

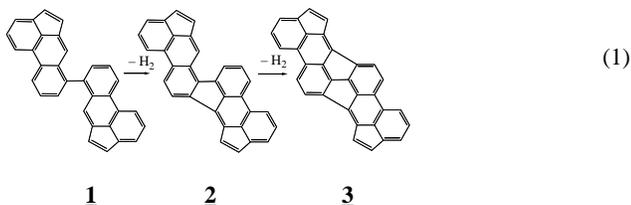
HYDROGEN ATOM CATALYZED ISOMERIZATION OF AROMATIC COMPOUNDS

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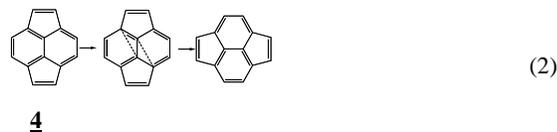
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Introduction

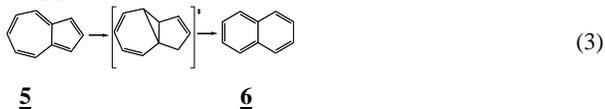
Isomerization of aromatic compounds plays an important role in the formation of flame-synthesized fullerenes, nanotubes, and in the growth of soot during combustion. During flame synthesis, unfavorable geometries often arise by the proposed zipper mechanism^{1,2} in which biaryl molecules zip together losing molecular hydrogen. For instance, the acephenanthrylene molecule, **1**, can zip together to form **3**. At flame temperatures (> 2000 K) the positive entropy of these reactions makes them significant. However, the resulting molecule, **3**, contains adjacent 5-membered rings, which is energetically undesirable. In fullerenes, the 5-membered rings are isolated by 6-membered rings and it is unlikely that a zipper mechanism will lead directly to this type of configuration. An isomerization needs to occur.



Fullerene modelers have often invoked the Stone-Wales (SW) rearrangement^{2,3} to explain annealing in aromatic compounds. In the simplest example of the SW reaction the 5-membered rings in pyracyclene, **4**, are shifted as shown in eq. 2. This mechanism can be used to isolate 5-membered rings in polycyclic aromatic compounds.



Another interesting annealing reaction is the isomerization of azulene, **5**, to naphthalene, **6**. This reaction may also be important in the zipper mechanism.



The calculated barriers for these reactions are fairly high [120 to 130 kcal mol⁻¹ for reaction (2) and > 83 kcal mol⁻¹ for reaction (3)] which might limit their extent during combustion. We have found that addition of a hydrogen atom to **4** and **5** dramatically reduces the barrier for these reactions and since hydrogen atom is fairly abundant in flames, this catalytic effect may increase the likelihood of these isomerization reactions.

Computational Techniques

The calculations in this study were carried out using the Gaussian 98 suite of programs at the following level: B3LYP/6-31+G(d,p)

Local minima and transition states were found using Berny optimizations. Starting geometries for the transition state optimizations were often located using a potential energy scan, where one internal coordinate was systematically changed while all other coordinates were allowed to relax. The geometry at the calculated maximum of this scan was used as a starting geometry for a TS optimization. Stable structures had only positive vibrational frequencies while transition states had one imaginary frequency. The transition states were confirmed by visual inspection of the imaginary frequency using the Molden visualization package. The transition states were also confirmed using IRC calculations.

Results and Discussion

Stone-Wales

We have considered two mechanisms for the SW reaction in pyracyclene; a two-step mechanism involving cyclopropyl transition states and a cyclobutyl intermediate and one-step mechanism⁵ with an sp³ carbon atom in the transition state. The calculated potential energies for the transition states of these mechanisms are shown in **Figure 1**. Since the product and reactant are the same for this molecule, the two cyclopropyl transition states are necessarily equivalent. As can be seen, the barriers for both of these processes are high (129.8 kcal mol⁻¹ for the sp³ mechanism and 119.3 kcal mol⁻¹ for the cyclopropyl mechanism). Furthermore, the level of theory used often underpredicts barrier energies by up to 5 kcal mol⁻¹. These barriers are high enough that other processes, such as C-H bond scissions (*DH* ~ 110 kcal mol⁻¹) will be more likely.

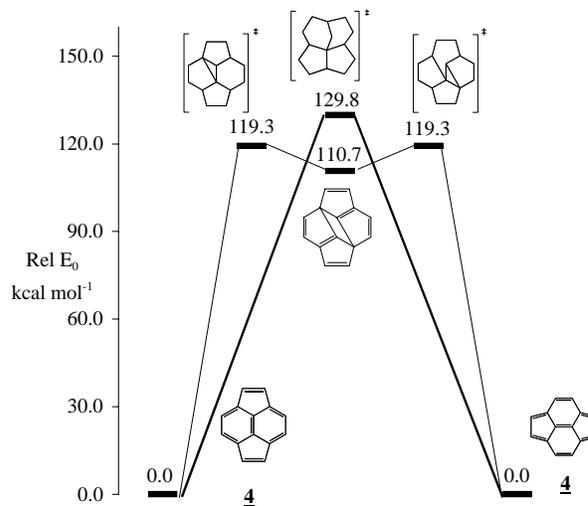


Figure 1. A potential energy plot of the calculated relative energies for the SW reaction in pyracyclene. The energies include the zero point energy.

The addition of a hydrogen atom to the central atom of pyracyclene significantly reduces the reaction barriers for the SW reaction. This is shown in **Figure 2**. As can be seen the relative energy of the cyclopropyl transition state drops from 119.3 kcal mol⁻¹ for neat pyracyclene to 66.9 kcal mol⁻¹ for H+pyracyclene and the sp³ transition state dropped from 129.8 kcal mol⁻¹ for the neat pyracyclene to 73.3 kcal mol⁻¹ for H+pyracyclene. In addition to the lower energy barrier, there is a chemical activation energy that would be available when hydrogen atom adds to pyracyclene. For the molecule shown in **Figure 2** the chemical activation energy is 20.4 kcal mol⁻¹. We have calculated the reaction energetics when a hydrogen atom is added to the external bridge carbon atoms on pyracyclene. The results are shown in Table I. As can be seen,

hydrogen atoms attached to these carbon atoms have a larger chemical activation energy, but have a smaller reduction in the reaction barrier relative to the neat pyracyclene

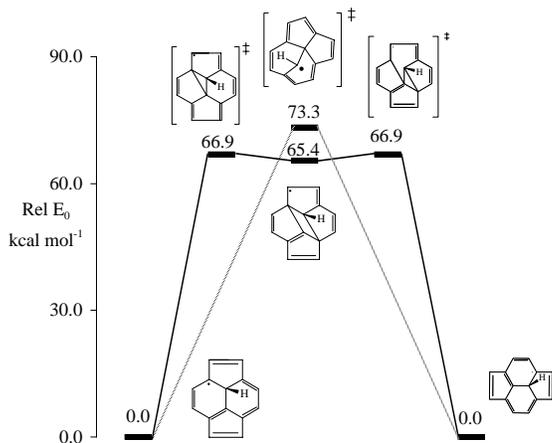


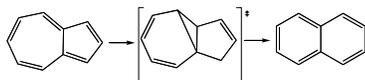
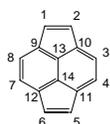
Figure 2. A potential energy plot of the calculated energies for the SW reaction in pyracyclene

Table I Calculated relative energies^a for SW for pyracyclene and pyracyclene + H atom. (kcal mol⁻¹)

React ^c	chem	sp ³		cyclopropyl		Prod.	
	act. ^b	mech.	TS	c-C4	TS2		
neat			129.8	119.3	110.7	119.3	0.0
H-C13	20.4	73.3	66.9	65.4	66.9	66.9	0.0
H-C9	34.5		105.3	97.4	105.3	105.3	0.0
H-C1	54.4		128.0	118.8	125.9	125.9	14.6

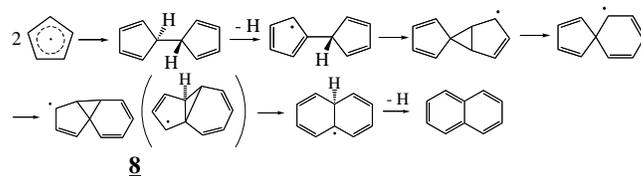
^aIncludes zero point energy ^bThe energy of the adduct relative to the energy of H atom + pyracyclene ^cThis shows where the H atom is attached on the pyracyclene. See carbon numbering scheme below:

Azulene/Naphthalene Isomerization



This rearrangement has been the subject of experimental⁶⁻⁸ and theoretical studies¹¹. We find a single transition for the neat molecule with a barrier energy of $E_0 = 83.4$ kcal mol⁻¹. With the addition of a hydrogen atom to a bridge carbon atom, the energetics changes considerably. **Figure 3** shows a plot of the calculated energies of the intermediates relative to the energy of azulene + H atom. As can be seen, the adduct formed from the addition of H atom to the bridge carbon is -30.9 kcal mol⁻¹ lower in energy than the reactants. This chemical activation energy is sufficient to surmount the barriers to naphthalene formation. In this case H atom catalysis makes the isomerization facile.

This mechanism also has an interesting consequence on aromatic formation from the recombination of cyclopentadienyl radical (C₅H₅). It has been proposed that in combustion two cyclopentadienyl radicals can react to form naphthalene by a mechanism which involves two cyclopropyl intermediates. 9,10



The intermediate, **8**, in this mechanism is identical to the cyclopropyl intermediate in the H atom catalyzed transformation of azulene to naphthalene shown in **Figure 3**. Thus, it is possible that the recombination of cyclopentadienyl radicals could lead to the formation of azulene in addition to naphthalene.

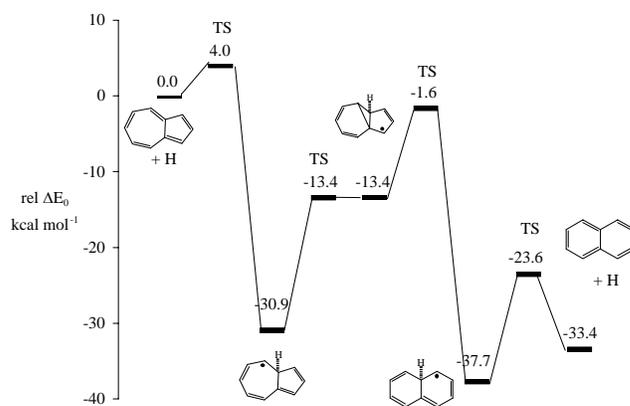


Figure 3. Relative energies of intermediates in the H atom catalyzed isomerization of azulene to naphthalene.

In summary, we have found that rearrangements of 5,6-rings and 5,7-rings in simple compounds that are designed to model more complex rearrangements in fullerenes have barriers that are significantly lowered by the addition of an H-atom to the rearranging framework. The resulting radicals, which are likely to exist in relatively high concentrations due to the high concentrations of H-atoms in flame environments, represent a possible low energy catalytic pathway for the SW and related rearrangements in fullerenes.

Acknowledgment

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