

Public Abstract

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Title:A TWO-FOLD APPROACH TOWARDS UNDERSTANDING PROPERTIES OF TWO SELF-ASSEMBLED MACROCYCLES: RESORCIN[4]ARENE AND PYROGALLOL[4]ARENE

Self-assembled macrocycles, molecular entities that are connected together spontaneously in a cyclic manner, are studied herein. Pyrogallol[4]arene (PgC) and resorcin[4]arene (RsC), self-assembled macrocycles made from four units of pyrogallol and four units of resorcinol, respectively, are the main focus of this work.

The first two topics discussed are metal-coordination of PgC and RsC. PgC forms both dimeric and hexameric metal-organic nanocapsules (MONCs); however, these types of architectures have not yet been observed for RsC. In our attempt to create analogous MONCs involving RsC, manganese and cobalt complexes were encapsulated inside a hydrogen-bonded dimeric capsule of RsC. The investigation into metal-coordinated PgC MONCs led to additional metal-coordination on the exterior of the MONCs, thus creating metal-organic frameworks using MONCs. Both of these systems have potential in the applications of molecular magnetism, gas sorption/separation, and encapsulation of other molecules.

PgC and RsC also may be used to encapsulate pharmaceuticals, e.g. Humalog and gabapentin. In this work, cocrystallization of RsC with pregabalin, a pharmaceutical similar to gabapentin in both structure (GABA functional group) and usage, was attempted. Unexpectedly, pregabalin underwent a cyclization to 4-isobutylpyrrolidone-2, a compound known in polymer synthesis. Both pregabalin and 4-isobutylpyrrolidone-2 are linked to important industrial applications.

The final chapter discusses the study of the various stereoisomers of RsCs by means of electronic structure calculations, in both the gas and solution phase. Stereoisomers are structures of a molecule for which the atoms are orientated differently in space but the molecule retains its identity. It was found from these calculations that the cone conformer, where the hydroxyl-substituted side (top) of all four resorcinol subunits point up, is most stable when the tail group of the macrocycle is a hydrogen. The chair stereoisomer, where top of one subunit points up, the top of the opposite subunit points down, and tops of the remaining two subunits lie in the plane, is most stable when the tail group of the macrocycle is a phenyl.

These studies are of importance to the synthetic work on this macrocycle, which affects all further studies on the macrocycle.