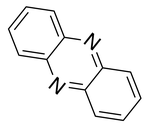

Computational Exploration of the Thermodynamic and Electronic Properties of Quinoxalines

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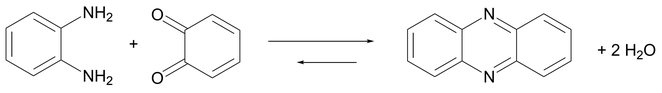
Introduction

- We are interested in the synthesis and self assembly of semi conductive organic small molecules and polymers
- Organic semi conductors can be made more flexible and lightweight than their inorganic counterparts
- Potential applications in flexible electronic devices and solar energy
- Previous lab work with boronate ester derivative frameworks have been moderately successful
- Quinoxalines may be a better platform due to their increased conjugation

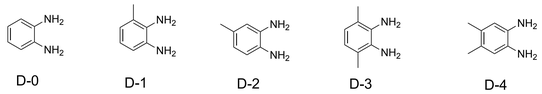
Methods and Motivations

- Eight diamines and nine quinones that are commercially available were studied along with their 84 possible quinoxaline combinations.
- The range of substituents allows us to study how electron donating and withdrawing groups (EDGs and EWGs), as well as extended conjugation affects quinoxaline formation and their electronic properties.
- The ΔG^o, ΔH^o, and HOMO & LUMO energies were computationally calculated using Gaussian software.
- The diamines, quinones and quinoxalines were optimized at B3LYP/6-311G(d) and M062x/6-311G(2d,p) levels of theory.
- Looking for ΔG^o values that are near thermoneutral, so that the reaction is reversible, and a thermodynamic product can be made via dynamic covalent assembly.
- Looking for a HOMO-LUMO gap between 0-3 eV, the general range of a semi conducting materials.

General Reaction



Diamine Chemical Structures



Quinone Chemical Strucutres

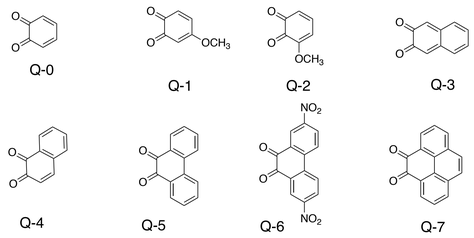
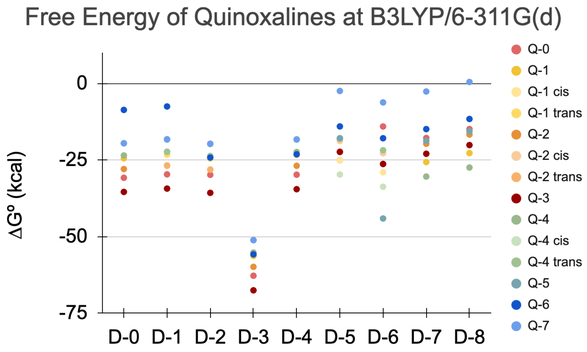


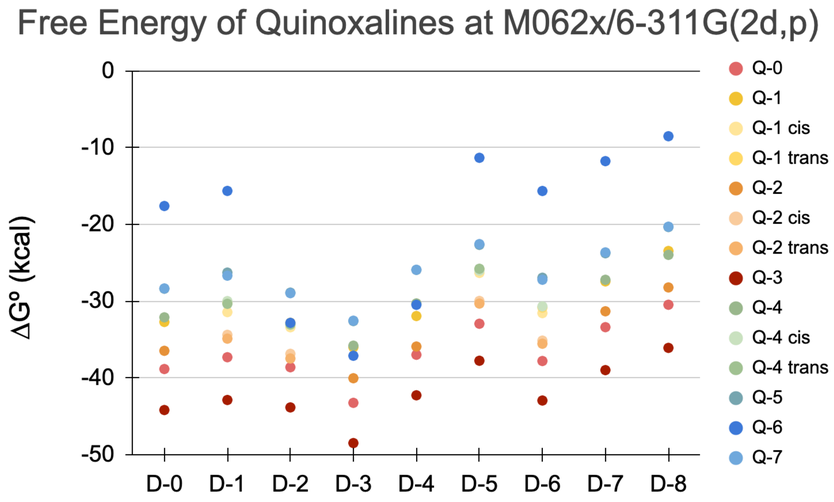
Figure 1: The general reaction of diamines and quinones to form quinoxalines, and the additional diamines and quinones used to form more substituted quinoxalines

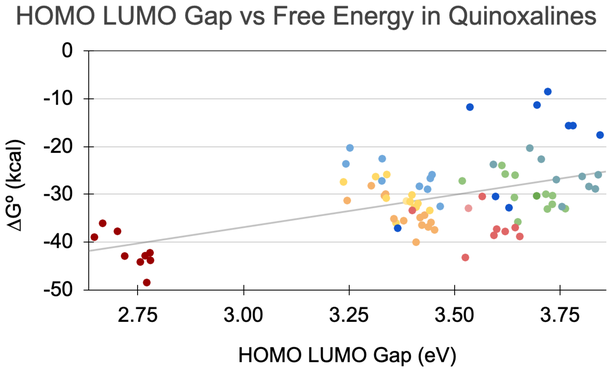
Thermodynamics of Quinoxaline Formation



- The formation of all quinoxalines are favored (ΔG^o<0).
- Quinoxalines with quinones containing EWGs (Q-6) are significantly less thermodynamically favorable.
- Quinoxalines containing diamines with EDGs (D 1-4) are slightly more thermodynamically favorable
- Quinoxalines containing diamines with EWGs (D 5-8) are slightly less favorable

Figures 2 and 3: The relationship between structure and free energy





- HOMO-LUMO gaps range from 2.5-4 eV, the lower end of which aligns with the values of semi conductive materials
- Low HOMO-LUMO gaps slightly correspond to more thermodynamic favorability
- The colored quinone functional groups tend to predict HOMO-LUMO gaps in addition to ΔG^o

Figure 4: The relationship between the HOMO LUMO gaps of quinoxalines and their ΔG^o values. Functional groups are colored (See Figure 3). Data from M062x/6-311G(2p,d) level of theory

Acknowledgements:

I want to thank Professor Northrop for his guidance on this project, and his flexibility with managing this summer's research virtually. Also thank you to Sophie Wazlowski who has been an incredible fellow student researcher and friend in the Northrop Lab.

Energetic Properties of Quinoxalines

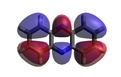
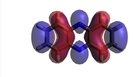
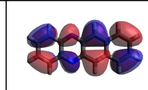
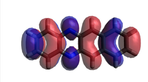
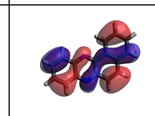
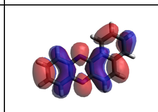
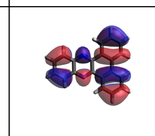
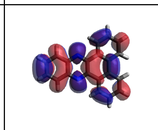
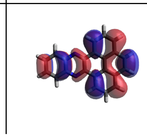
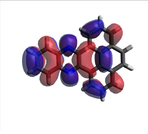
Quinoxaline	HOMO	LUMO	Gap (eV)
D-0 + Q-0			3.65
D-0 + Q-3			2.76
D-0 + Q-4			3.73
D-0 + Q-5			3.82
D-0 + Q-7			3.42

Figure 5: The extent of conjugation is shown in the HOMO and LUMO images and is also reflected in their HOMO LUMO gap.

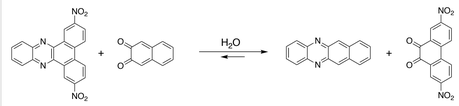
- Increased conjugation generally leads to lower HOMO-LUMO gaps
- However geometry plays an important role: more linear arrangements of aromatic rings result in lower HOMO-LUMO gaps

Summary

- Formation of **all** quinoxalines were thermodynamically favored (ΔG^o<0)
- Quinoxalines made of quinones with EWGs tend to be less thermodynamically favored (ie. Q-6)
- Quinoxalines made of diamines with EDGs tend to be slightly more thermodynamically favored (ie. D 1-4)
- Quinoxalines made of diamines with EWGs tend to be slightly less thermodynamically favored (ie. D 5-8)
- HOMO-LUMO gaps range between 2.5-4 eV
- Low HOMO LUMO gap correlates to more thermodynamic favorability
- Linearity of quinoxalines correlates to a lower HOMO-LUMO gap

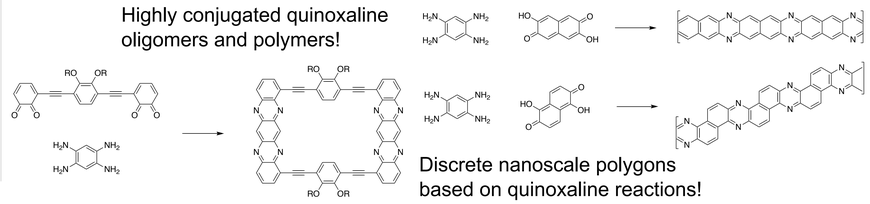
Future Works

This study is this lab's the first inquiry into quinoxalines as possible monomers for a semi conductive organic polymer materials. It opens the door for many directions of future work, including experimental tests of reversibility and construction of larger assemblies of quinoxalines.



Reversibility via dynamic covalent exchange!

Highly conjugated quinoxaline oligomers and polymers!



Discrete nanoscale polygons based on quinoxaline reactions!