What about the spin preferences of diradicals?

What are the electronic structure factors that control spin states in diradical organic molecules? (i.e., systems that have two weakly interacting electrons).

**Singlet or triplet?**

Chapter 4

---

General results: Weakly interacting radicals will produce a weak preference for the singlet state. However, when the nodal properties of the system are “co-extensive” in space significant exchange interactions results and this can produce the triplet ground state (Hund’s rule).

Disjoint (=non co-extensive) alternate hydrocarbons will have small singlet-triplet energy gaps, with the singlet likely to be the ground state. Non-disjoint (co-extensive) alternate hydrocarbons will have large singlet-triplet gaps, with a triplet ground state.

The pair of half-occupied near degenerate nonbonding MOs have their lobes coinciding significantly (co-extensive, the exchange integral is large).

The lobes coincide to very small extent (disjoint MOs), the spin coupling is small (S=1 and S=0) are almost degenerated.

Chapter 4
What about the spin preferences of diradicals?

The Trick of Borden and Davidson: to decide if the two nonbonding molecular orbitals are disjoint or not for alternate hydrocarbons by “starring” alternate carbons. If the difference between the number of starred ($n^*$) and unstarred ($n$) carbons is zero, then the molecule will have disjoint NBOs.

$$n^* - n = 0$$

$$n^* - n = 2$$

Representative alternate hydrocarbons with starred and unstarred carbon atoms.

Chapter 4
Tetramethyleneethane (TME) and Trimethylenemethane (TMM)

TME is a singlet but the triplet state is very close in energy.

TMM has a triplet ground state

Chapter 4

Tetramethyleneethane (TME)

1970 (Dowd, ESR): TME was assigned a triplet ground state.

…..computations in disagreement with this result.

1998  Clifford, gas-phase negative ion photoelectron spectroscopy: the electron loss gives two different states of TME. Based on the population distribution, they found the singlet state to be about 2 kcal mol⁻¹ below the triplet state.

Chapter 4
Tetramethylenethane (TME)

The triplet state $^3B_1$ can be described by a single configuration. The singlet $^1A_1$ state require at least two configurations. Any computations that does not account for the multiconfigurational nature of the singlet will run into difficulties.

Most computations at multireference levels predict:

\[
\begin{array}{c|c}
\text{state} & \text{configuration} \\
\hline
^3B_1 & (\pi^3, \sigma^3) \\
^1A_1 & (\pi^1, \sigma^1) \\

\end{array}
\]

- For all conformations, the singlet is lower than the triplet but those states are very close in energy. The smallest singlet-triplet gap, 1.3 kcal mol$^{-1}$ is obtained at an angle of 45° (with multireference coupled cluster methods)

- The gas phase PES experiment agrees with the computations. The ground state of TME is a singlet but metastable triplet could be trapped explaining the ESR results of Dowd.

Trimethylenemethane (TMM)

Is TMM a ground state singlet or triplet?

\[
\begin{array}{c|c|c|c|c|c|c}
^3A_2 & ^1A_1 & ^1B_2 & ^3B_1 & ^1B_1 & MCP \\
\hline
\text{method} & ^3A_2 & ^1A_1 & ^1B_2 & ^3B_1 & ^1B_1 & MCP \\
\hline
\text{MCSCF}(2,2)/cc-pVDZ & 0.0 & 10.5 & 16.7 & 13.9 & 15.1 & -29.5 \\
\text{MCSCF}(4,4)/cc-pVDZ & 0.0 & 19.5 & 19.9 & 13.4 & 14.7 & -21.5 \\
\text{MCSCF}(10,10)/cc-pVDZ & 0.0 & 19.2 & 19.5 & 13.8 & 15.9 & -18.9 \\
\text{MCSCF}(10,10)/cc-pVTZ & 0.0 & 18.9 & 19.3 & 13.8 & 15.8 & -19.8 \\
\text{CASPT2N}(2,2)/cc-pVDZ & 0.0 & 23.0 & 19.7 & 15.1 & 16.9 & -17.8 \\
\text{CASPT2N}(4,4)/cc-pVDZ & 0.0 & 20.1 & 19.8 & 14.1 & 15.8 & -20.7 \\
\text{CASPT2N}(10,10)/cc-pVTZ & 0.0 & 19.1 & 19.1 & 13.9 & 15.7 & -20.9 \\
\text{zero-point energies$^a$} & 0.0 & -1.6 & -2.9 & -1.3 & -1.2 & 2.4 \\
\end{array}
\]

$^a$ Relative energies in kcal/mol. $^b$ MCSCF geometries were fully

\[\text{Chapter 4}\]
Chapter 4

Trimethylenemethane (TMM)

Thermal rearrangement of methylenecyclopropane derivatives

Proposal: biradical TMM is produced

Resonance stabilization

Preparation of TMM and selected reactions

Chapter 4

Trimethylenemethane (TMM)

Thermal rearrangement of methylenecyclopropane derivatives

Berson’s trick to avoid rapid ring closure

Demonstration of the different natures of singlet and triplet biradicals

Chapter 4
The world of Benzyne

The Bergman cyclization

The unusual chemical structural feature of potent antibiotics: an enediyne fragment within the ring

What is the mechanism underlying the biological activity?

Chapter 4

The world of Benzyne

The Bergman cyclization

The diradical abstract hydrogen atoms from the DNA molecule leading to its scission.

How to convert 12 into 13?

Chapter 4
The world of Benzyne

The Bergman cyclization

The original experiment (1972)

Reactions typical of a free radical behavior suggesting the formation of 41.

Experimental reaction and activation enthalpies ($\Delta H^{\ddagger}$ in kcal mol$^{-1}$):
- $39 \rightarrow 41$: 28.2 (470 K)
- $42 \rightarrow 43$: 27.4
- $43 \rightarrow 42$: 16.0
- $43 \rightarrow 44$: 10.0

The cyclization has a large activation barrier and depend on the $cd$ distance

The world of Benzyne

Theoretical Considerations

The inherent multiconfigurational nature of 41 and 40 was early recognized: CASPT2, large CI or DFT appears as the most promising options but without potential difficulties.

<table>
<thead>
<tr>
<th>Method</th>
<th>TS</th>
<th>Product</th>
</tr>
</thead>
<tbody>
<tr>
<td>CASSCF(12,12)/TZ2P</td>
<td>43.64</td>
<td>27.0</td>
</tr>
<tr>
<td>CASPT2//CASSCF(12,12)/ANO</td>
<td>23.87</td>
<td>3.84</td>
</tr>
<tr>
<td>CCSD(T)/6-31G9d,p with MP2 Frequencies</td>
<td>28.5</td>
<td>8.0</td>
</tr>
<tr>
<td>Composite Approach</td>
<td>27.7</td>
<td>11.0</td>
</tr>
<tr>
<td>UB3LYP/6-311+H(3df, 3dp)</td>
<td>29.9</td>
<td>8.5</td>
</tr>
<tr>
<td>Expt.</td>
<td>28.2</td>
<td>8.5</td>
</tr>
</tbody>
</table>
The world of Benzyne

The cd Criteria and Cyclic Enediynes

<table>
<thead>
<tr>
<th>cd</th>
<th>$\Delta H$</th>
<th>cd</th>
<th>$\Delta H$</th>
</tr>
</thead>
<tbody>
<tr>
<td>4.52</td>
<td>27.07</td>
<td>2.152</td>
<td>NA</td>
</tr>
<tr>
<td>4.54</td>
<td>30.99</td>
<td>2.636</td>
<td>NA</td>
</tr>
</tbody>
</table>

values computed at the BPW91/6-311G** level.

The cyclization has a large activation barrier, which depend on the cd distance and on the strain in the resulting product.

Chapter 4

Benzynes

Benzynes are challenging for both experiment and theory. All three isomers are ground state singlets, but with a differing extent of diradical character.

<table>
<thead>
<tr>
<th></th>
<th>$\Delta E_{ST}$ (in kcal mol$^{-1}$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>$o$-benzyne</td>
<td>-2.9  (Triplet ground state)</td>
</tr>
<tr>
<td>$m$-benzyne</td>
<td>33  (singlet ground state)</td>
</tr>
<tr>
<td>$p$-benzyne</td>
<td>5.8</td>
</tr>
</tbody>
</table>

diradical character: 11% 20% 65%

Chapter 4
Chemical Properties of $p$-Benzyne

The S-T gap control the reactivity of $p$-Benzyne

\[ \Delta E_{ST} \text{ (in kcal mol}^{-1}\text{)} \]
\[
\text{CASPT2/cc-pVDZ } \begin{array}{c}
5.4 \\
17.2 
\end{array}
\]

Efficiencies for H-transfer from tetrahydrofuran

\[
\begin{array}{c|c|c|c}
& \text{0.007%} & \text{none} & \text{8%} & \text{13%} \\
\end{array}
\]

The decrease radical reactivity result from the need to partially uncouple the biradical electrons in the transition state.


Chapter 4

Chemical Properties of $p$-Benzyne

\[ \Delta E_{ST} \text{ (in kcal mol}^{-1}\text{)} \]
\[
\text{CASPT2/cc-pVDZ } \begin{array}{c}
5.4 \\
17.2 
\end{array}
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\end{array}
\]

The decrease radical reactivity result from the need to partially uncouple the biradical electrons in the transition state.


Chapter 4
Relative Energies of Benzynes

Relative energies (kcal mol\(^{-1}\))

<table>
<thead>
<tr>
<th>Method</th>
<th>otho</th>
<th>meta</th>
<th>para</th>
</tr>
</thead>
<tbody>
<tr>
<td>CASPT2</td>
<td>0.0</td>
<td>10</td>
<td>21.9</td>
</tr>
<tr>
<td>B3LYP/cc-pVTZ</td>
<td>0.0</td>
<td>12.2</td>
<td>37.2</td>
</tr>
<tr>
<td>CCSD(T)/cc-pVTZ</td>
<td>0.0</td>
<td>14.9</td>
<td>26.4</td>
</tr>
<tr>
<td>Latest Expt.</td>
<td>0.0</td>
<td>16</td>
<td>31.9</td>
</tr>
</tbody>
</table>

Chapter 4

Structures of \(m\)-Benzyne

Does \(m\)-Benzyne exist as the monocyclic biradical or as bicyclic closed-shell species?

Or

Comparisons of Spectroscopic Data

<table>
<thead>
<tr>
<th>Expt</th>
<th>CCSD(T)</th>
<th>B3LYP/cc-pVTZ</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>(\nu (\text{cm}^{-1}))</td>
<td>(\nu (\text{cm}^{-1}))</td>
</tr>
<tr>
<td></td>
<td>(\Gamma)</td>
<td>(\Gamma)</td>
</tr>
<tr>
<td>90</td>
<td>950</td>
<td>950</td>
</tr>
<tr>
<td>350</td>
<td>945</td>
<td>945</td>
</tr>
<tr>
<td>350</td>
<td>940</td>
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<td>350</td>
<td>935</td>
<td>935</td>
</tr>
<tr>
<td>350</td>
<td>930</td>
<td>930</td>
</tr>
</tbody>
</table>

Chapter 4
**Mini Quiz 5**

1. Using what you have learned about the difference between the number of starred ($n^*$) and unstarred ($n$) carbons, give the spin state of the following molecule.

   ![Molecule Image]

2. What is the biggest challenge in the computation the electronic structure and reaction mechanisms of diradicals and carbenes?

3. Propose an intermediate for the formation of cyclopentenones from vinylallene oxides.

   ![Intermediate Image]

4. The ESR signal of 17 depends on the temperature. What does it mean?

   ![ESR Signals Image]

---

**An interesting case: the phenalenyl radical**

The phenalenyl radical is a prototypical open-shell graphene fragment, proposed for use in organic electronics. 9b-azaphenalene is a closed-shell analogue of phenalenyl radical.

![Radicals Image]

1. Which physical forces dominate the interactions of the 9b-azaphenalene dimer?
2. What about the phenalenyl-radical dimer(s)? Which dimer is bound more strongly?
3. Which X-ray structures do you expect for 2,3,8-$\text{Bu}$-phenalenyl-radical and the unsubstituted molecule?
4. Which computational level would you choose to compute the interaction energy profile of 9b-azaphenalene? Do you expect the same methods to be accurate for the phenalenyl dimers?
5. If you remove one electron from the phenalenyl-radical dimer (giving a doublet cationic dimer), do you expect the interaction energy to increase or decrease? How could you verify your prediction?