

Molecule Within a Molecule

May 12 2006

All children are fascinated by Russian dolls: when the largest outer wooden figure is opened, a second, smaller, nearly identical doll appears. This one can also be opened and so on.... This toy could well have inspired T. Shinmyozu, H. Takemura, M. Yasutake, and K. Sato in Japan to synthesize their cyclophane within a cyclophane.

Cyclophanes are nonplanar polycyclic aromatic compounds, benzene rings in which two opposite carbon atoms are linked by a handle-like bridge. The simplest example would be a benzene ring “basket” with an alkane “handle”. Of course, this cannot be used to make tubes, so the Japanese scientists synthesized larger rings made of several building blocks whose opening is large enough to enclose larger molecules.

They thus allowed pyromellitic dianhydride (benzene-1,2,4,5-tetracarboxylic acid dianhydride) to react with 1,4-bis(aminomethyl)-2,5-dimethoxybenzene. The acid anhydrides combine with the amino groups to form acid imides, which results in rigid rings made of six building blocks with alternating acid imide and dimethoxybenzene units.

X-ray structure analyses show that these rings are not perfectly round but are shaped more like a triangle. At its widest point, the diameter of the ring is 1.2 to 1.3 nm. That is large enough to take up two molecules of the solvent p-xylene. In doing this, two of the cyclophane rings stack on top of each other to form longer smooth tubes. If the solvent for the crystallization was switched to toluene instead of p-xylene, the rings could enclose three solvent molecules. However, in this case the tubes

were no longer smooth but had a zig-zag structure instead.

The researchers were interested in trying to incorporate larger molecules, such as a smaller cyclophane made of three benzene rings each bound to the others by a C₂H₄ bridge. This little cyclophane also has a triangular structure and is able to lodge in the larger cyclophane like a “doll within a doll”. These structures also organized themselves into longer, smooth tubes.

Citation: Teruo Shinmyozu, Cyclophanes Within Cyclophanes: The Synthesis of a Pyromellitic Diimide-Based Macrocyclic Unit in a Molecular Tube and Its Inclusion Phenomena, *Angewandte Chemie International Edition* 2006, 45, No. 22, 3643–3647, doi: 10.1002/anie.200504499

Source: Angewandte Chemie

Citation: Molecule Within a Molecule (2006, May 12) retrieved 24 April 2024 from <https://phys.org/news/2006-05-molecule.html>

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