Division of Synthetic Chemistry
- Structural Organic Chemistry -

http://www.scl.kyoto-u.ac.jp/~kouzou/K_eHP_F/main.html

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Dr MARGETIC, Davor Rudjer Boskovic Institute, Croatia, 9 November 2009

Scope of Research

Fundamental studies are being conducted for creation of new functional π-systems with novel structures and properties. The major subjects are: organo-chemical transformation of fullerenes C_{60} and C_{70}, specifically organic synthesis of endohedral fullerenes by the technique of molecular surgery; generation of ionic fullerene species and their application for the synthesis of functional material; synthesis of new π-systems with curved structure by the use of transition metal complex.

Research Activities (Year 2009)

Publications

Horsewill AJ, Panesar KS, Rols S, Johnson MR, Murata Y, Komatsu K, Mamone S, Danquigny A, Cuda F, Maltsev S, Grossel MC, Carravetta M, Levitt MH: Quantum Translator-Rotator: Inelastic Neutron Scattering of Dihydrogen Molecules Trapped inside Anisotropic Fullerene Cages, *Phys. Rev. Lett.*, **102**, 013001 (4 pages) (2009).

Kohama Y, Rachi T, Jing J, Li Z, Tang J, Kumashiro R, Izumisawa S, Kawaji H, Atake T, Sawa H, Murata Y, Komatsu K, Tanigaki K: Rotational Sublevels of an Ortho-Hydrogen Molecule Encapsulated in an Isotropic C_{60} Cage, *Phys. Rev. Lett.*, **103**, 073001 (4 pages) (2009).

Presentations

Synthesis and Properties of Novel Open-Cage Fullerenes and Endohedral Fullerenes, Murata Y, Murata M, Kurotobi K, Kato K, Morinaka Y, Komatsu K, 13th International Symposium on Novel Aromatic Compounds, 20 July 2009, Luxembourg City, Luxembourg.

Synthesis and Reaction of Fullerene C_{70} Encapsulating Two Molecules of H_2, Murata M, Maeda S, Morinaka Y, Murata Y, Komatsu K, 13th International Symposium on Novel Aromatic Compounds, 20 July 2009, Luxembourg City, Luxembourg.

Synthesis and Properties of Novel Open-Cage C_{60} Derivatives, Kurotobi K, Murata M, Murata Y, The 11th International Kyoto Conference on New Aspects of Organic Chemistry, 12 November 2009, Kyoto, Japan.

Synthesis and Reaction of Fullerene C_{70} Encapsulating Two Molecules of H_2, Murata M, Maeda S, Morinaka Y, Murata Y, Komatsu K, The 11th International Kyoto Conference on New Aspects of Organic Chemistry, 12 November 2009, Kyoto, Japan.

Grants

Murata Y, Synthesis of Novel Endohedral Fullerenes by Molecular Surgery Approach and Development of Their Function, PRESTO, Japan Science and Technology Agency, October 2005–March 2009.

Murata M, Synthesis and Properties of Carbon π-Systems with Curved Structures, Grant-in-Aid for Young Scientists (B), April 2007–March 2009.

Murata Y, Synthesis and Properties of Bowl-shaped π-Systems by Top-down Approach, Grant-in-Aid for Young Scientists (A), April 2008–March 2011.

Murata Y, Creation and Function of Spherical π-Space

Oxidation of the Open-Cage C_{60} Derivative

Open-cage fullerene derivatives have drawn significant attention for the molecular surgical approach toward organic synthesis of endohedral fullerenes. Since the size of an opening is crucial for insertion of a small molecule inside the fullerene cage, chemical modification to make an opening larger and smaller is important. Previously, we reported chemical reaction on the rim of the opening for an open-cage C_{60}. However, we found that different reactions take place on its structural isomer **1** under the similar reaction conditions. Oxidation of **1** with one equiv of *m*-CPBA in CS_2 afforded open-cage C_{60} **2** with a transannular bridge at the rim of the 13-membered ring opening. This compound is formed via oxidation of a sulfide group followed by addition of a water molecule to the carbonyl group on the five-membered ring on **1**. When a larger amount of *m*-CPBA (5 equiv) was used in *o*-dichlorobenzene instead of CS_2, another reaction took place to give open-cage C_{60} **3** having a 14-membered ring opening with a lactone moiety. The size of opening was large enough for a neon atom to be inserted into the fullerene cage under high-pressure conditions.

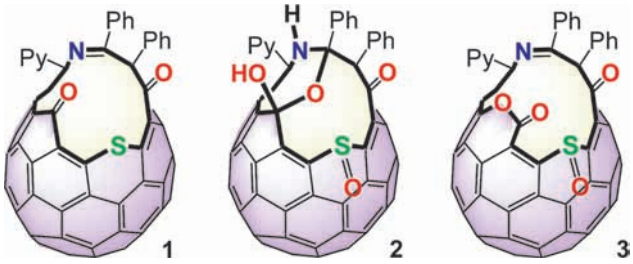

Figure 1. Structure of open-cage C_{60} derivatives. .

Expansion of 3D π-System with 2D π-System

It is very interesting to construct an extended π-system because unique photophysical and electrochemical properties are expected owing to the small HOMO-LUMO gap of the system. We recently synthesized open-cage C_{60} derivative **1** by way of functionalization of the rim of an opening. UV-vis spectrum of **1** showed maximum absorptions at 330 (sh), 400 (sh), 450 (sh) and 730 nm extended to ca. 900 nm which is not seen for many examples of fullerene derivatives. When the redox properties were investigated by cyclic voltammetry in benzonitrile, the first reduction wave was observed in less negative potential by 0.3 V from that of pristine C_{60}, indicating the lower-lying LUMO level. Furthermore, an irreversible oxidation wave was detected at 1.0 V, which was less positive than that of C_{60}. These properties are ascribed to expansion of 3D π-system of the C_{60} moiety (colored in blue) with 2D π-system of the terphenyl moiety (colored in red) by sharing a part of π-system of the naphthalene moiety (highlighted in yellow).

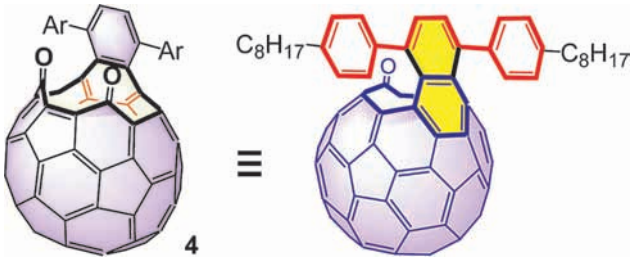

Figure 2. Open-cage C_{60} derivative with expanded π-system.

Theoretical Investigation into Interaction of C_{70} with Encapsulated H_2 Molecules

Is the reactivity of spherical π-system affected from inside? We have found that the equilibrium constant for Diels-Alder reaction of 9,10-dimethylanthracene with $(H_2)_2@C_{70}$ is slightly smaller by 19% at 30 °C than that with $H_2@C_{70}$, studied by ^{1}H NMR analysis in *o*-dichlorobenzene-d_4. In order to get insights into the interaction of C_{70} cage with encapsulated H_2 molecules, DFT calculations by MPWB1K/6-31G** were performed. When attention was paid to the optimized structures of C_{70}, $H_2@C_{70}$, and $(H_2)_2@C_{70}$, the difference in size was observed. The longer axis of $(H_2)_2@C_{70}$ is larger by 0.25%, whereas the shorter axis of $(H_2)_2@C_{70}$ is smaller by 0.30%, than that of $H_2@C_{70}$, respectively. Furthermore, small difference in the encapsulation energies of one and two H_2 molecules into C_{70} as well as H_2C_{70}, as a model compound for the Diels-Alder adduct, were observed, which might account the experimental results.

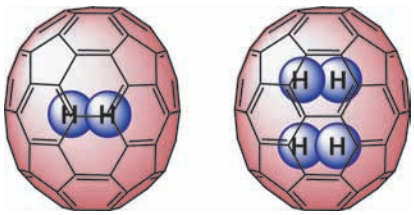

Figure 3. Endohedral C_{70} encapsulating H_2 molecules.

Encapsulating an Active Small Molecule, Grant-in-Aid for Scientific Research on Innovative Areas "π-Space", December 2009-March 2014.

Award

Morinaka Y, The Best Poster Award, The 20th Symposium on Fundamental Organic Chemistry, 30 September 2009.