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ORIGINAL PAPER

Silabenzene through divalent precursors at theoretical levels

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Abstract Based on geometries and relative energies, three different mechanisms are proposed for the rearrangements of five isomers of silacyclohexadienylidenes to silabenzene at B3LYP and MP2 levels: (1) [1,2]-hydrogen migration through a planar transition state, (2) [1,4]-hydrogen migration through a boat transition state, and (3) zip-zap mechanism, comprised of three successive [1,2]-hydrogen migrations. The above results are compared and contrasted to rearrangements of the corresponding cyclohexadienylidenes to benzene.

Keywords Ab initio · DFT · Hydrogen migration · Silabenzene · Zip-zap mechanism

Introduction

Silaethylenes and their related silylene isomers have been under both experimental and theoretical investigations since the synthesis research directed by Chapman in late 1976 [1–18]. In 1979, Schaefer suggested that the [1,2]-hydrogen migration connects silaethylene with both methylsilylene and silylmethylene [19]. The rearrangement between such isomers can also be considered for silabenzene (**1**), one of the most important aromatic rings in organometallic chemistry, which Barton and Burns [20] reported the first unambiguous evidence for its existence in 1978. Schlegel predicted the structure of **1** at the SCF STO-3G level in the same year [21]. A year later, Blustin used an adaptation of Frost's floating spherical Gaussian orbital (FSGO) model to calculate the geometric structure of this compound [22]. In 1983, Chanderasekhar et al. [23] reported 3-21G* calculations on **1** and several of its isomers and determined their relative stabilities and aromaticity. These calculations showed silylene isomers, silacyclohexa-2,4-dienylidene (**2**) and silacyclohexa-2,5-dienylidene (**3**), lie 84–105 kJ mol^{-1} higher in energy than **1**. Based on these relative energies, it is predicted that **1** might be obtained by hydrogen migration from suitable precursors **2** or **3**. Now, one may ask: to what extent is this preliminary prediction reliable? What are the possible mechanisms of such rearrangements? Can 2-silacyclohaxa-3,5-dienylidene (**4**) and 4-silacyclohaxa-2,5-dienylidene (**5**) also serve as suitable precursors for the preparation of **1** (Scheme 1)?

Hence, in the current research, the possibility of reaching at **1** through rearrangements of **2**–**5** is investigated at B3LYP/6-311++G**//B3LYP/6-31G* and MP4(SDTQ)/6-311+G*//MP2/6-31G* levels of theory. In the course of suggesting mechanisms for the above rearrangements, we will encounter other isomers of C_5SiH_6 including silafulvene (**6**), isosilabenzene (**7**), and 4-silacyclohexa-2,4-dienylidene (**8**). The obtained results are compared and contrasted to the formation of benzene (**9**) from the corresponding C_6H_6 divalent isomers, i.e., cyclohexa-2,4-dienylidene (**10**) and cyclohexa-2,5-dienylidene (**11**) (Scheme 1).

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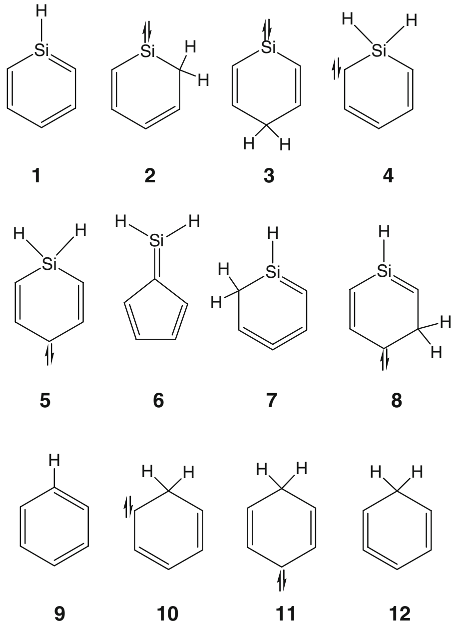


Scheme 1

Results and discussion

Considering the great interest in silabenzene (**1**) and its similarities to benzene, we examined the possibility of reaching at **1** through rearrangements of silacyclohaxa-2,4-dienylidene (**2**), silacyclohaxa-2,5-dienylidene (**3**), 2-silacyclohaxa-3,5-dienylidene (**4**), and 4-silacyclohaxa-3,5-dienylidene (**5**) (Scheme 1). Our calculated data at B3LYP/6-311++G**//B3LYP/6-31G* and MP4(SDTQ)/6-311+G*//MP2/6-31G* levels appear consistent, so our discussion is restricted to the single point calculations at B3LYP/6-311++G**//B3LYP/6-31G*. All the optimized structures are depicted (Fig. 1), and the representative transition states (TSs) are summarized in the supporting information.

Relative energies

The planar and aromatic form **1** is the most stable C_5SiH_6 isomer on its potential energy surface [23, 24] (Scheme 2). Isomers **2** and **3** are computed to be 102.3 and 114.1 kJ mol^{-1} higher in energy than **1**, respectively. These values confirm the 84–105 kJ mol^{-1} range defined by Chanderasekhar et al. [23] at the 3–21G* level. Employing more advanced methods, **2** is calculated to be 11.76 kJ mol^{-1} more stable than **3**, which is possibly related to the higher π delocalization in the former. Among **1**–**5**, the two least stable isomers are singlet silylcarbenes **4** and **5** (Scheme 2). This is consistent with the $CSiH_4$ system, where silylcarbene is much less stable than either methylsilylene or silaethylene [22, 25–32]. Interestingly, the energy gap between benzene (**9**) and its carbene isomers **10** and **11** (359.70 and 367.90 kJ mol^{-1}, respectively) is about four times larger than the corresponding gap between silabenzene (**1**) and its silylene isomers **2** and **3** with 102.30 and 114.10 kJ mol^{-1}, respectively (Scheme 2).

The possible mechanisms

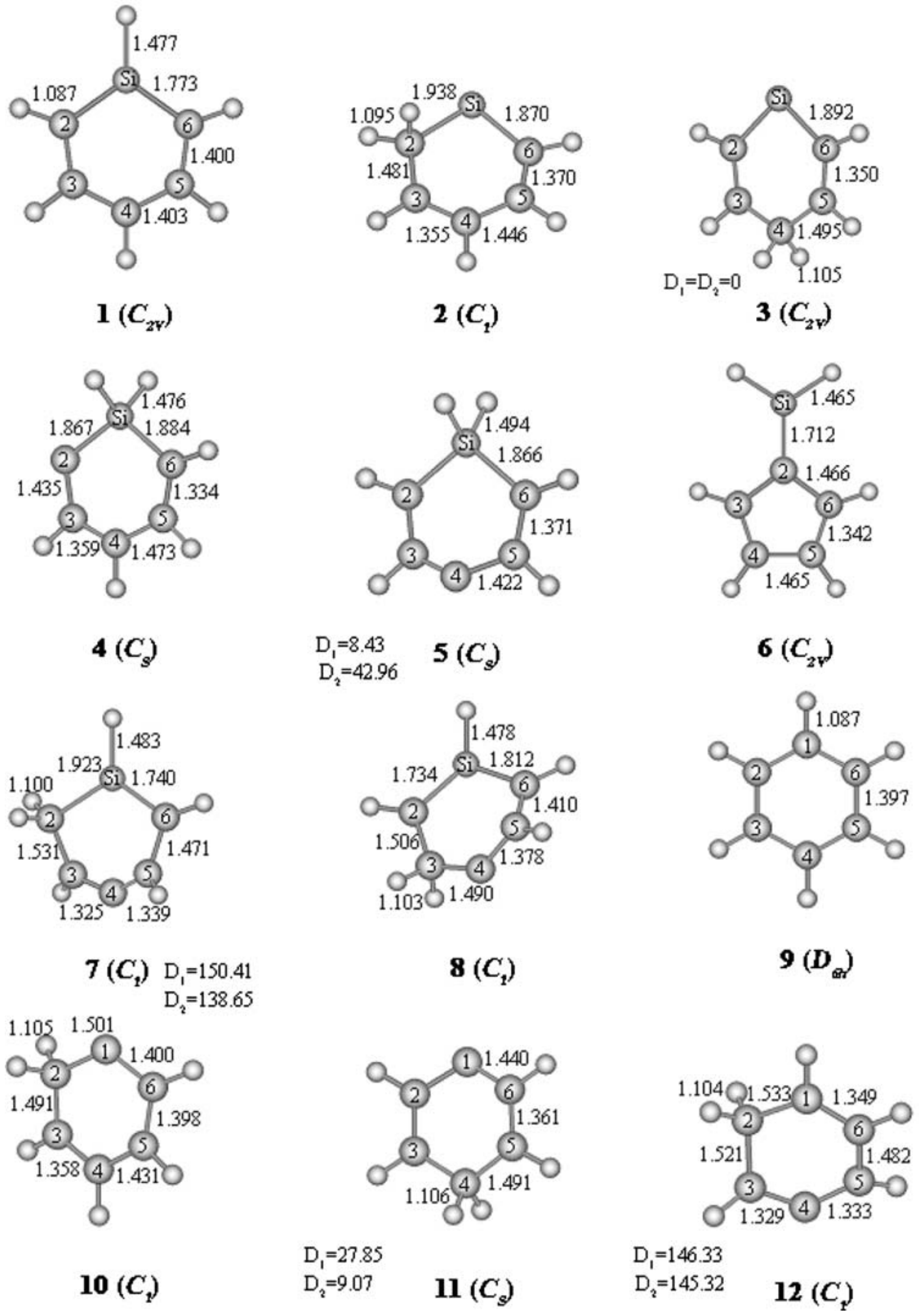
Firstly, we examine the rearrangements of **2** and **3** to **1**, originally suggested by Chandrasekhar et al. [23]. Rearrangement of **2** → **1** is a one step [1,2]-hydrogen migration, passing through a nonplanar transition state, with a 66.65 kJ mol^{-1} energy barrier (Fig. 2). In contrast, the rearrangement of **3** → **1** appears to occur through space, with a one-step [1,4]-hydrogen migration, which requires a boat transition state. Since the initial structure of **3** is planar, changing both dihedrals of the molecule from 0° to 69.50° and 51.18° requires a large energy barrier (169.03 kJ mol^{-1}) (Fig. 1).

The rearrangement of **4** → **1** through [1,2]-hydrogen migration requires only 13.47 kJ mol^{-1} activation energy (Fig. 3). This energy barrier is 53.18 kJ mol^{-1} less than the corresponding barrier for analogous **2** (Fig. 2). This difference is related to the strength of the C–H bond that is going to be formed and the weakness of the Si–H bond that is breaking for **4** → **1** and the reversed process for **2** → **1** [23]. In other words, the Si–H bond (with a typical length of 1.480 Å and bond energy of 410 kJ mol^{-1}) is 0.390 Å longer than C–H bond (with a typical length of 1.090 Å and bond energy of 393 kJ mol^{-1}). However, it should be mentioned that **1** is the thermodynamic product that results from [1,2]-hydrogen migration in **4**, while silafulvene (**6**) with relative energy of 94.85 kJ mol^{-1} is the kinetic product obtained from migration of the dienyl group through a lower energy barrier of 1.21 kJ mol^{-1} (Fig. 3). This result confirms the experimental report of Sekiguchi and Ando [33].

On the other hand, the rearrangement of **5** → **1** proceeds via a [1,4]-hydrogen migration, through space, which has 89.12 kJ mol^{-1} energy barrier (Fig. 4). This is 79.91 kJ mol^{-1} less than the corresponding energy barrier for **3** → **1** rearrangement due to the shallow boat form of **5** compared to the planar form of **3** (Fig. 2). Apparently, it is easier for **5** to reach at the boat transition state, as the dihedrals of **5** change from 8.43° to 48.00° and from 42.96° to 71.44° (Fig. 1). Another reason is the breakage of the longer and weaker Si–H bond in **5** compared to the breakage of rather stronger C–H bond in **3**. Now, it can be said that [1,2]-hydrogen migration for **5** is easier than **3**.

The interesting aspect of the **5** → **1** rearrangement is the alternative three [1,2]-hydrogen migration (zip-zap) where first step possesses a competitive energy barrier of

Fig. 1 The principle geometry parameters for eight isomers of C_5SiH_6 (**1**–**8**) and four isomers of C_6H_6 (**9**–**12**) calculated at B3LYP/6–311++G**//B3LYP/6-31G*, where in **3**, **5**, and **11**, dihedral angles D_1 and D_2 are representative of $C_6Si_1C_2C_3$ and $C_2C_3C_4C_5$, respectively, while in **7** and **12**, they represent $HC_3C_4C_5$ and $C_3C_4C_5H$, respectively



1 (C_{2v}) **2** (C_1) $D_1=D_2=0$ **3** (C_{2v})

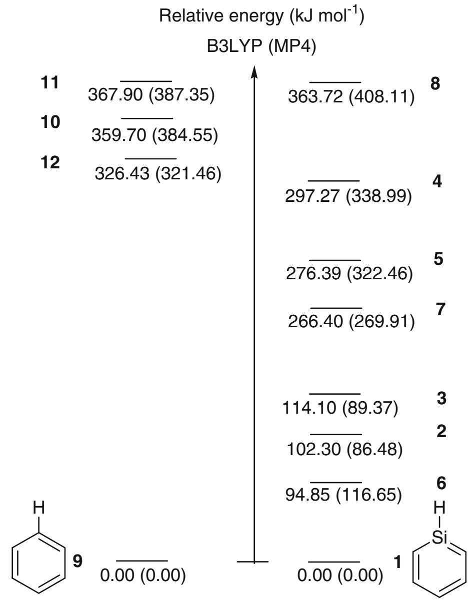
4 (C_s) $D_1=8.43$ $D_2=42.96$ **5** (C_s) **6** (C_{2v})

7 (C_1) $D_1=150.41$ $D_2=138.65$ **8** (C_1) **9** (D_{6h})

10 (C_1) $D_1=27.85$ $D_2=9.07$ **11** (C_s) $D_1=146.33$ $D_2=145.32$ **12** (C_1)

103.47 kJ mol^{-1} (Fig. 4). The first intermediate is named isosilabenzene (**7**) (with relative energy of 266.40 kJ mol^{-1}), a silicon analogue of isobenzene (**12**) [34], and the second one is 4-silacyclohexa-2,4-dienylidene (**8**) (with relative energy of 363.72 kJ mol^{-1}) in which the silicon atom is involved in a double bond. The second step, **7** → **8**, has a transition state lying 161.92 kJ mol^{-1} higher than **7**, while **8** readily rearranges to **1** as a barrier-free final step. Compared to the other C_5SiH_6 isomers discussed up to now, **8** turns out to be the least stable one (with relative energy of 369.28 kJ mol^{-1}) due to the substitution of a C=C double bond with a weaker Si=C one.

It is so fascinating to compare the mechanism of the rearrangements of carbene isomers of the parent C_6H_6 formula to the renowned stable aromatic benzene ring (**9**). Similar to those mentioned for **2** → **1** and **4** → **1**, the rearrangement of **10** → **9** is a [1,2]-hydrogen migration with only 0.75 kJ mol^{-1} energy barrier (Fig. 5). Again, the rearrangement of **11** → **9** exhibits two distinct mechanisms similar to **5** → **1**, but different in energy barriers. The first



Scheme 2

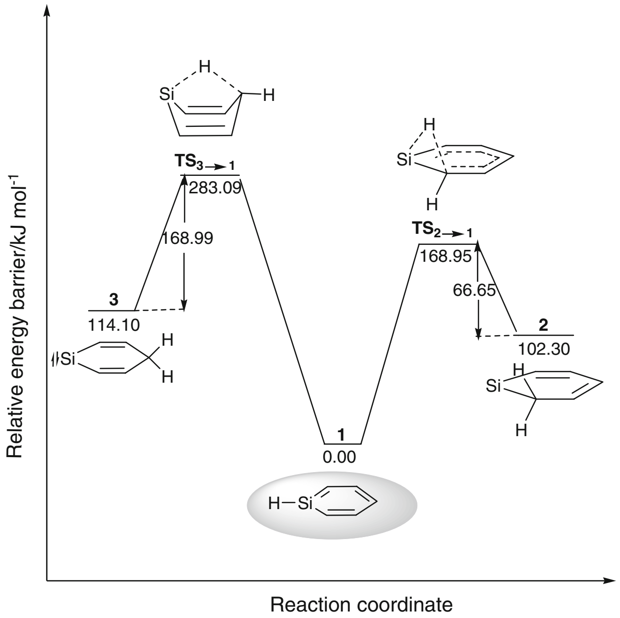


Fig. 2 The schematic energy diagram for **3** → **1** and **2** → **1** rearrangement pathways at B3LYP/6-311++G**//B3LYP/6-31G* level of theory

mechanism is a [1,4]-hydrogen migration through space, and the second one is the zip-zap mechanism through isobenzene intermediate with 159.16 and 76.73 kJ mol^{-1} energy barriers (Fig. 5). Therefore, the preference for the zip-zap mechanism in **11** → **9** is in a clear contrast to the competitive nature of the two pathways in **5** → **1**. The higher energy barrier for [1,4]-hydrogen migration is due to the great distortion imposed on the molecule in going from **11** to the corresponding boat transition state. The dihedrals of **11** should be changed from 9.07° to 59.61° and from 27.85° to 72.97°, while there is not such a great distortion going from **11** to the isobenzene intermediate at the first step of the zip-zap mechanism (Fig. 1).

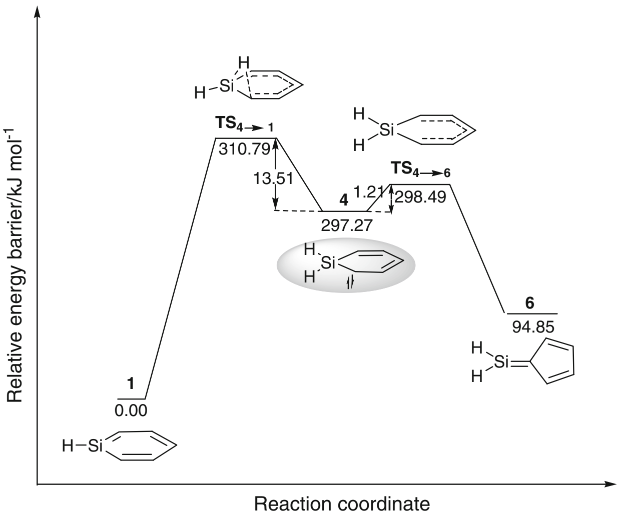


Fig. 3 The schematic energy diagram for **4** → **1** and **4** → **6** rearrangement pathways at B3LYP/6-311++G**//B3LYP/6-31G* level of theory

In summary, the **2** → **1** and **4** → **1** rearrangements proceed through [1,2]-hydrogen migrations, while our mechanism for **3** → **1** is a one-step [1,4]-hydrogen migration through space, after passing a boat TS. For the rearrangement of **5** → **1**, we propose two competitive mechanisms: [1,4]-hydrogen migration through space and the three [1,2]-hydrogen migrations, zip-zap mechanism ($\Delta E^{\ddagger} = 103.47$ vs. 89.12 kJ mol^{-1}, respectively). The carbene **11** also exhibits the two mechanisms, but prefers the zip-zap pathway over the [1,4]-hydrogen migration ($\Delta E^{\ddagger} = 76.73$ vs. 159.16 kJ mol^{-1}, respectively). Carbene analogues of **2**–**5** appear to rearrange to benzene through similar pathways. Finally, among **2**–**5**, based on both relative energies and energy barriers, we suggest **2** as the most suitable precursor for reaching at **1**.

Methods

The geometry optimizations are accomplished by means of ab initio and DFT calculations performed with the Gaussian98 code [35], MP2/6-31G* [36] and B3LYP/6-31G* [37, 38] levels of theory. The B3LYP hybrid functional includes a mixture of Hartree-Fock [39] exchange with DFT [40] exchange correlation, given by Becke's three-parameter functional [41] with the Lee, Yang, and Parr correlation functional, which includes both local and

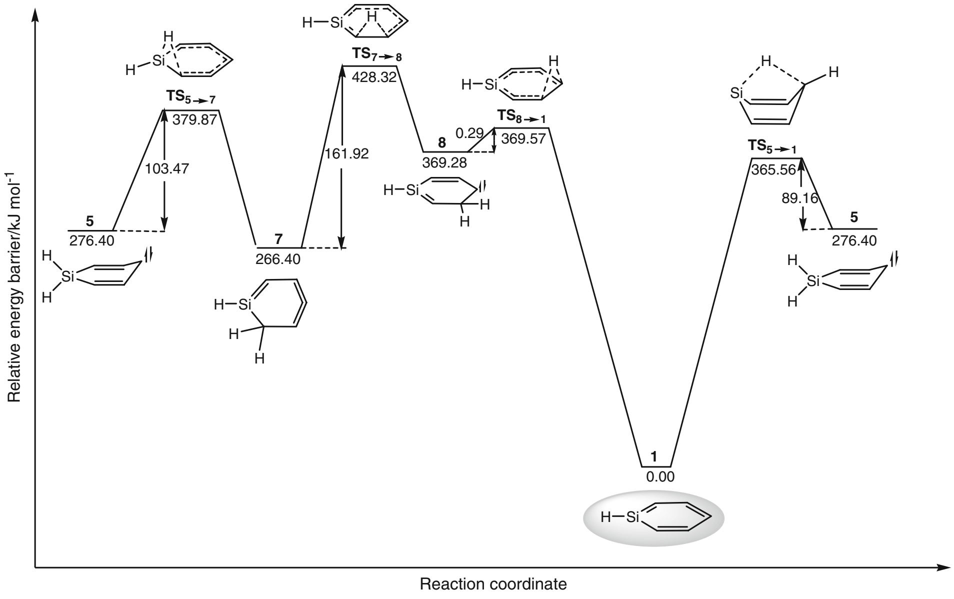


Fig. 4 The schematic energy diagram for **5** → **1** rearrangement pathways, [1,4]-hydrogen migration through space (*right*), and zip-zap mechanism (*left*) at the B3LYP/6-311++G**//B3LYP/6-31G* level of theory

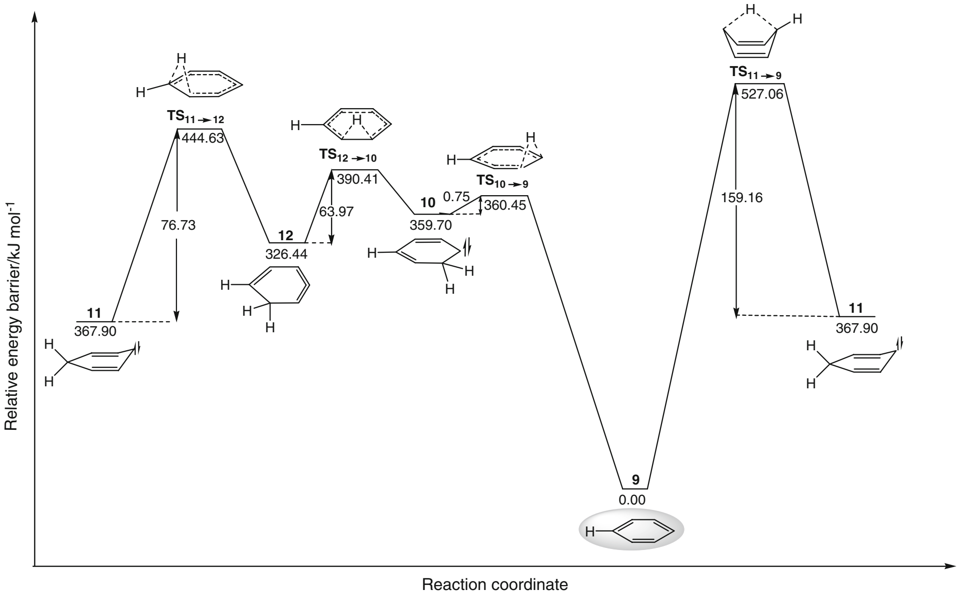


Fig. 5 The schematic energy diagram for **11** → **9** rearrangement pathways [1,4]-hydrogen migration through space (*right*), and zip-zap mechanism (*left*) at the B3LYP/6-311++G**//B3LYP/6-31G* level of theory

nonlocal terms [42, 43]. All the optimized geometries are the result of full optimizations without any symmetry constraints. The Pople's 6-31G* basis set [44] has been used for geometry optimization in the well-known Gn method developed by Curtiss and co-workers for highly accurate predictions of molecular energies [45]. Single-point calculations are performed at B3LYP/6-311++G**//B3LYP/6-31G*, and MP4(SDTQ)/6-311+G*//MP2/6-31G* levels of theory for more accurate energetic data. MP4(SDTQ) is applied to the MP2 optimized geometries as a high-level electron correlation method [46–48]. The TSs linking the initial and final structures are found using the reactants-products quasi-synchronous transit (QST2) algorithm [35]. The TSs are further characterized by vibrational analysis showing a single imaginary frequency at both levels of theory. Zero point vibrational energy (ZPVE) corrections are calculated at both levels [49].

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