

Synthesis and Characterization of Tetrakis-Silylated C₆₀ Isomers

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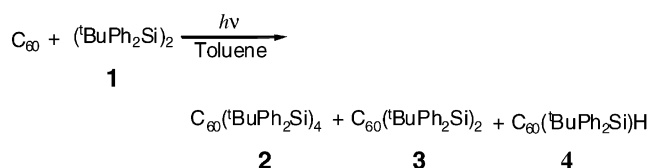
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Abstract: A photochemical reaction of C₆₀ with disilane in a 2:3 ratio affords the isomer mixture of the tetrakis-adduct of C₆₀(^tBuPh₂Si)₄ as the major product. The use of a three-stage HPLC separation system isolated three of their isomers. Their structural assignments were based on FAB mass, UV-vis, NMR, and cyclic voltammetry (CV) measurements. The CV analysis showed that the tetrakis-adduct has lower oxidation and higher reduction potentials than the bis-adduct C₆₀(^tBuPh₂Si)₂ and the parent C₆₀.

Much attention has focused on the chemical derivatization of C₆₀, the third allotropic form of carbon.¹ C₆₀ can be derivatized three-dimensionally, and hence, the derivatives possess some specific electronic and optical properties.² The electrochemical properties of C₆₀ are affected by the nature, number, and position of the addends.³ C₆₀ is known as a good electron acceptor.⁴ Meanwhile, disilane can act as an electron donor.⁵ We found that the combination of C₆₀ and disilane produces a new class of silylfullerenes,⁶ which have lower oxidation and higher reduction potentials than the analogous

SCHEME 1



carbon-substituted derivatives as well as C₆₀ itself.⁷ We also reported the preparation of the bis-silylated 1,6-adduct of C₆₀, which consists of lower oxidation and higher reduction potentials than the 1,2- and 1,4-silylated adducts.⁸ Multisilylated 1,6-adduct would possess more exciting electronic properties. We now report the preparation and characterization of the tetrakis-silylated 1,6-adduct of C₆₀.

Photo-irradiation of a toluene solution of C₆₀ (0.2 mM) and 1,1,2,2-tetraphenyl-1,2-di-*tert*-butyl-1,2-disilane (**1**,⁹ 0.3 mM) in a degassed quartz tube with a low-pressure mercury-arc lamp afforded the tetra-adduct **2** in moderate yield along with two minor products, bis-**3**⁸ and the mono-adduct **4**¹⁰ (Scheme 1).

Figure 1 illustrates the HPLC profile for the separation of the tetrakis-adduct isomers. The products **2** were isolated in 12.5% yield from fraction no.1 as a mixture of the isomeric form by using a Buckyclutcher column with a mixture of toluene and hexane (1:5). A Buckyclutcher column readily isolated the derivative **2b** (36%), while it was very difficult to separate **2a** and **2c** at this stage. A gel permeation chromatographic separation was performed to separate **2a** (15%) and **2c** (49%) with a series of Jaigel 1H + 2H columns using toluene as the eluent. The FAB mass analysis of three isomers of the tetrakis-adduct exhibits a peak at *m/z* 1683–1676 for C₁₂₄H₇₆Si₄ with two other peaks at *m/z* 1442–1438 for C₁₀₈H₅₇Si₃ and 723–720 for C₆₀. The latter peaks appeared to be due to the loss of one and four ^tBuPh₂Si groups from C₆₀(^tBuPh₂Si)₄, respectively.

The ¹H NMR spectrum of **2a** displays one *tert*-butyl signal at 1.51 ppm and two sets of multiplet signals between 8.5 and 7.0 ppm. The ¹³C NMR spectrum of **2a** displays 15 signals in an almost equal intensity for the carbons on C₆₀, indicative of C_{2h} symmetry for the molecule. The ¹H NMR spectrum of **2b** consists of two *tert*-butyl signals at 1.47 and 1.35 ppm along with two sets of multiplet signals in the aromatic region. The ¹³C NMR spectrum of **2b** shows 30 signals corresponding to the skeletal carbons of C₆₀, which suggests that **2b** has a C₂ symmetry. The ¹H NMR spectrum of compound **2c** gives three peaks at 1.43, 1.35, and 1.26 ppm (the ratio of their intensities is 2:1:1) for the ^tBu groups and two

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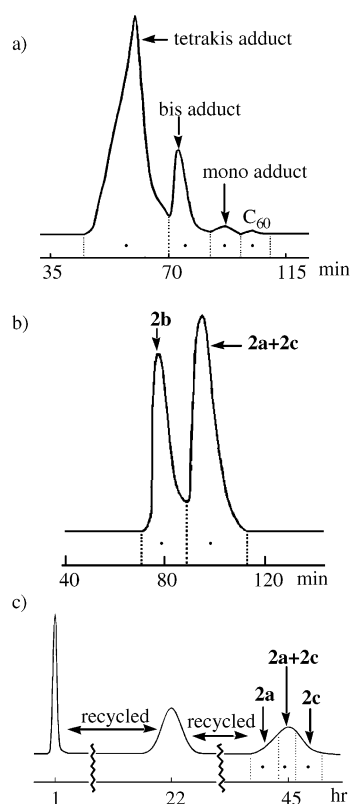


FIGURE 1. Three-stage HPLC separation of tetrakis-silylated C_{60} isomers: (a) reaction mixture; (b) fraction 1; (c) fraction 6.

TABLE 1. Relative Energies and the Number of Double Bonds at the 5,6-Junction of Possible Tetrakis Isomers

isomer	symmetry ^a	no. of double bonds at 5,6-junction	rel energy ^b
A (1, 16, 43, 56)	C_{2h}	4	0.0
B (1, 16, 38, 56)	C_2	4	1.1
C (1, 16, 27, 41)	C_1	4	4.7
D (1, 16, 39, 44)	C_2	4	9.6
E (1, 16, 23, 53)	C_2	4	11.2
F (1, 16, 42, 57)	D_2	4	12.8
G (1, 16, 25, 47)	C_1	4	15.3

^a The symmetries with free rotation of $Si(Ph)_2Bu$ groups.

^b Calculated at the AM1 level.

sets of multiplet signals from 8.5 to 7.0 ppm. Its ^{13}C NMR spectrum shows 55 sp^2 resonances in the fullerene region (one has a relative intensity of 2) with four sp^3 carbons, supporting the theory that **2c** has C_1 symmetry.

The addition of two bulky $tBuPh_2Si$ groups on the C_{60} cage at the 1,2- and 1,4-positions can be ruled out due to the steric hindrance.⁸ In this context, the 1,6-addition mode in $C_{60}(tBuPh_2Si)_2$ is the most stable among the 1,2-, 1,4-, and 1,6-additions⁸ (Schlegel diagram's 1,16- and 1,29-addition positions are labeled the 1,6-addition). Consequently, it is undoubtedly certain that the 1,6-addition affords the tetrakis-adduct. The clue to understanding the structures of **2a–c** can be provided from the AM1 molecular orbital calculation¹¹ of seven possible isomers of tetrakis-silylated C_{60} derivatives. Table 1 shows seven isomers of $(tBuPh_2Si)_4C_{60}$ accompanied by the corresponding relative energies, symmetry, and the

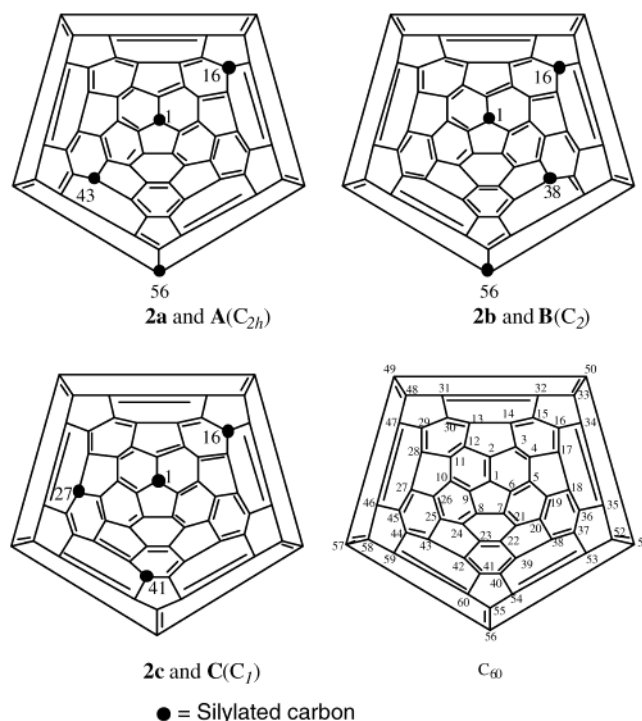


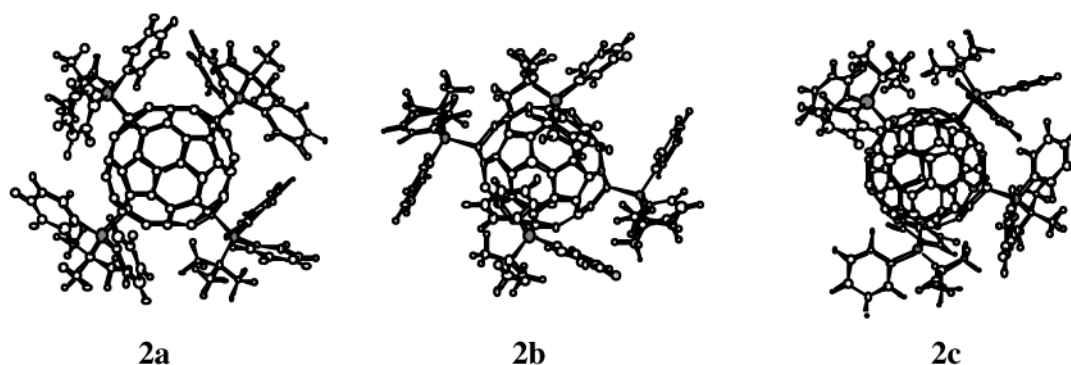
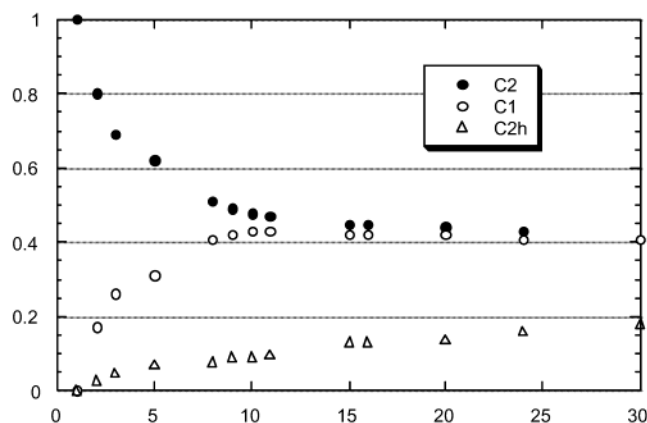
FIGURE 2. Schlegel diagram of tetrakis isomers **2a–c**, **A–C**, and C_{60} .

number of double bonds at the 5,6-junction. Isomer **A** is found to be the most stable among these isomers. Although isomer **B** is 1.1 kcal/mol less stable than **A**, it is the most stable of the isomers which have C_2 symmetry. Isomer **C** is less stable than **A** and **B**, but **C** is more stable than **G**. On the basis of these observations, **2a–c** may correspond to isomers **A**, **B**, and **C**, which have C_{2h} , C_2 , and C_1 symmetries, respectively. Figure 2 shows the Schlegel diagrams of isomers **A**, **B**, and **C**, and the optimized structures of the **2a–c** are shown in Figure 3.

The tetrakis-adduct isomers **2a–c** are very stable and can be stored several months in the solid state, but in solution, it has been found to undergo a facile migration process which leads to the formation of a mixture of the tetrakis-adduct isomers from each individual isomer. For example, the **2b**(C_2) isomer gives an isomer mixture within 1 month at room temperature as shown in Figure 4. The migration process proceeds under air, suggesting that the migration might take place in a concerted manner.

Table 2 summarizes the redox behaviors of C_{60} , **2a–c**, and the bis-silylated compounds, **3**, **5**, and **6**, recorded in 1,2-dichlorobenzene. The isomers **2a** and **2b** have two reversible reduction and two irreversible oxidation potentials, whereas **2c** shows three reversible reduction and two oxidation potentials. These isomers reveal very similar oxidation and reduction potentials. There are two salient features for the tetrakis-adduct isomers. (1) **2a–c** have lower oxidation potentials than any of the other silylated C_{60} derivatives. To the best of our knowledge, the silylated C_{60} derivatives show the lowest oxidation potentials of the previously reported C_{60} 's.^{8,12} These observations indicate that tetrakis-silylation is very effective for increasing the electron donor ability of C_{60} . (2) Although the bis-silylated fullerenes **3**, **5**, and **6** have only

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FIGURE 3. Optimized structures of **2a–c**.FIGURE 4. Isomerization of **2b** in $\text{CS}_2/\text{CDCl}_3$ at room temperature.

one low oxidation potential, the second oxidation potentials of **2a–c** are also very low. We recently reported that the 1,6-bis-silylated C_{60} **3**, due to its unique structure, has a lower oxidation potential than that of the 1,2- or 1,4-bis-silylated C_{60} . The 1,6-addition to the C_{60} cage produces a highly strained dihydronaphthalene frame, where two short double bonds lie between the pentagon and the hexagon of the 1,6-adduct. This strain energy can be released in its cationic form. All the tetrakis-adducts **2** have two strained dihydronaphthalene frames on the fullerene cage. These dihydronaphthalene frames must exist independently, because the tetrakis-adduct **2** has two lower oxidation potentials. On the other hand, the reduction potential of **2b** is cathodically shifted in comparison to **3**, which suggests that the introduction of four silyl groups results in a decreasing electron-accepting property. These lower oxidation and higher reduction potentials are due to the influence of the four short double bonds on the C_{60} cage for each isomer as mentioned above.

In conclusion, it has been demonstrated that the tetrakis-silylation of C_{60} readily takes place by a silyl radical photochemically generated from the simple disilane.^{8,14}

TABLE 2. Redox Potentials of C_{60} , **2a–c**, **3**, **5**, and **6**

3

5

6

Dep = 2,6-diethylphenyl

compd	oxE ₂ ^{b,c}	oxE ₁ ^{b,c}	redE ₁	redE ₂	redE ₃
2a	+0.38	+0.24	−1.20	−1.67	
2b	+0.40	+0.22	−1.41	−1.78	
2c	+0.41	+0.22	−1.24	−1.69	−2.19
3 ^d	+1.20	+0.33	−1.19	−1.59	−2.18
5 ^d	+1.26	+0.73	−1.22	−1.61	−2.12
6 ^d	+1.22	+0.60	−1.29	−1.67	−2.18
C_{60}		+1.21	−1.12	−1.50	−1.95

^a Values are relative to ferrocene/ferrocenium couple. Conditions: 0.1 M (*n*-Bu)₄NPF₆ in 1,2-dichlorobenzene; working electrode, Pt wire as working and counter electrode; reference electrode, Ag/0.01 M AgNO₃ and 0.1 M (*n*-Bu)₄NClO₄ in CH₃CN. CV: scan rate, 20 mV/s. ^b Irreversible. ^c Values were obtained by DPV: pulse amplitude, 50 mV; pulse width, 50 ms; pulse period, 200 ms; scan rate, 20 mV/s. ^d Reference 8.

The redox properties of C_{60} can be controlled not only by the electronegativity of the substituents and regiochemistry of its functionality but also by the number of substituents.¹⁵ It is expected that the thus-derivatized fullerene, which is endowed with a strikingly low oxidation potential, opens up a new application of C_{60} as an electron donor.

Experimental Section

A three-stage HPLC separation technique was applied to isolate three tetrakis-adduct isomers. In the first stage, a gel

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permeation chromatographic separation was performed on a preparative HPLC with a series of Jaigel 1H + 2H columns (Japan Analytical Industry Co., Ltd.) to separate the tetrakis-adduct mixture from minor products. In the second stage, the purification of **2b** was achieved by Buckyclutcher column (Regis, Morton Grove, IL: 21 500 mm) with a 1:5 v/v mixture of toluene/hexane as eluent. In the third stage, the purification of **2a** and **2c** were accomplished on a GPC column. In first and third stages, toluene was used as eluent.

Cyclic voltammetric and differential pulse voltammetric (DPV) measurements were carried out at 1 mM concentration in an *o*-dichlorobenzene solution with 0.1 M supporting electrode (*n*-Bu)₄NPF₆; platinum wire was used as working and counter electrode; a Ag/AgNO₃ (CH₃CN) was used as the reference electrode. Ferrocene (0.5 mM) was added as an internal reference. The scan rate was 20 mV/s. The scan rate was 20 mV/s. Pulse amplitude, pulse width, and pulse period were 50 mV, 50 ms, and 200 ms, respectively.

Geometries were fully optimized with the semiempirical AM1 method¹¹ using the Gaussian 98 program.¹³

Photolysis of 1,1,2,2-Tetraphenyl-1,2-di-*tert*-butyldisilane (1a) with C₆₀. A toluene solution (38 mL) of C₆₀ (144 mg, 0.2 mmol) and **1a** (143 mg, 0.3 mmol) was irradiated with a low-pressure mercury-arc lamp for 2 h. The tetrakis-adduct isomers were isolated by preparative HPLC in 12.5% yield.

Compound **2a**: dark brown solid; ¹H NMR (CDCl₃) δ 8.10–8.05 (m, 16 H), 7.40–7.30 (m, 24 H), 1.51 (s, 36 H); ¹³C NMR (CDCl₃) δ 168.94 (s), 160.32 (s), 155.35 (s), 149.61 (s), 148.08 (s), 145.69 (s), 144.92 (s), 143.05 (s), 142.98 (s), 139.75 (s), 139.65 (s), 137.87 (s), 137.66 (s), 137.56 (d), 137.37 (d), 137.07 (d), 132.54 (s), 129.78 (d), 129.66 (d), 127.39 (d), 127.30 (d), 65.27 (s), 29.19 (q), 22.28 (s); ²⁹Si NMR (CDCl₃) δ –4.30; UV–vis (λ_{max}, toluene) 467, 556 nm; FABMS (toluene/NBA) *m/z* 1676 (M), 720 (C₆₀); symmetry C_{2h}. Compound **2b**: dark brown solid; ¹H NMR (CDCl₃) δ 8.00–7.78 (m, 16 H), 7.42–7.24 (m, 24 H), 1.47 (s, 18 H), 1.35 (s, 18 H); ¹³C NMR (CDCl₃) δ 166.90 (s), 160.57 (s), 158.87 (s), 157.74 (s), 152.22 (s), 152.14 (s), 151.79 (s), 150.43 (s), 148.13 (s), 147.04 (s), 146.27 (s), 145.00 (s), 144.92 (s), 144.80

(s), 144.25 (s), 142.81 (s), 142.43 (s), 142.35 (s), 141.32 (s), 140.79 (s), 138.55 (s), 138.37 (s), 138.02 (s), 137.47 (d), 137.31 (d), 137.29 (d), 137.11 (d), 135.89 (s), 135.70 (s), 135.45 (s), 134.37 (s), 129.80 (d), 129.73 (d), 129.57 (d), 127.44 (d), 127.35 (d), 127.28 (d), 127.10 (d), 62.55 (s), 61.68 (s), 29.16 (q), 29.05 (q), 22.08 (s), 21.76 (s); ²⁹Si NMR (CS₂/CDCl₃/99.3 MHz) δ –3.12, –4.80; UV–vis (λ_{max}, toluene) 469, 505, 586 nm; FABMS (toluene/NBA) *m/z* 1676 (M), 720 (C₆₀); symmetry C₂. Compound **2c**: dark brown solid; ¹H NMR (CDCl₃) δ 8.11–7.81 (m, 16 H), 7.41–7.27 (m, 24 H), 1.43 (s, 18 H), 1.31 (s, 9 H), 1.25 (s, 9 H); ¹³C NMR (CDCl₃) δ 170.82 (s), 170.00 (s), 168.26 (s), 166.21 (s), 161.61 (s), 160.83 (s), 160.74 (s), 157.88 (s), 155.60 (s), 152.85 (s), 152.59 (s), 152.22 (s), 150.53 (s), 150.12 (s), 150.06 (s), 149.68 (s), 148.87 (s), 148.50 (s), 148.10 (s), 147.86 (s), 147.69 (s), 147.36 (s), 146.99 (s), 146.95 (s), 146.31 (s), 146.09 (s), 145.77 (s), 145.32 (s), 144.72 (s), 144.66 (s), 144.49 (s), 144.47 (s), 144.35 (s), 144.32 (s), 143.63 (s), 143.42 (s), 142.66 (s), 142.63 (s), 142.56 (s), 142.44 (s), 141.85 (s), 141.76 (s), 141.30 (s), 141.15 (s), 140.88 (s), 140.84 (s), 140.63 (s), 140.40 (s), 139.79 (s), 139.62 (s), 139.60 (s), 139.00 (s), 138.97 (s), 138.01 (s), 137.52 (d), 137.49 (d), 137.31 (d), 137.28 (d), 136.75 (s), 136.25 (s), 135.51 (s), 129.80 (d), 129.74 (d), 129.58 (d), 129.49 (d), 127.46 (d), 127.39 (d), 127.31 (d), 127.25 (d), 64.28 (s), 63.73 (s), 62.84 (s), 61.91 (s), 29.14 (q), 22.29 (s), 22.14 (s), 21.90 (s), 21.64 (s); ²⁹Si NMR (CDCl₃) δ –4.04, –4.20, –4.61, –5.43; UV–vis (λ_{max}, toluene) 466, 569 nm; FABMS (toluene/NBA) *m/z* 1676 (M), 720 (C₆₀); symmetry C₁.

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Supporting Information Available: Spectroscopic data of **2a–c** and computational data of **A–G**. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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