Division of Synthetic Chemistry
- Structural Organic Chemistry -

http://hydrogen.kuicr.kyoto-u.ac.jp/K_eHP_F/main.html

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Mr JOHNSON, Jeremiah Columbia University, USA, 6 June–22 July 2008

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.

Research Activities (Year 2008)

Publications

Murata M, Ochi Y, Tanabe F, Komatsu K, Murata Y: Internal Magnetic Fields of Dianions of Fullerene C_{60} and Its Cage-Opened Derivatives Studied by Encapsulated H_2 as an NMR Probe, *Angew. Chem. Int. Ed.*, **47**, 2039-2041 (2008).

Murata Y, Maeda S, Murata M, Komatsu K: Encapsulation and Dynamic Behavior of Two H_2 Molecules in an Open-Cage C_{70}, *J. Am. Chem. Soc.*, **130**, 6702-6703 (2008).

Murata M, Maeda S, Morinaka Y, Murata Y, Komatsu K: Synthesis and Reaction of Fullerene C_{70} Encapsulating Two Molecules of H_2, *J. Am. Chem. Soc.*, **130**, 15800-15801 (2008).

Presentations

Synthesis of Endohedral Open-Cage Fullerenes and Studies on Non-Covalent Interaction between Encapsulated Species and Fullerene Cage, Murata Y, Cuang S-C, Murata M, Komatsu K, 213th ECS Meeting, 19 May 2008, Phoenix, USA (invited).

Organic Synthesis of Endohedral Fullerenes, Murata Y, Symposium on H_2@C_{60}, 15 August 2008, New York, USA (invited).

Synthesis and Properties of Novel Open-Cage Fullerene Derivatives, Kurotobi K, Murata M, Murata Y, PRiME 2008, 12 October 2008, Honolulu, USA.

Generation of Ionic [60] Fullerene Derivatives Encapsulating Molecular Hydrogen, Murata M, Ochi Y, Tanabe F, Murata Y, Komatsu K, PRiME 2008, 13 October 2008, Honolulu, USA.

Grants

Murata Y, PRESTO, Japan Science and Technology Agency, October 2005–March 2009.

Murata Y, Grant-in-Aid for Scientific Research on Priority Areas, "Molecular Theory for Real Systems", April 2007–March 2009.

Murata M, Grant-in-Aid for Young Scientists (B), April 2007–March 2009.

Murata Y, Grant-in-Aid for Young Scientists (A), April 2008–March 2011.

Murata Y, Grant-in-Aid for Scientific Research on Innovative Areas, December 2009–March 2014.

Encapsulated H_2 Molecule as an NMR Probe

Magnetic properties of inside of fullerenes are very interesting because ring current effects of three-dimensional π-system of fullerenes are reflected critically. We measured ^{1}H NMR chemical shifts of molecular hydrogen encapsulated in dichloromethyl-C_{60} cation and (1-octynyl)-C_{60} anion in order to clarify the difference in magnetic shielding effects inside the fullerene cages. The signals of the H_2 molecule inside both cationic and anionic C_{60} cages appeared in lower fields as compared to those of neutral counterparts. In contrast, upon ^{1}H NMR measurement of $H_2@C_{60}^{2-}$, a signal of the encapsulated H_2 appeared at extraordinarily low magnetic field such as δ = +26.36 ppm in acetonitrile-d_3. According to the results of NICS calculations for $H_2@C_{60}^{2-}$, magnetic properties of hexagons and pentagons on C_{60} were shown to be totally reversed as compared to those of neutral C_{60}.

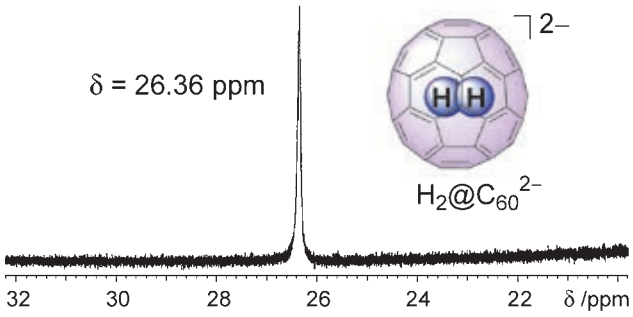

Figure 1. ^{1}H NMR spectrum (300 MHz, CD_3CN) of $H_2@C_{60}^{2-}$.

Encapsulation and Dynamic Behavior of Two H_2 Molecules in an Open-Cage C_{70}

Encapsulation of small molecules in a small space with sub-nanometer size are currently attracting wide interests from the view point of basic science as well as storage purpose. Open-cage fullerenes are one of the ideal systems with a hollow space inside the carbon cage. In contrast with open-cage C_{60}, examples of open-cage C_{70} are quite limited. Recently, we synthesized an open-cage C_{70} derivative, which has an opening large enough for hydrogen molecule to pass through. Under the high pressure of hydrogen, this open-cage C_{70} encapsulated not only one H_2 molecule but also two H_2 molecules reflecting the larger inner space than C_{60}. The two H_2 molecules trapped inside the open-cage C_{70} showed a rapid exchange of their relative positions as observed by the ^{1}H NMR measurement at room temperature. This exchange slowed down at low temperature. The ^{1}H NMR at –100 °C clearly showed two sharp signals corresponding to two individual H_2 molecules encapsulated in the open-cage C_{70}. This is the first example of observing the dynamic behavior of two hydrogen molecules in a tightly confined space.

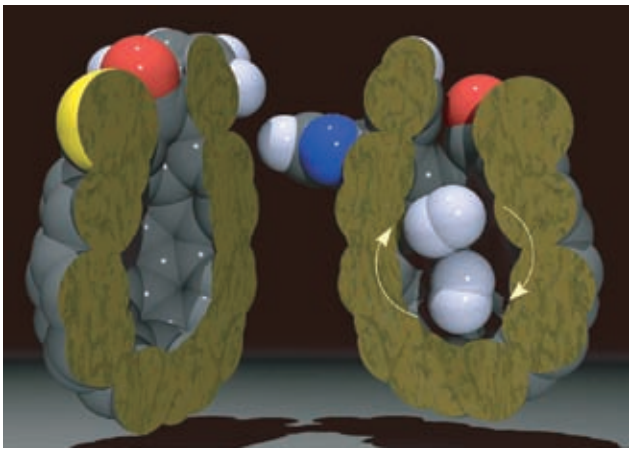

Figure 2. Cut-out view of open-cage C_{70} derivative encapsulating two molecules of hydrogen.

Synthesis and Reaction of $H_2@C_{70}$ and $(H_2)_2@C_{70}$

We have previously established a methodology to realize endohedral fullerene C_{60} containing one molecule of H_2 by organic synthesis, so-called "molecular surgery". In the present research, the scope of the molecular surgery method is extended to the representative higher fullerene, C_{70}, to provide a novel endohedral fullerene C_{70} encapsulating one and two molecules of H_2 from their open-cage derivatives. Actually, $H_2@C_{70}$ and $(H_2)_2@C_{70}$ were synthesized and characterized. For the clarification of difference in reactivity between $H_2@C_{70}$ and $(H_2)_2@C_{70}$, the equilibrium constants for the Diels-Alder reaction of $H_2@C_{70}$ and $(H_2)_2@C_{70}$ with 9,10-dimethylanthracene (DMA) have been determined at 30, 40, and 50 °C. The decreased equilibrium constants of $(H_2)_2@C_{70}$ to the addition of DMA as compared to that of $H_2@C_{70}$ has been demonstrated.

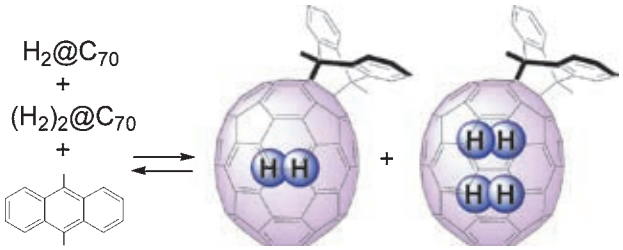

Figure 3. Reaction of $H_2@C_{70}$ and $(H_2)_2@C_{70}$ with 9,10-Dimethylanthracene.