Theoretical Studies of Potential Redox-Activated Organic Switch Involving Electrocyclic Reactions of Substituted Benzocyclobutenes and O-Xylylenes

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Molecular Switches

The Concept:
- “At the atomic level, we have new kinds of forces and new kinds of possibilities, new kinds of effects.”
  -- Richard P. Feynman (1959)

Criteria for a Switch:
- Reversible by non-destructive means
- Stable at room temperature
- Observable States (“on” and “off”)
- Color
- NMR shift
- Electrochemical potential

Background

General Reaction

Thermal pericyclic reaction that undergoes a conrotatory ring-fusion and fission to form benzocyclobutene
Once oxidized, the radical cation undergoes a thiol-cycloaddition ring-opening to form the more stable ortho-xylylene

The Goal
- Modify the above system to design a switch that is reversible and barrierless for use as a hybrid molecular electronic (HME) device

Computational Method

Optimization and frequencies of minimum and transition structures calculated with B3LYP/6-31G(d)
Benchmark calculations of the parent system carried out with HF/6-31G(d), B3LYP/6-31G(d), MP2/6-31G(d), BPRW91/6-31G(d), and MPW1K/6-31+G(d,p), and compared to known experimental values
All calculations carried out with Gaussian 98

Benchmark Calculation on the Thermal Ring-Opening Process of the Neutral Parent System

<table>
<thead>
<tr>
<th>Method</th>
<th>E (kcal/mol)</th>
<th>E_{rxn} (kcal/mol)</th>
</tr>
</thead>
<tbody>
<tr>
<td>HF/6-31G(d)</td>
<td>-14.95</td>
<td>-11.92</td>
</tr>
<tr>
<td>B3LYP/6-31G(d)</td>
<td>-16.93</td>
<td>-13.90</td>
</tr>
<tr>
<td>MP2/6-31G(d)</td>
<td>-16.76</td>
<td>-13.73</td>
</tr>
<tr>
<td>CAS-APSW311G(2df,2p)</td>
<td>-11.76</td>
<td>-8.73</td>
</tr>
<tr>
<td>BPRW91/6-31G(d)</td>
<td>-11.72</td>
<td>-8.70</td>
</tr>
<tr>
<td>MPW1K/6-31+G(d,p)</td>
<td>-11.57</td>
<td>-8.54</td>
</tr>
</tbody>
</table>

Benchmark Calculation on the Electrochemical Potential

<table>
<thead>
<tr>
<th>System</th>
<th>Reduction</th>
<th>Oxidation</th>
</tr>
</thead>
<tbody>
<tr>
<td>HF/6-31G(d)</td>
<td>-14.96</td>
<td>-11.96</td>
</tr>
<tr>
<td>B3LYP/6-31G(d)</td>
<td>-17.00</td>
<td>-14.00</td>
</tr>
<tr>
<td>MP2/6-31G(d)</td>
<td>-16.76</td>
<td>-13.73</td>
</tr>
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</tr>
</tbody>
</table>

Transition Structures for Neutral and Radical Cationic Species

Neutral:
- A concerted conrotatory C-symmetric process
- Substituents at position stabilize the TS
- Substituents at β position may stabilize or destabilize the TS

Radical Cation:
- A concerted conrotatory C-symmetric process
- TS with substituent at β position is most stable
- Similar to the TS of cyclohexane radical cation

Insight into Possible Pathways for the Radical Cation Species

OH-substituted radical cation TS:
- Length of the breaking bond is shorter than the parent system
- The TS is a dissociative, rather than conrotatory mechanism

Divinyl radical cation system:
- A transition structure that is ~13.9 kcal/mol from the divinyl benzocyclobutene
- Possible stepwise mechanism for the ring-opening of radical cationic divinyl cyclobutene

Phenyl Substitution

- Diphenyl-substituted benzocyclobutene spontaneously opens to the ortho-xylylene once the system is oxidized
- <3H and -OH added to model phosphohydrox and phosphohydroxyl

Other Systems

Applications

Conclusion

Reversible interconversion of a benzocyclobutene and ortho-xylylene derivative is a simple system that can be utilized as an organic switch

Additional modifications are necessary for a barrierless interconversion

A bottom-up approach using computational methods is suitable for the design of a hybrid molecular electronic device, since experimental data are difficult to obtain especially for the radical cationic species

Acknowledgements

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