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[1] 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].
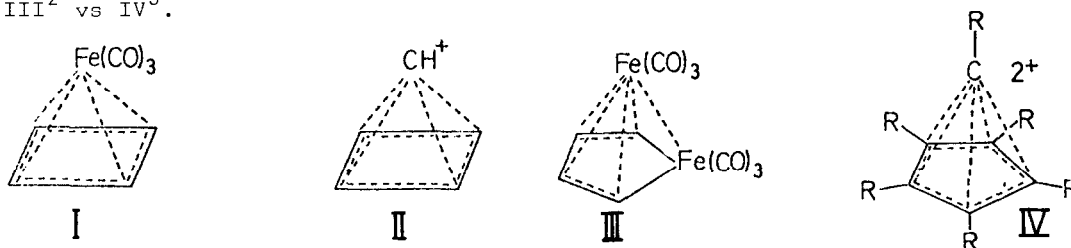

Since several trimethylenemethane $Fe(CO)_3$ complexes (e.g. V) have been characterized,[6] we may well expect CH^+ to form stable complex VI with trimethylenemethane.[7] The compatibility of orbitals between the CH^+ and the C_4H_6 fragments is quite like those describing the electronic structures of II[4] and IV.[5] The six interstitial[8] 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).
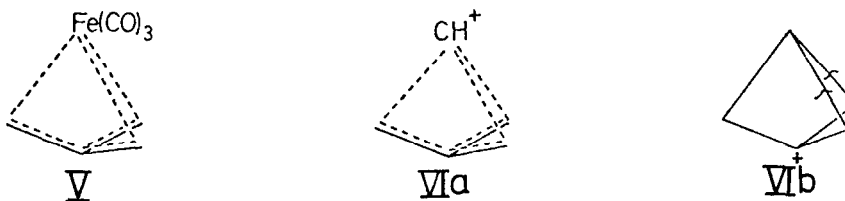
This cation has been studied by Wiberg as a putative solvolysis intermediate.[9]

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)[10] 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.[7]
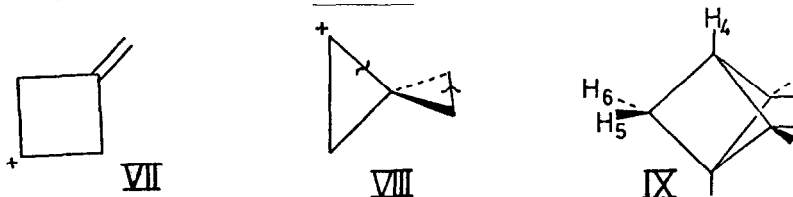
We have studied the nature of the 1-bicyclo[1.1.1]pentyl cation (VI) theoretically,
using both MINDO/3 semi-empirical[11] and RHF/STO-3G _ab initio_ methods.[12]

At both these levels, VI _is_ _a_ _local_ _minimum_ on the $C_5H_7^+$ potential energy
surface. With MINDO/3 the $\underline{C_{3v}}$ 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[13] showed the
$\underline{C_{3v}}$ structure rigorously to be an energy minimum. However, the MINDO/3 barrier
for conversion of VI to VII along the symmetry allowed $\underline{C_s}$ 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),[14] 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 1.890Å, 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
1.640Å, 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.[8]

The non-involvement of VI in the rearrangement of the spiropentyl cation VIII to
VII can be attributed to orbital symmetry prohibitions. Following Pearson,[15] the
bonds broken and formed during the conversion of VIII to VI can be classified in
terms of the $\underline{C_s}$ 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.[16] Further reports will be presented subsequently.

Acknowledgements

Table. Calculated Structures and Energies of VI and IX[a]

| | VI (C_{3v}) | | IX (D_{3h}) | |
	MINDO/3[b]	RHF/STO-3G[c]	MINDO/3[b]	RHF/STO-3G[c]
$r_{C_1C_2}$	1.497 (0.998)	1.507 (0.671)	1.549 (0.952)	1.552 (0.677)
$r_{C_2C_3}$	1.593 (0.867)	1.597 (0.581)	1.549 (0.952)	1.552 (0.677)
$r_{C_1C_3}$	1.583 (0.331)	1.640 (-0.092)	1.862 (0.028)	1.890 (-0.279)
$r_{C_3H_4}$	1.093 (0.873)	1.090 (0.548)	1.107 (0.907)	1.088 (0.752)
$r_{C_2H_5}$	1.106 (0.945)	1.088 (0.698)	1.112 (0.952)	1.087 (0.770)
$<C_1C_2H_{56}$	151.9	150.8	143.1	142.5
$<H_5C_2H_6$	108.5	115.7	104.3	111.1
Energy	253.4[d]	-190.75749[e]	58.8[d]	-191.61541[e]
		(-192.72309)[e,f]		(-193.60941)[e,f]

[a] Bond lengths in Å, angles in degrees. [b] Bond indexes in parentheses. [c] Mulliken overlap populations in parentheses. [d] ΔH_f^o in kcal/mole. [e] Total energy in Hartrees. [f] Energy using the 4-31G basis with STO-3G optimized geometry.

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