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# A Comprehensive Exploration of the Conformational and Energetic Landscape of a Rotaxane System: A Molecular Dynamics Study

Kentaro Bodzewski  
*Concordia University - Portland*

Andrew Johnson  
*Concordia University - Portland*, andjohnson@cu-portland.edu

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# A Comprehensive Exploration of the Conformational and Energetic Landscape of a Rotaxane System: A Molecular Dynamics Study

Kentaro Bodzewski, Andrew Johnson  
Concordia University, Portland, OR

## Abstract / Introduction

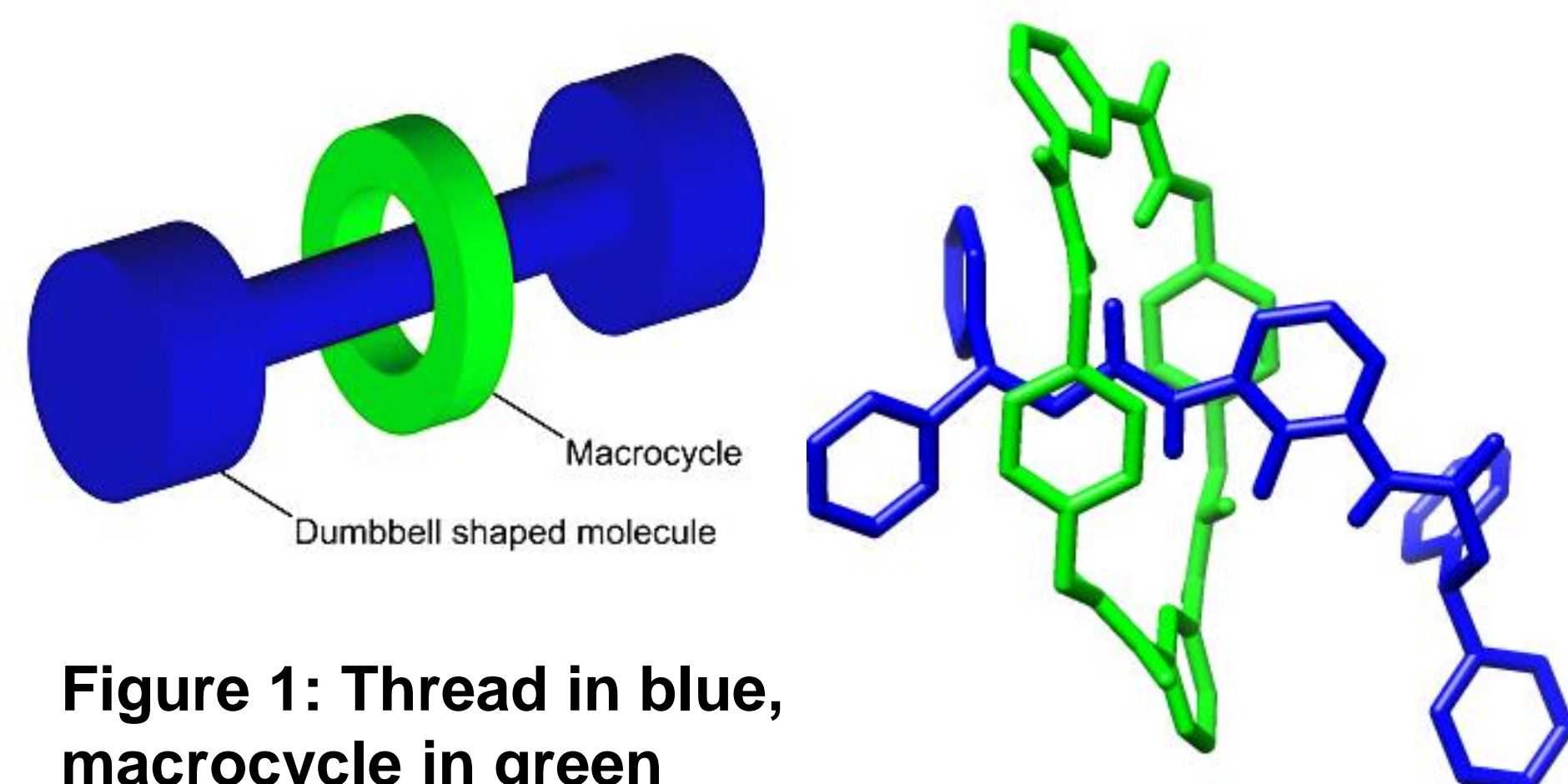


Figure 1: Thread in blue, macrocycle in green

Rotaxanes are composed of a dumbbell shaped molecule threaded through a ring shaped macrocycle; see Figure 1. Rotaxanes are used in molecular machines due to the thread's ability to rotate (pirouette) within the macrocycle. This rotation is often coupled with a shuttling movement as well making them especially useful. Unfortunately, rotaxanes are extremely difficult to synthesize, making it a challenge to study them. By being able to study them using molecular dynamics, one can predict their conformational energies before having to create them. In a previous study, energy barrier values were found for three DAP based rotaxane pirouettes using NMR spectroscopy<sup>3</sup>. Our study looked at two of the previous study's DAP based rotaxanes (figures 2 and 3). We intend to show that molecular dynamics is a viable approach to calculating energy barriers of rotaxane pirouettes.

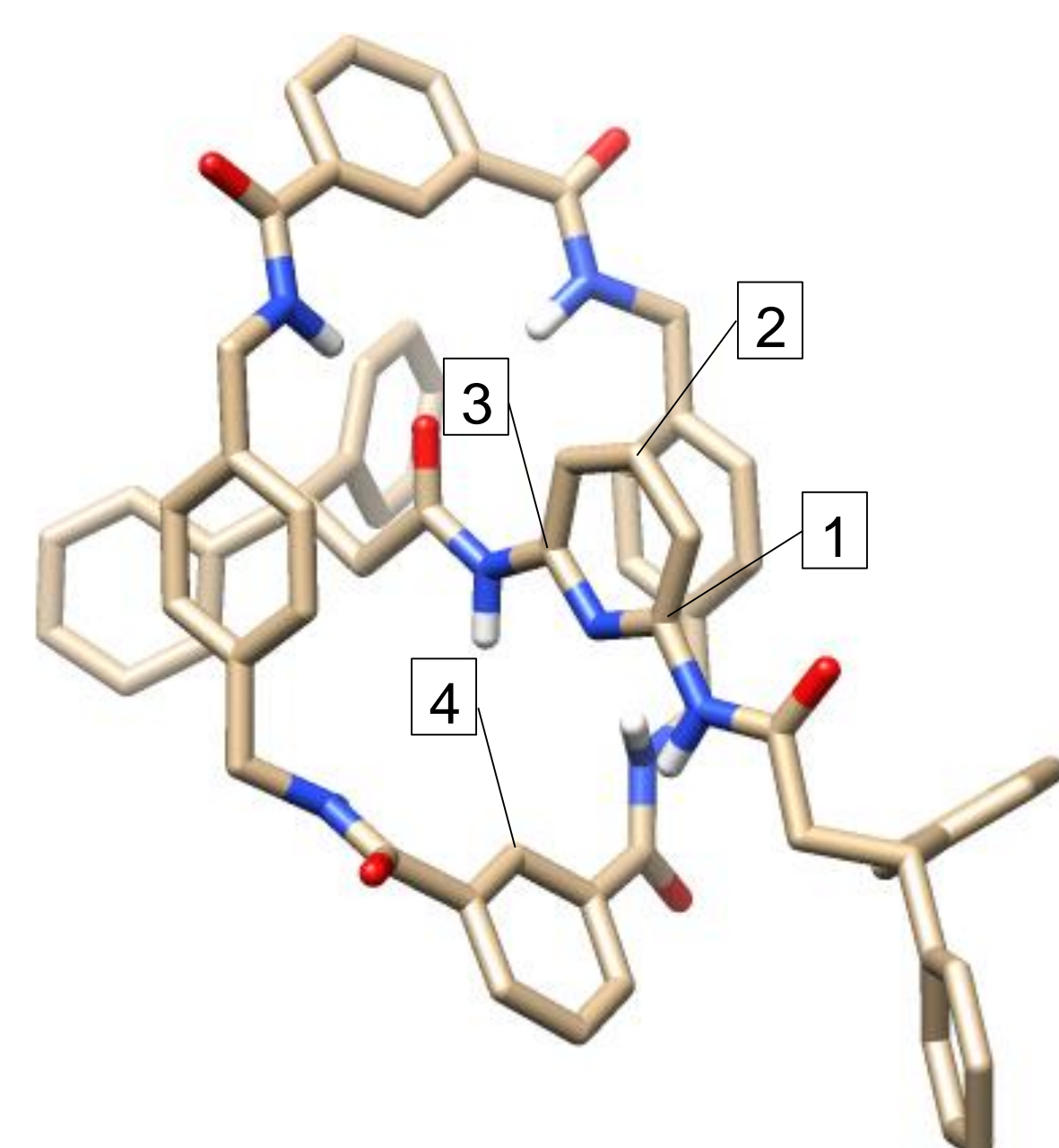


Figure 2: DAP-2A with labeled dihedral

## Abstract / Introduction

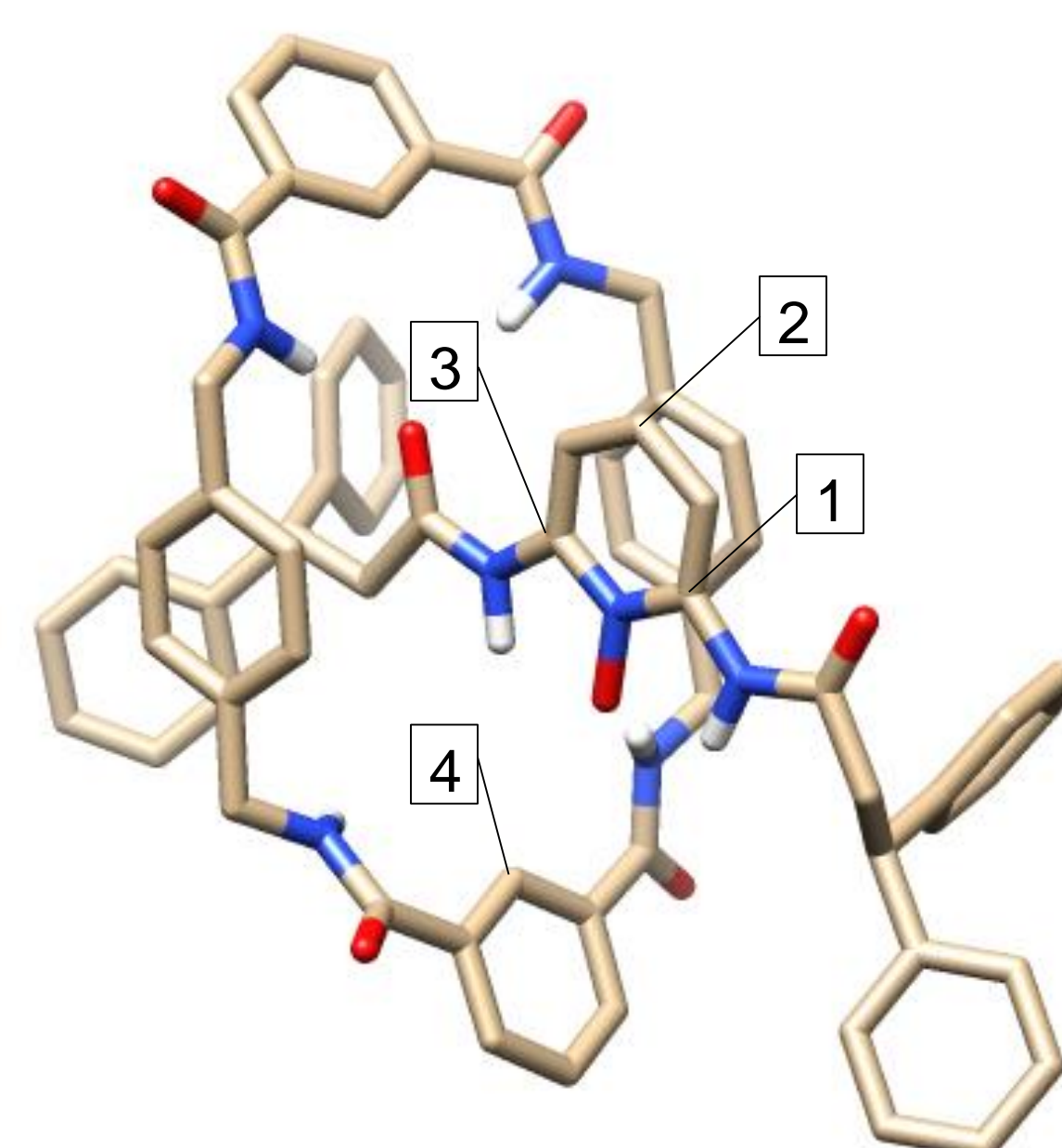


Figure 3: DAP-2B with labeled dihedral

## Materials & Methods

Geometries for the two DAP based rotaxanes were optimized using Firefly, and RESP charge fitting was performed using R.E.D. server<sup>1,4</sup>. The rotaxane was then explicitly solvated with chloroform and minimized. In the first minimization of the system, the rotaxane was held in place with restraints. In the second minimization restraints were removed. The system was then heated slowly to 300 K at constant volume (NVT ensemble) with small restraints on the rotaxane that allowed for some movement. Next it was equilibrated for 50 nanoseconds at constant pressure (NPT ensemble) broken up into 2 nanosecond segments. At this point the system was prepared for biased sampling to take place; the biased runs all began from the last step of equilibration. There were three methods of biased sampling that were applied to the rotaxane: adaptive biasing force, metadynamics, and umbrella sampling. In all three cases a dihedral was defined using 3 atoms on the thread and 1 atom on the macrocycle, with a force being applied to cause pirouetting of the thread. Minimizations, equilibrations, and biased simulations were all run using NAMD<sup>2</sup>.

## Results

Figure 4: Visualization of DAP-2B pirouette

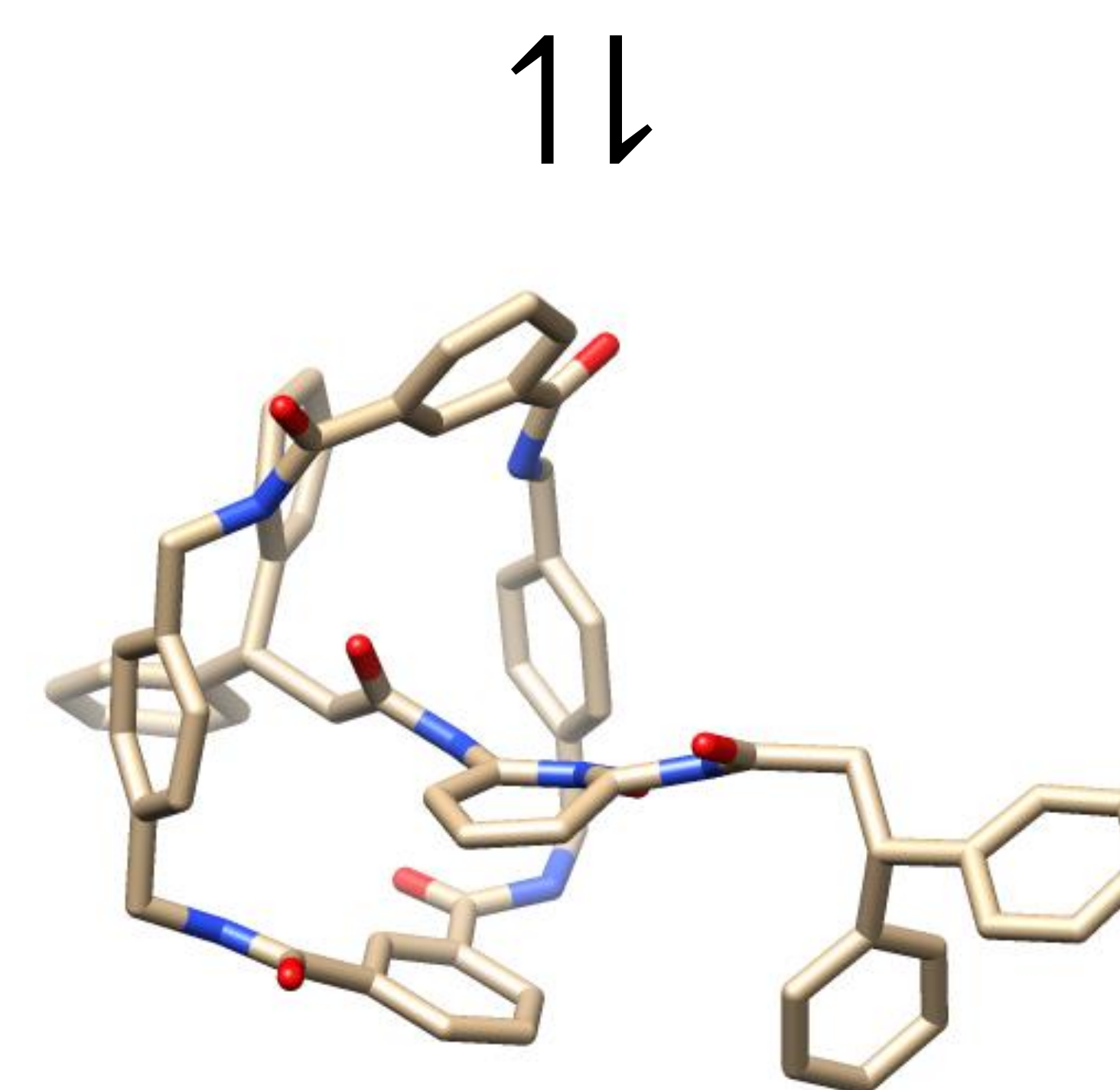
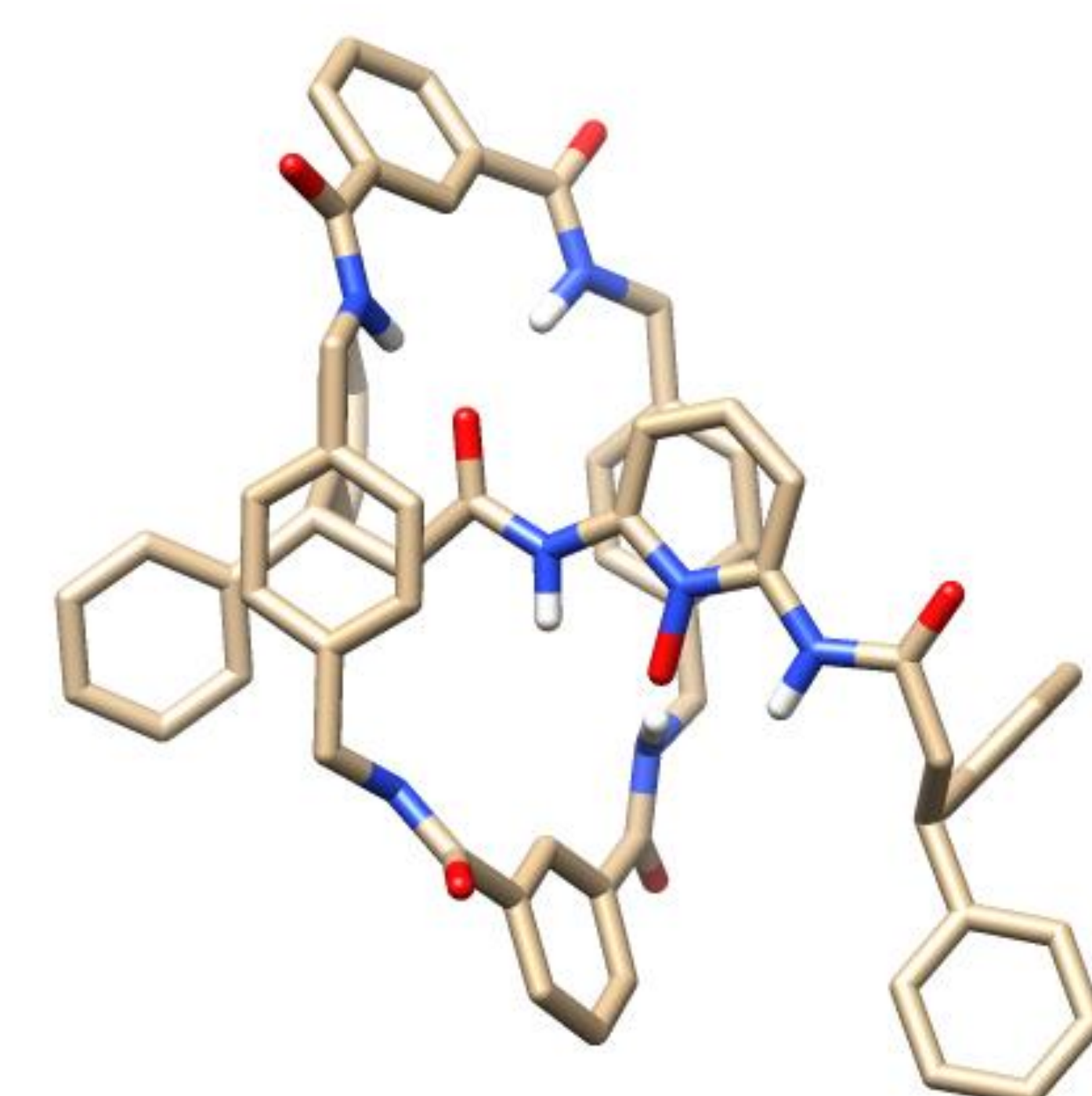
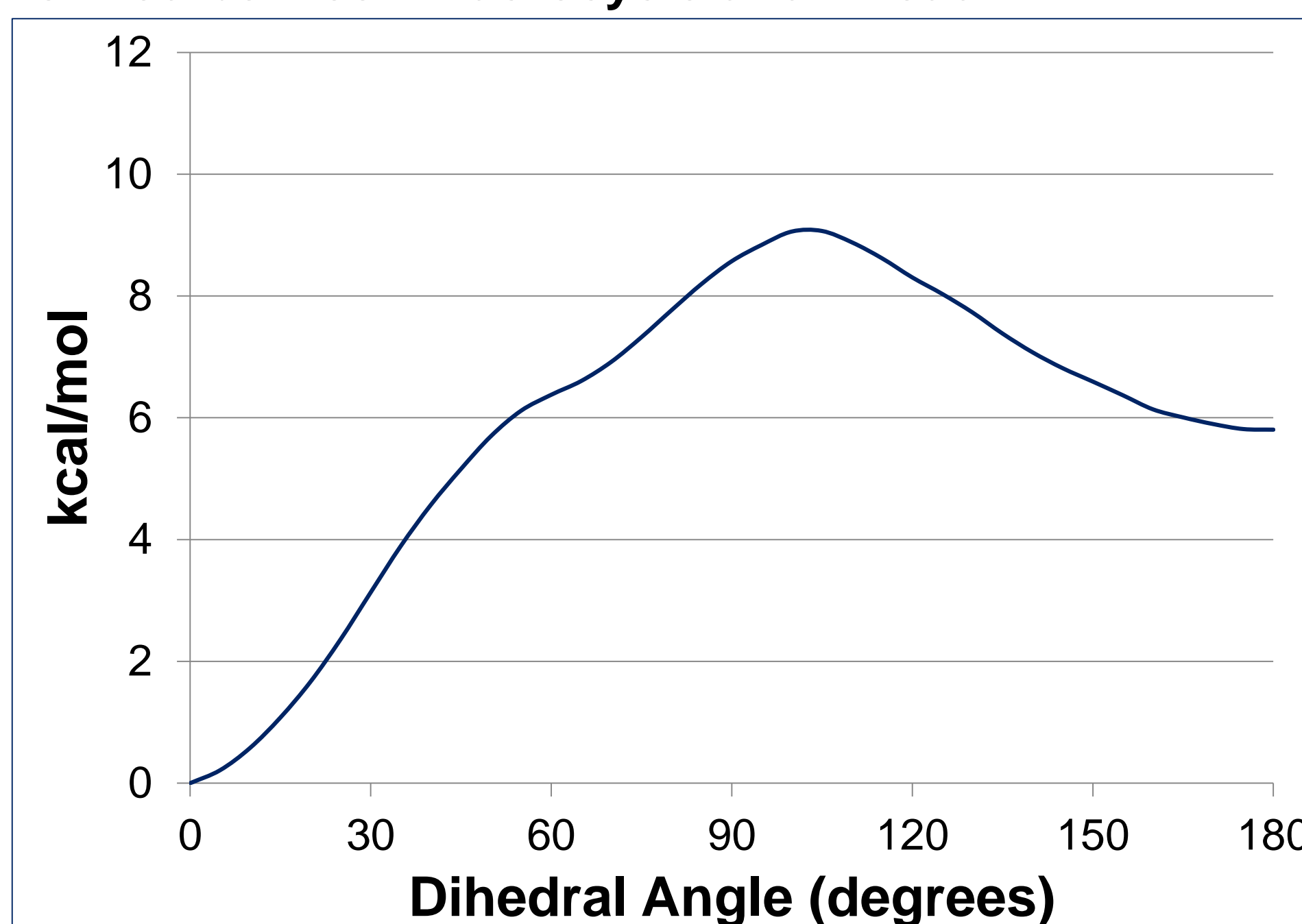
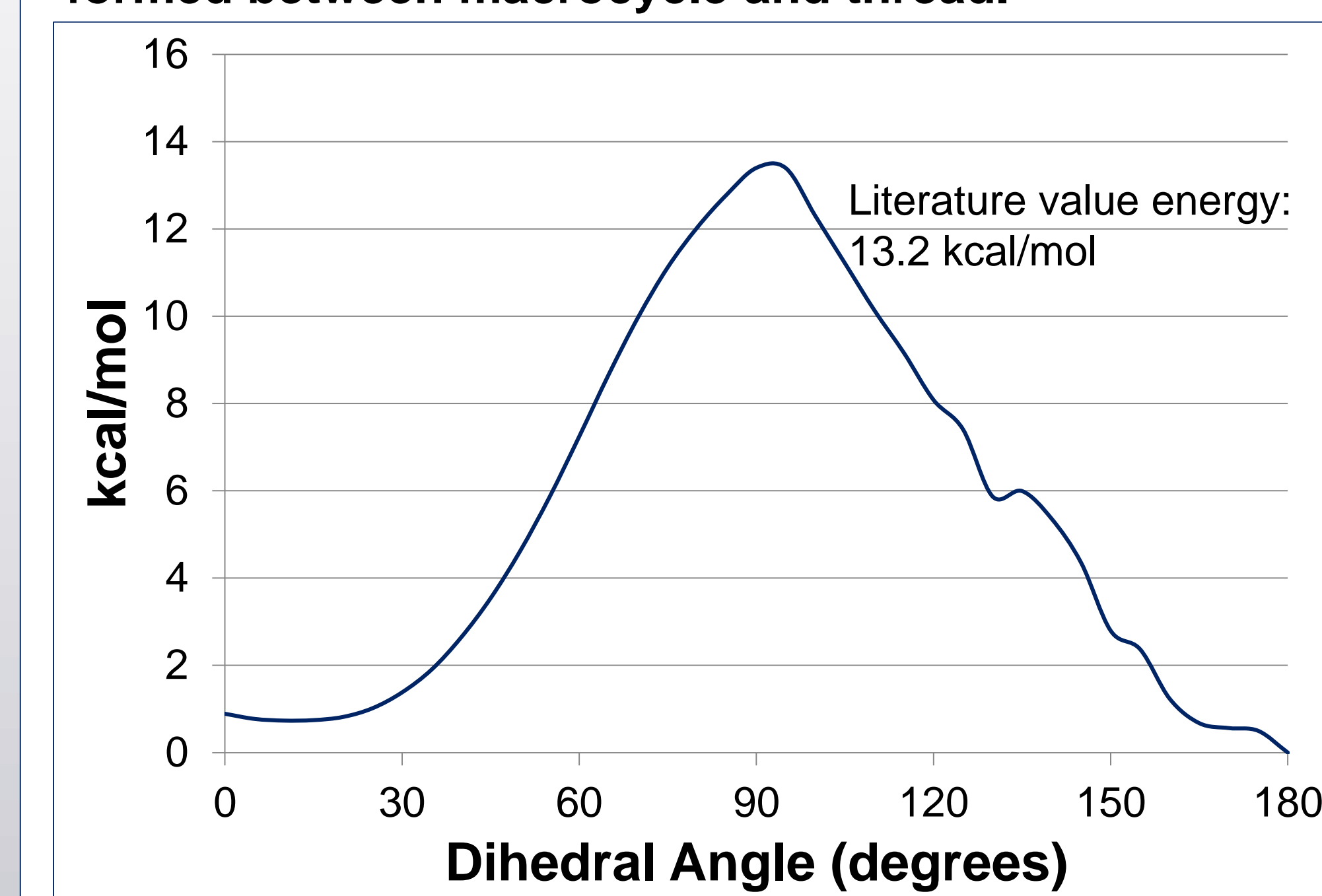


Figure 5: DAP-2A Free energy vs. dihedral angle formed between macrocycle and thread.



## Results

Figure 6: DAP-2B Free energy vs. dihedral angle formed between macrocycle and thread.



## Conclusions

Of the three methods used to measure the energy required for a 180° rotation of the two DAP based rotaxanes, adaptive biasing force had the most success. Umbrella sampling and metadynamics both calculated values that were much lower than found in a previous study using NMR spectroscopy<sup>1</sup>. When taking a closer look at the simulations it was found that often times the thread would be bent out of shape as a means of changing the dihedral angle without actually pirouetting. Though we found some data which aligned with past results, there were also inconsistencies with this data. Using molecular dynamics as a viable means of studying rotaxanes seems promising but by no means perfected.

## References

- <sup>1</sup>Alex A. Granovsky, Firefly version 8, [www http://classic.chem.msu.su/gran/firefly/index.html](http://classic.chem.msu.su/gran/firefly/index.html)
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- <sup>3</sup>Martinez-Cuevas, A., Pastor, A., Cioncoloni, G., Orenes, R., Alajarin, M., Symes, M., & Berna, J. (2015). Versatile control of the submolecular motion of di(acylamino)pyridine-based [2] rotaxanes. *Chemical Science*, 6(5), 3087-3094.
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