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Azide Addition to an Endohedral Metallofullerene: Formation of Azafulleroids of $Sc_3N@I_h$-C_{80}

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Supporting Information

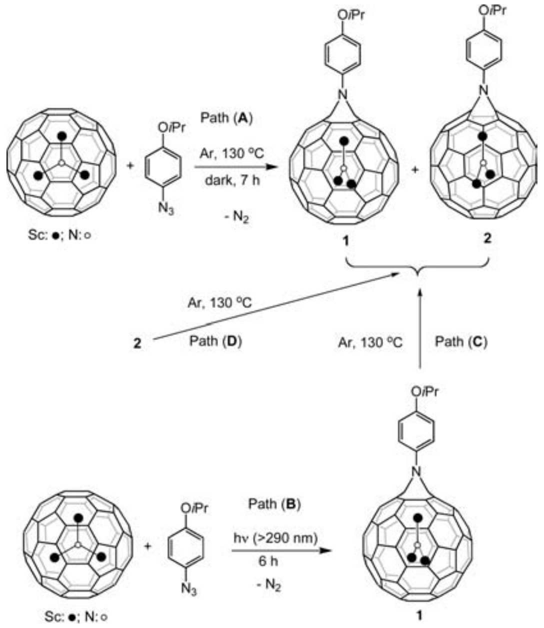
ABSTRACT: The reaction of an organic azide with an endohedral metallofullerene has been investigated for the first time. Isomeric [5,6]- and [6,6]-azafulleroids can be obtained from the thermal reaction of $Sc_3N@I_h$-C_{80} with 4-isopropoxyphenyl azide, while photoirradiation leads exclusively to the [6,6]-azafulleroid. An unprecedented thermal interconversion between the two isomeric azafulleroids has also been discovered.

Endohedral metallofullerenes (EMFs), a new family of carbon clusters, are generated by encapsulating metal atom(s) or metallic clusters in fullerene cages. Because of the interaction between the encapsulated metallic species and the carbon cage, these fascinating molecules display structural and electronic properties that are quite different from the properties of empty fullerenes.[1] Potential applications in nanoscience, organic solar cell development, and biomedicine have been proposed.[2] Exohedral chemical functionalization of EMFs is essential for the generatation of novel diversified metallofullerene materials. To date, various types of chemical transformations such as Diels–Alder reactions, Prato reactions, Bingel reactions, [2+2] cycloadditions with benzynes, [2+1] cycloadditions with carbenes, disilylations, and free-radical reactions have been utilized to modify EMFs.[2] Functionalization of EMFs has also been realized by the reactions of their cations and anions.[3] Reactions of diazo and azido compounds with empty fullerenes have been demonstrated to be a powerful tool for the synthesis of various fullerene derivatives.[4] Although diazo compounds,[5] 2-adamantane-2,3-[3*H*]-diazirine (AdN_2),[6] and 3-chloro-3-phenyldiazirine ($PhClN_2$)[6l] have been widely employed in the derivatization of EMFs, the reaction of organic azides with EMFs remains unexplored. Here we report for the first time the thermal and photochemical reactions of $Sc_3N@I_h$-C_{80} with 4-isopropoxyphenyl azide, which afford [6,6]- and [5,6]-azafulleroids.

Initially, the thermal reactions of $Sc_3N@I_h$-C_{80} with 4-isopropoxyphenyl azide were investigated. No adduct could be detected when the reaction of $Sc_3N@I_h$-C_{80} with the aryl azide was carried out at room temperature in the dark and under an argon atmosphere. Under similar conditions, the more reactive C_{60} undergoes a facile cycloaddition with aryl azides.[7] When the reaction temperature was raised, we found that the reaction of $Sc_3N@I_h$-C_{80} with 60 equiv of 4-isopropoxyphenyl azide in *o*-dichlorobenzene (ODCB) at 130 °C for 7 h afforded products **1** and **2** in yields of 13 and 7%, respectively, along with recovery of 53% of the $Sc_3N@I_h$-C_{80} starting material (Scheme 1, Path (**A**)).

Intriguingly, photoirradiation of a reaction mixture of $Sc_3N@I_h$-C_{80} and 4-isopropoxyphenyl azide (60 equiv) in a degassed sealed tube for 6 h at room temperature using a high-pressure

Scheme 1. Reactions of $Sc_3N@I_h$-C_{80} with 4-Isopropoxyphenyl Azide



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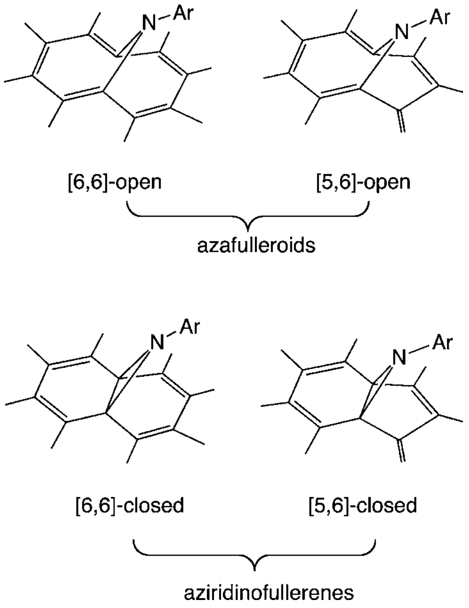
mercury arc lamp (λ > 290 nm) gave **1** in 21% yield along with 58% recovery of $Sc_3N@I_h$-C_{80} (Scheme 1, Path (**B**)). Compound **2** was not detected as a product of this photochemical reaction.

Adducts **1** and **2** were characterized by MALDI-TOF mass spectrometry and ^1H NMR and UV−vis−NIR spectroscopies. The structure of **2** was unequivocally determined by single-crystal X-ray diffraction. The mass spectra of **1** and **2** both gave the same mass peak at m/z 1259, indicating that they are isomeric monoadducts $Sc_3N@I_h$-C_{80}-p-$NC_6H_4OC_3H_7$.

Only two types of reaction sites are available for the functionalization of the I_h-symmetric C_{80} cage. One is the pyrene-type site, a C−C bond at a [6,6] ring junction, and the other is the corannulene-type site, a C−C bond at a [5,6] ring junction. Thus, there are four possible structures for **1** and **2**: [5,6]-closed, [5,6]-open, [6,6]-closed, and [6,6]-open (Scheme 2).

Scheme 2. Possible Cycloaddition Products of $Sc_3N@I_h$-C_{80}



NMR spectroscopy is usually an effective tool for structural characterization of fullerene derivatives. The ^1H NMR spectra of **1** and **2** are shown in Figure 1. The spectral patterns for the two isomers are similar, with only slight changes in the chemical shifts. The limited quantities and low solubilities of **1** and **2** precluded acquisition of their ^{13}C NMR spectra. Thus, whether the C−C bond at the addition site of $Sc_3N@I_h$-C_{80} is closed or open could not be determined by NMR spectroscopy.

As shown in Figure 2, the UV−vis−NIR spectral patterns of **1** and **2** resemble that of the pristine $Sc_3N@I_h$-C_{80}, indicating that the electronic structure of the C_{80} cage was only minimally altered in each of the addition products. In contrast to the results in Figure 2, [6,6]-closed regioisomers of $Sc_3N@I_h$-C_{80} display a characteristic absorption centered at 800 nm, while [5,6]-closed isomers exhibit a weak absorption centered at 955 nm.[8] No corresponding features are seen in Figure 2. On the other hand, the UV−vis−NIR absorption spectra of fulleroids generated by carbene additions, Bingel reactions, or electrochemical syntheses of several endohedral fullerenes are similar to those of the corresponding pristine endohedral fullerenes.[3,5,6] Therefore, adducts **1** and **2** are azafulleroids.

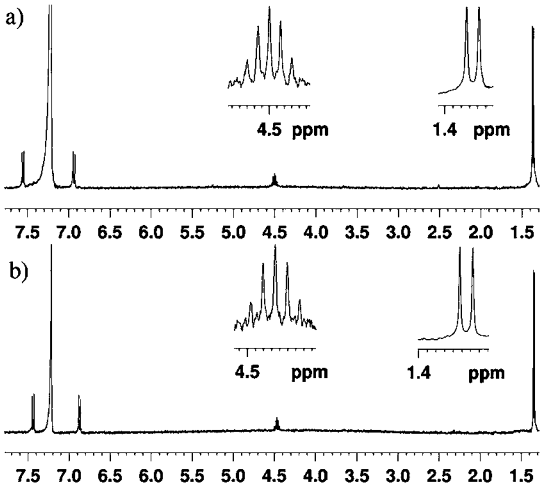


Figure 1. Proton NMR spectra of (a) **1** and (b) **2** in $CS_2/CDCl_3$ solution.

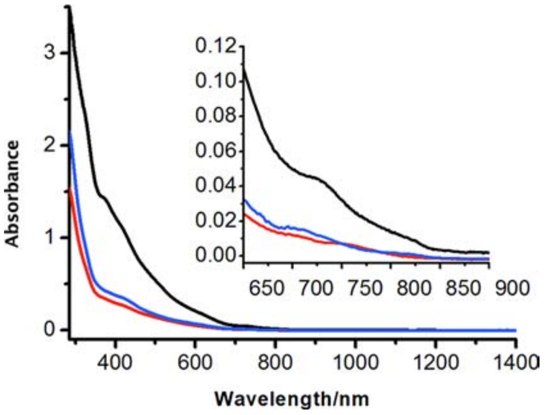


Figure 2. UV−vis−NIR spectra of $Sc_3N@I_h$-C_{80} (black), **1** (red), and **2** (blue) in toluene solution.

Additionally, the structure of **2** was unequivocally established as the [5,6]-azafulleroid by single-crystal X-ray crystallography. Black plates of the solvate $Sc_3N@I_h$-C_{80}[5,6]-open-p-$NC_6H_4OC_3H_7\cdot 0.88C_6H_6\cdot 0.12CS_2$ were obtained by slow evaporation of a solution of adduct **2** in a mixture of carbon disulfide and benzene.[9] Addition occurred at a [5,6] ring junction, as shown by the drawing in Figure 3. The C−C bond at the site of nitrene addition is clearly broken: the C1···C2 separation in **2** is 2.161(2) Å. For comparison, the average C−C bond distance at a [5,6] ring junction in $Sc_3N@I_h$-C_{80} is 1.437(15) Å. The C1−N2 and C2−N2 distances are nearly equal [1.4163(17) and 1.4156(18) Å, respectively]. N2 is pyramidal; the sum of the three C−N−C angles that surround it is 340.19°. The Sc_3N unit, which is disordered over two sites, is planar. The sum of the three Sc−N−Sc bond angles for the major site, with 0.759(2) fractional occupancy, is 360.00°. Sc1 is positioned near the site of adduct formation, as is usual for endohedral fullerenes when a C−C bond in a fullerene cage is broken as a result of external functionalization, as seen, for example, in the structure of $Y_3N@I_h$-C_{80}[6,6]-open-C-$(CO_2CH_2Ph)_2$.[10]

For C_{60} derivatives, interconversions between azafulleroids and aziridinofullerenes have been achieved under photoirradiation[7,11,12] or heating.[12,13] However, photolysis (λ > 290 nm) of solutions of **1** or **2** under an argon atmosphere for 2 h

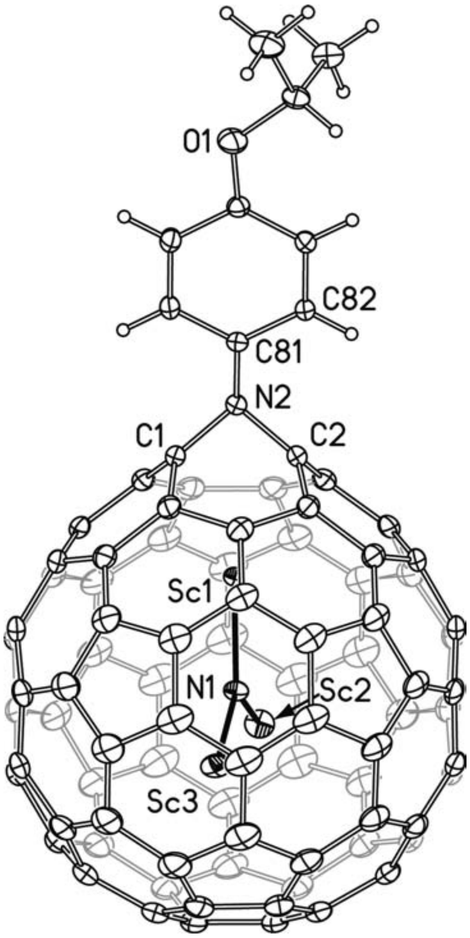
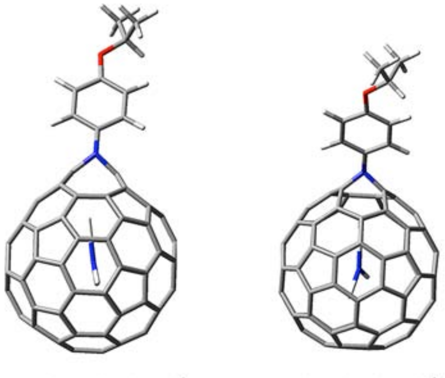


Figure 3. Single-crystal X-ray crystallographic structure of product **2**. Thermal ellipsoids are shown at the 50% probability level. Only the major site for the three scandium ions with 0.759(2) fractional occupancy is shown. The minor site for the three scandium ions has Sc4 positioned very near Sc1 while Sc5 and Sc6 are further from Sc2 and Sc3, suggesting that the Sc_3N unit is somewhat free to rotate about the Sc1−N1 axis. The molecules of benzene and carbon disulfide and the minor disorder in the isopropyl group are not shown.

led only to the formation of insoluble precipitates. Under these conditions, no evidence was found for the formation of aziridinofullerenes or for isomerization. Nevertheless, when a mixture of **1** and **2** in a 67:33 ratio (as determined by ^1H NMR spectroscopy) was heated at 130 °C for 7 h, the **1**:**2** ratio changed to 37:63. When the conversion was conducted at higher temperature (180 °C), the formation of some $Sc_3N@I_h$-C_{80} was observed as a result of a retroaddition reaction. The interconversion of the two azafulleroids was also investigated with pure samples of **1** and **2**. When pure **1** was heated at 130 °C for 7 h, a mixture of **1** and **2** was formed in a ratio of 44:56 (Scheme 1, Path (**C**)). In comparison, when pure **2** was heated at 130 °C for 14 h, a mixture of **1** and **2** was formed in a 16:84 ratio (Scheme 1, Path (**D**)). Therefore, adduct **1**, which is formed exclusively under photoirradiation, is a kinetic product, while adduct **2**, which is generated thermally, is the thermodynamic product.

Theoretical studies at the B3LYP/6-31G*/LANL2DZ(Sc) level showed that azafulleroid **2** is more stable than azafulleroid **1** by 2.05 kcal mol^{-1} and produced the structures shown in Figure 4. In addition, attempts to optimize the structures of the corresponding [6,6]- and [5,6]-aziridinofullerenes always led to azafulleroids **1** and **2**, respectively. These theoretical results suggest that both aziridinofullerenes of $Sc_3N@I_h$-C_{80} are much less stable, thus accounting for the failure of the attempts to convert **1** and **2** into the isomeric aziridinofullerenes under photoirradiation or thermal treatment. The interconversion between isomeric azafulleroids is unprecedented in fullerene chemistry, although interconversions between azafulleroids and aziridinofullerenes can be promoted photochemically or thermally.[7,11−13]



1 (2.05 kcal·mol^{-1}) **2** (0.00 kcal·mol^{-1})

Figure 4. Optimized structures and relative energies of **1** and **2** at the B3LYP/6-31G*/LANL2DZ(Sc) level.

It has been reported that aryl azides react photochemically[7,14] or thermally[14] with C_{60} to produce aziridinofullerenes as the products. In contrast, the azafulleroid **1** was exclusively formed from $Sc_3N@I_h$-C_{80} and 4-isopropoxyphenyl azide under our photochemical conditions. In view of the lower stability of **1** relative to **2**, our observations clearly demonstrate that the *in situ* generated nitrene is more reactive toward the [6,6] ring junction than the [5,6] ring junction of $Sc_3N@I_h$-C_{80}. The same reactivity trend and similar [6,6]-open products were also observed in the reactions of $Sc_3N@I_h$-C_{80} with carbenes formed from diazo compounds.[5d,f] The formation of adducts **1** and **2** from the thermal reaction of $Sc_3N@I_h$-C_{80} with 4-isopropoxyphenyl azide might proceed via the 1,3-dipolar cycloaddition of 4-isopropoxyphenyl azide to $Sc_3N@I_h$-C_{80} followed by loss of N_2.[7,13,14] However, attempts to isolate the expected triazolinofullerene intermediate failed even at lower reaction temperatures.

In conclusion, the first study of azide addition to EMFs, which affords aza-bridged annulene-type metallofulleroids, has been reported. The thermal reaction of $Sc_3N@I_h$-C_{80} with 4-isopropoxyphenyl azide provides both [6,6]- and [5,6]-azafulleroids, while the corresponding photochemical reaction generates only the [6,6]-azafulleroid isomer. Computational studies have shown that the [6,6]-azafulleroid isomer is less stable than the [5,6]-azafulleroid isomer and indicated that the *in situ* generated nitrene preferentially reacts with the [6,6] ring junction of $Sc_3N@I_h$-C_{80} to give a kinetic product. An unprecedented interconversion between two azafulleroid isomers has also been disclosed for the first time. Further studies of the reactions of other azides with EMFs are underway.

■ ASSOCIATED CONTENT

Ⓢ Supporting Information

Experimental procedures; spectral data, spectra, and optimized structures and Cartesian coordinates for **1** and **2**; and a CIF file for the single-crystal X-ray structure of **2**. This material is available free of charge via the Internet at http://pubs.acs.org.

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Notes

The authors declare no competing financial interest.

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