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

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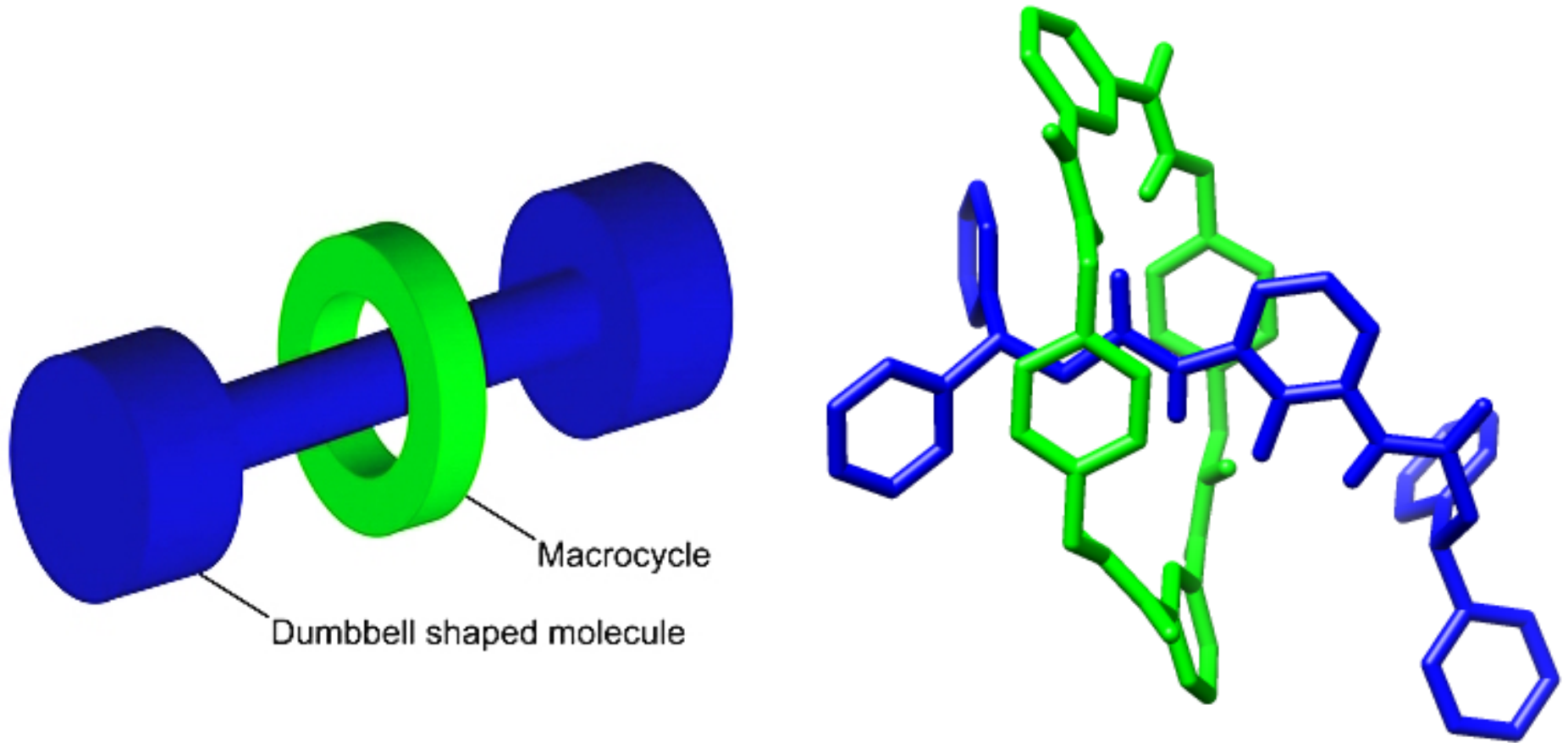
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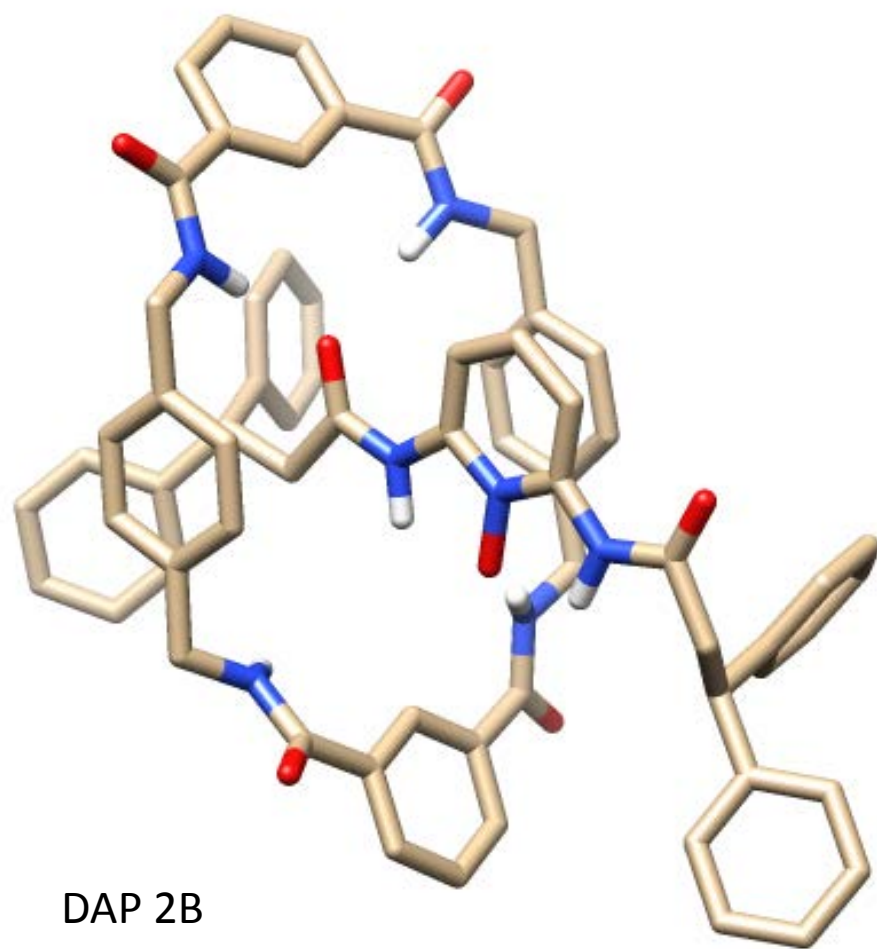
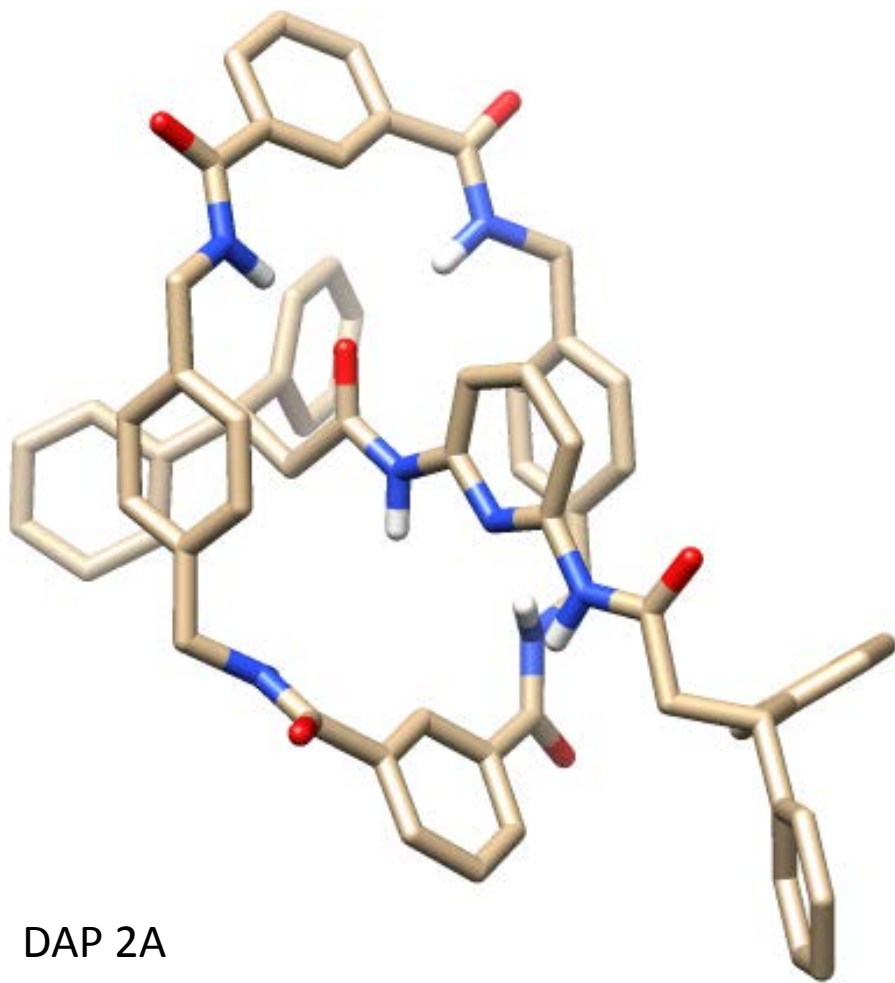
A Comprehensive Exploration of the
Conformational and Energetic Landscape
of a Rotaxane System: A Molecular
Dynamics Study.

Ken Bodzewski

Rotaxanes

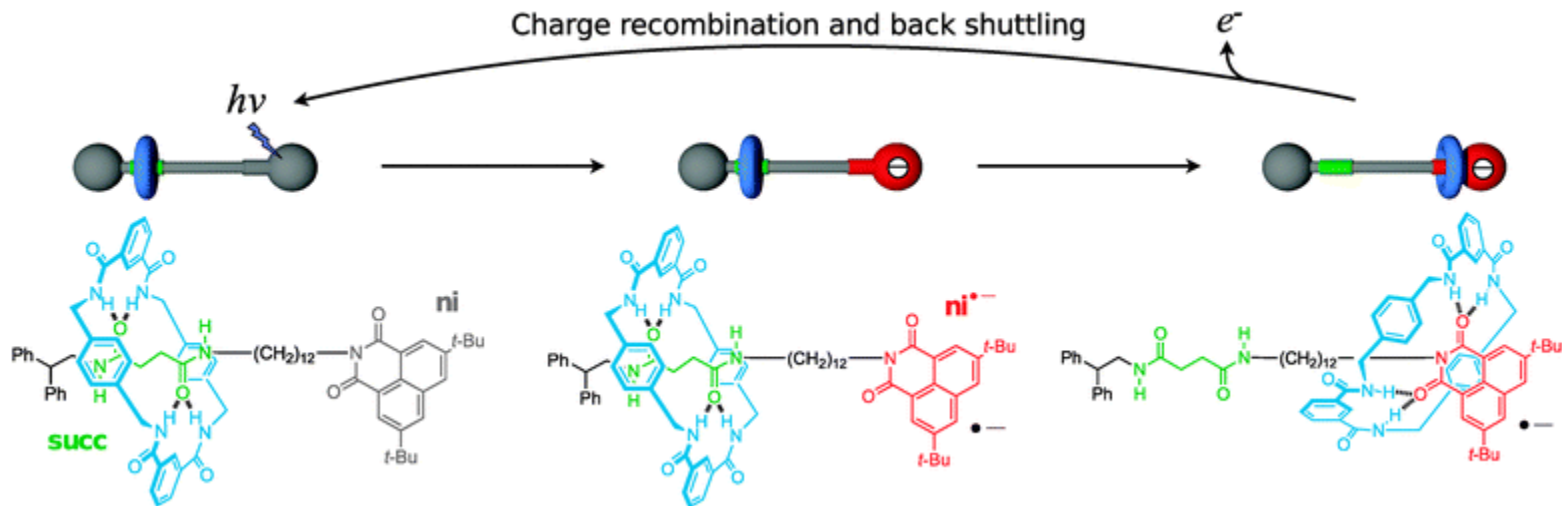


Di(acylamino)pyridine (DAP) based rotaxanes



Relevance

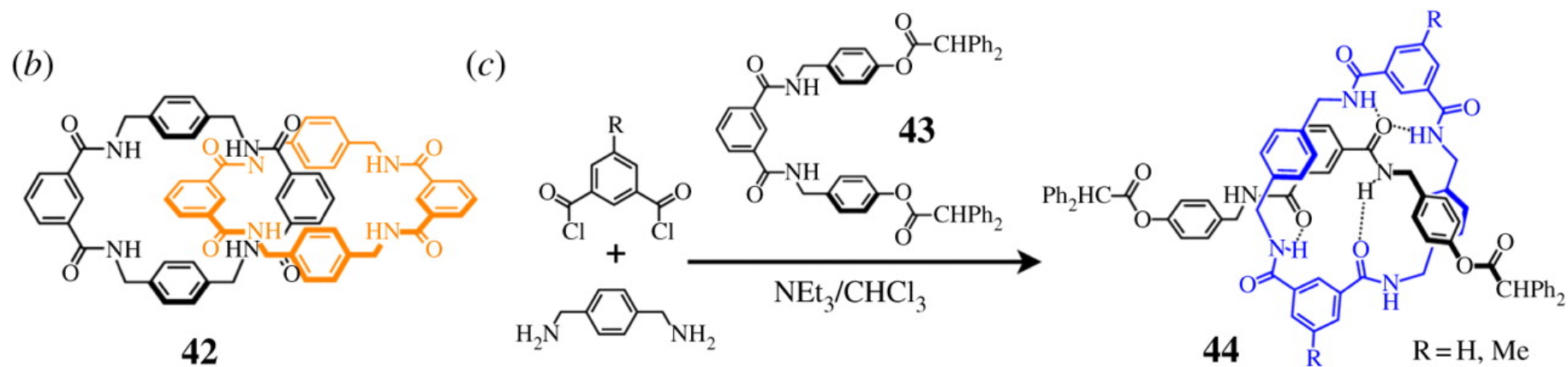
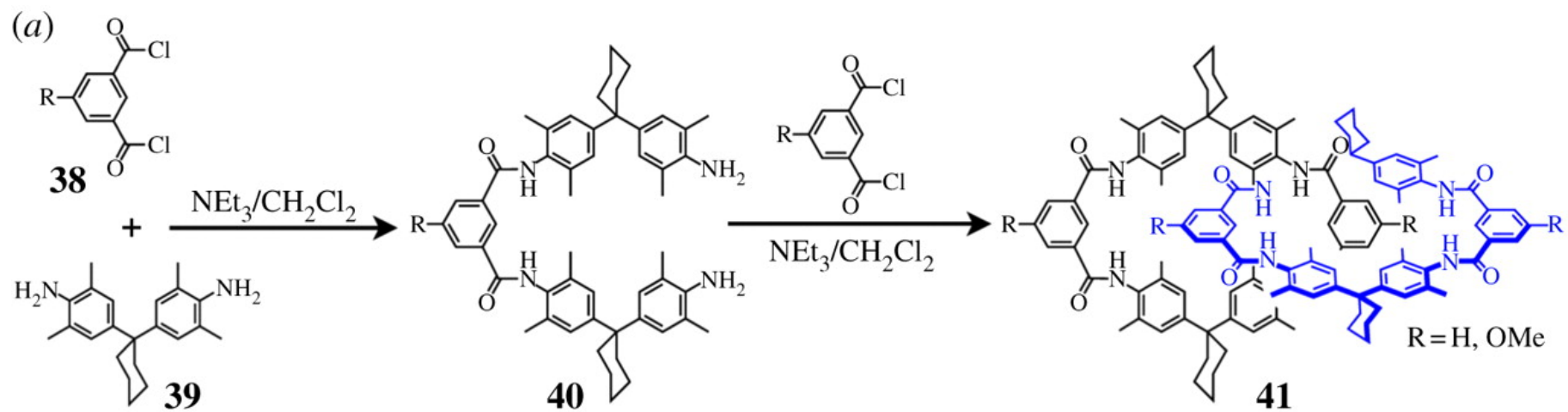
- Rotaxanes are being used more and more.
 - Molecular machines.
 - Switches to turn them “on” and “off”
 - Rotation is often paired with a sliding or “shuttling.”



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

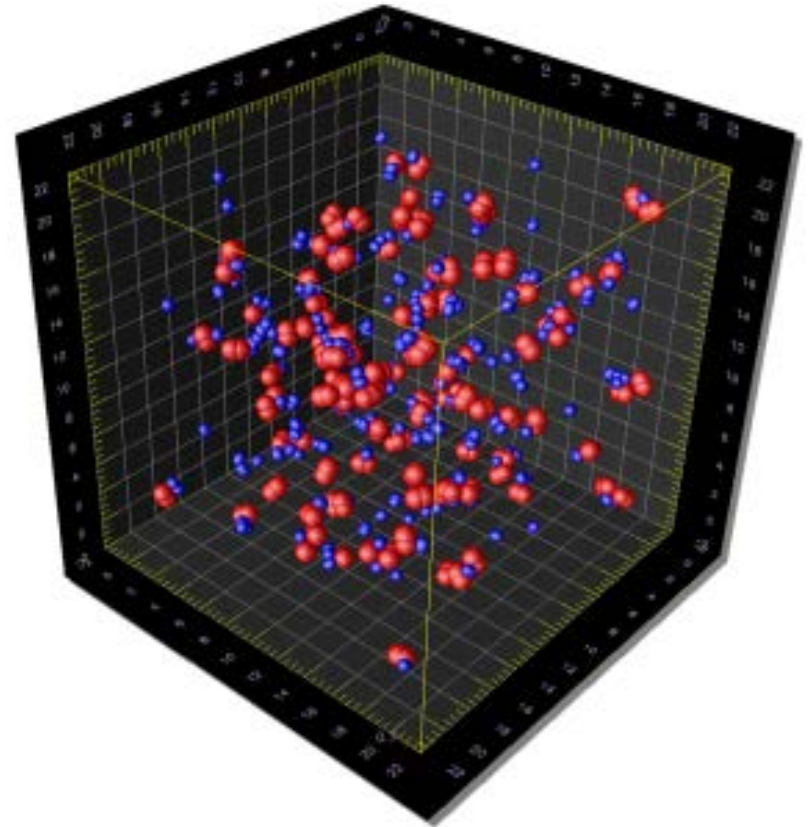


(Gokhan Barin, Ross S. Forgan, J. Fraser Stoddart

Proc. R. Soc. A 2012 468 2849-2880; DOI: 10.1098/rspa.2012.0117. Published 24 August 2012)

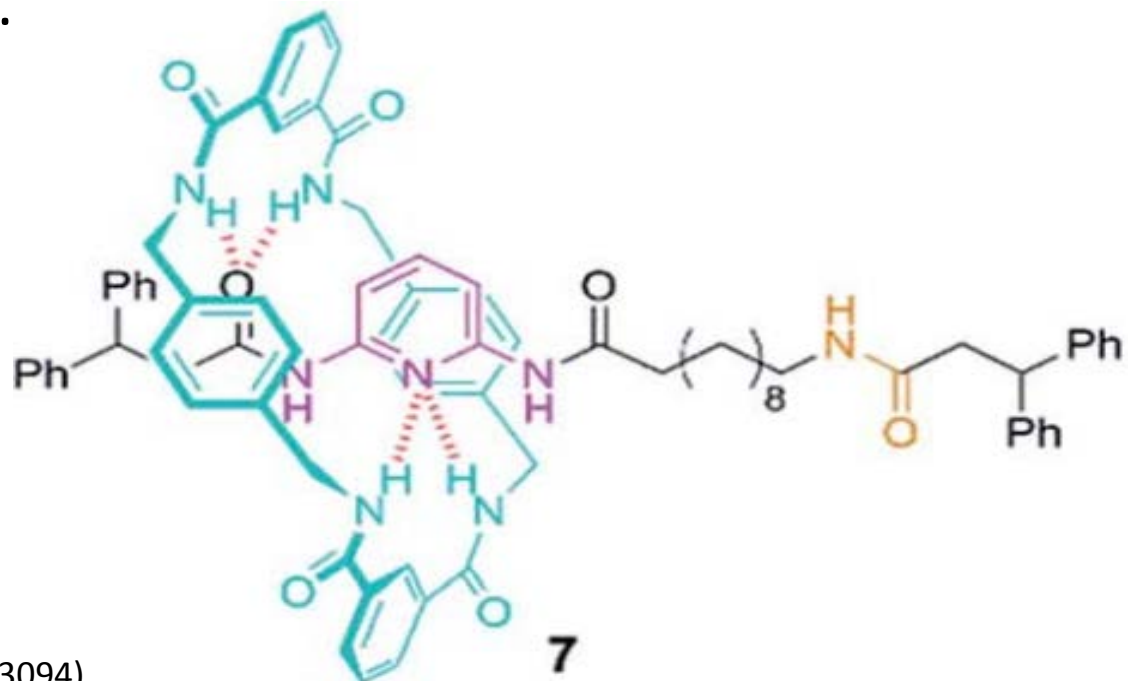
Molecular Dynamics

- 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.

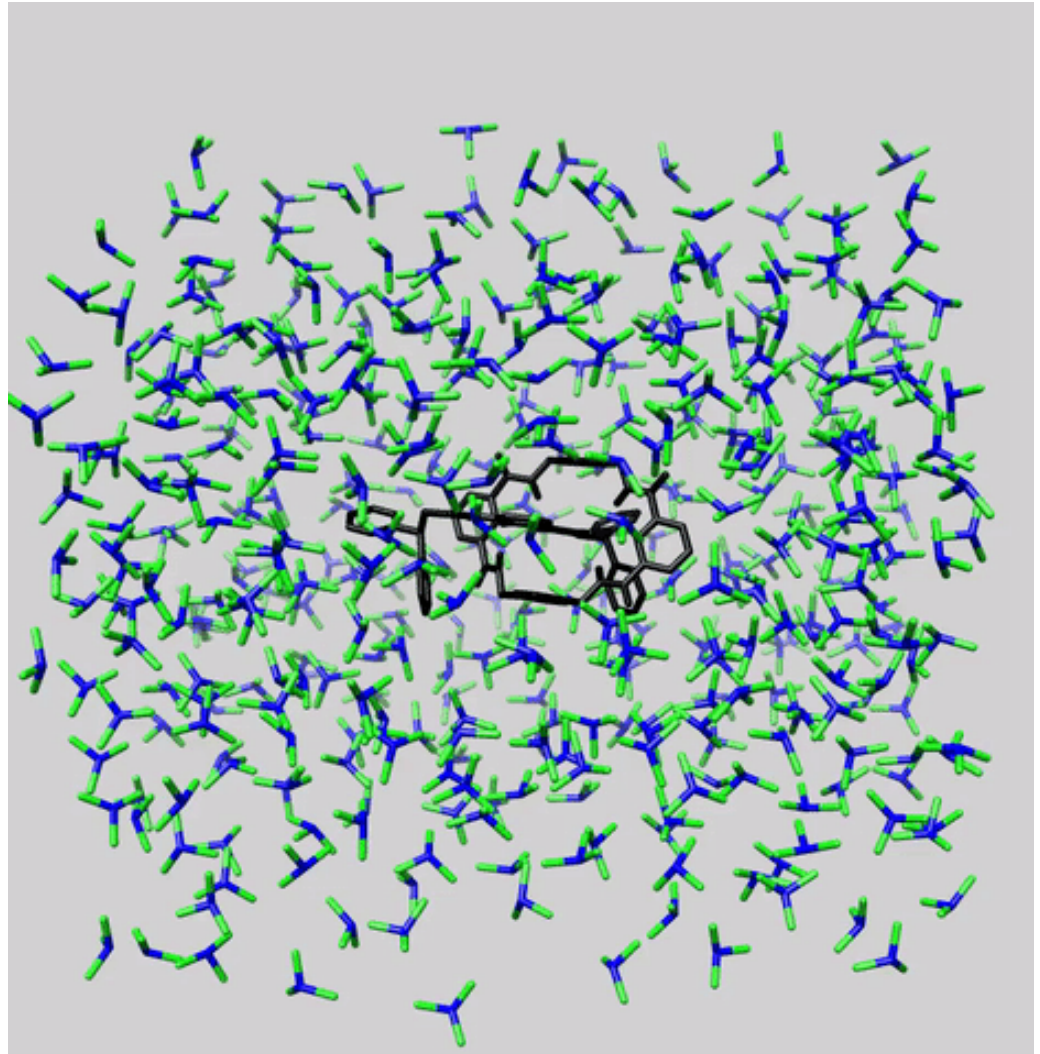


Procedure

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

Procedure

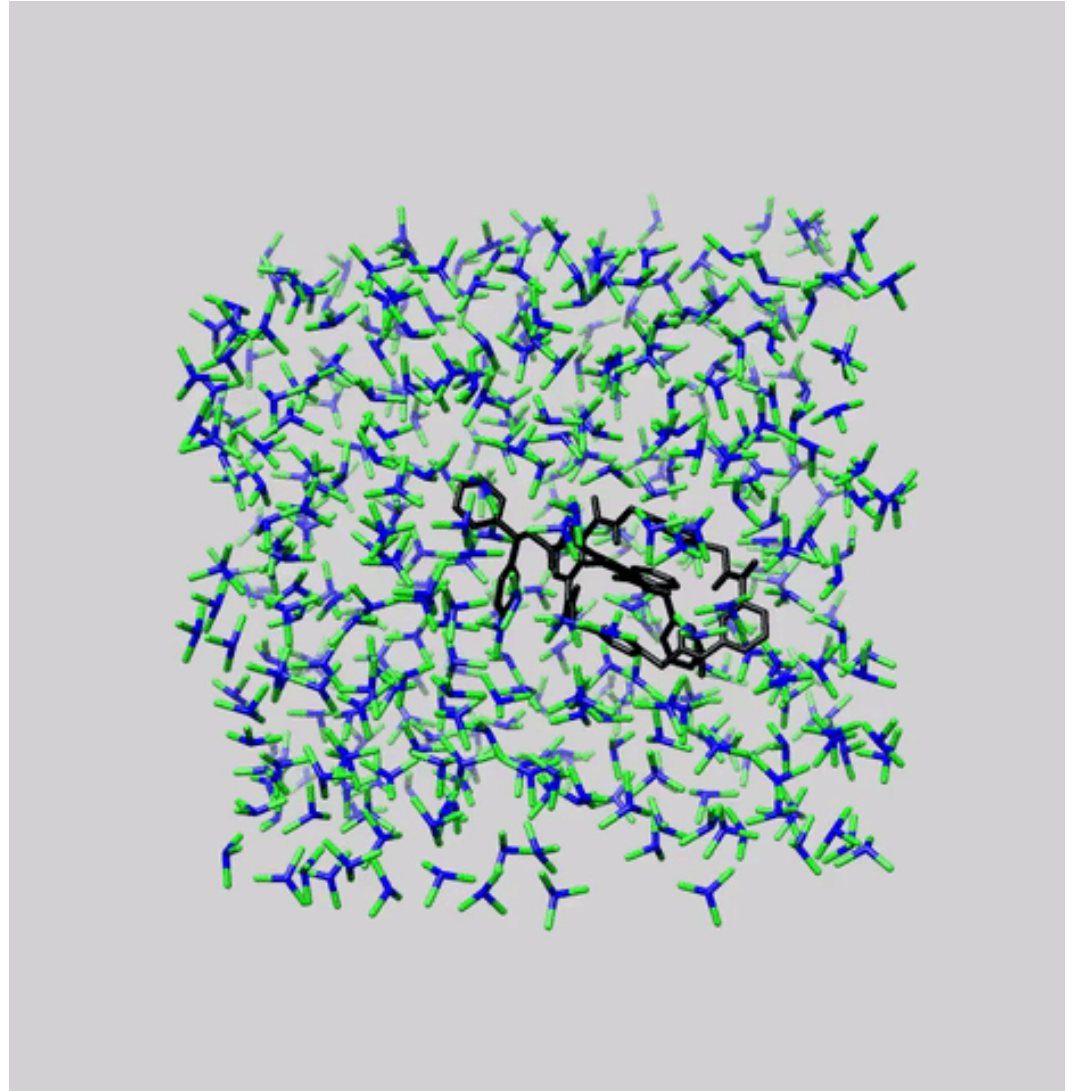
- Rotaxane held still while chloroform is relaxed.
- Whole system is relaxed.



(visualized with chimera)

Procedure

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



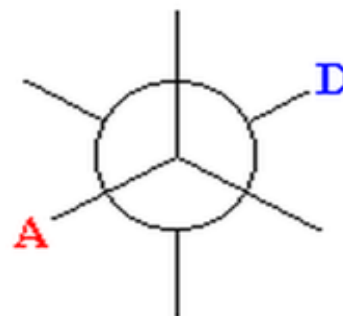
(visualized with chimera)

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.

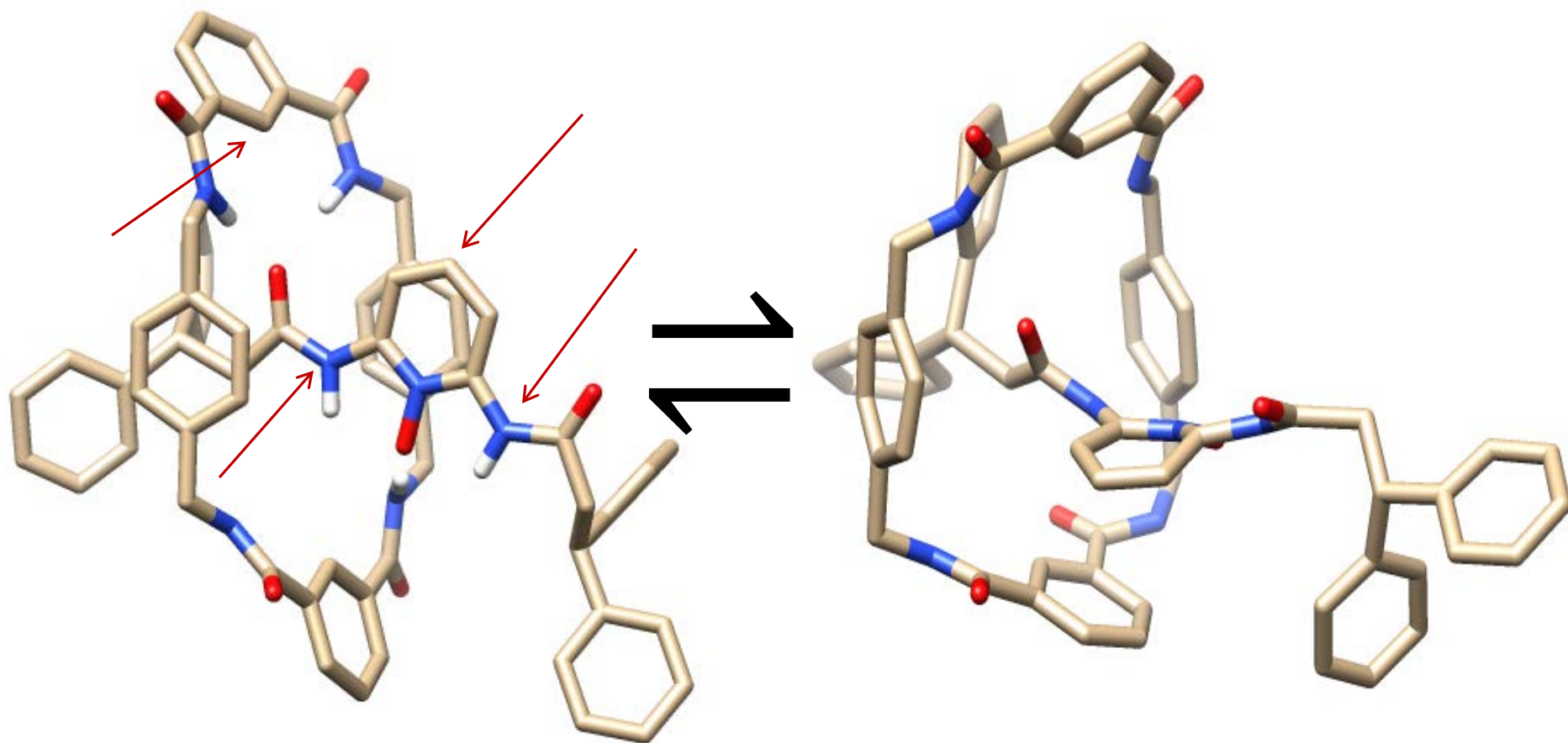


Sawhorse projection



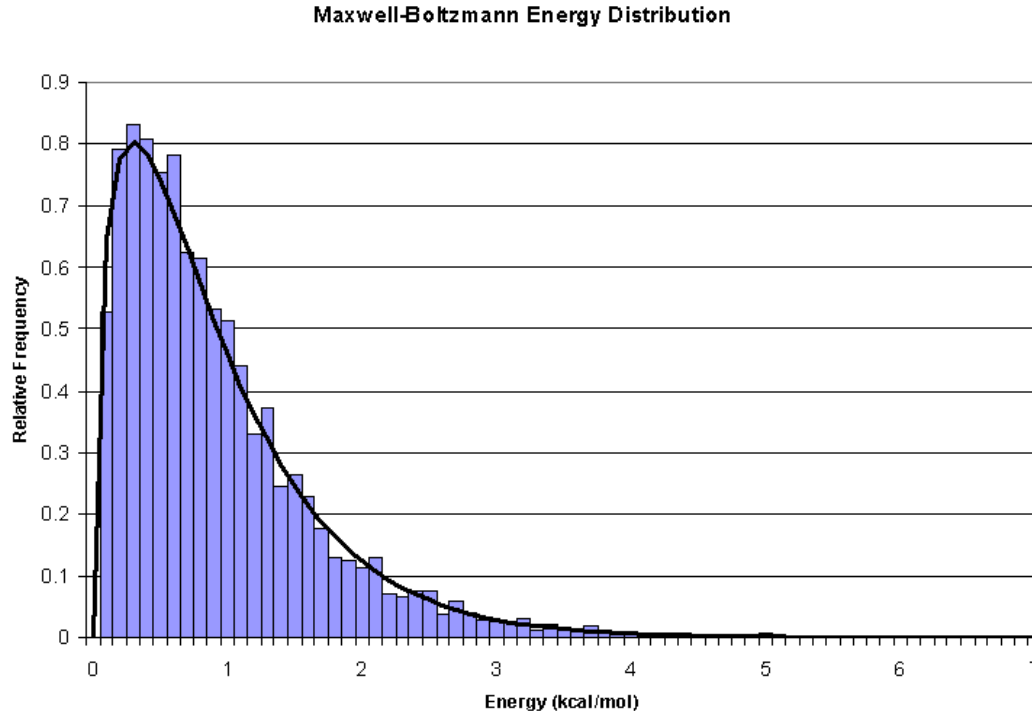
Newman projection

Simulated Rotation



Biased Sampling

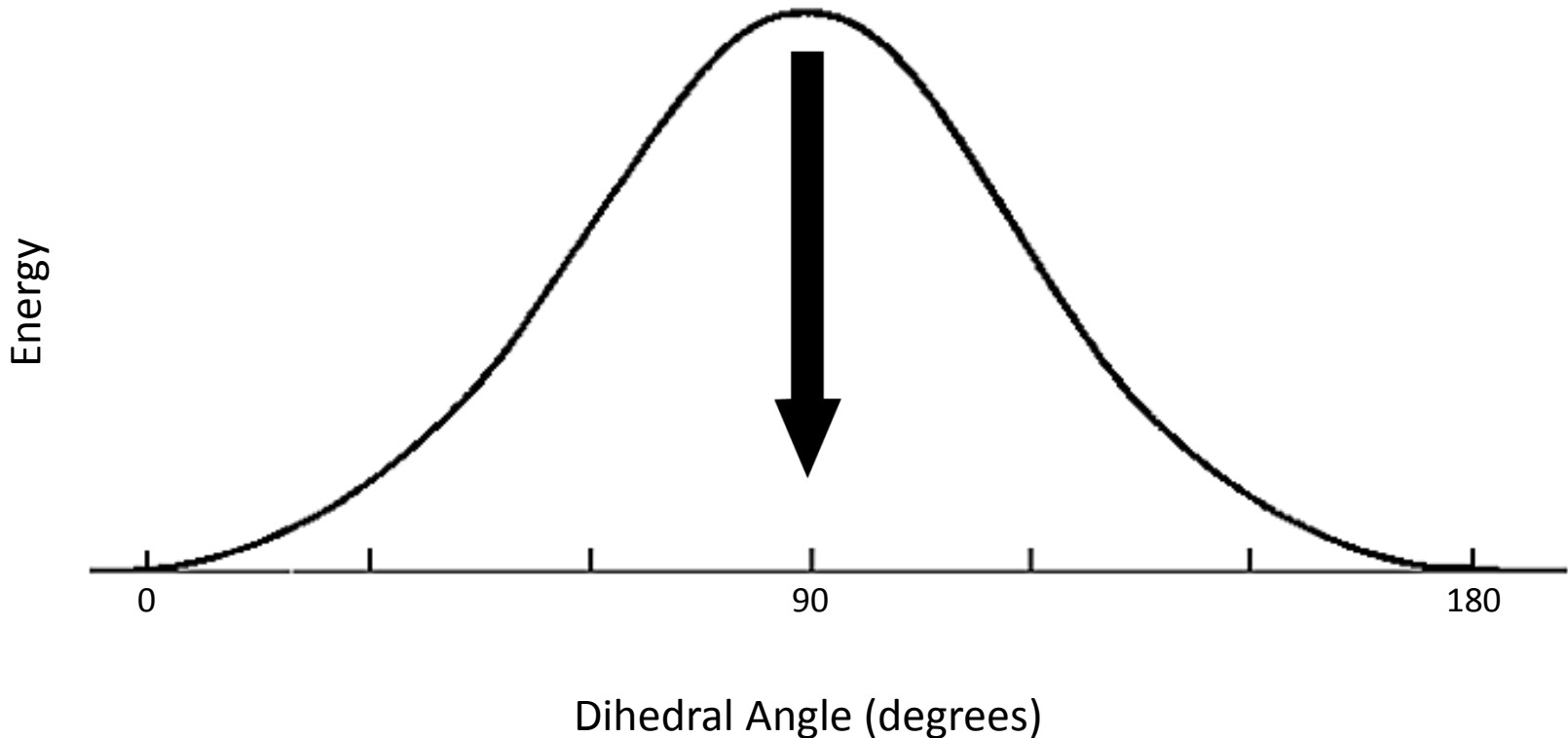
- Adaptive Biasing Force, Metadynamics, and Umbrella Sampling.
- Apply force on the system to allow molecules to go through otherwise unfavorable conformations.
- Took 3-4 hours to produce 1 nanosecond simulation.
- Much more efficient way of mapping free energy barriers.



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

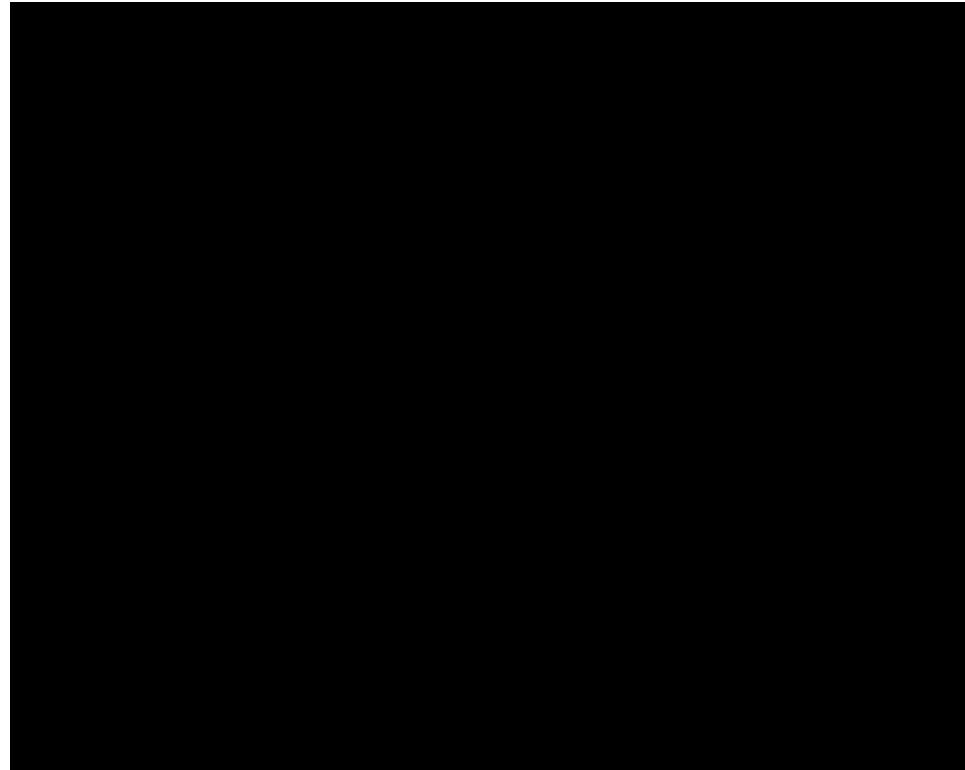
Adaptive Biasing Force

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



Metadynamics

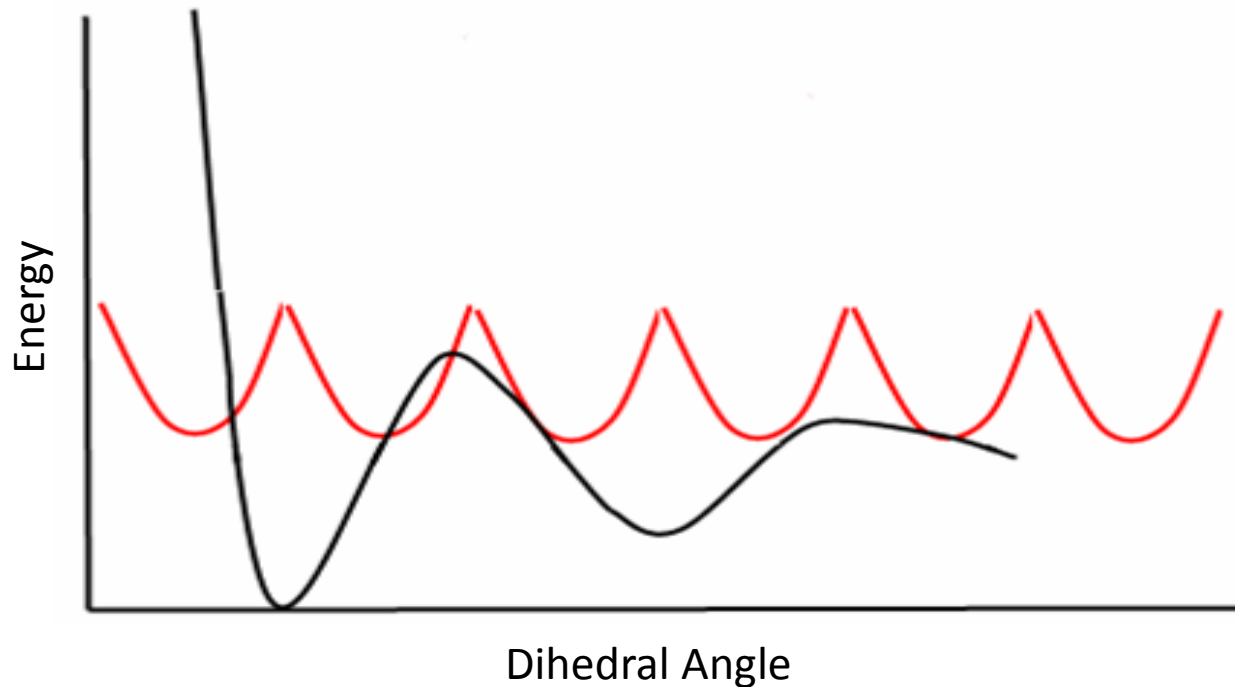
- Metadynamics
 - Flooding low energy areas to fill up energy valleys.
- Allows for more sampling at high energy states.



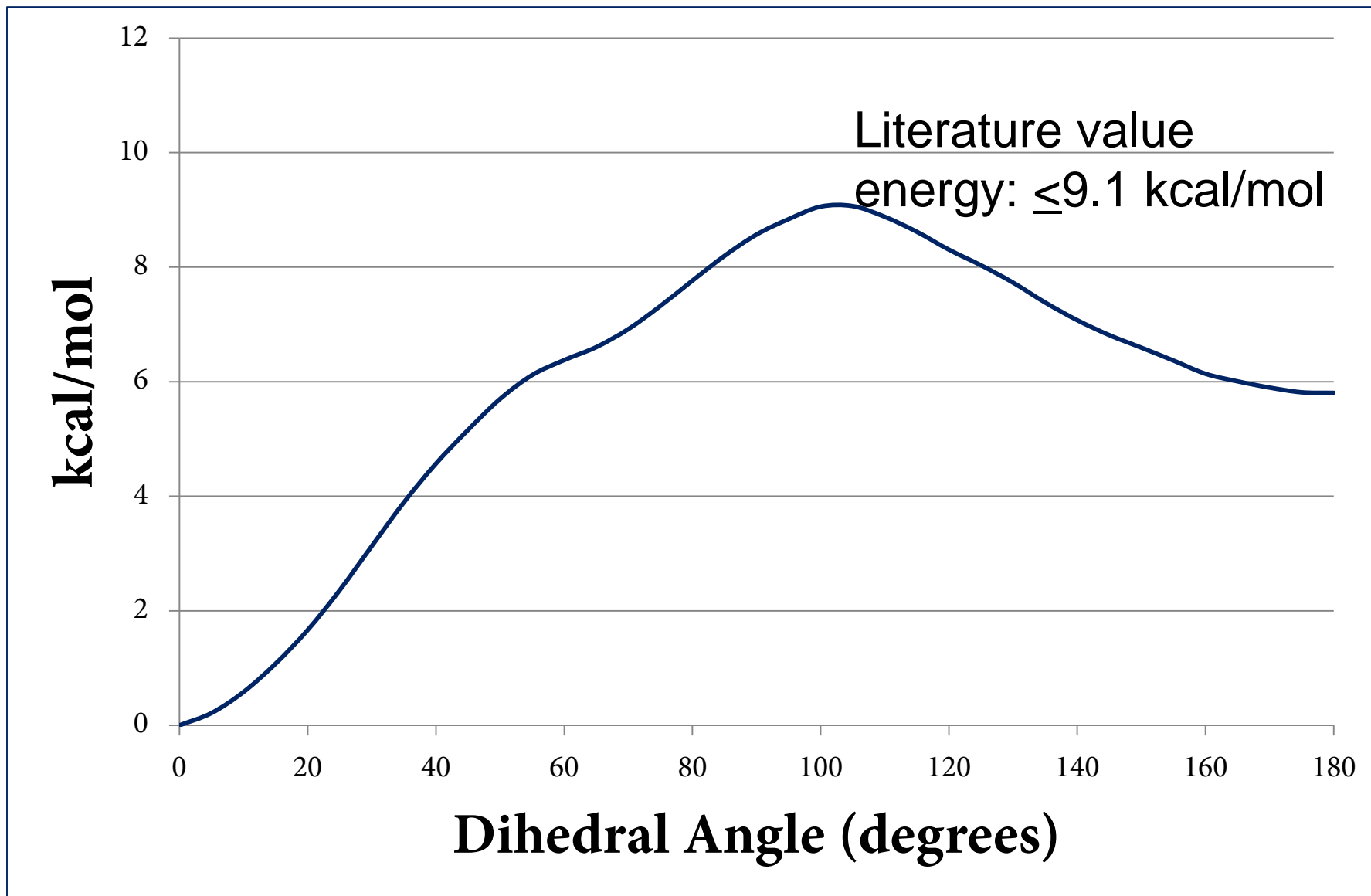
Umbrella Sampling

– Umbrella Sampling

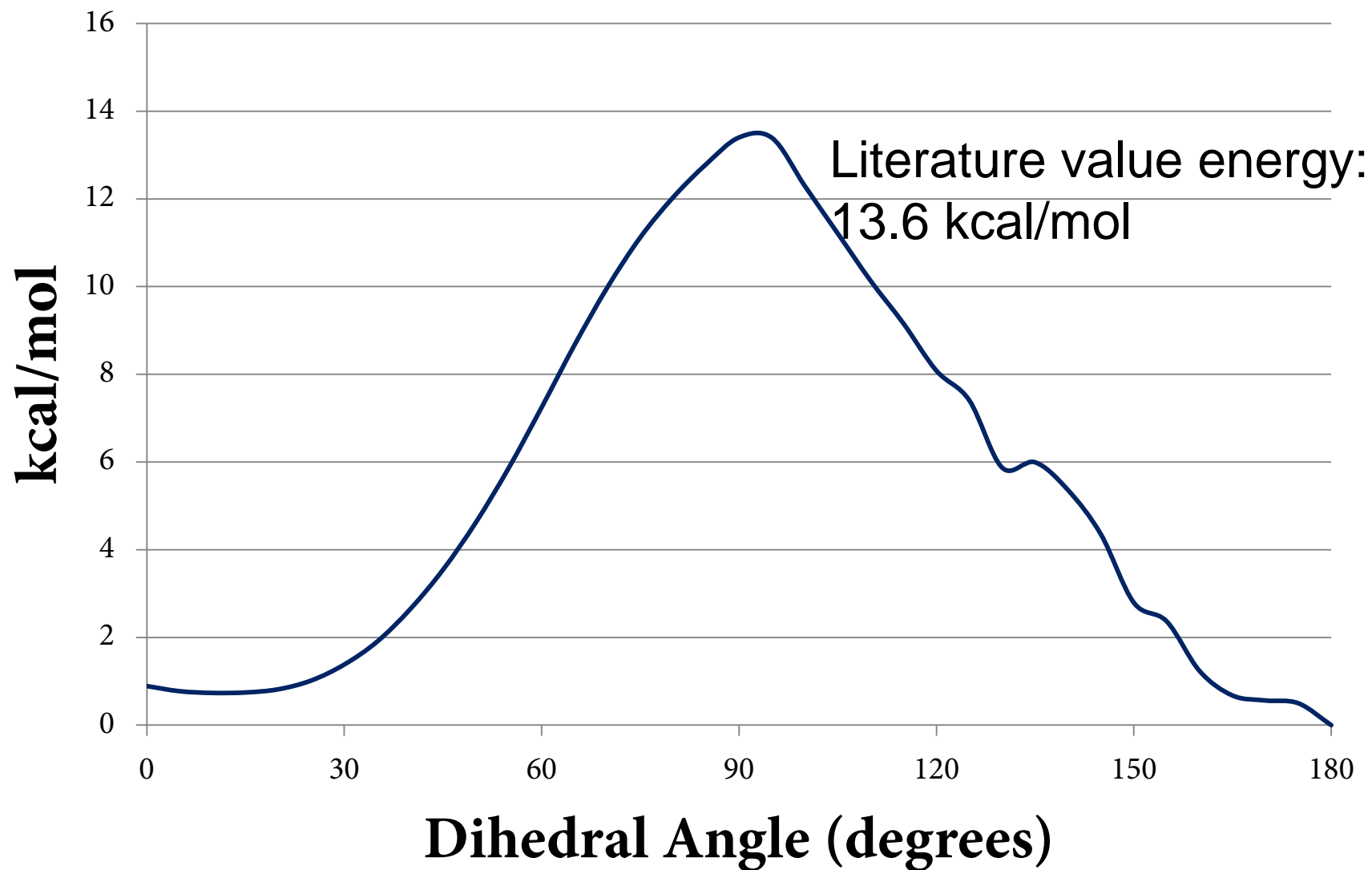
- Multiple runs held at different angle ranges.
 - 0 to 180 degrees, 5 degrees apart.



DAP 2A (ABF)

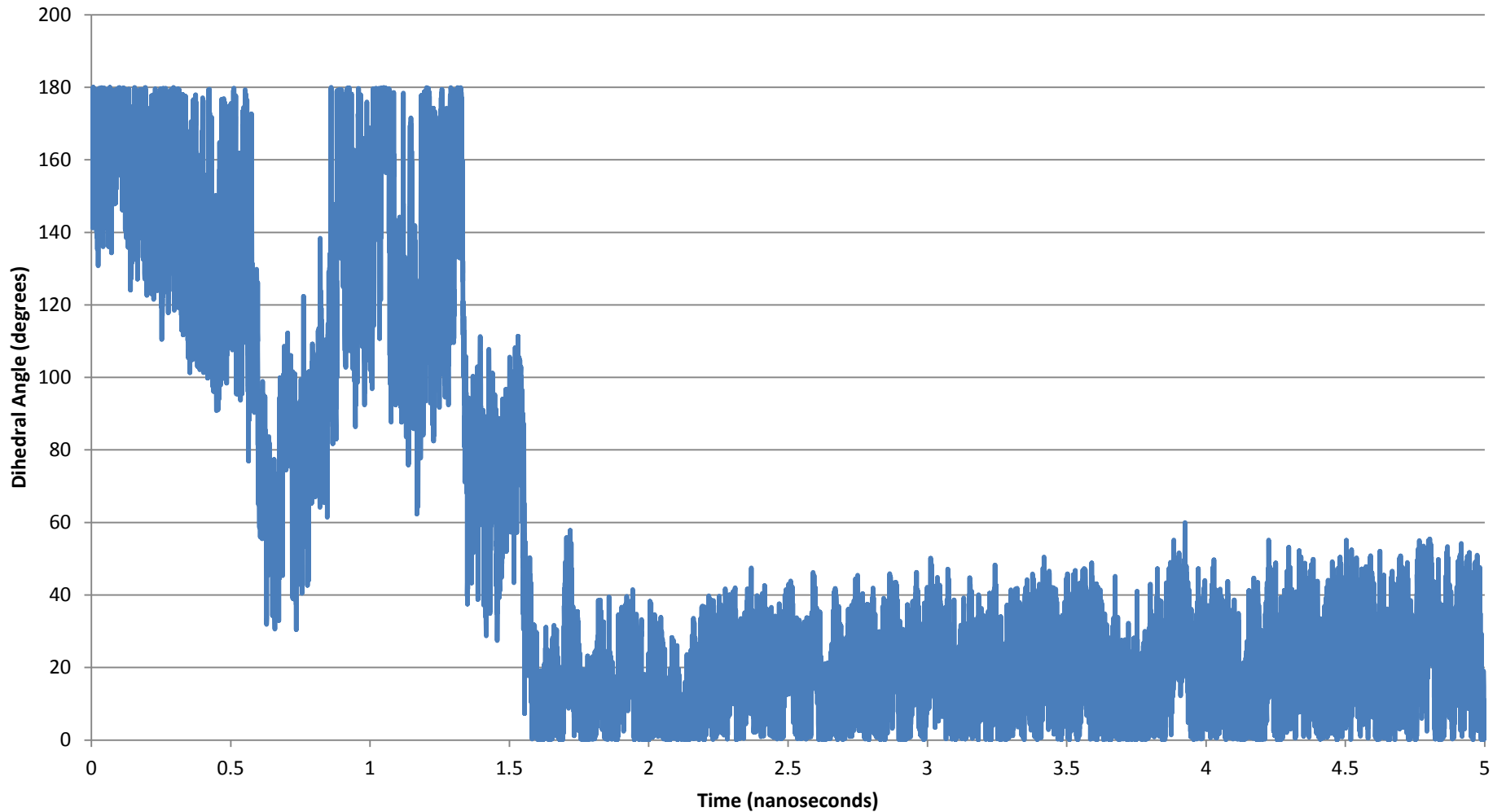


DAP 2B (ABF)



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

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