Synthesis, Structure, and Properties of Novel Open-Cage Fullerenes Having Heteroatom(s) on the Rim of the Orifice

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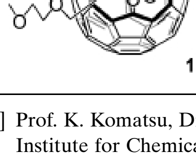
Dedicated to Emeritus Professor Soichi Misumi on the occasion of his 77th birthday

Abstract: A thermal liquid-phase reaction of fullerene C_{60} with 3-(2-pyridyl)-5,6-diphenyl-1,2,4-triazine afforded aza-open-cage fullerene derivative **5** having an eight-membered-ring orifice on the fullerene cage. Compound **5** was found to undergo oxidative ring-enlargement reactions with singlet oxygen under photo-irradiation to give azadioxo-open-cage fullerene derivatives **9** and **10**, which have a 12-membered-ring orifice, in addition to a small amount of azadioxa-open-cage fullerene derivative **11**, which has a 10-membered-ring orifice. A thermal reaction of **9** with elemental sulfur in the presence of tetrakis(dimethylamino)ethylene resulted in further ring-enlargement to give azadioxothia-open-cage fullerene derivative **15**, which has a 13-membered-ring orifice. The structures of **5** and **15** were determined by X-ray crystallography, while those of **9**, **10**, and **11** were confirmed by the agreement of observed ^{13}C NMR spectra with those obtained by DFT-GIAO calculations. These reactions were rationalized based on the results of molecular orbital calculations. Following electrochemical measurements, compounds **9** and **10**, which have two carbonyl groups on the rim of the orifice, were found to be more readily reduced than C_{60} itself (the first reduction potential was found to be 0.2 V lower than that of C_{60}), while the first reduction potentials of other open-cage fullerene derivatives, **5**, **11**, and **15**, were nearly the same as that of C_{60}.

Keywords: density functional calculations · electrochemistry · fullerenes · insertion · sulfur · X-ray diffraction

Introduction

Compared to the abundant studies of chemical modification of the exterior of fullerene cages utilizing the reactivity of the π bond,[1] those concerning transformation of the σ framework of fullerene cage leading to the formation of open-cage fullerenes are quite limited. Thus, in his pioneering work, Wudl and co-workers utilized the reaction of C_{60} with organic azide to create an azafulleroid derivative for the synthesis of the first open-cage fullerene **1**,[2] which has an 11-membered-ring orifice with a ketolactam functionality. The compound **1** was subsequently employed as a precursor to novel azafullerenes,[3] $(C_{59}N)_2$[4] and $C_{59}NH$.[5]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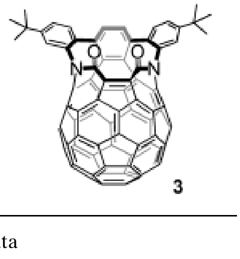
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On the other hand, Rubin and co-workers have discovered a versatile method leading to a bisfulleroid **2**, which is looked upon as an open-cage fullerene with an eight-membered-ring orifice. They demonstrated that when a 1,3-cyclohexadiene moiety is fused to C_{60}, a photochemical intramolecular [4+4] cycloaddition followed by a retro [2+2+2] reaction can cause the formation of an eight-membered-ring orifice on the C_{60} cage.[6] According to essentially the same reaction pathway, several derivatives of open-cage fullerene **2** have been prepared by the use of the reactions of C_{60} with nickelacyclopentadiene derivatives,[7] palladacyclopentadiene derivatives,[8] and phthalazine.[9] Subsequently, the eight-membered-ring orifice on the C_{60} cage in these derivatives was found to be enlarged into the 12-membered-ring by oxidative cleavage of the double bond with photochemically generated singlet oxygen.[10]

These transformations of the σ framework of fullerene cages are of great importance because of the possibility in organic synthesis of endohedral fullerene complexes encapsulating materials such as rare gases, molecular hydrogen, and particularly metals. It has been proposed by Rubin and co-workers that organic syntheses of these endohedral fullerene complexes could be realized if we can establish the method-

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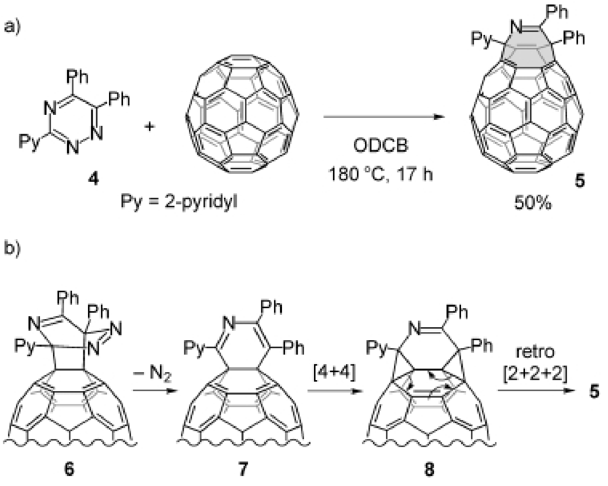
ologies for "cracking open fullerenes" and "zipping up fullerene precursors".[11] In connection with the latter "zipping up" process, the formation of C_{60} has been detected by mass spectrometry of various precursors,[12] and, most importantly, the actual organic synthesis of C_{60} has recently been achieved by Scott and co-workers using flash vacuum pyrolysis as the final step of the synthesis.[13] Although this strategy appears quite promising for providing access to various kinds of known or as yet unknown fullerenes, it has not been applied to the synthesis of endohedral fullerene complexes. Some limited success has, however, been attained in the "cracking open" strategy for the endohedral complexes. As the simplest example, rare gases such as helium, neon, argon, krypton, and xenon have been incorporated into pristine C_{60} under forced conditions (such as 600 °C, 3000 atm) to afford C_{60} containing these gases, albeit in yields typically as low as 0.1 %,[14] that is only one molecule of C_{60} out of approximately 1000 molecules contains the gas atom. It is supposed that in the transition state, a bond on the C_{60} cage is cleaved to form a window that can incorporate these gas atoms under such conditions.[15] In a recent study, Rubin and co-workers synthesized a bislactam derivative of C_{60} having a 14-membered-ring orifice **3**,[16] and succeeded in the encapsulation of a helium atom (1.5 %) or molecular hydrogen (5 %) under the conditions of 300 °C and 475 atm or 400 °C and 100 atm, respectively.[17]

In our previous work, we demonstrated that the course of the reaction of C_{60} with nitrogen-containing aromatic compounds, such as phthalazine,[9] 3,6-di(2-pyridyl)-1,2,4,5-tetrazine,[18] and 4,6-dimethyl-1,2,3-triazine,[10c] shows a large dependence on the reaction phase (solid state or liquid phase) and the liquid-phase thermal reactions particularly with phthalazine[9] and with 4,6-dimethyl-1,2,3-triazine[10c] afford new derivatives of open-cage fullerenes. Interestingly, the above-mentioned intramolecular [4+4] and retro [2+2+2] reactions can also take place under the thermal conditions employed in our work, probably by a radical mechanism.

With the continuation of this study, we became interested in a thermal reaction of C_{60} with a 1,2,4-triazine derivative. This reaction is expected to give a novel aza-open-cage fullerene, that is, the one containing an eight-membered-ring orifice incorporating an unsaturated nitrogen atom on the rim of the orifice. It appeared interesting to clarify the electronic effects of the presence of this nitrogen atom on the properties and reactivity of the fullerenyl π system of this new derivative of an open-cage fullerene. In the present study we succeeded in obtaining a series of new open-cage fullerene derivatives with 10-, 12-, and 13-membered-ring orifice containing heteroatom(s) on the rim from the first-formed aza-open-cage fullerene derivatives. Here we report on the synthesis, structure, and properties of a series of these newly formed derivatives of open-cage fullerenes.

Results and Discussion

Open-cage fullerene derivatives having an eight-membered-ring orifice: To avoid the problem of obtaining a product with low solubility, we chose a 1,2,4-triazine derivative **4** (Scheme 1) having a 2-pyridyl group at the 3-position and two phenyl groups at the 5- and 6-positions. We conducted a thermal reaction with one equivalent of C_{60} in *o*-dichlorobenzene (ODCB) at 180 °C for 17 h. The reaction was found to proceed smoothly, giving almost a single product, which exhibits a purple color in solution, together with unreacted C_{60} in 41 % recovery. The product, which was highly soluble in common organic solvents such as $CHCl_3$, toluene, CS_2, and ODCB, was determined as an aza-open-cage fullerene derivative **5** (Scheme 1 a) based on the characterization described below. Its yield was 50 %, or 85 % based on consumed C_{60}, and no bisfunctionalized product was isolated.



Scheme 1. Synthesis of open-cage fullerene derivative **5**.

The structure determination of open-cage fullerene **5** was first attempted by spectroscopy. The FAB mass spectrum showed the molecular ion peak at *m*/*z* 1003 ([*M*+1]) corresponding to $M = C_{80}H_{14}N_2$, which clearly indicates that **5** is formed by addition of triazine **4** to C_{60} followed by extrusion of N_2. While the ^{1}H NMR spectrum displayed the signals for aromatic protons only, the ^{13}C NMR spectrum showed 65 signals in the sp^2-carbon region between $\delta = 167.96$ and 122.47 ppm, in which nine signals are apparently overlapped, in addition to two signals at $\delta = 73.02$ and 56.35 ppm for the sp^3-carbon atoms, suggesting that **5** has C_1 symmetry. The purple color observed for the solution of **5** in $CHCl_3$ and its maximum absorption at 533 nm in the electronic spectrum (closely resembling the spectrum of C_{60}), indicate that the 60 original fullerene carbon atoms retain their sp^2 hybridization in a π-conjugated system.[6–9]

The structure of **5** was unambiguously determined by X-ray crystallography of a single crystal obtained from a solution in benzene. As shown in Figure 1, an eight-membered-ring orifice composed of C1 – C7 and N1 is present on the fullerene cage of **5**. In the eight-membered ring, the C2–C3 (1.406(4) Å), C4–C5 (1.403(4) Å), and C7–N1 (1.270(4) Å) bonds have double bond character, whereas the others are single bonds. The eight-membered ring is a tub-form with the C1-C2-C3-C4 and C3-C4-C5-C6 dihedral angles being −39.0(4) and 38.8(4)°, respectively, deviating significantly from 0°. The butadiene system, C2-C3-C4-C5, is almost planar

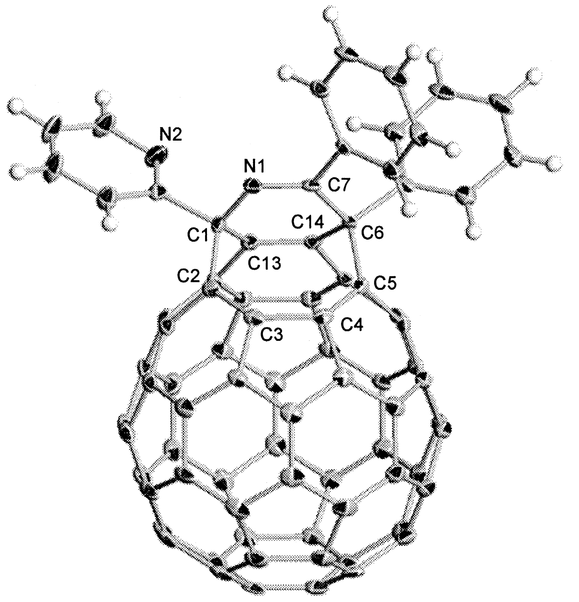


Figure 1. The X-ray structure of open-cage fullerene derivative **5** with displacement ellipsoids drawn at the 50% probability level. Selected distances [Å], bond angles [°], and dihedral angles [°]: C1−C2 1.521(4), C2−C3 1.406(4), C3−C4 1.511(4), C4−C5 1.403(4), C5−C6 1.517(4), C6−C7 1.540(4), C7−N1 1.270(4), N1−C1 1.457(3), C2−C13 2.274(4), C5−C14 2.279(4); C1-C2-C3 124.0(3), C2-C3-C4 129.8(2), C3-C4-C5 128.7(2), C4-C5-C6 124.6(2); C1-C2-C3-C4 −39.0(4) C3-C4-C5-C6 38.8(4), C2-C3-C4-C5 0.4(5).

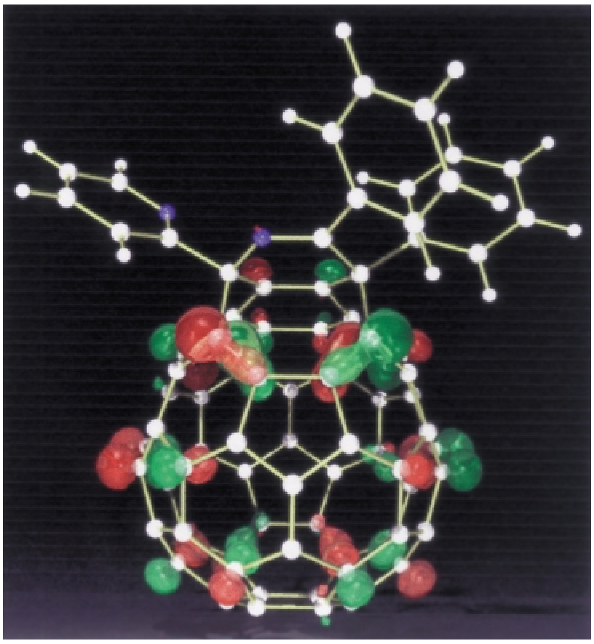


Figure 2. The optimized structure of open-cage fullerene derivative **5** with the contour of the HOMO, calculated at the B3LYP/6−311G** level of theory.

with the dihedral angle between the two double bonds being only 0.4(5)°.

A probable reaction mechanism for the formation of **5** is shown in Scheme 1b. A [4+2] cycloaddition of triazine **4** to C_{60} affords **6**, and the following extrusion of nitrogen gives 2-aza-1,3-cyclohexadiene-fused C_{60} derivative **7**, which would undergo a formal intramolecular [4+4] cycloaddition to give **8**, and then a retro [2+2+2] reaction affords **5**.

Enlargement of the orifice in open-cage fullerene 5: It has been reported both by us and another group that one of the double bonds in the eight-membered-ring orifice in an open-cage fullerene can undergo oxidative cleavage by the action of photochemically generated singlet oxygen.[10]

To clarify the reactivity of **5**, DFT calculations were conducted. The geometry of **5** was fully optimized at the B3LYP/6−311G** level of theory[19] to give a structure with the HOMO shape shown in Figure 2. The HOMO was found to be localized primarily at the two double bonds, C2−C3 and C4−C5, in the same manner as reported for the carbon analogues,[10] whereas the LUMO was found to be spread over almost all the sp^2-carbon atoms on the fullerene cage. The absolute values of the coefficients of HOMO were 0.33 for C2, 0.22 for C3, 0.21 for C4, and 0.32 for C5. Thus, the electrophilic addition of the singlet oxygen was expected to take place on these double bonds.

In fact, when the photochemical reaction of **5** with oxygen was conducted in a CCl_4 solution under irradiation with a high-pressure mercury lamp for 6 h, the HPLC separation of the reaction mixture afforded three oxidation products **9**, **10**, and **11**, all having the molecular formula corresponding to **5** with the addition of O_2 as shown by FAB MS, in 60%, 31%, and 2% yields, respectively. The IR spectra of **9** and **10** exhibited strong carbonyl stretching bands at 1747 and 1748 cm^{-1}, respectively, whereas no carbonyl band was observed for **11**.

Because comparison of the experimental and calculated ^{13}C NMR spectra seemed to be crucial for the structural determination of **9**, **10**, and **11**, we first examined the validity of such a comparison using the spectrum of compound **5**, for which the structure was confirmed by X-ray crystallography. To determine which level of theory is the most accurate for reproducing the experimental ^{13}C NMR spectrum of **5**, the gauge-independant atomic orbital (GIAO)[20,21] calculations on **5** were conducted using Hartree−Fock (HF) and density functional theory (B3LYP[22] and B3PW91[23]) methods with both the 6−311G** and TZV[24] basis sets, based on the structure optimized at the B3LYP/6−311G** level of theory.[25] All chemical shifts are given as the values relative to that of tetramethylsilane, also calculated using the same method at the same level of theory as those used for the corresponding GIAO calculations.

As shown in Figure 3a , the experimentally observed spectrum of **5** is characterized by two sp^2-carbon signals at $\delta = 167.96$ and 164.81 ppm, which are notably downfield shifted, the rest of the sp^2-carbon signals appearing in the range $\delta = 149.10-122.47$ ppm (63 signals observed out of 76 expected signals for fullerenyl and aryl carbon atoms), and two sp^3 carbon signals at $\delta = 73.02$ and 56.35 ppm. As shown in Figures 3b−g, all six GIAO calculations, conducted with B3PW91/6−311G**, B3LYP/6−311G**, B3PW91/TZV, B3LYP/TZV, HF/6−311G**, and HF/TZV, reproduced the general characteristics of the experimental ^{13}C NMR spectrum fairly well. Of the six calculations, DFT methods were shown to be generally superior to HF methods in reproducing

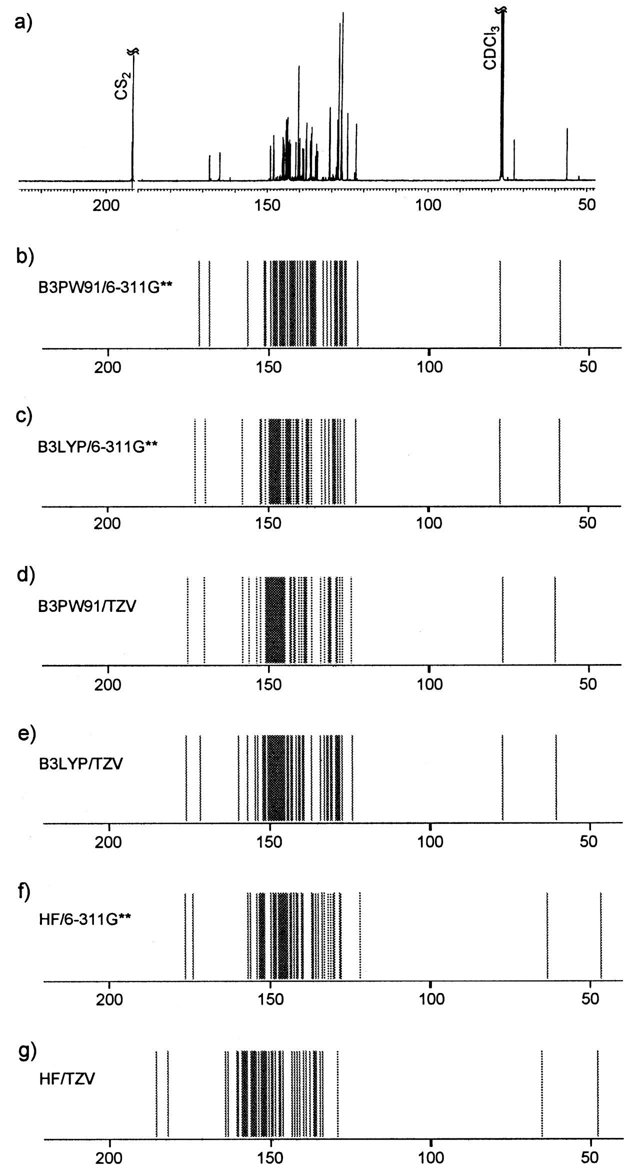
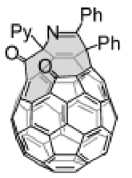


Figure 3. The experimental and calculated ^{13}C NMR spectra of **5**. The GIAO calculations were conducted at different levels of theory and basis sets using the optimized structure at the B3LYP/6–311G** level of theory: a) experimental spectrum, b) GIAO-B3PW91/6–311G**, c) GIAO-B3LYP/6–311G**, d) GIAO-B3PW91/TZV, e) GIAO-B3LYP/TZV, f) GIAO-HF/6–311G**, and g) GIAO-HF/TZV.

the experimental spectrum, regardless of the basis sets. The contribution of electron correlations[26] seems to play an important role in the properties of compound **5**. A similar trend has also been observed in the calculated ^{13}C NMR chemical shifts on a naphthalene derivative.[27] As shown by the comparison of Figure 3a with Figure 3b, the GIAO-B3PW91/6–311G** calculation was found to be the best method for reproducing the experimental ^{13}C NMR spectrum for compound **5**.

Based on the results of the FAB MS and IR spectroscopy described above, possible structures of the two major photo-oxidation products of **5** are supposed to be diketo-compounds **9** and **10**, which could be formed by oxidative cleavage of the C2–C3 bond and C4–C5 bond, respectively. The GIAO-B3PW91/6–311G** calculations conducted for **9** and **10** are shown in Figure 4 together with the experimentally observed spectra. From the fairly good agreement of the observed spectra with the calculated ones, the structural assignment of **9** and **10** is considered to be correct.[28]



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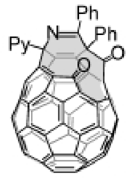

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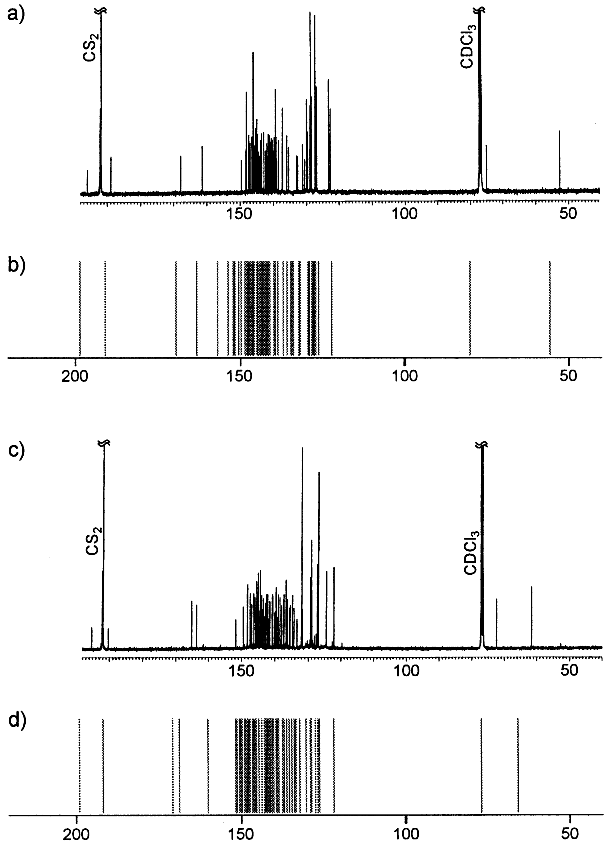
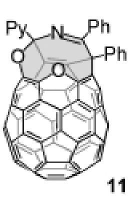


Figure 4. The experimental and calculated ^{13}C NMR spectra of **9** and **10**. The GIAO calculations were conducted at the B3PW91/6–311G** level of theory: a) observed for **9**, b) calculated for **9**, c) observed for **10**, and d) calculated for **10**.

For the minor product **11**, obtained in 2% yield from the photochemical oxidation of **5**, the experimental ^{13}C NMR spectrum shown in Figure 5a displayed no peak corresponding to a carbonyl carbon, while the FAB MS data indicated that two oxygen atoms were incorporated in **5**. In comparison



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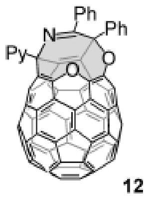

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with the ^{13}C NMR spectrum of starting material **5**, a notable downfield shift was observed for one of the sp^3-carbon signals (a signal at $\delta = 73.02$ ppm for **5** was shifted to $\delta = 96.47$ ppm for **11**), whereas another sp^3-carbon signal remained relatively unchanged ($\delta = 56.35$ ppm for **5** and $\delta = 53.26$ ppm for **11**). Because the signals at $\delta = 73.02$ and 56.35 ppm for **5** are assigned to the C1 and C6 carbon atoms, respectively, by the GIAO calculations described above, it is implied that the reaction with oxygen has taken place near the C1 carbon atom of **5** without any formation of additional sp^3-carbon atom(s). Thus the most probable structure for this minor product is considered to be **11**, shown below, with a 10-membered-ring orifice on the fullerene cage, resulting from insertion of each of the two oxygen atoms into C1–C2 and C3–C4 single bonds of **5**. This assignment was verified by comparison of the ^{13}C NMR spectra calculated by the GIAO-B3PW91/6-311G** method for **11** and its positional isomer **12** with the experimental ^{13}C NMR spectrum. Clearly, a better agreement was observed for compound **11**, as shown in Figure 5.

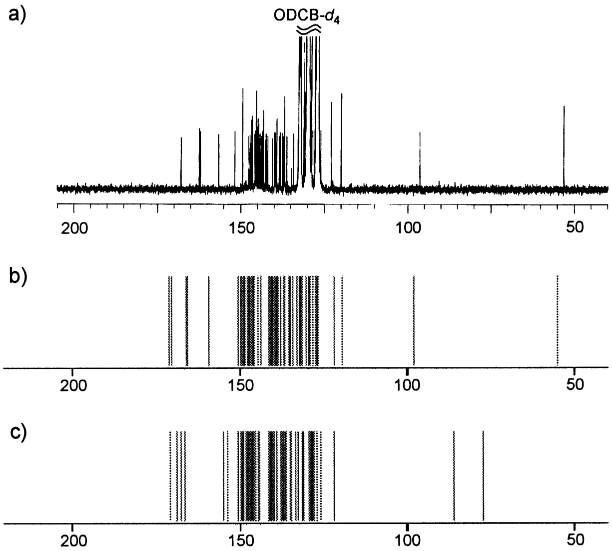
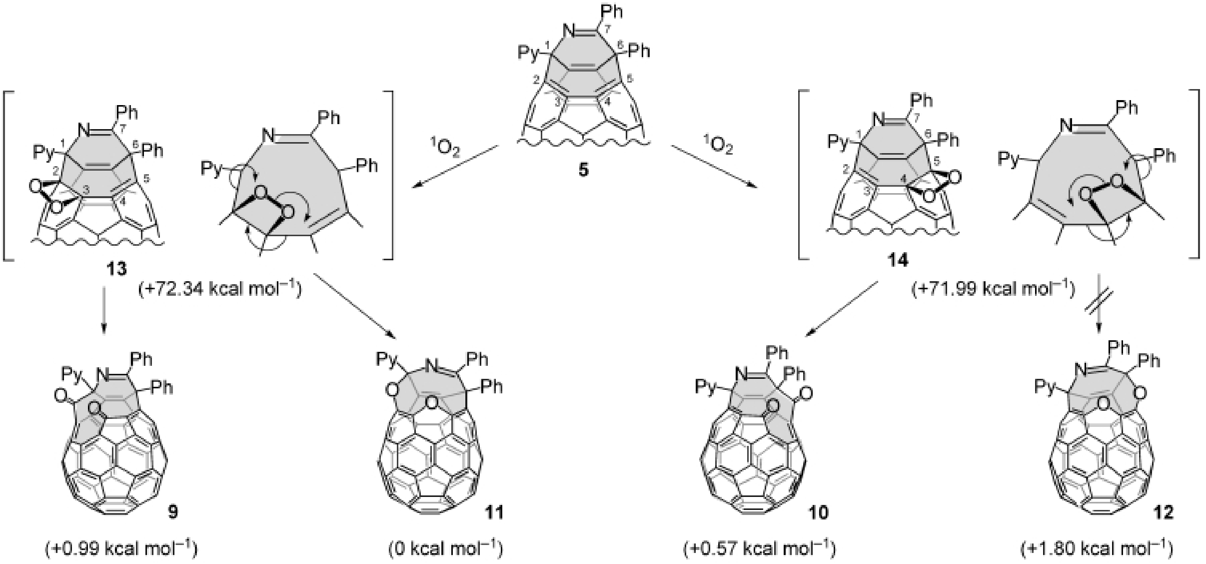


Figure 5. The experimental ^{13}C NMR spectrum of the minor product and calculated ^{13}C NMR spectra of **11** and **12**. The GIAO calculations were conducted at the B3PW91/6-311G** level of theory: a) observed for the minor product, b) calculated for **11**, and c) calculated for **12**.

The formation of three oxidation products **9**, **10**, and **11** by the reaction of **5** with photochemically generated singlet oxygen is explained as follows. As shown in Scheme 2, singlet oxygen is considered to add electrophilically to the C2–C3 and C4–C5 double bonds having relatively high coefficients of the HOMO to form intermediate dioxetanes **13** and **14**, respectively. The optimized structures and relative energies of dioxetanes **13** and **14** as well as diethers **11** and **12** were also calculated at the same level of theory (B3LYP/6-311G**). Although the addition of singlet oxygen to the C2–C3 bond would be slightly unfavorable as judged from the relative energy of dioxetanes **13** and **14** calculated at the B3LYP/6-311G** level of theory, it would be kinetically favorable compared with the addition to the C4–C5 bond when the presence of two bulky phenyl groups in close proximity is considered. Diketone **9** is formed from dioxetane **13** by the cleavage of the C2–C3 single bond and the O–O bond, whereas diether **11** is produced by means of the insertion of each oxygen atom into the C1–C2 bond and the C3–C4 bond with the concomitant cleavage of the O–O bond. A similar reaction pathway can be supposed for the formation of diketone **10** from dioxetane **14**, but the formation of diether **12**, which is calculated to be 1.8 kcal mol^{-1} less stable than **11**, was not observed under the present reaction conditions.

An open-cage fullerene derivative having a 13-membered-ring orifice: To further enlarge the 12-membered-ring orifice of **9**, a reaction to cause insertion of a heteroatom at the rim of the orifice appeared quite appealing. It has been shown that a sulfur atom can be inserted into an activated C–C single bond.[29] We therefore attempted a thermal reaction of **9** with elemental sulfur in ODCB and found that the desired reaction



Scheme 2. Formation of open-cage fullerene derivatives **9**, **10**, and **11**. The relative energies calculated at the B3LYP/6-311G** level of theory with reference to **11** are shown in parentheses.

actually takes place in the presence of tetrakis(dimethylamino)ethylene (TDAE). Heating a mixture of **9**, elemental sulfur (8 equiv), and TDAE (1 equiv) in refluxing ODCB for 30 min successfully afforded a single product with a FAB MS data exhibiting a molecular ion peak at m/z 1067 corresponding to **9**+S+H, in 77 % yield.

In this reaction, TDAE, a typical π-electron donor,[30] is supposed to activate **9** either by one-electron transfer or by complexation so that the electrophilic addition of elemental sulfur to **9** can readily take place. The theoretical calculations for **9** at the B3LYP/6–311G** level of theory demonstrated that the LUMO of **9** is relatively localized at the conjugated butadiene part, C9–C10–C11–C12, on the rim of the orifice (Figure 6); the numbering is shown in Scheme 3. The absolute values of the coefficients of the LUMO at C9, C10, C11, and C12 of **9** are 0.29, 0.35, 0.32, and 0.25, respectively. Thus, it is assumed that the sulfur atom has been inserted into the C10–C11 bond to give the novel open-cage fullerene derivative **15** having a 13-membered-ring orifice (Scheme 3). The ^{13}C NMR spectrum of this product exhibited two signals for the carbonyl carbon atoms at $\delta = 193.06$ and 185.02 ppm, 52 signals (out of possible 76 signals) corresponding to the fullerenyl and aryl sp^2-carbon atoms in the range $\delta = 166.40$ to 122.68 ppm, and two signals corresponding to the sp^3-carbons at $\delta = 74.42$ and 52.33 ppm (Figure 7 a). This spectrum showed good agreement with the spectrum calculated for the structure **15** by the GIAO–B3PW91/6–311G** method using the optimized structure at the B3LYP/6–311G** level of theory (Figure 7 b).[28] Finally, the validity of the assignment of the structure **15** to this product was proved by the X-ray crystallography for the single crystal grown from a solution in toluene (Figure 8).

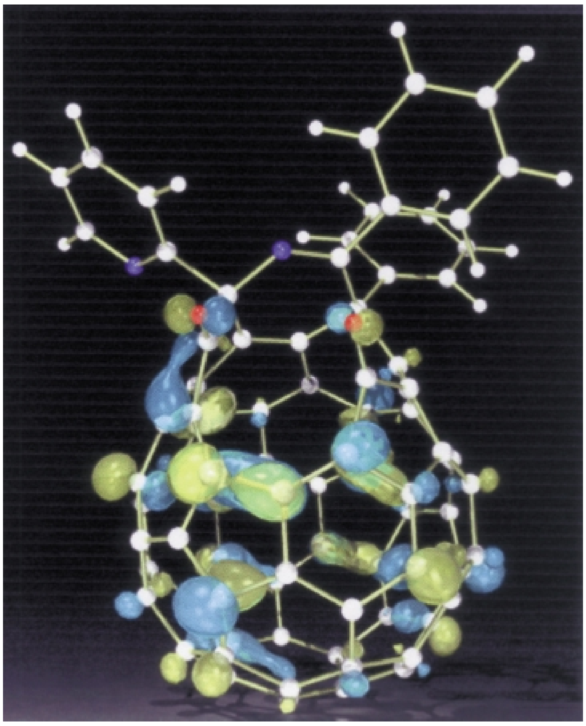
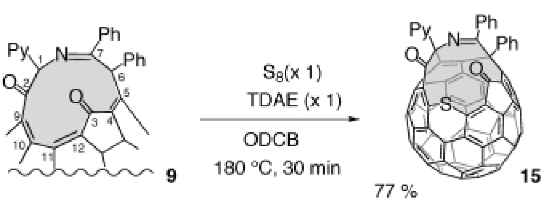


Figure 6. The optimized structure of open-cage fullerene derivative **9** with the contour of the LUMO, calculated at the B3LYP/6–311G** level of theory.



Scheme 3. Synthesis of open-cage fullerene derivative **15**.

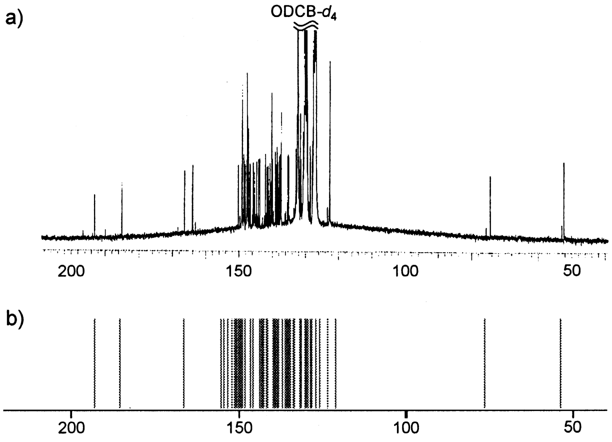


Figure 7. The experimental and calculated ^{13}C NMR spectra of **15**. The GIAO calculations were conducted at the B3PW91/6–311G** level of theory: a) observed for **15** and b) calculated for **15**.

As shown by the X-ray crystal structure given in Figure 8 a, compound **15** has a 13-membered-ring orifice on the fullerene cage (shown in red) containing sulfur and nitrogen atoms. The bond lengths of C9–C10, C10–S1, S1–C11, and C11–C12 are 1.398(4), 1.780(3), 1.754(3), and 1.367(4) Å, respectively. Thus a divinyl sulfide moiety was formed in the 13-membered ring as a result of the sulfur-atom insertion into the C10–C11 bond of **9**. Determination of this X-ray structure also confirmed the validity of the structural assignment of the starting material **9**, which was made based on the comparison with the DFT–GIAO calculated spectrum, as described above.

From the top view of the X-ray structure shown in Figure 8 b, it can be seen that the 13-membered-ring orifice in **15** has a somewhat more circular shape as compared to the rather elliptic shape observed for the 14-membered-ring orifice (counting the fused benzene-ring carbon atoms) in the bislactam derivative of an open-cage fullerene **3** reported by Rubin and co-workers.[16, 17] This is the largest hole constructed thus far on the surface of C_{60}. Thus, the insertion of a small molecule or atom is expected to be possible through the 13-membered-ring orifice in **15**.

Properties of open-cage fullerene derivatives: The UV/Vis spectra of the obtained open-cage fullerene derivatives, **5**, **9**, **10**, **11**, and **15**, taken in $CHCl_3$ are shown in Figure 9. As mentioned previously, compound **5**, having an eight-membered-ring orifice, displayed a similar absorption pattern to that of C_{60} itself, reflecting the fact that **5** retains the conjugated system composed of 60 sp^2-carbon atoms.[6–9]

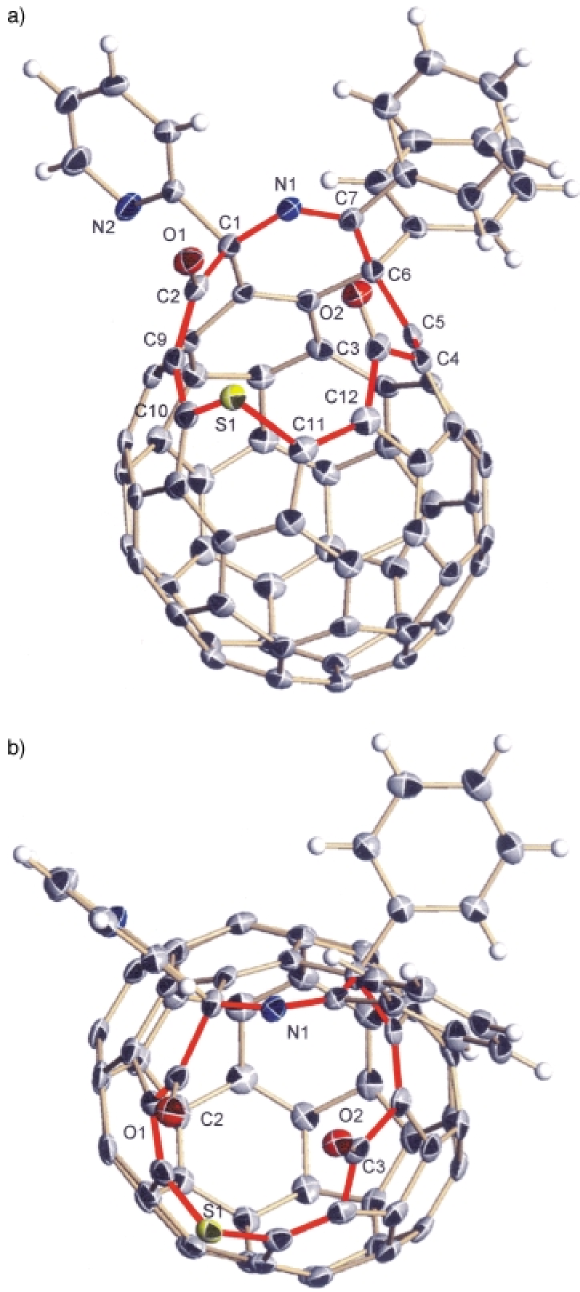


Figure 8. The X-ray structure of open-cage fullerene derivative **15** with the displacement ellipsoids model drawn at the 50 % probability level: a) side view and b) top view. Selected distances [Å]: N1−C1 1.445(3), C1−C2 1.584(4), C2−O1 1.209(3), C2−C9 1.492(4), C9−C10 1.398(4), C10−S1 1.780(3), S1−C11 1.754(3), C10−C11 2.546(4), C11−C12 1.367(4), C12−C3 1.518(4), C3−O2 1.202(3), C3−C4 1.553(4), C4−C5 1.380(4), C5−C6 1.552(3), C6−C7 1.545(4), C7−N1 1.281(3).

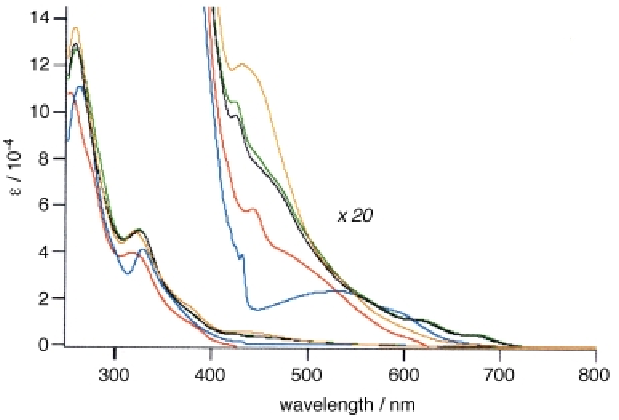
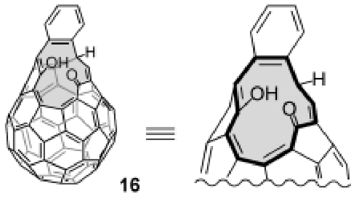


Figure 9. UV/Vis spectra of open-cage fullerene derivatives: blue line (**5**), black (**9**), green (**10**), red (**11**), and brown (**15**).

Compounds **9** and **10**, which are isomeric, showed quite similar absorptions, that is, strong maximum absorptions in the UV region (257 and 325 nm for **9**; 259 and 324 nm for **10**), which are commonly observed in C_{60} derivatives, and a small absorption in the visible region (424 nm for **9**; 423 nm for **10**) as well as the long-wavelength visible absorption extending to approximately 700 nm. These absorptions are different from those of an enol-ketone derivative **16**, which has a similar 12-membered-ring orifice. This showed maximum absorptions at 453 and 751 nm.[10a] Compound **11** showed maximum absorptions at 253, 317, and 442 nm. Compound **15**, which has the largest orifice among the compounds examined in this study, showed maximum absorptions at 257 and 319 nm as well as a broad absorption at 430 nm. With the increase in the size of the orifice in the order **5**, **9** and **10**, and **15**, the absorption at the visible region lost their structure. The colors of the solutions of **5**, **9**, **10**, **11**, and **15** in $CHCl_3$ were purple, brown, brown, red-brown, and bright red, respectively.



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To examine the electronic properties of the open-cage fullerene derivatives **5**, **9**, **10**, **11**, and **15**, their redox behaviors were studied by cyclic voltammetry (CV) and differential pulse voltammetry (DPV) in ODCB using Bu_4NBF_4 as a supporting electrolyte. Despite the significant change in the π-electronic system resulting from the transformation in the fullerene skeleton made for these derivatives, all compounds showed four quasi-reversible redox waves in the negative scans upon CV. These were quite similar to those observed for C_{60} itself. The corresponding four one-electron reduction peaks were observed upon DPV measurements. As an example, the CV and DPV results for compound **10** are shown in Figure 10, together with those for C_{60}.

The reduction potentials determined by DPV are summarized in Table 1, together with the LUMO energy levels calculated by the B3LYP/6–31G* level of theory. As shown by the values in Table 1, the reduction potentials of compounds **5** and **11** were found to be rather similar to those of C_{60}, indicating that the fully conjugated π-electron systems made of 60 sp^2 carbons in **5** and **11** retain the high electron affinities characteristic of C_{60}. Most noteworthy is the observation that compounds **9** and **10** exhibited first reduction waves at potentials as low as −0.97 and −0.98 V versus the ferrocene/ferrocenium couple, respectively, which are approximately 0.2 V lower than that of C_{60} measured under the

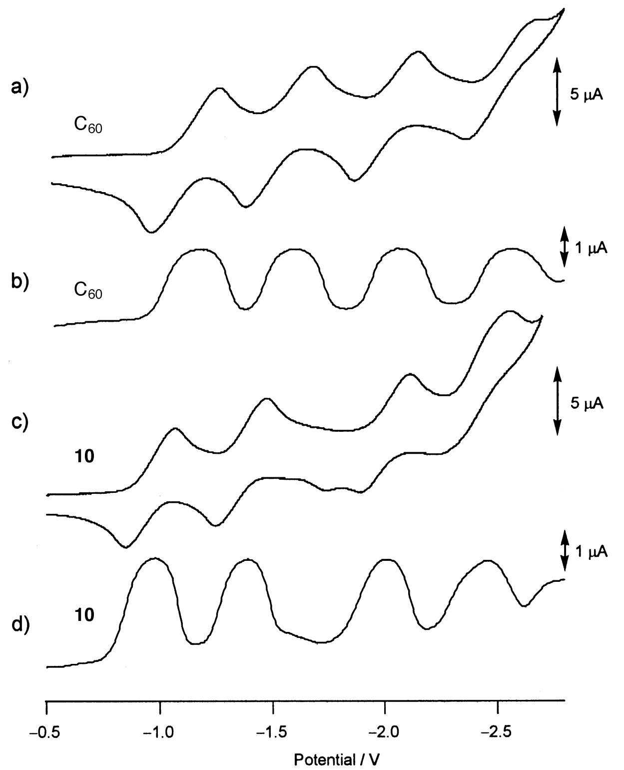

Figure 10. CV and DPV of C_{60} and **10**: 1 mM in ODCB, 0.05 M $TBABF_4$, scan 0.02 V s^{-1}; a) CV of C_{60}, b) DPV of C_{60}, c) CV of **10**, and d) DPV of **10**.

Table 1. Reduction potentials[a] and calculated LUMO levels.[b]

Compound	E_{red}^{1}[a]	E_{red}^{2}[a]	E_{red}^{3}[a]	E_{red}^{4}[a]	LUMO [eV][b]
C_{60}	-1.17	-1.59	-2.06	-2.56	-3.23
5	-1.21	-1.62	-2.11	-2.62	-3.03
9	-0.97	-1.40	-2.01	-2.43	-3.32
10	-0.98	-1.39	-2.00	-2.44	-3.34
11	-1.18	-1.58	-2.20	-2.70	-3.13
15	-1.15	-1.56	-2.05	-2.52	-3.16
16[10a]	-1.07	-1.43	-1.99	-2.29	-3.26

[a] V versus ferrocene/ferrocenium: All reduction potentials were measured by DPV (1 mM sample, 0.05 M Bu_4NBF_4 in ODCB, scan rate 0.02 V s^{-1}). [b] Calculated at the B3LYP/6–31G* level of theory.

same conditions. The second to fourth reduction potentials were also lower than those of C_{60}. This enhanced reducibility could be ascribed to the presence of two carbonyl groups directly connected to the partially broken fullerenyl π system. Actually, the reduction potentials observed for **9** and **10** are lower than those of the monocarbonyl analogue of the similar open-cage fullerene **16**[10a] by about 0.1 V. Thus, one carbonyl group connected to the fullerenyl π system is considered to decrease the reduction potential by approximately 0.1 V. This effect is nearly comparable to that of the two cyano groups connected by sp^3-carbon atoms to the C_{58} fullerenyl π system in $C_{60}(CN)_2$.[31] In contrast, the sulfur-containing derivative **15** displayed its first reduction at -1.15 V, which is more negative than that of **9** and **10** and close to that of C_{60} despite the presence of two carbonyl groups. This is considered to reflect the strong electron-donating effect of a sulfur atom directly bonded to the π system. As shown in Table 1, the lowered reduction potentials observed for **9** and **10** are in agreement with the low levels of LUMO predicted for these compounds by theoretical calculations at the B3LYP/6–31G* level of theory.[32]

Conclusion

In summary, an open-cage fullerene derivative having a nitrogen-containing, eight-membered-ring orifice (**5**) was synthesized in high yield (85% based on consumed C_{60} at 59% conversion) by a liquid-phase thermal reaction of C_{60} with 3-(2-pyridyl)-5,6-diphenyl-1,2,4-triazine (**4**) in one pot. The eight-membered-ring orifice was further enlarged to a 10-membered ring containing ether linkages (**11**) and a 12-membered ring containing two carbonyl carbon atoms (**9** and **10**) by photochemical oxidation with singlet oxygen. The structures of these compounds were characterized by spectroscopy and DFT calculations, as well as by the X-ray crystallography for **5**. In particular, the GIAO calculation was found to be a powerful method for structural determination of derivatives such as **9**, **10**, and **11** by comparison of the calculated with the observed ^{13}C NMR spectra.

A novel sulfur-atom insertion into the central C–C bond in the butadiene unit of the rim of the 12-membered-ring orifice was found. It gave a novel fullerene derivative **15** with a 13-membered-ring orifice containing both nitrogen and sulfur atoms on the rim. The X-ray crystallography on this compound indicated that the shape of the orifice is closer to a circle than to an ellipse compared with compound **3**, which has the largest orifice reported thus far.[17] The energy barrier for insertion of a helium atom through the orifice was calculated to be approximately 5.5 kcal mol^{-1} lower for compound **15** than for **3**.[33] This finding is a good indicator that the preparation of endohedral fullerene complexes by means of organic synthesis, which was initiated by Rubin and coworkers,[17] is indeed possible. Work in this field is now under way using compound **15**.

Experimental Section

General: The ^{1}H and ^{13}C NMR measurements were carried out on Varian Mercury 300 and JEOL AL-400 instruments and referenced to TMS or to the solvent signals: $\delta_H = 2.05$ ppm for [D$_6$]acetone and $\delta_C = 132.35$ ppm for [D$_4$]*o*-dichlorobenzene ([D$_4$]ODCB). UV/Vis spectra were recorded on a Shimadzu UV-2100PC spectrometer. IR spectra were recorded with a Shimadzu FTIR-8600 spectrometer. MS spectra were recorded on a JEOL MStation JMS-700. Cyclic voltammetry and differential pulse voltammetry were conducted on a BAS Electrochemical Analyzer CV-100 W using a three-electrode cell with a glassy carbon working electrode, a platinum wire counter electrode, and a Ag/0.01 M $AgNO_3$ reference electrode. The potentials were corrected against ferrocene used as an internal standard which was added after each measurement. Fullerene C_{60} was purchased from Matsubo Co. 3-(2-Pyridyl)-5,6-diphenyl-1,2,4-triazine and tetrakis(-dimethylamino)ethylene were purchased from Aldrich Co. and used as received, while elemental sulfur was purchased from Nacalai Tesque and used as received. *o*-Dichlorobenzene (ODCB) was distilled over CaH_2 and stored over 4 Å molecular sieves.

Computations: All calculations were conducted by using the Gaussian 98 series of electronic structure programs.[19] The geometries were fully optimized with the restricted Becke hybrid (B3LYP) method[22] for all compounds. The GIAO calculations were performed at HF/6–311G**,

B3LYP/6–311G**, B3PW91/6–31G**, HF/TZV, B3LYP/TZV, and B3PW91/TZV level of theory using the optimized structure at the B3LYP/6–311G** level of theory.

Open-cage fullerene derivative 5: A mixture of fullerene C_{60} (50 mg, 0.069 mmol) and 3-(2-pyridyl)-5,6-diphenyl-1,2,4-triazine (**4**) (21 mg, 0.068 mmol) in *o*-dichlorobenzene (ODCB, 4 mL) was refluxed at 180 °C for 17 h under an argon atmosphere. The resulting dark purple solution was directly subjected to flash column chromatography over silica gel. Elution with CS_2 gave unreacted C_{60} (20 mg, 41 %) while the following elution with CS_2-ethyl acetate (20:1) gave open-cage fullerene derivative **2** (35 mg, 0.035 mmol, 50 %) as a brown powder. M.p. >300 °C; IR (KBr): $\tilde{\nu} = 1749\ cm^{-1}$ (C=N); UV/Vis ($CHCl_3$): λ_{max} (log ε) = 262 nm (5.05), 329 (4.62), 431 (3.29), 533 (3.07); ^1H NMR (300 MHz, CS_2:$[D_6]$acetone (7:1)): δ = 8.68 (m, 1H), 8.00–7.90 (m, 2H), 7.76–7.69 (m, 2H), 7.44–7.37 (m, 2H), 7.22–7.10 ppm (m, 7H); ^{13}C NMR (100 MHz, CS_2:$CDCl_3$ (1:2)): δ = 167.96, 164.81, 149.10, 148.10, 147.96, 145.40, 145.21, 145.14, 145.12, 145.06, 144.85, 144.37, 144.34, 144.20, 144.15, 144.02, 143.96, 143.94, 143.80, 143.77, 143.71, 143.65, 143.59, 143.54, 143.50, 143.40, 143.35, 143.31, 143.21, 143.19, 143.16, 143.13, 143.02, 142.86, 141.29, 140.53, 140.49, 140.32, 140.23, 140.20, 139.96, 139.18, 138.77, 138.09, 137.92, 136.73, 136.69, 136.57, 136.48, 136.35, 135.18, 135.02, 134.88, 134.60, 134.48, 130.78, 130.65, 128.36, 128.21, 128.00, 127.18, 127.04, 125.17, 125.08, 122.47, 73.02, 56.35 ppm; HRMS (+FAB): calcd for $C_{80}H_{15}N_2$ ([*M*+1]): 1003.1235, found 1003.1238.

Open-cage fullerene derivatives 9, 10, and 11: A purple solution of compound **5** (66 mg, 0.066 mmol) in CCl_4 (65 mL) in a Pyrex flask was irradiated by a high-pressure mercury lamp (500 W) from a distance of 20 cm for 6 h under air. The resulting brown solution was evaporated and the residual black solid was dissolved in ODCB (3 mL). This was subjected to preparative HPLC using a Cosmosil 5PBB column (10 × 250 mm) eluted with ODCB (flow rate, $2\ mL\,min^{-1}$) to afford open-cage fullerene derivatives **9** (40 mg, 0.038 mmol, 60 %, retention time: 8.7 min), **10** (21 mg, 0.020 mmol, 31 %, retention time: 9.2 min), and **11** (1 mg, 0.001 mmol, 2 %, retention time: 9.1 min), after nine recycles, all as brown powders.

When the photoirradiation of **5** (41 mg, 0.041 mmol) was conducted in CS_2 (50 mL) in the presence of trifluoroacetic acid (30 µL, 0.39 mmol) under the same conditions as described above and the reaction mixture was neutralized by addition of triethylamine (55 µL, 0.40 mmol) before evaporation of the mixture, the separation by preparative HPLC gave **9** (22 mg, 0.021 mmol, 53 %), **10** (4 mg, 0.004 mmol, 10 %), and **11** (3 mg, 0.002 mmol, 6 %).

9: M.p. >300 °C; IR (KBr): $\tilde{\nu}$ = 1747, 1700 cm^{-1} (C=O); UV/Vis ($CHCl_3$): λ_{max} (log ε) = 257 (5.11), 325 (4.69), 424 nm (3.70); ^1H NMR (300 MHz, CS_2:$[D_6]$acetone (7:1)): δ = 8.52 (m, 1H), 8.37 (m, 1H), 8.07–7.98 (m, 3H), 7.82 (m, 1H), 7.37–7.03 ppm (m, 8H); ^{13}C NMR (100 MHz, CS_2:$CDCl_3$ (1:2)): δ = 196.04, 188.96, 167.84, 161.38, 149.53, 148.22, 148.18, 148.04, 147.43, 147.32, 147.29, 147.15, 146.92, 146.37, 145.99, 145.85, 145.67, 145.53, 145.44, 145.38, 145.32, 145.25, 145.20, 145.19, 144.96, 144.85, 144.67, 144.35, 144.20, 143.79, 143.71, 143.51, 142.87, 142.38, 142.17, 141.95, 141.57, 141.46, 141.11, 140.77, 140.56, 140.24, 140.13, 139.89, 139.73, 139.58, 139.27, 139.13, 138.96, 138.35, 137.30, 137.21, 137.16, 135.97, 135.92, 135.35, 132.90, 132.54, 131.08, 130.48, 129.96, 129.85, 129.78, 129.51, 128.88, 128.69, 128.37, 127.27, 127.17, 126.76, 123.13, 122.60, 74.97, 52.63 ppm; HRMS (+FAB): calcd for $C_{80}H_{15}N_2O_2$ ([*M*+1]): 1035.1134, found 1035.1132.

10: M.p. >300 °C; IR (KBr): $\tilde{\nu}$ = 1748 cm^{-1} (C=O); UV/Vis ($CHCl_3$): λ_{max} (log ε) = 259 (5.10), 324 (4.70), 423 nm (3.72); ^1H NMR (300 MHz, CS_2:$[D_6]$acetone (7:1)): δ = 8.58 (m, 1H), 8.20–8.17 (m, 2H), 8.02 (m, 1H), 7.93 (m, 1H), 7.37–7.21 ppm (m, 9H); ^{13}C NMR (100 MHz, CS_2:$CDCl_3$ (1:2)): δ = 195.31, 190.36, 165.18, 163.66, 151.71, 149.50, 148.38, 148.20, 147.48, 147.40, 147.34, 147.00, 146.37, 145.99, 145.96, 145.61, 145.55, 145.29, 145.22, 145.20, 145.12, 145.10, 144.98, 144.52, 144.39, 144.25, 144.11, 143.89, 143.78, 143.51, 143.05, 142.80, 142.43, 142.06, 141.80, 141.56, 141.49, 140.79, 140.69, 140.62, 140.07, 139.92, 139.63, 139.58, 139.49, 139.27, 138.96, 138.40, 138.00, 137.48, 137.23, 136.58, 136.55, 136.18, 135.51, 135.44, 134.73, 134.23, 133.33, 132.01, 131.91, 131.68, 129.35, 129.32, 128.95, 127.21, 126.87, 124.44, 122.15, 72.42, 61.58 ppm; HRMS (+FAB): calcd for $C_{80}H_{15}N_2O_2$ ([*M*+1]): 1035.1134, found 1035.1151.

11: M.p. >300 °C; UV/Vis ($CHCl_3$): λ_{max} (log ε) = 317 (4.64), 442 nm (3.52); ^1H NMR (300 MHz, CS_2:$[D_6]$acetone (7:1)): δ = 8.64 (m, 1H), 8.48 (m, 1H), 8.03–7.89 (m, 4H), 7.66 (m, 1H), 7.39–7.21 ppm (m, 7H); ^{13}C NMR (100 MHz, $[D_4]$ODCB): δ = 167.97, 162.52, 162.16, 156.68, 151.84, 149.55, 147.73, 147.37, 147.09, 146.84, 146.82, 146.56, 145.89, 145.75, 145.67, 145.54, 145.45, 145.34, 145.30, 145.18, 145.03, 144.99, 144.67, 144.65, 144.60, 144.41, 144.23, 144.00, 143.81, 143.54, 143.27, 142.68, 142.50, 142.40, 142.00, 140.61, 139.99, 139.91, 139.77, 139.69, 139.54, 139.30, 138.62, 138.52, 138.47, 138.31, 138.18, 137.67, 137.48, 137.15, 137.04, 136.99, 136.91, 136.31, 134.37, 134.30, 132.94, 126.58, 126.15, 123.01, 120.04, 96.47, 53.26 ppm (some signals in the region δ = 132.7–126.9 ppm overlap with the $[D_4]$ODCB peaks); HRMS (+FAB): calcd for $C_{80}H_{15}N_2O_2$ (M+1): 1035.1134, found 1035.1121.

Open-cage fullerene derivative 15: To a heated and stirred solution of compound **9** (32 mg, 0.031 mmol) and elemental sulfur (8 mg, 0.031 mmol as S_8) in ODCB (15 mL) was added tetrakis(dimethylamino)ethylene (7.1 µL, 0.031 mmol) at 180 °C. The solution was refluxed at 180 °C for 30 min then the resulting dark red-brown solution was concentrated by evaporation to about 3 mL. This was added to pentane (30 mL) with vigorous stirring to give brown precipitates. The precipitates, collected by centrifuge, were dissolved in ODCB (2 mL). The resulting solution was subjected to flash chromatography on silica gel eluted with toluene/ethyl acetate (30:1) to give open-cage fullerene derivative **15** (25 mg, 0.023 mmol, 77 %) as a brown powder. M.p. >300 °C; IR (KBr): $\tilde{\nu}$ = 1748 cm^{-1} (C=O); UV/Vis ($CHCl_3$): λ_{max} (log ε) = 257 (5.14), 319 (4.69), 430 nm (3.78); ^1H NMR (300 MHz, CS_2:$[D_6]$acetone (7:1)): δ = 8.60 (m, 1H), 8.23 (m, 1H), 8.18–8.15 (m, 2H), 8.02 (m, 1H), 7.53 (m, 1H), 7.36 (m, 1H), 7.30–7.25 (m, 3H), 7.04–6.88 ppm (m, 4H); ^{13}C NMR (75 MHz, $[D_4]$ODCB): δ = 193.06, 185.02, 166.40, 164.00, 150.18, 149.19, 149.06, 148.64, 148.57, 148.53, 148.43, 148.23, 148.03, 147.71, 147.59, 147.56, 147.49, 147.40, 147.35, 147.33, 147.20, 146.82, 146.75, 146.56, 145.81, 145.60, 145.28, 144.67, 144.14, 143.73, 142.12, 141.65, 141.32, 141.09, 140.73, 140.30, 140.15, 139.93, 139.13, 138.91, 138.58, 138.54, 138.50, 138.32, 137.97, 137.88, 137.54, 137.39, 137.31, 135.44, 135.19, 135.10, 132.91, 122.68, 74.42, 52.33 ppm (signals in the range δ = 132.4–126.9 ppm overlap with the signals of $[D_4]$ODCB); HRMS (+FAB): calcd for $C_{80}H_{15}N_2O_2S$ ([*M*+1]): 1067.0854, found 1067.0814.

Table 2. Crystallographic data for open-cage fullerene derivatives.

	5·3(C_6H_6)	**15**·0.5(C_7H_8)
empirical formula	$C_{98}H_{32}N_2$	$C_{83.5}H_{18}N_2O_2S$
formula weight	1237.26	1113.06
crystal system	triclinic	triclinic
space group	$P\bar{1}$	$P\bar{1}$
a [Å]	13.750(2)	10.0158(8)
b [Å]	15.237(2)	13.1987(10)
c [Å]	15.498(2)	17.5019(14)
α [°]	63.891(3)	98.638(2)
β [°]	71.078(4)	91.309(2)
γ [°]	85.258(3)	98.317(2)
V [$Å^3$]	2751.4(7)	2261.0(3)
Z	2	2
T [K]	100(2)	100(2)
λ [Å]	0.71073	0.71073
μ [mm^{-1}]	0.086	0.142
θ range [°]	1.55–25.50	1.82–25.60
limiting indices	$-14 \leq h \leq 16$ $-18 \leq k \leq 18$ $-18 \leq l \leq 18$	$-11 \leq h \leq 12$ $-15 \leq k \leq 16$ $-21 \leq l \leq 13$
ρ_{calc} [$g\ cm^3$]	1.493	1.635
data/restraints/parameters	10201/0/957	8357/34/829
unique reflections	10201	8357
completeness [%]	99.4	98.2
absp correction	SADABS	SADABS
R_{int}	0.0357	0.0188
$R1$ [$I > 2\sigma(I)$][a]	0.0613	0.0559
$wR2$ [$I > 2\sigma(I)$][b]	0.1318	0.1348
$R1$ (all data)[a]	0.1093	0.0792
$wR2$ (all data)[b]	0.1499	0.1439
GOF on F^2	0.931	0.969

[a] $R1 = \Sigma||F_c| - |F_o||/\Sigma|F_o|$. [b] $wR2 = \{\Sigma[w(F_o^2 - F_c^2)^2]/\Sigma[w(F_o^2)^2]\}^{1/2}$.

0947-6539/03/0907-1608 $ 20.00+.50/0

X-ray structural analysis of 5 and 15: Single crystals of compounds **5** and **15** suitable for X-ray crystallography were obtained by slow evaporation of the solutions in benzene and in toluene, respectively, over three days at room temperature. Single-crystal X-ray data were collected on a Bruker SMART diffractometer equipped with a CCD area detector using $Mo_{K\alpha}$ radiation. Single-crystal diffraction data were collected at 100 K. All structure solutions were obtained by direct methods and refined using full-matrix least-squares with a Bruker SHELXTL (Version 5.1) Software Package. The crystal parameters are summarized in Table 2. CCDC-197761 (**5**) and CCDC-197762 (**15**) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge at www.ccdc.cam.ac.uk/conts/retrieving.html (or from the Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; fax: (+44) 1223-336-033; or deposit@ccdc.cam.uk).

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