

Acid/Base Control of the Amplitude of Shuttling Motions in Amide-Type [2]Rotaxanes?

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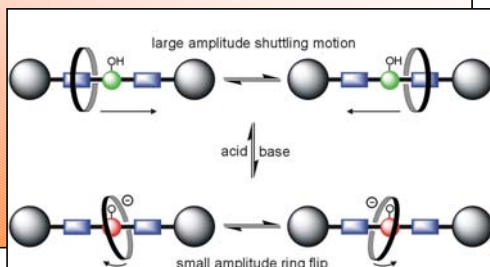
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I. Introduction:

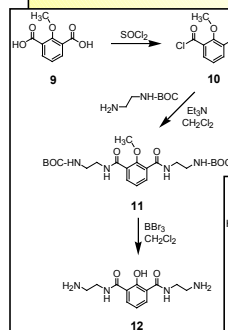
Rotaxanes are under intense research in supramolecular chemistry. They are not only interesting with respect to their topological properties, but also deliver insight into complex binding behavior such as self-assembly or template effects.

Due to their mechanical bond, they are especially suited for implementing molecular switches and shuttles. The motion of the wheel along the axle can often be controlled by external stimuli such as pH, light, or electrons.

We present the synthesis of new axle-functionalized amide rotaxanes which are intended to form the basis of acid/base-controlled molecular shuttles. One example is schematically shown in the Figure. The OH group incorporated in the axle may have a significant influence on the shuttling behavior of the rotaxane permitting to control the dynamics of the molecular motion of the wheel along the axle.

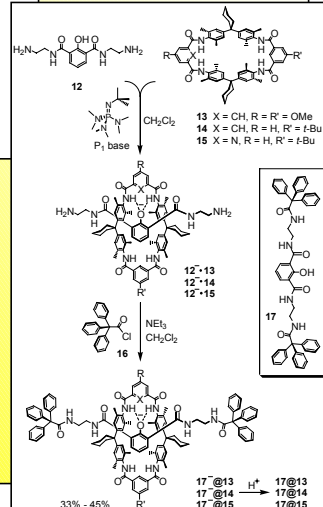


II. Rotaxane synthesis:



The amide-type [2]rotaxanes have been synthesized with a recently developed anionic template effect. A phenolic OH group mediates the template effect through strong hydrogen bonding with the wheel.

The same OH group will serve for controlling the properties of the final rotaxane.

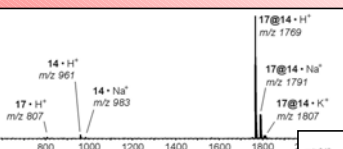


The deprotected center piece was deprotonated with Schwesinger's P₁ base. The base forms a large lipophilic counter ion and increases the solubility of the axle center piece even in solvents such as dichloromethane.

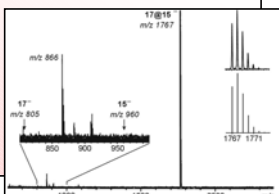
The center piece is bound within the macrocycle through a bifurcated hydrogen bond. The rotaxane is formed in 33 - 45% yield by addition of the acid chlorides of the stopper groups.

III. Evidence of rotaxane formation

a) Mass Spectrometry



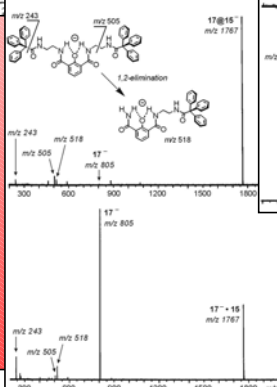
In the positive-mode MALDI mass spectrum (left figure) of 17@14, all characteristic signals for the rotaxane are observed. A control experiment with a mixture of 17 and 14 under the same ionization conditions did not yield intense signals at the rotaxane mass.



Also, conclusive results come from negative ion MS/MS spectra (right figure). The collision-induced dissociation (CID) of 17@15 shows that the axle decomposes thereby releasing the wheel as a neutral fragment.

Several fragments of the axle are observed, which correspond to covalent bond cleavages and 1,2-elimination reactions as indicated in the figure.

A mixture of 17 and 15 leads to the axle wheel complex 17@15 under exactly the same ionization conditions. As expected, the loss of wheel 15 is observed and the negatively charged, intact axle 17 is formed as the major product at $m/z = 807$.

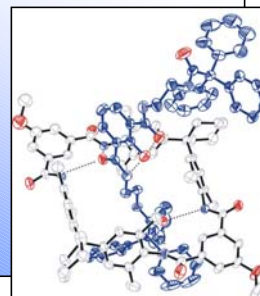


Negative mode ESI mass spectra (top figure) confirm the formation of rotaxanes. Deprotonation of 17@15 can easily be achieved (top). A 1:1 mixture (beneath) of axle 17 and wheel 15 shows strong signals for 17- and 15-. Just a small peak for the hydrogen-bonded complex of 17 and 15 is observed at $m/z = 1767$.

b) Crystal structure

Evidence for rotaxane formation also comes from the crystal structure. The Ortlep plot shows unambiguously the axle to be threaded through the wheel with one stopper bound on each side.

The axle center piece bears an in/out conformation of the two amide groups near to the phenolate, stabilized through a N-H...O-H...O=C hydrogen-bonding pattern.

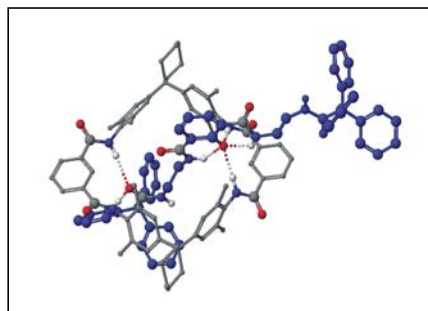
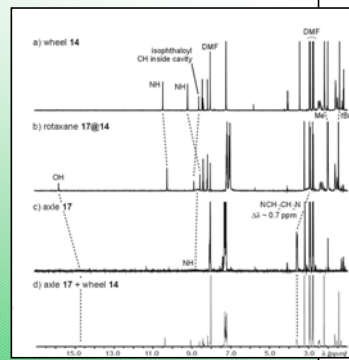


c) ¹H-NMR

The third piece of evidence for the formation of the rotaxanes comes from ¹H-NMR experiments. The figure compares the spectra of free wheel 14 (a), rotaxane 17@14 (b), the axle 17 (c) and a 1:1 mixture of axle 17 and wheel 14 (d) in [D₂]-DMF at 333 K.

While the mixture of both components is more or less a superposition of the two spectra of axle and wheel, significant shifts are observed in the rotaxane spectrum.

A major shift of $\Delta\delta = 0.8$ ppm and sharpening is observed for the OH signal and smaller shifts of the amide hydrogen atoms of the wheel ($\Delta\delta = 0.3$ and 0.6 ppm) are found. Most importantly, the shift of the signals for the ethylene diamine spacer indicates the wheel to be located on one of the arms of the axle as revealed by the crystal structure.



Related rotaxanes with longer and rigid spacer units connecting the axle center piece and the stoppers will be synthesized in the near future for comparison.

IV. Outlook

In agreement with each other, calculations and NMR experiments indicate the wheel to bind to the phenolate oxygen and the more remote carbonyl group in the deprotonated state.

The dynamic behavior and the switching of the rotaxanes between their protonated and deprotonated states are under investigation, which will provide insight into their utility as molecular machines.

P. Ghosh, C. A. Schalley, D. Haase, W. Saak, A. Lützen, G. Federwisch, R. Gschwind, in preparation for J. Am. Chem. Soc.

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