# 6+4 Cycloadditions As Covalent Adaptable Networks

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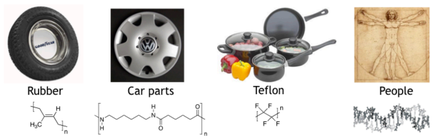
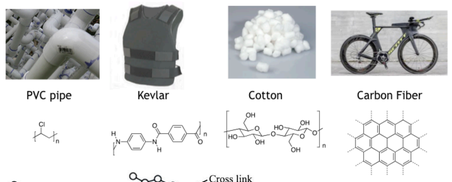
## Introduction

### Background

- polymers: very large molecules containing many repeating subunits
  - Examples of synthetic polymers:
    - Nylon
    - Polyethylene
    - Polyester
    - Teflon
    - Epoxy

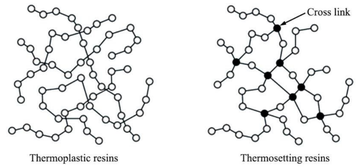



- **Recycling** and **reusing** polymers is very important when finding ways to reduce environmental impacts of plastics used in mass production settings




**Thermoplastics vs Thermosets**

**Thermoplastics** do not have cross links and are more recyclable, but less durable







**Thermosets** have cross links that make them more durable but they are less recyclable (they usually decompose over time)

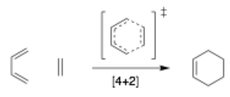
### Covalent Adaptable Networks (CANs) and Cycloadditions

**Covalent Adaptable Networks (CANs)** are

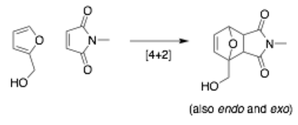
- Reversible covalent bond forming reactions that can allow for cross links to be able to be broken and reformed, thus the polymer can be recycled and reused

**Diels Alder Reactions** are an example of a cycloaddition that forms covalent bonds with no byproducts

Butadiene + ethylene (440 K, 900 atm: difficult reaction to drive and **nonreversible**)



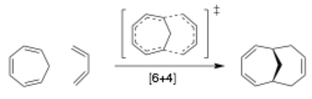

The substituted furan + maleimide reaction below is an example of a reversible Diels Alder




(also *endo* and *exo*)

These reactions are examples of **4+2 cycloadditions** because each has one reactant with 4 pi electrons and another with 2 pi electrons.

Question: Are there **reversible 6+4 cycloadditions?**

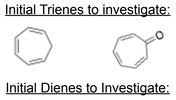



### Plan

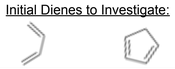
- Explore cycloadditions computationally
  - First, starting with known reactions to test and evaluate the accuracy of different computational methods
  - Computationally model new possibilities of 6+4 cycloadditions to pre-screen reaction viability and in the future be compared with experiments to verify

**Building 6+4 reactions:**

Initial Trienes to investigate:



Initial Dienes to Investigate:

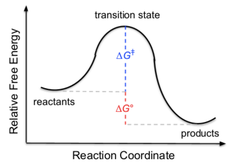


## Results

Computations were carried out using the program Gaussian19 at the following four levels of theory:

- B3LYP/6-31G(d)
- M062X/6-31G(d)
- M062X/6-311++G(d,p)
- CBS-QB3

Reaction and transition state enthalpies and free energies were computed. All results reported below are in kcal/mol, some calculations are still in progress as indicated.



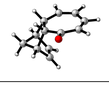

Favorable reaction parameters for dynamic covalent reversibility:
• Transition state free energy barrier <30 kcal/mol, ideally <25 kcal/mol
• Reaction free energy between -0.5 to -4.5 kcal/mol

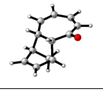
### 4+2 Cycloadditon Results

| | Transition state | | Reaction | |
|---|---|---|---|---|
| | ΔH | ΔG | ΔH | ΔG |
| b3lyp/6-31g(d) | 20.2 | 32.9 | -41.9. | -27.6 |
| M06 | 15.9 | 28.8 | -41.8 | -26.7 |
| m06P | 17.8 | 30.6 | -36.2 | -21.1 |
| Cbs-qb3 | - | - | - | - |
| Experimental | 23.2 | 36.1 | -39.6 | -27.1 |

| | Transition state | | Reaction | |
|---|---|---|---|---|
| | ΔH | ΔG | ΔH | ΔG |
| B3lyp | 21.1 | 34.4 | -20.3 | -5.7 |
| M06 | 15.4 | 28.9 | -31.3 | -16.7 |
| m06P | 17.3 | 30.8 | -26.2 | -11.6 |
| Cbs-qb3 | - | - | - | - |
| Experimental | 22.5 | 32.1 | -26.4 | -9.4 |

| | Endo transition state | | Exo transition State | | Endo reaction | | Exo reaction | |
|---|---|---|---|---|---|---|---|---|
| | ΔH | ΔG | ΔH | ΔG | ΔH | ΔG | ΔH | ΔG |
| B3lyp | 20.3 | 32.4 | 19.8 | 31.4 | -3.4 | 9.6 | -6.2 | 7.0 |
| M06 | 10.6 | 24.5 | - | - | -17.0 | -2.1 | -19.3 | -4.3 |
| m06P | 11.8 | 26.6 | 12.2 | 26.6 | -14.7 | 0.9 | -16.6 | -0.8 |
| Cbs-qb3 | - | - | - | - | - | - | - | - |
| Experimental | N/A | 24.9 | N/A | 25.2 | N/A | -1.9 | N/A | -3.7 |

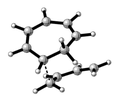


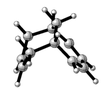


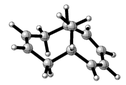
| | Endo transition state | | Exo transition State | | Endo reaction | | Exo reaction | |
|---|---|---|---|---|---|---|---|---|
| | ΔH | ΔG | ΔH | ΔG | ΔH | ΔG | ΔH | ΔG |
| B3lyp | - | - | 24.0 | 37.9 | 2.0 | 16.8 | 2.0 | 16.8 |
| M06 | - | - | - | - | - | - | - | - |
| m06P | - | - | - | - | - | - | - | - |
| Cbs-qb3 | - | - | 13.5 | 27.6 | -13.5 | 1.2 | -12.6 | 2.2 |

## Results and Discussion

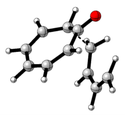
### 6+4 Cycloaddition Results

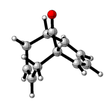




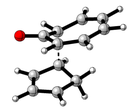


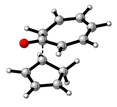
| | Endo transition state | | Exo transition State | | Endo reaction | | Exo reaction | |
|---|---|---|---|---|---|---|---|---|
| | ΔH | ΔG | ΔH | ΔG | ΔH | ΔG | ΔH | ΔG |
| B3lyp | 33.3 | 46.6 | 23.0 | 36.0 | -23.9 | -9.1 | -21.2 | -6.5 |
| M06 | 31.3 | 44.8 | - | - | -38.1 | -23.3 | - | - |
| m06P | 28.2 | 40.9 | - | - | -30.6 | -15.5 | - | - |
| Cbs-qb3 | 26.1 | 68.9 | - | - | -32.0 | -16.4 | - | - |

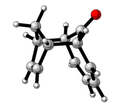


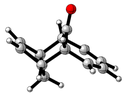


| | Endo transition state | | Exo transition State | | Endo reaction | | Exo reaction | |
|---|---|---|---|---|---|---|---|---|
| | ΔH | ΔG | ΔH | ΔG | ΔH | ΔG | ΔH | ΔG |
| B3lyp | 21.7 | 35.2 | - | - | -13.3 | 1.2 | - | - |
| M06 | 15.5 | 29.5 | - | - | -31.4 | -16.8 | - | - |
| m06P | - | - | - | - | - | - | - | - |
| Cbs-qb3 | 14.2 | 28.5 | - | - | -26.7 | -11.3 | - | - |







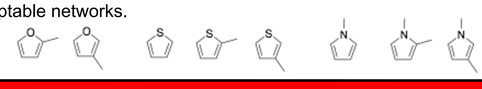


| | Endo transition state | | Exo transition State | | Endo reaction | | Exo reaction | |
|---|---|---|---|---|---|---|---|---|
| | ΔH | ΔG | ΔH | ΔG | ΔH | ΔG | ΔH | ΔG |
| B3lyp | 20.0 | 34.4 | 20.0 | 63.7 | 0.2 | 16.0 | -5.5 | 10.4 |
| M06 | 11.4 | 26.5 | 11.4 | 26.5 | -19.6 | -3.7 | -25.2 | -9.2 |
| m06P | - | - | - | - | - | - | - | - |
| Cbs-qb3 | 9.2 | 23.8 | 9.2 | 23.8 | -18.8 | -2.9 | -24.2 | -8.2 |

### Conclusions & Future Works

A 6+4 cycloaddition reaction could be a potential candidate for use in covalent adaptable networks if its ΔG for the transition state is at least below 30 kcal/mol and, preferably, below 25 kcal/mol. Another indicator of reaction viability is the ΔG° for the cycloaddition reaction should ideally be between -4.5 and -0.5 kcal/mol. Pertinent data is highlighted in green if it's an indicator of a reaction being likely viable and highlighted in orange if it's an indicator that a reaction could be viable.

Based on this, future work will include completion of the computations currently under study, inclusion of more potential triene and dienes (such as the heterocyclic below), and ultimately synthesis of target candidates for testing of reversibility and incorporation into covalent adaptable networks.

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