THE 1-BICYCLO[1.1.1]PENTYL CATION AS A CH⁺ TRIMETHYLENEMETHANE COMPLEX

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Recognition of the equivalence of certain transition metal fragments and groups
comprised of first row atoms and hydrogen° casts new light onto old problems.
For example, Fe(CO)₃ and CH⁺ (or BH) are isolobal; ² both contribute two vacant
orbitals and a pair of electrons to structures in which they participate.¹
Hence, analogous geometrical arrangements are anticipated: I ³ vs II ⁴,⁵ and
III ² vs IV ⁵.

Since several trimethylenemethane Fe(CO)₃ complexes (e.g. V) have been
characterized,⁶ we may well expect CH⁺ to form stable complex VI with trimethyl-
енемethane.⁷ The compatibility of orbitals between the CH⁺ and the C₄H₅
fragments is quite like those describing the electronic structures of II ⁴ and
IV ⁵. The six interstitial⁸ electrons in II, IV, and VIa fill strongly stabilized
a and e orbitals, and the CH binding indicated by dotted lines in II, IV, and
VIa results. VIa may be recognized as a "nonclassical" form of the 1-bicyclo-
[1.1.1]pentyl cation (VIb).

This cation has been studied by Wiberg as a putative solvolysis intermediate."
For a highly strained bridgehead system, 1-bicyclo[1.1.1]pentyl chloride reacts remarkably rapidly, three times faster (not many powers of ten slower) than t-butyl chloride. However, the products, 3-methylenecyclobutyl derivatives formed via VII, are exclusively ring opened. This suggests that relief of ring strain concerted with ionization might be responsible for the enhanced rate, rather than any special stability of VI. In addition, a recent study showed that the spiropentyl cation VIII formed VII without the intervention of VI.

We have studied the nature of the 1-bicyclo[1.1.1]pentyl cation (VI) theoretically, using both MINDO/3 semi-empirical and RHF/STO-3G ab initio methods. At both these levels, VI is a local minimum on the C_5H_7^+ potential energy surface. With MINDO/3 the C_{3v} structure VI was obtained by Davidon-Fletcher-Powell optimization without symmetry constraints. At STO-3G, evaluation of the pertinent force constants using analytically calculated gradients showed the C_{3v} structure rigorously to be an energy minimum. However, the MINDO/3 barrier for conversion of VI to VII along the symmetry allowed C_{3v} reaction coordinate was only 1.8 kcal/mole. Such a low value is consistent with the observation of ring opened products during solvolysis, but suggests that this opening is not concerted with ionization.

The STO-3G optimized structure of VI (Table) supports its description as a CH^+ trimethylenemethane complex (VIa). In comparison with the STO-3G structure of the parent hydrocarbon, bicyclo[1.1.1]pentane (IX, Table), the C_1C_2 bonds in VI are lengthened, and the C_2C_3 bonds are shortened significantly. Noteworthy is the flattening which takes place in the cation. The C_1C_3 distance in VIII is calculated to be 1.89 Å, the shortest nonbonded C-C separation known; that these bridgehead carbons are strongly repulsive is indicated by their strongly negative overlap population (-0.279) (Table). In cation VI, C_1C_3 shortens to 1.64 Å, but the overlap population (-0.092) indicates that the antibonding character of the interaction is largely eliminated. This confirms a speculation of Wiberg that reduction of the nonbonded repulsion between bridgehead atoms upon ionization might contribute to the observed rate enhancement.

The non-involvement of VI in the rearrangement of the spiropentyl cation VIII to VII can be attributed to orbital symmetry prohibitions. Following Pearson, the bonds broken and formed during the conversion of VIII to VI can be classified in terms of the C_5 symmetry maintained during the reaction. The bonds broken
(indicated in VIII) transform as a' + a' while the bonds formed transform as a' + a'' (see VIb). Thus the process is symmetry forbidden.

Besides II, IV, and IV, a number of carbocations can be equated to isolobal transition metal equivalents, but this is not always successful. Further reports will be presented subsequently.

Acknowledgements

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Table. Calculated Structures and Energies of VI and IXa

<table>
<thead>
<tr>
<th></th>
<th>VI (C\textsubscript{3v})</th>
<th>IX (D\textsubscript{3h})</th>
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</thead>
<tbody>
<tr>
<td></td>
<td>MINDO/3\textsuperscript{b}</td>
<td>RHF/STO-3G\textsuperscript{c}</td>
</tr>
<tr>
<td>r\textsubscript{C1C2}</td>
<td>1.497 (0.998)</td>
<td>1.507 (0.671)</td>
</tr>
<tr>
<td>r\textsubscript{C2C3}</td>
<td>1.593 (0.867)</td>
<td>1.597 (0.581)</td>
</tr>
<tr>
<td>r\textsubscript{C1C3}</td>
<td>1.583 (0.331)</td>
<td>1.640 (-0.092)</td>
</tr>
<tr>
<td>r\textsubscript{C2H4}</td>
<td>1.093 (0.273)</td>
<td>1.090 (0.548)</td>
</tr>
<tr>
<td>r\textsubscript{C2H5}</td>
<td>1.106 (0.945)</td>
<td>1.088 (0.698)</td>
</tr>
<tr>
<td>&lt;C\textsubscript{1}C\textsubscript{2}H\textsubscript{5}</td>
<td>151.9</td>
<td>150.8</td>
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<tr>
<td>&lt;H\textsubscript{5}C\textsubscript{2}H\textsubscript{6}</td>
<td>108.5</td>
<td>115.7</td>
</tr>
<tr>
<td>Energy</td>
<td>253.4\textsuperscript{a}</td>
<td>-190.75749\textsuperscript{e}</td>
</tr>
<tr>
<td></td>
<td>(-192.72309)\textsuperscript{e,f}</td>
<td>(-192.60941)\textsuperscript{e,f}</td>
</tr>
</tbody>
</table>

\textsuperscript{a} Bond lengths in Å, angles in degrees. \textsuperscript{b} Bond indexes in parentheses. \textsuperscript{c} Mulliken overlap populations in parentheses. \textsuperscript{d} \(\Delta H^o\) in kcal/mole. \textsuperscript{e} Total energy in Hartrees. \textsuperscript{f} Energy using the 4-31G basis with STO-3G optimized geometry.
References

12. The Gaussian 70 series of programs were used: W. J. Hehre, W. A. Lathan, R. Ditchfield, M. D. Newton, and J. A. Pople, Program No. 236, Quantum Chemistry Program Exchange, Indiana University, Bloomington, Ind.

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