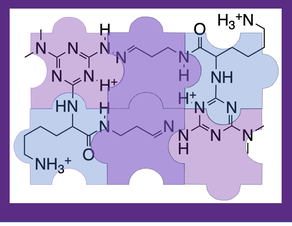

From Macroscopic to Molecular: Investigating the Behavior of Self-Assembling Hinges

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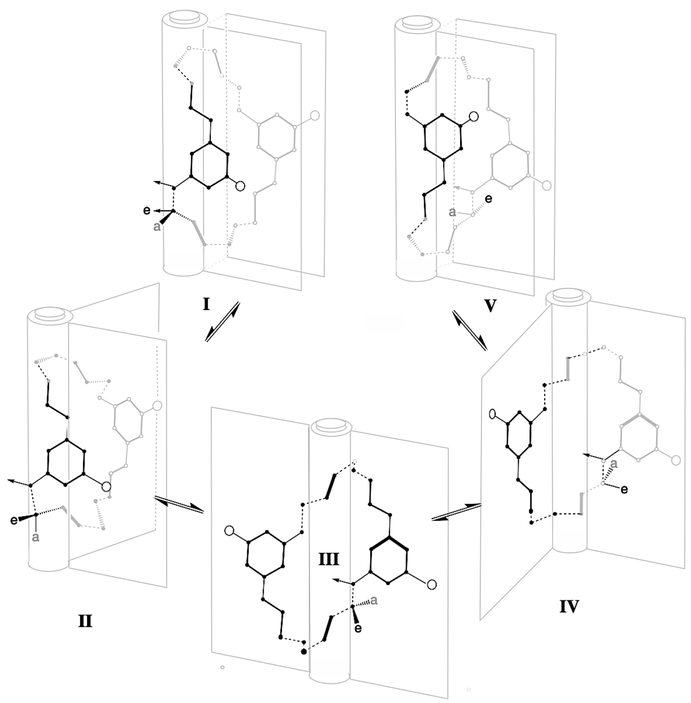
Hinges are pervasive in the world today. Most common is a simple mortise door hinge - defined by the flush stacking of leaves and fully revolute motion. Chemists have long sought to reproduce such structures on the molecular scale. Here, the hinge behavior of large, cyclic molecules is described. Moreover, hinge motion can be controlled by "gumming up" the parts responsible for motion. While dirt and debris work in the macroscopic world, additional atoms are used in these molecular mimics. Specifically, by increasing the size of groups in the hinge domain, the rate of hinging decreases. Hinge motion is visualized by variable temperature NMR spectroscopy where in, at low temperatures the hinging both faces of the leaves (inside and outside) can be observed. At high temperatures, the hinging speeds up and the inside and outside exchange too quickly to be observed. Unlike hinges of everyday use that require human assembly, the molecular hinges described here assemble themselves. As a result, hinges with identical leaves as well as hinges with mismatched leaves can be prepared. Surprisingly, the results of this assembly process are biased: a statistical distribution of hinges is not observed. Further studies to understanding this steric (gumming) sorting are ongoing.

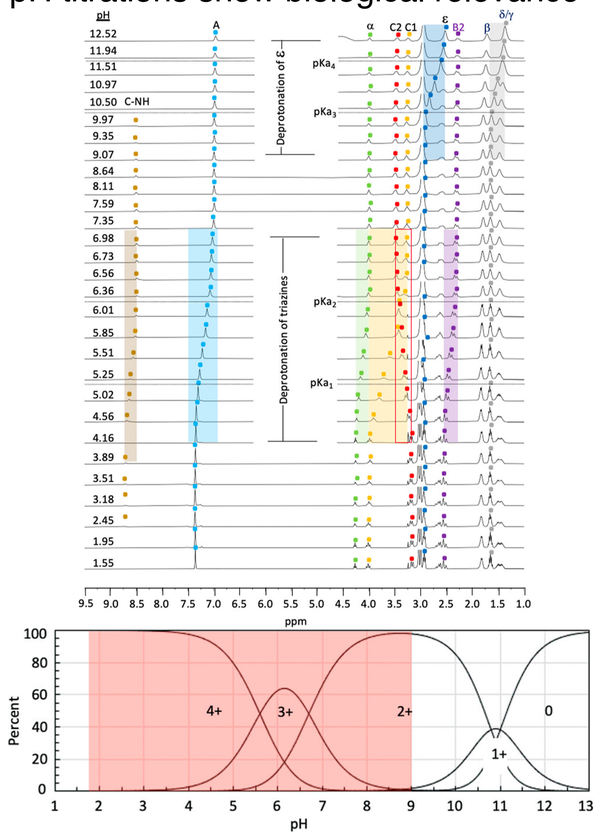
Synthesis[1-5]

Dynamic motion of mortis hinges[4]



	R = R'	CD_3OD	CD_3CN	DMSO-d_6	D_2O*	Pyr-d_5*	Average
G-G	H	13.3 ± 0.3	12.8 ± 0.2	—	—	—	13.3 ± 0.1
Aib-Aib	Me	16.2 ± 0.2	16.1 ± 0.1	16.1 ± 0.1	16.9 ± 0.2	16.6 ± 0.1	16.4 ± 0.2
Acp-Acp		—	—	15.7 ± 0.1	—	—	15.7 ± 0.1
Acb-Acb		—	—	17.3 ± 0.3	—	—	17.3 ± 0.3

pH titrations show biological relevance[5]

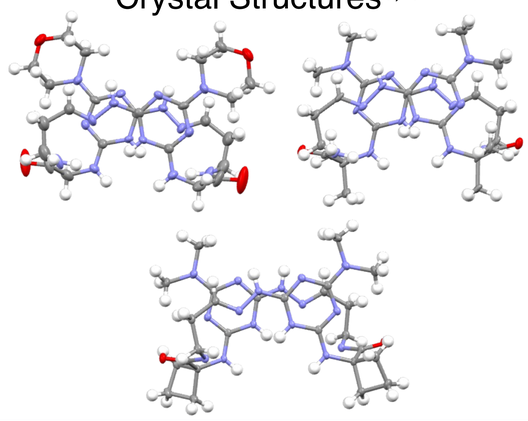


Conclusions

- Can control $\Delta G^{\ddagger}$ with steric bulk around the hinge axis
- Changing the side chain does not largely change the structure
- Computation shows that mechanism of folding is likely caused by phi/psi rotation

Computation when done

Crystal Structures[1, 4]



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