



Contribution ID: 106

Type: E-Poster

## X-ray Structure Investigation of Confused-Prism[5]arene: a Conformationally Adaptive Host with Stereoselective Opening of its 1,4-bridged Naphthalene Flap

X-ray Structure Investigation of Confused-Prism[5]arene: a Conformationally Adaptive Host with Stereoselective Opening of its 1,4-bridged Naphthalene Flap

Neal Hickey<sup>a</sup>, Paolo Della Sala<sup>b</sup>, Rocco Del Regno<sup>b</sup>, Placido Neri<sup>b</sup>, Carmine Gaeta<sup>b</sup> and Silvano Geremia<sup>a</sup>

<sup>a</sup> Centro di Eccellenza in Biocristallografia, Dipartimento di Scienze Chimiche e Farmaceutiche, Università di Trieste, Trieste, Italy. Presenting author, e-mail: nhickey@units.it

<sup>b</sup> Laboratory of Supramolecular Chemistry, Department of Chemistry and Biology "A. Zambelli", University of Salerno, Fisciano, I-84084, Italy.

We have recently reported a new class of macrocycle, denoted prism[*n*]arenes, composed of *n* (*n*=5,6) methylene-bridged naphthalene units, each with two identical alkoxy substituents (R = Me, Et, Pr) at the 2, 6 positions [1,2]. The new molecules possess chiral planes and show high structural flexibility as well as a strong tendency to encapsulate ammonium cations. Symmetric prism[*n*]arenes are characterised by all the methylene bridges at the 1, 5 positions of the naphthalene units. However, a variation of this bridging pattern was obtained for a 1,4-confused-prism[5]arene (c-PrS[5]Me), for which 1/5 of the naphthalene rings is bridged at the 1,4-positions. In this case, the asymmetric macrocycle is self-filled by the confused naphthalene moiety and its two C-C bridging single bonds are aligned so that the naphthalene can rotate more freely than its PrS[5]Me analogue.

Here we show that c-PrS[5]Me shows adaptive conformational behaviour. The X-ray structures of host-guest complexes of c-PrS[5]Me with 1,4-dihexyl-DABCO and with *n*-butylammonium were obtained using synchrotron radiation. A stereoselective opening of the 1,4-bridged naphthalene flap toward the homochiral conformation of the host, inverting its planar chirality, occurs during the complexation. X-ray studies, supported by NMR spectra and DFT calculations, show that the homochiral complexes are stabilized by C-H... $\pi$  interactions. Furthermore, the *n*-butylammonium directional axle produces up/down directional isomers. Therefore, symmetry breaking introduced by the 1,4 link in c-PrS[5]Me creates a new scenario in terms of the stereochemistry of these systems, characterized by an adaptive macrocycle which can open the 1,4-bridged naphthalene flap in a stereoselective and directional manner.

Figure 1: Stereoselective insertion of ammonium guests in c-PrS[5]Me

[1] P. Della Sala, R. Del Regno, C. Talotta, A. Capobianco, N. Hickey, S. Geremia, M. De Rosa, A. Spinella, A. Soriente, P. Neri, C. Gaeta, Prismarenes: A New Class of Macrocyclic Hosts Obtained by Templatation in a Thermodynamically Controlled Synthesis, *J. Am. Chem. Soc.* 2020, 142, 4, 1752–1756

[2] P. Della Sala, R. Del Regno, L. Di Marino, C. Calabrese, C. Palo, C. Talotta, S. Geremia, N. Hickey, A. Capobianco, P. Neri, C. Gaeta, An intramolecularly self-templated synthesis of macrocycles: self-filling effects on the formation of prismarenes, *Chem. Sci.* 2021, 12, 9952–9961

**Primary author:** HICKEY, Neal (University of Trieste)

**Co-authors:** DELLA SALA, Paolo; DEL REGNO, Rocco; NERI, Placido; GAETA, Carmine; GEREMIA, Silvano (University of Trieste)

**Presenter:** HICKEY, Neal (University of Trieste)

**Session Classification:** E-Poster Session

**Track Classification:** Investigating Molecular Crystals: Methods and Applications