

# Photoisomerization of Perfluoroaryltetrahedranes to Perfluoroarylcyclobutadienes

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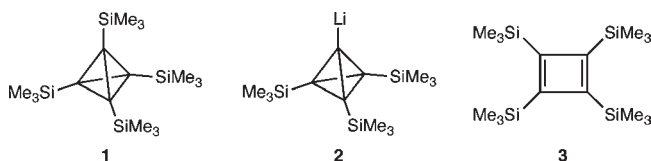
Supporting Information

**ABSTRACT:** Two perfluoroaryl-substituted cyclobutadiene derivatives, **6** and **7**, were prepared as air- and moisture-sensitive red solids by the photochemical isomerization of the corresponding tetrahedranes (**4** and **5**, respectively). Remarkably, the 9,10-dicyanoanthracene-sensitized photochemical reaction of **4** also proceeded, giving **6**, and the mechanism of this reaction is also discussed. The first aryl-substituted cyclobutadienes were characterized by spectroscopic data as well as by X-ray crystallography for **6**, showing a distorted rectangular structure with extremely long C–C single bonds.

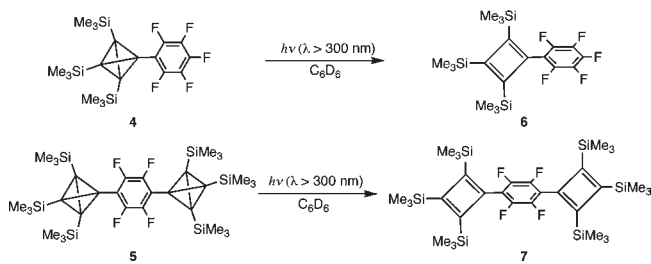
Cyclobutadiene (CBD) is a cyclic unsaturated compound with four  $\pi$ -electrons within a rectangular planar four-membered ring, as found both experimentally and theoretically.<sup>1</sup> CBD is also a valence isomer of the highly strained cage compound, tetrahedrane (THD).<sup>2</sup> The thermal concerted pericyclic isomerization of THD to CBD is a symmetry-forbidden process with a high activation barrier.<sup>3</sup> Despite this, Maier et al. were able to perform the thermal isomerization of tetra-*tert*-butyltetrahedrane to the corresponding CBD at 130 °C.<sup>4</sup> However, they proposed a diradical pathway. The highly strained tetrahedrane skeleton can be sterically and electronically stabilized if the <sup>t</sup>Bu groups are replaced by  $\sigma$ -donating trimethylsilyl groups. Maier and our group succeeded in synthesizing tetrakis(trimethylsilyl)tetrahedrane (**1**) by photochemical isomerization of tetrakis(trimethylsilyl)cyclobutadiene (**3**) (Chart 1).<sup>5</sup> Unlike tetra-*tert*-butyltetrahedrane, **1** is stable up to 300 °C. We have also reported a new procedure for synthesizing **1** by one-electron oxidation of **3** with tris(pentafluorophenyl)borane.<sup>6</sup> Furthermore, we demonstrated that **1** could be transformed into tris(trimethylsilyl)tetrahedranylithium (**2**) by reaction with methylithium (Chart 1).<sup>7</sup> Since then, sulfur-substituted derivatives have been accessible from **2**.<sup>8</sup> Very recently, we also successfully synthesized perfluoroaryl-substituted tetrahedranes **4** and **5**, the first stable aryl-substituted tetrahedranes.<sup>9</sup> As mentioned, the thermal isomerization of THD to CBD is known;<sup>1,4</sup> however, the photochemical isomerization of THD to CBD has remained elusive because of the synthetic difficulty in preparing THD derivatives with a chromophore.

In a previous paper, we reported that X-ray analysis and the UV–vis absorption spectrum of tetrahedranes **4** and **5** suggest there is a  $\sigma$ – $\pi$  conjugation of the strained tetrahedrane core with the benzene ring, which causes a considerable bathochromic shift.<sup>9</sup> Herein, we report the first photochemical isomerization of

**Chart 1.** Tetrakis(trimethylsilyl)tetrahedrane (**1**), Tris(trimethylsilyl)tetrahedranylithium (**2**), and Tetrakis(trimethylsilyl)cyclobutadiene (**3**)



**Scheme 1.** Photoisomerization of Perfluoroaryltetrahedranes **4** and **5** to Perfluoroarylcyclobutadienes **6** and **7**, respectively



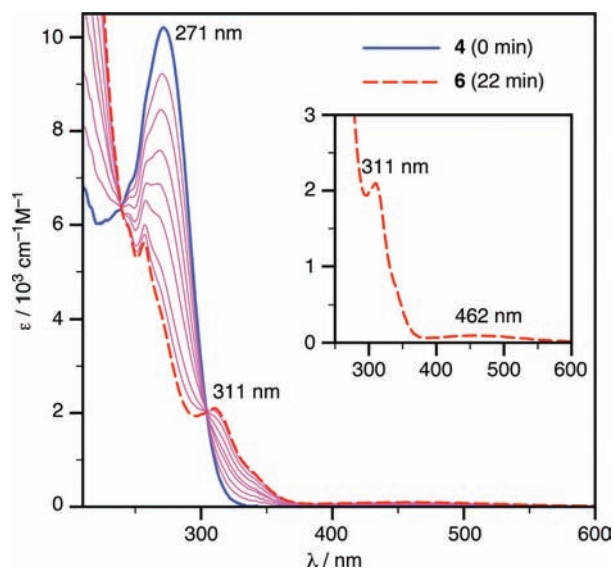
**4** and **5** to the corresponding **6** and **7** by UV irradiation under mild conditions, as well as the electronic spectra of **6** and **7** and the crystal structure of **6**. Notably, **6** and **7** are the first examples of aryl-substituted cyclobutadienes. We also found that **4** isomerized to **6** by 9,10-dicyanoanthracene (DCA)-mediated oxidation, and the mechanism of this reaction is also discussed.

A  $C_6D_6$  solution of **4** was irradiated by a high-pressure mercury lamp ( $\lambda > 300$  nm) at 10 °C. Upon irradiation, the color of the solution immediately changed from pale yellow to red. After 4 h, **4** was quantitatively converted to the corresponding **6** and isolated as air- and moisture-sensitive red crystals in 81% yield (Scheme 1).<sup>10</sup> We examined the solvent effects on the rate of this isomerization. It appears that the reaction is about twice as fast in polar solvents (THF and  $CH_3CN$ ) as in nonpolar hexane (see the Supporting Information). Under similar conditions, bis(tetrahedrane) **5** can be transformed into **7**, which was obtained as air- and moisture-sensitive red crystals in 57% yield.<sup>10</sup>

The photoisomerization of **4** was monitored by UV–vis spectroscopy in hexane. As the intensity of the 271 nm band of **4** decreased, the intensity of a new absorption band at 311 nm

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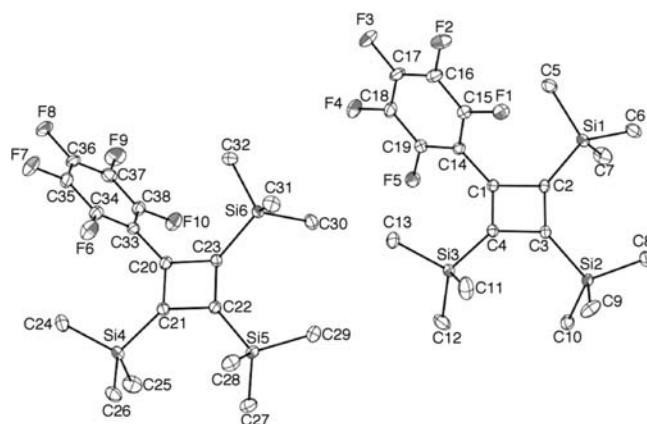


**Figure 1.** UV-vis spectroscopy monitoring of the photoisomerization of **4** to **6** in hexane, measured every minute.

increased, as depicted in Figure 1. The observation of isosbestic points indicates that this isomerization proceeds very cleanly. In addition to the absorption maximum at 311 nm ( $\epsilon = 1900 \text{ M}^{-1} \text{ cm}^{-1}$ ), a fairly weak broad band was observed at 462 nm ( $\epsilon = 90 \text{ M}^{-1} \text{ cm}^{-1}$ ).<sup>11</sup> The UV-vis spectrum of **7** was also measured. Although the shape of the spectrum was almost the same as that of **6**, the absorption maxima at 502 ( $\epsilon = 300 \text{ M}^{-1} \text{ cm}^{-1}$ ), 431 ( $\epsilon = 900 \text{ M}^{-1} \text{ cm}^{-1}$ ), and 340 nm ( $\epsilon = 3900 \text{ M}^{-1} \text{ cm}^{-1}$ ) were red-shifted compared with those of **6**, probably because of the conjugation between the two cyclobutadiene units in **7**.

The characteristic  $^{13}\text{C}$  NMR signals of the cyclobutadiene skeleton were observed at 146.0 ( $\text{C}-\text{C}_6\text{F}_5$ ), 162.7 ( $\text{C}-\text{SiMe}_3$ ), and 168.2 ppm ( $\text{C}-\text{SiMe}_3$ ) for **6** and at 147.6 ( $\text{C}-\text{C}_6\text{F}_4-\text{C}$ ), 162.4 ( $\text{C}-\text{SiMe}_3$ ), and 168.3 ppm ( $\text{C}-\text{SiMe}_3$ ) for **7**, which are considerably downfield-shifted compared with those of the THD skeleton of **4** [ $-17.2$  ( $\text{C}-\text{SiMe}_3$ ) and  $-6.5$  ppm ( $\text{C}-\text{C}_6\text{F}_5$ )] and **5** [ $-17.3$  ( $\text{C}-\text{SiMe}_3$ ) and  $-6.0$  ( $\text{C}-\text{C}_6\text{F}_4-\text{C}$ ) ppm]. The  $^1\text{H}$  NMR signals of the trimethylsilyl groups were observed at  $-0.02$  and  $0.11$  ppm for **6**, and at  $0.04$  and  $0.13$  ppm for **7**, with the integration ratio of 2:1 in both cases. In the  $^{29}\text{Si}$  NMR spectrum, the two signals of the trimethylsilyl groups were observed at  $-14.4$  and  $-13.9$  ppm for **6**, and at  $-14.1$  and  $-13.9$  ppm for **7**. The observation of only two signals for the three trimethylsilyl groups in the  $^1\text{H}$  and  $^{29}\text{Si}$  NMR spectra indicates a fast auto-merization reaction occurring in solution on the NMR time scale.<sup>12</sup> The nucleus-independent chemical shift (NICS) was calculated for the optimized structure (optimized at the B3LYP/6-31G(d) level) of **6** at the GIAO-B3LYP/6-311+G(3d,p) level. The NICS(0) value of 29.1 and the NICS(1) value of 14.7 are indicative of the anti-aromatic character of this compound.<sup>13</sup>

Single crystals of **6** were obtained by recrystallization from toluene. The molecular structure of **6** was determined by X-ray crystallographic analysis, and there are two crystallographically independent molecules (**A** and **B**) of **6** in the unit cell (Figure 2).<sup>10</sup> The cyclobutadiene skeleton has a distorted rectangular structure with C-C bond alternation. The  $\text{C}(\text{sp}^2)-\text{C}(\text{sp}^2)$  single bond lengths of **6** [1.565(2) (C1-C2) and 1.605(2) Å (C3-C4) for **A**, 1.536(3) (C20-C23) and

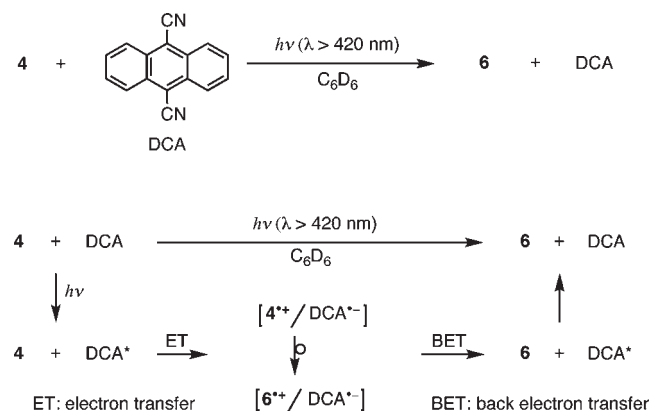


**Figure 2.** ORTEP drawing of **6** (30% thermal ellipsoids). Hydrogen atoms are omitted for clarity. Selected bond lengths (Å) and angles (deg) for molecule **A** (right): C1-C2, 1.565(2); C2-C3, 1.365(3); C3-C4, 1.605(2); C4-C1, 1.350(3); C1-C14, 1.473(3); C2-Si1, 1.8769(19); C3-Si2, 1.8697(19); C4-Si3, 1.8679(19); C4-C1-C2, 93.11(15); C3-C2-C1, 88.62(15); C2-C3-C4, 90.76(14); C1-C4-C3, 87.51(14); C4-C1-C14, 134.91(17); C14-C1-C2, 131.98(16); C3-C2-Si1, 139.07(15); C1-C2-Si1, 132.20(13); C2-C3-Si2, 137.63(15); C4-C3-Si2, 131.60(13); C1-C4-Si3, 133.69(15); C3-C4-Si3, 138.65(14). Selected bond lengths (Å) and angles (deg) for molecule **B** (left): C20-C23, 1.536(3); C23-C22, 1.394(3); C22-C21, 1.580(3); C21-C20, 1.367(3); C20-C33, 1.471(3); C23-Si6, 1.877(2); C22-Si5, 1.857(2); C21-Si4, 1.866(2); C21-C20-C23, 93.09(16); C22-C23-C20, 88.75(15); C23-C22-C21, 90.20(15); C20-C21-C22, 87.94(16); C21-C20-C33, 134.08(18); C33-C20-C23, 132.81(18); C22-C23-Si6, 138.05(15); C20-C23-Si6, 132.95(14); C23-C22-Si5, 138.50(16); C21-C22-Si5, 130.99(14); C20-C21-Si4, 133.04(15); C22-C21-Si4, 138.62(15).

1.580(3) Å (C22-C21) for **B**] are significantly stretched compared with the  $\text{C}(\text{sp}^3)-\text{C}(\text{sp}^3)$  single bond lengths (1.554 Å) of cyclobutane, except for C20-C23.<sup>14</sup> The skeletal single bonds of CBD are known to be quite long from theoretical studies, regardless of the bulkiness of the substituents.<sup>1m</sup> Therefore, the exceptional stretching of the skeletal single bonds of **6** may originate from its antiaromaticity. The  $\text{C}(\text{sp}^2)=\text{C}(\text{sp}^2)$  double bond lengths of **6** [1.365(3) (C2-C3) and 1.350(3) Å (C4-C1) for **A**, 1.394(3) (C23-C22) and 1.367(3) Å (C21-C20) for **B**] are slightly stretched compared with that of cyclobutene (1.335 Å).<sup>14</sup> As a consequence of the different substituents ( $\text{Me}_3\text{Si}$  vs  $\text{C}_6\text{F}_5$ ), the four-membered ring structure in **6** does not show ideal  $D_{2h}$  symmetry but is almost planar. The folding angle of the CBD ring in **6** is  $0.48(2)^\circ$  for **A** and  $1.42(2)^\circ$  for **B**. The presence of an electron-withdrawing group leads to a shortening of the CBD skeletal bond lengths: the bonds with two  $\text{Me}_3\text{Si}$  groups are longer than the bonds adjacent to the electronegative  $\text{C}_6\text{F}_5$  group because of steric and electronic effects. Thus, C2-C3 (1.365(3) Å) in **A** is longer than C4-C1 (1.350(3) Å), and C3-C4 (1.605(2) Å) is longer than C1-C2 (1.565(2) Å). Molecule **B** shows a similar tendency. The dihedral angle between the cyclobutadiene ring and the perfluorophenyl ring is  $58.5^\circ$ , which is attributable to large steric hindrance.

An electron-transfer photoreaction of **4** using DCA as a singlet sensitizer was also carried out. It became apparent that chemical oxidation is also effective for the valence isomerization of **4** to **6**. Because **4** has no absorption bands longer than 350 nm, only DCA can be excited by using longer-wavelength light.<sup>15</sup> A  $\text{C}_6\text{D}_6$  solution of **4** and a catalytic amount of DCA (0.8 mol %) was

**Scheme 2. 9,10-Dicyanoanthracene-Sensitized Isomerization of 4 to 6 and Proposed Mechanism of This Transformation via an Electron-Transfer Reaction**



irradiated ( $\lambda > 420 \text{ nm}$ ) at  $10^\circ \text{C}$ , and **4** was cleanly converted to **6** (93% yield) (Scheme 2). On the other hand, under the same photochemical conditions in the absence of DCA, no **6** was formed. The oxidation potential ( $E_{1/2}^{\text{Ox}}$ ) of **4** (+0.700 V vs Fe/Fe<sup>+</sup>, +1.08 V vs SCE in acetonitrile) is low enough to promote oxidation of **4** with the excited singlet DCA in acetonitrile by electron transfer, as suggested by the calculated free energy change ( $\Delta G_{\text{ET}} = -20.4 \text{ kcal/mol}$ ).<sup>16,17</sup> These results strongly suggest a mechanism that involves initial generation of the cation radical **4**<sup>•+</sup>, which rapidly isomerizes to the cation radical **6**<sup>•+</sup>, as depicted in Scheme 2. This cation radical undergoes back-electron-transfer to the DCA, which yields neutral **6**.<sup>18</sup> According to theoretical calculations at the B3LYP/6-31G(d) level, the cation radical **6**<sup>•+</sup> is 11.8 kcal/mol more stable than the cation radical **4**<sup>•+</sup>, which further confirms this mechanism.

Although the mechanism of the photoinduced valence isomerization of **4** and **5** to **6** and **7**, respectively, shown in Scheme 1, is not certain, we can consider the photoinduced intramolecular electron transfer from the tetrahydrofuran moiety to the perfluorobenzene moiety as the general pathway for this type of transformation. Solvent effects on the rate of photoisomerization of **4** to **6** also support this possibility (see the Supporting Information).

## ASSOCIATED CONTENT

**S** **Supporting Information.** Experimental procedures and spectral data for **6** and **7**, solvent effects on the rate of photoisomerization of **4** to **6**, and tables of crystallographic data, including atomic positional and thermal parameters, and CIF files for **6**. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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- (10) For the experimental procedures, spectral data for **6** and **7**, solvent effects on the rate of photoisomerization of **4** to **6**, and crystal data for **6**, see the Supporting Information.
- (11) TD-DFT calculations at the B3LYP/6-31G(d) level were carried out for the assignment of the absorptions. A weak absorption at 462 nm can be assigned to a HOMO ( $\pi$  of cyclobutadiene)—LUMO ( $\pi^*$  of cyclobutadiene) transition, and the absorption at 311 nm can be assigned to a HOMO ( $\pi$  of cyclobutadiene)—LUMO+1 ( $\pi^*$  of perfluorobenzene) transition.
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- (17) In the intermolecular electron-transfer process, the change in Gibbs free energy,  $\Delta G$ , can be estimated by the following eq:

$$\Delta G_{\text{ET}} = (E_{1/2}^{\text{Ox}} - E_{1/2}^{\text{Red}}) - E_{0-0} - \omega_p \quad (1)$$

where  $E_{1/2}^{\text{Ox}}$  is the half-wave potential of the electron donor's oxidation wave (V),  $E_{1/2}^{\text{Red}}$  is the half-wave potential of the electron acceptor's reduction wave (V),  $E_{0-0}$  is the lowest excitation energy (eV), and  $\omega_p$  ( $= e^2/\epsilon r$ ) is a coulomb term (eV). The cyclic voltammetry of **4** in acetonitrile containing 0.1 M  $[n\text{-Bu}_4\text{N}]^+\text{ClO}_4^-$  was measured. An irreversible oxidation wave was observed, and the peak potential of the oxidation wave was used instead of  $E_{1/2}^{\text{Ox}}$ . The values of  $E_{1/2}^{\text{Red}}$  ( $-0.950$  V vs SCE),  $E_{0-0}$  (2.91 eV), and  $\omega_p$  ( $\approx 0.00$  V) in acetonitrile were taken from the following references: (a) Gould, I. R.; Ege, D.; Moser, J. E.; Farid, S. *J. Am. Chem. Soc.* **1990**, *112*, 4290. (b) Ikeda, H.; Akiyama, K.; Takahashi, Y.; Nakamura, T.; Ishizaki, S.; Shiratori, Y.; Ohaku, H.; Goodman, J. L.; Houmam, A.; Wayner, D. D. M.; Tero-Kubota, S.; Miyashi, T. *J. Am. Chem. Soc.* **2003**, *125*, 9147.

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