Relationship between the Molecular Structure and the π–π* Transition Energy of a Lattice-Framework Disilene: A DFT Study

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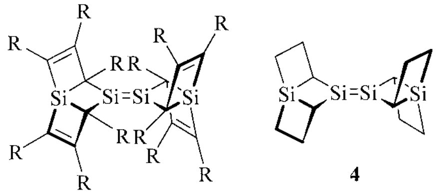
The origin of a significantly red-shifted π–π* transition observed in a unique lattice-framework disilene, 2,3,4,6,7,8,2′,3′,4′,6′,7′,8′-dodeca-*tert*-butyl[5,5′]bi{1,5-disilatricyclo[4.2.0.0^{1,4}]octylidene}-2,7,2′,7′-tetraene, has been elucidated by time-dependent density functional calculations and MO energy calculations. An intramolecular through-space interaction between the $\pi^*_{Si=Si}$ orbital and the $\pi^*_{C=C}$ orbitals in the lattice framework strongly stabilizes the LUMO, resulting in a small HOMO–LUMO energy gap.

Introduction

Silicon–silicon doubly-bonded species (disilenes)[1–4] are pale yellow to red-orange, while carbon–carbon doubly bonded species, such as ethylene, are colorless. The longest wavelength absorptions of disilenes, which correspond to the HOMO–LUMO transition, are generally assigned to the $\pi_{Si=Si}$–$\pi^*_{Si=Si}$ transition and are responsible for the color of the disilenes. It has been postulated that the π–π* transition energy of disilenes is governed by both geometric and electronic effects. For example, steric repulsion caused by the bulkiness of the substituents and electron delocalization between the Si=Si bond and substituents result in a shift of the π–π* absorption wavelength of the disilenes.[4] Substituent effects on the geometry and bond energy of disilenes are of particular interest in theoretical calculations, because of large the differences in the bonding nature between the Si=Si bond and the C=C bond.[5–11] However, to the best of our knowledge, there are few theoretical investigations on the relationship between molecular structures and electron-transition energies of disilenes.[12,13]

Very recently, we reported the synthesis of a novel lattice-framework disilene **1** (Scheme 1).[14] An X-ray crystallographic analysis of **1** reveals that the geometry around the Si=Si bond is almost planar (177.8° for the Si···Si=Si angle) and the Si=Si bond is relatively long (2.262 Å) and slightly twisted (12.1°). Surprisingly, this unique tetraalkyldisilene has the π–π* absorption maximum at 493 nm (2.52 eV) in hexane, which is significantly red-shifted relative to the absorption maximum of tetramethyldisilene (344 nm or 3.60 eV)[15] measured in an argon matrix. The small π–π* transition energy of **1** suggests that the lattice framework surrounding the Si=Si bond should strongly influence the energy levels of the HOMO and LUMO. In this study, to elucidate factors controlling the π–π* transition energy of **1**, we have performed density functional theory (DFT) calculations. The electron transition energies of **1** are evaluated by using a time-dependent DFT (TD-DFT) calculation. The HOMO and LUMO energies of **1** are compared with those of four model disilenes **2**–**5** (Scheme 1).



1: R = *tert*-Butyl
2: R = CH_3
3: R = H

$(H_3C)_2Si{=}Si(CH_3)_2$
5

Scheme 1.

Results and Discussion

As described in our previous report, **1-opt** reproduces the experimental crystal structure of **1** well.[16] The result of the TD-DFT calculation of **1-opt** is shown in Figure 1, together with the experimental UV/Vis absorption spectrum of **1**. It is noteworthy that the TD-B3LYP calculation of **1-opt** with moderate-size basis sets quantitatively reproduce not only

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the positions of the absorption bands but also the relative intensity of the bands.[17] Also, this calculation demonstrates that the longest-wavelength absorption of **1** is assigned to the π–π* transition.

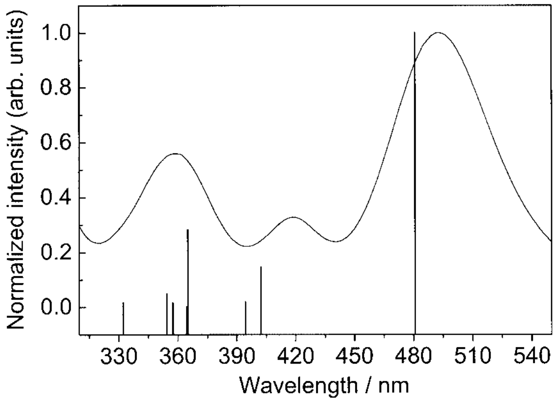

Figure 1. Electron transition energies of **1-opt** calculated by the TD-B3LYP method (vertical line). The UV/Vis spectrum of **1**, in which the intensities are nomalized, is also shown for comparison. Normalized oscillator strengths are used for the calculated intensities.

Although the red-shifted π–π* absorption of **1** was successfully reproduced using the TD-B3LYP method, this calculation does not give information on the factors determining the small π–π* transition energies of **1**. Here we chose four model disilenes **2**–**5** (Scheme 1) and compared the MO energies of the model disilenes with those of **1**. The π–π* transition energies calculated by the TD-B3LYP method are listed in Table 1. The HOMO–LUMO energy gaps (HLGs) as well as the HOMO and LUMO energies are also summarized in Table 1.

Table 1. π–π* transition energies, MO energies, and HOMO–LUMO energy gaps (HLGs) of disilenes **1**–**5** (in eV).

Disilene	π–π* Transition energy[a]	HOMO energy[b]	LUMO energy[b]	HLG
1-fix	2.58[c] (2.52)[d]	–4.18 (0)	–1.24 (0)	2.94
2-fix	2.63	–4.40 (–0.22)	–1.38 (–0.14)	3.03
3-fix	2.56	–4.62 (–0.44)	–1.89 (–0.65)	2.89
4-fix	3.53	–4.77 (–0.59)	–1.15 (+0.09)	3.47
5-fix	4.07	–4.85 (–0.67)	–1.18 (+0.06)	3.67
5-opt	3.45 (3.60)[e]	–4.85 (–0.67)	–1.31 (–0.07)	3.54

[a] Obtained by the TD-B3LYP method. The employed basis sets are described in the text. Experimental values are presented in parentheses. [b] Calculated at the B3LYP/6-311+G(d,p) level. The MO energies relative to **1-fix** are presented in parentheses. [c] Calculated for **1-opt**. [d] Ref.[14] [e] Ref.[15]

Firstly, the result of the DFT calculations for disilenes **1**–**3** are compared in order to evaluate electronic properties depending on the bulkiness of the substituents R (R = *tert*-butyl, CH_3, H). Disilenes **2-fix** and **3-fix** have a structure in which the geometric parameters for the lattice framework are fixed to those of **1-fix**. All the *tert*-butyl groups in **1-fix** are replaced by methyl groups in **2-fix** and by hydrogen atoms in **3-fix**. The π–π* transition energies of **1-fix** (2.58 eV) are almost similar to those of **2-fix** (2.63 eV) and **3-fix** (2.56 eV). The HLGs of these molecules are also very similar to each other, while both the HOMO and LUMO energy levels gradually become lower as the size of the substituents increases in all the molecules. The order of the lowering of the MO energy levels corresponds to the order of the electron-donating ability of the substituents (*tert*-butyl group > methyl group > hydrogen atom). Thus, reducing the size of the substituent R lowers the energy levels of the HOMO and LUMO, whereas it does not change the π–π* transition energy and the HLGs.

Secondly, to discuss how the lattice-framework structure influences the MO energy levels and the π–π* transition energy, the results for **3-fix** are compared with those for **4-fix**, **5-fix** and **5-opt**. Disilene **4-fix** has a lattice-framework structure like **3-fix**, but the C=C bonds are replaced by CH–CH bonds. In **4-fix**, the geometric parameters for doubly bonded silicon atoms and four carbon atoms bound to the silicon atoms are fixed to the parameters of **1-fix** during optimization. Tetramethyldisilene **5-fix** has a structure in which the Si=Si and Si–C bond lengths as well as the C–Si–C bond angle are fixed to those of **1-fix**. The other parameters are optimized in **5-fix**. Tetramethyldisilene **5-opt** has the lowest-energy structure with a trans-bent Si=Si bond.

For a comparison between **3-fix** and **4-fix**, the HLG of **4-fix** (3.47 eV) is significantly larger than that of **3-fix** (2.89 eV), due to the increasing LUMO energy of **4-fix** (+0.71 eV relative to **3-fix**). Thus, the presence of the C=C bonds in the lattice framework is essential for reproducing the small π–π* transition energy observed for **1**. The HOMO and LUMO energies of **4-fix** are calculated to be –4.77 and –1.15 eV, respectively. These values are comparable with the HOMO and LUMO energies of **5-fix** (–4.85 and –1.18 eV, respectively) and **5-opt** (–4.85 and –1.31 eV, respectively). This comparison reveals that geometric changes around the Si=Si bond, such as elongation, flattening, and twisting of the Si=Si bond, play a minor role in changing the HOMO and LUMO energies. Also, replacement of the methyl groups in **5** by the condensed four-membered ring has only a slight influence on the shift in the

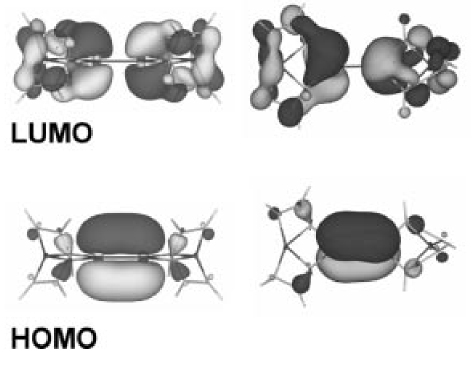

Figure 2. Spatial distribution of the HOMO and LUMO of **3-fix**. Both the side-view (left) and top-view (right; tilted by 60°) images are presented to clarify the interaction between the Si=Si bond and the C=C bonds in the lattice framework.

HOMO and LUMO energies. To explain the large difference in the π–π* transition energy between **3-fix** and **4-fix**, the frontier orbitals of **3-fix** are shown in Figure 2. In the LUMO of **3-fix**, an intramolecular through-space interaction can be found between the Si=Si bond and the four C=C orbitals surrounding the Si=Si bond. The $\pi^*_{C=C}$ orbital overlaps with the $\pi^*_{Si=Si}$ orbitals, as depicted in Figure 3. This π*–π* overlap strongly stabilizes the LUMO of **3-fix**. In the HOMO of **3-fix**, on the other hand, no significant interactions are found between the Si=Si bond and the lattice framework. Because the shape of the frontier orbitals of **1-fix** (or **1-opt**) is almost similar to **3-fix** and the calculated π–π* transition energy of **1-opt** is very close to that of **3-fix**,[18] we can conclude that the stabilization of the LUMO significantly contributes to the small π–π* transition energy of **1**.

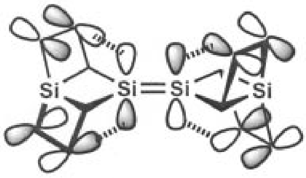

Figure 3. Schematic view of an intramolecular through-space interaction between $\pi^*_{Si=Si}$ and $\pi^*_{C=C}$ orbitals in the LUMO of **1**.

Conclusions

The TD-B3LYP calculation of the lattice-framework disilene **1** combined with moderate-size basis sets quantitatively reproduces the experimental UV/Vis spectrum. The TD-B3LYP calculation would be useful for a full characterization of the electron transitions of "real" disilenes. The red-shifted π–π* absorption maximum observed for **1** can be ascribed to the stabilization of the LUMO. A comparison of the MO energies of **1** and model disilenes **2-5** reveals that an intramolecular through-space interaction between the $\pi^*_{Si=Si}$ and $\pi^*_{C=C}$ orbitals lowers the LUMO energy of **1**. This π*–π* overlap is effectively achieved in **1**, because the four C=C bonds surrounding the Si=Si bond locate nearly perpendicularly to the Si=Si bond. Geometric changes around the Si=Si bond play a minor role in shifting the energy levels of the HOMO and LUMO of **1**.

Computational Methods

All calculations were carried out with the Gaussian98 program.[19] The optimized structure of **1** (**1-opt**) was computed with the B3LYP hybrid functional.[20,21] The 6-31G(d) basis sets were used for the Si and C atoms, except for the atoms consisting of 12 *tert*-butyl groups. For the C and H atoms included in the *tert*-butyl groups, the 3-21G basis sets were employed. The TD-B3LYP calculation[22–25] for **1-opt** was performed at the same level of theory. For model disilenes **2**–**5**, all calculations including the TD calculations were performed at the B3LYP/6-311+G(d,p) level.[25] The MO energies of **1** were also obtained with the B3LYP/6 311+G(d,p) level calculation at the geometry of the experimental crystal structure[14] (represented as **1-fix**). The MO energy calculation of **1** required large basis sets to give converged results, unlike the TD-B3LYP calculation.

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