J|A|C|S
COMMUNICATIONS

Perfluoroaryltetrahedranes: Tetrahedranes with Extended σ–π Conjugation

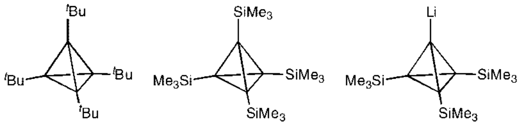
Masaaki Nakamoto, Yusuke Inagaki, Motoaki Nishina, and Akira Sekiguchi*

Department of Chemistry, Graduate School of Pure and Applied Sciences, University of Tsukuba, Tsukuba, Ibaraki 305-8571, Japan

Received December 25, 2008; E-mail: sekiguch@chem.tsukuba.ac.jp

Tetrahedrane (tricyclo[1.1.0.0^{2,4}]butane) is one of the most strained organic molecules, containing four cyclopropane rings in a fused system.[1] The parent tetrahedrane is thermodynamically unstable and is still an unknown compound, even under matrix-isolation conditions; however, its derivatives with four bulky, σ-donating substituents have been isolated (Chart 1). In 1978, Maier and co-workers succeeded in synthesizing tetrakis(*tert*-butyl)tetrahedrane (**1**),[2] in which the four bulky ^{t}Bu substituents kinetically stabilize the tetrahedrane skeleton against ring-opening bond cleavage. However, when one of the ^{t}Bu substituents in **1** was replaced by a smaller group, such as a phenyl or methyl group, tetrahedrane derivatives were not detected, even at low temperature.[1] However, the highly strained tetrahedrane skeleton can be sterically and electronically stabilized if the ^{t}Bu groups are replaced by σ-donating groups, such as trimethylsilyl groups. Thus, Maier and we succeeded in synthesizing tetrakis(trimethylsilyl)tetrahedrane (**2**),[3,4a] which is stable up to 300 °C, by the photochemical isomerization of tetrakis(trimethylsilyl)cyclobutadiene.[4,5] Furthermore, we demonstrated that compound **2** could be transformed into tris(trimethylsilyl)tetrahedranyllithium **3**,[6] which reacts with a variety of electrophiles to give isolable substituted tetrahedranes with H and Me as substituents.[6] Recently, we also reported the synthesis of hexakis(trimethylsilyl)tetrahedranyltetrahedrane,[7] which has a very short linking C−C bond [1.436(3) Å] resulting from the high s-character of the central bond, by the oxidative coupling of **3** using CuCN.

Chart 1

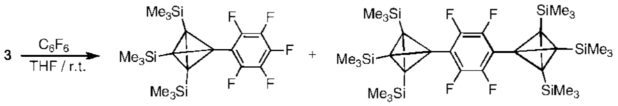


1 **2** **3**

Because tetrahedrane has an extremely strained skeleton, the ring strain raises the energy levels of the C−C σ-bond orbitals.[1,8] Therefore, σ–π conjugation between the tetrahedrane σ framework and the adjacent π-orbital system would be expected. However, all attempts to prepare aryl-substituted tetrahedranes have been unsuccessful, and no report of a stable tetrahedrane with a π system, such as a phenyl group, has appeared. Herein, we report a simple and straightforward method for the synthesis of three perfluoroaryl-substituted tetrahedranes, **4**–**6**, which are the first stable aryl-substituted tetrahedrane derivatives; **4**–**6** have been characterized by NMR spectroscopy and **4** and **6** by X-ray diffraction. We also report the unusual electronic properties of these tetrahedranes, which are caused by σ–π conjugation between the strained tetrahedrane core and the aromatic ring.

A 10-fold excess of hexafluorobenzene was added at room temperature to a solution of **3** in THF. The reaction occurred immediately, and the reaction mixture turned from the dark-brown solution of **3** to black. The reaction mixture was separated by HPLC to give the two products **4** and **5** as colorless crystals in 36 and 25% isolated yields, respectively (Scheme 1).[9] The second substitution to produce **5** occurred regioselectively at the para position, as expected in view of the fact that the nucleophilic aromatic substitution reactions of many nucleophiles with hexafluorobenzene proceed regioselectively at the 1 and 4 positions.[10] Because the second substitution is faster than the first, it was difficult to obtain **4** selectively, even when a large excess of hexafluorobenzene was used. Both of the compounds **4** and **5** are stable in air and at temperatures of up to 170 °C.

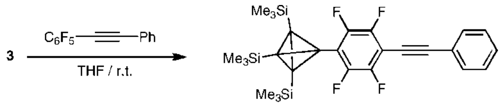
Scheme 1



4 **5**

The tetrahedrane unit could also be introduced into an extended π-conjugation system of the phenylene−ethynylene type by the same method as for the reaction of **3** with hexafluorobenzene. Thus, tetrahedranyllithium **3** was treated with [(pentafluorophenyl)ethynyl]benzene in THF to give the product **6** in 31% isolated yield; **6** is stable in air and has a melting point of 73.5−75.5 °C (Scheme 2).[9] As expected, the substitution reaction took place at the position para to the ethynyl group.

Scheme 2



6

The ^{13}C NMR signals of the tetrahedrane skeleton were observed at −6.5 ppm (C−C$_6$F$_5$) and −17.2 ppm (C−SiMe$_3$) for **4**; −6.0 ppm (C−C$_6$F$_4$) and −17.3 ppm (C−SiMe$_3$) for **5**; and −4.7 ppm (C−C$_6$F$_4$) and −15.5 ppm (C−SiMe$_3$) for **6**. Although an upfield shift of the skeletal C atoms is typical for tetrahedrane,[2,3] significant downfield shifts relative to **2** (−20.5 ppm) and **3** [−27.0 ppm (ring C−Li) and −22.0 ppm (ring C)] were observed for the aryl-substituted carbon atom: +14.0 ppm for **4**, +14.5 ppm for **5**, and +15.8 ppm for **6** relative to **2**.[3] These remarkable downfield NMR chemical shifts could be attributed to the considerable electronic effect of the perfluoroaryl group on the tetrahedrane skeleton.

The molecular structure of **4**, as determined by X-ray crystallographic analysis, is shown in Figure 1.[9] The C1(tetrahedrane skeleton)−C14(ipso-C of C$_6$F$_5$) bond length is 1.450(2) Å, which is significantly shorter than the typical C(sp^3)−C(sp^2) single-bond length (1.507 Å).[11] The bond shortening of the C1−C14 bond indicates the σ–π conjugation between the highly strained tetrahedrane framework and the benzene ring (seen in HOMO−3). The

10.1021/ja810055w CCC: $40.75

calculated s character of the C1−C14 bond at the NBO/B3LYP/6-31G(d) level is $sp^{1.57}$. As a consequence of the difference in the electronegativity of the substituents (Me_3Si vs C_6F_5), the core structure in **4** does not show ideal T_d symmetry. Thus, the $C(C_6F_5)-C(SiMe_3)$ bond lengths (C1−C2, C1−C3, and C1−C4) in **4** range from 1.475(2) to 1.504(2) Å [av 1.485(2) Å], whereas the $C(SiMe_3)-C(SiMe_3)$ bond lengths (C2−C3, C2−C4, and C3−C4) range from 1.504(2) to 1.524(2) Å [av 1.512(2) Å]. Obviously, the presence of an electron-withdrawing group leads to a shortening of the tetrahedrane bond lengths [av 1.485(2) vs av 1.512(2) Å]. It should be noted that the distorted core of **3** shows the opposite behavior: that is, the $C(Li)-C(SiMe_3)$ bond lengths are longer [av 1.543(2) Å] than the others [av 1.499(2) Å].[6]

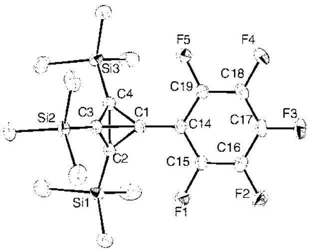


Figure 1. ORTEP drawing of **4** (30% probability level). Hydrogen atoms have been omitted for clarity. Selected bond lengths (Å): C1−C14, 1.450(2); C1−C2, 1.475(2); C1−C3, 1.504(2); C1−C4, 1.475(2); C2−C3, 1.507(2); C2−C4, 1.524(2); C3−C4, 1.504(2); Si1−C2, 1.8363(17); Si2−C3, 1.8327(18); Si3−C4, 1.8377(18). Selected bond angles (deg): C2−C1−C3, 60.80(11); C2−C1−C4, 62.21(12); C3−C1−C4, 60.65(11); C3−C2−C4, 59.51(11); C2−C3−C4, 60.79(11); C2−C4−C3, 59.70(11).

We also carried out the X-ray analysis of **6** and found that its tetrahedrane core structure is quite similar to that of **4** (Figure 2).[9] The C1(tetrahedrane skeleton)−C14(ipso-C of C_6F_4) bond length is 1.438(2) Å in **6**.

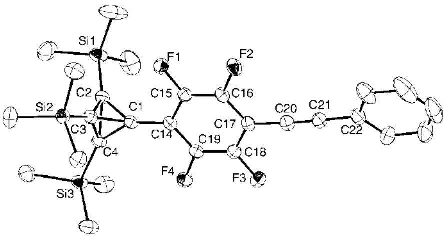


Figure 2. ORTEP drawing of **6** (30% probability level). Hydrogen atoms have been omitted for clarity. Selected bond lengths (Å): C1−C14, 1.438(2); C1−C2, 1.497(2); C1−C3, 1.501(2); C1−C4, 1.463(2); C2−C3, 1.491(2); C2−C4, 1.527(2); C3−C4, 1.523(2); Si1−C2, 1.8328(17); Si2−C3, 1.8277(16); Si3−C4, 1.8337(16); C20−C21, 1.195(2). Selected bond angles (deg): C2−C1−C3, 59.65(10); C2−C1−C4, 62.11(11); C3−C1−C4, 61.82(10); C3−C2−C4, 60.60(10); C2−C3−C4, 60.86(11); C2−C4−C3, 58.53(10).

The HOMO−3 (bonding interaction) and HOMO (antibonding interaction) of **4** calculated at the B3LYP/6-31G(d) level are shown in Figure 3. The tetrahedrane has two higher-energy σ orbitals, which are degenerate because of the highly symmetric structure.[12] The two σ orbitals can conjugate with the π orbital (Ψ_s) of the benzene ring to form two conformational isomers (one coplanar with and one perpendicular to the benzene ring); $\sigma-\pi$ conjugation over the tetrahedrane unit and benzene ring can be achieved in both cases (see the Supporting Information), but the energy difference of the two conformers is very small.[13]

The extended $\sigma-\pi$ conjugation in **4**−**6** is reflected in the electronic spectra (Figure 4). The absorption maxima of the UV−vis absorption spectra of **4**, **5**, and **6** in hexane were observed at 271 nm ($\varepsilon = 6200\ cm^{-1}\ M^{-1}$) for **4**, 303 nm ($\varepsilon = 9600\ cm^{-1}\ M^{-1}$) for **5**, and 324 nm ($\varepsilon = 30\,500\ cm^{-1}\ M^{-1}$) for **6**. The considerable bathochromic shift of **4**−**6** relative to hexafluorobenzene ($\lambda_{max} = 231$ nm)[14] could serve as evidence for $\sigma-\pi$ conjugation between the tetrahedrane σ framework and the perfluoroaryl π system.

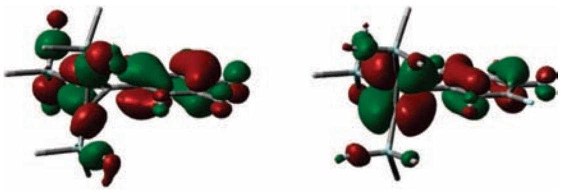


Figure 3. (left) HOMO−3 and (right) HOMO of **4** calculated at the B3LYP/6-31G(d) level.

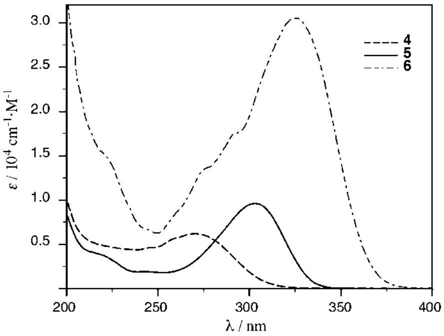


Figure 4. UV−vis spectra of **4**−**6** in hexane.

Supporting Information Available: Experimental procedures and spectral data for **4**, **5**, and **6**, computational results and MO diagram for **4**, and tables of crystallographic data, including atomic positions and thermal parameters, and CIF files for **4** and **6**. This material is available free of charge via the Internet at http://pubs.acs.org.

References

(1) For reviews on tetrahedrane, see: (a) Maier, G. *Angew. Chem., Int. Ed. Engl.* **1988**, *27*, 309. (b) Maier, G. *Pure Appl. Chem.* **1991**, *63*, 275. (c) Lee, V. Ya.; Sekiguchi, A. In *Strained Hydrocarbons*; Dodziuk, H., Ed.; Wiley-VCH: Weinheim, Germany, 2009; Chapter 2.
(2) (a) Maier, G.; Pfriem, S.; Schäfer, U.; Matusch, R. *Angew. Chem., Int. Ed. Engl.* **1978**, *17*, 520. (b) Maier, G.; Pfriem, S.; Schäfer, U.; Malsch, K.-D.; Matusch, R. *Chem. Ber.* **1981**, *114*, 3965.
(3) Maier, G.; Nuedert, J.; Wolf, O.; Pappusch, D.; Sekiguchi, A.; Tanaka, M.; Matsuo, T. *J. Am. Chem. Soc.* **2002**, *124*, 13819.
(4) (a) Maier, G.; Neudert, J.; Wolf, O. *Angew. Chem., Int. Ed.* **2001**, *40*, 1674. (b) Sekiguchi, A.; Tanaka, M.; Matsuo, T.; Watanabe, H. *Angew. Chem., Int. Ed.* **2001**, *40*, 1675.
(5) For recent reviews of silyl-substituted cyclobutadienes, see: (a) Matsuo, T.; Sekiguchi, A. *Bull. Chem. Soc. Jpn.* **2004**, *77*, 211. (b) Sekiguchi, A.; Matsuo, T. *Synlett* **2006**, 2683.
(6) Sekiguchi, A.; Tanaka, M. *J. Am. Chem. Soc.* **2003**, *125*, 12684.
(7) Tanaka, M.; Sekiguchi, A. *Angew. Chem., Int. Ed.* **2005**, *44*, 5821.
(8) (a) Mo, Y. *Org. Lett.* **2006**, *8*, 535. (b) Nemirowski, A.; Reisenauer, H. P.; Schreiner, P. R. *Chem.—Eur. J.* **2006**, *12*, 7411.
(9) For experimental procedures and spectral data for **4**−**6** and crystal data for **4** and **6**, see the Supporting Information.
(10) Brooke, G. M. *J. Organomet. Chem.* **1977**, *86*, 1.
(11) Allen, F. H.; Kennard, O.; Watson, D. G.; Brammer, L.; Orpen, A. G.; Taylor, R. *J. Chem. Soc., Perkin Trans. 2* **1987**, S1.
(12) Heilbronner, E.; Jones, T. B.; Krebs, A.; Maier, G.; Malsch, K.-D.; Pocklington, J.; Schmelzer, A. *J. Am. Chem. Soc.* **1980**, *102*, 564.
(13) One of the edges (the C1−C3 bond) of the tetrahedrane skeleton in **4** is perpendicular to the benzene ring: the dihedral angles C15−C14−C1−C3 and C19−C14−C1−C3 are 89.4(3) and−91.6(3)°, respectively. On the other hand, one of the edges of the tetrahedrane skeleton in **6** was found to be almost coplanar to the benzene ring: the dihedral angles C15−C14−C1−C4 and C19−C14−C1−C4 are 173.5(4) and−6.8(2)°, respectively. DFT calculations of the barrier for rotation about the C1−C14 single bond in **4** at the B3LYP/6-31G(d) level indicated that the energy difference of the two conformers is very small (0.75 kcal/mol). The slightly less favorable perpendicular structure in **4** found from the X-ray analysis (see Figure 1) may be due to crystal-packing forces.
(14) Saik, V. O.; Lipsky, S. *J. Phys. Chem. A* **2001**, *105*, 10107.

JA810055W