Synthesis and Structure of an Open-Cage Thiafullerene $C_{69}S$: Reactivity Differences of an Open-Cage C_{70} Tetraketone Relative to Its C_{60} Analogue

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S *Supporting Information*

ABSTRACT: An open-cage C_{70} fullerene with a 13-membered ring-opening and a bis(hemiacetal) moiety was synthesized by the reaction of the corresponding open-cage C_{70} diketone with nucleophilic oxidizing agents. The size of the cage opening could be expanded by a subsequent dehydration reaction. Reaction of the thus obtained open-cage C_{70} tetraketone with elemental sulfur in the presence of tetrakis(dimethylamino)ethylene resulted in the formation of the first example of an open-cage $C_{69}S$ thiafullerene with a 12-membered ring-opening. The formation of this sulfur-containing heterofullerene reflects a significantly different chemical reactivity for the open-cage C_{70} tetraketone relative to its C_{60} analogue. The structures of all novel compounds were unambiguously determined by single crystal X-ray diffraction analyses, in addition to which the electrochemical properties of the thiafullerene $C_{69}S$ were examined and compared with those of the corresponding C_{70} analogue.

Heterofullerenes, where at least one carbon atom of the fullerene cage is replaced by other atoms such as boron, nitrogen, or oxygen, are very interesting compounds as their chemical reactivity, photophysical properties, and solid-state characteristics can be tuned relative to the original carbon-cage fullerenes and are expected to be very exciting and even unprecedented.[1] Although the generation of these molecules in the gas phase has been reported,[2] viable synthetic routes to heterofullerenes on a macroscopic scale have only been successful for azafullerenes such as $C_{59}N$, $C_{69}N$, $M_2@C_{79}N$ (M = Y, Gd, Tb) and their derivatives.[1] In contrast, studies on thiafullerenes, i.e., sulfur-containing heterofullerenes, are very rare and so far remain limited to theoretical studies on $C_{59}S$[3] and the gas-phase detection of $C_{58}S$, $C_{56}S_2$, $C_{52}S_4$, and $C_{50}S_5$.[4]

In order to synthesize heterofullerenes in a controlled fashion under mild reaction conditions, open-cage C_{60} and C_{70} derivatives,[5] which are also used for the synthesis of endofullerenes, should be promising precursors. Azafullerenes $C_{59}N$[6−8] and $C_{69}N$,[9] e.g., were prepared from the open-cage C_{60} and C_{70} derivatives, respectively. The successful formation of $C_{58}N_2$[10] and $C_{58}O_2$[11] in the gas phase was reported for laser irradiation of open-cage C_{60} derivatives under MALDI-TOF MS conditions. Open-cage $C_{59}O$[12] and $C_{59}S$[13] derivatives, and also

$CO@C_{59}O_6$,[14] have been synthesized by unprecedented decarbonylation reactions in solution. However, the cages of these C_{60} fullerenes were severely modified during the reactions, and several functional groups are present on the rim of the openings, rendering these compounds rather unsuitable precursors for the synthesis of closed heterofullerene cages.

Although some examples of open-cage C_{60} derivatives have been reported,[15] there are only a limited number of examples for open-cage C_{70} derivatives. Until now, it has been acknowledged that C_{70} exhibits, similar to C_{60}, the typical reactivity of electron-deficient olefins.[16] The lower symmetry of C_{70} relative to that of C_{60} often causes difficulties during the separation and characterization (especially by ^{13}C NMR) of the usually isomeric reaction products.[17] Despite these difficulties, some examples of open-cage C_{70} derivatives have been isolated, including an ester,[18] ketolactams,[19] and a diketosulfide.[20] Developing synthetic strategies toward open-cage C_{70} derivatives is not only desirable from an academic perspective but also justified by their photophysical properties, which are very different from the C_{60} analogues. So is, e.g., the absorption of visible light stronger,[21] the lifetime of the excited triplet state by 2 orders of magnitude longer[22] and the behavior as an n-type semiconductor in polymer solar cells much better.[23] Moreover, open-cage C_{70} fullerene derivatives are also considered crucial for the generation of the corresponding hetero- and endofullerenes.[24,25]
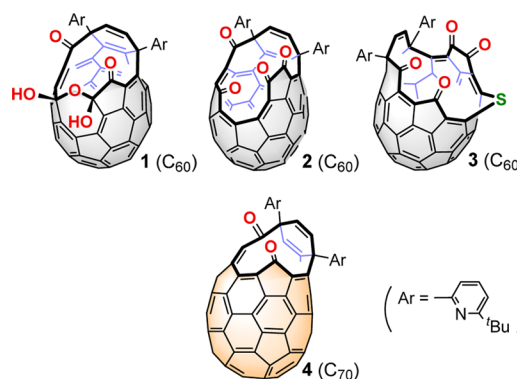
Previously, we reported the thermal reaction of C_{70} with 3,6-di(2-pyridyl)-pyridazine, which resulted in the formation of two open-cage C_{70} derivatives, both containing an eight-membered

ring-opening. The subsequent photochemical treatment of the major isomer afforded two diketone derivatives, each containing a 12-membered ring-opening.[20] We also reported that a similar reaction sequence should be applicable to the C_{60} derivative.[26] Open-cage C_{60} bis(hemiacetal) 1[27] with a 13-membered ring-opening was transformed into tetraketone 2 with a 16-membered ring-opening,[13,27] which gave access to tetraketosulfide 3 with a 17-membered ring-opening.[13] In the interest of discovering the previously mentioned synthetic pathways to hetero- and endofullerenes, it should be desirable to establish whether similar reactivity can be observed for the corresponding C_{70} analogues of the open-cage C_{60} derivatives. Herein, we report the synthesis of open-cage C_{70} diketone 4 and some reactions, which demonstrate that this C_{70} derivative exhibits a remarkably different reactivitiy compared to its C_{60} analogue. Ultimately, these reactions resulted in the formation of the first example of an open-cage $C_{69}S$ thiafullerene 8.

The open-cage C_{70} diketone 4 was synthesized from the reaction of the parent closed C_{70} fullerene with 3,6-bis(6-(*t*-butyl)pyridin-2-yl)pyridazine, followed by photochemical oxidation. After each reaction step, the resulting mixtures of isomers were carefully separated by chromatography on silica gel.[20] The *t*-butyl groups on the pyridyl rings of the pyridazine reagent were introduced in order to increase the solubility of 4 during the following reaction steps.[27] The size of the cage opening in 4 was subsequently expanded by nucleophilic oxidation reactions (Scheme 1). The reaction of 4 with N-methylmorpholine N-

Scheme 1
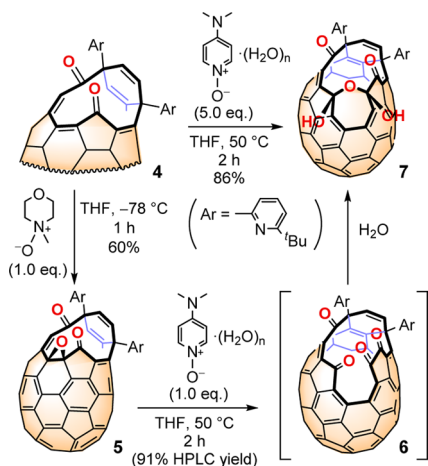
oxide (NMO) at room temperature, i.e., under optimized reaction conditions described for the C_{60} analogue 1, resulted in the formation of complex product mixtures, indicative of different reactivity patterns between the C_{70} and C_{60} derivatives. Presumably due to the milder nucleophilicity of the oxidizing agent, reaction of 4 with 4-dimethylaminopyridine N-oxide (DMAPO) yielded bis(hemiacetal) 7 in 86%.[28] We assumed that the reaction proceeds via the initial formation of epoxide 5, which would afford tetraketone 6[24] after reaction with a second equivalent of the oxidant, followed by the addition of one molecule of water to one of the carbonyl groups, thus generating 7. This mechanism was corroborated by the isolation of epoxide 5 in 60% yield from the reaction of 4 with 1 equiv of NMO at −78 °C. Consistent with the different reactivity observed for the C_{70} analogue 4, the corresponding epoxide based on the C_{60} analogue of the open-cage diketone could neither be detected

nor isolated under similar conditions.[27] A subsequent sequential reaction of epoxide 5 with a second equivalent of DMAPO afforded 7 in high yield (91% estimated by HPLC analysis).

Single crystals of 5 and 7 were obtained from hot toluene solutions of 5 in the presence of nickel(II) octaethylporphyrin and the slow evaporation of THF solutions of 7, respectively, allowing the unambiguous determination of the molecular structures by X-ray diffraction (XRD) analyses (Figure 1). The
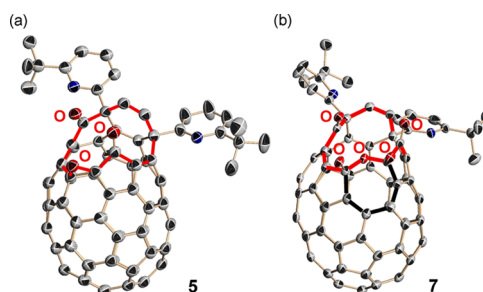

Figure 1. Single crystal XRD structures of 5 (a) and 7 (b) with thermal ellipsoids set at the 30% and 50% levels, respectively. Hydrogen atoms, solvent molecules, and nickel(II) octaethylporphyrin were omitted for clarity, and only selected atoms were labeled.

epoxide moiety in 5 is formed selectively next to the carbonyl group of the five-membered ring. The subsequent nucleophilic attack of the second equivalent of DMAPO should accordingly proceed from the front, as the back side is sterically encumbered due to the cage structure.[29] The opening of 7 contains both a diketone and bis(hemiacetal) moieties, which adopt the same structural motif as in the C_{60} analogue 1. This structural congruence prompted us to consider the possibility to obtain opening expanded 6 from a dehydration reaction of 7 (see Scheme 2), whereby a water molecule should be accommodated inside the cage of 6, as reported for the C_{60} analogue 1.[27]

Scheme 2
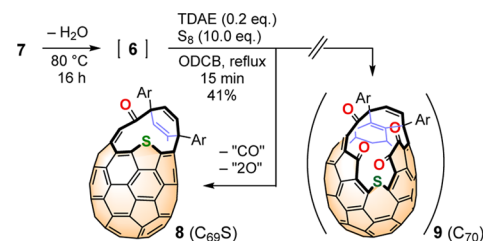
In order to examine the size of the opening in 6 from a theoretical perspective, DFT calculations[30] were conducted for the model compounds 2′ and 6′, in which the *t*-butyl groups on the pyridyl rings were replaced with hydrogen atoms. To avoid unnecessary levels of complexity potentially arising from hydrogen bond interactions in case of H_2O insertion, we decided to model the insertion process with an Ar atom instead. The energies for an Ar atom required to pass through the opening of 2′ and 6′ were calculated at the M06-2X/6-31G* level of theory to be 34.2 and 38.8 kcal/mol, respectively. These results demonstrate that despite their similar structures, the opening in the C_{70} derivative 6′ is smaller compared to that in the C_{60} analogue 2′. This result can be explained by the larger degree of strain release in the C_{60} cage[16] by the larger opening relative to the C_{70} derivative, in which the 10 additional carbon atoms in the fullerene cage may already defuse the present strain to some

extent. The smaller size of the opening in the C_{70} derivative is experimentally supported by the presence of mere trace amounts of water encapsulated inside **7**, after treatment with water in toluene at 120 °C under 9000 atm. Under similar conditions, C_{60} analogue **1** quantitatively encapsulated a molecule of water inside the cage.

For the open-cage C_{60} diketone[26,31] and tetraketone **2**,[13] as well as for the open-cage C_{70} diketone **4**,[20] the insertion of sulfur on the rim of the opening has been reported as an effective procedure to expand the cage opening. Since the open-cage C_{70} tetraketone **6** shares a similar opening motif with the C_{60} analogue **2**, we expected a similar reaction product from a simple insertion reaction with sulfur. However, when tetraketone **6** was subjected to similar reaction conditions as **2**, we observed an unprecedented reaction. Dehydration of bis(hemiacetal)-diketone **7** at 80 °C for 16 h resulted in the generation of **6**, which was dissolved in *o*-dichlorobenzene (ODCB) and heated to 180 °C for 15 min in the presence of 1 equiv of elemental sulfur and 0.2 equiv of tetrakis(dimethylamino)ethylene (TDAE) (Scheme 2).[13,20,26,31] After column chromatography on silica gel, followed by recycling HPLC separation using Buckyprep columns, the unexpected open-cage $C_{69}S$ thiafullerene **8** was isolated in 41% yield, whereas the expected product **9** with a 17-membered ring-opening could not be observed. A possible explanation for the formation of **8** instead of **9** is outlined in Scheme 3. As previously

Scheme 3
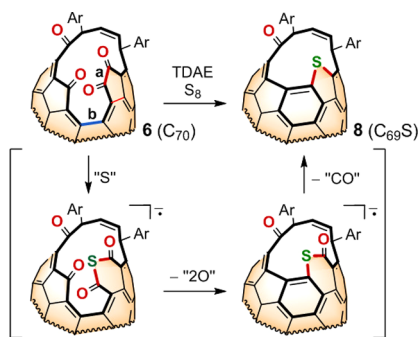
mentioned, the LUMO of **2**, the C_{60} analogue of **6**, is localized to a relatively high degree on the conjugated butadiene unit.[13] The LUMO of the C_{70} derivative **6**, however, is not observed at the corresponding C–C bond "b" (blue), thus explaining the absence of **9**. Instead, sulfur should insert into the more reactive C(O)–C(C) bond "a" (red), probably during the anion radical state. The insertion of sulfur should be followed by a carbonyl coupling reaction under concomitant loss of two oxygen atoms. A subsequent decarbonylation should then afford **8** after a transfer of one electron to the starting material **6**, which is more electronegative than **8**.

Single crystals suitable for XRD analysis were obtained from hot toluene solutions of **4** and hot chlorobenzene solutions of **8**, respectively, which allowed the assignment of the molecular structures (Figure 2). The loss of two oxygen atoms from the two carbonyl groups in starting material **6** is evident from the contracted 12-membered ring-opening in **8** (Figure 2a). More importantly, the opening in **8** consists of 11 carbon atoms and one sulfur atom. In contrast, the molecular structure of diketone **4** (Figure 2b) shows that the carbonyl group in the five-membered ring, which formed part of the C_{70} cage, has been replaced with a sulfur atom in **8**. The larger van der Waals radius of sulfur relative to carbon leads to a shortend (O)C···S distance
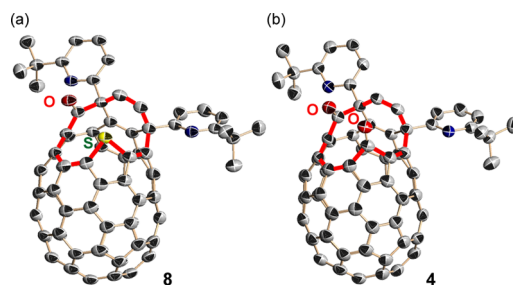
Figure 2. Single crystal XRD structures of **8** (a) and **4** (b) with thermal ellipsoids set at the 50% level. Hydrogen atoms and solvent molecules were omitted for clarity, and only selected atoms were labeled.

of 2.0735(10) Å between the carbonyl carbon and the sulfur atom. Compared to the corresponding (O)C···C(O) distance of 3.104(8) Å between the carbonyl carbon atoms in **4**, this represents a significant contraction of the opening. Thiafullerene **8** is the first example of a heterofullerene with an open-cage $C_{69}S$ structure. It is worth noting that due to the similar molecular structure of **4** and **8**, the resulting packing structures are also quite similar. In order to examine the effects of sulfur doping and decarbonylation on the redox behavior, **4** and **8** were examined by cyclic votammetry (CV) and differential pulse voltammetry (DPV). The cyclic voltammogram of open-cage C_{70} diketone **4** exhibited a pseudoreversible first reduction wave and several other reduction waves at more negative potentials (Figure 3a),
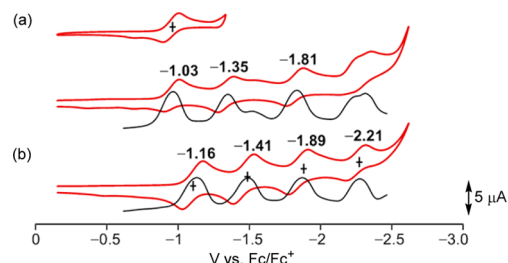
Figure 3. Cyclic (red) and differential pulse (black) voltammograms of **4** (a) and **8** (b). Conditions: 1 mM sample with 0.1 M *n*-Bu$_4$NBF$_4$ in ODCB at a scan rate of 20 mV s^{-1}.

indicating electrochemical instability of the anionic species of **4**. The observed instability stems most likely from the two adjacent carbonyl groups on the rim of the opening, which should be susceptible to pinacol coupling under the conditions applied. However, for open-cage $C_{69}S$ thiafullerene **8**, four pseudoreversible reduction waves were observed (Figure 3b), demonstrating significantly higher stability toward electrochemical reduction compared to **4**. The individual redox potentials of **4** were determined by DPV at −1.03, −1.35, and −1.81 V (vs the Fc/Fc$^+$ couple). Under the same conditions, **8** displayed more negative redox potentials at −1.16, −1.41, −1.89, and −2.21 V, respectively. The difference in redox potentials of **8** compared to **4** can be explained by the electropositive nature of the sulfur atom and the loss of one of the electronegative carbonyl groups. DFT calculations at the B3LYP/6-31G* level of theory are in close agreement with the observed trend: the calculated LUMO level of **8** (−3.05 eV) is significantly higher than that of **4** (−3.23 eV). Within the electrochemical window of ODCB, no oxidation peak was observed for **8**, even though the HOMO level of **8** (−5.54 eV) was calculated to be higher than that of **4** (−5.69 eV). The similar absorption bands of **8** and **4** observed in the UV−vis

spectra suggest the absence of significant differences with respect to the HOMO−LUMO gap.

In conclusion, we synthesized a series of open-cage C_{70} fullerene derivatives. The opening in **7** was expanded by a dehydration reaction to give tetraketone **6**. The reaction of **6** with elemental sulfur in the presence of TDAE afforded open-cage $C_{69}S$ thiafullerene **8**, which is evidence for a remarkably different chemical reactivity of the C_{70} tetraketone **6** relative to its C_{60} analogue **2**. The molecular structure of **8**, which is the first example of a thiafullerene derived in a controlled fashion from a higher C_{70} fullerene, was determined by single crystal XRD analysis. The electronic properties of **8**, which is less electronegative than **4**, supported the notion that the LUMO of fullerene derivatives can be tuned by embedding a heteroatom such as sulfur. The exploration of the electronic properties of thiafullerene **8** is expected to provide a very interesting study area for the future, as intermolecular interactions are most likely increased in the solid state due to the larger van der Waals radius of sulfur relative to carbon. Research on the development of further molecular transformations as well as investigations into the solid-state properties of the discussed compounds are currently in progress in our laboratory.

■ ASSOCIATED CONTENT

Ⓢ Supporting Information

Experimental details and crystallographic data; full ref 30. 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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