

Radical Catalyzed Skeletal Rearrangement of the Tetracene Series

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Introduction

Polycyclic aromatic hydrocarbons are potentially carcinogenic combustion byproducts listed by the EPA as persistent toxins. Our research group has actively contributed research on PAH's in order to understand the formation and interconversion of these species.

The Johnson group has done extensive work on the skeletal rearrangements with respect to the anthracene/phenanthrene ¹ and the tetracene ² series catalyzed with trifluoromethanesulfonic acid in solution. These rearrangements proceed through an aryl pirouette mechanism, involving the formation of a spirocyclic intermediate. ³ (Figure 1)

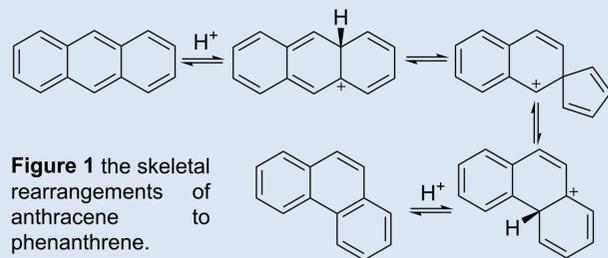


Figure 1 the skeletal rearrangements of anthracene to phenanthrene.

It was then theorized that this rearrangement could occur through a radical route similar to the cationic route. This was investigated by microwave flash pyrolysis in which hydrocarbons are heated to high temperatures in the absence of oxygen on graphite. ⁴ Catalytic hydrogen atoms are believed to be generated under these conditions. With much deliberation, pathways were found between each of the tetracene isomers as shown in Figure 2.

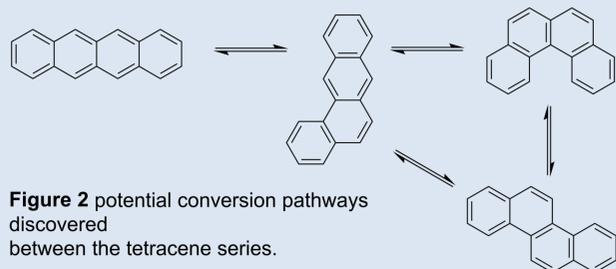


Figure 2 potential conversion pathways discovered between the tetracene series.

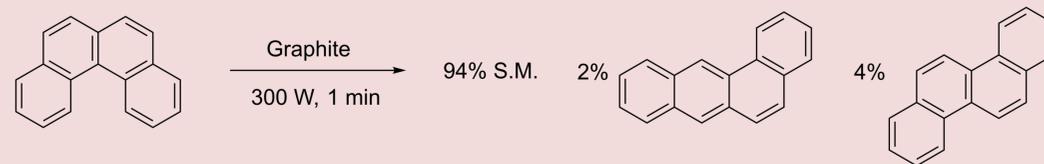
In these reactions, we saw limited but measurable rearrangements of the arenes. Using computational chemistry a mechanism was investigated and proposed for the interconversion of these species focusing on the tetracene series. A sample of this can be viewed in Scheme 1.

Objectives

To develop a computational model to illustrate the potential energy surface of all the hydrogen atom catalyzed rearrangements in the tetracene series. Four isomers may be interconverted.

To verify the computational model developed using experiment.

Experimental



Scheme 1 initial rearrangement experiments were completed by Sarah Joiner using MFP technique. Upon heating with graphite, rearrangement is observed under conditions thought to generate a hydrogen atom rich environment. Conditions need to be optimized to increase rearrangement yield.

One Portion of the Proposed Energetic Pathway B3LYP/6-311+G(d,p)

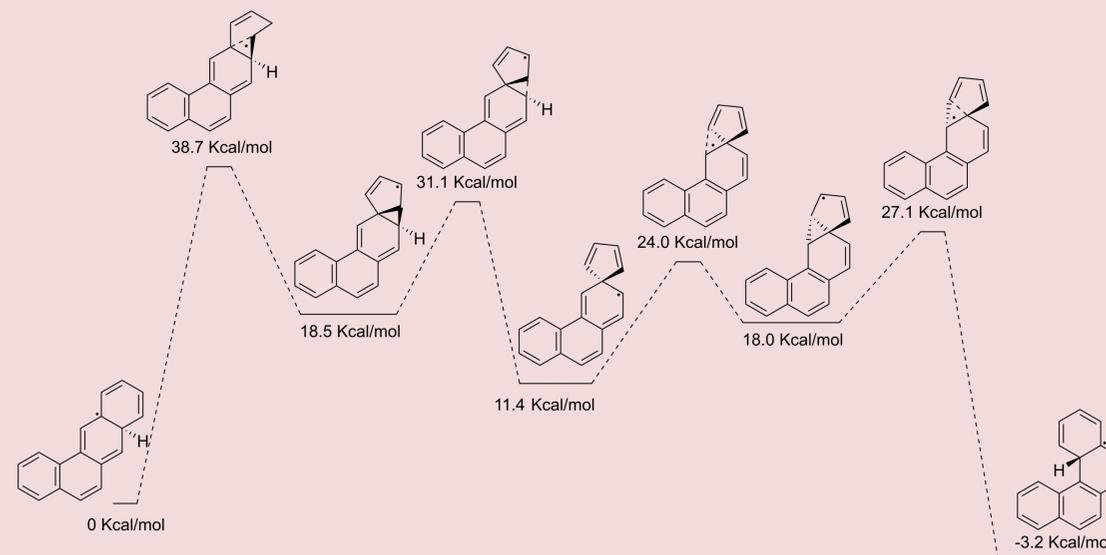


Figure 3 shows the proposed pathway, including all transition states and intermediates, for the interconversion of benz[a]phenanthrene to 4-helicene. This is the best characterized pathway having energies calculated for each intermediate. The entire potential surface is far more complex.

Anatomy of a Quantum Chemical Calculation ⁵

1. Model the system that is to be investigated using an electronic equivalent of a model kit.
2. Make an estimation at the geometry of the system you are trying to investigate.
3. Optimize with a low level of theory to improve on the estimated geometry.
4. Optimize with the level of theory chosen for your research.

Discussion

It is found that the rearrangement of the tetracene series through a radical mechanism has a higher barrier than for similar rearrangement through a cationic mechanism. However, the rearrangement is still possible under combustion conditions as shown in the microwave flash pyrolysis.

The proposed mechanism for the rearrangement is similar to the proposed cationic mechanism, but has an additional cyclopropyl intermediate which manifests itself as a shallow minimum on the potential energy curve.

Results

It was found that hydrogen atoms do have the potential to catalyze the rearrangement of PAH's. The tetracene series do appear to undergo rearrangement under high temperature, hydrogen atom rich conditions.

A proposed mechanism was developed for the rearrangement of PAH's under hydrogen atom addition conditions. This mechanism was modeled using DFT B3LYP/6-311+G(p,g) method. This model has proposed energy of activation and should be useful in determining equilibrium conditions.

Future Work

To complete this research I plan to run Microwave Flash Pyrolysis with a greater variety of PAH to better generalize this rearrangement.

More computations should be done to complete the entire potential energy surface, encompassing all of the possible hydrogen atom addition sites and transition states.

A better reaction scheme should be developed to increase rearrangement yield. Research into metal complexes or other sources for the hydrogen atom donor is ongoing.

Investigate potential solutions to minimizing cyclopropyl carbonyl radical TS. These represent shallow minima.

Acknowledgements

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Citations

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