

Production of a 15-membered Ring Orifice in Open-cage Fullerenes by Double Photooxygenation of Azafulleroid

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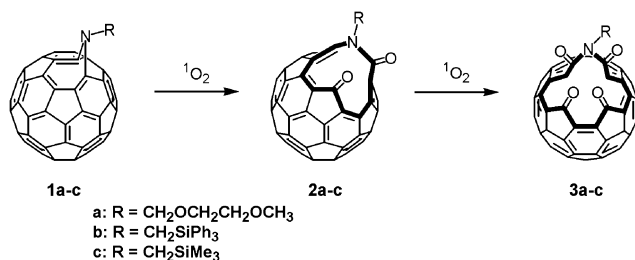
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Photooxygenation of silyl-modified azafulleroids **1b** and **1c** gave open-cage fullerenes having keto lactam **2b** and **2c** or diketo imide **3b** and **3c** functional groups on 11- or 15-membered ring orifices. The high reactivity of the bridgehead double bonds was estimated by π -orbital axis vector (POAV) analysis comparing the bisfulleroid derivatives **5d**, **5e**, **6d**, and **6e**.

Among surface modification reactions of C_{60} , singlet oxygen (1O_2) oxygenation of azafulleroid and bisfulleroid is the key reaction in the production of open-cage-,¹ hetero-,² and endohedral-fullerenes.³ The [2 + 2] addition of 1O_2 to the electron-rich bridgehead double bonds of these fullerenes, followed by symmetrical ring opening, results in the opening of a hole in the fullerenes surface.^{1a,1d-1i} When the first cage-opening reaction of azafulleroid **1a** was reported by Wudl and co-workers,^{1a} diketo imide **3a** was suggested as an alternative possible structure in addition to the keto lactam **2a**, as shown in Scheme 1. However, the diketo imide **3a** has remained unobserved to date. Recently, we reported the selective synthesis of silyl benzene azafulleroids.⁴ⁱ Herein, we report the photooxygenation of these silyl-modified azafulleroids **1b** and **1c** undergoing stepwise oxidation to afford the first diketo imide **3b** and **3c** via the keto lactam **2b** and **2c** as shown in Scheme 1. It was demonstrated that whether the double photooxygenation of azafulleroid and the related bisfulleroid takes place or not can be predicted by π -orbital axis vector (POAV) analysis⁵ of the bridgehead double bonds.

A solution of either **1b** or **1c** in *o*-dichlorobenzene in a pyrex tube was irradiated with a halogen lamp under bubbling oxygen for 5 h. The 1H NMR signals of methylene protons for **1b** and **1c** at 4.23 and 3.44 ppm disappeared completely (**1b** is shown in Figure 1). The new signals for **2b** and **2c** at 4.52/5.68 and 3.83/4.93 ppm with doublet couplings were observed together with aziridinofullerenes **4b** and **4c** at 4.03 and 3.25 ppm (**2b** and **4b** are shown in Figure 1). After column chromatography through silica gel (eluent: CS_2), **2b** and **2c** were obtained in 85 and 90% yields, as dark brown solid together with 11 and 10% yield of the aziridinofullerene **4b** and **4c**, formed by the photo-



Scheme 1.

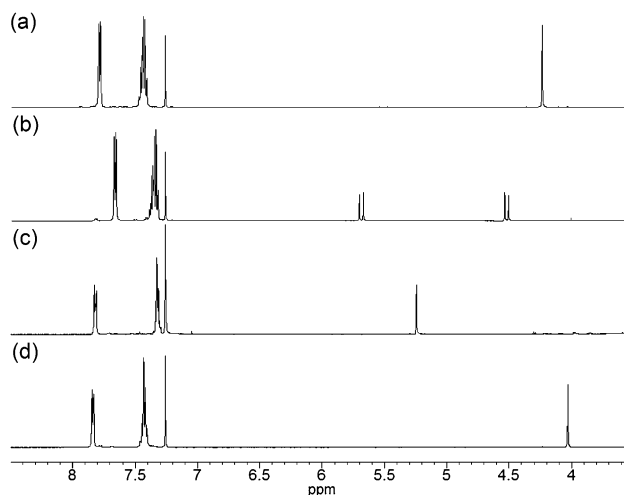


Figure 1. 1H NMR spectra in $CDCl_3$ solution; (a) **1b**, (b) **2b**, (c) **3b**, and (d) **4b**.

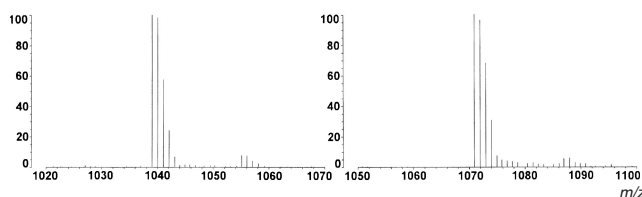


Figure 2. MALDI-TOF mass spectra of **2b** (left) and **3b** (right) in negative-ion reflectron mode.

chemical isomerization of **1b** and **1c**.⁴ The MALDI-TOF mass spectra of **2b** and **2c** show molecular ion peaks at m/z 1039 (M^-) and 853 (M^-) (**2b** is shown in Figure 2), indicating that the product was formed by the addition of O_2 to **1b** and **1c**. The ^{13}C NMR spectra display two carbonyl carbons at 161/194 and 161/194 ppm for keto lactams **2b** and **2c**. In the fullerene skeleton regions, 59 and 56 signals were observed, respectively, indicating C_1 symmetry for **2b** and **2c**. The IR spectra show two pairs of carbonyl groups at 1682/1726 and 1681/1726 cm^{-1} , respectively.

Next, a solution of either **1b** or **1c** in *o*-dichlorobenzene in a pyrex tube was irradiated for 30 h. The reaction mixtures were monitored by 1H NMR spectroscopy. During the prolonged irradiation, the signals for **2b** and **2c** decreased in intensity with a concomitant increase in the singlet peaks at 5.24 and 4.49 ppm (**3b** is shown in Figure 1). After chromatographic separation (eluent: $CHCl_3$), **3b** and **3c** were isolated in 9 and 11% yields, with 58 and 44% yields of **2b** and **2c** recovered.⁶ The final products are suggested to be the diketo imide **3b** and **3c** on the basis of the observed 1H and ^{13}C NMR and MALDI-TOF mass spectra. The molecular ion peaks at m/z 1071 (M^-) and 885 (M^-)

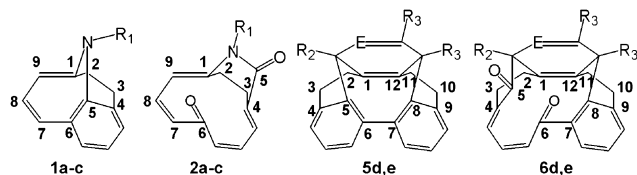


Figure 3. Partial atomic numbering of **1a–1c**, **2a–2c**, **5d**, **5e**, **6d**, and **6e**.

Table 1. The π -orbital misalignment angles (Φ°) of **1a–1c**, **2a–2c**, **5d**, **5e**, **6d** and **6e** (calculated geometries^a)

Fulleroid/ketolactam	1 (C1–C9, C5–C6)	2 (C1–C9)
a: $R_1 = \text{CH}_2\text{OCH}_2\text{CH}_2\text{OCH}_3$	29.7, 30.1	28.8
b: $R_1 = \text{CH}_2\text{SiPh}_3$	30.2, 30.7	29.5
c: $R_1 = \text{CH}_2\text{SiMe}_3$	30.1, 30.3	29.6
Bisfulleroid/diketone	5 (C5–C6, C7–C8)	6 (C7–C8)
d: $E = \text{N}$, $R_2 = \text{Py}$, $R_3 = \text{Ph}$	29.5, 29.9	14.1
e: $E = \text{CCO}_2\text{Me}$, $R_2 = R_3 = \text{CO}_2\text{Me}$	29.3, 29.7	13.6

^aAll geometries optimized using the B3LYP/6-31G** basis set.

are due to the addition of O_2 to **2b** and **2c** (**3b** is shown in Figure 2). The ^{13}C NMR spectra show two pairs of carbonyl carbons at 161/188 and 162/189 ppm with 32 and 32 signals in the fullerene skeleton regions supporting C_s symmetry for **3b** and **3c**. The IR spectra show two carbonyl groups at 1651/1744 and 1647/1743 cm^{-1} , respectively. The observed stepwise reaction of molecular oxygen with the azafulleroid observed is attributed to the self-sensitizing ability of C_{60} and its derivatives.⁷ Comparing **1b**, **1c** to **2b**, **2c**, the fullerene first acts as an O_2 sensitizing agent in ambient light and then reacts with the $^1\text{O}_2$ generated to give **2b**, **2c** and **3b**, **3c** respectively. Of note is the fact that in order to make the second oxidation more facile, when using C_{60} or dyes (TPP or rose bengal) as sensitizer, nothing need be changed.

The structures of the products having been established, the reactivity of the bridgehead double bond (**1a–1c** and **2a–2c**) toward $^1\text{O}_2$ was estimated by the POAV misalignment angles (Φ°),⁵ as shown in Figure 3 and Table 1. These values are defined as the two-center dihedral angles between the two carbon dihedral angles on bonded pairs of carbons. Komatsu and Murata have reported the single photooxygenation of bisfulleroids **5d** and **5e** to afford diketones **6d** and **6e** in spite of the bridgehead double bond remaining. The geometries utilized for the azafulleroids **1a–1c**, keto lactams **2a–2c**, bisfulleroid **5d** and **5e**, and diketone **6d** and **6e** were obtained at the B3LYP/6-31G** level of theory. The misalignment angles of the bridgehead double bonds of **1a–1c**, **5d** and **5e** are far larger than in C_{60} ($\Phi = 0^\circ$), as shown in Table 1. However, in the keto lactams **2a–2c**, the misalignment angle of the remaining C1–C9 double bond is similar to those of **1a–1c**.⁸ In the diketones **6d** and **6e** the angle of the remaining C7–C8 double bond is far less than those of **5d** and **5e**. However, it would appear that some elaboration is in order.

In conclusion, we have demonstrated that the double photooxygenation of silyl-modified azafulleroid **1b** and **1c** provides the first diketo imide **3b** and **3c** via the keto lactam intermediate **2b** and **2c**. The sizes of 15-membered ring orifice of **3b** and **3c** were theoretically estimated to be 5.7 Å along the long axis and 3.3 Å along the short axis.⁶ The reactivity of the bridgehead

double bond of the fulleroid and related bisfulleroid were estimated by POAV misalignment angles to predict the difference between the keto lactam **2a–2c** and the diketones **6d** and **6e**.

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- Our preliminary experiment of double photooxygenation of **1a** was carried out at the same condition of **1b** and **1c** for 30 h. The resulting crude product is suggested to be a mixture of keto lactam **2a** and diketo imide **3a** observed by ^1H NMR and MALDI-TOF mass spectra. This preliminary result to be published, disclosed the remaining C1–C9 double bond of **2a** having the same reactivity as **2b** and **2c** predicted by POAV analysis.