Fullerenes

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Rigid Tether Directed Regioselective Synthesis and Crystallographic Characterization of Labile 1,2,3,4-Bis(triazolino)[60]fullerene and Its Thermolized Derivatives

Muqing Chen[+], *Lipiao Bao*[+], *Ping Peng, Shushu Zheng, Yunpeng Xie, and Xing Lu*[*]

Abstract: *Labile bis-triazoline adducts of C_{60} are supposed to be the precursors of bis-azafulleroids, but the formation mechanism is still unclear because of the incomplete isolation of the thermolized products and the lack of X-ray structures. A rigid-tethered reagent 1,2-bis(azidomethyl)benzene (**1**) was used to regioselectively synthesize the labile 1,2,3,4-bis(triazolino)[60]-fullerene (**2**), the structure of which was determined by single-crystal X-ray crystallography. Further thermolysis of **2** produces four products (**3a**–**3d**), which were all characterized by X-ray crystallography. Although **3a** and **3b** have traditional bis-azafulleroid structures, as proposed previously, **3c** and **3d** show unprecedented structures with either the coexistence of [5,6]-open and [6,6]-closed patterns or an oxidized structure with an 11-membered ring on the cage. A thermolysis mechanism is proposed to clarify long-term confusion about the transformation process from bis-triazoline adducts to bis-azafulleroids of C_{60}.*

Chemical modification of fullerenes is a key step to alter their inherent properties so as to realize their applications in different areas.[1–4] Recent results show that regioisomerically pure bis-adducts of C_{60} perform better as acceptor materials in organic photovoltaic solar cells than the corresponding isomeric mixtures or the monoadducts.[5,6] However, the regioselective synthesis of bis-adducts of fullerenes is still a challenging work because it always produces a large number of regioisomers. For instance, even the highly symmetric C_{60} has two types of C–C bonds, that is, [6,6]-bonds and [5,6]-bonds, giving at least 8 possible isomers for a bis-adduct with two identical addends.[7,8]

To obtain regioisomerically pure bis-adducts, the tether-directed method that was first proposed by Diederich and co-workers is proved to be very useful.[8–10] It was later recognized that the length, rigidity, and symmetry of the spacers affect strongly the regioselectivity of the reactions and even the properties of the adducts.[11] Up to now, the tether-directed methodology has been widely adopted to synthesize pure regioisomers of fullerene bis-adducts following different synthetic strategies, such as the Bingel–Hirsch reaction,[12] Prato reaction,[13] Diels–Alder cycloaddition,[14] and Diazo cycloaddition.[15]

Meanwhile, the reaction of organic azides is another important method for the functionalization of fullerenes, which has shown its effectiveness to produce many novel derivatives with different structures.[16–20] The bis-addition reactions of azides with C_{60} are more complicated because of the large number of isomers that may form in the mixture and the difficulties lying in the complete isolation and concrete structural characterization of the bis-adducts, leaving a long confusion about the thermolysis mechanism of bis-triazoline derivatives of fullerenes.[21] As a result, the tether-directed strategy was also adopted for the regioselective synthesis of bis-adducts of C_{60} following the azide addition.[22–24] Considering the fact that no X-ray result of either the bis-triazoline adducts of fullerenes or the bis-azafulleroids have been reported so far,[22,23,25,26] we speculate that the use of soft tethers in the previous studies may have hindered the successful growth of single crystals of these compounds.

Accordingly, we herein designed a novel azide reagent containing a rigid 1,2-dimethylbenzene tether (**1**) to functionalize C_{60}, which shows high regioselectivity to afford only one isomer of the labile 1,2,3,4-bis-triazoline C_{60} derivative (**2**). Furthermore, the thermolysis of **2** was studied in more detail, and the utilization of high-performance liquid chromatography (HPLC) ensured the complete isolation of all of the soluble thermolized isomers (**3a**, **3b**, **3c**, and **3d**) in addition to pristine C_{60} (Scheme 1). More significantly, the rigid phenyl tether facilitates the single crystal growth of all the derivatives (**2**, **3a**, **3b**, **3c**, and **3d**) and the unambiguous X-ray crystallographic results enable us to make an in-depth understanding about the mechanism of the thermolysis process of **2** to form the bis-adduct isomers, some of which show very interesting addition patterns that have rarely been reported before.

In a typical reaction (Scheme 1), a chlorobenzene solution containing 72 mg C_{60} (0.1 mmol) and 62 mg **1** (0.33 mmol) was heated to 75 °C under stirring, and the reaction process was monitored with HPLC (Supporting Information, Figure S1). After 1 h, along with the peak of C_{60} at 5.2 min, a new peak appeared at 6.3 min which was attributed to the product **2**. When the reaction proceeded to 10 hours, the peak of **2** became the most prominent one but some tiny peaks appeared at 4–5 min, which were assigned to the decomposed

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[*] Dr. M. Chen,[+] Dr. L. Bao,[+] Prof. P. Peng, Dr. S. Zheng, Prof. Y. Xie, Prof. X. Lu
State Key Laboratory of Materials Processing and Die & Mould Technology, School of Materials Science and Engineering
Huazhong University of Science and Technology
1037 Luoyu Road, Wuhan 430074 (P.R. China)
E-mail: lux@hust.edu.cn
Dr. M. Chen[+]
Department of Materials Physics, School of Physics and Mechanical & Electronical Engineering, Hubei University of Education
129 Gaoxin 2nd Rd, Wuhan Hi-Tech Zone
Wuhan 430205 (P.R. China)

[+] These authors contributed equally to this work.

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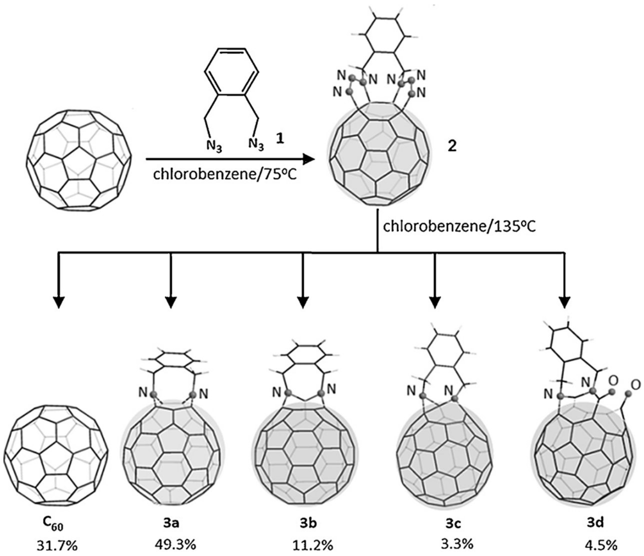


Scheme 1. Formation of **2** and its conversion into the thermolysis adducts (**3a**, **3b**, **3c** and **3d**) along with C_{60}.

products of **2**. Accordingly, the reaction was terminated and the mixture was subjected to HPLC separation, which gave pure **2** in 49% yield based on HPLC peak areas.[27] The molecular ion peak of **2** is clearly observed at m/z 908.1 in the matrix-assisted laser desorption/ionization time-of-flight (MALDI-TOF) mass spectrum (Supporting Information, Figure S2), which is in perfect agreement with the theoretical value of $C_{60}(C_8H_8N_6)$.

The molecular structure of **2** is unambiguously determined by single-crystal X-ray diffraction crystallography (Figure 1). To the best of our knowledge, this is the first X-ray result of a bis-triazoline adduct of fullerenes. It is clear that **2** is truly a 1,2,3,4-bis-triazoline adduct with the two triazoline rings fusing onto two [6,6]-bonds on a hexagonal face, possessing a *cis*-1 addition pattern.[28] The distances between the carbon atoms at the sites of addition, that is, 1.572(3) Å for C1–C6 and 1.577(4) Å for C4–C5, indicate that **2** has a closed-cage structure. The bond lengths of N3–N5 (1.251(3) Å) and N4–N6 (1.251(3) Å) suggest their N=N double bond features, whereas N2–N4 (1.342(3) Å) and N1–N3 (1.339(3) Å) are single bonds. Although a similar 1,2,3,4-bis-triazoline adduct has been proposed by Luh and coworkers,[25] they were not able to unambiguously confirm whether the spacer was linked to N1–N2 or to N5–N6 based on their NMR results. Here we unequivocally confirm that only one bis-triazoline isomer **2** exists in the reaction and establish its absolute structure with single-crystal X-ray crystallography.

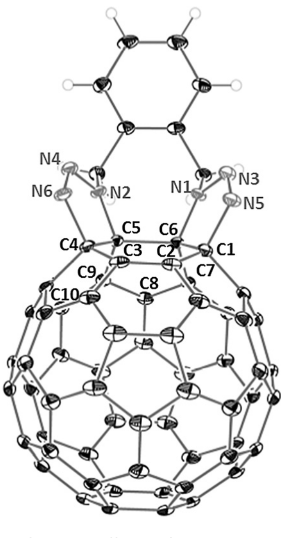


Figure 1. ORTEP of **2** showing ellipsoids set at 30% probability. Solvent molecules are omitted for clarity.[30]

It has been proposed that bis-triazoline adducts of C_{60} can convert into bis-azafulleroids under heating, but the mechanism is not fundamentally clear because of the incomplete isolation of the thermolized products and the lack of their X-ray structures.[24,25] We investigated the thermolysis reaction of **2**, and to avoid missing any soluble bis-azafulleroids even with a trace yield, we used HPLC technique to separate all the products, some of which are difficult to isolate with conventional column chromatography. The thermolysis of **2** is carried out in chlorobenzene at 135°C (Scheme 1). The reaction process was monitored by HPLC (Supporting Information, Figure S3). After 15 min, **2** quickly decomposed to five products as C_{60}, **3a**, **3b**, **3c**, and **3d** (Scheme 1). When the reaction proceeded for 60 min, the peak of **2** had almost completely disappeared and then the reaction was terminated. According to the HPLC peak areas,[27] it is demonstrated that nearly one third (31.7%) of **2** is changed to pristine C_{60} by the complete detachment of the bis-triazoline moiety. As to the thermolized products, **3a** is the most abundant one with 49.3% yield, while others are 11.2% for **3b**, 3.3% for **3c** and 4.5% for **3d** (Supporting Information, Figure S4). It is noteworthy that the latter two compounds (**3c** and **3d**) with such low yields are difficult to obtain without the assistance of HPLC. More importantly, owing to the rigid tether, the molecular structures of all the products (**3a**, **3b**, **3c** and **3d**) are determined by single-crystal X-ray crystallography, which enables us to understand the thermolysis mechanism accurately.

The structure of **3a** is shown in Figure 2a. The addition occurs at two [5,6]-junctions of a fluorene moiety of C_{60}, which is different from the situation in the precursor **2** where a phenanthrene unit is involved in the reaction (Supporting Information, Figure S5a). The C–C distances of C6–C7 (2.258(3) Å) and C5–C9 (2.265(3) Å) confirm that the two [5,6]-bonds are broken and the structure can be assigned as a conventional (1,2)-[5,6]+(3,4)-[5,6]-bis-azafulleroid.[22] **3b** has an unusual structure that has rarely been reported for C_{60} derivatives.[18,21] The reaction occurs at two [5,6]-junctions of an acenaphthene unit and the two N atoms of the addend share a common cage carbon atom to exhibit a (1,2)-[5,6]+(2,3)-[5,6]-bis-azafulleroid pattern (Figure 2b; Supporting Information, Figure S5b). The broken bonds of C5–C9 (2.284(8) Å) and C5–C6 (2.216(8) Å) reveal the fulleroid feature. To the best of our knowledge, this is the first X-ray result for such a novel bis-azafulleroid structure containing a shared cage carbon atom.[21] Furthermore, the fact that the addition of the bis-triazoline moiety occurs on a hexagonal

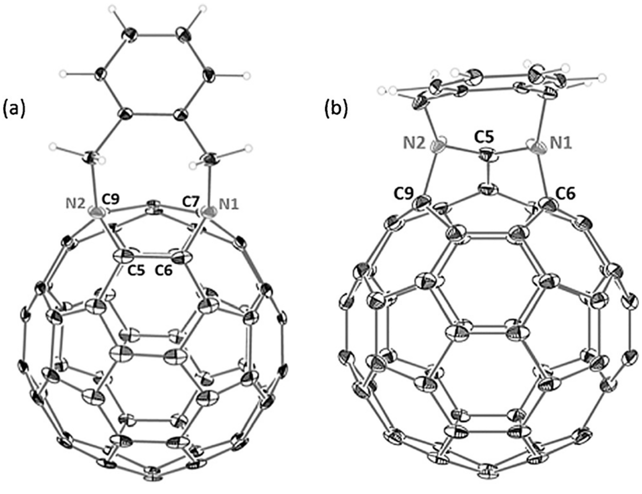


Figure 2. ORTEPs of a) **3a** and b) **3b** with ellipsoids set at 30% probability. Solvent molecules are omitted for clarity.[30]

ring in **2** but the addition sites are all concentrated on the carbon atoms at a pentagonal ring in **3a** and **3b**, suggesting that the short and rigid tether is responsible for the latter two bis-azafulleroid structures (see below).

The structure of **3c** is very interesting because of the coexistence of a [5,6]-open pattern and a [6,6]-closed pattern on a hexagonal ring, namely, a (1,2)-[6,6]-aziridino + (2,3)-[5,6]-azafulleroid structure (Figure 3a; Supporting Information, Figure S5c). To the best of our knowledge, such a structure has never been reported previously. The C−C distance of C5−C6 (2.277(4) Å) confirms that the bond is broken, producing a heptatomic ring on the cage. The distance of C4−C5 (1.555(4) Å) shows its [6,6]-closed configuration and the bond lengths are 1.504(4) Å for N2−C4 and 1.459(3) Å for N2−C5. The respective angles of the three membered ring are N2-C5-C4 (59.8(2)°), N2-C4-C5 (56.9(2)°), and C4-N2-C5 (63.3(2)°).

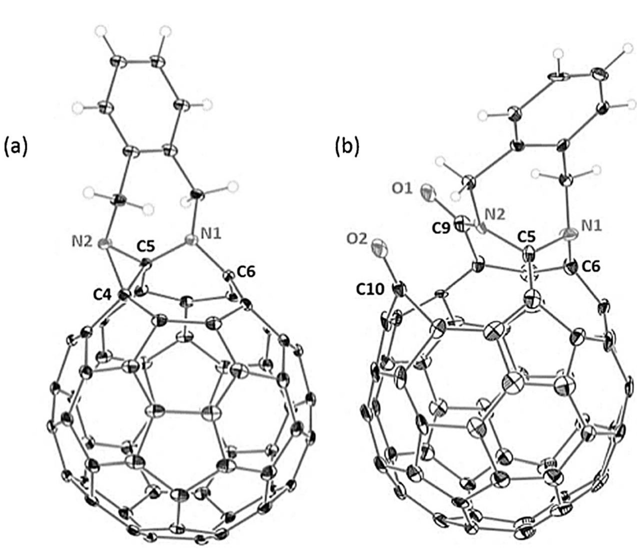
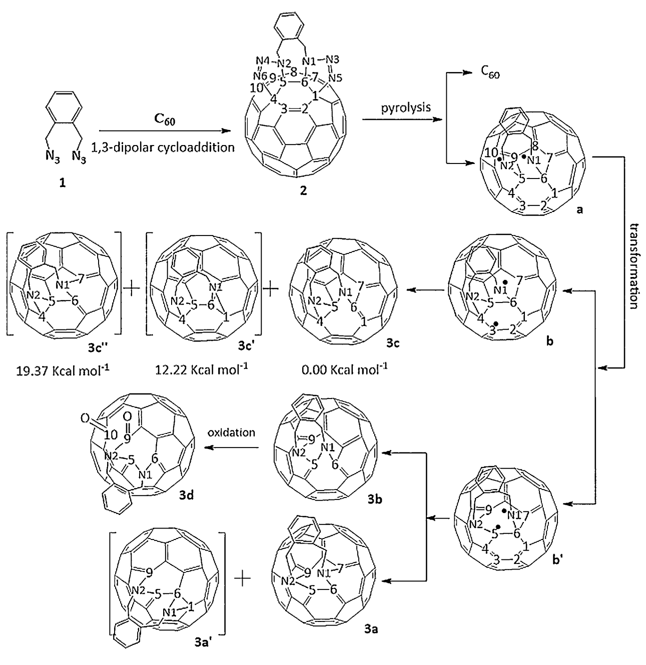


Figure 3. ORTEPs of a) **3c** and b) **3d** with ellipsoids set at 30% probability. Solvent molecules are omitted for clarity.[30]

The structure of **3d** displays two [5,6]-open structures on a pentagonal ring with the two nitrogen atoms sharing a common cage carbon atom C5. The C−C distances of C5−C6 and C5−C9 are 2.25(2) Å and 2.43(3) Å, respectively, confirming the fulleroid structure. Interestingly, two oxygen atoms break the [6,6]-bond between C9 and C10 adjacent to a site of nitrogen addition, forming two carbonyl groups and drilling an 11-membered ring orifice on the cage (Figure 3b; Supporting Information, Figure S5d). The bond lengths of C9−O1 (1.26(3) Å) and C10−O2 (1.19(3) Å) confirm their C=O double-bond character. Except the oxidized region, the structure of **3d** is identical to that of **3b**, which stimulates us to consider that **3d** is the oxidized product of **3b**. To verify this speculation, we checked the toluene solution of **3b** under ambient conditions by HPLC (Supporting Information, Figure S6). It was found that after the solution was exposed to air for 12 h, an obvious peak appeared at 8.4 min which was attributed to **3d**. When the time prolonged to 96 h, the peak of **3d** continued to increase and no other new peaks appeared, indicating the high regioselectivity of the conversion reaction from **3b** into **3d**.

Thanks to the unambiguous X-ray structures of all these derivatives shown above, we are able to propose a fundamentally clear mechanism to describe the thermolysis process of bis-triazoline adduct **2** so as to clarify the long-term confusion about the formation of bis-azafulleroids. As shown in Scheme 2, the tethered azide **1** as an 1,3-dipolar reagent first attacks the [6,6]-bonds of a hexagonal ring of C$_{60}$ to form the 1,2,3,4-bis-triazoline **2** in a highly regioselective manner. Under thermal conditions, the bis-triazoline moiety of **2** can be completely detached to form pristine C$_{60}$. Another possibility is that denitrogenation by breaking the C1−N5, C4−N6, N1−N3, and N2−N4 bonds forms intermediate **a** with



Scheme 2. Plausible reaction mechanism for the formation of **2**, **3a**, **3b**, **3c** and **3d**. The structures in the brackets represent undetected isomers from the thermolysis mixture of **2**. The black dots display radicals.

two nitrogen radicals (N1 and N2) linking to C6 and C5, respectively. The highly reactive intermediate **a** follows two routes to form the corresponding adducts **3a**, **3b**, **3c**, and **3d**. One is that the N2-radical first attacks the neighboring C4, forming **b** with a [6,6]-closed structure. Further transformation of **b** shows that N1-radical has the probabilities to react with the three adjacent cage carbons (C1, C5, and C7). However, only C5 is attacked to form **3c**. This result promotes us to investigate why C1 and C7 are precluded from the reaction of N1-radical to form **3c″** and **3c″**, respectively. We compared the thermodynamic stability of the three possible isomers **3c**, **3c′,** and **3c″** by theoretical calculations (Supporting Information, Figure S9), which show that **3c″** (19.37 kcal mol^{-1}) and **3c′** (12.22 kcal mol^{-1}) are much more unstable than **3c**. Accordingly, the formation of **3c′** and **3c″** may not take place during the process. Considering the rigid tether, we draw a preliminary conclusion that the spacer is too short to bear a 1,2,3,4-bis-aziridino pattern on a hexagonal ring for **3c′**, not to say that the addition occurring on two different ring faces for **3c″**. An alternative transformation of **a** is that N2-radical first attacks its neighboring C9 to form **b″** and thus N1-radical also has three possible addition sites (C1, C5, and C7) to further form bis-azafulleroid regioisomers **3a″**, **3b**, and **3a**, respectively. Experimental results indicate that N1-radical successfully combines with the carbon radicals of C5 or C7 to form **3b** or **3a**, respectively, but not with C1 to form **3a″,** which has a similar structure to that of **3c″** and is hard to form because of the rigidity of the short tether. The regioselective oxidation of **3b** to **3d** can be referred to the reported photo-oxygenation process because the C9−C10 bond has high HOMO coefficients to be attacked by the electrophilic $^1O_2$.[1,29]

In summary, a rigid tethered azide **1** has been designed to selectively synthesize the labile 1,2,3,4-bis(triazolino)-[60]fullerene **2**. Further thermolysis of **2** forms two bisazafulleroids **3a**, **3b**, one aziridino + azafulleroid adduct **3c** and an oxidized bis-azafulleroid product **3d** along with C_{60}. Importantly, the molecular structures of all these products (**2** and **3a**-**3d**) have been unambiguously established by single crystal X-ray crystallography. Although the bis-triazoline moiety in **2** is fused on a hexagonal ring, the addition sites in bis-azafulleroids **3a** and **3b** involve a pentagonal face instead. **3c** has an unprecedented structure with the coexistence of aziridino (5,6-open) and azafulleroid (6,6-closed) structures on a hexagonal ring. The structure of **3d** shows two azafulleroid structures on a pentagonal ring, with two carbonyl groups and an 11-membered ring orifice on the cage. Actually, **3d** is the oxidized product of **3b** and the conversion process is experimentally confirmed by HPLC. Based on these concrete X-ray results, we propose a precise thermolysis mechanism of **2** to elucidate the formation of **3a**–**3d**, clarifying the long confusion about the conversion from bis-triazoline adducts to bis-azafulleroids. Considering the high regioselectivity of this reaction and the high-efficiency of single crystal growth, this novel rigid tethered reagent can also be used to functionalize other fullerenes or even metallofullerenes for the regioselective synthesis of bis-aza-adducts, which may find applications in photovoltaics and materials science.

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[30] CCDC 1403988 (**2**), 1439083 (**3a/b**), 1409011 (**3c**), and 1439093 (**3d**) contain the supplementary crystallographic data for this paper. These data are provided free of charge by The Cambridge Crystallographic Data Centre.

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