ORGANIC LETTERS

2002
Vol. 4, No. 6
1039−1041

Mechanochemical Synthesis of a Novel C_{60} Dimer Connected by a Silicon Bridge and a Single Bond

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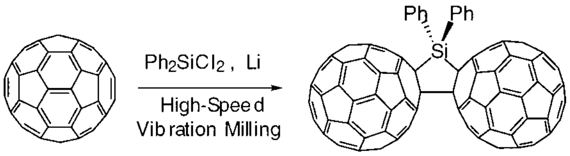
Received January 28, 2002

ABSTRACT



A novel C_{60} dimer connected by a silicon bridge and a single bond was synthesized by the mechanochemical solid-state reaction employing a high-speed vibration milling technique and fully characterized by the ^1H and ^{13}C NMR, APCI mass, and UV–vis spectroscopy. The presence of the electronic interaction between the two C_{60} cages was demonstrated by the electrochemical method.

We have shown that the mechanochemical solid-state reaction employing the high-speed vibration milling (HSVM) technique is particularly effective for the dimerization of fullerenes as exemplified by the synthesis of the C_{60} dimer, C_{120},[1] and the C_{60}/C_{70} cross-dimer, C_{130}.[2] In these dimers, the two fullerene cages are connected by sharing a cyclobutane ring. On the other hand, there have so far been only two reports on the C_{60} dimer connected by sharing a five-membered ring, i.e., $C_{120}X$; $X = O$,[3,4] CH_2.[3] We were interested in introducing a Group 14 element such as silicon into the central five-membered ring in order to examine its electronic effect on the properties of fullerene cages. Previously, silicon species such as silylene,[5] disilirane,[6] and silyllithium[7] have been reported to react with fullerene C_{60} to give the mono- or disilyl derivatives of C_{60}.[5−8] In our laboratory, the mechanochemical solid-state reaction of C_{60} with alkyl or aryl halide in the presence of alkali metals was found to cause alkylation or arylation of C_{60} possibly by the intermediacy of the C_{60} radical anion.[9] Here we report the synthesis of the first example of the C_{60} dimer fused with a silacyclopentane ring (**1**) by the use of the solid-state reaction of C_{60} with dichlorodiphenylsilane and lithium metal.

Fullerene C_{60} (50 mg, 0.069 mmol), dichlorodiphenylsilane (72 mg, 0.29 mmol), and lithium powder (3 mg, 0.4 mmol) were placed in a vibration-milling capsule together with a mixing ball under argon, and the mixture was vigorously vibrated at the rate of 3500 rpm for 30 min. The HPLC analysis on a Cosmosil “Buckyprep” column eluted with toluene demonstrated that a new single peak appeared at a retention time of 6.6 min with the HPLC peak area of 8%

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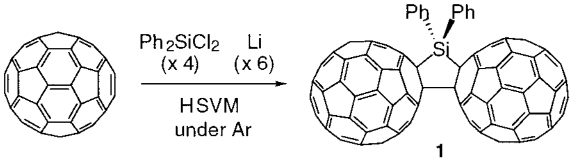
10.1021/ol025630f CCC: $22.00

Scheme 1



in addition to a peak for unreacted C_{60} (retention time, 7.8 min). The separation of the product using recycle HPLC (a SiO_2 column eluted with *o*-dichlorobenzene (ODCB) followed by a Cosmosil "5PBB" column eluted with ODCB) afforded dimer **1**[10] in 7.5% yield, while 67.4% of C_{60} was recovered unchanged. The structure of **1** was determined by MS, ^{1}H and ^{13}C NMR, and UV−vis spectroscopy. In the negative-ion mode atmospheric-pressure chemical ionization (APCI) MS spectrum, a molecular-ion peak at *m/z* 1622 corresponding to the molecular formula of $C_{132}H_{10}Si$ was observed. The ^{1}H NMR exhibited signals at δ 8.62 (dd), 7.58 (d), and 7.56 (m) ppm for meta, ortho, and para protons, respectively. The ^{13}C NMR (in ODCB-d_4 with $Cr(acac)_3$ as a relaxation reagent) exhibited 30 signals (4C × 28 and 2C × 2) for the sp^2 carbons of the C_{60} cage ranging from 158.46 to 134.23 ppm in addition to two signals (85.67 and 64.70 ppm) for the sp^3 carbons (Figure 1). These spectral data are in good agreement with the structure **1** having the C_{2v} symmetry. The ^{13}C NMR signals of the benzene-ring carbons, which were overlapped with ODCB-d_4 signals, were observed as four signals at 139.13, 132.19, 130.75, and 129.36 ppm when measured in $CS_2-CD_2Cl_2$ (3:1). The APT (attached proton test) measurement of ^{13}C NMR indicated both kinds of sp^3 carbons on C_{60} cages to be quaternary carbons. These results indicate that the structure of **1** consists of a silacyclopentane ring fused with two C_{60} cages at the 6−6 bonds. A ^{29}Si NMR signal of **1** was observed at 26.85 ppm, which is definitely (from 21.43 to 99.59 ppm) downfield shifted compared with that of C_{60} derivatives having silicon atoms directly attached to the C_{60} cage.[5−8] This downfield shift can be attributed to the deshielding effect of the two C_{60} cages.

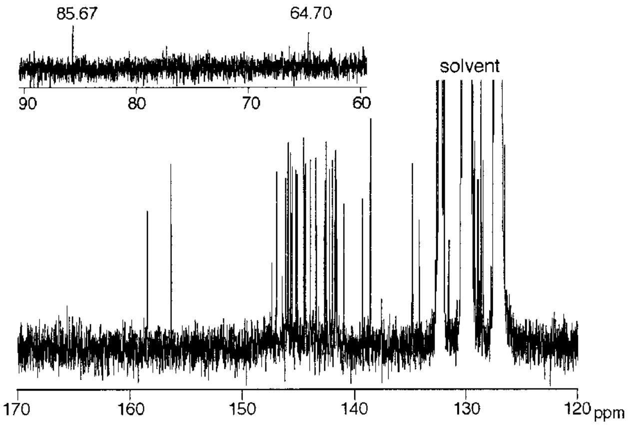


Figure 1. ^{13}C NMR spectrum (100 MHz, ODCB-d_4) of **1**.

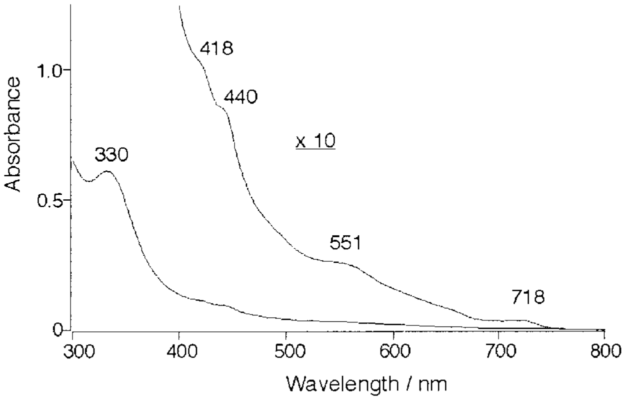


Figure 2. UV−vis spectrum of **1** in ODCB ($c = 6.42 \times 10^{-5}$ M).

In the UV−vis spectrum shown in Figure 2, two absorptions around 400 nm were observed as shoulders at 418 and 440 nm. These absorptions are characteristic of the C_{60} derivatives having directly attached silicon atoms as exemplified by a silacyclopropano[60]fullerene derivative (420 and 463 nm),[5] a 1′,3′-disilacyclopentano[4′,5′:1,2][60]fullerene derivative (424 and 457 nm),[6a] and a 1-silyl-1,2-dihydro-[60]fullerene derivative (417 and 445 nm).[7]

This new dimer **1** is stable as a solid but was found to be sensitive to moisture in solution and to be transformed into C_{60} and $C_{60}H_2$ after standing for a few days in a solution containing a trace of water. The precise mechanism for this decomposition is not clear for the moment, but the severe steric congestion around the silicon atom, as clearly seen in Figure 3, and the presence of the silicon atom at the allylic position on the C_{60} cage in **1** would be the reasons for such a cleavage. In support of such a ready cleavage of the allylic carbon−silicon bond by water, theoretical calculations on an HF/3-21G level indicated that coefficients of the HOMO are rather localized at the "allylic" double bonds and the C−Si bonds.

In the case of the oxygen-bridged C_{60} dimer, $C_{120}O$, an electrochemical study indicated that there is electronic communication between the two C_{60} cages and they are reduced stepwise at slightly different potentials.[11] In a similar manner, the cyclic voltammetry on dimer **1** indicated that

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[10] ^{1}H NMR (300 MHz, $CS_2-CD_2Cl_2$ (3:1)) δ 8.62 (dd, 2H), 7.58 (d, 2H), 7.56 (m, 1H); ^{13}C NMR (100 MHz, ODCB−d_4) δ 158.46, 156.35, 147.39 (2C), 147.00, 146.49 (2C), 146.18, 145.99, 145.95, 145.93, 145.74, 145.57, 145.26, 145.13, 144.56, 144.46, 144.42, 143.89, 143.48, 142.56, 142.54, 142.26, 142.03, 141.81, 141.72, 141.69, 141.62, 140.96, 139.34, 138.63, 134.89, 134.23, 85.67, 64.70 (carbon signals in the benzene ring were observed at 139.13, 132.19, 130.75, 129.36 by the measurement in $CS_2-CD_2Cl_2$ (3:1)); ^{29}Si NMR (79.4 MHz, ODCB−d_4) δ 26.85; UV−vis (ODCB) λ_{max} 330 nm (log ϵ 4.98), 418 sh (4.20), 440 sh (4.12), 551 (3.61), 718 (2.79); MS (−APCI) *m/z* 1622 (M^-).

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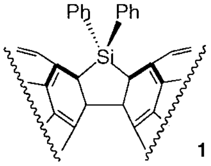

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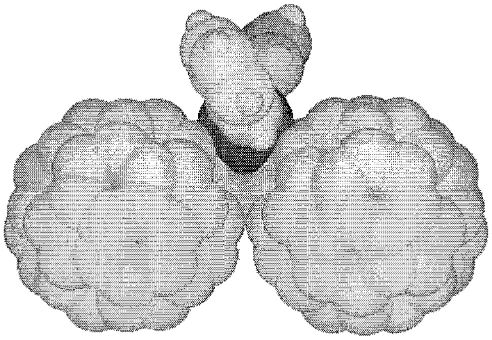

Figure 3. Space filling model of **1** as calcualted by HF/3-21G.

the two C_{60} cages in **1** were reduced stepwise as shown in Figure 4 at E_{pc} −1.04, −1.13, −1.46, −1.54, −1.94, and −2.08 V vs Fc/Fc$^+$, indicating the presence of an electronic interaction between the two C_{60} cages upon the electrochemical reduction. The corresponding reduction peaks for C_{60} were observed at E_{pc} −0.97, −1.40, and −1.88 V under the same conditions. On the other hand, the oxidation peak of **1** was observed at E_{pa} +1.07 V, which is 0.09 V less positive than C_{60} (+1.16 V). The observed general tendency of both the reduction and oxidation peaks to shift in a cathodic direction is attributed to the electronic effect of the silicon atom.[6,12]

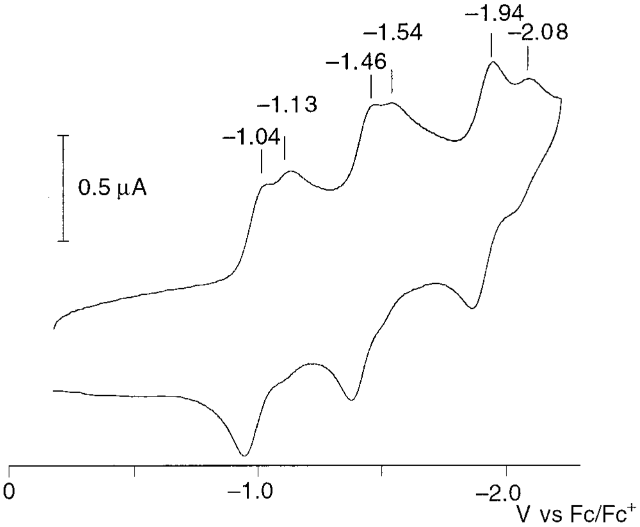

Figure 4. Cyclic voltammogram for **1** measured in ODCB−benzonitrile (1:1) ($c = 5 \times 10^{-4}$ M) with 0.05 M $Bu_4N^+BF_4^-$ as a supporting electrolyte: scan rate, 0.05 V/s.

Thus, a novel C_{60} dimer **1** connected by a silicon bridge and a single bond was obtained for the first time by the use of the HSVM technique. We suppose that the mechanism for the formation of **1** would involve the ionic reaction between dichlorodiphenylsilane and C_{60} radical anion formed by one-electron transfer from Li and radical coupling of the two C_{60} cages.

Acknowledgment. We thank the Ministry of Education, Culture, Sports, Science and Technology, Japan, for the Grant-in-Aid (12CE2005) for COE Reaserch on Elements Science. K.F. thanks JSPS for a Reaserch Fellowship for Young Scientists.

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