First Unsymmetrical Bisfullerene, C_{121}: Evidence for the Presence of Both Homofullerene and Methanofullerene Cages in One Molecule

Nita Dragoe,*,[‡] Hidekazu Shimotani, Jian Wang, Mitsuhiro Iwaya, Ana de Bettencourt-Dias,[†] Alan L. Balch,[†] and Koichi Kitazawa*

Contribution from the Department of Applied Chemistry, University of Tokyo and Japan Science and Technology Corporation, JST−CREST, Tokyo 113-8656, Japan

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Abstract: We report the isolation and characterization of the bisfullerene C_{121}, the first all-carbon molecule to contain a homofullerene (also called a fulleroid) cage. This unsymmetrical isomer of C_{121} ,along with a symmetrical isomer of C_{121} and C_{122}, were obtained by thermolysis of a mixture of $C_{60}CBr_2$ and C_{60} and separated by high performance liquid chromatography. The predominant isomer of C_{121} has a spiro carbon atom bridge that connects to one of the cages through an open [5.6] ring junction (i.e., between a pentagon and a hexagon) and to the other through a closed [6.6] ring junction. Ab initio calculations indicate that the unsymmetrical structure is more stable than either of the symmetrical alternatives, with the bridging carbon atom attached to both C_{60} cages through closed [6.6] ring junctions or attached to each cage through open [5.6] ring junctions. Experimental evidence for the unsymmetrical structure comes from the ^{13}C NMR and UV/vis spectra. Electrochemical reduction of this bisfullerene shows three pairs of distinct, reversible peaks that correspond to each of the first three reductions of the [60]fullerene cages. This is consistent with the presence of a homofullerene unit and shows the similarity of the redox behavior to that of C_{60}. The first reduction potential of C_{121} is slightly shifted toward more positive values than that of [60]fullerene.

Introduction

Fullerene dimers and other bisfullerenes have attracted attention as models for fullerene polymers, for example, C_{120};[1] as intermediates for the formation of endohedral fullerenes;[2] or as molecules with interesting properties, such as electronic interactions between the two cages.[3−5] Segura and Martin outlined the interest in the fullerene dimers in a recent review.[6] In particular, the all-carbon fullerene dimers are interesting as allotropic forms of carbon and potentially as starting materials for coalescence reactions of fullerenes. The coalescence reactions, which produce higher fullerenes that are multiples of the starting fullerenes, have been observed in gas-phase studies of [60]fullerene.[7] Recent studies by Shvartsburg et al. of the gas phase behavior of [60]fullerene and related clusters revealed the presence of several ball-and-chain dimers in which fullerenes are linked by linear arrays of carbon atoms.[8,9] These studies have provided experimental evidence that the inclusion and exclusion of C_2 units are involved in the formation of fullerenes in the "fullerene road" mechanism for fullerene growth.

Considerable attention has been given in recent years to the chemical modification and functionalization of fullerenes. This work has produced an array of new fullerenes including water-soluble fullerenes, optically active fullerenes, fullerenes with holes in their skeleton, etc.[10] Important insight has been provided into the reactivity and structure of chemically modified fullerenes. When a fullerene is modified through the addition of a CR_2 bridging unit, there are four hypothetical structural possibilities. These include addition to form open and closed [6.6] ring junctions and addition to open and closed [5.6] ring junctions. However, only the [6.6] closed and [5.6] open structures have been found experimentally.[11,12] Usually, the thermodynamically stable product has the [6.6] structure; that is, it is a methanofullerene. A fullerene derivative with a [5.6] open connection is called a *fulleroid* or *homofullerene*.[13] Several fulleroids have been reported so far. Although some fulleroids can be isolated and characterized, they are generally unstable in comparison to the corresponding methanofullerenes. Remarkably stable fulleroids include the parent $C_{61}H_2$, which has been isolated as both the homofullerene (fulleroid) and methanofullerene isomer,[14,15] and an amphiphilic derivative of [60]fullerene with a $CH(CH_2)_9COOEt$ group connected to a [5.6] junction.[16] The

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* To whom correspondence should be addressed.

[†] Department of Chemistry, University of California at Davis, Davis, CA 95616.

[‡] Permanent address: Department of Physical Chemistry, Faculty of Chemistry, University of Bucharest, Bucharest, Romania.

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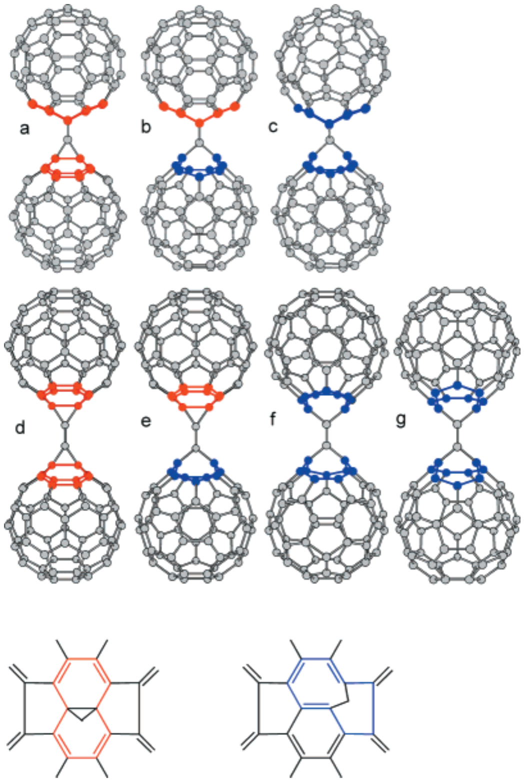

Figure 1. Possible isomers of C_{121} and C_{122} bisfullerenes (geometry optimized at HF/3-21G level). The cyclopropane and annulene-like connections are marked with red and blue, respectively (see the model). Compounds **f** and **g** are geometric isomers; the relative positions of the hexagons and pentagons of the two cages are trans or cis (note that for the bisfullerene **c**, there are two typical isomers). The compounds identified in this work are **1a**, **1b**, and **1d**.

latter is more stable in the homofullerene (fulleroid) form than in the corresponding methanofullerene form, and it was found that the methanofullerene-to-homofullerene isomerization occurs for this compound at room temperature.

For the reasons described above, we are interested in the synthesis and study of all-carbon derivatives of [60]fullerene, particularly in C_{121} and C_{122}.[17] Osterodt and Vogtle observed these species in mass spectroscopic studies of dibromomethano-[60]fullerene, $C_{60}CBr_2$, and proposed structures for them.[18] The preparation and isolation of C_{122} have also been reported by Strongin and co-workers.[19] We describe here the synthesis, separation, and characterization of a C_{121} fullerene, **1b**, which is the first all-carbon fullerene to contain a homofullerene unit. Among the products of the thermolysis of dibromomethano-[60]fullerene, we have also identified the high-symmetry C_{121} (D_{2d}, **1a**) and C_{122} (D_{2h}, **1d**) bisfullerenes whose structures are shown in Figure 1. Due to the low solubilities, small yields, and the difficulties of purification of these products, only **1b** could be fully characterized.

Results and Discussion

Theoretical Calculations. Among the possibilities of connecting a carbon atom to two [60]fullerene frameworks to produce C_{121}, three isomers can be envisioned (**1a**−**c**, Figure 1): [6.6]−[6.6], [5.6]−[6.6], and [5.6]−[5.6], where [6.6] denotes a closed methanofullerene structure and [5.6] signifies an open, homofullerene structure. Exploring the relative stabilities of the isomers **1a**−**c** through ab initio calculations, we have found that the [5.6]−[6.6] isomer **1b** should be the most stable of these (on the basis of the relative heats of formation of the three isomers). The calculations showed that **1a** and **1c** are less stable than **1b** by 3.12 kJ/mol and 20.21 kJ/mol. The stability difference increases at 750 K (the temperature of formation) to 8.46 and 23.20 kJ/mol, respectively. Having obtained this indication of stability of a fulleroid of C_{121}, we continued our efforts to isolate it.

We assume that the reason for a higher stability of **1b** compared to **1a** is a release of the strain that is involved in the spirane structure. There are many factors influencing the equilibrium geometry for strained structures as **1a** and **1b**. For instance, there is the release of the strain of the [60]fullerene cage by addition to a double bond, which actually governs the reactivity of fullerenes; the preference of the [5]radialene structure; and the occurrence of Bredt's Rule violations.[20] For such a complex system, it is difficult to accurately assess the determinant factors. We assume that the strain energy that is involved in building the rigid spirane unit between the fullerene cages is probably higher than that of the release of the strain associated with the addition to the sp^2 carbon atoms of [60]-fullerene.[21] Moreover, contrary to other cyclopropane or homofullerene derivatives, the geometry of the bridge carbon is affected from both sides of the molecule. Thus, for a $C_{61}H_2$ derivative, the H−C−H angle is not restricted by reasons other than energetic. For C_{121}, the bridge carbon is affected, and its geometry is restricted, by both fullerene cages. In the case of C_{122}, theoretical calculations showed that among the three possible isomers of C_{122} (**1d**−**f**), the one having D_{2h} symmetry, that is, **1d**, is by far the most stable.

Synthesis of C_{121}. Considering the theoretical data on the relative stability of these isomers, we explored the reaction conditions so as to obtain the homofullerene C_{121} isomer. In our experiments for the synthesis of C_{121}, we used thermolysis of a mixture of [60]fullerene and $C_{60}CBr_2$. This procedure is based on the fact that a C_{61} cluster seems to be relatively stable in the gas phase under MS conditions.[22] However, in our studies, the thermolysis reactions were conducted in solid state by heating a mixture of [60]fullerene/$C_{60}CBr_2$ at a rate of 5 K/min up to 723 K and then quenching the sample. The separation of the mixture by using preparative GPC yielded C_{122} and C_{121}. The latter was initially thought to consist of the highly symmetrical C_{121} isomer (D_{2d}, **1a**), but we later found that it is actually a mixture of two C_{121} isomers (**1a** and **1b**). The formation of **1b** and the lack of **1c** are consistent with the results of theoretical calculations concerning the relative stabilities of the three C_{121} isomers.

Thermogravimetric experiments on $C_{60}CBr_2$ showed that decomposition, presumably by bromine elimination, starts around 450 K and slowly evolves up to 750 K. Consequently, we performed a thorough investigation of the reaction process in this range of temperatures. When using 12 h of thermolysis

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reactions, we found the proper conditions to be in the range of 500−575 K. Under these conditions, mainly two fractions of bisfullerenes could be obtained, and these were subsequently identified as **1d** and **1b**. C_{122} (**1d**) is obtained as a byproduct in yields which are dependent on the sample preparation, usually in the 1−2% range. For example, a large excess of [60]fullerene in the starting material and/or coprecipitation of the products reduced the formation of C_{122}. The high-symmetry C_{121} isomer **1a** was found in a fraction eluting just before **1d** in the recycling HPLC on 5PBB columns, see later. Our work focused on the separation and characterization of the major product of this reaction, the unsymmetrical C_{121} isomer, **1b**. The yield of formation of **1b** is typically 5−10%.

A typical synthesis of this C_{121} isomer is described in the Experimental Section. The synthetic procedure is tolerant of adjustments such as temperature and scale, although the reaction yields have a dependency on the "history" of the sample; that is, the purity of the starting material, degree of crystallinity, etc.

HPLC Experiments

To illustrate the separation process, several HPLC experiments are shown in the Supporting Information.[23] The HPLC trace of the starting material (C_{60}:$C_{60}CBr_2$, 4:1) on a preparative Cosmosil Buckyprep column (20 × 250 mm) showed that $C_{60}CBr_2$ eluted slightly before [60]fullerene (7.4 vs 7.8 min). The HPLC trace of the thermolysis product (12 h at 330 °C) on the same column under the same conditions showed, besides a major peak for [60]fullerene, at least two bisfullerene fractions eluting between 19 and 22 min. The low solubility of the bisfullerenes in toluene and the large excess of [60]fullerene in the crude reaction product rendered these HPLC conditions to be of little preparative utility. We improved the process by initial removal of [60]fullerene from the reaction product and by using *o*-dichlorobenzene (ODCB) as the mobile phase on a semipreparative 5PBB column (Supporting Information). By using 5PBB column with ODCB as eluent, three fractions were obtained: I contained mainly [60]fullerene with traces of unreacted $C_{60}CBr_2$, II contained the bisfullerene mixture, and III contained trimers and possibly higher oligomers (MS). The HPLC of fraction II on a Buckyprep column and eluted with toluene is shown in Figure 2. The fractions of interest that were observed in this HPLC chart eluted around 20 min and were subsequently identified as **1a**, **1d**, and $C_{120}O$ (vide infra), in the peak at eluting at 19−20 min, and **1b**, in the peak eluting around 21 min. C_{60} elutes at 7.6 min. Several other minor fractions with elution times at 12, 16, 24, 26, 28, 30, and 34 min could be observed (see Supporting Information). These fractions were not characterized any further. They appeared to be unstable and yielded [60]fullerene and other materials after weeks of storage at room temperature. Moreover, the yields of these fractions were in the best cases about 0.1−0.2% (HPLC); hence, their identification was not possible. These fractions appeared to be significant when the thermolysis temperatures were low; hence, we believe they are the products of secondary radical reactions (for instance, the addition of bromine atoms to the bisfullerenes).

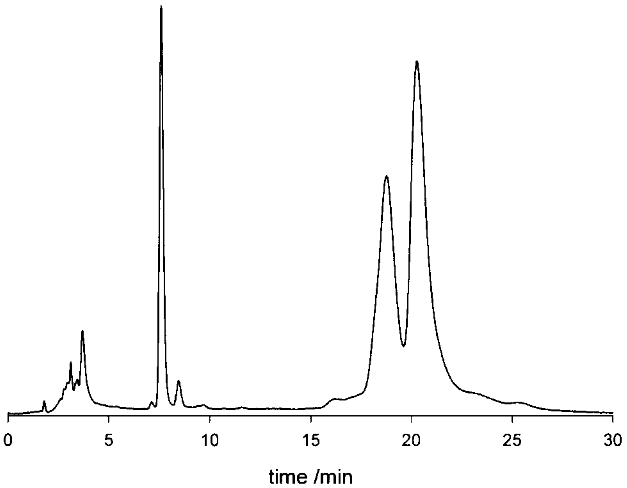

Figure 2. HPLC plot of the dimeric fraction dissolved in toluene; Cosmosil Buckyprep 20 × 250mm; toluene, 20 mL/min; 330-nm detection.

We explored the HPLC conditions that were suitable for the separation of the fraction II into pure compounds. Several separation strategies are possible. We examined the following: (I) HPLC separation with toluene as eluent on Buckyprep column and (II) HPLC separation with ODCB as eluent on a 5PBB column and incorporating recycling.

In the case of method I, the limiting step is the small solubility of the fullerene mixture in toluene, but this method is able to separate C_{121} (**1a**, **b**) and C_{122} (**1d**) isomers. If $C_{120}O$ and related dimers ($C_{120}O_2$) are not present in the sample, this method is appropriate for the purification of small amounts (a few milligrams) of these bisfullerenes. The advantages of method I are that it does not require recycling and the Buckyprep column is readily available. Method II requires long separation times and recycling. However, it is better than I because the solubility of the bisfullerenes in ODCB is much higher (at least 1 order of magnitude) than in toluene. We note that preparative GPC with toluene can also be used for the separation of these fullerenes. However, the main disadvantages of the GPC separations are its inability to separate the isomers **1a** and **1b** and the long time required, 24 h for a 12-mL portion of a toluene solution of bisfullerenes.

Procedure II uses two preparative 5PBB HPLC columns (20 × 250 mm), with ODCB as eluent, and recycling. Figure 3 shows the separation of the bisfullerenes by this method. It allows the separation of a 3-mL portion of an ODCB solution in about 6 h. There are three main fractions in this HPLC, identified as **1d**, $C_{120}O$, and **1b** (the major product). The small shoulder appearing before **1d** was assigned as D_{2d} C_{121} (**1a**) on the basis of MS experiments and its partial conversion to **1b**.

One of the difficulties of the separation and characterization of the C_{121} isomers was the presence of the oxygen-containing bisfullerene such as $C_{120}O$ and $C_{120}O_2$. $C_{120}O$ seems to be unavoidable in commercial [60]fullerene, as observed recently by Taylor and co-workers,[24] and it can be easily formed when samples of fullerenes stand in air. The presence of $C_{120}O$ with the same retention time as **1a** and a retention time similar to that of **1d** is intriguing, because $C_{120}O$ was reported to elute at 15−16 min on Cosmosil Buckyprep column. We find it eluting at 18.5−19 min on both analytical Cosmosil Buckyprep (4.6

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[23] The toluene solutions of the bisfullerenes were subjected to at least two HPLC separations, which were performed on a preparative Cosmosil Buckyprep HPLC column: 10 mm × 20 mm guard column coupled with a 20 mm × 250 mm column, 9 mL/min toluene flow, 330 nm detection, 9 mL injection volume. Compounds **1d** and **1b** elute at 42.1 and 44.8 min, respectively. On a semipreparative Cosmosil 5PBB HPLC column (guard column 5PBB 10 mm × 20 mm and 5PBB column of 10 mm × 250 mm) with 2.5 mL of chlorobenzene as eluent, detection at 340 nm, **1d** and **1b** elute at 29.8 and 32.3 min, respectively. With a Shodex ODS 4.6 × 20 guard column coupled to an analytical Cosmosil Buckyprep 4.6 × 250 mm, detection at 330 nm, toluene flow 1 mL/min, [60]fullerene elutes at 8.10 min and **1d** and **1b** elute at 19.6 and 20.9 min, respectively.

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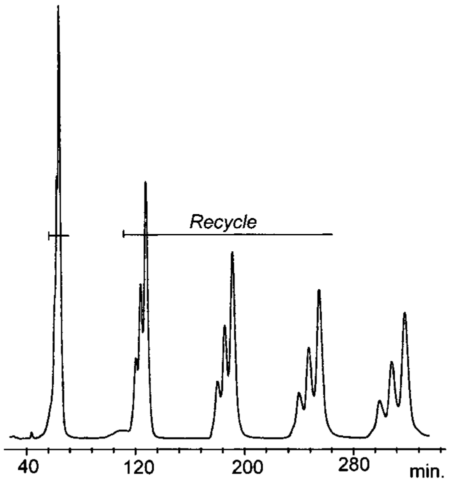

Figure 3. Recycling HPLC for the separation of the bisfullerenes using 4.2 mL/min ODCB flow and two preparative Cosmosil 5PBB columns. The continuous bar on top of the chart shows the recycling periods. The three major peaks in the order of elution are: **1d**, $C_{120}O$, and **1b** (**1a** eluted slightly before **1d**; it was removed from the mixture after the first cycle period).

mm × 250 mm, 1 mL/min toluene flow) and preparative Buckyprep column (20 × 250, 20 mL/min toluene flow), while [60]fullerene elutes at 7.5−7.8 min. This was rather surprising but the presence of $C_{120}O$ was confirmed by ^{13}C NMR spectroscopy, which produced spectra identical to those reported in the literature.[25] The presence of $C_{120}O$ in our samples was probably due to its presence in the commercial [60]fullerene and its formation when the fullerene samples were manipulated in air in the presence of light.

Mass Spectroscopy. The Maldi-TOFMS data for **1b** and **1d** are shown in Figure 4a. We have obtained accurate values of the molecular peaks, with absolute errors within 0.1 Da, and the isotopic distribution peaks compare well to the expected one. The bisfullerene **1b** was detected only when using a matrix, dithranol or 9-nitroanthracene. The LDI-TOFMS for these bisfullerenes showed strong fragmentation and products of ion reactions of fullerenes, which produces a series of clusters with the composition $C_{120} + nC_2$, as seen in Figure 4b. Similar results were obtained when using dithranol as the matrix and when spectra were obtained in the negative ionization mode. We note a possible pitfall in the LDI−MS analysis of fullerene derivatives: the systematic appearance of a peak due to C_{122} in the MS obtained from **1b** and **1d**. Additionally, depending upon the laser power, C_{120}, C_{123}, C_{124}, and C_{125} also can be observed in these spectra. The C_{122} peak originated in the addition/elimination reactions of C_2 units with fullerene-like clusters in the MS. C_{122} and related clusters (C_{120}, C_{121}, C_{123}, C_{124}, C_{126}, and trimers C_{182}, C_{183}, and C_{184}, etc.) are detected fairly easy in the LDI−MS experiments of the triply chromatographically separated $C_{60}CBr_2$ or many other methanofullerenes under appropriate conditions. We conclude that the use of LDI−MS should be used with caution unless MALDI techniques are used for comparison. This is especially the case for compounds having masses that are a multiple of C_{60} or C_{61}, in which case gas-phase reactions in the mass spectrometer can interfere with the true value of the mass.

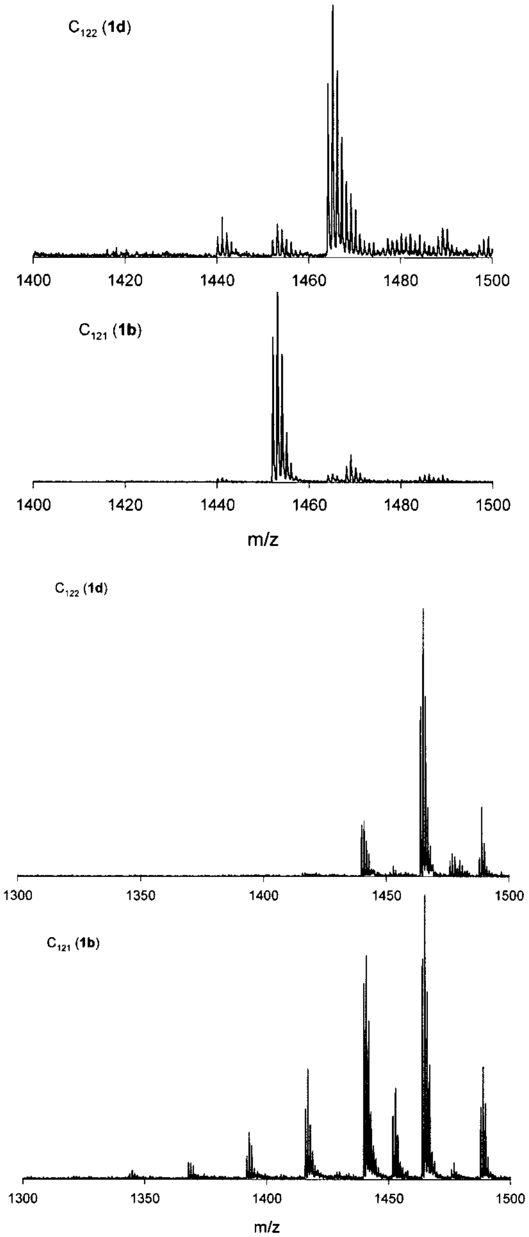

Figure 4. (a) Maldi-TOFMS (9-nitroanthracene as matrix) experiments of **1d** and **1b**. The small peak at C_{121} (1453.3 amu) in panel a originates in the presence of traces of **1a** in the material separated by recycling (see also Figure 3). (b) The LDI-TOFMS of **1d** and **1b**; **1d** is more resistant to fragmentation under these conditions. C_{121} is strongly affected by the laser power, resulting in mostly even-numbered carbon clusters.

Using the procedure described recently by Gross et al.,[26] we also performed LT−FAB MS experiments, and the parent C_{121} peak (1453 amu) could be observed only for **1b**, although with a small S/N.

^{13}C NMR

The ^{13}C NMR analysis of these isomers was difficult because of the limited solubility, as well as low symmetry, of **1b**. For that matter, the use of 1-chloronaphthalene as the solvent was essential, and resonances from the solvent completely covered the 124−137 ppm region. Of all of the solvents we tested, 1-chloronaphthalene was determined to be the best solvent for

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(25) $C_{120}O$ was also obtained from a sample of commercial [60]fullerene, and we found that it elutes at 19 min on a Buckyprep column. A ^{13}C NMR spectrum of this sample was found to be identical to those reported both by Lebedkin, S.; Ballenweg, S.; Gross, J.; Taylor, R.; Kratschmer, W. *Tetrahedron Lett.* **1995**, *36*, 4971 and by A. B. Smith III et al. (see ref 33).

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these bisfullerenes, yet the solubility is rather low, <3 mg/mL. Additionally, to maintain a high solubility we used 1-methylnaphthalene-d_{10}, another good solvent for fullerenes, as the lock reagent. We observed that **1b** was more soluble than **1d** in 1-chloronaphthalene. In other solvents, these bisfullerenes are only sparingly soluble. For instance, in CS_2 and ODCB, which are quite good solvents for fullerenes, the solubilities of **1d** and **1b** are <0.1 mg/mL. Because of the appearance of spin−spin coupling satellites and the low symmetry of the bisfullerenes, the use of ^{13}C-enriched [60]fullerene alone did not provide an alternative for a better ^{13}C NMR analysis. Because the key structural feature of these bisfullerenes is the bridging region, we performed ^{13}C NMR experiments on samples with the bridging carbon atoms enriched to 99% ^{13}C.

The ^{13}C NMR spectrum of **1d** (with natural abundance ^{13}C) is presented in Figure 5a.[27] Sixteen resonances are observed in the sp^2 region. Three of these have intensity four, and the others are eight-intensity resonances and are in agreement with a D_{2h} C_{122} dimeric structure. The spectrum is similar to that reported by Fabre et al.[19] except for the sp^3 region (the sp^3 carbon atoms of fullerene). In the sp^3 region, there was only one quaternary carbon resonance, whose intensity integrated for four carbons, located at 84.71 ppm. The carbon atoms in the bridging positions of C_{122} (the cyclopropylidene carbon atoms) resonate at 128.62 ppm in ^{13}C NMR experiments on 99% ^{13}C-enriched samples dissolved in CS_2.

For **1b**, 62 resonances are expected in the sp^2 region, with 6 being single-intensity and the rest being double-intensity resonances. Additionally, three single-intensity resonances should be observed in the sp^3 region. Indeed, three single-intensity resonances of the quaternary carbon atoms were observed in the sp^3 domain, which is in agreement with the [5.6]−[6.6] structure for the C_s symmetry C_{121} isomer. There is good agreement, particularly concerning the sp^3 resonances, between the experimental spectrum and the spectrum predicted by the GIAO method.[28] The resonance located at 56.4 ppm was confirmed as belonging to the bridge carbon atom following ^{13}C NMR experiments on a sample that was 99% ^{13}C-enriched at the bridging carbon atom. In the sp^2 region, 60 resonances with accidental overlap and within the limits of the resolution, 6 of them having single intensity, were observed. The sixth was assigned on the basis of the peak integration to the cluster at 145 ppm (Figure 5b).

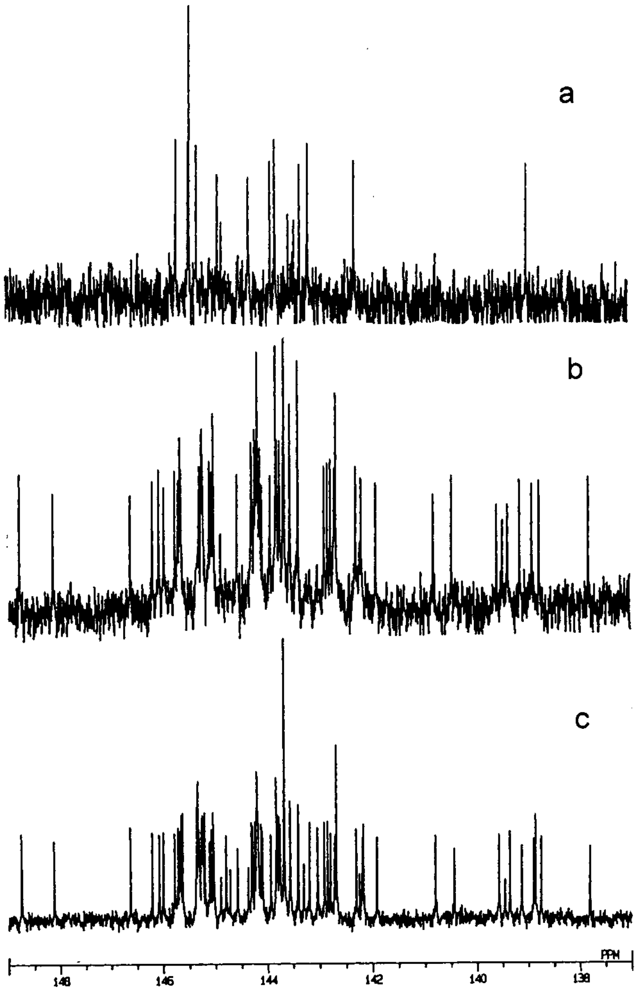

Figure 5. ^{13}C NMR of **1d** (top), **1b** (middle), and a 1:4 mixture of **1d**:**1b**. The spectra are consistent with D_{2h} and C_s symmetries of the bisfullerenes.

Several attempts[29] to uncover the missing sp^2 fullerene carbon atom resonances failed. One of the missing double-intensity resonance probably originates in the two sp^2 bridge-carbon atoms involved in the [5.6] connection. This resonance is expected to be strongly shifted upfield. With red and blue are marked Ab initio calculations predicted that the two sp^2 carbon atoms involved in the bridge structure should resonate at 132 ppm. We assigned the bridge carbon atoms of the [5.6] connection to sp^2 on the basis of the observation that addition across at a [5−6] bond yields *exclusively* the [5.6] open isomer. This assignment is also in agreement with the three single-intensity resonances located in the sp^3 region, as well as with the ab initio calculations, which showed a nonbonding distance between the two [5.6] carbon atoms.

We performed an experiment that supports the structural assignment for the isomer **1b**. A ^{13}C NMR spectrum obtained from a mixture of **1d** and **1b** in a 1:4 ratio showed that the eight-intensity resonances belonging to **1d** are of about the same intensity as the double-intensity resonances of **1b** (Figure 5c). This is in agreement with the additional symmetry elements in **1d**, as compared to **1b** isomer (D_{2h} vs C_s).

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[27] We had first considered that the fraction having 16 resonances in the ^{13}C NMR would be that of a C_{121} with high symmetry. We note that the distinction between C_{121} and C_{122} is not as straightforward as it might seem. The MS data on both of these bisfullerenes have peaks corresponding to C_{122}, which originates in ion reactions of fullerenes in the mass spectrometer. Moreover, the highest symmetry bisfullerenes (**1a**, **1d**) have indistinguishable ^{13}C NMR spectra in the sp^2 region. Thus, both of them should have sixteen ^{13}C NMR resonances in the 137−145 ppm range, and three of these should half the intensity of the others. The key features used to distinguish these bisfullerenes are the resonances of the carbon atoms that act as bridges between the fullerene cages. The highest symmetry bisfullerenes **1a** and **1d** have four sp^3 carbon atoms on the fullerene cages, and these carbon atoms are expected to produce resonances in the 50−80 ppm range. The bridge carbon atom in **1a** should produce only one resonance in the 20−60 ppm range, and this resonance should be 1/8 the relative intensity of the fullerene sp^2 carbon atoms resonances. The dimer **1d** should have one resonance of the sp^2 carbon atom region of 1/4 intensity, located in the 110−140 ppm range. Unfortunately, these distinctive features cannot be undoubtedly observed in ^{13}C NMR experiments, due to frequent impurities, solvent resonances, and the intrinsic low solubility of these bisfullerenes. The case of lower symmetry bisfullerenes is even more difficult, because the ^{13}C NMR spectra of these molecules have tens of resonances distributed over 1 ppm (see also the ^{13}C NMR section). Therefore, we were were compelled to use ^{13}C labeling for the analysis of these bisfullerenes. Samples having 99% ^{13}C-enriched carbon atoms bridges and 15% ^{13}C-enriched fullerene cage carbon atoms were synthesized. With the help of these experiments, we obtained convincing evidence that the two main bisfullerene products reported here have the structures **1b** and **1d**.

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[29] Several ^{13}C NMR experiments, 48−160 h acquisition on ^{13}C NMR (JEOL 67.7 MHz, and Varian 75 MHz), in ODCB-d_4 failed to provide a spectrum in which this resonance could be identified. Similar experiments in CS_2 with a high-field NMR (^{13}C, 125 MHz) were again unsuccessful.

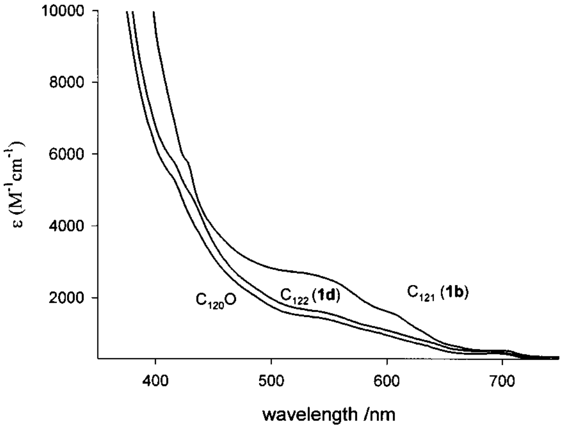

Figure 6. UV/vis spectra of **1b**, **1d**, and $C_{120}O$ in ODCB, determined using solutions of concentrations of 0.1 mg/mL.

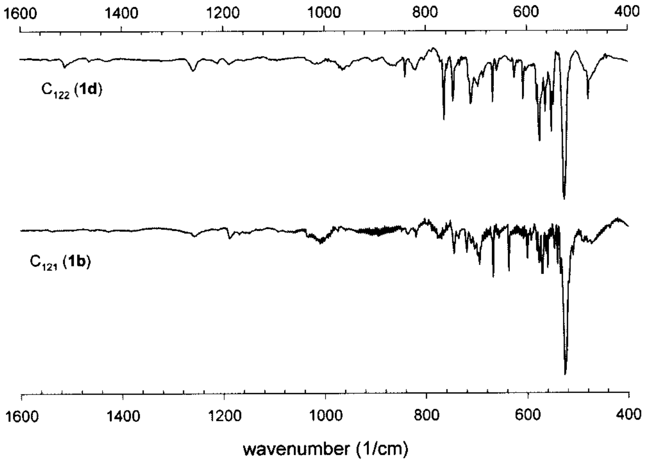

Figure 7. FTIR spectra of **1b** and **1d**.

Compelling evidence about the structures of **1b** and **1d** was obtained from ^{13}C NMR experiments of samples prepared by mixing $C_{60}CBr_2$ in which the cyclopropane bridge carbon atoms were 99% ^{13}C-enriched (the other 60 carbon atoms were not ^{13}C-enriched) with 15% ^{13}C-enriched [60]fullerene. Thermolysis of this mixture produced partially ^{13}C-enriched C_{121} and C_{122} samples whose ^{13}C NMR spectra were recorded. We note that C_{121} obtained in this way should have only one ^{13}C-enriched [60]fullerene cage, but the other should have natural abundance ^{13}C. For the case of C_{122}, both [60]fullerene cages should have natural abundance ^{13}C, and only the bridge carbon atoms should be enriched in ^{13}C. The ^{13}C NMR spectrum of **1d** showed the cyclopropylidene resonance as a singlet at 128.6 ppm, but the ^{13}C-enriched **1b** showed for the resonance at 56.4 ppm two types of spin−spin couplings, broadened and ∼7−8% in intensity. The presence of these two types of spin−spin couplings, of ∼13 and 23 Hz are indicative of both sp^3−sp^3 and sp^3−sp^2 couplings. This is the result of the scrambling of the ^{13}C-enriched [60]fullerene cages between the two possibilities, that is, closed and open structures. Spin−spin coupling measurements on related compounds were examined as a means of distinguishing between fulleroids and methanofullerenes.[30] The values of J_{cc} for the bridgehead carbon atoms of $C_{60}C(CH_3)_2$ were found to be 32 Hz for the fulleroid and 20 Hz for the methanofullerene isomers. For **1b**, J_{cc} for the bridging carbon atom is 23 Hz for coupling to the fulleroid cage and 13 Hz for coupling to the methanofullerene cage. Although these values are smaller than those of $C_{60}C(CH_3)_2$, they are in the expected range.[31] The differences may be due to the increased strain in the bridging carbon atom in C_{121} as well as the electronic influence of the adjacent fullerene cage.

The implications of these findings, which support the assignment of **1b** as containing a homofullerene cage, are discussed below in conjunction with the reaction mechanism.

Optical Spectroscopy. Optical spectroscopy allowed a straightforward identification of the homofullerene derivative. The UV/vis spectra of **1b** and **1d** dissolved in ODCB are shown in Figure 6. For comparison, the spectrum of the well-known bisfullerene, $C_{120}O$ is also shown. The spectra suggest that **1b** has a different type of structure from either $C_{120}O$ or **1d**. The spectrum of **1b** in ODCB is similar to that of a mixture of a homofullerene and a methanofullerene. The UV/vis spectra of methanofullerenes have characteristic absorptions at 430−440 nm and 690−710 nm. All of these bisfullerenes ($C_{120}O$, **1b**, and **1d**) have methanofullerene chromophores, and their spectra should resemble those of methanofullerenes. Indeed, all of them have 330-, 430-, and 700-nm absorption bands with different extinction coefficients. Contrary to the methanofullerenes, the homofullerenes have vis features similar to those of [60]fullerene, although they show hypsochromic shift and have the vis features diminished as compared to the [60]fullerene.[32] Moreover, the UV/vis spectra of bisfullerenes are also known to have diminished features.[33] Thus, the features in the vis region of the **1b** spectrum were assigned to a homofullerene chromophore (i.e., 60π electrons). It is noteworthy that the UV/vis spectra in toluene for the fractions **1d** and **1b** are very similar, rendering impossible a clear distinction between these isomers when using the UV/vis spectra in toluene. The toluene solutions of $C_{120}O$, **1a**, and **1d** are golden-yellow, as reported previously for C_{122}, and cannot be differentiated. This is probably due to the low solubility of these dimers in toluene. The ODCB and CS_2 solutions of $C_{120}O$, **1a**, and **1d** are all yellow-orange, but **1b** is red, thus rendering possible an easy distinction between the **1b** and the bisfullerenes containing only methanofullerene units. Recycling HPLC experiments on a system with a multiwavelength detector (200−900 nm) make possible the distinction between the fulleroid and methanofullerene isomers.

The FTIR spectra (KBr pellets measured under vacuum, 1024 scans, Ge/KBr beam splitter, and using a DTGS/KBr detector) of the two isomers (**1b**, **1d**) are shown in Figure 7. Their spectra are quite similar, although the isomer **1b** has diminished IR features when compared with **1d**. This is consistent with the symmetry of the two isomers. The breathing mode vibration of [60]fullerene is split and slightly shifted in the case of **1b**.

Electrochemical Measurements. As seen in Figure 8, the differential pulse voltammogram of **1b** shows six distinct peaks, which in pairs correspond to each of the first three reductions of the fullerene cage. The potentials of the peaks are: −1044, −1124, −1436, −1532, −1988, and −2160 mV vs ferrocene/ferricinium. Thus, the potential difference is roughly 80 mV for the first two sets of peaks and roughly 135 mV for the third and last set of peaks. Thus, the separation between pairs of peaks increases as reduction proceeds, as seen for $C_{122}H_4$ and $C_{120}O$. Cyclic voltammetry shows that these reductions are quasi-

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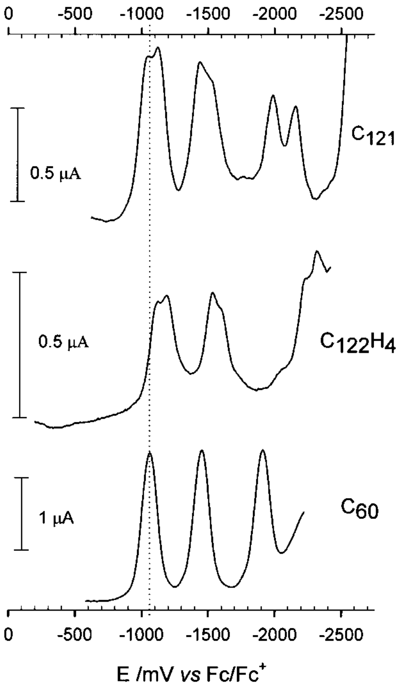

Figure 8. Differential-pulse voltammogram of C_{121} (top trace), square-wave voltammogram of $C_{122}H_4$ (middle trace), and C_{60} (bottom trace) in *o*-dichlorobenzene with 0.1 M TBAP as supporting electrolyte. For the DPV the parameters were scan rate, 20 mV/s; pulse amplitude, 50 mV; sample width, 17 ms; pulse width, 50 ms; and pulse period, 200 ms. For the SWV, the parameters were pulse step, 2 mV; square-wave frequency, 15 Hz; square-wave amplitude, 10 mV; and 256 samples/point for $C_{122}H_4$; pulse step, 4 mV; square-wave amplitude, 25 mV; square-wave frequency, 15 Hz; and 256 samples per point for C_{60}. The first reduction potential of C_{60} is shown by the dotted line.

reversible. In traces b and c of Figure 8, the differential pulse voltammograms of $C_{122}H_4$ and [60]fullerene are shown for comparison.

The reductions take place sequentially on each of the two distinct [60]fullerene cages, on both the homofullerene and the methanofullerene cages. The reduction potentials for isomeric fulleroids and methanofullerenes are reported to be essentially identical for the first two one-electron reductions, with isomerizations between the two forms occurring upon addition of a third electron.[34−36] Consequently, the pairwise splitting of peaks seen in Figure 8 does not necessarily arise from the intrinsic differences in the two fullerene cages in C_{121}. Rather, this splitting is a consequence of the successive addition of electrons to each fullerene cage. The magnitudes of the effects are similar to those seen in both $C_{120}O$ and $C_{122}H_4$ (trace b) in which the two fullerene cages are identical until electrons are introduced via reduction. However, the first reduction of C_{121} occurs at a potential that is slightly shifted to more positive potentials from that of [60]fullerene (trace c). For [60]fullerene adducts, shifts of the reduction potentials to more negative values are expected, and the lack of such a shift for C_{121} may reflect the unusual electronic structure that involves coupling of two dissimilar carbon cages.

Reaction Mechanism for Formation of 1b. For the formation of **1a** and **1b**, several reaction mechanisms can be proposed. The most significant are: (i) the formation of an intermediate carbene, [6.6]C_{61}; and (ii) a nucleophilic attack of a $C_{60}CBr^-$. For the path (i) the kinetically controlled reaction should yield a [6.6] structure, **1a**, because of a shorter [6.6] double bond than the [5.6] in [60]fullerene. For path (ii) a nucleophilic attack of $C_{60}CBr^-$ followed by a statistical distribution of ring formation between the [6.6] and [5.6] sites would allow both **1a** and **1b** to form, with the formation of the latter being preferred on the basis of statistical considerations (two 6−5 bonds for a given 6−6 bond). Because **1b** may be formed via a methanofullerene-to-fulleroid isomerization, in either of the two mechanisms, both of the isomers, **1a** and **1b**, should be obtained. The methanofullerene-to-fulleroid isomerization, known in fullerene chemistry, is also consistent with the relative stability of **1a** and **1b**. The mechanism of this rearrangement could be similar to that proposed earlier.[14,15] Extensive discussions on the reaction mechanisms of fulleroid/methanofullerene conversions can be found in references.[37−39]

An experiment devised to clarify the reaction mechanism involved the use of partially ^{13}C-enriched materials (see also the ^{13}C NMR section). The distribution of the spin−spin coupling satellites of **1b**, which was 99% ^{13}C-enriched at the bridging carbon atom, suggested the presence of both sp^3-sp^2 and sp^3-sp^3 couplings in **1b**. This can arise from the presence of a symmetrical intermediate during the reaction process as follows: (a) an interconversion of **1a** to **1b**, which would be nonselective relative to the fullerene cages (enriched or not), thus yielding bisfullerenes in which both types of cages, methanofullerene or homofullerene, have ^{13}C-enriched carbon atoms; or (b) an "inversion" of the **1b** structure, passing through **1a** as an intermediate.

The **1b** that is formed as a result of the nucleophilic attack of $C_{60}CBr^-$ should have only the homofullerene cage enriched with ^{13}C carbon atoms. Therefore, no sp^3-sp^3 couplings should be observed in the ^{13}C NMR. Given the fact that we observed sp^3-sp^3 couplings for the bridge structure of **1b** and considering that the conversion of **1b** to **1a** and back to **1b** is unlikely, we suggest that the mechanism involves a carbene attack by C_{61} on C_{60} followed by isomerization of **1a** to **1b**.

Conclusions

We present experimental data consistent with the fact that a C_{121} isomer, **1b**, with one fulleroid cage is more stable than the corresponding symmetrical isomers, **1a** and **1c**, with two methanofullerene cages or two fulleroid cages. These findings present a unique opportunity to study 58- and 60-π-electron chromophores and their intramolecular interactions.

Electrochemical measurements indicate that the two cages in the **1b** isomer of C_{121} exchange signals electronically. The first reduction potential of **1b** is unexpectedly shifted toward more positive values than that of [60]fullerene.

This interesting bisfullerene is the first example of a molecule that incorporates both types of cages, fulleroid and methanofullerene, and it is the first all-carbon fulleroid. Our continuing efforts are concentrated on the optical and electronic properties of these bisfullerenes and, in particular, on studies concerning the supramolecular complexes of calix[8]arene and **1b**. We assume that supramolecular complexes of **1b** with electron donors will show selectivity toward the complexation of one of the two [60]fullerene cages, thus holding the potential for

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practical applications as molecular switches and information storage materials.

Experimental Section

General. [60]fullerene (>99.5% purity) was purchased from Term Co. and purified by sublimation. The solvents were reagent grade and were dried and distilled before use. All reactions were performed under a dry argon atmosphere. UV/vis spectra were obtained using a Hitachi 9000 spectrophotometer with toluene, CS_2, or *o*-dichlorobenzene solutions. IR spectroscopy experiments were performed with a Bruker FTIR instrument on KBr micropellets. ^{13}C NMR spectra were obtained using a JEOL JNM270 (^1H 270 MHz) spectrometer in CS_2, 1,2-dichlorobenzene-d_4 (ODCB), or 1-chloronaphthalene solutions with Varian spectrometers (^1H frequencies of 300 and 500 MHz). Laser desorption and ionization time-of-flight mass spectroscopy (LDI-TOFMS) and matrix assisted LDI-TOFMS (MALDI) spectroscopy were performed using either a Perseptive Biosystems instrument or a Bruker Reflex instrument with a 337-nm laser. As matrix, we used dithranol or 9-nitroanthracene. HPLC experiments were performed with preparative (20 × 250) and analytical Cosmosil Buckyprep columns having toluene as eluent, or with a Cosmosil 5PBB column (10 × 250 and 20 × 250) with chlorobenzene or ODCB as eluents. The HPLC experiments were performed using either a preparative JAI-LC 908 system, an analytical Jasco instrument, or a diode-array MD1515 Jasco HPLC equipped with both gradient and recycling options.

Preparation and Isolation of C_{121}. In a flame-dried flask, NaH powder (55% in oil, 2.4 g, 55 mmol) was washed with two 10-mL portions of dry hexane. [60]fullerene (720 mg, 1 mmol) in 100 mL dry ODCB was added, and the flask was filled with argon, then cooled to 0 °C. Through a pressure-equalizing funnel, $CHBr_3$ in dry ODCB (1/10 v/v) was dropwise added under strong stirring while the reaction was followed by HPLC.[40] The reaction was quenched when the conversion of [60]fullerene reached about 60%, and an aqueous work-up, followed by extraction with ODCB, gave a red solution. The solution was dried and passed through a 10-cm silica/alumina plug. The solvent was evaporated in vacuo, and the black powder was dissolved in toluene. HPLC separation on a 5PBB column with elution with toluene afforded about 250 mg of $C_{60}CBr_2$. Subsequently, 50 mg $C_{60}CBr_2$ and 250 mg [60]fullerene were dissolved in 50 mL of ODCB. To this solution under stirring, 150 mL of acetone were added, which induced the coprecipitation of [60]fullerene and $C_{60}CBr_2$. The brown-yellow precipitate was filtered and then dried in vacuo. The powder was placed in an atmosphere-controlled furnace and heated under a 50 mL/min flow of argon for 20 h at 260 °C. The product was then dissolved in ODCB, and the [60]fullerene was removed using a semipreparative 5PBB column (10 × 250) having a 6 mL/min ODCB flow and a 4-mL injection volume. The [60]fullerene eluted at 8.1 min, and the C_{121} mixture eluted at 10.55 min. The mixture of bisfullerenes was collected, and the solvent was removed in vacuo at 80 °C to produce a brown powder. Subsequently, the bisfullerenes were subjected to preparative multistage HPLC or GPC for further separation. The typical yield for the bisfullerene **1b** ranged from 5 to 10%.

Theoretical Calculations. All calculations were made using the Gaussian 98W package.[41] Frequency analysis was made at STO-3G; energy and NMR-GIAO calculations were made at the HF/6−31(d) level; and geometry optimizations were made using the Becke-style 3 Parameter Density Functional Theory, using the Lee-Yang and Parr correlation functional, with a 6-31G(d) basis set.[42]

^{13}C NMR Spectroscopy. The ^{13}C NMR spectroscopic measurements at 67.7 MHz were performed in 1-chloronaphthalene with 20% v/v 1-methylnaphthalene-d_{10} for field/frequency lock in an instrument with a 10-mm ^{13}C NMR probe. $Cr(acac)_3$ was used as a relaxation agent at a concentration of 10 mM. Either the $-CD_3$ resonance at 19.2 ppm or the most upfield resonance of 1-chloronaphthalene, 124.32 ppm, was used as reference. For the spectra presented in Figure 6a−c, the following conditions were used: (a) 34464 scans, 90° pulses, 6.854-s pulse delay, 3.146-s acquisition time; (b) 44735 scans, 60° pulse, 2-s pulse delay, 3.146-s acquisition time; (c) 60716 scans, 45° pulse, 0.427-s pulse delay 3.146-s acquisition time.

Electrochemistry. Voltammetric experiments were performed on a BAS CV50−W electroanalytical system equipped with a three-electrode cell. The measurements were made by dissolving **1b** in 4 mL of ODCB with 0.10 M tetra(*n*-butyl)ammonium perchlorate as supporting electrolyte at a gold disk electrode equipped with a Pt wire counter-electrode and a Ag/Ag^+ reference electrode. The ferrocene/ferricinium couple occurs at 220 mV vs Ag/Ag^+ in this system. The DPV measurements were made at a scan rate of 20 mV/s, pulse amplitude of 50 mV, sample width 17 ms, pulse width 50 ms, and pulse period 200 ms.

Acknowledgment. N. D. gratefully acknowledges the continuous and generous support of Prof. Yohji Achiba of Tokyo Metropolitan University. We also thank Prof. Roger Taylor of Sussex University for help related to the identification of $C_{120}O$. The authors acknowledge support from CREST, Japan Science and Technology Corporation, and the U.S. National Science Foundation (Grant CHE0070291 to A.L.B.) and the Gulbenkian Foundation for a postdoctoral fellowship for A.de B.-D.

Supporting Information Available: ^{13}C NMR data of **1b** and **1d**, preparative HPLC chart of the starting material for the synthesis of **1b** (20 × 250 mm, 20 mL/min, toluene, 330 nm detection), the crude reaction product under the same conditions (20 × 250 mm, 20 mL/min, toluene, 330 nm detection), preparative HPLC of the reaction product completely dissolved in ODCB and eluted with ODCB on a semipreparative Cosmosil 5PBB column (10*250 mm, 2.5 mL/min), and analytical HPLC chart of the crude thermolysis product on a Cosmosil Buckyprep column (4.6 × 250 mm, 1 mL/min, toluene, 330 nm detection). This material is available free of charge via the Internet at http://pubs.acs.org.

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[40] The synthesis of $C_{60}CBr_2$ can be accomplished in several ways. One possibility is the use of bromoform and *t*-BuOK, as initially proposed by Ishida et al. (see ref 22) and Benito, A. M.; Darwish, A. D.; Kroto, H. W.; Meidine, M. F.; Taylor, R.; Walton, D. R. M. *Tetrahedron Lett.* **1996**, *67*, 1085. Another possibility is to use the Seyferth reagent, for instance (see ref 18). We obtained better yields by replacing *t*-BuOK with either NaH, DBU, or a toluene solution of $[(CH_3)_3Si]_2NNa$. In all but the last case, the reaction can be followed visually, because the formation of the methanofullerene is accompanied by a change of the color from magenta to red. The best yields (i.e., ∼40%) were obtained when using a 35% $[(CH_3)_3Si]_2NNa$ in toluene/cumene, which is commercially available from Wako.

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