

## Theoretical Study Of A Switchable [2]-Rotaxane

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In recent years, pioneering work carried out by Sauvage, Stoddart and co-workers<sup>[1], [2]</sup>, has focused on the development of synthetic methodologies and the characterization of catenanes and rotaxanes.

Catenanes and rotaxanes are examples of interlocked molecule. Unlike classical molecular structures, they consist of two or more separate components which are mechanically connected. Catenanes consist of two or more interlocked macrocyclic rings, while rotaxanes are constituted by a macrocyclic ring trapped on a linear unit, i.e., the thread, by two bulky stoppers

The submolecular units may undergo relative motions such as “circumrotation” (rotation of one ring inside the cavity of the other) and “shuttling” (linear motion along the thread), which may be addressed by external stimuli, such as photons, electrons and solvent variations. This property makes rotaxanes and catenanes prime candidates for the construction of artificial molecular-level machines and possibly for the fabrication of molecular electronic devices<sup>[3]</sup>, attracting considerable attention from chemists, physicists, and materials scientists. Controlling the location of a macrocycle between two or more (non-) equivalent sites in a catenane or a rotaxane has already been achieved<sup>[4]</sup>.

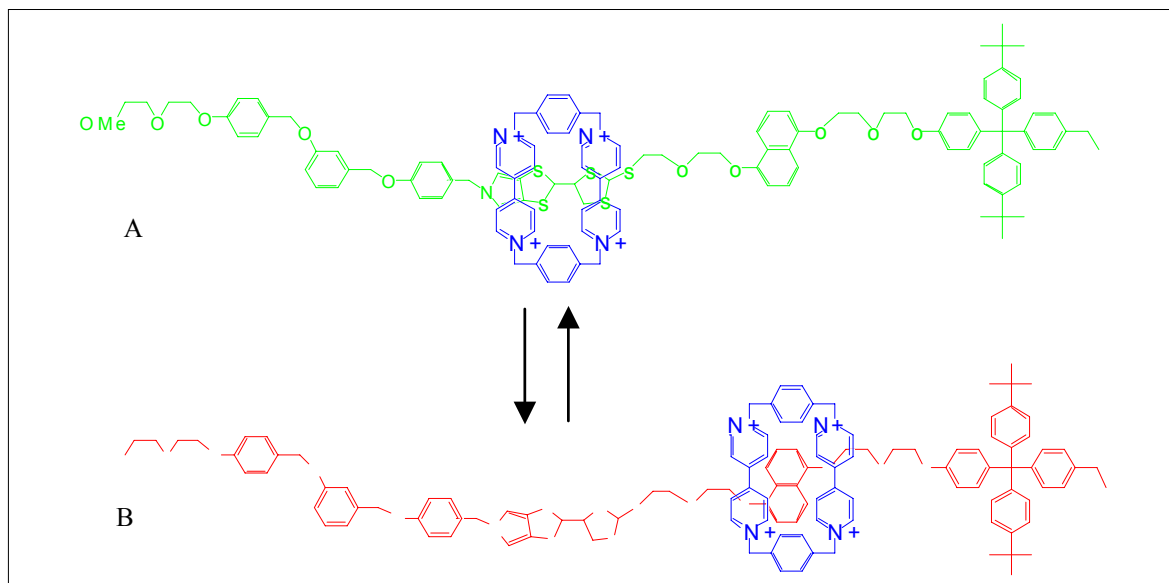
Unfortunately, little is yet known about the mechanisms by which mechanically interlocked components move with respect to each other.

Here we present a study where experimentally determined energy barriers, in the switching of a positive charged macrocycle between two electron-donor sites of a [2] rotaxane,<sup>[5]</sup> (see Figure 1) are accurately simulated by theoretical modelling studies.

The size of the complexes does not allow modelling with advanced *ab-initio* quantum mechanical methods. Thus, molecular dynamic simulations can be used as an alternative approach for the investigation.

A computational procedure has been applied to identify the energetically preferred conformations of the bistable [2]-rotaxane. Parametrization of an empirical force field was carried out in order to model rotaxane structure. Potential energy pathway describing the slippage mechanism was calculated both in the gas and in the solvent phase.

Solving the problem of choosing the adequate potential energy formalism to model this class of molecular systems, should allow future computational studies as a complement to the synthesis of new supramolecular systems.



**Figure 1.** Switchable [2]rotaxane structure, in the two isomeric form, A (**A-GREEN**) with the cyclophane interacting with the TTF unit, and B (**B-RED**) with the cyclophane interacting with the DNP unit.

### References:

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