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ELECTRONIC SPECTRA OF PYRAMIDAL DICATIONS, $(CCH_3)_6^{2+}$ AND $(CH)_6^{2+}$.

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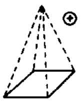
Interest is increasing in the preparation, chemistry, and unusual bonding properties of pyramidal carbonium ions, fascinating newcomers to the nonclassical group.[1-8] Representatives of two possible types of these ions, $(CH)_5^+$, 1, and $(CH)_6^{2+}$, 2, have already entered the recent literature. The parent $(CH)_5^+$ ion has been the subject of a number of calculations[1] and a methyl substituted derivative has been prepared.[2] Preparative work on several substituted homo-[3] and bishomo-$(CH)_5^+$ cations[4] has also been reported.



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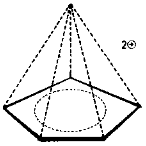

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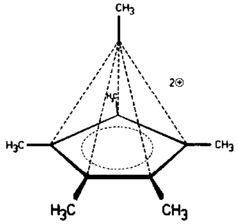

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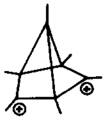

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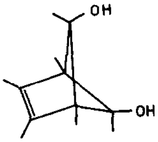
The hexamethyl derivative of 2, $(CCH_3)_6^{2+}$ dication 3, has been prepared in strongly acidic solutions from a variety of percursors.[5] A number of arguments, including nmr spectroscopic evidence and the chemical reactivity of 3, justifies expression of a strong preference for the nonclassical structure 3, rather than a rapidly equilibrating system of classical ions 4.[6]The nonclassical structure was substantiated also by ab initio quantum mechanical calculations on the parent ion 2.[7] We wish to present here experimental observations on the electronic spectrum of $(CCH_3)_6^{2+}$ as well as ab initio calculations on the electronic spectrum of $(CH)_6^{2+}$.

Strongly acidic solutions of dication 3 show no uv absorption that can be due to the dication itself. All observed absorptions (figure 1) can be assigned to other species. Preparation of solutions of 3 in $FHSO_3$-SbF_5 (1:1 molar ratio) from diol 5 or epoxide 6 as reported,[6] gives rise to a solution showing a maximum at 208 nm. This absorption is due to a species which is formed by reaction of the solvent with the water lost by 5 or 6 in the reaction to give 3. Also a shoulder is seen at 285 nm, which increases in intensity on standing at room temperature. This absorption is caused by a trace of hexamethylbenzenium ion 7[9] formed from the reported[6] hydride uptake by 3



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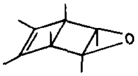

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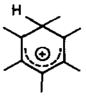

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under these conditions. These conclusions were confirmed by measuring the uv spectrum of a solution 3 prepared by an alternate route. Hexamethyldewarbenze, 8, was extracted at -40° from a 1,1,2-trichlorotrifluoroethane solution into $FHSO_3$-SbF_5 (1:2 molar ratio). The pmr spectrum of the acid layer showed the presence of 3, together with 5% of hexamethylbenzenium ion 7. Ion 3 presumably is formed by proton addition to 8 to give 9, followed by hydride abstraction.

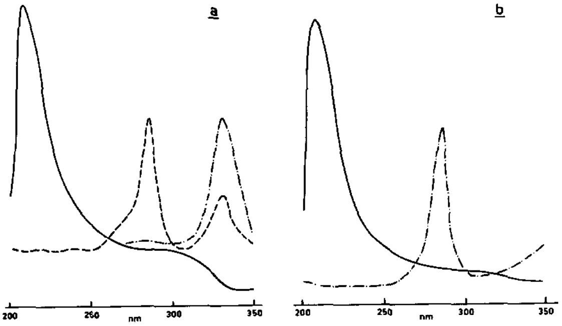


Fig. 1. Uv spectra in strongly acidic solutions. These spectra are obtained using a Beckman DB-G spectrofotometer and 1 mm quartz cells.

a. *Spectra of dication solutions,*

——— 3 mg/ml of 5 in $FHSO_3$-SbF_5 (1:1 molar ratio) at 0°, the maximum at 208 nm is due to a species formed on reaction of water, lost by 5, with the solvent. The shoulder at 285 nm is due to 7.

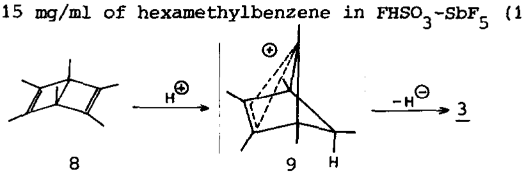
-.-.- the same solution, now recorded after 20 min at 20°, the intensity of the absorption at 285 nm (7) has increased and a new maximum at 332 nm (10) is present,

----- 3 mg/ml of 8 in $FHSO_3$-SbF_5 (1:2 molar ratio) at 20°, the maximum at 208 nm is absent, 7 is present in a larger amount, 10 shows absorptions at 332, 265, 240, and 220 nm (ref. 11).

b. reference spectra,

——— 0.55 mg/ml of water in $FHSO_3$-SbF_5 (1:1 molar ratio) at 20°,

-.-.- 0.15 mg/ml of hexamethylbenzene in $FHSO_3$-SbF_5 (1:2 molar ratio) at 20°.



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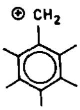

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Ion 7 can be formed thermally from intermediate 9.[10] The uv spectrum of this solution, prepared from a percursor losing no water, lacks the absorption at 208 nm. Due to the higher concentration of 7, the absorption at 285 nm is stronger than in the previous case. At temperatures higher than 0° all solutions of dication 3 slowly turn purple due to the formation of pentamethylbenzyl cation 10. The uv absorptions of this ion appear at the reported[11] wavelenghts as far as not obscured by stronger absorptions.

We conclude that no uv absorption for 3 with a molar extinction greater than 100, can be detected. A less strong absorption, however, can have been obscured by the absorptions of other species and might have escaped detection.

The best available models for a classical ion 4 are cyclopropylcarbinyl cations. These cations show absorptions with large molar extinctions ($\varepsilon > 10^4$) in the region 270-290 nm.[12] From this consideration it is difficult to see why classical structure 4 with two positive centers interacting with the cyclopropyl group would have no observable uv absorption. Unfortunately, no models are available for cation 3. However, *ab initio* calculations on the electronic structure of several states of parent ion 2 substantiate our interpretation that 3 does not absorb in the uv region.

Following the results of ref. 7, $(CH)_6^{2+}$ has C_{5v} symmetry and a closed shell $^1A_1$ ground state. The 40 electrons doubly occupy 6 MOs of species a_1, 8 of species e_1 and 6 of species e_2. Using the computed equilibrium geometry[7] we performed a SCFMO calculation on the ground state with a [63/3] gaussian basis set (*i.e.* 6s- and 3p-functions on each carbon atom and 3s-functions on each hydrogen) contracted into a [42/2] scheme. This basis is of "double-zeta" quality and has been used before for similar purposes.[13] Orbital energies and -types of the highest occupied MOs and of the first few virtual MOs are listed in table 1.

Table 1: $(CH)_6^{2+}$ ground state MOs

MO	orbital energy (hartrees)
$6a_1$ (occ)	-1.02048
$4e_1$ (occ)	- .89388
$7a_1$ (empty)	- .270301
$4e_2$ (empty)	- .26344
$5e_1$ (empty)	- .23438
$8a_1$ (empty)	- .15742

From these results a number of excited configurations were selected which might correlate with uv absorptions, and separate (open shell) SFC calculations were carried out for these configurations. We report here only results with a computed excitation energy of less than .36 au (corresponding to a wavelength > 126 nm), *i.e.* of the excitations from the ground state to the configurations $(4e_1)^3 7a_1$ and $(4e_1)^3 4e_2$. Table 2 gives total energies of the various states, as well as the differences, expressed in nm. We see clearly that the first spin allowed transition in this model system is computed to lie well below 200 nm.

Table 2: Total energies and energy differences with respect to the ground state for several excited configurations of $(CH)_6^{2+}$.

config.	s/t	E (hartrees)	ΔE (nm)
$(4e_1)^4$	s	-229.31987[a]	
$(4e_1)^3 7a_1$	t	-229.03153	158
	s	-229.01367	148
$(4e_1)^3 4e_2$	t	-228.99889	142
	s	-228.95989	126

[a] ground state; s = singlet; t = triplet.

These computations refer to a single ion in vacuum, whereas the spectrum was measured in solution. Moreover, cation 3 contains 6 methyl groups whereas 2 has hydrogen atoms only. However, if we make a generous estimate of the combined effects of the solvent and the methyl substitution[12] to be a red-shift of 40-50 nm, the first allowed transition still lies outside the uv region.

In conclusion, we may reiterate that spectroscopic and theoretical evidence supports the nonclassical, pyramidal structure of 3.

Footnotes and references.

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