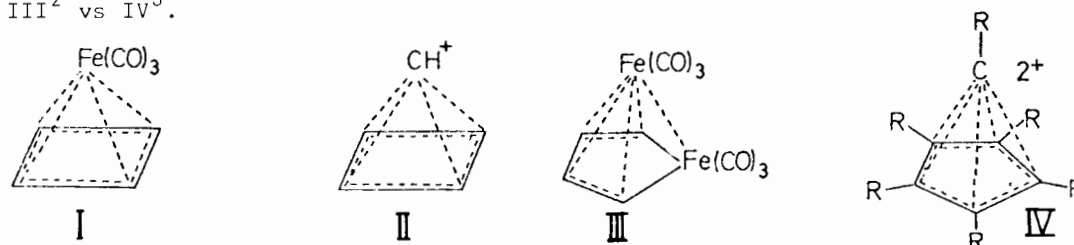


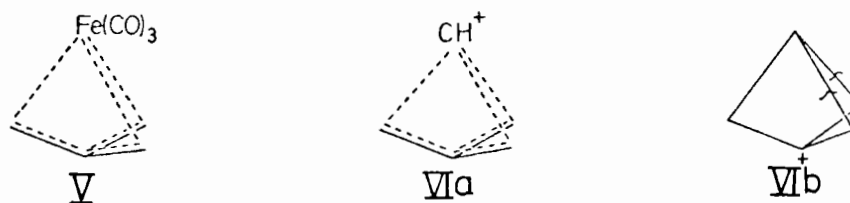
THE 1-BICYCLO[1.1.1]PENTYL CATION AS A CH^+ -TRIMETHYLENEMETHANE COMPLEX

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Recognition of the equivalence of certain transition metal fragments and groups comprised of first row atoms and hydrogen¹ casts new light onto old problems. For example, $\text{Fe}(\text{CO})_3$ 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: I³ vs II^{4,5} and III² vs IV⁵.

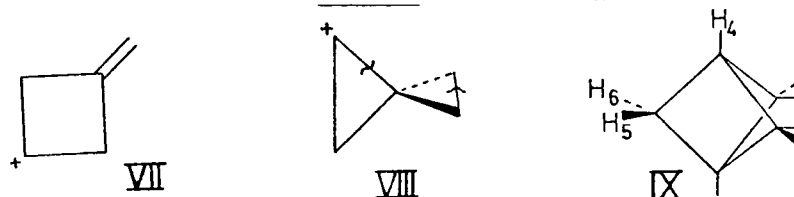


Since several trimethylenemethane $\text{Fe}(\text{CO})_3$ complexes (e.g. V) have been characterized,⁶ we may well expect CH^+ to form stable complex VI with trimethylenemethane.⁷ The compatibility of orbitals between the CH^+ and the C_4H_6 fragments is quite like those describing the electronic structures of II⁴ and IV.⁵ The six interstitial⁸ electrons in II, IV, and VIa fill strongly stabilized \underline{a} and \underline{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 spiro-pentyl 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-empirical¹¹ 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 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 gradients¹³ 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_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 1.890 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 1.640 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.⁸

The non-involvement of VI in the rearrangement of the spiro-pentyl 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 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.

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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)
$\langle C_1C_2H_5 \rangle$	151.9	150.8	143.1	142.5
$\langle H_5C_2H_6 \rangle$	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° in kcal/mole. ^e Total energy in Hartrees. ^f Energy using the 4-31G basis with STO-3G optimized geometry.

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