

1-1-2016

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

Kentaro Bodzewski
Concordia University - Portland

Follow this and additional works at: http://commons.cu-portland.edu/suri_msd



Part of the [Chemistry Commons](#)

Recommended Citation

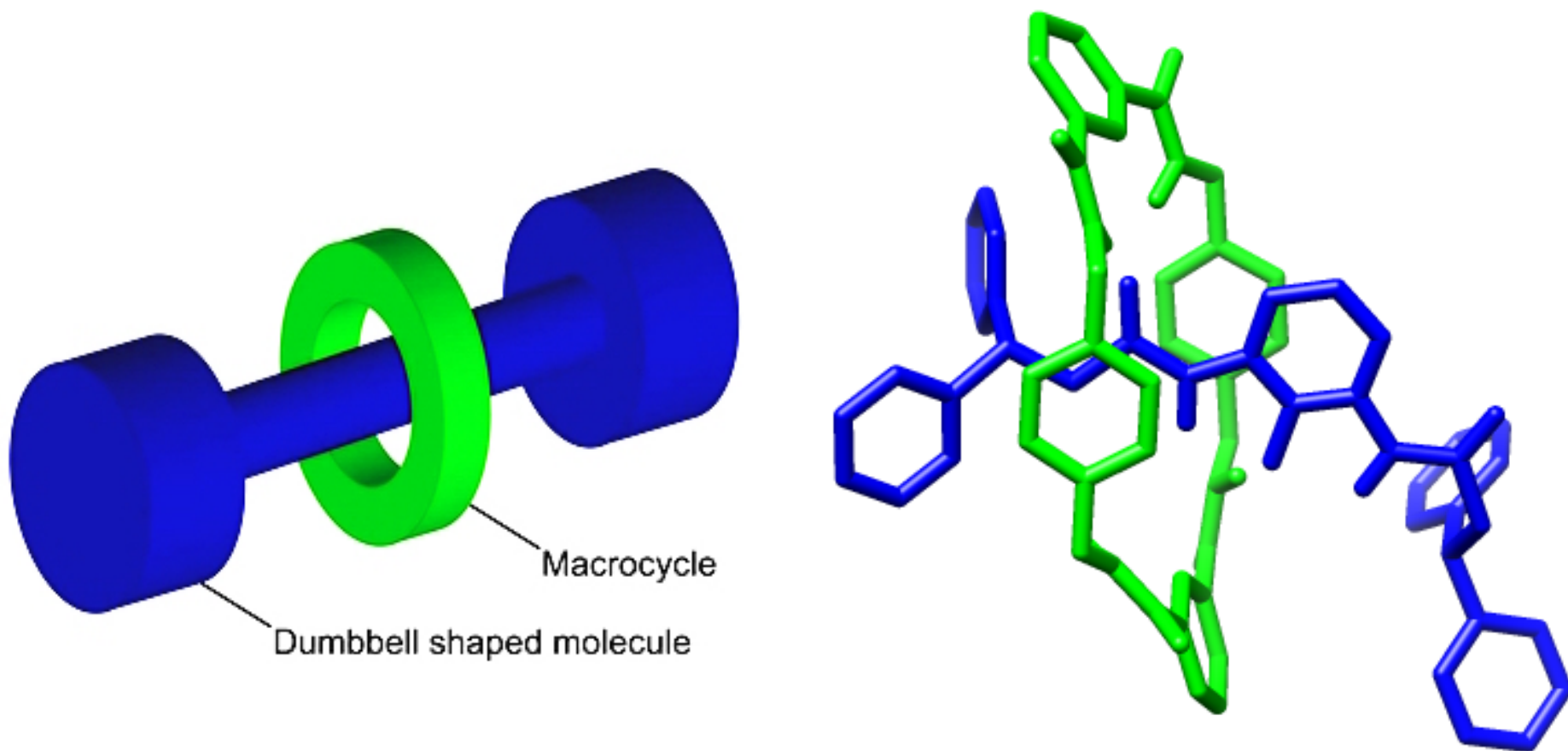
Bodzewski, Kentaro, "A Comprehensive Exploration of the Conformational and Energetic Landscape of a Rotaxane System: A Molecular Dynamics Study" (2016). *Math & Science Department (SURI)*. 16.
http://commons.cu-portland.edu/suri_msd/16

This Presentation is brought to you for free and open access by the Summer Undergraduate Research Institute (SURI) at CU Commons. It has been accepted for inclusion in Math & Science Department (SURI) by an authorized administrator of CU Commons. For more information, please contact libraryadmin@cu-portland.edu.

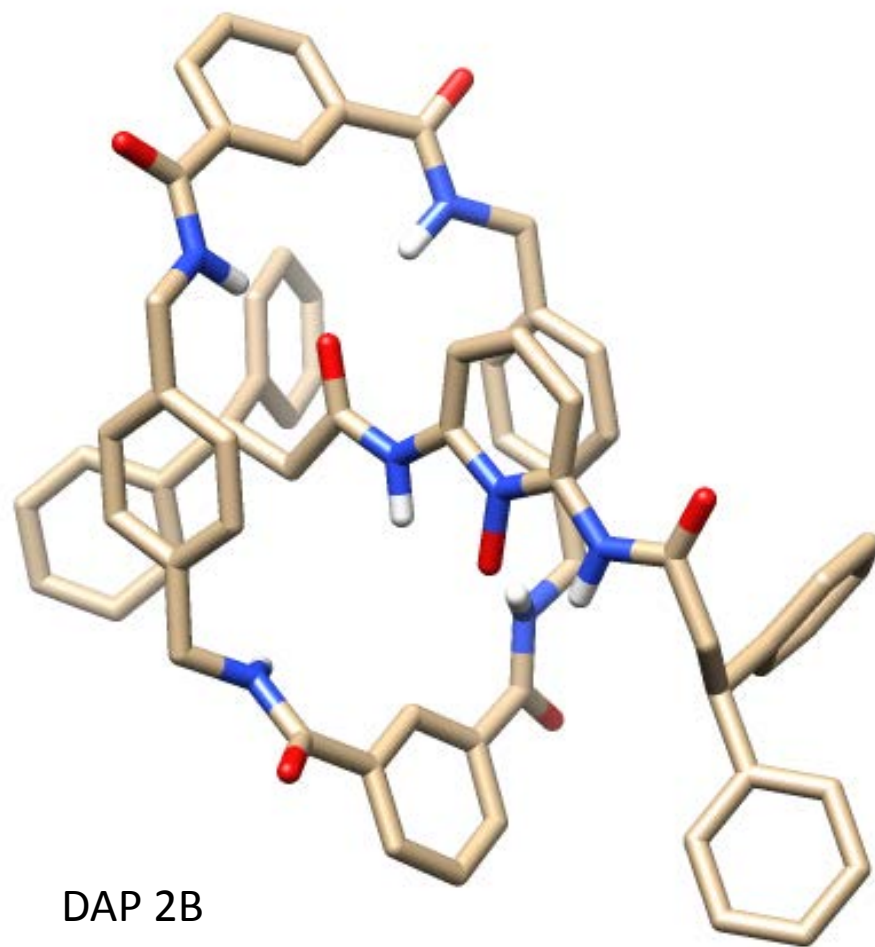
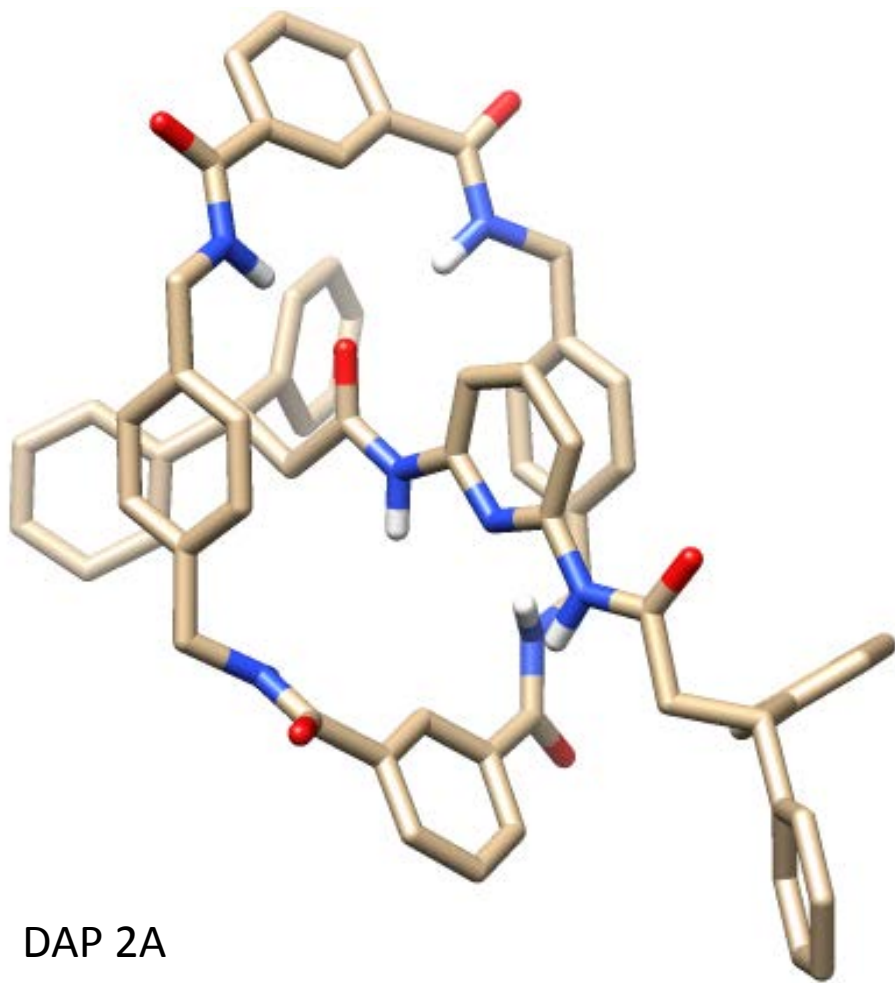
A Comprehensive Exploration of the Conformational and Energetic Landscape of a Rotaxane System: A Molecular Dynamics Study.

Ken Bodzewski

Rotaxanes

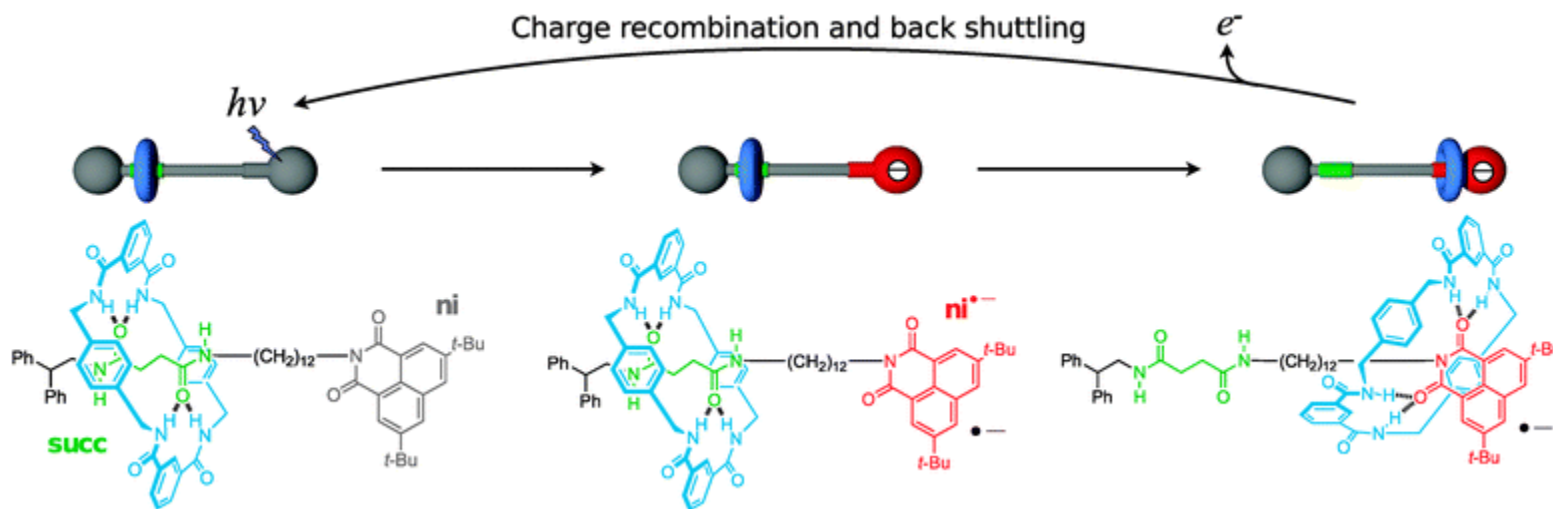


Di(acylamino)pyridine (DAP) based rotaxanes



Relevance

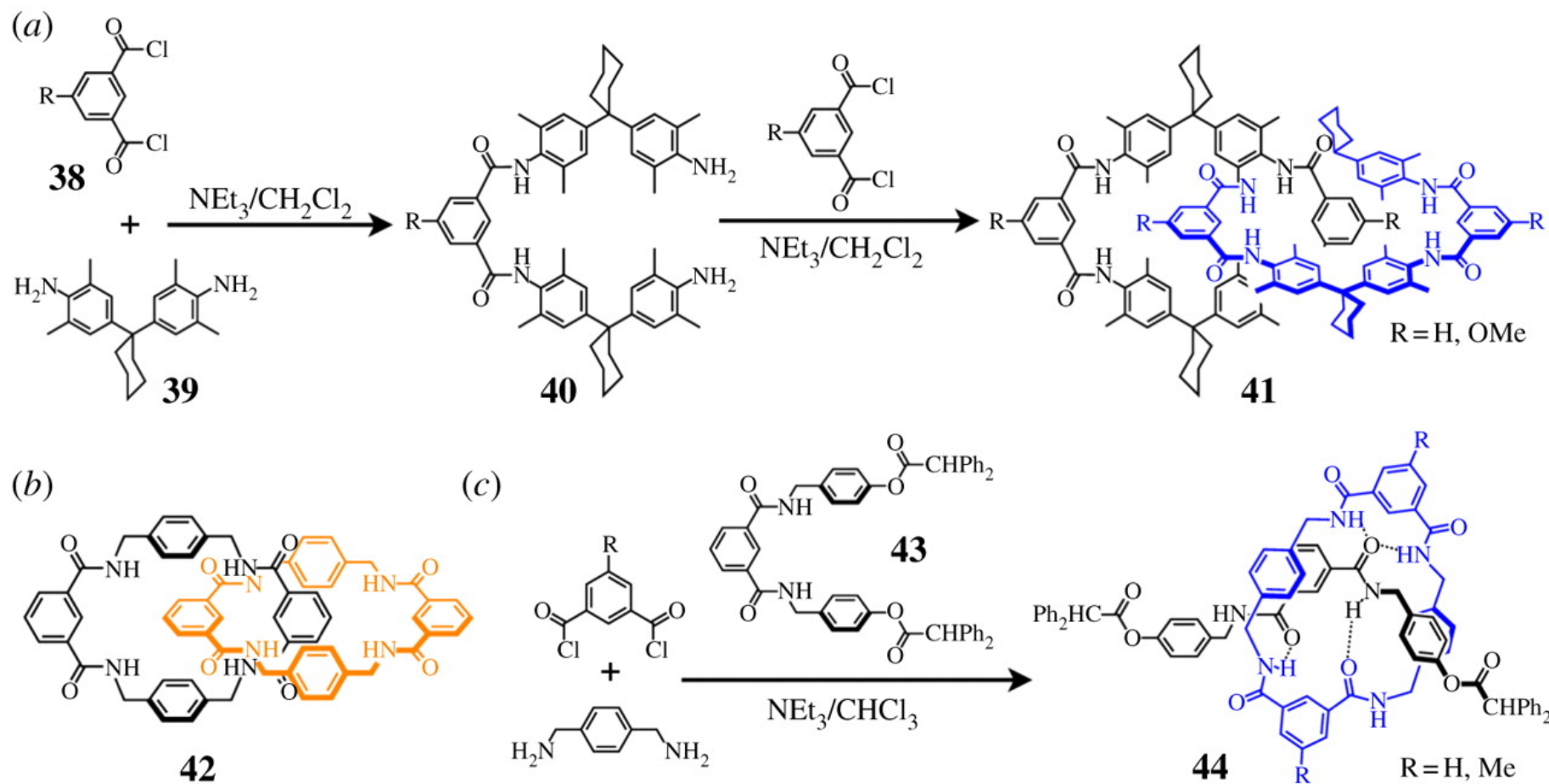
- Rotaxanes are being used more and more.
 - Molecular machines.
 - Switches to turn them “on” and “off”
 - Rotation is often paired with a sliding or “shuttling.”



Relevance

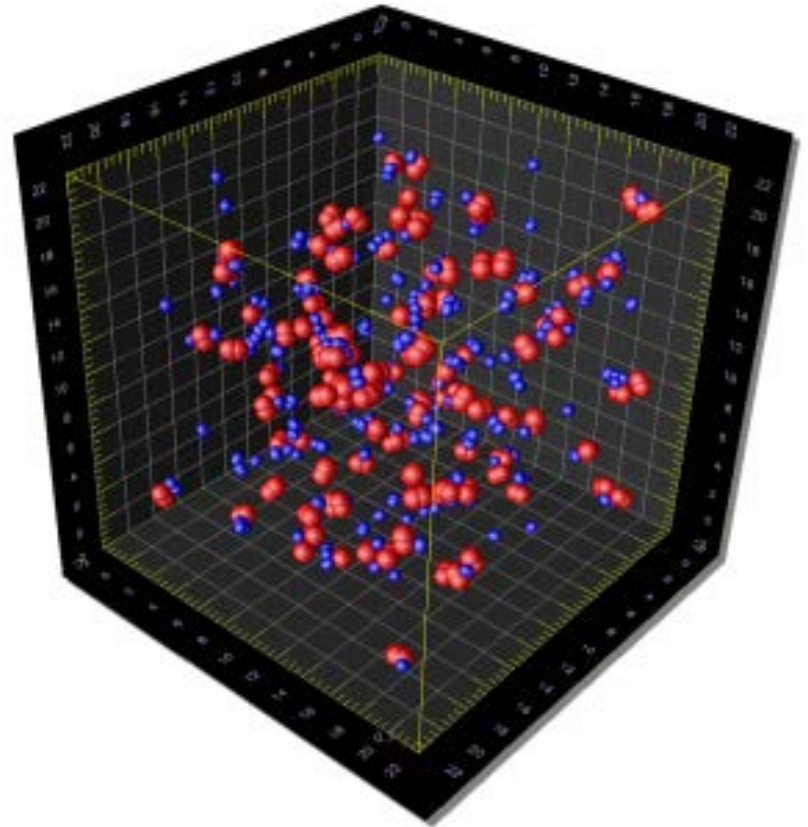
- Very difficult to make, low yield.
 - Molecular Dynamics as a way to study them before synthesizing them.
 - Use it as a predictor for how your rotaxane will respond.

Relevance



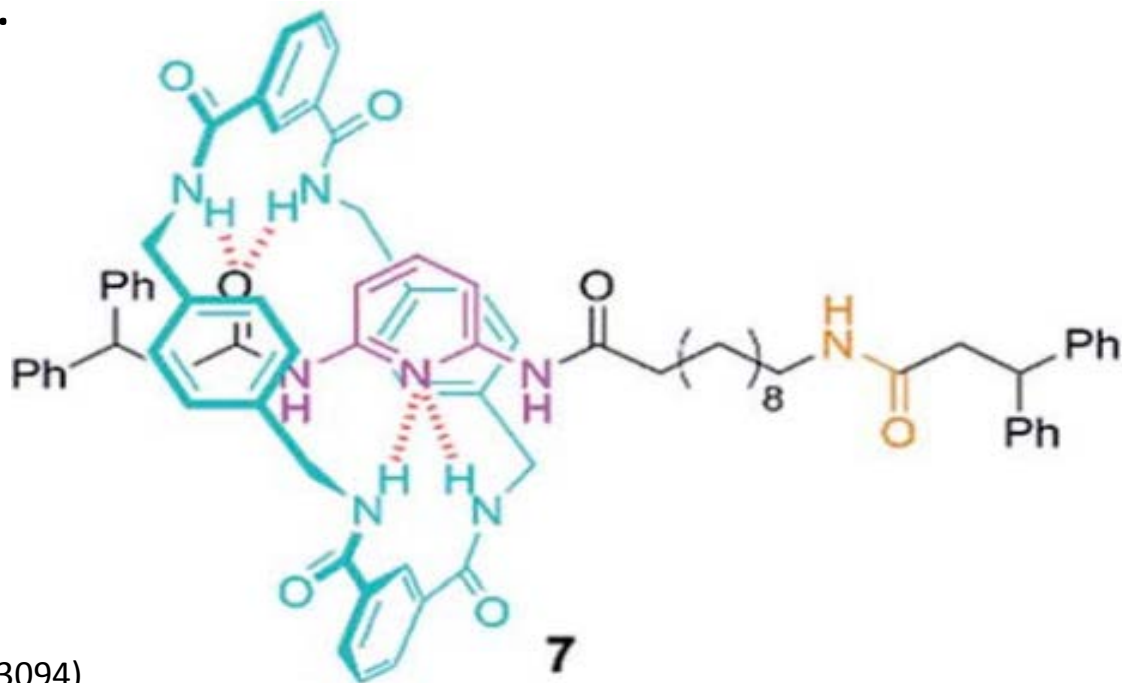
Molecular Dynamics

- Classical (Newtonian) mechanics.
- NAMD.
- VMD.
- Roughly 2,000 atoms in our systems.



Previous Study

- Used NMR spectroscopy to find energy required for rotaxane pirouette.
- Looked at three different rotaxanes.
 - We studied two of these three.
- Solvated in chloroform.

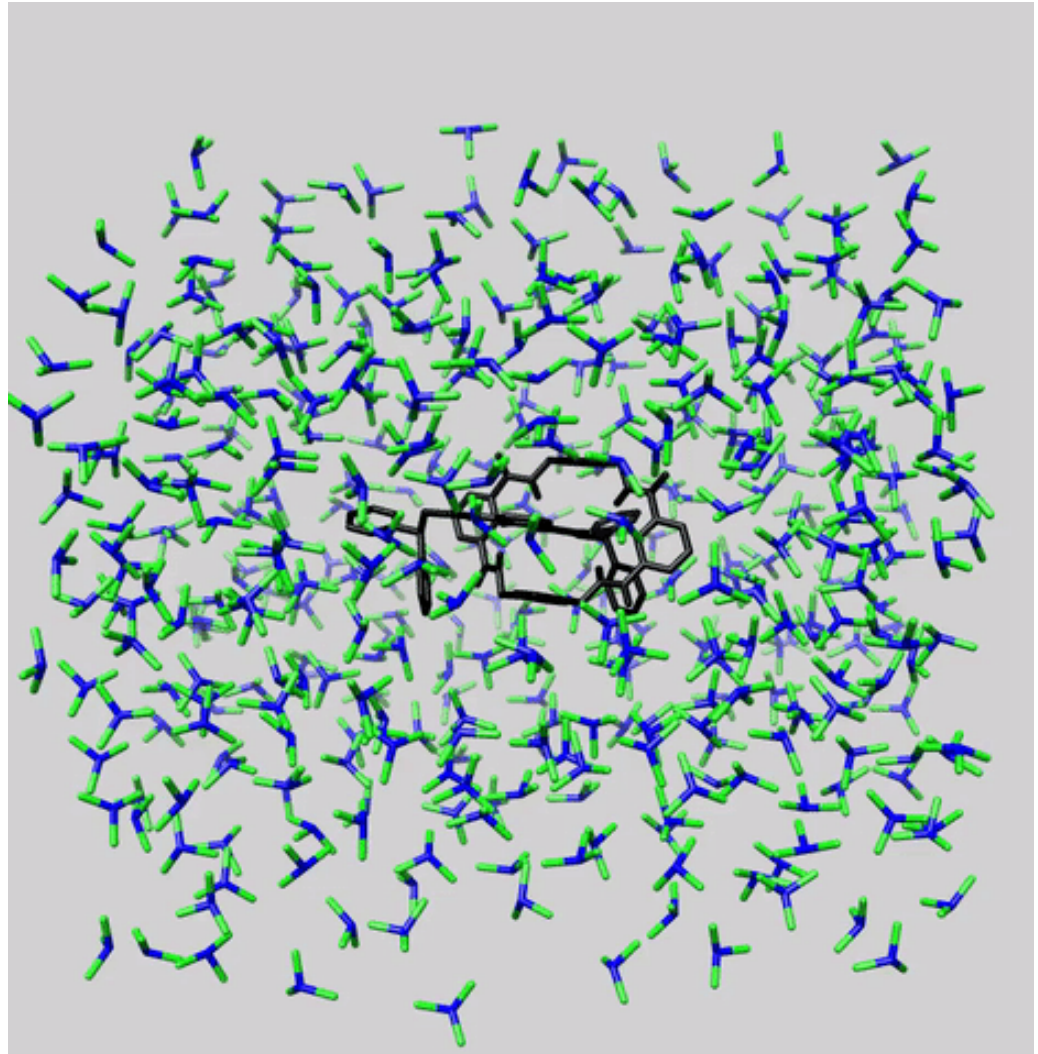


Procedure

- R.E.D.D. server to derive partial charges on our rotaxanes.
- System was created through the use of AmberTools.

Procedure

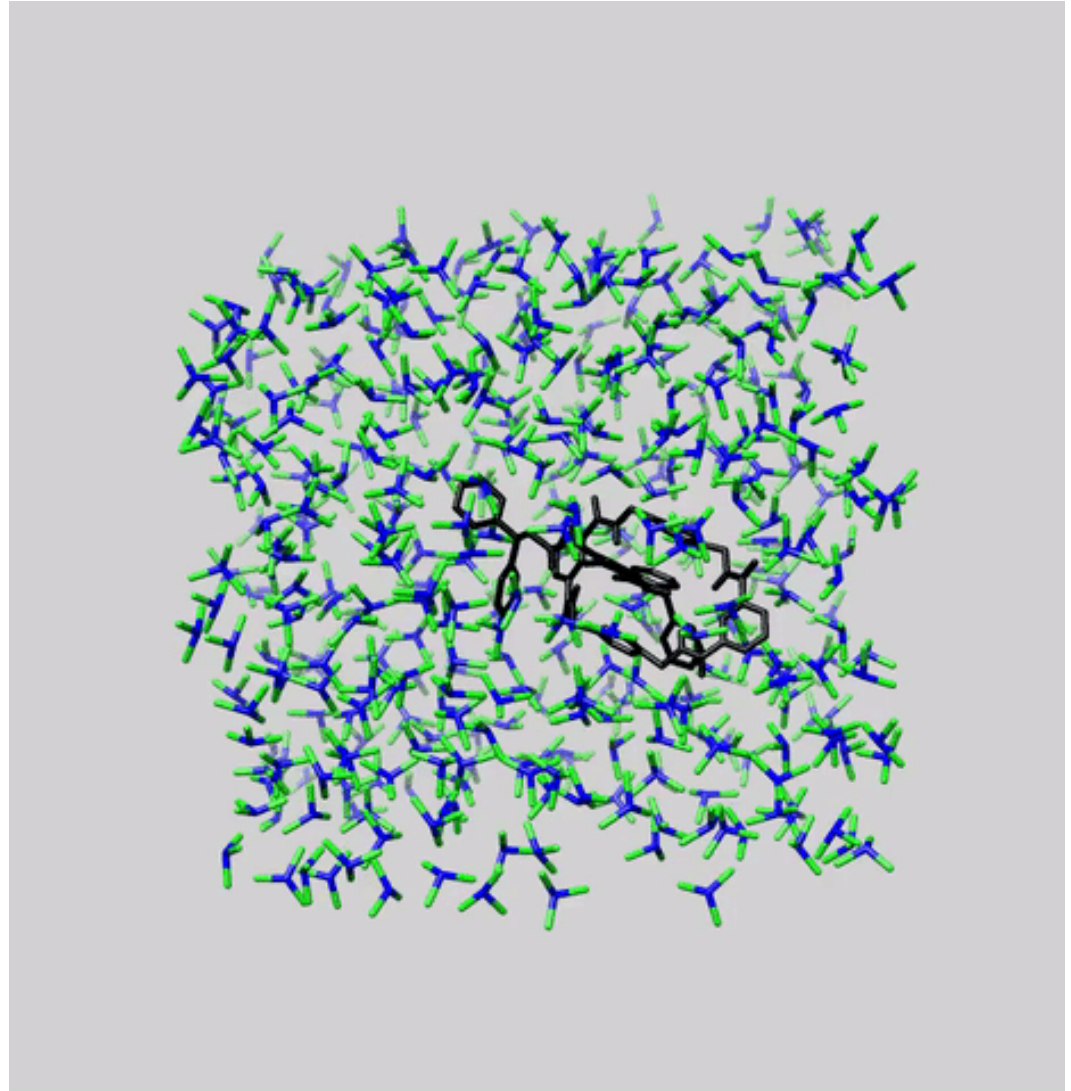
- Rotaxane held still while chloroform is relaxed.
- Whole system is relaxed.



(visualized with chimera)

Procedure

- Slowly heat up the system at constant volume.
- Equilibrate for 50 nanoseconds.



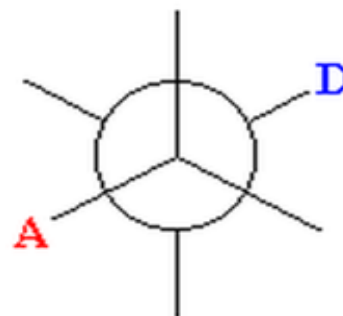
(visualized with chimera)

Dihedral Angle

- Angle made up of 4 atoms.
 - Created by first and fourth atom, second and third atom act as an axis.
- Defined three atoms on the thread and one on the macrocycle.
- Tried countless combinations.

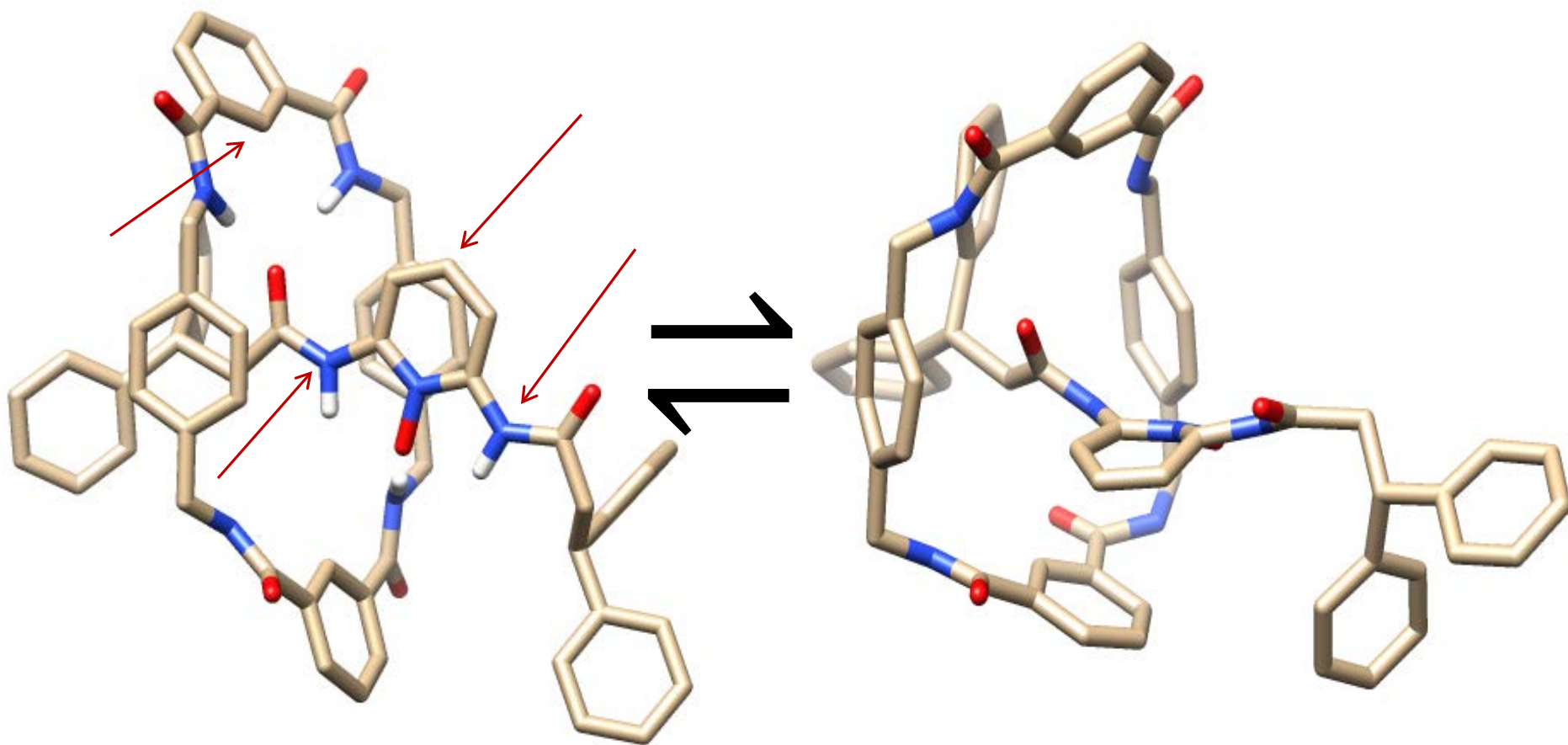


Sawhorse projection



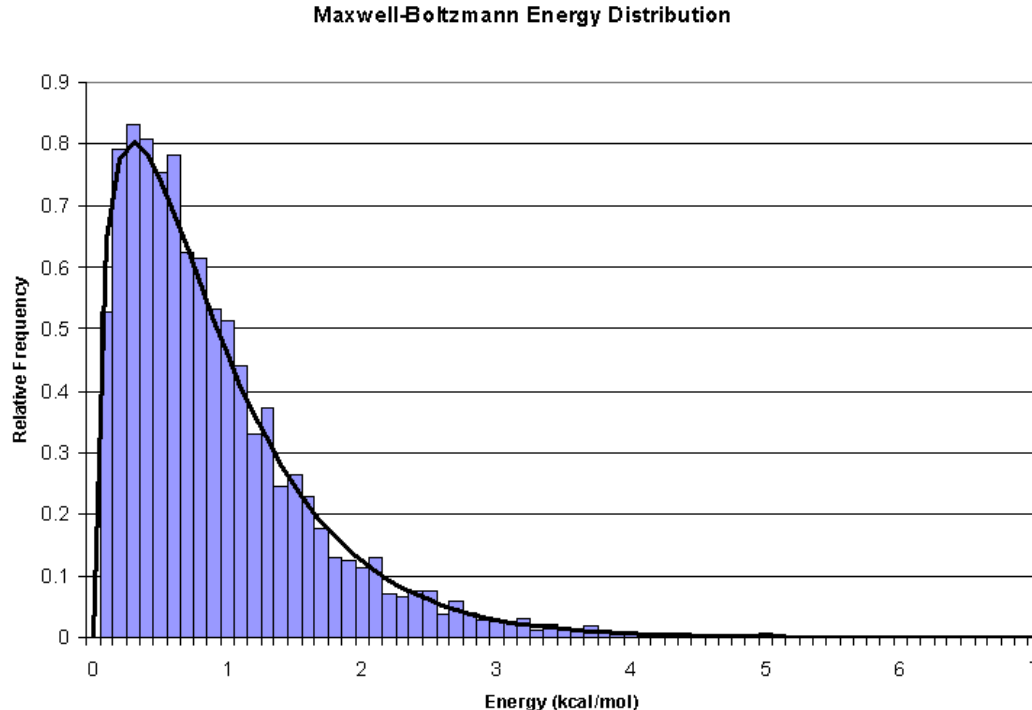
Newman projection

Simulated Rotation



Biased Sampling

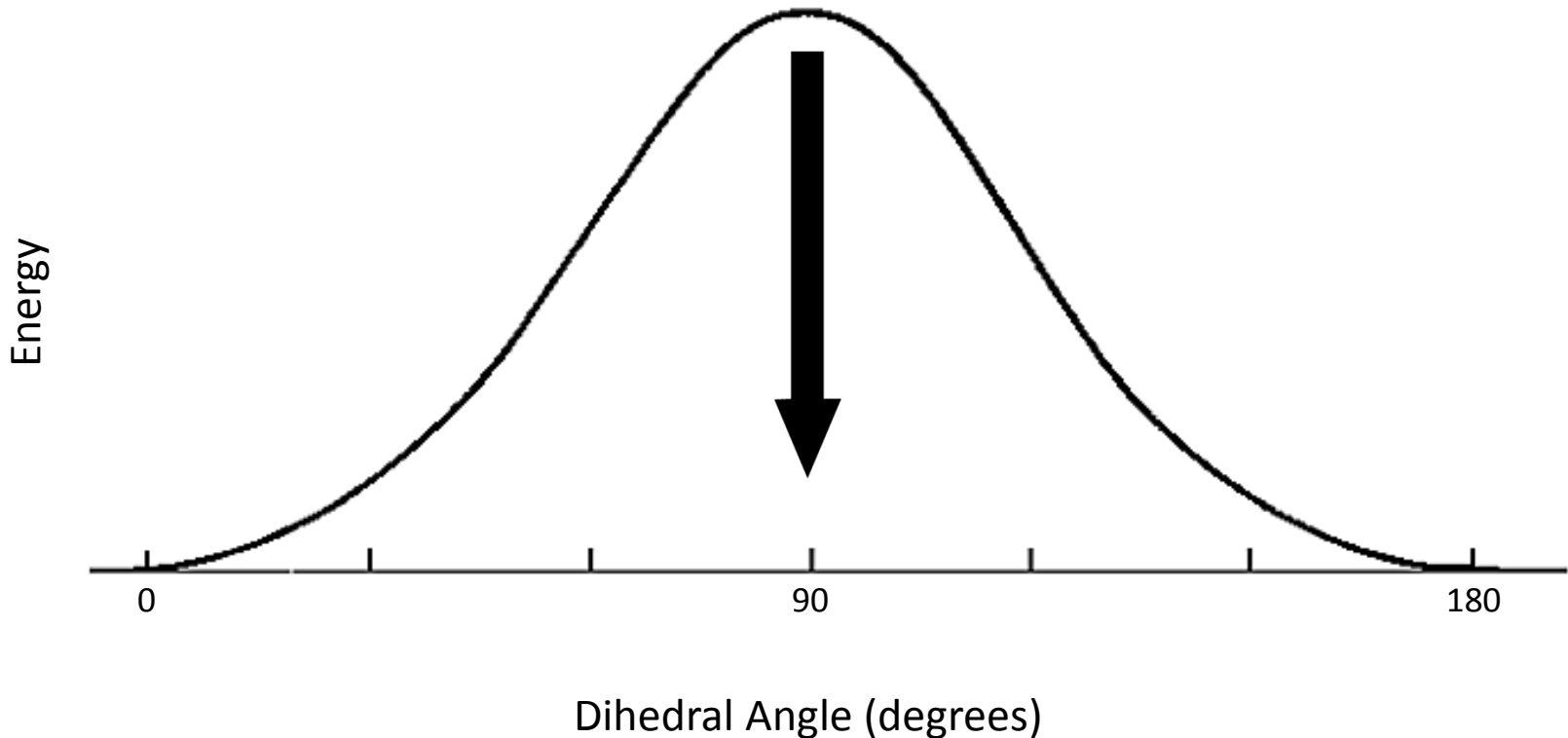
- Adaptive Biasing Force, Metadynamics, and Umbrella Sampling.
- Apply force on the system to allow molecules to go through otherwise unfavorable conformations.
- Took 3-4 hours to produce 1 nanosecond simulation.
- Much more efficient way of mapping free energy barriers.



(James C. Phillips, et al. Scalable molecular dynamics with NAMD. *Journal of Computational Chemistry*, 26:1781-1802, 2005.)

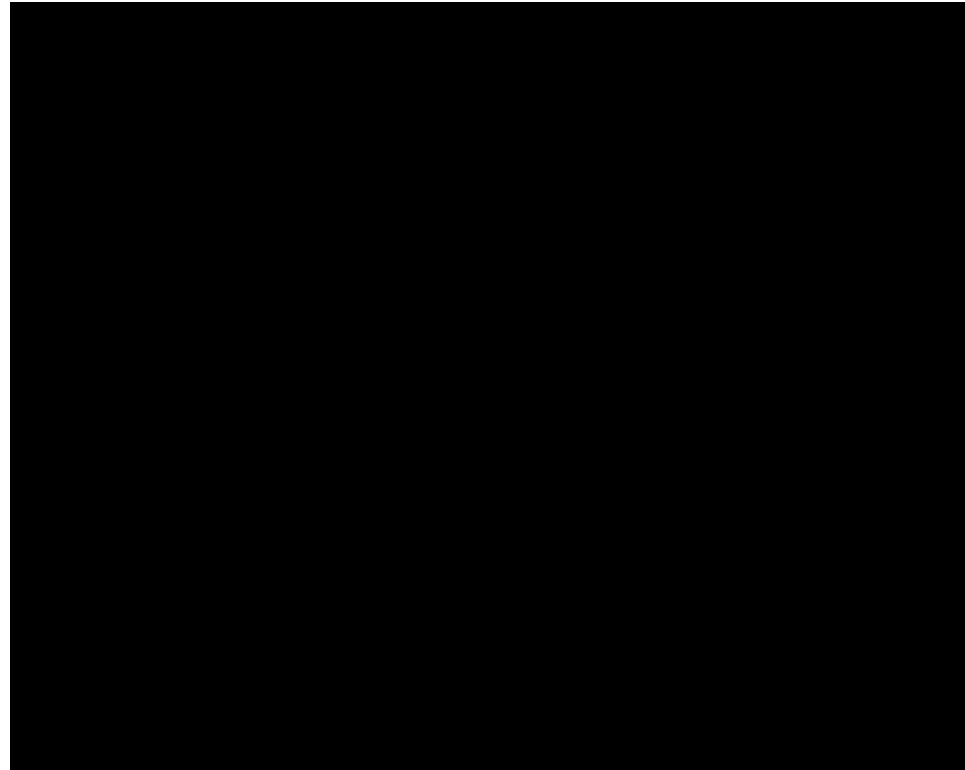
Adaptive Biasing Force

- Adaptive Biasing Force
 - Flattening out energy barriers to allow full sampling.



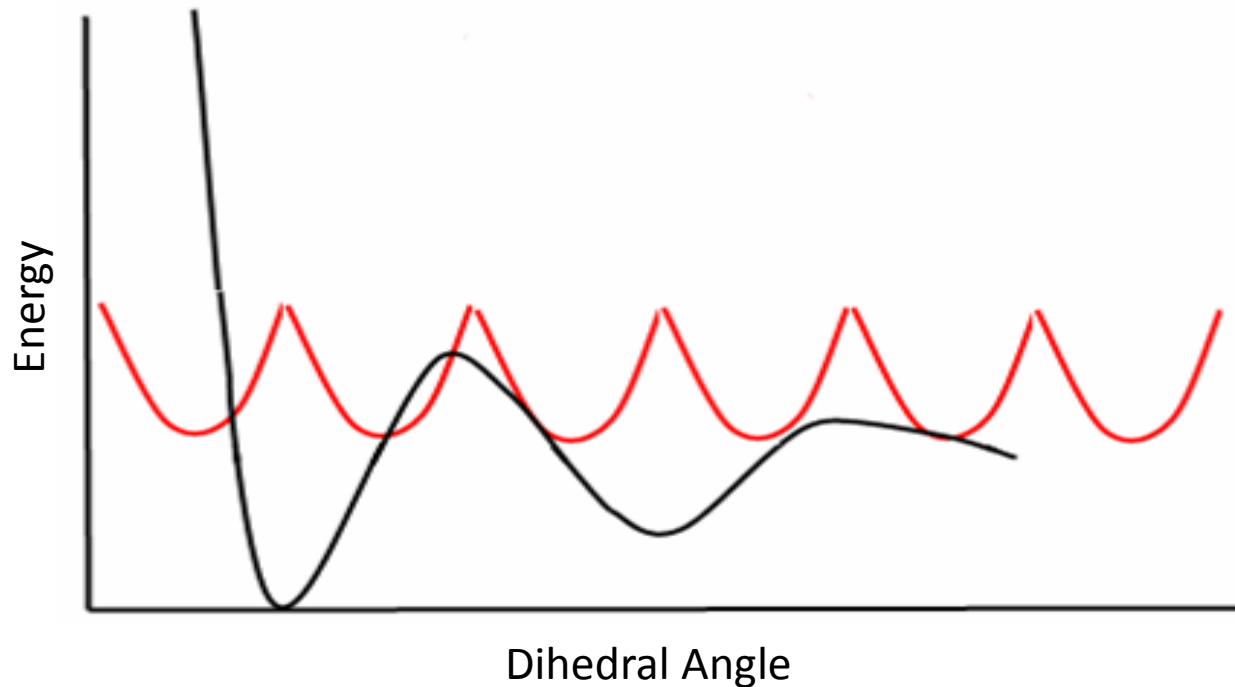
Metadynamics

- Metadynamics
 - Flooding low energy areas to fill up energy valleys.
- Allows for more sampling at high energy states.

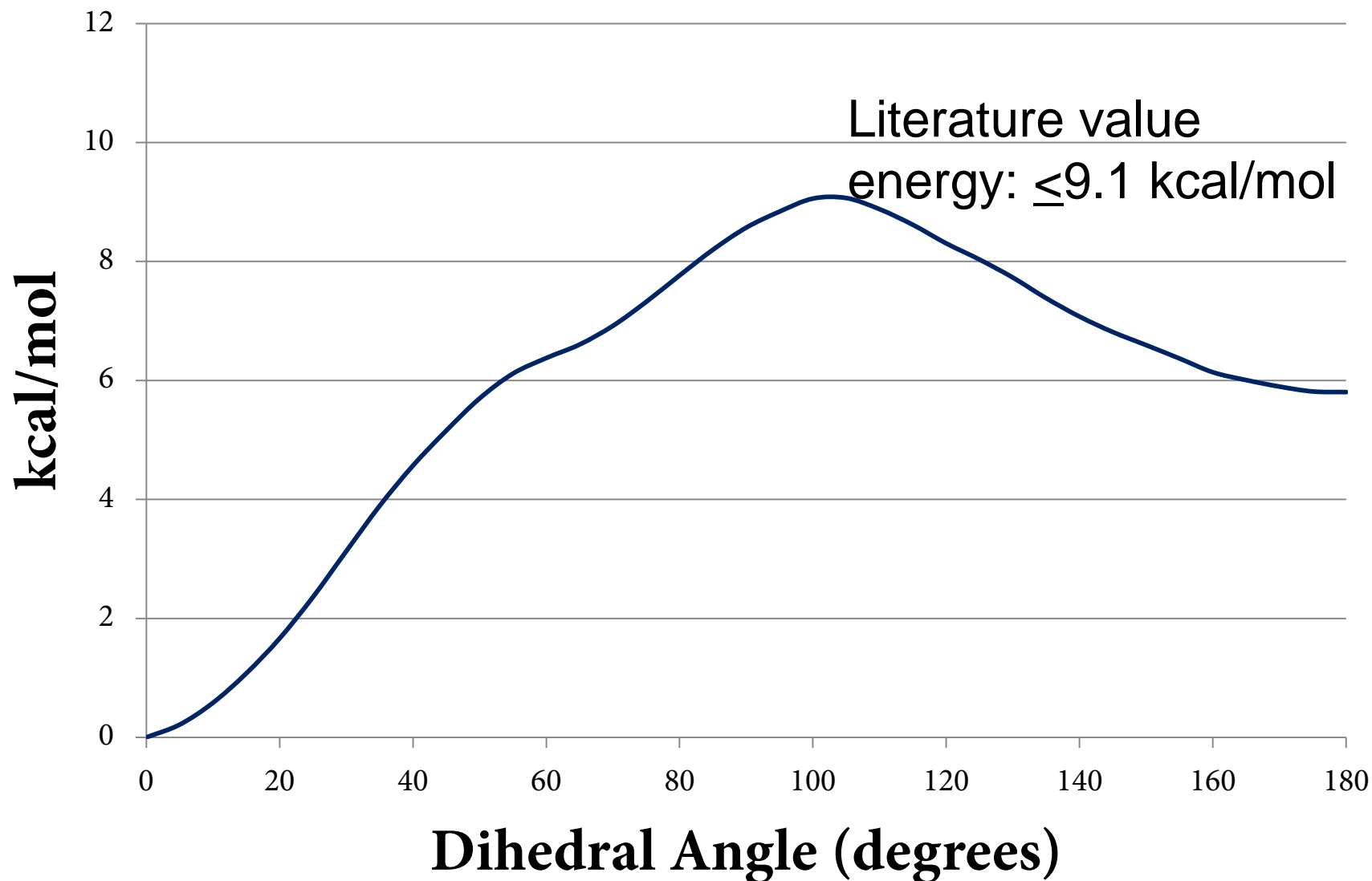


Umbrella Sampling

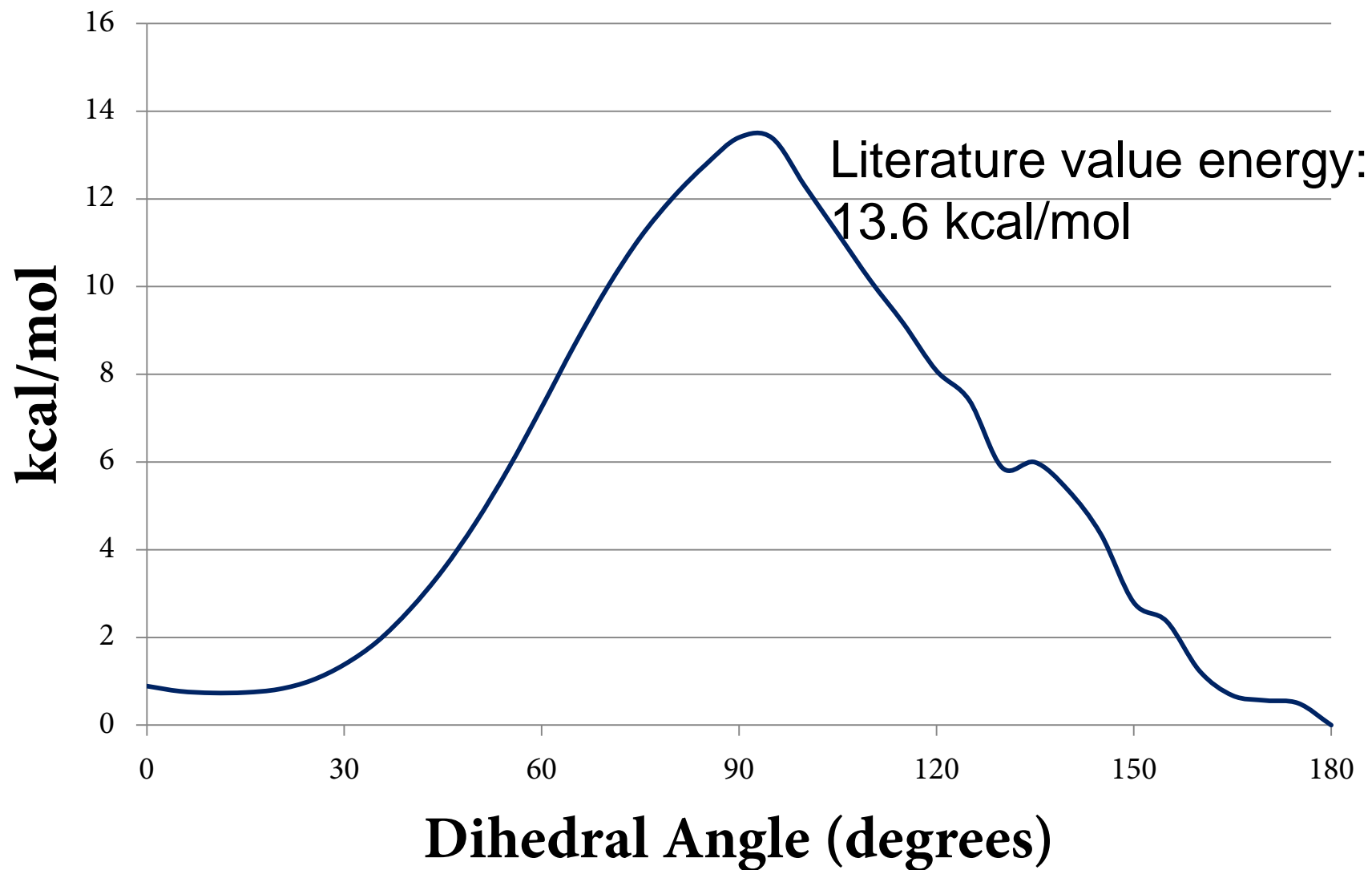
- Umbrella Sampling
 - Multiple runs held at different angle ranges.
 - 0 to 180 degrees, 5 degrees apart.



DAP 2A (ABF)

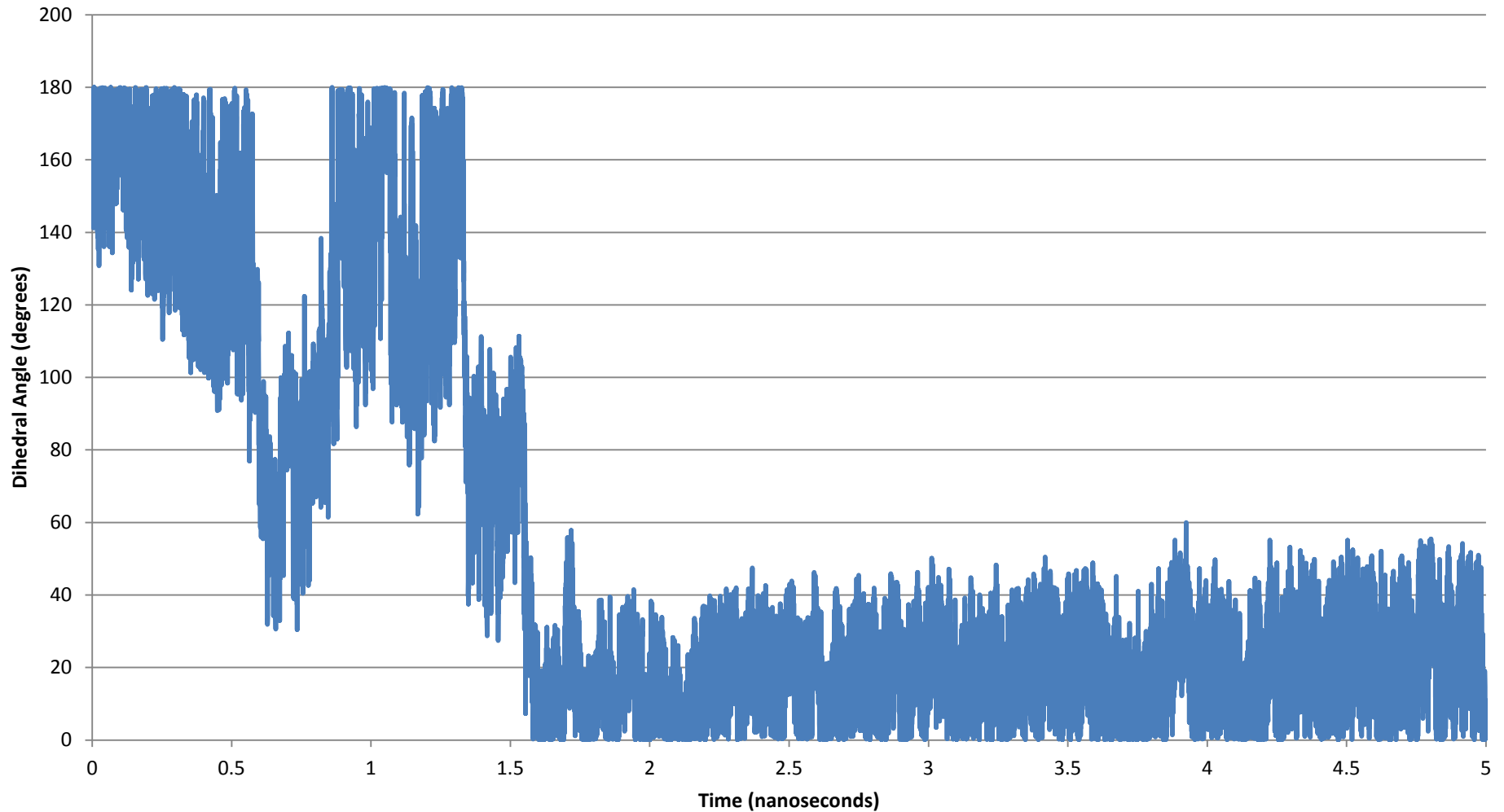


DAP 2B (ABF)



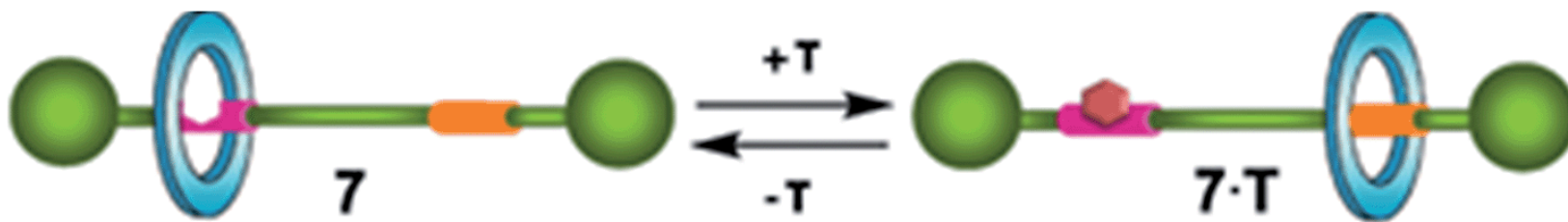
Sampling

Dihedral Angle vs Time



Future Direction

- Run ABF with a distance variable added.
 - Way of measuring energy involved in shuttling.
- Apply bias to allow thread to shuttle through macrocycle.



Acknowledgements

Concordia University
Summer Undergraduate Research Institute

Dr. Andrew Johnson

References

- Gokhan Barin, Ross S. Forgan, J. Fraser Stoddart Proc. R. Soc. A 2012 468 2849-2880; DOI: 10.1098/rspa.2012.0117. Published 24 August 2012
- Humphrey, W., Dalke, A. and Schulten, K., "VMD - Visual Molecular Dynamics", J. Molec. Graphics, 1996, vol. 14, pp. 33-38.
- James C. Phillips, Rosemary Braun, Wei Wang, James Gumbart, Emad Tajkhorshid, Elizabeth Villa, Christophe Chipot, Robert D. Skeel, Laxmikant Kale, and Klaus Schulten. Scalable molecular dynamics with NAMD. *Journal of Computational Chemistry*, 26:1781-1802, 2005.
- Martinez-Cuezva, A., Pastor, A., Cioncoloni, G., Orenes, R., Alajarin, M., Symes, M., & Bernal, J. (2015). Versatile control of the submolecular motion of di(acylamino)pyridine-based [2] rotaxanes. *Chemical Science*, 6(5), 3087-3094.
- Matthijs R. Panman, Pavol Bodis, Danny J. Shaw, Bert H. Bakker, Arthur C. Newton, Euan R. Kay, David A. Leigh, Wybren Jan Buma, Albert M. Brouwer and Sander Woutersen, Time-resolved vibrational spectroscopy of a molecular shuttle, *Phys. Chem.* 14, 2014