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REGULAR ARTICLE

Zwitterionic structures of strained *cis*-pyramidalized disilenes: fact or artifact

Zoran Glasovac · Ivana Antol · Mario Vazdar · Davor Margetić

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Abstract A series of *cis*-pyramidalized disilenes was modeled by ab initio and DFT methods with the special emphasis on character of the wavefunction. Spin restricted DFT (RDFT) and MP2 approaches predicted qualitatively different structures of disilenes as the minima (deformed zwitterionic and symmetrical diradicaloid, respectively). Additional CASSCF and broken symmetry spin unrestricted DFT (BS-UDFT) calculations confirmed symmetrical structures as more reliable minimum. The only exception is highly strained 1,4-disilabicyclo[2.2.0]hex-1,4-ene where deformed zwitterionic structure is corroborated by most of the applied methods including high-level MR-AQCC calculation. Analysis of the wavefunction obtained for both deformed and symmetrical minima indicates a strong tendency of the RDFT method to prefer structures possessing a closed shell wavefunction even though a strong electron density shift occurs. The results obtained at CASSCF level of theory showed that for a correct description of geometries of such systems, a two-configurational wavefunction is needed at least. The BS-UDFT and spin restricted MP2 methods describe such "diradicaloid" geometries of *cis*-pyramidalized disilenes qualitatively correct although from different reasons.

Keywords Quantum chemical calculations · Disilenes · Pyramidalization · Diradical character · Ring strain

1 Introduction

The structures of the compounds possessing a Si=Si double bond have attracted considerable attention ever since they were suggested as the intermediates in some organic reactions [1–6]. In contrast to compounds possessing a C=C double bond, the first isolable compounds with Si=Si bond were synthesized some 30 years ago [7]. It has been shown that the geometry of disilene double bond is highly dependent on the substituents attached to it [2, 8, 9]. In the case of electron donating substituents, the geometry deviates from the planarity with the silicon atoms being pyramidalized in a *trans*-manner. On the other hand, the presence of the electron withdrawing substituents leads to the planar Si=Si double bond.

Recently, Kira and co-workers [10] prepared the first stable compound possessing a disilene double bond shared between two 5-membered polysilane rings (Fig. 1a). Crystal structure analysis of this compound revealed the *cis*-pattern of pyramidalization of the Si=Si double bond (ca. 3°). Inspection of the bond angles adjacent to the double bond reveals significant deviation from the double bond found in Kira's disilene and tetrakis(*t*-butyldimethylsilyl)disilene [11] (110° against 122°, respectively, Fig. 1b). It has been shown earlier that similar *cis*-pyramidalization of C=C bond occurs in a number of *syn*-sesquinorbornene derivatives as a consequence of the molecular strain imposed to the double bond located between two carbon junction atoms [12–16]. Similar effect could also operate in strained *cis*-pyramidalized disilenes.

The widely accepted description of the geometry and electronic structure of disilenes was independently given by Trinquier and Malrieu [17, 18] and Carter and Goddard [19, 20] (so-called CGMT theory). Also, other theoretical approaches were adopted in order to explain structure and

Z. Glasovac (✉) · I. Antol · M. Vazdar · D. Margetić
Division of Organic Chemistry and Biochemistry,
Rudjer Bošković Institute, POB 180, 10002 Zagreb, Croatia
e-mail: glasovac@emma.irb.hr

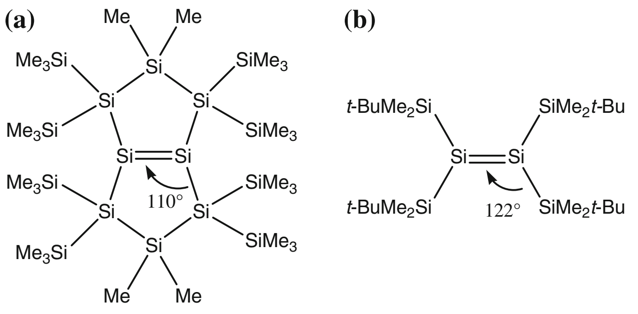

Fig. 1 Structures of the Kira's bicyclic disilene (**a**) and its unstrained analog (**b**)

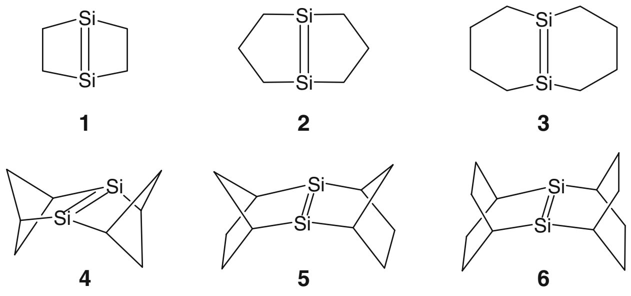

Fig. 2 Schematic representation of disilenes **1**–**6**

bonding in disilenes [21–24]. It was claimed that disilenes possess significant diradical character [25, 26], thus belonging to the group of "diradicaloids" [27]. Nevertheless, the theoretical investigations of *trans*-disilenes confirmed that the DFT methods reproduce their geometry qualitatively correctly [25, 28–30]. It has to be emphasized that all approaches successfully rationalize electronic effects that lead to the planar or *trans*-pyramidalized geometries found in disilenes. On the other side, in neither of these approaches *cis*-pyramidalized disilenes were even proposed and no discussion had been offered treating possible *cis*-pyramidalization in strained disilenes where, similarly to *trans*-disilenes and *cis*-pyramidalized alkenes [31, 32], significant diradical character is also expected. The only exception was recent DFT study of disila-analogue of both *syn*- and *anti*-sesquinorbornene where highly deformed structures with an asymmetric Si=Si double bond are predicted [33]. Electron structure analysis showed a strong polarization of the electron density along the Si=Si bond resulting in closed shell "zwitterionic-like" structure. Similarly, Ottosson [34] analyzed a number of different structures possessing an unsymmetrical highly polarized double bond with an incorporated silicon atom. He found that the RB3LYP method is able to correctly interpret geometries of both regularly and reverse polarized Si=C double bonds. These findings raise question whether the molecular strain can be driving force for formation of the zwitterionic structures in symmetrically substituted disilenes or will the structures be more stable as the singlet or triplet diradicals.

In the series of papers, Cremer and co-workers discussed four different types of diradicals [35–37] with emphasis on the ability of DFT methods to model such systems with sufficient accuracy. They pointed out that broken symmetry spin unrestricted (BS)-UDFT [38] can be successfully applied for the diradicals with some multiconfigurational character (type II diradicals [35]) when the singlet–triplet splitting is sufficiently small (<5 kcal mol^{-1}), but generally, these results should be checked with the multiconfigurational methods [37]. Such an approach could be necessary to correctly account for the partial diradical nature of the Si=Si double bond in pyramidalized disilenes. If so, the closed shell "zwitterionic-like" character of Si=Si double bond incorporated in strained sesquinorbornene skeleton as predicted in Ref. [33] might be an artifact of using restricted theoretical approach.

In order to analyze the geometrical and electronic structure of the strained *cis*-pyramidalized disilenes, we investigated several model bicyclic and pentacyclic structures (Fig. 2) by RDFT, BS-UDFT, MP2 and CASSCF methods. Special emphasis is laid upon effect of the ring strain on the pyramidalization of the double bond. Comparison of these methods is performed in order to analyze their accuracy and applicability to larger systems which would be of synthetic interest. In this respect, BS-UDFT is especially interesting due to its low demand for the computing resources compared to MPn and especially MCSCF methods.

2 Methodology

All structures were optimized at the RMP2/6-31G(d), RB3LYP/6-31G(d) and BS-UB3LYP/6-31G(d) levels of theory without any geometrical constraints (denoted as MP2, RDFT and BS-UDFT models, respectively).[1] Single point energies were further evaluated using 6-311G(d,p) basis set at each level of theory. BS-UDFT wavefunction is obtained starting from spin unrestricted wavefunction with mixed frontier orbitals (using Guess = mix keyword). The wavefunction is then optimized until stability conditions were satisfied. Subsequently, a geometry optimization was conducted starting from the optimal wavefunction. All attempts to obtain a broken symmetry spin unrestricted singlet structure of disilene **3** ended up in the same minimum with identical properties of the singlet wavefunction. Symmetrical structures obtained reflect either C_{2v} (**2**, **4** and

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[1] The disilene **2** was also optimized by B3LYP and MP2 approaches using 6-311+G(d,p) basis set. The optimization resulted with very similar structures to those obtained with 6-31G(d) basis set indicating very weak basis set effect on geometrical parameters.

5) or C_2 (**1** and **6**) point group symmetry and were interpreted accordingly. Deformed structures were obtained by full geometry optimization using spin restricted wavefunction at the B3LYP/6-31G(d) level of theory (hereafter denoted as RDFT model). Triplet structures were optimized using spin unrestricted approaches (UDFT or UMP2) without any constraints imposed.

The CASSCF calculations were performed using CAS(2,2) and CAS(4,4) active spaces which consisted of two electrons in two orbitals and four electrons in four orbitals, respectively. For example, active orbitals selected for the symmetric disilene **2** (structure **2a**) were shown in Fig. 3a. The largest coefficients in active orbitals are mainly located on both Si atoms in case of the symmetrical structures. Although the σ/π separation is broken owing to high deviation of Si=Si bond from planarity and mixing of σ- and π-contributions in all four orbitals is evident, we shall describe them as π-type (**2a$_1$** and **1b$_2$**) and σ-type orbitals (**1a$_1$** and **2b$_2$**). For the CASSCF(2,2) calculations, only π-type orbitals were selected as active ones. In the case of deformed structures (such as **2b**), active orbitals are mostly localized on either one of the silicon atoms (see **1a**–**4a** orbitals in Fig. 3b). This effect is particularly strong in **2a** and **3a** orbitals which closely correspond to the anionic lone pair and cationic empty p-type orbital.

All optimizations were performed with Gaussian03 program package [39] employing standard convergence criteria. Obtained minima were verified by vibrational analysis. Zero point vibrational energies (E_{ZPV}) were either scaled by 0.967 (MP2) as recommended by Scott and Radom [40] or used unscaled otherwise. In the case of the smallest molecule studied in this work (**1**), the multireference averaged coupled cluster (MR-AQCC) calculations with CAS(4,4) reference space were additionally performed using COLUMBUS suite of codes [41–44]. Atomic integrals were computed with DALTON program [45]. Molecular orbitals were viewed and plotted using Molden [46].

3 Results and discussion

3.1 Geometry of disilenes

Geometries of all selected compounds are calculated at four different levels of theory spanning from single determinant restricted B3LYP to multiconfigurational CASSCF method. The values of selected geometrical parameters are collected in Table 1 and typical structures are shown in Fig. 4. The MP2 optimizations resulted in highly symmetrical structures (practically of C_{2v} symmetry) for most of the compounds (**2**–**5**) despite of switching off all symmetry constrains during optimization. The two exceptions are molecules **1** and **6** where slight deformation from C_{2v} toward C_2 symmetry is obtained with α_1 versus α_2 angle difference of 3.8° and 1.1°, respectively.

In accordance with the previously published results [33], the RDFT approach gives the deformed structures as the most stable minimum for all molecules except **3**. Since the RDFT calculations are not time consuming, we re-optimized the structures of all investigated disilenes using the RB3LYP/6-311G(d,p) approach. Enlargement of the basis set to the triple zeta quality gave qualitatively the same results for all disilenes (Table 1) confirming that the deformed structures are not the consequence of the size of basis set employed. Illustrative example for the difference between symmetrical MP2 and deformed RDFT structure for molecule **2** is given in Fig. 4. In order to simplify the discussion and to clarify the difference between symmetrical and deformed structures, they will be denoted

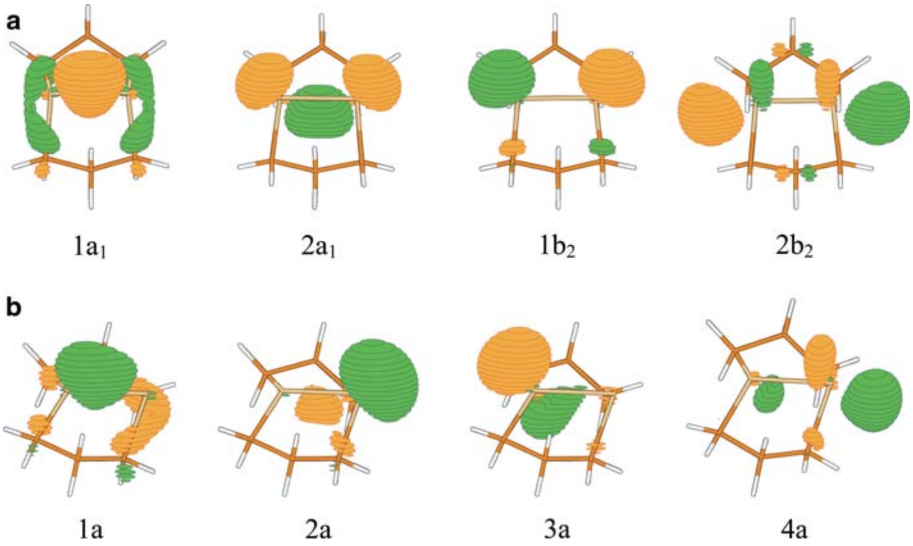


Fig. 3 Active orbitals for disilene structures **2a** (**a**) and **2b** (**b**) used in CASSCF calculations

Table 1 Selected geometrical parameters obtained for symmetrical (a) and deformed (b) structures of compounds **1–6** optimized by different methods

Mol.	r(Si1=Si2)[a] (Å)		β^{b} (°)	$\beta'^{\,b}$ (°)	α_1^{b} (°)	α_2^{b} (°)	$\alpha_1'^{\,b}$ (°)	$\alpha_2'^{\,b}$ (°)
	Singlet	Triplet						
MP2								
1a	2.329	2.356	−123.4	105.1	79.6	75.8	75.8	79.6
2a	2.198	2.326	−129.9	129.9	95.5	95.5	95.5	95.5
3	2.133	2.300	180.0	180.0	110.7	110.7	110.7	110.7
4a	2.269	2.313	−129.6	129.6	88.2	88.2	88.2	88.2
5a	2.220	2.320	−134.0	134.0	92.7	92.7	92.7	92.7
6a	2.202	2.304	−123.9	139.0	99.7	98.6	98.6	99.7
RDFT[c]								
1b	2.345 (2.350)	–	−119.0 (−118.7)	101.4 (101.1)	104.9 (105.2)	85.6 (85.4)	54.2 (53.9)	70.9 (71.0)
2b	2.262 (2.264)	–	−125.0 (−125.8)	125.0 (125.7)	112.2 (112.0)	112.0 (111.9)	75.8 (76.0)	76.2 (76.1)
3[d]	2.129 (2.124)	–	180.0 (180.0)	180.0 (180.0)	110.8 (180.0)	110.8 (180.0)	110.8 (180.0)	110.8 (180.0)
4b	2.277 (2.280)	–	−128.7 (−128.6)	128.7 (128.7)	103.7 (103.7)	103.7 (103.7)	73.0 (72.9)	73.0 (72.9)
5b	2.244 (2.246)	–	−134.5 (−134.5)	134.5 (134.5)	105.9 (105.9)	105.9 (105.9)	78.6 (78.5)	78.6 (78.5)
6b	2.227 (2.228)	–	−127.9 (−128.0)	136.8 (136.6)	112.9 (112.9)	112.3 (112.3)	84.5 (84.3)	83.4 (83.3)
BS-UDFT								
1a	2.418	2.391	−98.6	113.8	73.6	80.7	80.7	73.6
2a	2.299	2.346	−117.6	117.6	94.2	94.2	94.2	94.2
3[d]	2.129	2.319	180.0	180.0	110.8	110.8	110.8	110.8
4a	2.296	2.337	−126.2	126.2	88.1	88.1	88.1	88.1
5a	2.253	2.343	−131.2	131.2	92.3	92.3	92.3	92.3
6a	2.246	2.324	−122.6	134.3	98.7	98.5	98.5	98.7
CASSCF								
1b[e,f]	2.375 [2.353]	2.387 [2.390]	−117.6 [−117.7]	101.8 [99.3]	102.1 [104.4]	84.1 [85.1]	55.6 [54.2]	71.2 [71.0]
2a	2.309	2.356	−118.5	118.5	94.0	94.0	94.0	94.0
3	2.185	2.329	180.0	180.0	108.3	108.3	108.3	108.3
4a	2.307	2.303	−126.8	126.8	87.8	87.8	87.8	87.8
4b	2.334	–	−126.3	−126.3	102.0	102.0	72.6	72.6
5a	2.272	2.343	−131.9	131.9	92.0	92.0	92.0	92.0
6a	2.267	2.334	−123.2	135.2	98.4	98.2	98.2	98.4

[a] Bond distances r(Si1=Si2) are given for singlet and triplet structures

[b] Bond angles α_1, α_1', α_2 and α_2' and dihedral angles β and β' are defined in Fig. 4 and are given for the geometries of the singlet structures

[c] Geometrical parameters calculated at the RB3LYP/6-311G(d,p) level of theory are given in parentheses

[d] BS-UDFT and RDFT optimization on **3** resulted in the same closed shell structure

[e] Structure **1a** is not a minimum at the CASSCF level of theory

[f] Geometrical parameters of **1b** obtained at MR-AQCC(4,4)/CASSCF(4,4)/6-31G(d) level of theory are given in square brackets

hereafter as “a” and “b”, respectively. It is interesting to note that the optimization of molecule **2** by imposing C_{2v} symmetry constraint at the RDFT level resulted in **2a** structure which is identified as the saddle point between two identically deformed minima.

Since single determinant methods (RDFT and MP2) give qualitatively different results, we also tested the methods that can be successfully applied for certain multi-configurational problems such as BS-UDFT [35–37, 47] and CASSCF, the latter being considered as the reference method. In contrast to RDFT, the BS-UDFT calculation method gave symmetric structures (analogous to **2a**) lower in energy than deformed ones (by 1–15 kcal mol^{-1}). Moreover, geometry optimization starting from the deformed geometries, similarly to the MP2 method, did not yield deformed minima but rather converged to the symmetric structures. Comparable results were also obtained by CASSCF method, although in the case of **4** both minima were located. However, the deformed structure (**4b**) was found to be significantly higher in energy (by 10 kcal mol^{-1})

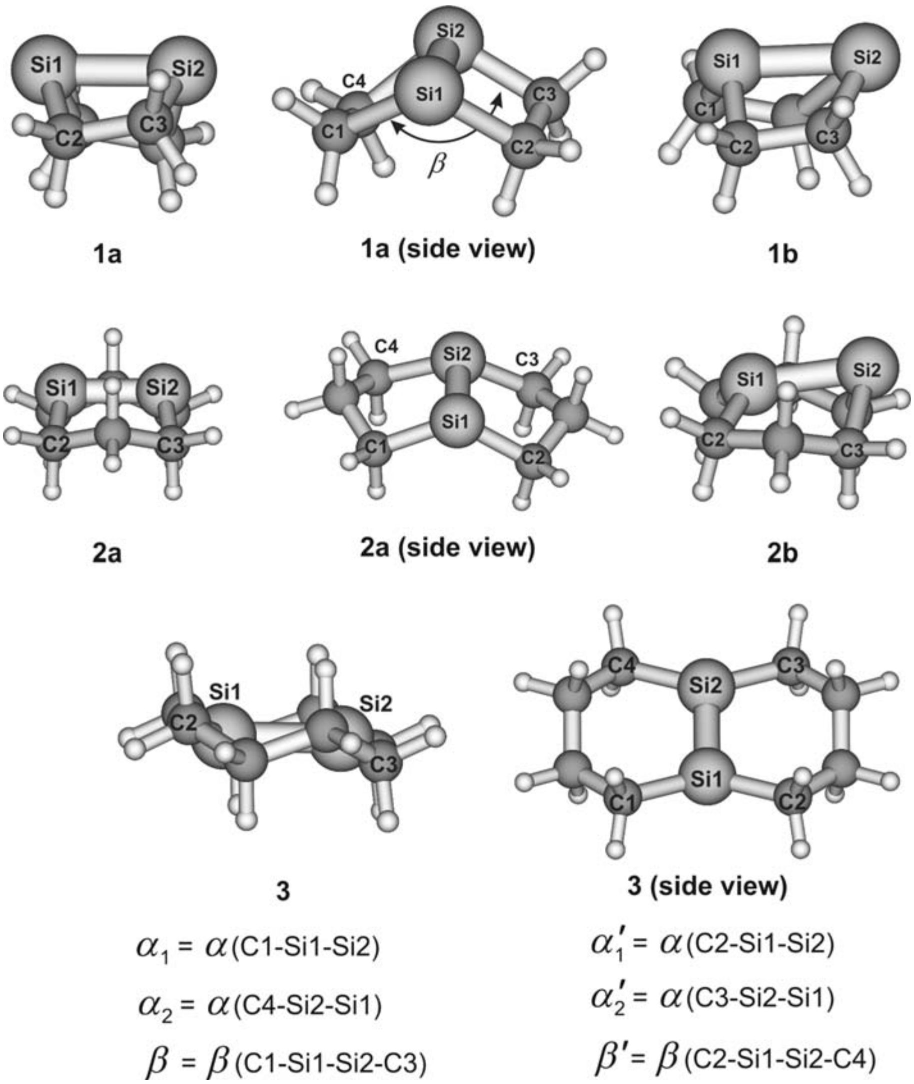


Fig. 4 Representation of the symmetrical (**Xa**) and deformed (**Xb**) structures of selected disilenes as optimized at the MP2/6-31G(d) and RDFT/6-31G(d) levels of theory, respectively. In the case of "unstrained" disilene **3**, both theoretical levels resulted in the *trans*-pyramidalized structure

than the symmetric one (**4a**). Geometrical parameters of disilenes obtained at BS-UDFT do not differ much from the MP2 results, although one may notice a systematic increase in Si=Si bond lengths when comparing to the MP2 results. The elongation of the Si=Si bonds calculated at the CASSCF level is even more pronounced. The change in Si=Si bond lengths is followed by a slight decrease in dihedral angles β, where BS-UDFT and CASSCF results show remarkable similarity. Disilene **1** can be again considered as an exception resulting in a deformed rather than a symmetrical structure irrespectively of the method applied.

cis-Pyramidalization of the central double bond imposed by the ring strain in all compounds, except disilene **3**, is evident. The other point worth noting is that the pyramidalization is slightly less pronounced in deformed structures. For instance, deviation of the disilene bond from planarity amounts 62.4° (calculated using BS-UDFT approach) and 55.0° (calculated using RDFT approach) in **2a** and **2b**, respectively, as determined from the dihedral angle β. In disilene **3**, the six-membered rings are flexible enough to allow *trans*-pyramidalization of the disilene double bond, which is found to be the lowest energy structure regardless of computational method applied.

The inspection of geometrical parameters given in Table 1 indicates a dependence of the pyramidalization of the Si=Si double bond on the deformation of bond angles α. Decrease in α is followed by increase in dihedral angle β and elongation of central Si=Si bond which culminates in values of 2.329 Å (MP2), 2.418 Å (BS-UDFT) and 2.345 Å (RDFT). These bond lengths closely correspond to the values of single Si–Si bonds found in disilanes [48]. Bond angles α_1, α'_1, α_2 and α'_2 adjacent to the Si=Si bond (**1a**–**6a**) vary between 76° and 100° across the series of compounds. Even though the structures **1a** and **6a** deviate from C_{2v} symmetry, difference between α_1 and α_2 within these structures is small and amounts ca. 4° and 1°, respectively, as calculated at the MP2 level of theory.

Strong asymmetry observed in the deformed structures (**2b**, **4b** and **5b**) is reflected in the bond angles α_1 and α_1' as well as α_2 and α_2' which are mutually markedly different. Furthermore, in the most strained disilene **1b** and in **6b**, all bond angles adjacent to the double bond are non-equivalent and different due to the close proximity of the bridgehead methylene groups which tend to avoid each other.

Geometry of disilene **1** deserves some additional comments. Small ring size in **1** induces strong pyramidalization of the structure (Fig. 4), with α_1, α_1', α_2 and α_2' bond angles assuming values similar to those found in propellanes. Consequently, the π-orbital is better described as two single occupied atomic orbitals which assume position almost co-linear with σ(Si–Si) bond. This is also reflected in the longest Si=Si bond distance of all investigated structures. It is well known that for propellanes, a multiconfigurational wavefunction is necessary for interpreting both bonding and energetics [49], hence the results for disilene **1** should be taken with a due care. Therefore, optimization at the MR-AQCC(4,4)/CASSCF(4,4)/6-31G(d) was performed for this structure and the selected geometrical parameters are given in Table 1. The results reveal **1b** type of the structure similar to the one obtained at the CASSCF level giving the credits to the deformed zwitterionic structure of **1** as the real minimum.

It is interesting to note that in the case of "unstrained" disilene **3**, the bond angle α is practically the same as in Kira's bicyclic disilene derivative. Consequently, a weak pyramidalization found in Kira's polysilene is not caused by the strain but more likely is a consequence of other electronic and/or crystal packing effects. More quantitative discussion on geometrical parameters would be required for the analysis of hyperconjugative interaction of the disilene double bond with unoccupied σ(Si–C) orbitals. This also involves analysis of the through-bond and through-space electron interactions as previously discussed for sesquinorbornene analogs [50–52] which is beyond the scope of this paper.

$$E_{S-T} = E_{tot}(\text{triplet}) - E_{tot}(\text{singlet}) \qquad (1)$$

As already mentioned in Sect. 1, diradicals of type II [35, 37] can be properly described by BS-UDFT approach as long as their singlet–triplet splitting is smaller than 5 kcal mol^{-1}. Although we are not dealing with a typical diradical, but with double bond where some amount of the diradical character is imposed by the strain (except in molecule **3**), we thought it is worthwhile to determine singlet–triplet energy gap ($E_{S–T}$) (Eq. 1). Therefore, all investigated disilenes were also optimized at triplet potential energy surface and their energies were compared with results obtained for singlets (Table 2). On going from singlet to triplet wavefunction, all methods led to symmetrical structures with somewhat elongated Si=Si double bond with respect to singlet structures (Table 1). The singlet structures of molecules **3–6** were found to be more stable than triplets. The opposite holds for disilene **2** where triplet has lower energy than singlet by 3.6, 0.5 and 1.7 kcal mol^{-1} as calculated at MP2, BS-UDFT and CASSCF levels of theory, respectively. Calculated singlet–triplet gap ($E_{S–T}$) is the biggest (>20 kcal mol^{-1}) for unstrained *trans*-pyramidalized compound **3**. In other molecules **2**, **4–6** (all being *cis*-pyramidalized), singlet–triplet gaps are small ranging between 0.3 and 3.6 kcal mol^{-1} at the CASSCF level. Similar values are obtained also with BS-UDFT and MP2 methods. This indicates that these structures satisfy Cremer's criterion for successful treatment of type II diradicals [35, 37].

The exception from the general trend is again "too strained" disilene **1**. For this molecule, MP2 method predicted that the triplet structure is strongly stabilized with respect to symmetric **1a** singlet structure by 17.4 kcal mol^{-1}. This is in strong contrast to the BS-UDFT results where symmetrical singlet and triplet structures have almost equal energies ($E_{S–T} = -1.0$ kcal mol^{-1}) while the deformed singlet **1b** is more stable by 13.8 kcal mol^{-1}. Such trend in energies of deformed singlet and triplet structures of **1** is also confirmed at the CASSCF and MR-AQCC levels where **1b** is more stable than triplet **1a** by 10.4 and 16.0 kcal mol^{-1}, respectively. On the basis of these results, it can be concluded that the molecule **1** is best described as the zwitterion with highly polarized Si=Si double bond.

3.2 Analysis of the wavefunction

The CASSCF single point calculations were performed at the MP2 and RDFT optimized geometries using both (4,4) and (2,2) active spaces. Thus, obtained natural orbital occupation numbers (NOON) and weights of the most important configurations (w_i) were compared with those obtained for CASSCF optimized structures (Table 3).

By examining NOON and w_i values presented in Table 3, a basic insight into origin of discrepancy between MP2 and RDFT calculations could be obtained. For this purpose, CASSCF wavefunction is calculated for the symmetrical (MP2 and CASSCF) and deformed (RDFT) geometries. In all symmetrical "**a**" structures, two configurations with considerably high weights (above 0.2) were found. While the first configuration (ϕ_1) represents a classical HF closed shell system, the second one (ϕ_2) arises from two electron excitations from the 2a$_1$ (π(Si=Si)) to the 1b$_2$ (π*(Si=Si)) orbital, thus describing typical diradical system. Contribution of the second configuration (w_2) increases proportionally with angular strain (with a decrease of bond angle α) (Table 1). The largest contribution of w_2 was found to be 0.343 for **1a**. CASSCF

Table 2 Total energies (E_{tot}) for singlet and triplet states and singlet–triplet energy differences ($E_{\mathrm{S-T}}$, see Eq. 1) for compounds **1**–**6** calculated using (U,R)DFT, MP2 and CASSCF(4,4) methods

	Symmetric structure				Deformed structure	
	E_{tot} (a.u.) MP2 singlet	E_{tot} (a.u.) Triplet	$E_{\mathrm{S-T}}$ (kcal mol^{-1})		E_{tot} (a.u.)	$E_{\mathrm{S-T}}$ (kcal mol^{-1})
1a	−734.54354	−734.57120	−17.4		[a]	–
2a	−812.94032	−812.94606	−3.6		[a]	–
3	−891.31111	−891.27325	23.8		[a]	–
4a	−888.85574	−888.85516	0.4		[a]	–
5a	−967.26785	−967.25589	7.5		[a]	–
6a	−1045.60928	−1045.60157	4.8		[a]	–
	BS-UB3LYP (RB3LYP[b,c]) singlet	Triplet			RB3LYP singlet	
1a	−736.09201 (−736.07598)	−736.09357	−1.0 (−11.0)	**1b**	−736.11550	13.8
2a	−814.71715 (−814.70041)	−814.71798	−0.5 (−11.0)	**2b**	−814.71684	−0.7
3	−893.33600 (−893.33833)	−893.30053	22.3 (23.7)	**3**[a]	−893.33611[a]	22.3[a]
4a	−890.82525 (−890.81216)	−890.82433	0.6 (−7.6)	**4b**	−890.82340	−0.6
5a	−969.48417 (−969.48137)	−969.47874	3.4 (1.6)	**5b**	−969.48440	3.6
6a	−1048.08344 (−1048.07929)	−1048.07901	2.8 (0.2)	**6b**	−1048.08257	2.2
	CASSCF(4,4) singlet	Triplet			CASSCF(4,4) singlet	
1a	[c]	−733.81639	–	**1b**	−733.83300	10.4
2a	−811.88168	−811.88446	−1.7	**2b**	−811.86812[d]	−10.3
3	−889.93684	−889.90421	20.5	**3**	−889.93682[a]	20.5
4a	−887.51025	−887.50982	0.3	**4b**	−887.49448	−9.6
5a	−965.60333	−965.59927	2.5	**5b**	−965.58812[d]	−7.0
6a	−1043.64032	−1043.63723	1.9	**6b**	−1043.62347[d]	−8.6

All energies were calculated at model/6-311G(d,p)//model/6-31G(d) levels of theory where model stands for MP2, (U,R)B3LYP or CASSCF(4,4) theoretical approaches

[a] Converged to symmetrical structure

[b] Values in parentheses refer to a single point RB3LYP/6-311G(d,p) calculations at the geometries of the corresponding symmetrical minima; NImag = 1 except for **1** (NImag = 2) and **3** (NImag = 0)

[c] Not a minimum

[d] NImag = 1, no deformed minima were found for disilenes **2**, **5** and **6**

wavefunctions obtained for deformed structures possess basically single configurational character, and it is expected that such structures will be preferred by single determinant methods such as RDFT. This finding is corroborated by the inspection of the active space orbitals of deformed systems (Fig. 3). One can clearly notice that the π-electron density in the Si=Si bond is dominantly shifted toward one silicon atom (more pyramidalized one) while the lack of the electron density is found at the second silicon atom. Polarization of the electron density results in structure with high zwitterionic character as previously observed and described in details by Margetić et al. [33]. The special case is disilene **3** which is symmetric but its wavefunction is basically single configurational. Consequently, similar geometries of the compound **3** obtained by all three computational approaches are not surprising.

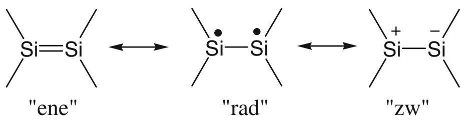
To get a more pictorial insight into the character of the Si=Si bond, we shall schematically depict it as the resonance of three most important valence structures. These valence structures represent a classical planar double bond ("ene"), a diradical structure ("rad") and a zwitterionic structure ("zw") (Scheme 1). The "ene" structure is strongly destabilized by pyramidalization and therefore its importance is lowered as pyramidalization increases. On the other hand, other two structures allow for distortion from planarity without being strongly destabilized due to formally single bond between the silicon atoms. Analysis of the CASSCF results indicates that "ene" and "rad" structures correspond to configurations ϕ_1 and ϕ_2 in the configurational state wavefunction obtained for symmetrical structures. The RDFT method, as a single configuration single determinant method, cannot properly describe

Table 3 Occupations of natural orbitals, configurational weights (w_i) and diradical character (n_{rad}) obtained from CASSCF(4,4) and CASSCF(2,2) calculations for symmetrical and deformed structures

Mol.	NOON (n_{occ})				w_1	w_2	n_{rad}
	1a$_1$	**2a**$_1$	**1b**$_2$	**2b**$_2$			
MP2 geometries (symmetrical)							
1a	1.96	1.26 [1.18]	0.74 [0.82]	0.03	0.617 [0.592]	0.343 [0.408]	[57.7]
2a	1.98	1.56 [1.50]	0.44 [0.50]	0.02	0.775 [0.749]	0.213 [0.215]	[35.5]
3	1.98	1.88 [1.86]	0.12 [0.14]	0.02	0.930 [0.929]	0.056 [0.071]	[10.0]
4a	1.97	1.41 [1.34]	0.59 [0.66]	0.02	0.697 [0.670]	0.288 [0.330]	[46.7]
5a	1.98	1.60 [1.53]	0.40 [0.47]	0.02	0.766 [0.765]	0.234 [0.235]	[33.3]
6a	1.98	1.57 [1.51]	0.43 [0.49]	0.02	0.777 [0.754]	0.212 [0.246]	[34.8]
Mol.	**1a**	**2a**	**3a**	**4a**	w_1	w_2	n_{rad}
RB3LYP geometries (deformed except in molecule 3)							
1b	1.96	1.94 [1.95]	0.08 [0.05]	0.03	0.948 [0.977]	0.023 [0.023]	[3.3]
2b	1.95	1.96 [1.95]	0.05 [0.05]	0.04	0.956 [0.977]	0.019 [0.023]	[3.2]
3	1.98	1.88 [1.86]	0.12 [0.14]	0.02	0.931 [0.930]	0.055 [0.070]	[9.9]
4b	1.93	1.96 [1.94]	0.07 [0.06]	0.03	0.949 [0.969]	0.027 [0.031]	[4.4]
5b	1.95	1.92 [1.94]	0.09 [0.06]	0.04	0.938 [0.969]	0.026 [0.031]	[4.4]
6b	1.96	1.93 [1.95]	0.08 [0.05]	0.04	0.944 [0.973]	0.022 [0.027]	[3.8]
Mol.	**1a**$_1$	**2a**$_1$	**1b**$_2$	**2b**$_2$	w_1	w_2	n_{rad}^{a}
CASSCF(4,4) geometries (symmetrical)							
1a	–	–[0.80]	–[1.20]	–	–[0.401]	–[0.599]	[84.7]
2a	1.98	1.32 [1.26]	0.68 [0.74]	0.02	0.653 [0.631]	0.335 [0.369]	[52.3]
3	1.98	1.83 [1.78]	0.17 [0.22]	0.02	0.906 [0.892]	0.082 [0.108]	[15.3]
4a	1.97	1.36 [1.30]	0.65 [0.70]	0.02	0.668 [0.648]	0.316 [0.352]	[49.8]
5a	1.98	1.53 [1.47]	0.47 [0.53]	0.02	0.757 [0.735]	0.228 [0.265]	[37.5]
6a	1.98	1.49 [1.44]	0.51 [0.56]	0.02	0.740 [0.718]	0.249 [0.282]	[39.9]

n_{occ} and w_i obtained at CASSCF(2,2) level of theory are given in square brackets

[a] Calculated for CASSCF(2,2) optimized geometries



Scheme 1 Three most important valence bond structures needed for the description of Si=Si double bond

contribution of “rad” structure and consequently cannot properly describe symmetrical systems. On the other hand, the “zw” structure is the only important configuration obtained for deformed structures, thus having single configuration single determinant character. Such systems can be properly described by the RDFT method and therefore these calculations result in the deformed geometry.

It is important to emphasize that each “ene” and “rad” structure can be described by a single determinant wavefunction, making the system similar to Cremer’s type II diradicals [35]. The wavefunction generated by a broken symmetry approach possesses certain two-configurational character [35] and properly describes such system. On the other hand, the MP2 approach, which is known to overestimate importance of the diradical structures [53], accounts for the contribution of the “rad” structure through the perturbation part leading to the correction of the initial HF wavefunction. Consequently, MP2 approach is able to correctly describe the geometry of the *cis*-pyramidalized disilenes in spite of their high diradical character.

In further analysis of the investigated disilenes, we shall turn to their diradical character (n_{rad}, Table 3). For this purpose, we adopted the approach of Bachler et al. [54] based on the absolute value of the coefficient of the doubly excited configuration (c_D) as given in Eq. 2. For this purpose, c_D coefficients are calculated by the CASSCF(2,2) method at three different optimized structures:

$$n_{rad} = 100|c_D|\sqrt{2} \qquad (2)$$

The diradical character calculated for the symmetrical MP2 structures **1a**, **2a** and **4a**–**6a** varies from 30 to 60%

while for disilene **3** it amounts to 10%. The latter is not surprising in view of the structure and the single configurational character of the CASSCF wavefunction. On the other hand, the diradical character of deformed RDFT structures **1b**, **2b**, **4b–6b** is below 10% what is in accordance with analysis of other descriptors of the CASSCF wavefunction. These numbers prove importance of the "rad" valence structure in description of symmetrical disilenes.

The analysis of the wavefunction in the examines disilenes leads to two main general trends observed: the wavefunction obtained for symmetrically pyramidalized disilenes shows significant two-configurational character and the electronic structures of the deformed disilenes practically reflects a closed shell zwitterionic system without significant diradical character. Consequently, only methods that correctly describe contribution of the diradical structure to the wavefunction will correctly predict their geometry. Our results show strong preference of the RDFT method toward a closed shell zwitterionic Si=Si double bond even when the double bond is not polarized. On the other hand, it is known that MP2 method prefers diradical valence structures [53]. In this respect, the similarity between BS-UDFT, MP2 and CASSCF results is not surprising in spite of the differences in theoretical aspects of the methods.

4 Conclusions

Quantum chemical investigations on the several polycyclic disilenes revealed that annelation of the Si=Si double bond by two small rings or ring systems resulted in *cis*-pyramidalized geometries with the significant diradical character. A strong dependence of the *cis*-pyramidalization of the central Si=Si double bond on the angular strain imposed was observed. Both pyramidalization and diradical character increased in parallel with the increase in strain. These findings were also corroborated by the analysis of the "unstrained" derivative **3** for which *trans*-pyramidalized geometry with weak diradical character was obtained.

Single configurational methods (MP2, BS-UDFT and RDFT) predicted qualitatively different optimal geometries for the *cis*-pyramidalized disilenes—symmetrical "diradicaloid" (MP2 and BS-UDFT) and deformed "zwitterionic" (RDFT) structure. The analysis of the wavefunction obtained for both deformed and symmetrical minima by the CASSCF calculations indicates importance of the diradical valence structures. A well-known fact that spin restricted DFT approach cannot be a suitable method for adequate treatment of "diradicaloid" systems is corroborated. Therefore, the unsymmetrical zwitterionic structures of *cis*-pyramidalized disilenes obtained by RDFT method are mostly artifacts of that computational level. Our results show that for successful modeling of *cis*-pyramidalized disilenes, at least BS-UDFT or MP2 approach is required, but the accuracy of each of these methods is still to be checked with appropriate benchmark calculations in extreme cases. Good example for that is provided by molecule **1** where high strain indeed leads to the unsymmetrical zwitterionic structure what is additionally corroborated by high-level MR-AQCC calculations. The RDFT approach is applicable only in the cases where the angular strain is not pronounced leading to the *trans*-pyramidalization of the Si=Si double bond and/or where the contribution of diradical valence structure is small.

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