

# **Syn-2,7-disilatetracyclo[6.2.1.1<sup>3,6</sup>0<sup>2,7</sup>]dodec-2(7)-ene: Structural Influence of Incorporation of Disilene into Sesquinorbornene Framework: A DFT Study**

Davor Margetić,\* Mario Vazdar, and Mirjana Eckert-Maksić

Laboratory for Physical Organic Chemistry,  
Department of Organic Chemistry and Biochemistry,  
Ruđer Bošković Institute, Bijenička c. 54, 10000 Zagreb, POB 180, Croatia

Received xxx; Preprint published xxx; Accepted xxx ; Published xxx

---

*Internet Electron. J. Mol. Des.* 2003, 1, 000–000

**Abstract.** Quantum chemical calculations of disilene bridge incorporated in sesquinorbornene skeleton using density functional theory at the B3LYP/6-31G\* level are reported. Calculated structures of *syn*- and *anti*-derivatives of disilasesquinorbornenes showed significant non-planarity and asymmetry of the central Si=Si double bond. The influence of the replacement of the carbon atoms by silicon on molecular and electronic structure of these molecules has been investigated.

**Method.** All geometry optimizations were carried out with the *Gaussian 98* suite of programs<sup>26</sup> employing the density functional theory (DFT) hybrid B3LYP method using 6-31G\* basis set.<sup>27,28</sup> The natures of the stationary points were characterized by the vibrational frequency calculations. Bonding characteristics of the calculated molecules were analysed using NBO hyperconjugative interaction parameters.<sup>29</sup> All calculations were conducted on the dual Athlon MP and Pentium III personal computers under the Linux Redhat 8.0 operating system.

**Introduction.** Extensive literature evidence shows that norbornenes (bicyclo[2.2.1]hept-2-enes) possess pyramidalized terminal olefinic carbon atoms with hydrogens bent towards the *endo*-direction.<sup>1-3</sup> The *syn*-sesquinorbornenes exhibits almost twice as much bending of the central  $\pi$ -bond.<sup>4</sup> There are several theoretical papers dealing with pyramidalization in sesquinorbornenes and related polycyclic systems.<sup>5</sup> While all-carbon sesquinorbornenes are studied in detail, both experimentally and theoretically, hetero-sesquinorbornenes have not attracted so much attention.<sup>6-9</sup> All of the studies published so far are dealing with replacement of carbon bridge (C<sub>11</sub> and C<sub>12</sub>) with heteroatoms, while molecular and electronic structures of sesquinorbornenes possessing heteroatoms at the central double bonds have not been investigated so far.

Molecular structure of disilenes exhibits some very interesting features. It is known

---

\* Correspondence author; phone: 385-1-4561-008; fax: 385-1-4680-195; E-mail: margetid@emma.irb.hr

experimentally that double bonds in disilenes and digermenes ( $R_2M=MR_2$ ,  $M=Si, Ge$ )<sup>10-13</sup> are not planar ( $\Psi > 0^\circ$ ) and that there is a twist ( $\tau$ ) in the structure, in which two organometallic atoms are pyramidalized in *anti*- fashion (Chart 1).<sup>14,15</sup> It was also shown, both experimentally<sup>16-18</sup> and theoretically<sup>19-23</sup> that the degree of disilene bond bending strongly depends on the nature of substituents. In this regard, it should be noted that carbon substituted disilenes generally adopt *trans*- bent structures with  $C_{2h}$  symmetry (planar structure of disilene has  $D_{2h}$  symmetry).<sup>24</sup> Tetraalkyl disilenes revealed some degree of *trans*- pyramidalization. Furthermore, a slight twisting of the double bond by the angle  $\tau$  may also occur in order to reduce steric overcrowding. The observed disilene bond deviations is attributed to hyperconjugative interactions between the  $Si=Si$   $\pi$  bond and  $\sigma$  orbitals of the appropriate symmetry on the substituents. Kira and co-workers assumed that electronic effects play an important role in defining digermene structures.<sup>25</sup>

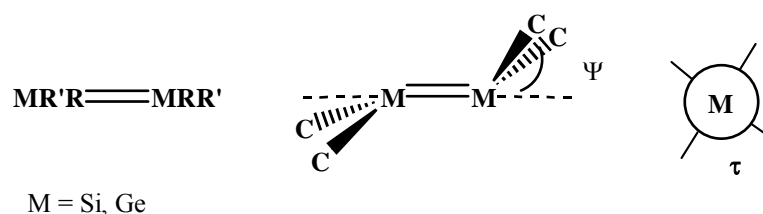


Chart 1.

The replacement of the olefinic carbon atoms in sesquinorbornene with the IVA group elements on the extent of double bond bending, has not been considered so far. The aim of this computational study is to determine molecular and electronic structure of disilene embedded in sesquinorbornene skeleton (Chart 2). Both *syn*-2,7-disilatetracyclo [6.2.1.1<sup>3,6</sup>0<sup>2,7</sup>]dodec-2(7)-ene (**1**) and *anti*-2,7-disilatetracyclo[6.2.1.1<sup>3,6</sup>0<sup>2,7</sup>]dodec-2(7)-ene (**2**) systems are studied and effects on the molecule examined. It was expected that rigid and strained norbornene skeleton influences the flexibility of disilene bending, favoring *syn*-fashion.

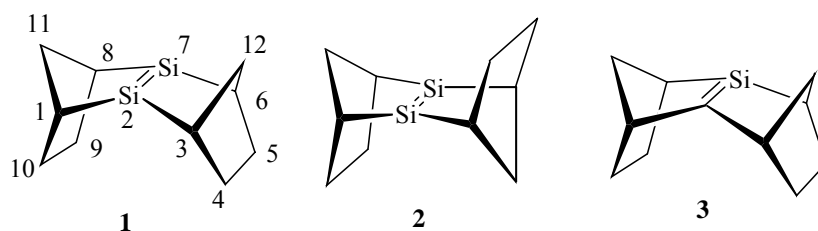
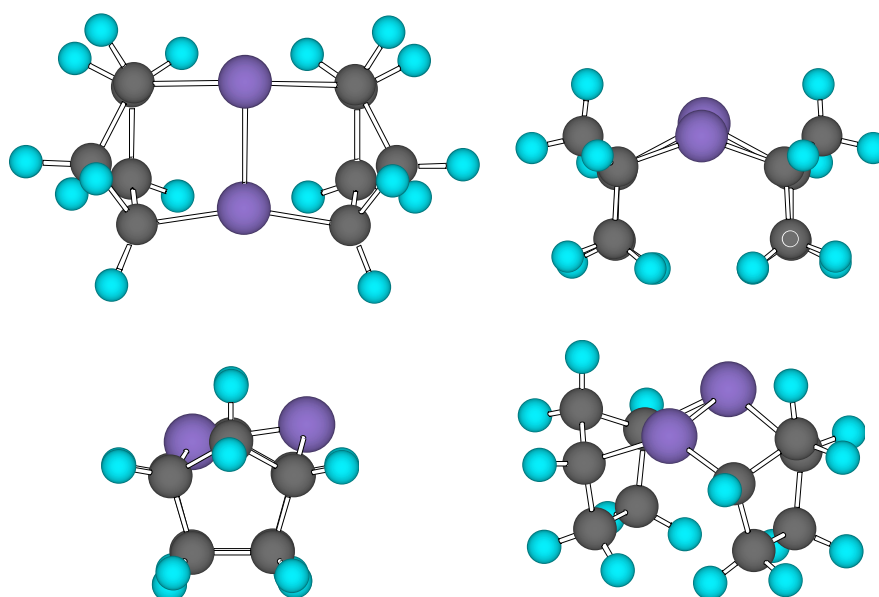


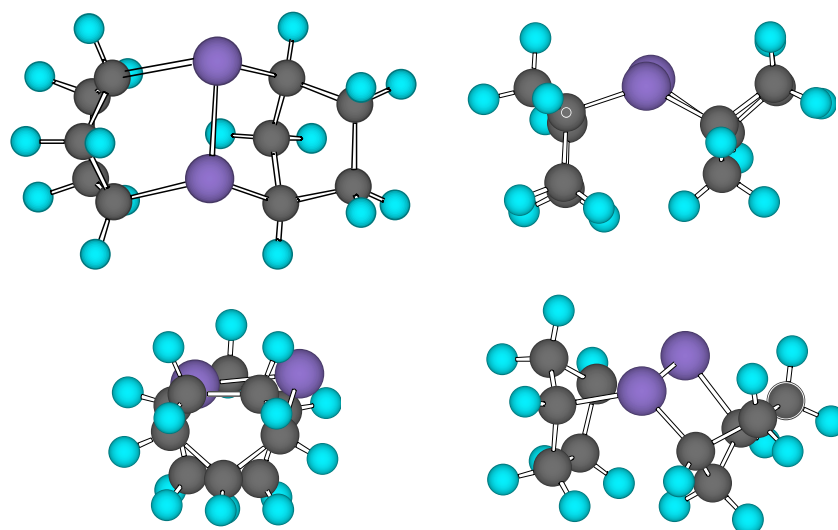
Chart 2.

**Results and discussion.** The B3LYP/6-31G\* optimized geometries of molecules **1-3** are

shown in Figures 1-3. Their total energies and selected geometrical parameters are collected in Table 1, while Table 2 lists orbital interaction parameters.



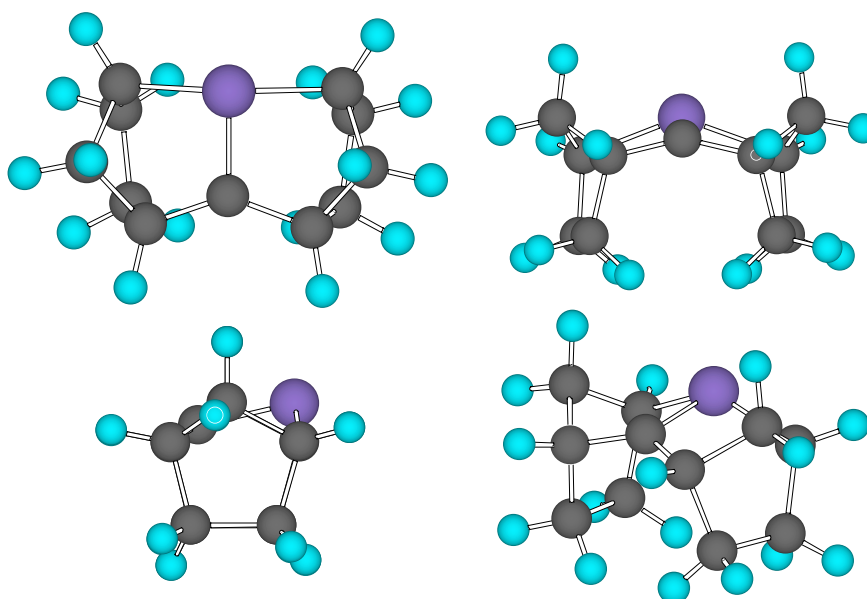
**Figure 1.** B3LYP optimized structure of **1**



**Figure 2.** B3LYP optimized structure of **2**

**Molecular structure.** As depicted in Figures 1 and 2, structures of molecules **1** and **2** possess  $C_1$  symmetry, while *syn*- and *anti*- sesquiorbornenes have higher,  $C_{2v}$  and  $C_{2h}$  symmetry, respectively. Remarkable large butterfly bending values were found in structures **1** and **2**:  $36.1^\circ$  and

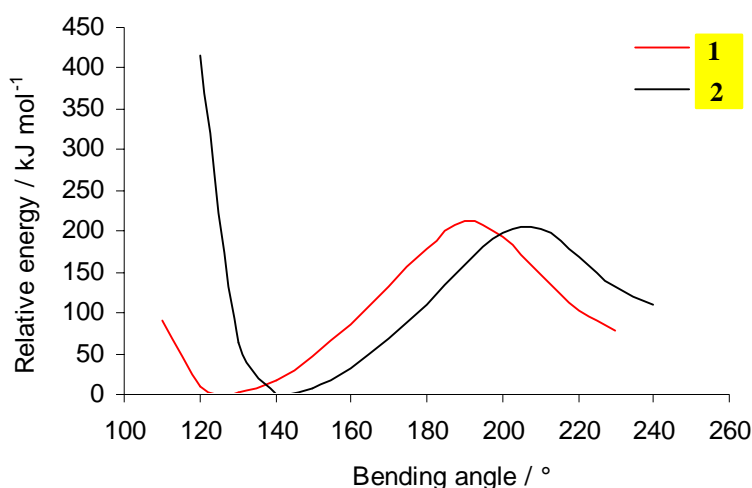
54.3° around Si<sub>2</sub> and Si<sub>7</sub> atoms in molecule **1**, while for molecule **2** corresponding values are 44.7° and 54.0° (Table 1).<sup>30</sup> There are only a few examples of comparably large pyramidalized sesquinorbornenes reported in literature.<sup>31</sup> However, the computed extent of butterfly bending in molecules **1** and **2** is much larger than the most pyramidalized disilene reported so far (tetramesityl disilene  $\Psi=13.0^\circ$ ).<sup>17</sup> Similar large extent of butterfly bending was found for related molecule **3** (Figure 3), where silene is incorporated in sesquinorbornene moiety ( $\Psi_2=41.1^\circ$ ). The butterfly bending around the carbon atom is of similar value to these previously found for *syn*-sesquinorbornenes ( $\Psi_1=16.5^\circ$ ).



**Figure 3.** B3LYP optimized structure of **3**

Other important structural features include twisting angle, C-Si-C angles and the length of the central double bond. Both structures, due to geometrical constraints imposed by sesquinorbornene skeleton show minimal twisting angle ( $\tau$ ) between two silicon atoms. Furthermore, calculated C-Si-C angles for molecules **1-3** are significantly larger than experimental ones (the range is 112.5–116.8°). The B3LYP calculated length of Si<sub>2</sub>=Si<sub>7</sub> central double bond in **1** and **2** is 2.244 and 2.280 Å, respectively. These lengths are within the range of experimentally measured values for various disilenes (2.143–2.260 Å). Comparison of the calculated structures with that of corresponding disilanorbornene, *i.e.* 2,3 disilatricyclo[2.2.1]hept-2-ene, revealed similar geometrical features around the Si=Si bond and double bond hydrogen trans- twisting.

**Energetics.** Calculations revealed that *syn*- **1** is by 2.86 kJmol<sup>-1</sup> energetically more stable than *anti*- **2**. Energy comparison showed significantly smaller energy difference between two isomers than previously calculated for *syn/anti*- dioxas and *syn/anti*- sesquinorbornene pairs, (6.1 and 10.7 kJmol<sup>-1</sup>, respectively).<sup>32</sup> This difference may be associated with the fact that *anti*-sesquinorbornene and *anti*-dioxasesquinorbornene have planar structures, while their *syn*-counterparts are pyramidalized.



**Figure 4.** Torsional energy surfaces for compounds **1** and **2**

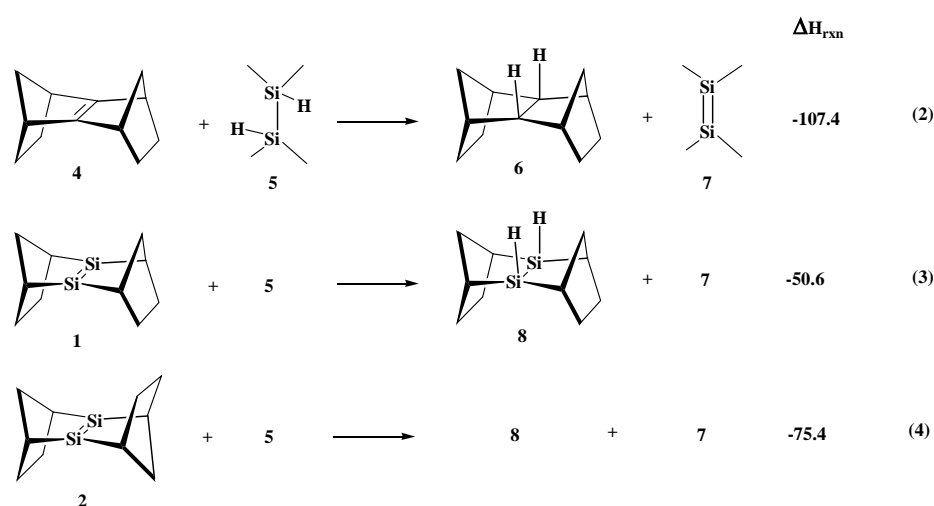
Torsional energy surfaces for compounds **1** and **2** (Figure 4) were obtained by single-point energy estimation at each point of the scan (with 10 degrees increment, going from *endo*- to *exo*-bending). Both structures possess energy minima with the butterfly bending towards *endo*- face of the norbornene skeleton and a structure with energy maximum for ( $\psi=190^\circ$  and  $200^\circ$ , respectively).<sup>33</sup>

Furthermore, olefin strain energies (OSE) for molecules **1** and **2** were calculated as a difference between the energy of hydrogenation of the alkene and the heat of hydrogenation of the corresponding unstrained alkene (Eq. 1).<sup>34,35</sup>

$$\text{OSE} = \Delta H_{\text{hydrog}}(\text{strained alkene}) - \Delta H_{\text{hydrog}}(\text{unstrained alkene}) \quad (1)$$

Firstly, we have calculated the relative OSE of *syn*-sesquinorbornene, as compared with 2,3-dimethyl-2-butene as an reference alkene, using equation 2 (Scheme 1). Relative OSE of molecules **1** and **2** were obtained according to equations (3) and (4). For a comparison with silicon systems, we have chosen tetramethyldisilene as reference disilene. Relative OSE of *syn*-sesquinorbornene

and molecules **1** and **2** were recalculated using Equations 2-4. Calculations at B3LYP/6-31G\* level indicate that *anti*- isomer **2** has larger OSE than **1** by 49.8 kJ/mol. A comparison made with *syn*-sesquinorbornene **4** showed that this molecule is much more strained and its calculated OSE is 107.4 kJ/mol, which is by 56.8 kJ/mol larger than the corresponding value for **1**. This difference may be attributed solely to strain relief obtained by elongation of C-Si bonds and further distortion of molecule **1**.



Scheme 1

**Electronic structure.** The energy levels of the  $\sigma$ -bonds of disilenes are raised by the ring strain. Accordingly, the stereoelectronic interactions between the strained CC  $\sigma$  bonds and the SiSi  $\pi$  bond become effective.<sup>36</sup> The UV/VIS absorption maximum of the  $\pi$ - $\pi^*$  transition in strained disilenes is 493 nm. This indicates that the transition is red-shifted relative to the typical values for tetraalkyl disilenes (400-470 nm).<sup>37</sup> This remarkable shift is mainly due to the lengthening and twisting of the central double bond. Stereo-electronic interactions are also important, which were successfully revealed by theoretical calculations. Calculations at the RHF/6-31G\*\*/B3LYP/6-31G\* level have shown that frontier orbital energies for **1** are -6.82 and 0.84 eV, whereas for *anti*- isomer **2** the corresponding values are -7.24 and 0.89 eV, respectively.<sup>38</sup> HOMO of *syn*-disilasesquinorbornene **1** has electron density mainly located on silicon atom Si<sub>7</sub>, with considerable contribution of  $\sigma$ -orbitals associated with the C<sub>5</sub>C<sub>6</sub> and C<sub>8</sub>C<sub>9</sub> bonds (Figure 5). On the contrary, LUMO has electron density mainly located on silicon Si<sub>6</sub>, and substantial contributions from the  $\sigma$  hyperconjugative interactions with  $\sigma$ -orbitals of the C<sub>3</sub>C<sub>4</sub> and C<sub>1</sub>C<sub>10</sub> bonds. Figure 6 depicts FMO of *anti*- isomer **2**. Here, in both orbitals depicted, the electron density is mainly localized on Si<sub>7</sub>. Difference in FMO gap between **1** and **2** is reflected in their calculated  $\pi$ - $\pi^*$  transitions. For molecule **1**  $\pi$ - $\pi^*$  transition wavelength was calculated by using the TDDFT method<sup>39</sup> to be 576.5 nm, while for *anti*- isomer **2** the value of 587.9 nm was obtained.

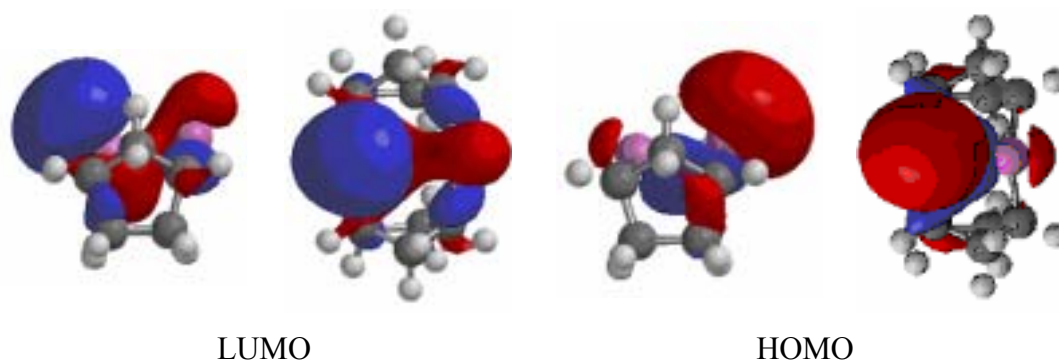


Figure 5. FMOs of molecule 1

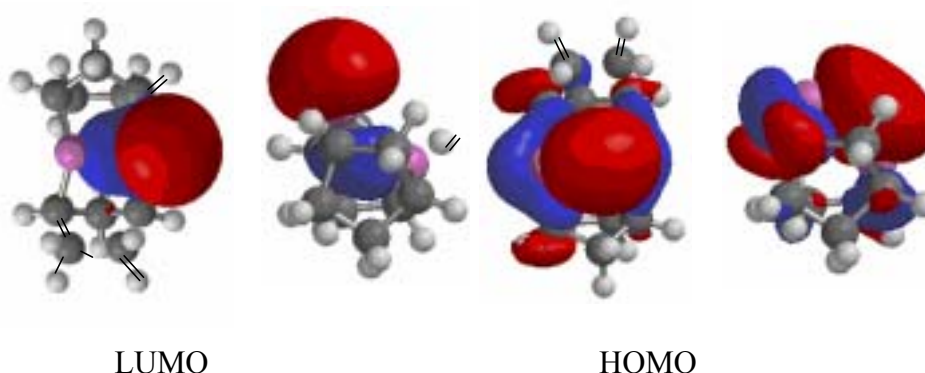


Figure 6. FMOs of molecule 2

Tables 2-4 list NBO interaction parameters for the studied molecules. An inspection of these results shows that  $\pi \rightarrow \sigma^*$  hyperconjugative interactions in the series of molecules studied are almost absent. This result is in contrast with previous calculations showing that  $\pi(\text{C}_2\text{C}_7) \rightarrow \sigma^*(\text{C}_5\text{C}_6)$  and  $\pi(\text{C}_2\text{C}_7) \rightarrow \sigma^*(\text{C}_6\text{C}_{12})$  interactions are dominant in *syn*-sesquinorbornene and *syn*-dioxasesquinorbornene.<sup>40</sup> Calculations indicate that elongation of the  $\text{Si}_2\text{Si}_7$  and  $\text{C}_1\text{Si}_2$  bonds greatly diminishes these interactions in molecules **1** and **2**. Instead, interactions of double bond with bridge hydrogen  $\sigma$  bonds, ( $\pi(\text{Si}_2\text{Si}_7) \rightarrow \sigma^*(\text{C}_6\text{H}_6)$ ) are much larger. The strongest interactions are calculated to be these of  $\sigma$  bonds with LP of silicon atom:  $\sigma(\text{C}_6\text{Si}_7) \rightarrow \text{LP}^*(\text{Si}_2)$  and  $\sigma(\text{Si}_2\text{C}_3) \rightarrow \sigma^*(\text{C}_1\text{Si}_2)$  interactions. Furthermore,  $\pi \rightarrow \sigma^*$  interactions of the central double bond with bridgehead hydrogens has been detected  $\pi(\text{Si}_2\text{Si}_7) \rightarrow \sigma^*(\text{C}_{11}\text{H}_{11\text{out}})$ . Interactions of identical nature and of similar extent were found also in a hypothetical molecule **1symm** with forced  $\text{C}_s$  symmetry having C-Si and Si=Si bonds lengths constrained to 2.060 Å and 2.240 Å, respectively, and pyramidalization angle

constrained to 15°. This fact indicates that replacement of the C=C bridge with the Si=Si bond causes significant changes in the nature of the orbital interactions within a molecule. Further insight into electronic structure of disilene **1** was obtained by analysing *syn*-sesquinorbornene molecule **1a**, obtained by using optimized geometry of **4**, where C=C atoms were replaced by Si=Si without optimization, thus forming disilene **1** possessing geometry of **4**. In both molecules, similar orbital interactions of comparable size were found. This result indicates that difference in orbital interactions between **1** and **4** are caused mainly by different geometries and bond elongation, rather than by replacement of carbon by silicon. Finally, for molecules **3** and **4** similar hyperconjugative interactions were found as expected, due to a greater similarity of these two structures.

**Chemical shifts.** Due to asymmetry of the considered molecules, two silicon atoms possess different  $^{29}\text{Si}$  NMR chemical shifts. The GIAO/B3LYP/6-31G\*// B3LYP/6-31G\* nuclear magnetic shielding tensors calculated for molecule **1** are estimated to be for Si<sub>2</sub> 188.5 and Si<sub>7</sub> -124.8 ppm, while in **2** Si<sub>2</sub> 260.1 and Si<sub>7</sub> -171.5 ppm. Corresponding  $\delta^{29}\text{Si}$  NMR values are 225.9 and 539.3 ppm for **1**, while 154.4 and 585.9 ppm for **2**, relative to TMS.  $\delta^{29}\text{Si}(\text{TMS})$  is calculated as 414.3 ppm.<sup>41</sup> For a comparison,  $\delta^{29}\text{Si}$  for Me<sub>2</sub>Si=SiMe<sub>2</sub> calculated at the same level of theory amounts 278.9 ppm. Obtained values indicate unusual magnetic environment around disilene bond in **1** and **2** as compared with available experimental data for distorted disilenes.<sup>42</sup>

**Table 1.** Selected B3LYP/6-31G\* geometrical parameters and total energies of molecules **1** - **3**

Distance / Å	<b>1</b>	<b>2</b>	<b>3</b>
M <sub>2</sub> Si <sub>7</sub>	2.244	2.280	1.778
C <sub>1</sub> M <sub>2</sub> /C <sub>3</sub> M <sub>2</sub>	1.909	1.905/1.907	1.500
C <sub>8</sub> Si <sub>7</sub> /C <sub>6</sub> Si <sub>7</sub>	2.075	2.103/2.068	1.969
C <sub>1</sub> C <sub>10</sub> /C <sub>3</sub> C <sub>4</sub>	1.561	1.560/1.553	1.576
C <sub>8</sub> C <sub>9</sub> /C <sub>5</sub> C <sub>6</sub>	1.552	1.549/1.558	1.559
C <sub>1</sub> C <sub>11</sub> /C <sub>3</sub> C <sub>12</sub>	1.546	1.550/1.558	1.555
C <sub>8</sub> C <sub>11</sub> /C <sub>6</sub> C <sub>12</sub>	1.555	1.543/1.554	1.553
C <sub>9</sub> C <sub>10</sub> /C <sub>4</sub> C <sub>5</sub>	1.558	1.560/1.566	1.556
Angle / °			
C <sub>1</sub> M <sub>2</sub> C <sub>3</sub>	131.8	123.2	133.9
C <sub>6</sub> Si <sub>7</sub> C <sub>8</sub>	121.5	112.5	138.9
C <sub>1</sub> M <sub>2</sub> Si <sub>7</sub> /C <sub>3</sub> M <sub>2</sub> Si <sub>7</sub>	105.9	107.8/108.3	111.6
C <sub>8</sub> Si <sub>7</sub> M <sub>2</sub> /C <sub>6</sub> Si <sub>7</sub> M <sub>2</sub>	78.7	75.3/73.6	88.1
C <sub>1</sub> C <sub>11</sub> C <sub>7</sub> /C <sub>3</sub> C <sub>6</sub> C <sub>12</sub>	100.5	99.5/100.0	98.9
Dihedral angle / °			
C <sub>1</sub> M <sub>2</sub> Si <sub>7</sub> C <sub>3</sub>	143.2	135.3	163.5
C <sub>6</sub> Si <sub>7</sub> M <sub>2</sub> C <sub>8</sub>	125.7	126.0	138.9



$C_6Si_7M_2C_8$	125.7	126.0	138.9
Butterfly bending /°			
$\Psi_1$	36.8	44.7	16.5
$\Psi_2$	54.3	54.0	41.1
$E_{tot}/a.u.$	-969.581825	-969.580735	-718.205661

**Table 2.** RHF/6-31G\*//B3LYP/6-31G\* NBO orbital interaction parameters for molecules **1** and **2**

<b>1</b>	<b>2</b>
$\pi(Si_2Si_7) \rightarrow \sigma^*(C_6H_6)$ (2.61)	$\pi(Si_2Si_7) \rightarrow \sigma^*(C_6H_6)$ (4.48)
$\pi(Si_2Si_7) \rightarrow \sigma^*(C_3H_3)$ (1.12)	$\pi(Si_2Si_7) \rightarrow \sigma^*(C_3H_3)$ (0.65)
	$\sigma(C_9H_{10}) \rightarrow \pi^*(Si_2Si_7)$ (0.61)
	$\sigma(C_3C_4) \rightarrow \pi^*(Si_2Si_7)$ (0.61)
	$\pi(Si_2Si_7) \rightarrow \sigma^*(C_8H_8)$ (2.34)
	$\pi(Si_2Si_7) \rightarrow \sigma^*(C_3H_3)$ (2.09)
	$\pi(Si_2Si_7) \rightarrow \sigma^*(C_9H_9)$ (0.69)
	$\pi(Si_2Si_7) \rightarrow \sigma^*(C_{10}H_{10})$ (0.65)
	$LP(Si_7) \rightarrow \sigma^*(C_8C_9)$ (2.82)
	$LP(Si_2) \rightarrow \sigma^*(C_1C_{10})$ (0.63)
	$LP(Si_7) \rightarrow \sigma^*(C_6C_{12})$ (4.33)
	$LP(Si_2) \rightarrow \sigma^*(C_3C_{12})$ (0.63)
$\pi(Si_2Si_7) \rightarrow \sigma^*(C_1Si_2)$ (9.57)	$\sigma^*(C_3C_{12}) \rightarrow LP^*(Si_2)$ (6.41)
$\pi(Si_2Si_7) \rightarrow \sigma^*(C_6Si_7)$ (5.12)	$LP(Si_2) \rightarrow \pi^*(Si_2Si_7)$ (4.70)
$LP^*(Si_2) \rightarrow \pi^*(Si_2Si_3)$ (4.54)	$\sigma(Si_7C_8) \rightarrow LP^*(Si_2)$ (36.88)
$\sigma(C_6Si_7) \rightarrow LP^*(Si_2)$ (27.81)	$\sigma(C_6Si_7) \rightarrow LP^*(Si_2)$ (29.33)
$\sigma(C_1Si_2) \rightarrow \sigma^*(Si_2C_3)$ (10.75)	$\pi(Si_2Si_7) \rightarrow \sigma^*(Si_2C_3)$ (12.70)
$\sigma(Si_2C_3) \rightarrow \sigma^*(C_1Si_2)$ (10.75)	$\pi(Si_2Si_7) \rightarrow \sigma^*(Si_2C_1)$ (13.81)
	$\sigma(Si_2C_3) \rightarrow \sigma^*(Si_2C_1)$ (10.59)
	$\sigma(Si_2C_{10}) \rightarrow \sigma^*(Si_2C_3)$ (10.18)
	$\pi(Si_2Si_7) \rightarrow \sigma^*(Si_7C_8)$ (5.86)
	$\pi(Si_2Si_7) \rightarrow \sigma^*(Si_7C_6)$ (3.88)
$\pi(Si_2Si_7) \rightarrow \sigma^*(C_{11}H_{11out})$ (2.48)	$\pi(Si_2Si_7) \rightarrow \sigma^*(C_{11}H_{11out})$ (2.12)
	$\sigma(Si_2C_3) \rightarrow \sigma^*(C_{12}H_{12out})$ (5.61)
	$\sigma(Si_2C_{10}) \rightarrow \sigma^*(C_{11}H_{11out})$ (6.21)

**Table 3.** RHF/6-31G\*//B3LYP/6-31G\* NBO orbital interaction parameters for molecules **1-symm** and **3**

<b>1-symm<sup>a</sup></b>	<b>3</b>
$\pi(Si_2Si_7) \rightarrow \sigma^*(C_5C_6)$ (2.04)	$\pi(C_2Si_7) \rightarrow \sigma^*(C_3C_4)$ (3.20)
$\pi(Si_2Si_7) \rightarrow \sigma^*(C_6H_6)$ (1.06)	$\pi(C_2Si_7) \rightarrow \sigma^*(C_3H_3)$ (3.55)
$\sigma(C_4H_4) \rightarrow \sigma^*(Si_2C_3)$ (4.46)	$\pi(C_2Si_7) \rightarrow \sigma^*(C_8C_9)$ (1.50)

$\sigma(\text{C}_1\text{C}_{11}) \rightarrow \sigma^*(\text{C}_8\text{H}_8)$ (4.07)	$\pi(\text{C}_2\text{Si}_7) \rightarrow \sigma^*(\text{C}_8\text{H}_8)$ (1.83)
$\pi(\text{Si}_2\text{Si}_7) \rightarrow \sigma^*(\text{C}_6\text{C}_{12})$ (0.63)	$\sigma(\text{C}_1\text{H}_1) \rightarrow \pi^*(\text{C}_2\text{Si}_7)$ (2.00)
	$\sigma(\text{C}_3\text{H}_3) \rightarrow \sigma^*(\text{C}_3\text{C}_{12})$ (1.46)
	$\sigma(\text{C}_2\text{C}_3) \rightarrow \sigma^*(\text{C}_1\text{C}_{11})$ (0.69)
	$\sigma(\text{C}_3\text{C}_{12}) \rightarrow \sigma^*(\text{C}_1\text{C}_2)$ (4.71)
	$\sigma(\text{C}_3\text{C}_{12}) \rightarrow \pi^*(\text{C}_2\text{Si}_7)$ (0.51)
	$\sigma(\text{C}_3\text{C}_{12}) \rightarrow \sigma^*(\text{C}_6\text{H}_6)$ (2.46)
$\sigma(\text{C}_1\text{Si}_2) \rightarrow \sigma^*(\text{Si}_2\text{C}_3)$ (10.39)	$\pi(\text{C}_2\text{Si}_7) \rightarrow \sigma^*(\text{C}_6\text{Si}_7)$ (8.94)
$\sigma(\text{C}_{11}\text{C}_{11\text{out}}) \rightarrow \sigma^*(\text{C}_1\text{Si}_2)$ (3.26)	$\sigma(\text{C}_2\text{C}_3) \rightarrow \sigma^*(\text{C}_{12}\text{H}_{12\text{out}})$ (1.59)
$\sigma(\text{C}_1\text{C}_{10}) \rightarrow \sigma^*(\text{C}_{11}\text{H}_{11\text{in}})$ (3.26)	$\sigma(\text{C}_3\text{C}_4) \rightarrow \sigma^*(\text{C}_{12}\text{H}_{12\text{in}})$ (2.59)

<sup>a</sup>molecule **1** with forced  $C_s$  symmetry, C-Si and Si=Si bonds lengths constrained to 2.060 Å and 2.240 Å, and pyramidalization angle constrained to 15°

**Table 4.** RHF/6-31G\*//B3LYP/6-31G\* NBO orbital interaction parameters for molecules **1a** and **4**

<b>4</b> → <b>1a</b> <sup>a</sup>	<b>4</b>
$\pi(\text{Si}_2\text{Si}_7) \rightarrow \sigma^*(\text{C}_3\text{C}_4)$ (1.99)	$\pi(\text{C}_2\text{C}_7) \rightarrow \sigma^*(\text{C}_3\text{C}_4)$ (3.38)
$\pi(\text{Si}_2\text{Si}_7) \rightarrow \sigma^*(\text{C}_1\text{H}_1)$ (7.21)	$\pi(\text{C}_2\text{C}_7) \rightarrow \sigma^*(\text{C}_1\text{H}_1)$ (1.33)
$\sigma(\text{C}_1\text{C}_{10}) \rightarrow \pi^*(\text{Si}_2\text{Si}_7)$ (1.55)	$\sigma(\text{C}_1\text{C}_{10}) \rightarrow \pi^*(\text{C}_2\text{C}_7)$ (3.40)
$\sigma(\text{C}_1\text{H}_1) \rightarrow \pi^*(\text{Si}_2\text{Si}_7)$ (0.56)	$\sigma(\text{C}_2\text{C}_3) \rightarrow \sigma^*(\text{C}_7\text{C}_8)$ (3.45)
$\sigma(\text{C}_1\text{C}_{11}) \rightarrow \sigma^*(\text{Si}_2\text{C}_3)$ (9.33)	$\sigma(\text{C}_1\text{C}_{11}) \rightarrow \sigma^*(\text{C}_2\text{C}_3)$ (5.90)
$\sigma(\text{C}_1\text{C}_{11}) \rightarrow \sigma^*(\text{Si}_2\text{Si}_7)$ (3.22)	$\sigma(\text{C}_1\text{C}_{11}) \rightarrow \sigma^*(\text{C}_1\text{H}_1)$ (3.27)
$\sigma(\text{C}_1\text{Si}_2) \rightarrow \sigma^*(\text{Si}_7\text{C}_6)$ (8.13)	
$\pi(\text{Si}_2\text{Si}_7) \rightarrow \sigma^*(\text{C}_{11}\text{H}_{11\text{out}})$ (3.84)	$\pi(\text{C}_2\text{C}_7) \rightarrow \sigma^*(\text{C}_{11}\text{H}_{11\text{out}})$ (0.79)
	$\sigma(\text{C}_6\text{C}_7) \rightarrow \sigma^*(\text{C}_{12}\text{H}_{12\text{out}})$ (2.02)
	$\sigma(\text{C}_8\text{C}_9) \rightarrow \sigma^*(\text{C}_{11}\text{H}_{11\text{in}})$ (2.44)

<sup>a</sup>geometry of **4** used, C=C atoms replaced by Si=Si without optimization

**Acknowledgments.** This work was supported by Croatian Ministry of Science, Education and Sport (Projects Nos. 0098147 and 0098056).

**Conclusions.** Density functional calculations have been used to estimate the influence of replacing central C=C bridge with the disilene double bond in sesquinorbornene molecular structure. This results in large distortion of the molecular structure and considerable increase in pyramidalization angles relative to sesquinorbornene, as well as to a large butterfly bending. It is also shown that hyperconjugative interactions between the central double bond and norbornene  $\sigma$  skeleton are greatly diminished.

#### References.

- [1] W. T. Borden, Pyramidalized Alkenes, *Chem. Rev.* **1989**, 89, 1095-1099.
- [2] P. A. Carrupt, and P. Vogel, Double bond pyramidalization in bicyclic alkanes. *Ab initio* MO calculations on bicyclo[2.2.1]hept-2-ene, bicyclo[2.1.1]hex-2-ene, and bicyclo[3.2.1]oct-6-ene derivatives, *J. Mol. Struct. (THEOCHEM)* **1985**, 124, 9-23.
- [3] W. Luef, and R. Keese, Strained olefins: structure and reactivity of nonplanar carbon-carbon double bonds, *Topics in Stereochemistry* **1991**, 20, 231-318.
- [4] IUPAC name for sesquinorbornene: tetracyclo[6.2.1.13,602,7]dodec-2(7)-ene, the numbering system used in this

paper follows IUPAC rules.

- [5] M. C. Holthausen, and W. Koch, Double-bond geometry in norbornene, sesquinorbornenes, and related compounds: a high-level quantum chemical investigation, *J. Phys. Chem.* **1993**, *97*, 10021-10027.
- [6] J. Spanget-Larsen, and R. Gleiter, Structure and reactivity of norbornene and syn-sesquinorbornene, *Tetrahedron* **1983**, 3345-3350.
- [7] I. Antol, M. Eckert-Maksić, D. Margetić, Z. B. Maksić, K. Kowski, and P. Rademacher, Molecular and Electronic Structure and Gas-phase Pyrolytic Generation of 7,7'-dioxasesquinorbornenes, *Eur. J. Org. Chem.* **1998**, 1403-1408.
- [8] D. Margetić, M. Eckert-Maksić, I. Antol, Z. Glasovac, and R. N. Warrener, A DFT Study of Pyramidalized Alkenes: 7-Oxasesquinorbornenes and 7,7'-Dioxasesquinorbornenes, *Theor. Chem. Acc.* **2003**, *109*, 182-189.
- [9] M. Eckert-Maksić, I. Antol, D. Margetić, and Z. Glasovac, *syn*-Sesquinorbornenyl Carbocations and Their Boron Analogues. *Ab Initio* and DFT Study, *J. Chem. Soc. Perkin 2* **2002**, 2057-2063.
- [10] J. T. Snow, S. Murakami, S. Masamune, and D. J. Williams, Synthesis and characterization of tetrakis(2,6-diethylphenyl)digermene, *Tetrahedron Lett.* **1984**, *25*, 4191-4.
- [11] N. Tokitoh, K. Kishikawa, R. Okazaki, T. Sasamori, N. Nakata, and N. Takeda, Synthesis and characterisation of an extremely hindered tetraaryl-substituted digermene and its unique properties in the solid state and in the solution, *Polyhedron* **2002**, *21*, 563-567.
- [12] M. Weidenbruch, M. Sturmman, H. Kilian, S. Pohl, and W. Saak, Compounds of germanium and tin. Part 21. A tetraaryldigermene with a short germanium-germanium double bond and a nearly planar environment of both germanium atoms, *Chem. Ber.-Recueil* **1997**, *130*, 735-738.
- [13] M. Stender, L. H. Pu, and P. P. Power, Stabilized Terphenyl-Substituted Digermene Derivatives of Simple Organic Groups and Their Halide Precursors: Preference for Symmetrically Bonded Structures, *Organometallics* **2001**, *124*, 1820-1824.
- [14] Y. Apeloig, Theoretical Aspects of Organosilicon Compounds, in: *The chemistry of organic silicon compounds*, Part 1, Eds. S. Patai, and Z. Rappoport, Wiley, Chichester, **1989**, pp. 57-225.
- [15] M. Driess, and H. Grützmacher, Main Group element analogs of carbenes, olefins, and small rings, *Angew. Chem. Int. Ed. Engl.* **1996**, *35*, 828-856.
- [16] S. Matsumoto, S. Tsutsui, E. Kwon, and K. Sakamoto, Formation of a stable, lattice-framework disilene: A strategy for the construction of bulky substituents, *Angew. Chem. Int. Ed. Engl.* **2004**, *43*, 4610-4612.
- [17] M. Kira, T. Maruyama, C. Kabuto, K. Ebata, and H. Sakurai, Stable tetrakis(trialkylsilyl)disilylenes; synthesis, x-ray structural analysis and UV/VIS spectra, *Angew. Chem. Int. Ed. Engl.* **1994**, *33*, 1489-1491.
- [18] M. Kira, S. Ohya, T. Iwamoto, M. Ichinohe, and C. Kabuto, Facile Rotation around Si:Si Double Bonds in Tetrakis(trialkylsilyl)disilylenes, *Organometallics* **2000**, *19*, 1817-1819.
- [19] W.-C. Chen, M.-D. Su, and S.-Y. Chu, Substituent Effects on Shape Deformation and Energies of the Silicon and Germanium Double Bond, *Organometallics* **2001**, *20*, 564-567.
- [20] L. Sari, M. C. McCarthy, H. F. Schaefer III, and P. Thaddeus, Mono- and Dibringed Isomers of Si<sub>2</sub>H<sub>3</sub> and Si<sub>2</sub>H<sub>4</sub>: the True Ground State Global Minima. Theory and Experiment in Concert, *J. Am. Chem. Soc.* **2003**, *125*, 11409-11417.
- [21] C. Liang, and L. C. Allen, Group IV double bonds: shape deformation and substituent effects, *J. Am. Chem. Soc.*

1990, 112, 1039-1041.

- [22] M. Karni, and Y. Apeloig, Substituent effects on the geometries and energies of the silicon-silicon double bond, *J. Am. Chem. Soc.* **1990**, 112, 8589-8590. flat bending potential for disilene, even severe bending in disilene requires relatively little energy
- [23] H. Jacobsen, and T. Ziegler, Nonclassical double bonds in ethylene analogs: influence of Pauli repulsion on trans bending and  $\pi$ -bond strength. A density functional study, *J. Am. Chem. Soc.* **1994**, 116, 3667-3679.
- [24] M. Kira, and T. Iwamoto, Stable cyclic and acyclic persilyldisilenes, *J. Organomet. Chem.* **2000**, 611, 236-247.
- [25] M. Kira, T. Iwamoto, T. Maruyama, C. Kabuto, and H. Sakurai, Tetrakis(trialkylsilyl)digermenes. Salient Effects of Trialkylsilyl Substituents on Planarity around the Ge:Ge Bond and Remarkable Thermochromism, *Organometallics* **1996**, 15, 3767-3769.
- [26] Gaussian 98, Revision A.5, M. J. Frisch, G. W. Trucks, H. B. Schlegel, G. E. Scuseria, M. Robb, J. R. Cheeseman, V. G. Zakrzewski, J. A. Montgomery Jr., R. E. Stratmann, J. C. Burant, S. Dapprich, J. M. Millam, A. D. Daniels, K. N. Kudin, M. C. Strain, O. Farkas, J. Tomasi, V. Barone, M. Cossi, R. Cammi, B. Mennucci, C. Pomelli, C. Adamo, S. Clifford, J. Ochterski, G. A. Petersson, P. Y. Ayala, Q. Cui; K. Morokuma, D. K. Malick, A. D. Rabuck, K. Raghavachari, J. B. Foresman, J. Cioslowski, J. V. Ortiz, B. B. Stefanov, G. Liu, A. Liashenko, P. Piskorz, I. Komaromi, R. Gomperts, R. L. Martin, D. J. Fox, T. Keith, M. A. Al-Laham, C. Y. Peng, A. Nanayakkara, C. Gonzalez, M. Challacombe, P. M. W. Gill, B. Johnson, W. Chen, M. W. Wong, J. L. Andres, C. Gonzalez, M. Head-Gordon, E. S. Replogle, and J. A. Pople, Gaussian, Inc., Pittsburgh PA, **1998**.
- [27] A. D. Becke, A new mixing of Hartree-Fock and local-density-functional theories, *J. Chem. Phys.* **1993**, 98, 1372-1377.
- [28] C. Lee, W. Yang, W. and R. G. Parr, Development of the Colle-Salvetti correlation-energy formula into a functional of the electron density, *Phys. Rev. B* **1988**, 37, 785-789.
- [29] J. E. Carpenter, and F. Weinhold, Analysis of the geometry of the hydroxymethyl radical by the "different hybrids for different spins" natural bond orbital procedure, *J. Mol. Struct. (Theochem)* **1988**, 169, 41-62.; A. E. Reed, R. B. Weinstock, and F. Weinhold, Natural population analysis, *J. Chem. Phys.* **1985**, 83, 735-746.
- [30] Structure of the digermene conterpart of compound **2** has similar geometrical features as **2** - butterfly bending of 48.4 and 56.1 deg. We were unable to locate stable structure of *syn*- digermene conterpart of compound **1**.
- [31] A. G. Griesbeck, T. Deufel, G. Hohlneicher, R. Rebentisch, and J. Steinwascher, Synthesis, structure and properties of twofold bridged sesquinorbornenes, *Eur. J. Org. Chem.* **1998**, 1759-1762.
- [32] D. Margetić, R. N. Warrener, M. Eckert-Maksić, I Antol, and Z. Glasovac, A DFT Study of Pyramidalized Alkenes: 7-Oxasesquinorbornenes and 7,7'-Dioxasesquinorbornenes, *Theor. Chem. Acc.* **2003**, 109, 182-189.
- [33] We again report all pyramidalization results in terms of the butterfly bending angle ( $\square$ ) which is defined in our earlier paper: D. Margetić, R. V. Williams, R. V.; and R. N. Warrener, Pyramidalized Olefins: A DFT Study of the Homosquinorbornene and Sesquibicyclo[2.2.2]octene Nuclei, *J. Org. Chem.* **2003**, 68, 9816-9819.
- [34] B. Yates, Olefin strain energies and platinum complexes of highly pyramidalized alkenes, *J. Organomet. Chem.* **2001**, 635, 142-152.
- [35] D. A. Hrovat, and W. T. Borden, *Ab initio* calculations of the olefin strain energies of some pyramidalized alkenes, *J. Am. Chem. Soc.* **1988**, 4710-4718.
- [36] K. Komatsu, Cyclic  $\pi$ -conjugated systems annelated with bicyclo[2.2.2]octene: synthesis, structures, and

properties, *Bull. Chem. Soc. Jpn.* **2001**, 74, 407-419.

- [37] T. Tsumuraya, S. A. Batcheller, and S. Masamune, Compounds with silicon-silicon, germanium-germanium, and tin-tin double bonds in addition to strained ring systems with the silicon-, germanium-, and tin-framework, *Angew. Chem. Int. Ed. Engl.* **1991**, 30, 902-930.
- [38] For comparison, experimental values for vertical ionization energies ( $I_{v,j}$ ) of *syn*- and *anti*- sesquinorbornenes are 8.12 and 7.90 eV, respectively.
- [39] M. E. Casida, C. Jamorski, K. C. Casida, and K. D. R. Salahub, Molecular excitation energies to high-lying bound states from time-dependent density-functional response theory: characterization and correction of the time-dependent local density approximation ionization threshold, *J. Chem. Phys.* **1998**, 108, 4439-4449.
- [40] D. Margetić, I. Antol, and M. Eckert-Maksić, Effect of Silicon and Germanium Bridges on Pyramidalization of Olefinic Carbon Atoms in *syn*-Sesquinorbornene Framework, *J. Organomet. Chem.*, submitted.
- [41] B. Wrackemeyer, W. Milius, M. H. Bhatti, and S. Ali, [4+2]Cycloadditions of organometallic-substituted siloles with dimethyl acetylenedicarboxylate and tetracyanoethylene, *J. Organomet. Chem.* **2003**, 665, 196-204.
- [42] R. West, Chemistry of the silicon-silicon double bond, *Angew. Chem. Int. Ed. Engl.* **1987**, 99, 1231-1241.

**Supplementary Material.** Cartesian coordinates of B3LYP/6-31G\* calculated structures **1-3** (2 pages).

**Keywords.** Pyramidalized alkenes, DFT calculations, sesquinorbornenes, disilenes

#### Abbreviations and notations

DFT, density functional theory	OSE, olefin strain energy
TMS, tetramethylsilane	UV, ultraviolet
HOMO, highest occupied molecular orbital	LUMO, highest unoccupied molecular orbital
FMO, frontier molecular orbital	NBO, natural bond orders
RHF, restricted Hartree-Fock method	B3LYP, Becke3 method with Lee, Young and Parr functionals

#### Biographies

**First Author** is research scientist working in Laboratory for Physical Organic Chemistry, at Department of Organic Chemistry and Biochemistry, Ruđer Bošković Institute in Zagreb, Croatia.

**Second Author** is computational chemist working on his Ph.D. project under the supervision of Dr. Mirjana Eckert-Maksić.

**Third Author** is senior research scientist and head of Laboratory for Physical Organic Chemistry.