Institut Européen de Chimie et Biologie

I E C B

Molecular encapsulation of dynamic systems inside the crystalline cages.

Mihail BARBOIU

Adaptive Supramolecular Nanosystems Group, Institut Européen des Membranes, ENSCM-UMII-CNRS 5635, Montpellier, FRANCE.

Guest molecules confined inside hollow confined space show unexpected structural behaviors compared to unprotected environment.

Various water clusters may be confined within complex artificial porous architectures. They have attracted a lot interest in a variety of fundamental processes such us the water cluster self-assembly, specific interactions with the host porous matrix or dynamic diffusional phenomena under confined conditions. Amazingly, there has been less progress in the area of synthetic water channels. Whatever the objective, the main point is the water-conduction function – the ability of the system to selectively mediate the translocation of water through a barrier hydrophobic membrane.

On the other hand, Cyclobutadiene (CBD), the smallest cyclic hydrocarbon bearing double bonds, has long intrigued chemists, but the parent compound and intermediates have eluded crystallographic characterization. The CBD precursor, 4,6-dimethyl-α-pyrone has been captured in a crystalline network. UV irradiation of the crystals transforms the 4,6-dimethyl-α-pyrone into a 4,6-dimethyl-β-lactone Dewar and 1,3-dimethylcyclobutadiene Me_2CBD.

Another case is related to the coiling behavior of alkane chains in rigid molecular cages. It has been found that coiling may occur and a large number of possible conformers have been theoretically and spectroscopically described. No direct evidence concerning the exact conformation of the chains has been presented. We present here the compression mechanisms of linear of 1,ω-diammonium-alkanes, confined with different degrees of compression, within a molecular cage. The exact coiling behavior is determined from atomic resolution X-ray diffraction and shows crenel-like conformations in the compressed states which are possibly assisted by slight attractive dihydrogen contacts. These findings may provide insight in areas ranging from nanomechanics to biological pathways.

References

1) Y.M. Legrand, A. van der Lee, M. Barboiu, Single-crystal X-ray structure of 1,3-dimethylcyclobutadiene by confinement in a crystalline matrix, *Science*, **2010**, 329, 299-302.
2) Y.M. Legrand, A. Gilles, E. Petit, A. van der Lee, M. Barboiu, Unprecedented synthesis of 1,3-dimethyl-cyclobutadiene in solid state and aqueous solution, *Chem. Eur J.* **2011**, 17, 10021-10028.
3) Y. Le Duc, M. Michau, A. Gilles, V. Gence, Y.-M. Legrand, A. van der Lee, S. Tingry, M. Barboiu, *Imidazole-quartet water and proton dipolar channels*. Angew. Chem. Int. Ed. **2011**, 50, 11366-11372.
4) M. Barboiu & A. Gilles, *From natural to bio-assisted and biomimetic artificial water channel systems*. Acc. Chem. Res. **2013**, 46 (12), pp 2814–2823
5) D. Dumitrescu, Y.-M. Legrand, E.Petit, A. van der Lee and M. Barboiu Progressive compression of 1,ω-diammonium-alkanes inside a rigid crystalline molecular cage, *Chem. Commun.*, **2014,** *50*, 14086-14088.

Institut Européen de Chimie et Biologie
2, rue Robert Escarpit - 33607 Pessac, France
Tél. : +33(0)5 40 00 30 38 - Fax. : +33(0)5 40 00 22 15
www.iecb.u-bordeaux.fr