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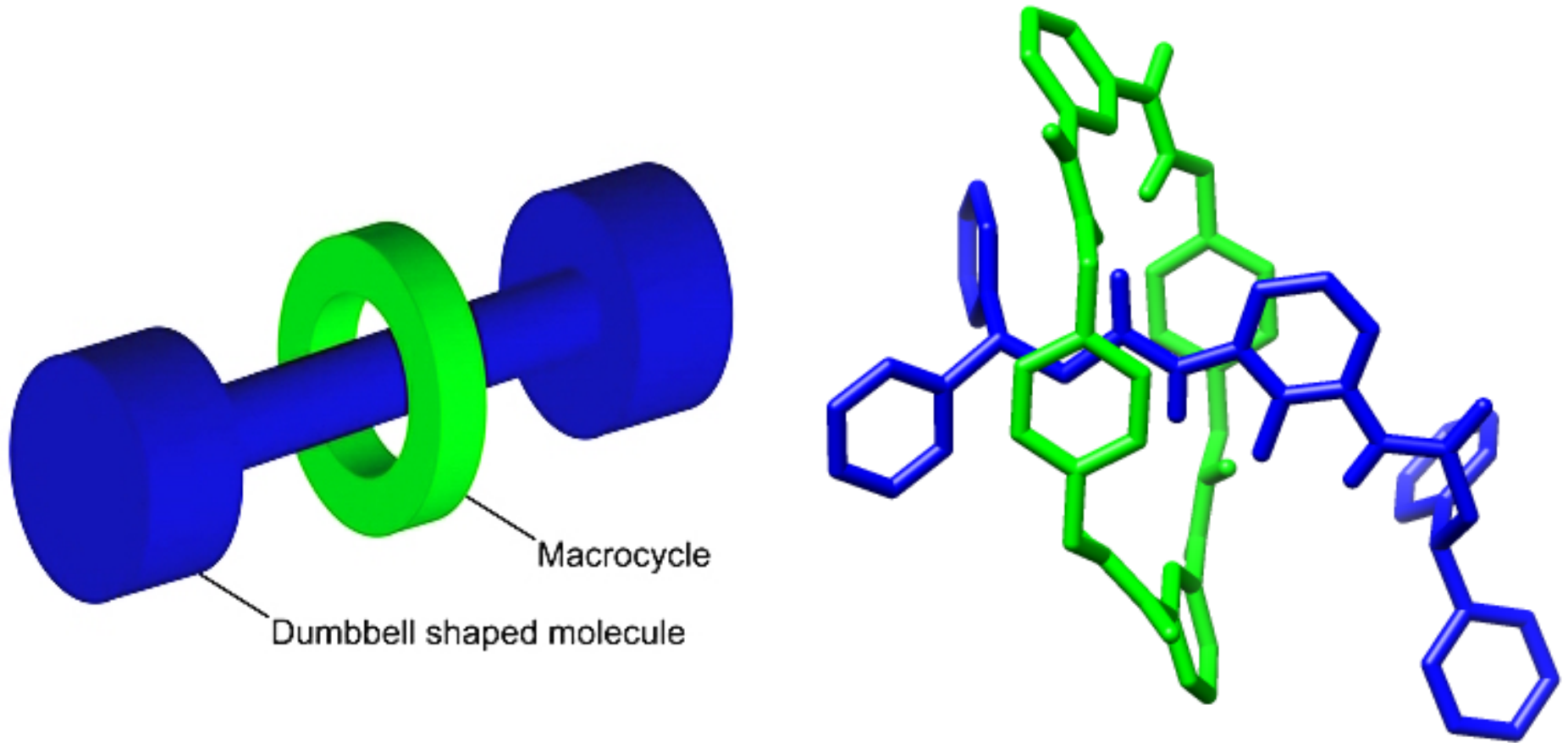
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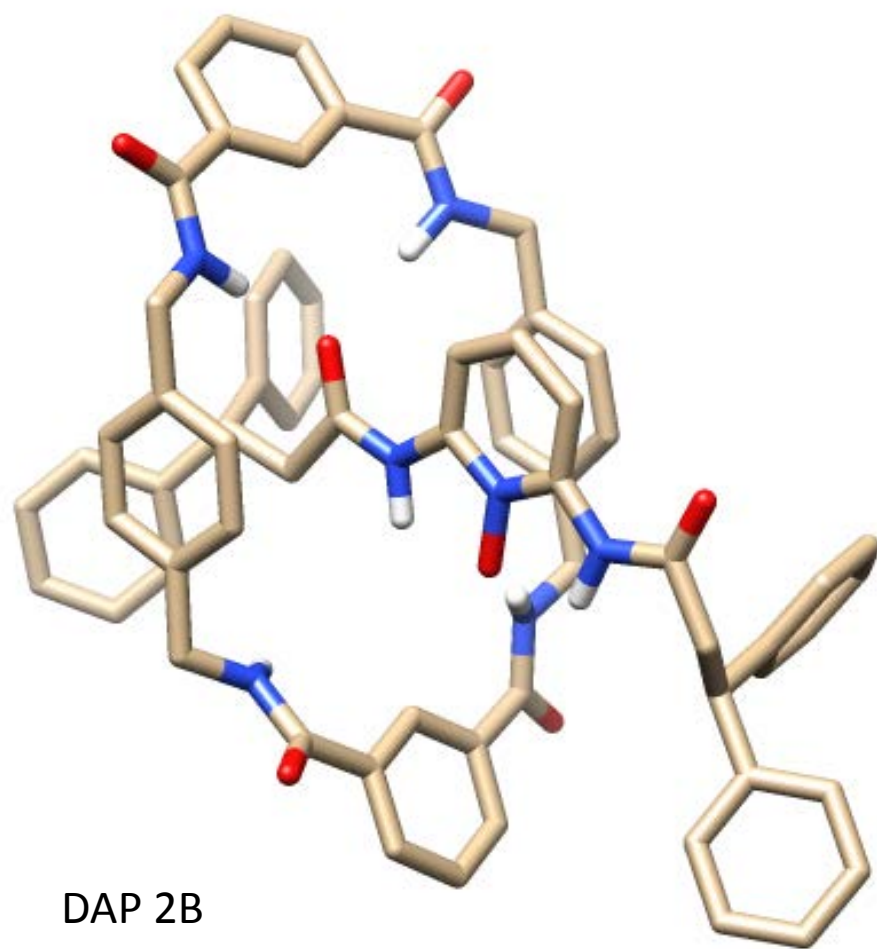
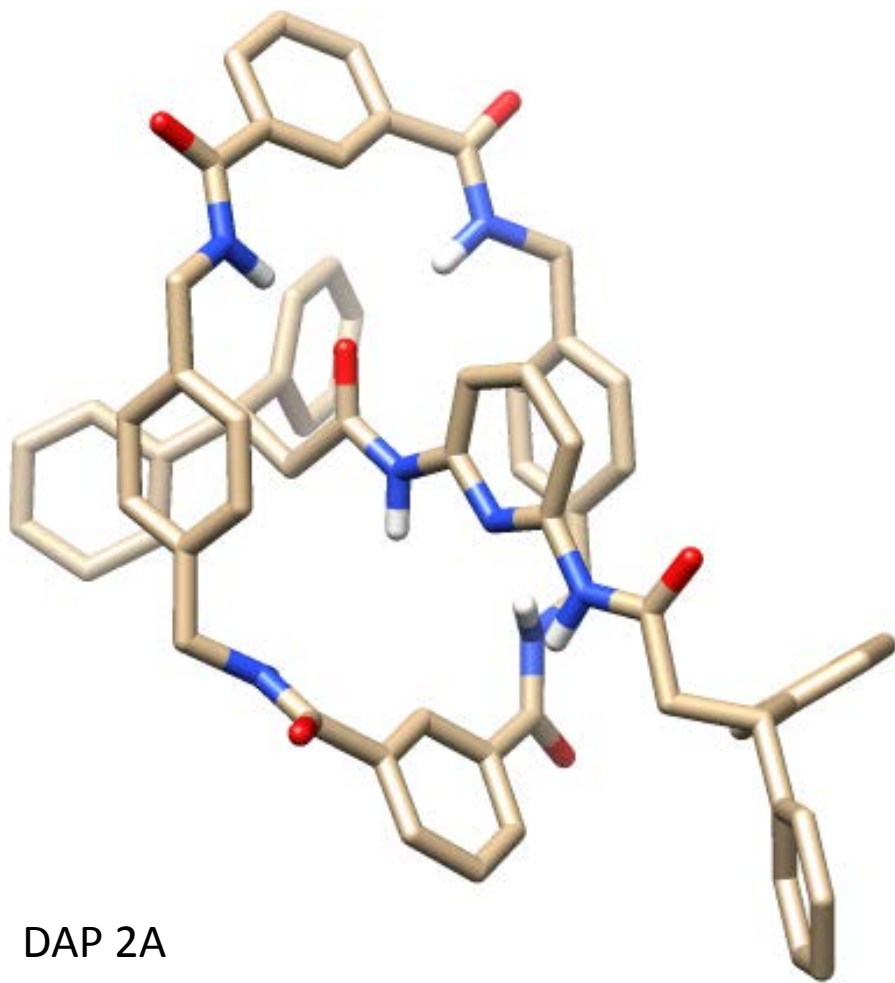
A Comprehensive Exploration of the  
Conformational and Energetic Landscape  
of a Rotaxane System: A Molecular  
Dynamics Study.

Ken Bodzewski

# Rotaxanes

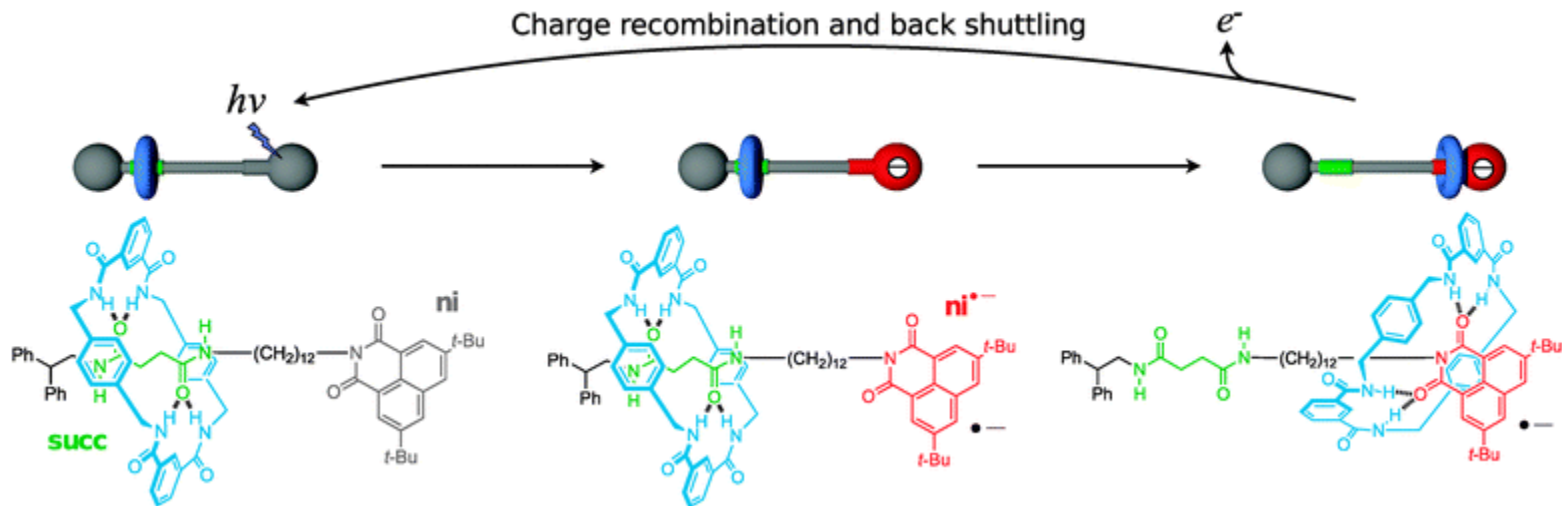


# Di(acylamino)pyridine (DAP) based rotaxanes



# Relevance

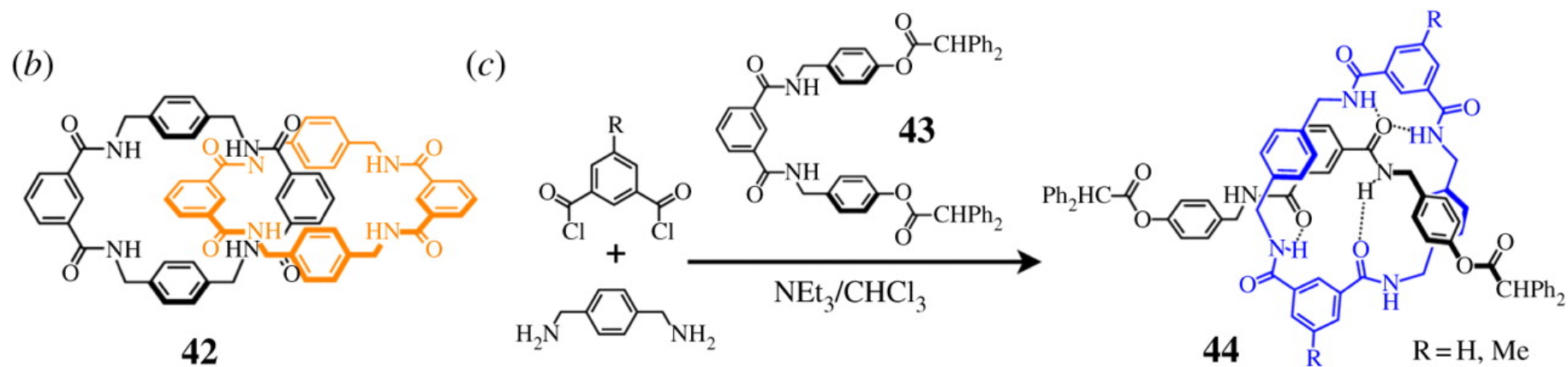
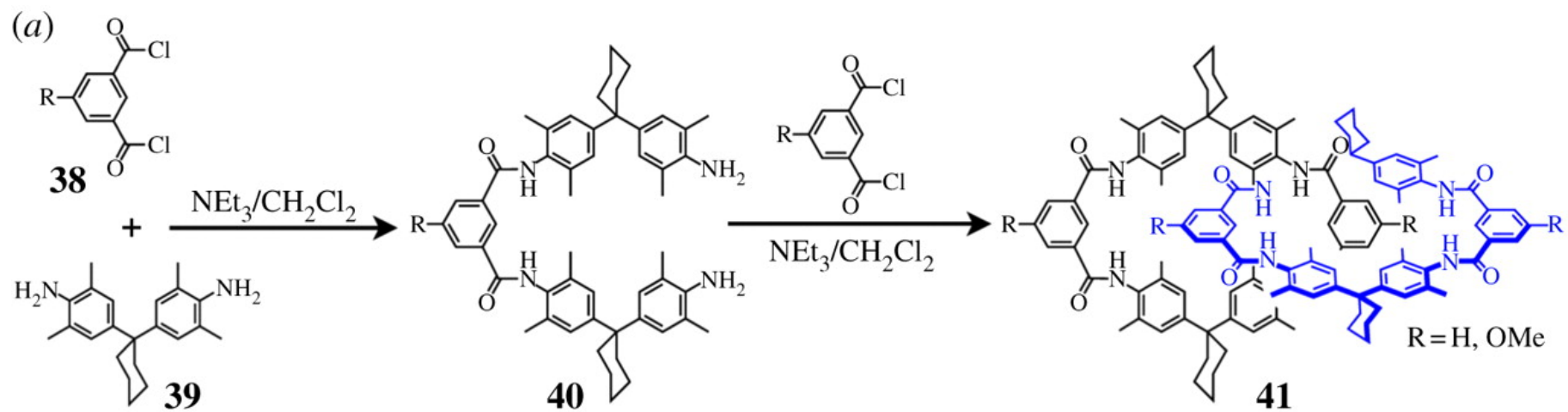
- Rotaxanes are being used more and more.
  - Molecular machines.
    - Switches to turn them “on” and “off”
    - Rotation is often paired with a sliding or “shuttling.”



# Relevance

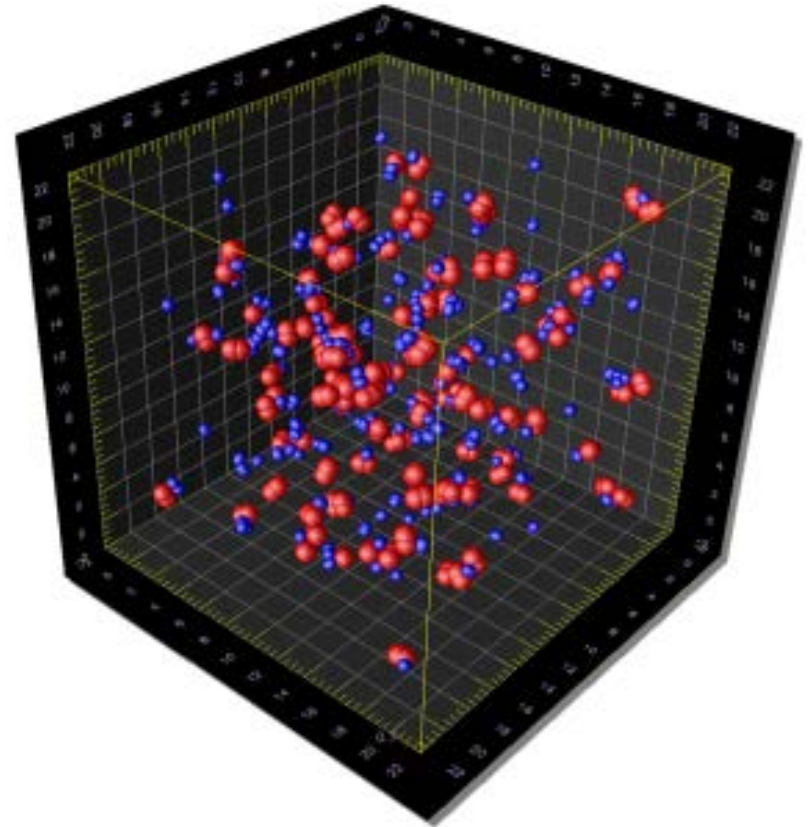
- Very difficult to make, low yield.
  - Molecular Dynamics as a way to study them before synthesizing them.
    - Use it as a predictor for how your rotaxane will respond.

# Relevance



# Molecular Dynamics

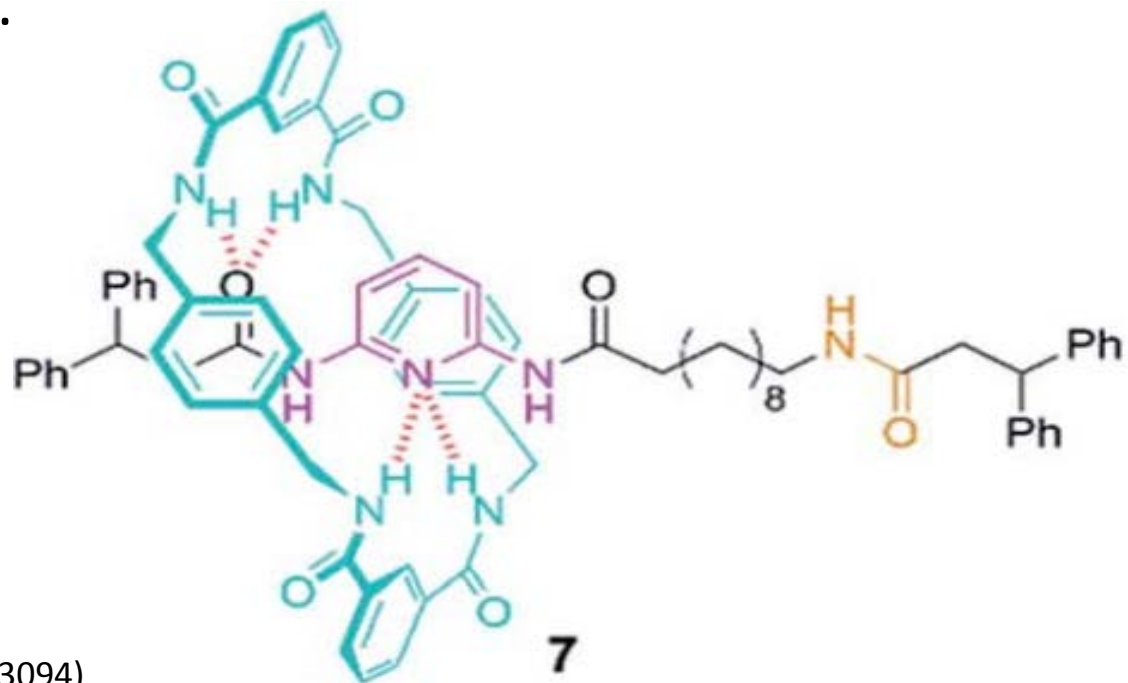
- Classical (Newtonian) mechanics.
- NAMD.
- VMD.
- Roughly 2,000 atoms in our systems.





# 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.

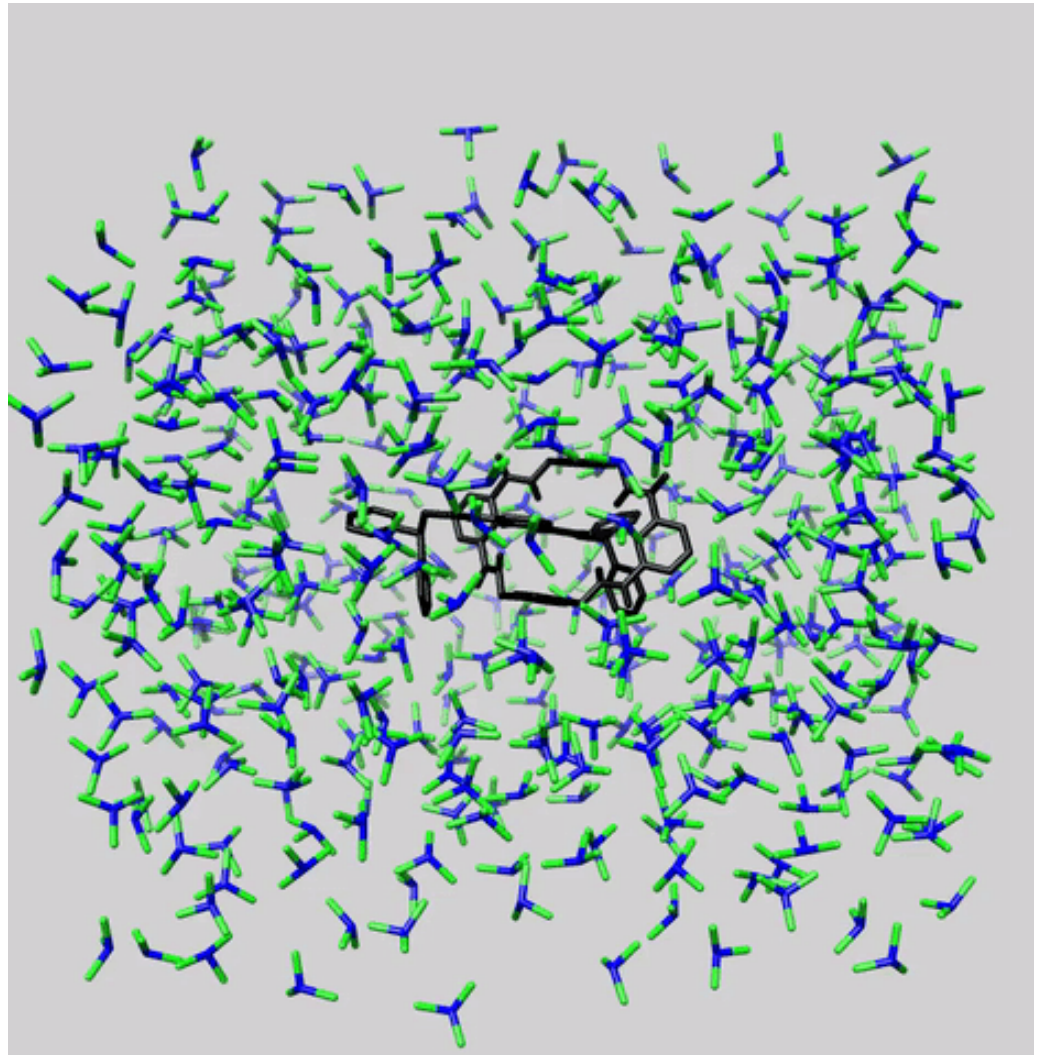


# Procedure

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

# Procedure

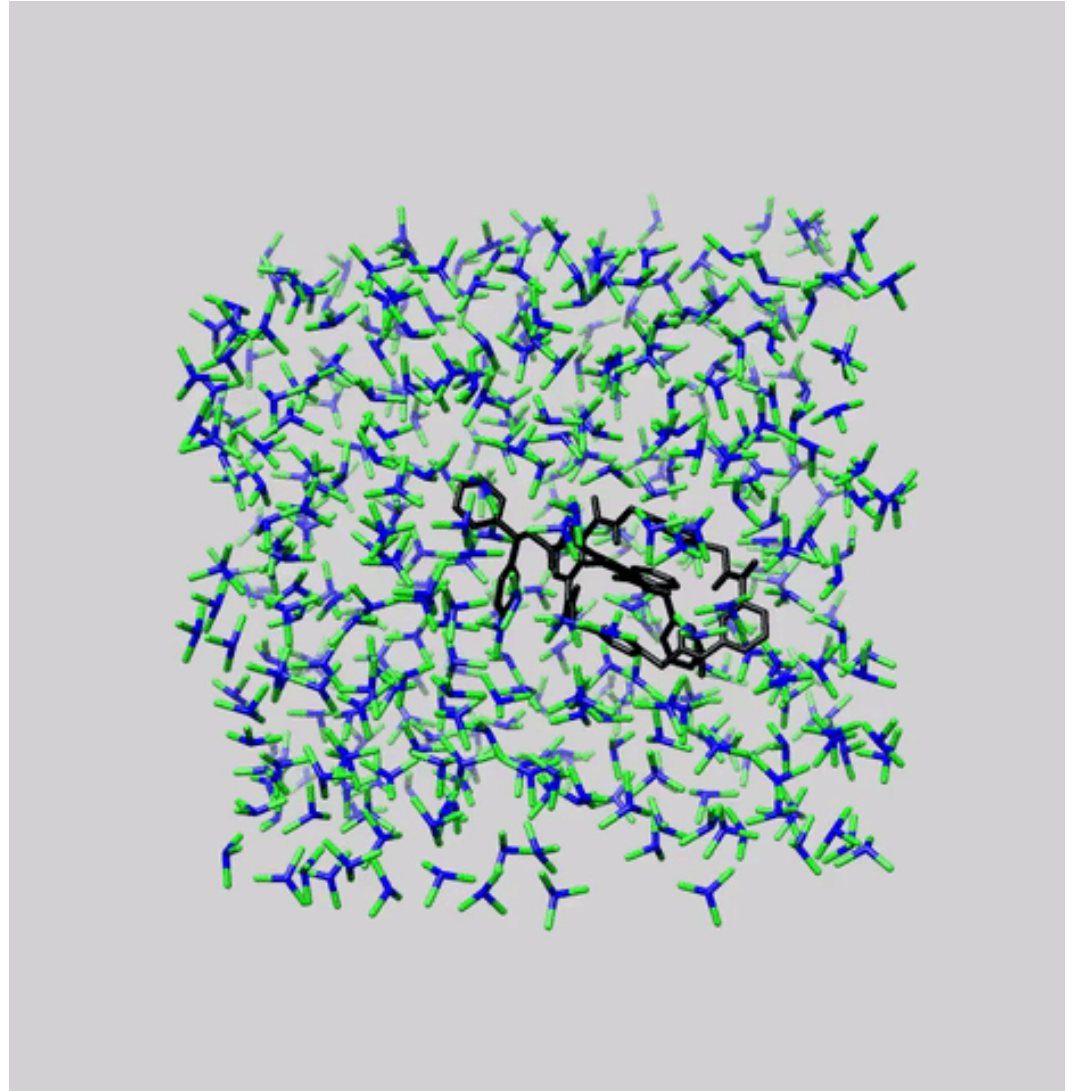
- Rotaxane held still while chloroform is relaxed.
- Whole system is relaxed.



(visualized with chimera)

# Procedure

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



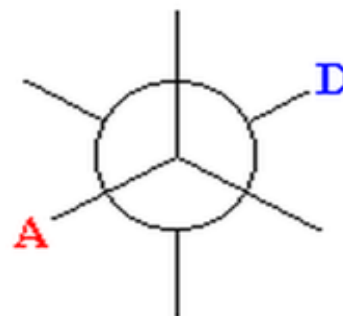
(visualized with chimera)

# 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.

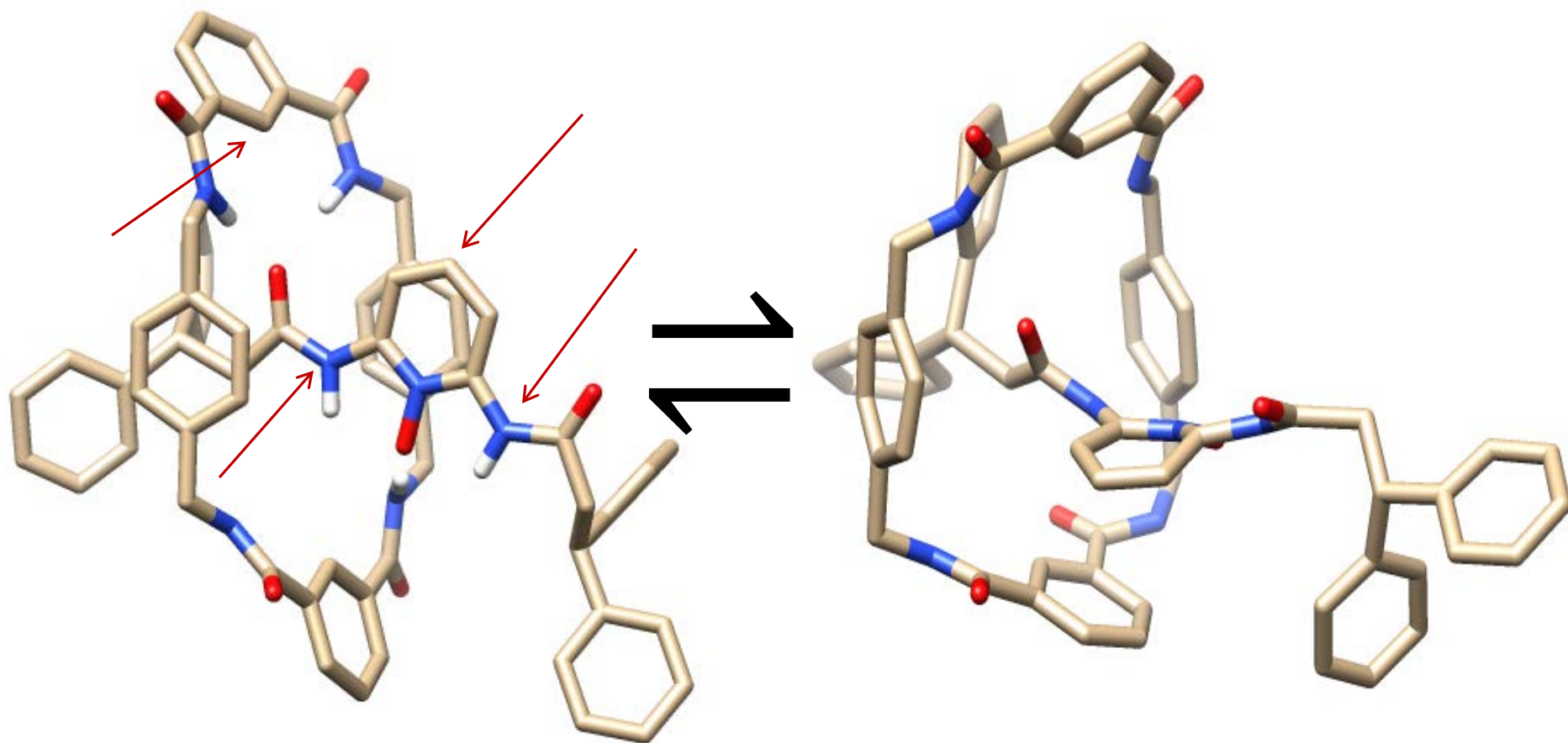


**Sawhorse projection**



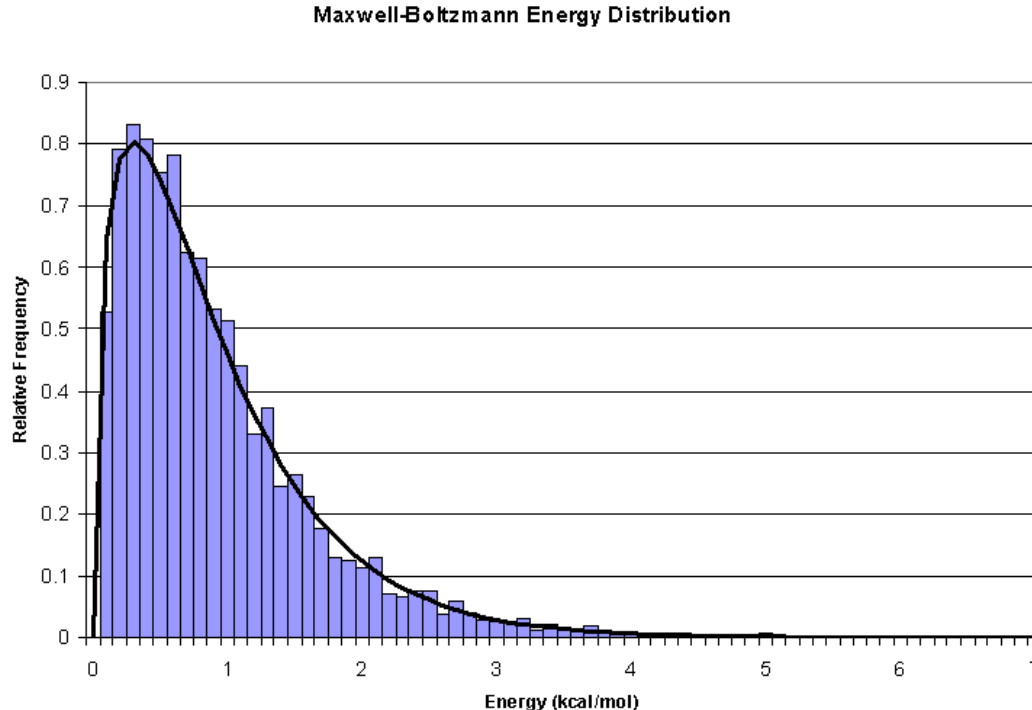
**Newman projection**

# Simulated Rotation



# Biased Sampling

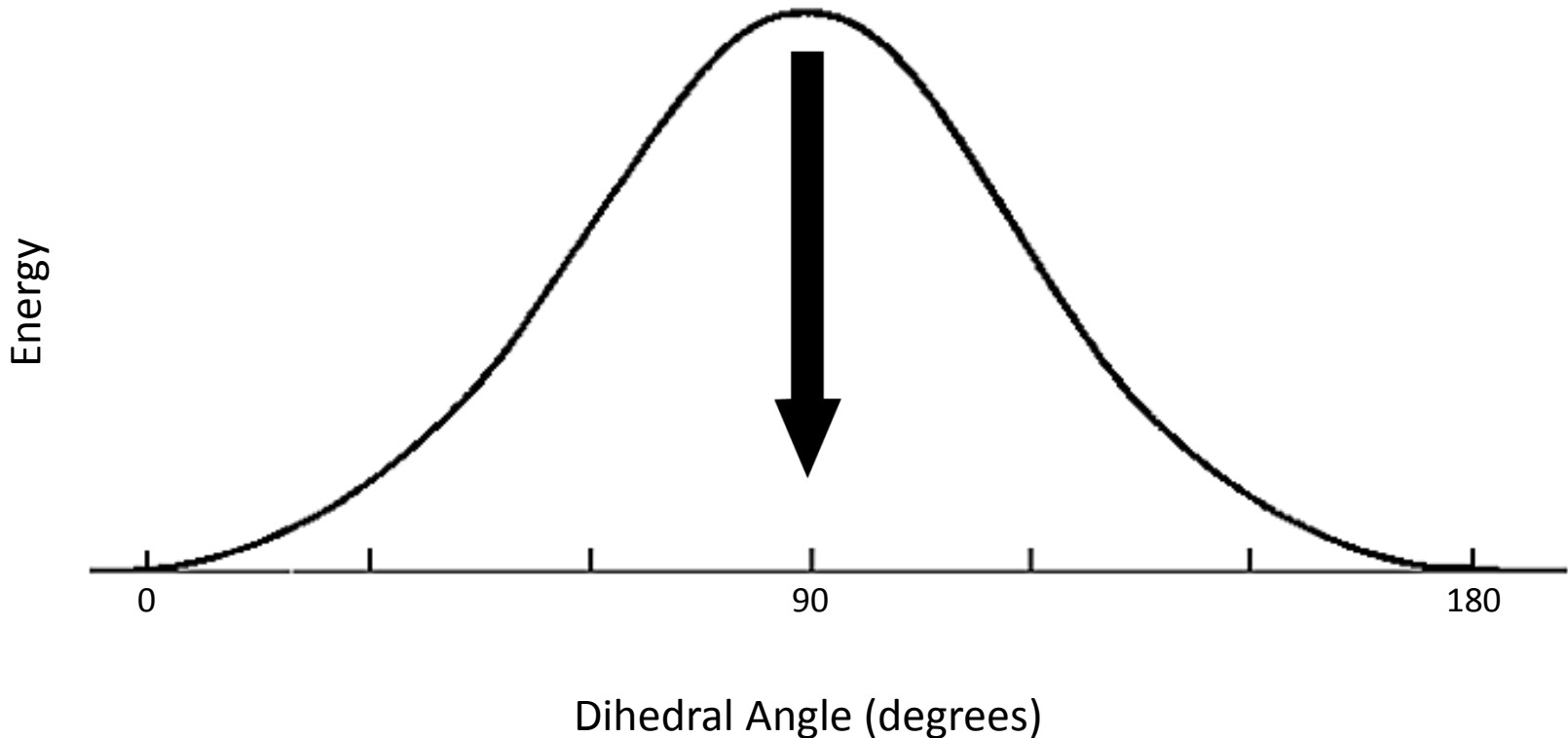
- Adaptive Biasing Force, Metadynamics, and Umbrella Sampling.
- Apply force on the system to allow molecules to go through otherwise unfavorable conformations.
- Took 3-4 hours to produce 1 nanosecond simulation.
- Much more efficient way of mapping free energy barriers.



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

# Adaptive Biasing Force

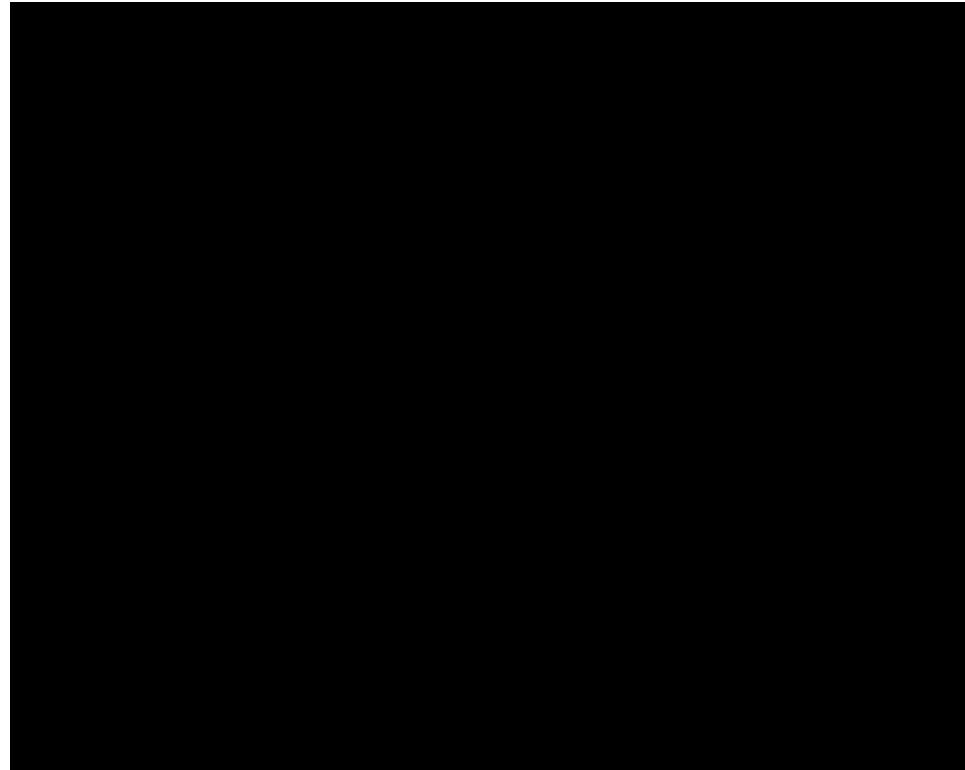
- Adaptive Biasing Force
  - Flattening out energy barriers to allow full sampling.





# Metadynamics

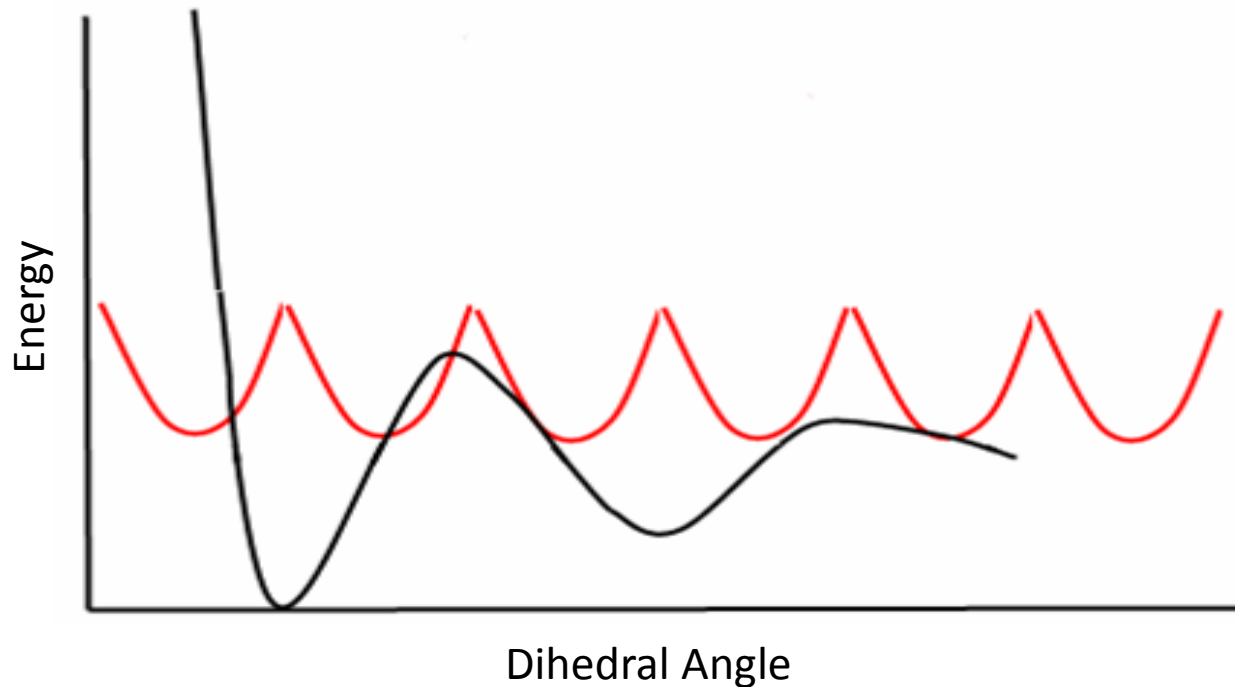
- Metadynamics
  - Flooding low energy areas to fill up energy valleys.
- Allows for more sampling at high energy states.



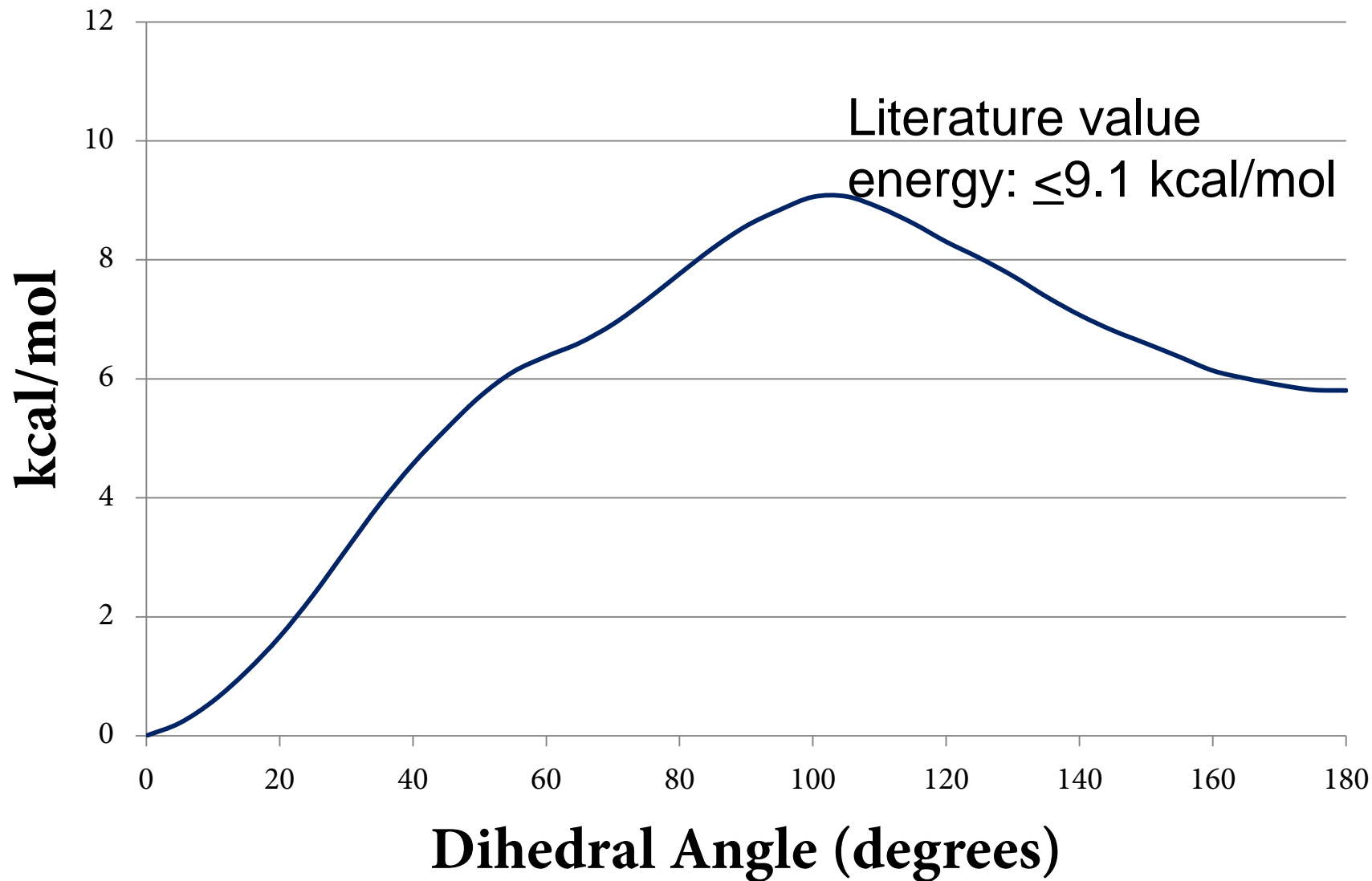
# Umbrella Sampling

## – Umbrella Sampling

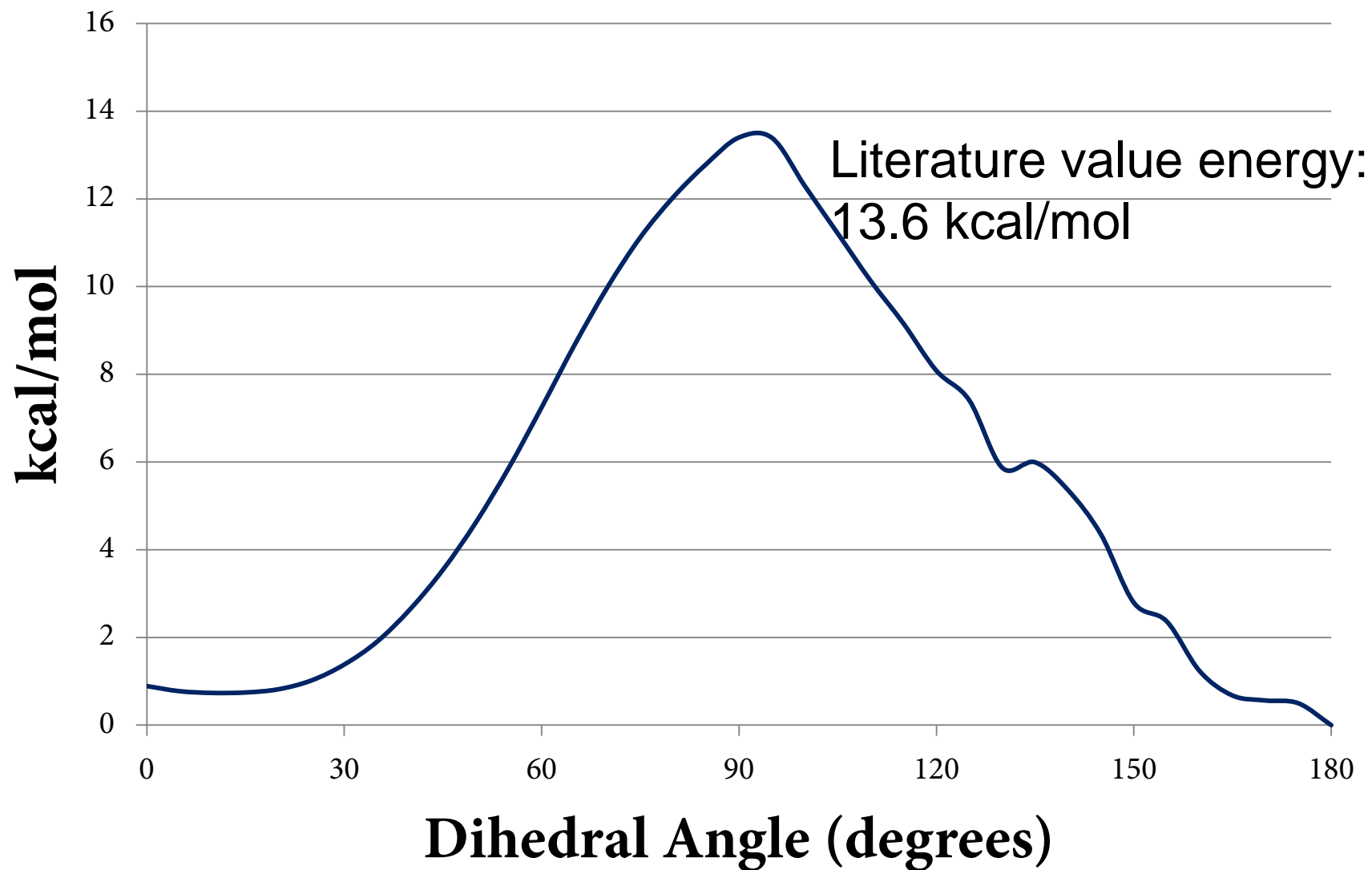
- Multiple runs held at different angle ranges.
  - 0 to 180 degrees, 5 degrees apart.



# DAP 2A (ABF)

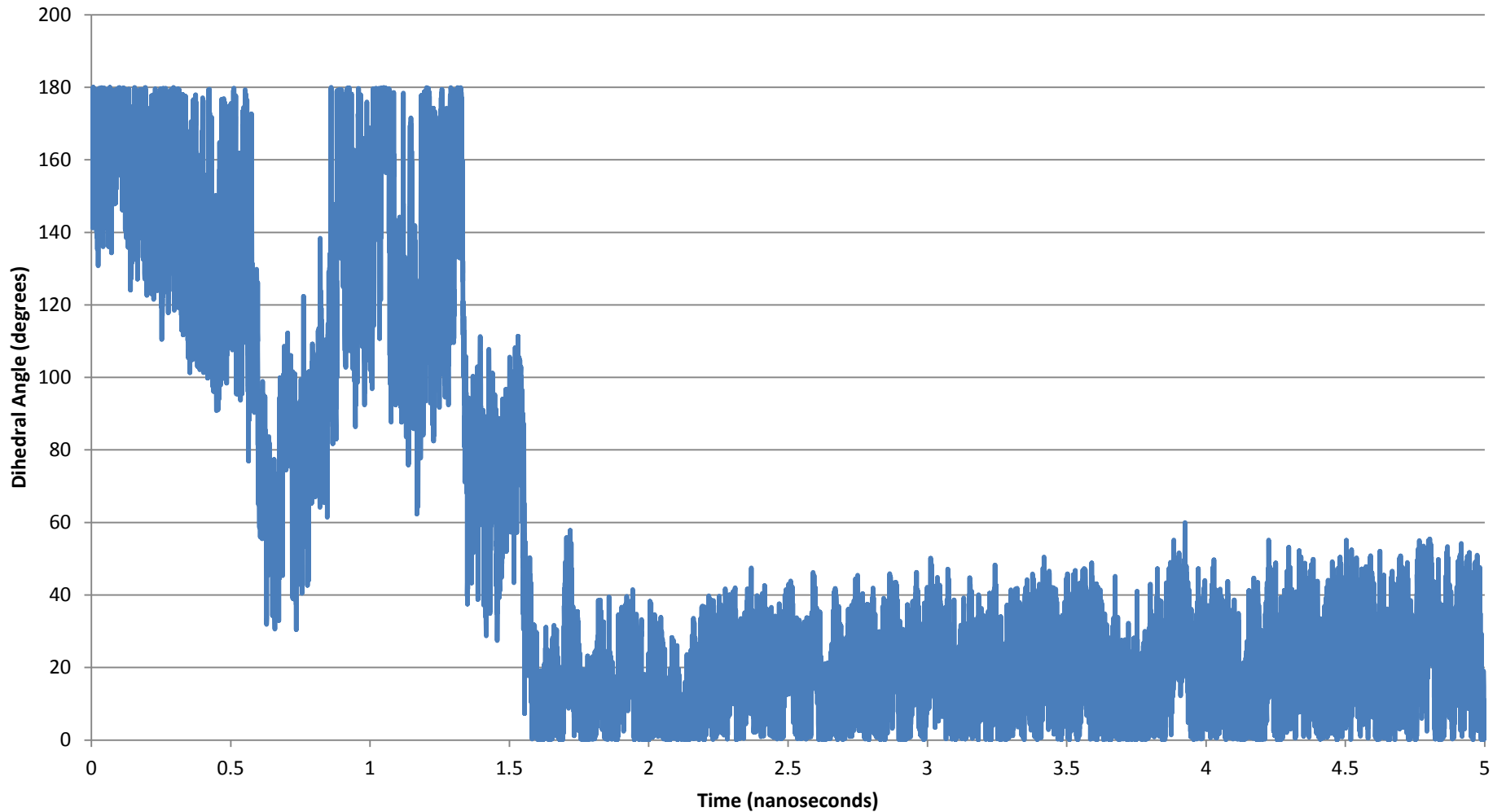


# DAP 2B (ABF)



# 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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