Association- and recognition-driven synthesis of new chiral cavitands and molecular capsules as well as investigation of their structures

Michał Wierzbicki, M.Sc., Eng.

supervisor: Assoc. Prof. Agnieszka Szumna

For many years supramolecular chemists have been trying to obtain chemical compounds in the forms of molecular capsules and cavitands. Such capsules may be capable to complex small molecules, which leads to their separation from the outside environment. This allows for their application as sensors, for storage of reactive molecules and even as nanoreactors.

The present dissertation concerns research on the synthesis of novel chiral molecular capsules and cavitands. Throughout the presented work I have used resorcin[4]arene as a fundamental building block, due to its rigid structure and ease of modification. Based on the accomplishments of the research group IX at the Institute of Organic Chemistry PAS, I have conducted the synthesis of novel molecular capsules through the Mannich reaction. I have obtained both homochiral and hybrid heterochiral capsules (the latter in partially reversible processes). I have carefully analyzed the course of the reaction and explained the reasons for the formation of particular products. The obstacles encountered during the determination of solid-state structures have caused me to turn to the methods of protein crystallography, especially the Molecular Replacement (MR) algorithms. Employment of the PHASER computer program has allowed to solve the structure of one of the capsules, which was impossible to solve using traditional methods. I have then explored the capabilities of the program regarding the size of the model required for obtaining a successful solution.

In order to use reversible reactions in the synthesis of capsules I have performed the synthesis of a previously not known building block – tetrafotmylresorcin[4]arene. Subsequently in the reactions between this new compound and primary amines I have obtained a set of inherently chiral cavitands capable of effective self-sorting. I have observed asymmetric induction in case of chiral amines. Tetraformylresorcin[4]aren has served as a scaffold for novel chiral molecular capsules synthesized in our research group. I have determined solid-state structures for three of them with help of the MR methods.

In reactions between tetraformylresorcin[4]arene and amino acid hydrazides I have obtained four new molecular capsules. I have found that they are formed in dynamic processes and I have proven that they are capable of chiral self-sorting. I have performed complexation of fullerenes inside the capsules through chemical and mechanochemical methods. I have determined the structures of two of the capsules as well as C_{60} and C_{70} complexes in the solid state using synchrotron radiation sources and Molecular Replacement methods.