that compare silanediimine barriers and various structural features as a function of size also follow.



#### 3.1. Five-membered ring

Geometry optimization of the planar, five-membered silanediimine (**3**) yields a ring opened silylene (**4**),  $(CH_2=N)_2Si$ : (Eq. (4)) with a dihedral angle of  $\sim 82^\circ$ . The bold, underlined atoms **C–N–Si–N–C** define what is called the dihedral angle throughout in distinction to the vicinal **H–C–C–H** dihedral angle discussed later and described as the vicinal dihedral angle. In contrast, the five-membered carbodiimide ring structure is a minimum on the potential energy surface and is potentially isolable despite its small size [33]. The expectation that the dihedral angle will be  $90^\circ$  ( $sp^2-sp-sp^2$ ) in  $RN=El=NR'$  species ( $El = Si$  or  $C$ ) cannot be realized either for the five-membered

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