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Mechanochemical Synthesis and Characterization of the Fullerene Dimer C_{120}

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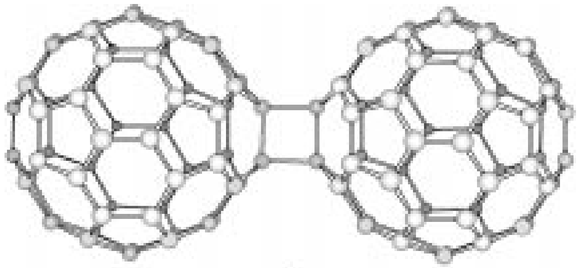
The bulk synthesis of the [2 + 2] dimer of fullerene C_{60} was achieved by the solid-state mechanochemical reaction of C_{60} with KCN by the use of a high-speed vibration milling (HSVM) technique. This reaction took place also by the use of potassium salts such as K_2CO_3 and CH_3CO_2K, metals such as Li, Na, K, Mg, Al, and Zn, and organic bases such as 4-(dimethylamino)- and 4-aminopyridine. Under optimum conditions, the reaction afforded only the dimer C_{120} and unchanged C_{60} in a ratio of about 3:7 (by weight) regardless of the reagent used. The dimer C_{120} was fully characterized by IR, UV−vis, ^{13}C NMR, and TOF MS spectroscopies, cyclic voltammetry, and differential scanning calorimetry. Comparison of the IR and ^{13}C NMR spectral data of C_{120} with those reported for all-carbon C_{60} polymers implied that the [2 + 2] dimer C_{120} represents the essential subunit of these polymers. The dimer C_{120} underwent facile dissociation into two C_{60} molecules by heat, HSVM treatment, exposure to room light, or electrochemical reduction. The dimer C_{120} encapsulating ^3He in one of the C_{60} cages was synthesized and was used to confirm the scrambling of a C_{60} cage between the monomer and the dimer during the HSVM reaction. A possible mechanism for the selective formation of the dimer C_{120} is proposed.

Introduction

The preparation and structure of the fullerene dimer as well as the all-carbon fullerene polymers are currently attracting great interest in the fullerene chemistry. Many theoretical studies on the C_{60} dimer have indicated that the [2 + 2]-type dimer (C_{120}, **1**) is the lowest energy and most plausible one among the possible isomers including those with the shape of peanut shells.[1,2] Dimer **1** was also proposed as an essential subunit of the all-carbon fullerene polymers produced by photoirradiation,[3] under high pressure,[4] and by alkali-metal doping.[5]

Thus, it is of great significance to clarify the detailed structure as well as the physical and chemical properties of the [2 + 2]-type dimer for better understanding the nature of fullerene polymers. However, the above reaction conditions for the fullerene polymerization could not stop the reaction at the stage of dimerization, and the synthetic approach to the dimer C_{120} has remained as a challenge to organic chemists.



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As to the synthesis and characterization of directly bonded dimeric fullerenes, reports have been made for $C_{120}O$ (**2**)[6,7] and $C_{121}H_2$ (**3**)[7] having two C_{60} cages connected by tetrahydrofuran and cyclopentane rings, re-

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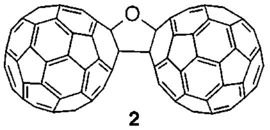
10.1021/jo981319t CCC: $15.00

spectively, and $C_{120}O_2$ (**4**)[8] having two C_{60} cages connected by a cyclobutane ring and also by two other oxygen bridges. On the other hand, the recent X-ray powder diffraction study showed the presence of dianion of singly bonded dimer of C_{60} in the metastable phases of RbC_{60} and KC_{60}.[9] The neutral singly bonded dimer was also formed from $C_{59}N$ radical[10] and from the alkyl-C_{60} radical, but the dimer from the latter is in equilibrium with the monomeric radical by facile dissociation.[11] Another type of fullerene dimer, C_{119}, has also been isolated in a low yield (2%) from the thermal solid-state reaction of the oxygen-containing dimer **2**.[12] However, there had been no experimental evidence for a structure of the simplest all-carbon [2 + 2] dimer, C_{120} (**1**), until our preliminary report.[13,14] Here we describe a full account of the first bulk and selective synthesis of the [2 + 2] dimer C_{120} (**1**), which was achieved by a unique solid-state mechanochemical reaction of C_{60} under high-speed vibration milling. This dimer can be dubbed "bucky dumbbells" on the basis of its molecular shape. Also, we describe the spectral and chemical properties of this new molecule of C_{120}.



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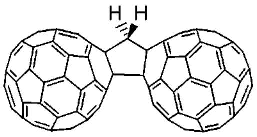

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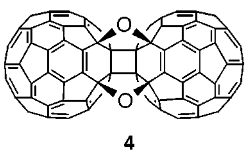

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Results and Discussion

Synthesis of C_{120} (1) by the Reaction with KCN. The solid-state organic reaction has extensively been studied by Toda,[15] but it has not been applied to the organic functionalization of fullerene C_{60} although this technique should be quite advantageous for the reaction of fullerenes which are poorly soluble in common organic solvents. Recently we developed a new technique of mechanochemical solid-state reaction which made use of "high-speed vibration milling" (abbreviated as HSVM), and applied it to organic functionalization of C_{60}.[16] Because of the absence of any solvent molecule and due to the mechanical energy given to the reacting system, a mechanochemical reaction is expected to produce highly activated local sites in the reacting species.[17] In this respect, our HSVM technique should be particularly advantageous because it involves the vigorous mechanical motion, that is, rapid vibration of a stainless steel capsule containing a stainless steel milling ball and reacting species at the rate of 3500 cycle per minute. It should be noted that, in a completely independent work from ours, Braun et al. also proved the feasibility of the use of a mechanochemical ball-milling technique for the complexation of C_{60} with γ-cyclodextrin.[18]

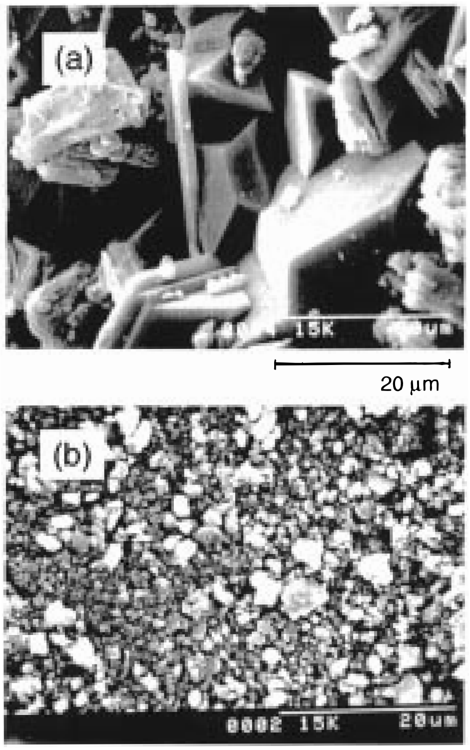

Figure 1. Scanning electron microscope photographs of C_{60} (a) before and (b) after high-speed vibration milling (HSVM) for 30 min.

When treated with our HSVM technique for 30 min, the crystalline C_{60} was pulverized into particles with the size of less than 1 μm as examined by the scanning electron microscope (Figure 1). In our previous work, application of such a powerful pulverizing and mixing procedure to the reaction of C_{60} with an organozinc reagent was found to give expected products in fairly good yields.[16] We intended to widen the scope of this method and applied it to the reaction of C_{60} with KCN. In contrast to the reaction in a liquid phase, which gave the cyanated product $C_{60}H(CN)$[19] after protonation, a totally different product was selectively produced, that is, the fullerene dimer C_{120} (**1**) (Scheme 1).

As a standard procedure, 50 mg of C_{60} and 10 mg (2 molar equiv) of KCN were placed in a capsule and were allowed to react by vigorous mixing under the HSVM

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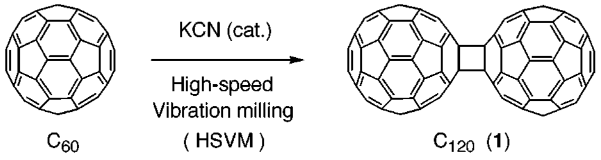
Scheme 1



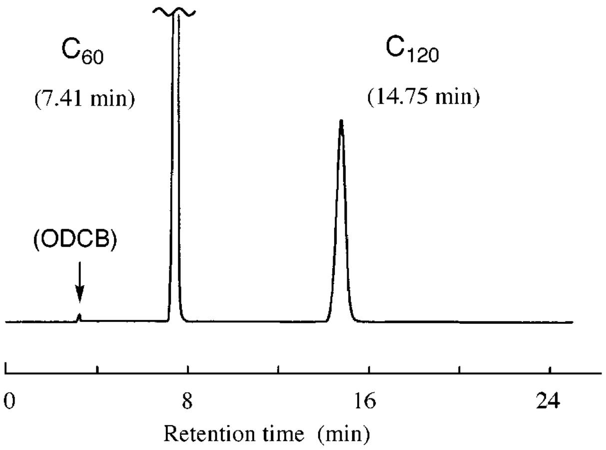


Figure 2. HPLC chart of the reaction product. Column: Cosmosil Buckyprep (4.6 mm × 250 mm). Solvent: toluene. Flow rate: 1 mL min^{-1}.

conditions for 30 min in a glovebox filled with nitrogen. Analysis of the reaction mixture by high-pressure liquid chromatography (HPLC) indicated the presence of only one product (a peak with retention time of 14.75 min over a Buckyprep column eluted with toluene) besides unchanged C_{60} (retention time of 7.41 min) in the peak area ratio of 30:70, which is approximately the same as the weight ratio (see Experimental Section), as shown in Figure 2. Separation by flash chromatography, by HPLC, or by reprecipitation from 1,2-dichlorobenzene (ODCB)/hexane gave unchanged C_{60} in 70% recovery and C_{120} (**1**) in 20–25% isolated yield. The structure of **1** was unequivocally determined as the [2 + 2] dimer of C_{60} on the basis of the evidence described below. When the reaction was conducted under air, the yield of C_{120} decreased to 15–17% (HPLC) with the formation of unidentified materials and a small amount of $C_{60}O$[20] which were difficult to be removed during the course of separation procedure.

To confirm that the metal surface of the capsule was not chemically affecting the reaction, the solid-state reaction was also carried out by the use of C_{60} and KCN in a Teflon capsule and a ceramic milling ball. The result was essentially the same except that the yield of C_{120} was decreased to 9.1% possibly because the surface of the mixing materials was softer and hence the mechanical energy was decreased.

Contrary to our previous report,[13] treatment of 50 mg of C_{60} itself under high-speed vibration milling in the absence of KCN resulted in the formation of a small amount of C_{120} (2%, as examined by HPLC analysis) and a larger amount of supposed C_{60} polymer that did not dissolve in ODCB. The amount of the latter material increased as the reaction time was elongated while the amount of C_{120} remained almost constant as shown in Figure 3a for the reaction using 20 mg of C_{60} as a starting material. In contrast, no such ODCB-insoluble material was formed in the reaction of C_{60} with KCN. Instead, the reaction appears to reach a kind of equilibrium state with the yield of C_{120} being nearly 30% after the reaction time of about 30 min as shown in Figure 3b. This is in agreement with the presence of a dissociation step of C_{120}, as will be discussed later. The amount of KCN need not be equivalent to that of C_{60}; a smaller amount is sufficient as shown in Figure 4.

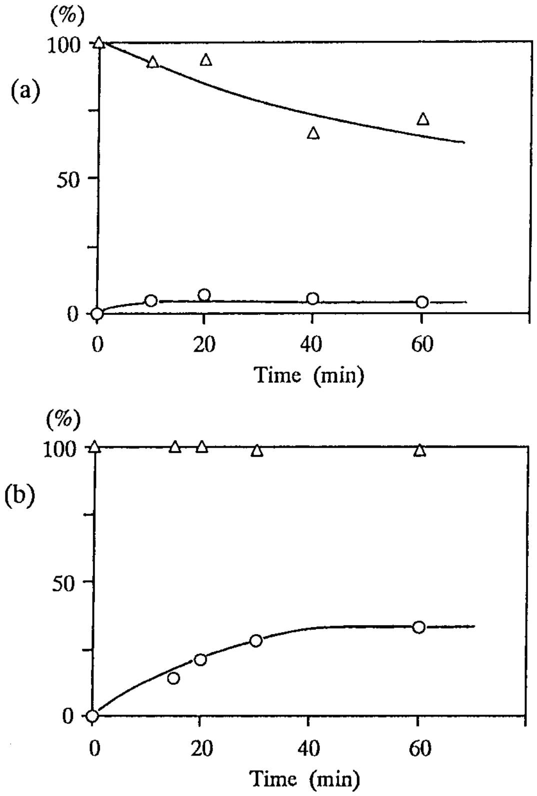


Figure 3. (a) Time dependence of the reaction mixture obtained by the HSVM treatment of C_{60} in the absence of any added reagent. (b) Time dependence of the reaction mixture of C_{60} and KCN under the HSVM conditions. ○: C_{120}. △: C_{120} + C_{60}.

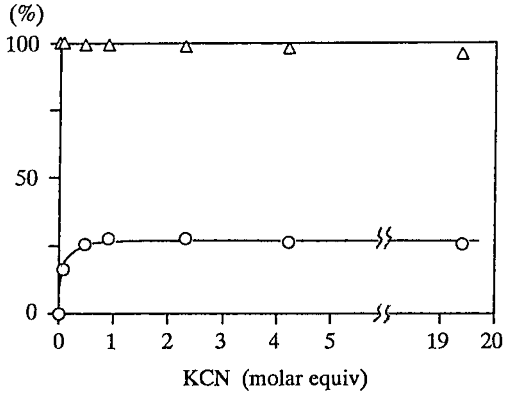


Figure 4. Dependence of the reaction mixture upon the molar amount of KCN used under the HSVM conditions. ○: C_{120}. △: C_{120} + C_{60}.

Synthesis of C_{120} (1) by Other Reagents. Other than KCN, potassium salts such as KCl, KBr, KI, KCNO, and $KMnO_4$ were also examined, but turned out to be ineffective for dimerization of C_{60}. On the other hand,

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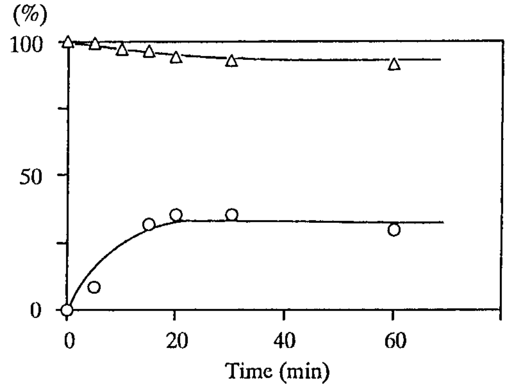

Figure 5. Time dependence of the reaction of C_{60} and Na under the HSVM conditions. ○: C_{120}. △: C_{120} + C_{60}.

the salts such as K_2CO_3 and CH_3CO_2K, which contain nucleophilic anions, were found to be as effective as KCN.

Alkali metals (Li, Na, and K) and other metals such as Mg, Al, and Zn were also found to be effective for dimerization of C_{60} while Ni and Cu were not effective. All the metals effective for dimerization are characterized by the reduction potentials,[21] which are much more negative (i.e., more strongly reducing) than −0.20 V versus standard hydrogen electrode, that is, the reduction potential of C_{60}.[22] As in the reaction with KCN, the reaction of C_{60} with these metals reaches an apparent equilibrium state giving a mixture of C_{60} and C_{120} in a weight ratio of about 7:3 as is shown by the reaction with Na as an example in Figure 5. However, to effect the clean formation of C_{120}, these metals had to be used in a very small amount (i.e., 0.1 to 1 equiv in the case of alkali metals), or otherwise the yield of the ODCB-insoluble material increased accompanying the increase in the metal used. The relationship between the amount of each of the representative metals and product components is shown in Figure 6.

Among the organic solids which can act as an electron donor, 4-(dimethylamino)- and 4-aminopyridine were found to be effective for dimerization of C_{60} under the HSVM conditions while tetrathiafulvalene was not effective. Particularly the reaction with 4-aminopyridine is advantageous because C_{120} can be isolated in satisfactory yield (30%) and 4-aminopyridine can be readily removed by washing with common organic solvents.

In the case when ODCB-insoluble materials were formed, the HPLC analysis (Buckyprep/toluene) of an ODCB-soluble portion indicated the formation of a very small amount (0.5−1%) of a component which gave rather broad peaks centering at the retention times of 27.49 and 31.19 min. This component could possibly be an isomeric mixture of the C_{60} trimer, C_{180}, but for the moment we have no further experimental evidence for the structural identification of this material because of its poor solubility and the scarceness of the sample.

Structural Characterization of C_{120} (1). The FT-IR spectrum of **1** exhibited more infrared-active peaks than C_{60} as shown in Figure 7 and resembled the IR spectrum of C_{60} polymer prepared by photoirradiation.[3a] This can be taken as the evidence for the presence of the [2 + 2] structure in the photoproduced polymer. The color of a solution of **1** in ODCB is brown, and it exhibited a UV absorption at 328 nm and visible absorptions at 434 and 700 nm, which are typical for 1,2-dihydrofullerene derivatives, as shown in Figure 8.

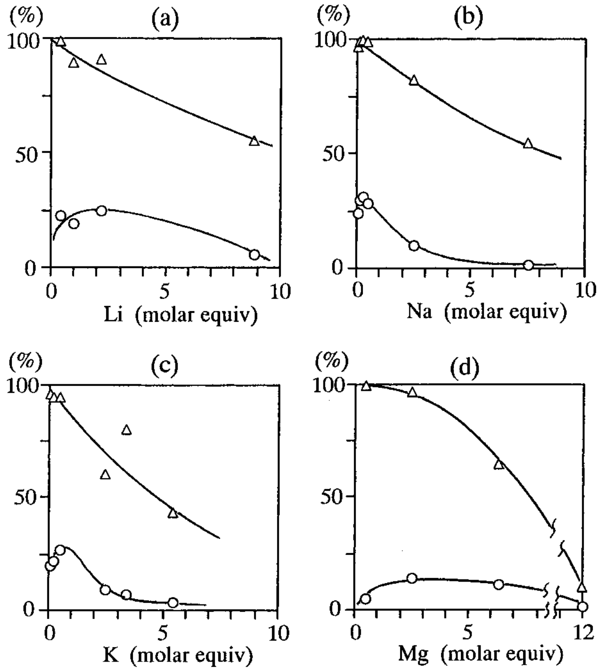

Figure 6. Dependence of the reaction mixture upon the molar amount of various metals used under the HSVM conditions: (a) Li; (b) Na; (c) K; (d) Mg. ○: C_{120}. △: C_{120} + C_{60}.

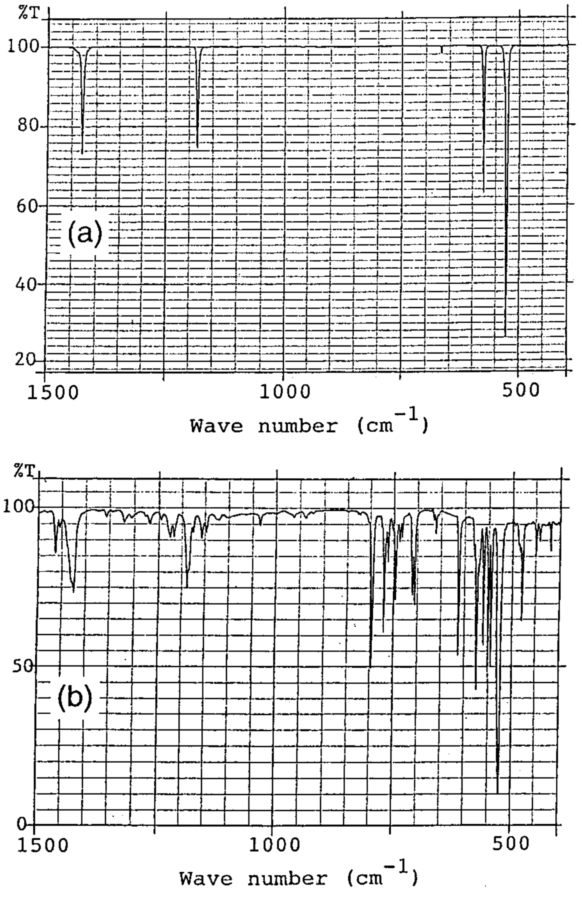

Figure 7. IR spectrum (KBr disk) of (a) C_{60} and (b) C_{120} (**1**).

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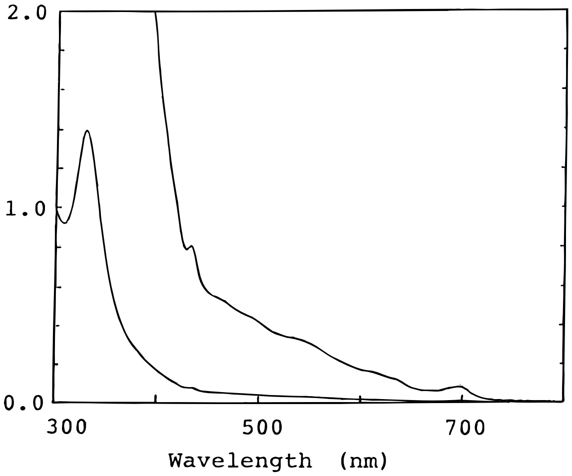


Figure 8. UV−vis spectrum of C_{120} (**1**) in ODCB (8 × 10^{-5} M).

The ^{13}C NMR spectrum in ODCB-d_4 exhibited 16 signals at δ 151.42 (8C), 147.14 (4C), 146.09 (8C), 146.08 (8C), 145.97 (8C), 145.65 (8C), 145.48 (4C), 145.18 (8C), 144.37 (8C), 142.97 (4C), 142.73 (8C), 142.56 (8C), 142.02 (8C), 141.99 (8C), 140.70 (8C), and 139.02 (8C) for sp^2 carbons and one signal at 76.22 ppm for a sp^3 carbon, which are fully consistent with the [2 + 2] structure with D_{2h} symmetry as has been determined by X-ray crystallography.[13] A comparison of the present data with the solid-state MAS ^{13}C NMR spectra of C_{60} polymers prepared under high pressure (e.g., 149.1, 147.9, 145.2, 139.6, 134.8, and 73.5[4d] and 144 (broad) and 77[4e]), again, supports that the dumbbell-shaped C_{120} is indeed the essential subunit of these polymers.

By using various mass spectral techniques such as EI, FAB, APCI, and ESI, in both positive- and negative-ion modes, no molecular ion peak of **1** was observed, but a strong peak for C_{60} was. However, the MALDI TOF mass spectrum showed a weak peak at *m/z* 1442 ($M^+ + 2$) together with a series of peaks corresponding to the loss of C_{2n} ($n = 1-5$) from C_{120} and a base peak at *m/z* 720 for C_{60} indicating the facile cleavage of the central cyclobutane's intercage bonds. The similar spectrum was observed more clearly and with higher precision by the positive-ion Fourier transform ion cyclotron resonance mass spectroscopy.[13]

Properties of C_{120} (1). Dimer **1** is a dark brown powder, which is hardly soluble in most organic solvents. The solubility highly depends on the purity, the purer sample being less soluble. In particular, the sample hardly goes into solution when once isolated as powdery crystals. The solubility of the powdery sample of **1** of the highest purity in the solvents frequently used for fullerenes is the following: 0.4 mg per mL (2.8 × 10^{-4} M) in 1-chloronaphthalene, 0.1 mg per mL (8 × 10^{-5} M) in ODCB, and 0.003 mg per mL (2 × 10^{-6} M) in toluene. However, the solubility increases by about 10 times for the sample of ca. 98% purity.

Previously, C_{60} polymers were reported to be converted back to C_{60} at about 200−300 °C.[3b,4a−d] According to the results of differential scanning calorimetry (DSC), this process is endothermic, suggesting that the polymer phase is more stable.[4b] In the case of dimer **1**, the DSC conducted in the range of 80−220 °C at a rate of 1 °C min^{-1} exhibited an endothermic peak centering at 162 °C in the heating process, while no such peak was observed in the cooling scan. This peak would be due to either the solvent evaporation or the bond breaking in **1**. Actually, dimer **1** was found to dissociate quantitatively into C_{60} when heated at 175 °C in ODCB for 15 min.

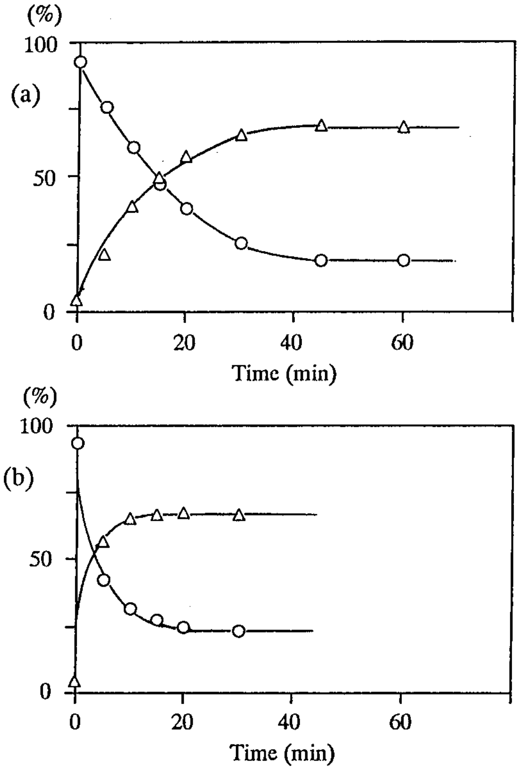
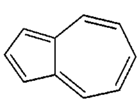


Figure 9. Time dependence of the reaction mixture of the HSVM treatment of C_{120} (20.7 mg) (a) with KCN (4.1 mg) and (b) with Na (0.5 mg). ○: C_{120}. △: C_{60}.

The dissociation of dimer **1** was also observed under the present high-speed vibration milling (HSVM) conditions both in the presence and absence of an added reagent. Thus, when **1** was treated with 2 molar equiv of KCN or 0.8 molar equiv of Na metal under the HSVM conditions, the dissociation occurred to give a mixture of C_{60} and C_{120} in a ratio of about 7:2.5 by weight as shown in Figure 9. It is to be noted that the final product ratio is nearly the same as that observed in the HSVM reactions of C_{60} with these reagents (see above), suggesting that a chemical equilibrium is established, either starting from monomer or dimer, despite such heterogeneous solid-state reaction conditions. In the absence of any added reagent, the HSVM treatment of C_{120} for 30 min afforded a mixture composed of C_{60} and C_{120} in a weight percent of 32:57, which changed into 46:36 after another 30-min period of HSVM. In the absence of added reagent, however, the formation of ODCB-insoluble material became notable just as in the case of HSVM treatment of C_{60} itself (see above).

To examine if the above-mentioned dissociation was affected by the rise of temperature of the reaction capsule, some organic compounds which are known to undergo thermal reaction were tested as a temperature probe. Any new product or any change in the starting material was not detected when 50 mg of azulene (**5**) or 7-(triphenylmethyl)-1,3,5-cycloheptatriene (**6**) was placed in a capsule and treated for 30 min under HSVM



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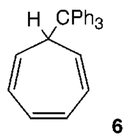

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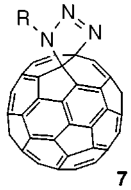

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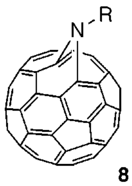

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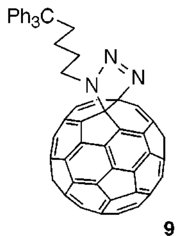
(R = CH_2CO_2Me, CH_2Ar)



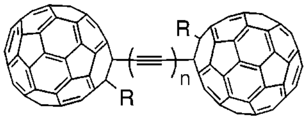
9

conditions. Azulene is known to isomerize to naphthalene at the temperature of 270 °C,[23] and **6** has been shown to undergo thermal dissociation at <100 °C [24] and 1,5-hydride shift at around 150 °C.[25] Furthermore, fullerenotriazolines **7** are known to undergo transformation into azafulleroids **8** with nitrogen extrusion at 100 °C.[26] Again, triazoline **9**[27] was found to be stable under the present HSVM conditions. These results indicate that the temperature of the content of a capsule in our HSVM technique does not even reach up to 100 °C, the temperature that is much lower than that for C_{120} to dissociate into two molecules of C_{60}.

From these results, the dissociation of C_{120} (**1**) under HSVM conditions is supposed to have occurred not only by the chemical effect of the added reagent but also by the local pressure effect. When high pressure is applied to the C_{120} molecules, distortion of each C_{60} cage would occur, which can lead to the cleavage of the bonds connecting the two cages.[28] Actually, when a powdery sample of C_{120} was subjected to the hydraulic pressure of 100 kg/cm^2 for 30 min, 0.8% of C_{60} was produced. Apparently the local pressure generated in the present HSVM method must be much higher than this pressure.

The C_{120} molecule also underwent photochemical dissociation into C_{60} at the rate of 2% per day when an ODCB solution (4×10^{-5} M) was exposed to room light, the rate being dependent upon the distance to and the type of the light source. The dissociation was negligible when the solution was kept in the dark.

There have been electrochemical studies on various fullerene dimers. In the case of the dimer with two C_{60} cages connected by sharing a tetrahydrofuran ring (**2**) and the azafullerene dimer, the two cages are directly connected so that they are strongly interacting with each other. As a result, the two cages are reduced not simultaneously but consecutively at each step in three-step six-electron reduction as examined by cyclic voltammetry.[29] On the other hand, in the case of ethyne-1,2-diyl and butadiyne-1,4-diyl bisfullerenes (**10**), two cages are located too far away for such interaction, and the two cages are reduced simultaneously at each of the three-step reduction with two-electron transfer at each step.[30]



10 (n = 1, R = $C_{12}H_{25}$; n = 2, R = CH_2Ph, CH_2OThp)

The electrochemical behavior of the present dimer **1** was found to be different from either of these cases. Thus, cyclic voltammogram of **1** exhibited three reversible reductions at $E_{1/2}$ −1.14, −1.53, −1.99 V vs ferrocene/ferrocenium (Figure 10a), which are almost identical to those of C_{60} (−1.12, −1.52, −1.99 V) observed under the same conditions. The only noticeable difference between **1** and C_{60} is the presence of a slight shoulder at the first reduction peak of **1**, which is discernible in the differential pulse voltammetry (Figure 10b). These results converge to indicate that dimer **1** readily dissociates into two C_{60} units immediately after C_{120} acquires extra negative charge. This is attributable to very weak bonding between the two cages in **1**.

Synthesis of $^3He@C_{120}$ and Scrambling of the C_{60} Cage. The encapsulation of ^{3}He is a particularly valuable method for labeling the fullerene cage since the C_{60} cage containing ^{3}He atom ($^3He@C_{60}$) can be unequivocally monitored by ^{3}He NMR.[31] The ^{3}He NMR chemical shift has been shown to be highly sensitive to the change in magnetic shielding environment of the fullerene cage.[32] In a present study, the C_{120} molecule containing ^{3}He in one of the C_{60} cages was synthesized from $^3He@C_{60}$ using KCN by the method described above. The approximate ratio of $^3He@C_{60}$ to empty C_{60} is about 1:1000 in the starting material (expressed as "$^3He@C_{60}$"), so that the probability for the formation of C_{120} containing ^{3}He atom in both of the C_{60} cages ($^3He_2@C_{120}$) is as small as 1:10^6 assuming that there is no significant difference in reactivity between $^3He@C_{60}$ and C_{60}. The product mixture of the dimerization of "$^3He@C_{60}$" exhibited an HPLC chart which was similar to that shown in Figure 2 and gave the ^{3}He NMR spectrum shown in Figure 11. From the comparison of these data, and also on the basis of the previously reported ^{3}He NMR chemical shift for $^3He@C_{60}$,[31,32] the signal at δ −6.29 (relative to free helium-3) is assigned to unchanged $^3He@C_{60}$ (**11**) and the one at −8.81 to the produced $^3He@C_{120}$ (**12**). This upfield shift

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[27] Murata, Y.; Komatsu, K. Unpublished result. For **9**: mp > 300 °C; ^{1}H NMR (CS_2−acetone-d_6 (7:1)) δ 7.23−7.05 (m, 15H), 4.28 (t, 2H), 2.69 (m, 2H), 2.23 (m, 2H), 1.38 (m, 2H); ^{13}C NMR (CS_2−acetone-d_6 (7:1)) δ 147.95, 147.76, 147.45, 146.58, 146.43, 146.33, 146.30, 146.28, 146.06, 145.85, 145.54, 145.51, 145.38, 145.04, 144.82, 144.31, 143.53, 143.40, 143.24, 143.11, 143.06, 142.90, 142.60, 142.58, 142.48, 142.29, 141.44, 141.14, 140.59, 136.93, 136.32, 129.63, 128.43, 126.41, 106.39, 81.90, 56.95, 48.87, 40.54, 30.98, 23.96; HRMS (+FAB, nitrobenzyl alcohol) calcd for $^{12}C_{82}{}^{13}CH_{23}N_3$ 1062.1926, found 1062.1924. Anal. Calcd for $C_{83}H_{23}N_3$: C, 93.86; H, 2.18; N, 3.96. Found: C, 93.58; H, 2.39; N, 3.79.

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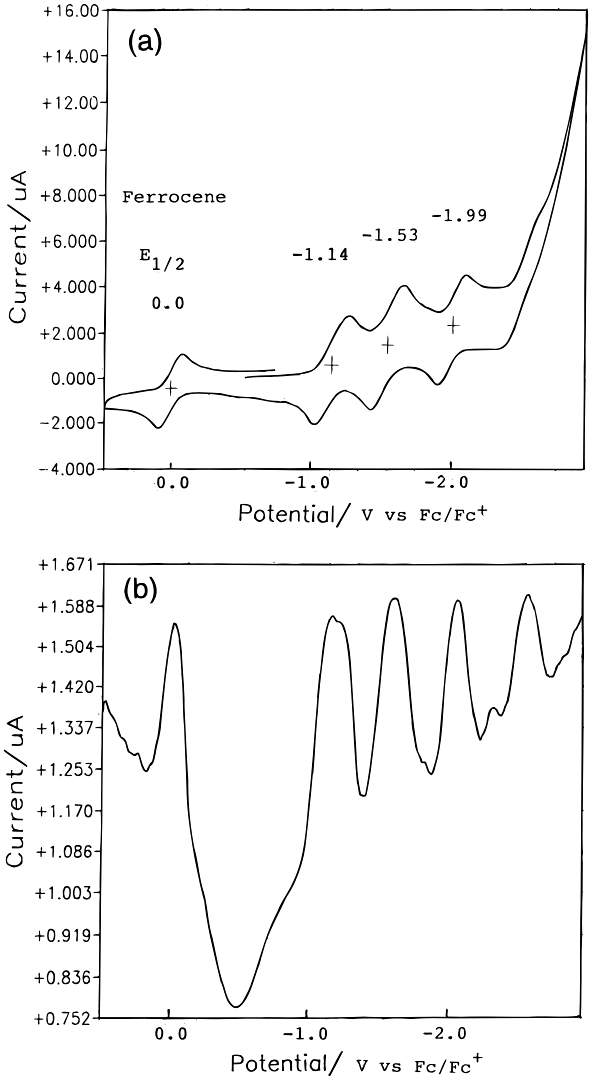


Figure 10. (a) Cyclic voltammogram and (b) differential pulse voltammogram of C_{120} (**1**); recorded in ODCB/0.05 M Bu_4NBF_4; Pt disk and Pt wire as working and counter electrodes; scan rate, 20 mV s^{-1}.

($\Delta\delta$) of 2.52 ppm for $^3He@C_{120}$ relative to that of $^3He@C_{60}$ is larger than that for a derivative fused by a three-membered ring (**13**) and is rather closer to the $\Delta\delta$ for the benzyne−C_{60} adduct **14** or other derivatives fused by a cyclobutane ring such as **15** for example (Figure 12).[31] Attachment of extra C_{60} cage was found to exert only a slight deshielding effect as compared with the benzene ring in **14**.

To confirm the presence of an apparent equilibrium between C_{120} and C_{60} as mentioned above, the scrambling of $^3He@C_{60}$ was examined using $^3He@C_{120}$ (**12**). Thus, "$^3He@C_{120}$" (a mixture of $^3He@C_{120}$ and empty C_{120} in a ratio of approximately 1:1000) was treated with empty C_{60} (9 molar equiv) and KCN (13 molar equiv) under the HSVM conditions for 30 min, and the product mixture was examined with ^3He NMR. There were observed the signals for $^3He@C_{60}$ and $^3He@C_{120}$ in a peak−height ratio of about 3:1 in fair agreement with the equilibrium ratio of 7:3 for the product ratio of C_{60} and C_{120} in the HSVM conditions as has been described, thus demonstrating the scrambling of $^3He@C_{60}$.

Possible Mechanism for the Dimerization of C_{60}. Formally there are at least two possible mechanisms conceivable for the formation of C_{120} by the solid-state reaction of C_{60} with KCN under the HSVM conditions, i.e., dimerization via nucleophilic addition and dimerization via coupling through an electron-transfer (ET) step. As shown in Scheme 2, both mechanisms involve the formation of the anion $C_{60}(CN)^-$ (**16**) (reaction i). In the nucleophilic addition the anion **16** is supposed to react with C_{60} in the 1,4-addition mode to give dimeric anion **17**, which could undergo an intramolecular S_N2' reaction furnishing the [2 + 2] dimer **1** (reaction ii). On the other hand, in the ET dimerization, the anion **16** is supposed to transfer one electron to C_{60} to give the radical anion $C_{60}^{\bullet-}$ (**18**) (reaction iii), which would couple with a neutral molecule of C_{60} to give $C_{120}^{\bullet-}$ (**19**) (reaction iv); a

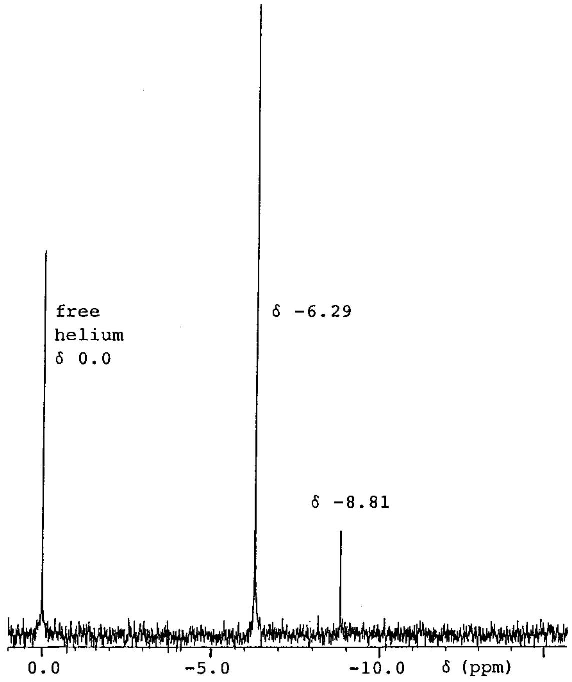


Figure 11. ^3He NMR spectrum of the product mixture of the mechanochemical HSVM reaction of $^3He@C_{60}$ with KCN measured in 1-methylnaphthalene−ODCB-d_4 (2:1).

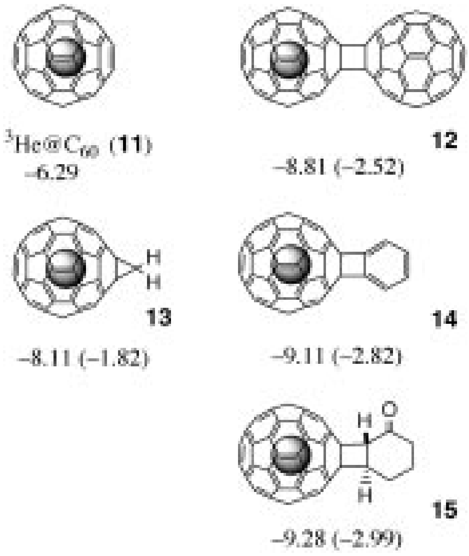
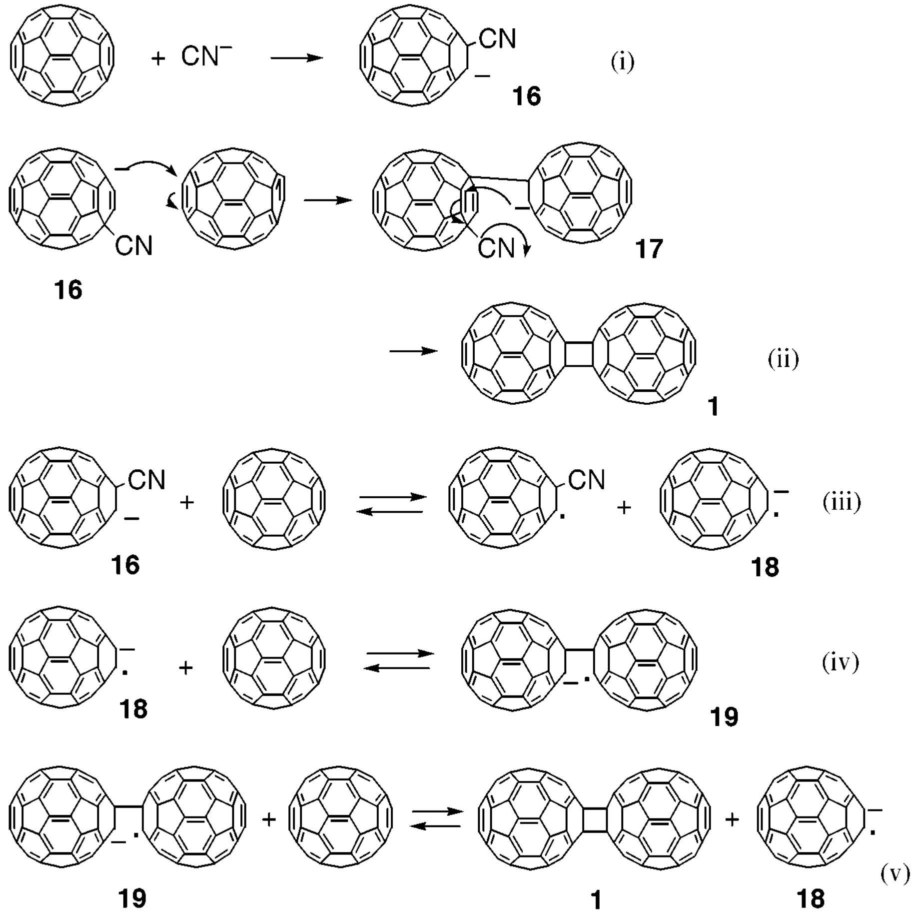


Figure 12. ^3He NMR chemical shifts (ppm) of **11** and **12** and other representative derivatives **13**−**15**.[31] $\Delta\delta$ values (relative to **11**) are given in parentheses.

Scheme 2



subsequent ET to another C_{60} molecule would furnish neutral C_{120} (**1**) (reaction v). Thus, once the radical anion **18** is formed, it would trigger the chain reactions iv and v. Since a small amount of reducing metals is effective in dimerization of C_{60}, the mechanism involving electron transfer appears to be more probable. The experimentally observed dissociation of C_{120} in the presence of a small amount of sodium metal is also in agreement with the presence of equilibrium for the reactions iv and v. Such equilibria seem to be the key feature of the present HSVM technique, which resulted in the selective formation of [2 + 2] dimer C_{120} (**1**).

The typical organic base, like amines, is known to undergo one-electron transfer to C_{60},[33] and thus it is supposed that under the HSVM conditions the reaction of 4-aminopyridines upon C_{60} worked to generate radical anion **18** to cause the selective formation of **1**.

Also in support of the intermediacy of the fullerenyl anion for the reaction of C_{60} by the action of carbon nucleophiles, the dimerization was observed upon HSVM treatment of C_{60} (40 mg) with a catalytic amount (1.4 or 1.5 mg; 3 mol % relative to C_{60}) of the potassium salt of the fullerenyl anion, t-BuC_{60}^- [34] or $C_{60}(CN)^-$,[34] in the presence of 100 mg of KCl as an solid diluent. After 30 min, an equilibrium mixture of C_{60} and C_{120} (67.5:31.2 or 93.4:5.9 by HPLC for the reaction of t-BuC_{60}^- or $C_{60}(CN)^-$, respectively) was obtained, while no ODCB-insoluble material was produced.

Summary

In the present study we have demonstrated that the formal [2 + 2] addition of the 6−6 bond of C_{60} can take place to give dumbbell-shaped dimer **1** in a highly selective manner by means of a technique of the high-speed vibration milling (HSVM) in the presence of a nucleophilic anion, metal powders, or 4-aminopyridine. This method is characteristic in providing the equilibrium state between monomer (C_{60}) and dimer (C_{120}), which is supposed to play an important role for the highly selective formation of the dimer. Under the present HSVM conditions, the stability of C_{120} appears to be comparable to that of two C_{60} molecules in agreement with the results of ab initio and density functional calculations.[2] Although the C_{120} molecule readily undergoes dissociation upon heating or one-electron reduction, this does not cause any rearrangement into the peanut-shaped isomer as has been anticipated theoretically. Comparison of the spectral data such as IR and ^{13}C NMR with those previously reported for all-carbon C_{60} polymers implies that the present dumbbell-shaped dimer is actually the essential subunit of the C_{60} polymers. There might be a possibility of the presence of C_{120} (**1**) in what has been regarded as C_{60} polymers prepared by various methods, and the investigation along this line is now in progress.

Experimental Section

Caution: *KCN and the evolving gas (HCN) are highly toxic and should be quenched by aqueous solution of sodium hypochlorite immediately after use.*

General Procedures. Fullerene C_{60} was the commercial material (>99.5%) perchased from Term Co. All inorganic

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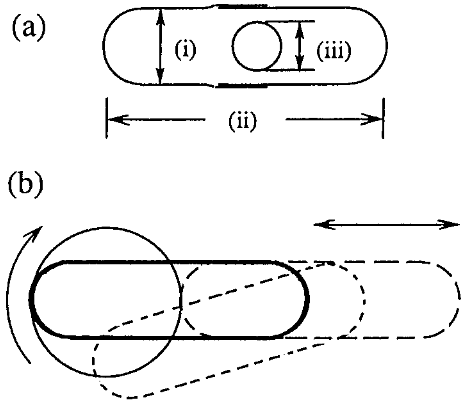

Figure 13. (a) A mixing capsule with a milling ball: (i) inner diameter, 9.0 mm; (ii) inner length, 26 mm; (iii) diameter, 6.0 mm. (b) Schematic representation of the movement of the capsule: one end moves around a circle while the other end moves horizontally.

reagents were commercial materials of the reagent grade and were used after drying under vacuum (<10^{-4} mmHg) at 100 °C for 24 h for KCN or for 3 h for other materials. 1,2-Dichlorobenzene (ODCB) was distilled over CaH_2.

IR spectrum was recorded on a Shimadzu 8600 FT IR spectrometer. UV−vis spectra were obtained on a Shimadzu UV-2100PC spectrometer. ^{13}C NMR spectrum was recorded on a JEOL JNM-Lambda 600 spectrometer (150 MHz). ^{3}He NMR spectra were obtained on a Bruker AM-500 NMR spectrometer in 1-methylnaphthalene−ODCB-d_4 (2:1) containing $Cr(acac)_3$ as a relaxation agent with ^{3}He gas bubbled in as the reference. MALDI TOF mass spectra were taken on a Finnigan-Mat VISION 2000 spectrometer. The high-pressure liquid chromatography (HPLC) was performed on a Shimadzu LC10A liquid chromatograph with a UV detector at 326 nm, using a Cosmosil Buckyprep column (4.6 mm × 250 mm) with toluene as an eluent for analytical purpose and a Cosmosil 5PBB column (10 mm × 250 mm) with ODCB as an eluent for preparative purpose. Electrochemical measurements were performed on a BAS CV-50W electrochemical analyzer. Differential scanning calorimetry was conducted on a Perkin-Elmer DSC-7 calorimeter.

High-Speed Vibration Mill. Throughout the present study, we used a mill which consisted of a capsule and a milling ball made of stainless steel (Fe−Cr−Ni with a composition of 74:18:8 wt %) (Figure 13a). The capsule containing the milling ball was fixed in a home-built vibrating machine so that the capsule was shaken along its long axis horizontally with a slight fluctuation (rotating motion) as schematically shown in Figure 13b at a rate of 3500 cycles per min. For the purpose of comparison, a capsule manufactured from Teflon and a milling ball made of ceramic, both with the same size as the stainless steel ones, were used.

Reaction of C_{60} with KCN. A Typical Procedure. In a glovebox filled with nitrogen, C_{60} (53.2 mg, 0.0738 mmol) and KCN (10.2 mg, 0.157 mmol) were weighed into a stainless steel capsule together with a milling ball. The capsule was vigorously shaken for 30 min by the use of a high-speed vibration mill. The reaction mixture was then washed into a two-necked flask containing a stirring bar and equipped with a septum seal and an outlet tube, using a total amount of 20 mL of 1,2-dichlorobenzene (ODCB). To the stirred mixture in ODCB was added 0.1 mL of CF_3CO_2H through a rubber septum, and a very small amount of evolved gas was led into another flask containing an aqueous solution of sodium hypochlorite through an outlet tube. The mixture in ODCB was filtered through a short column of silica gel (length 15 mm) and evaporated under reduced pressure to give a dark brown solid. The HPLC analysis (Buckyprep) of an ODCB solution of this solid exhibited only two peaks of C_{60} and C_{120} (the area ratio, 69.7:29.5) at the retention times of 7.41 and 14.75 min, respectively. From the correction factor between the peak area ratio and the weight ratio of these components, found to be 1.01 by an independent experiment, the HPLC yield of C_{120} was found to be 29.8% while 69.7% of C_{60} was unchanged.

The mixture was dissolved in 30 mL of ODCB and was subjected to flash chromatography over silica gel (Merck SiO_2 60). Elution with 200 mL of hexane−toluene (3:1) afforded C_{60} (36.0 mg, 67.7%). Subsequent elution with 100 mL of toluene−ODCB (1:1) and 100 mL of ODCB gave C_{120} (11.8 mg, 22.2%). In another experiment, the separation was made by preparative HPLC using a Cosmosil 5PBB column with ODCB as an eluent to give a similar result.

For C_{120} (**1**): mp > 300 °C (transformation into C_{60} at around 175 °C); IR (KBr) 1463.9, 1425.3, 1188.1, 796.5, 769.5, 761.8, 746.4, 710.7, 705.9, 612.4, 573.8, 560.3, 550.6, 544.9, 526.5, 479.3, 449.4, 418.5 cm^{-1}; UV−vis (ODCB) λ_{max} (nm) (log ϵ) 328 (5.24), 434 (3.99), 700 (2.93); ^{13}C NMR, see text; MS [MALDI TOF, with 2,5-dihydroxybenzoic acid as a matrix; *m*/*z* (% rel intensity)] 1442 ($M^+ + 2$, 1), 1418 (5), 1394 (4), 1370 (3), 1346 (2), 1322 (1), 721 ($M^+ + 1$, 100). Anal. Calcd for C_{120}: C, 100.00; H, 0.00; N, 0.00. Found: C, 96.59; H, 0.00; N, 0.00 (incomplete combustion).

In a separate experiment starting from 49.5 mg of C_{60}, the crude product was dissolved in ODCB (10 mL) and the solution was added dropwise into rapidly stirred hexane (25 mL). The dark brown precipitates were filtered, redissolved in ODCB (17 mL), and reprecipitated from hexane (70 mL) to give dark brown powder (11.4 mg), which was 97% pure C_{120} according to HPLC analysis (22.3% yield). From the hexane solution was recovered unchanged C_{60} (34.3 mg, 69.3%).

Reaction was also conducted using 25.1 mg of C_{60} and 20 equiv of KCN in a Teflon capsule with a ceramic mixing ball in a same way as described above for the reaction in a stainless steel. The product mixture was obtained in 24.6 mg which contained 90.0% of C_{60} and 9.1% of C_{120} as determined by HPLC (Buckyprep).

Reaction of C_{60} with Other Reagents. The reactions with other reagents were conducted in a similar way using C_{60} (48 mg, 0.067 mmol). After the reaction, the mixture was washed with 20 mL of ODCB, filtered through a short column of silica gel, examined by HPLC (Buckyprep), and evaporated under reduced pressure. The product yield was calculated from the weight of the residual solid and the HPLC peak area. The reagent (mg, mmol) and the yield of C_{120} determined by HPLC are as follows: Li (1.0 mg, 0.14 mmol), 27.6%; Na (0.4 mg, 0.02 mmol), 31.5%; K (1.4 mg, 0.03 mmol), 29.1%; Mg (10.2 mg, 0.42 mmol), 17.6%; Al (9.0 mg, 0.33 mmol), 33.8%; Zn (13.0 mg, 0.20 mmol), 19.3%; 4-(dimethylamino)pyridine (8.9 mg, 0.073 mmol), 29.0%; 4-aminopyridine (5.0 mg, 0.053 mmol), 43.0%.

Dissociation of C_{120}. A solution of C_{120} in ODCB (4×10^{-5} M) was placed in a Pyrex glass flask under usual room light. The solution was examined by HPLC (Buckyprep) and indicated that C_{60} was formed in ~2% yield per day. The reaction was followed for total of 15 days until C_{60} was formed in 32.4%. No such change was observed when the solution was stored in the dark.

A solution of C_{120} in ODCB of the same concentration was placed in a test tube and heated at 175 °C for 15 min. The resulting solution was examined by HPLC and indicated that all starting material was converted into C_{60}.

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