Synthesis of Open-Cage Fullerene Derivatives and Encapsulation of Small Molecules

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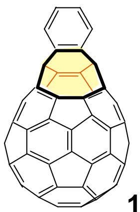
Preparation of open-cage fullerenes is of great importance in a challenging task aiming at the organic synthesis of endohedral fullerene complexes.

Previously, we found that a thermal reaction of C_{60} with various nitrogen-containing aromatic compounds can lead to the formation of open-cage fullerene derivatives having an 8-membered-ring orifice such as **1**,[1] **2**,[2] and **3**.[3] The size of the orifice can be further enlarged to a 12-membered ring by aerobic oxidative cleavage of a double bond at the rim of the orifice under photochemical conditions, thus giving **4**,[4] **5**,[2] and **6**.[3]

Then, we found that elemental sulfur can be inserted into the rim of the orifice of comound **6** quite effectively by heating **6** in the presence of an electron acceptor such as tetrakis(dimethylamino)ethylene. Thus a novel open-cage fullerene derivative **7** with a 13-membered-ring orifice was obtained in 77% yield.[3] The structures of **3** and **7** were unambiguously determined by X-ray crystallography.

Theoretical calculations indicated that the energy barrier for insertion of small molecules such as neon and hydrogen should be rather low, i.e. 26.2 and 30.1 kcal/mol respectively. Actually, a remarkably large amount of hydrogen was found to be encapsulated in the derivative **7** under high pressure (800 atm) and high temperature (200 °C) conditions. The ^{1}H NMR chemical shift of the encapsulated hydrogen was observed at such a high field as –7.25 ppm due to strong shielding effects of the fullerene cage.

The detailed properties of H_2@**7** will be reported together with the results on the encapsulation of smaller molecules such as rare-gases.



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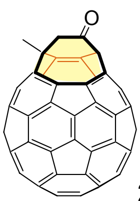

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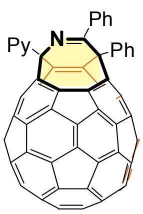

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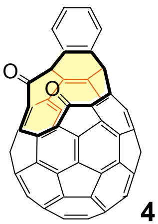

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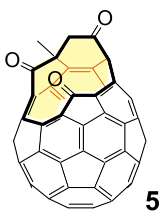

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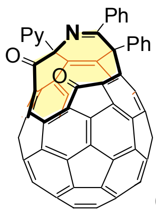

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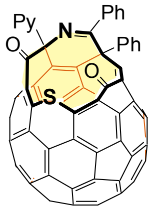

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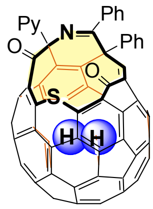
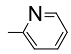


H_2@**7**

(Py = )

References:

1. Murata, Y.; Kato, N.; Komatsu, K. *J. Org. Chem.*, **2001**, *66*, 7235.
2. Murata, Y.; Murata, M.; Komatsu, K. *J. Org. Chem.*, **2001**, *66*, 8187.
3. Murata, Y.; Murata, M.; Komatsu, K. *Chem., Eur. J.*, **2003**, *9*, in press.
4. Murata, Y.; Komatsu, K. *Chem. Lett.*, **2001**, 896.