DIRECT OBSERVATION OF A REMARKABLY STABLE DICATION OF UNUSUAL STRUCTURE: $(CCH_3)_6^{2\oplus}$.[1]

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Recently we reported on the observation of the bishomocyclopropenyl cations 1 and 2 in methylene chloride solution[2,3] at low temperatures. We have now obtained evidence that these ions in strong acid solutions are converted into a remarkable stable dication for which we propose structure 3.

1

$- = CH_3$
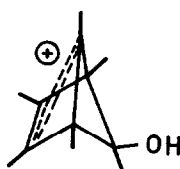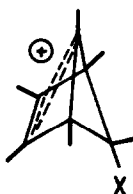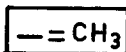
2

a. X = Cl
b. X = Br

3

Solutions of diol 4[3,4] in $FHSO_3$ and in SbF_5/SO_2 and diether 5[3] in $FHSO_3$ prepared at -60° provided identical PMR spectra[5] at -60°: 2.65 (s, 5CH_3) and 1.96 (s, 1CH_3). On extracting a methylene chloride solution of ion 2a[2] with $FHSO_3/SbF_5$ (5:1 v/v) a solution was obtained which showed the same PMR spectrum at -60°. The PMR spectra were temperature independent in the range from -140° to +40°,[6] whereas at higher temperatures an irreversible reaction was observed, via intermediates that are still under investigation, to hexamethylbenzenium ion 7[7]. This reaction was

shown to be faster in FHSO$_3$ than in FHSO$_3$/SbF$_5$ (5:1 v/v). The CMR spectrum[8] of 3 in FHSO$_3$ at -60°

showed peaks at 126.3 and 22.5 ppm (intensity ratio 5:1), which remained singlets in proton off

resonance decoupled spectra, and at 10.6 and -2.0 (intensity ratio 5:1) showing methyl quartets

using the off resonance technique.

On quenching solutions of 3 in FHSO$_3$ with NaOCH$_3$/CH$_3$OH at -60°, and after workup, a

reaction mixture was obtained, containing 95% of 5[3] (determined by PMR). On standing in the air

at room temperature 5 showed the reported[3] conversion into 4, which was isolated in 80% yield

(calculated on the basis of ion precursors). When quenched with KOH/C$_2$H$_5$OH at -60° 8[3] was obtained

(80%, determined by PMR) and on conversion in the air at room temperature 65% of 4 was isolated.[3]
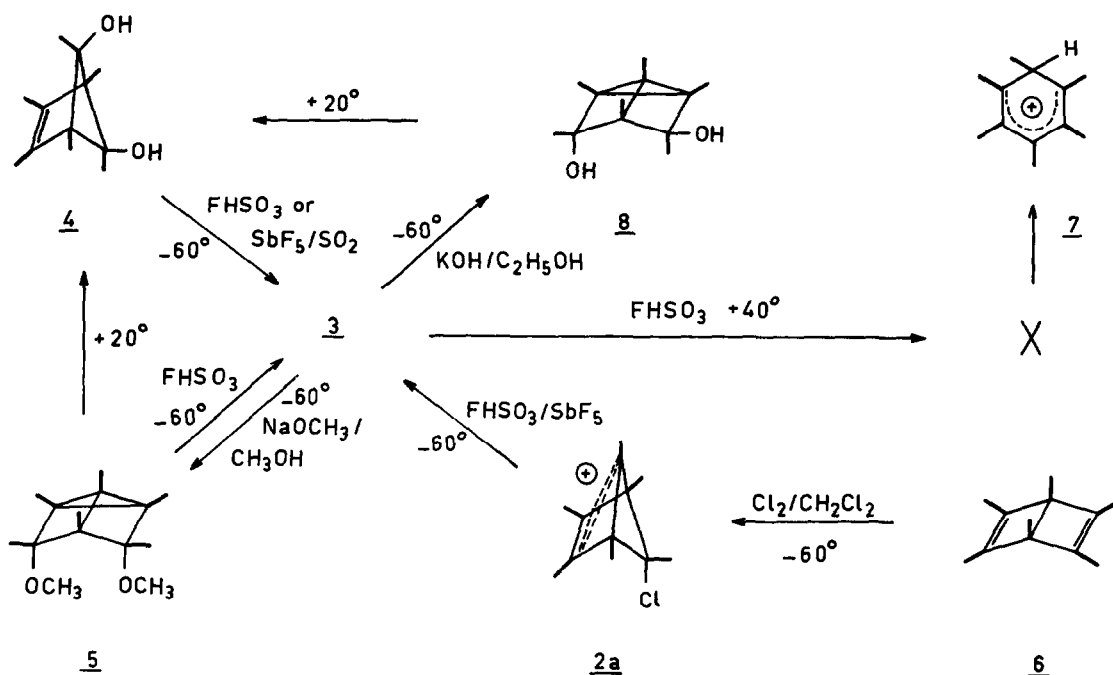
The PMR and CMR chemical shifts, being far downfield from those of the monocations 1 and

2[2,3] strongly suggest 3 to be a dication. This is confirmed by the fact that precursors containing

different substituents on treatment with acid yield solutions of the same ion. Because of possible

rearrangements[9] several structures for this cation have to be discussed. The antiaromatic structure

9 has to be rejected because of incompatibility with the PMR and CMR spectra and the impossibility

of yielding 5 and 8 as quenching products. For the same reasons the stabilised pericyclic[10] cations

10 and 11 are ruled out. Expanding the discussion of Goldstein and Hoffmann[10] on longicyclic sta-

9   10   11

12   13   14
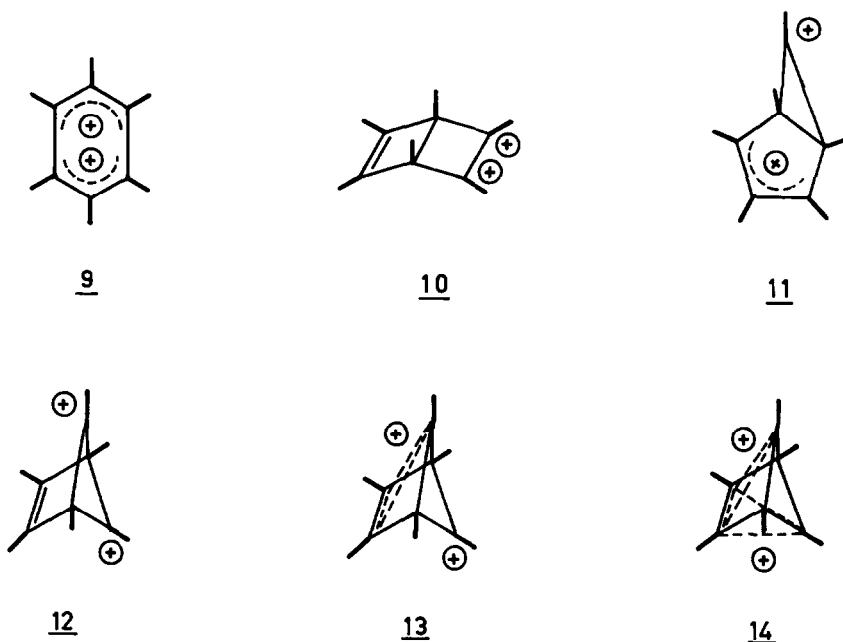
bilisation to dipositive ions, 12 must be regarded as stabilised because of its modal description

(0,0,2). However neither 12, nor the delocalised descriptions 13 and 14 account for the 5:1 peak

ratios in the PMR and CMR spectra. The static description 15 does not show the necessary symmetry

either, but the peak ratio could be rationalised with the depicted fivefold degenerate rearrange-

ment if sufficiently rapid to make five carbon atoms (with the attached methyls) equivalent on the

NMR time scale. From the absence of line broadening at -140° in the PMR spectrum it is concluded

that the free enthalpy of activation of such a rearrangement would be $<$ 5 kcal/mole. It should be

noted that this only holds for a rapid Wagner-Meerwein shift of bonds (a) and not of bond (b) be-

cause the latter type would involve intermediate 16, giving rise to complete scrambling of the

six carbon atoms (with the attached methyls). The alternative is the highly delocalised structure

3, which we prefer because of the following reasons:

A frequently used method for discerning between a rapidly equilibrating system and a

delocalised structure[11] depends on a comparison of the observed CMR chemical shifts with the cal-

culated average of the equilibrating carbon atoms by use of suitable model compounds. The average

of the five equilibrating skeleton carbons of 15 is calculated with use of the CMR chemical shift

of C$^{\oplus}$ in dimethylcyclopropylcarbinyl cation (281.4 ppm)[12] and the chemical shifts of carbon atoms

2 (45.0 ppm)[8] and 4 (47.7 ppm)[8] of 1̲7̲[13] to be (2 x 281.4 + 2 x 45.0 + 47.7)/ 5 = 140.1 ppm. This

value needs correction for positive charge adjacent to the quaternary carbon atoms of the five

membered ring.[11] In the cyclopentyl cation case it was shown that 13 ppm is a realistic value[11]

to correct the calculated average for one positive charge in a five membered ring. Using this

factor an average value of 166.1 ppm is calculated for the five membered ring containing two po-

sitively charged carbon atoms. Olah[14] reported that no deviations from the observed value larger

than 10 ppm would occur on calculating the average CMR chemical shifts in classical ions, there-

fore the observed chemical shift of 126.3 ppm cannot be explained with rapid equilibration of lo-

calised structures 1̲5̲. Additional evidence for structure 3̲ is gained from the single methyl CMR

peak at δ = -2.0 ppm. The chemical shift of the methyl attached to carbon atom 1 of 1̲7̲[13] was found

to be 4.3 ppm.[8] As structure 1̲5̲ has approximately the same geometry as 1̲7̲, one would expect a

downfield shift, rather than an upfield shift on introduction of localised positive charges at

carbon atoms 3 and 5, that is going from 1̲7̲ to 1̲5̲. The observed upfield shift of 6.3 ppm, however,

is readily explained with structure 3̲, with the methyl at the top carbon atom being in the shiel-

ding cone of the ring current of the five membered ring.

1̲5̲   1̲5̲   1̲5̲

1̲6̲   1̲6̲   1̲7̲
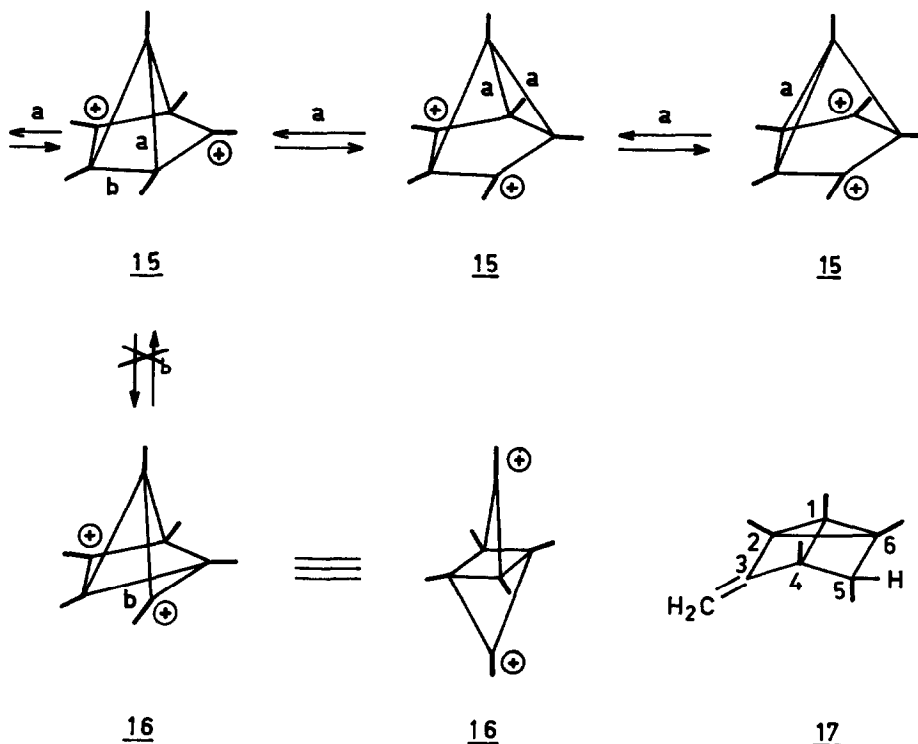
Structure $\underline{3}$ strongly resembles structure $\underline{18}$, once suggested as a possible description

of the norbornadienyl cation[15] ($(CH)_7^{\oplus}$ species) and structure $\underline{19}$, recently reported[16] to be an

energy minimum of the $(CH)_5^{\oplus}$ species. Formally $\underline{3}$ can be seen as sp hybridised $^{\oplus}C\text{-}CH_3$ interacting

with a pentamethylcyclopentadienyl cation ($\underline{20}$). The interaction diagram showing how the orbitals

of $\underline{3}$ are constructed in this way is given below. From the CMR chemical shifts indicating low po-

sitive charge at the top carbon, it is concluded that net electron donation takes place from the

ring towards the $C^{\oplus}\text{-}CH_3$. The stabilising orbital interactions discussed here are held responsible

for the thermal stability of $\underline{3}$, which is very high compared with the aromatic tetramethylcyclo-

butenium dication, which was reported[14] to be more than 80% decomposed in a $FHSO_3/SbF_5/SO_2$ solu-

tion at -78° after 6 hr.
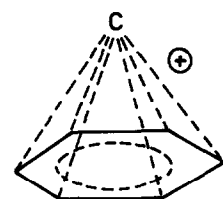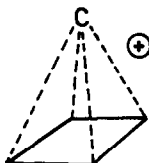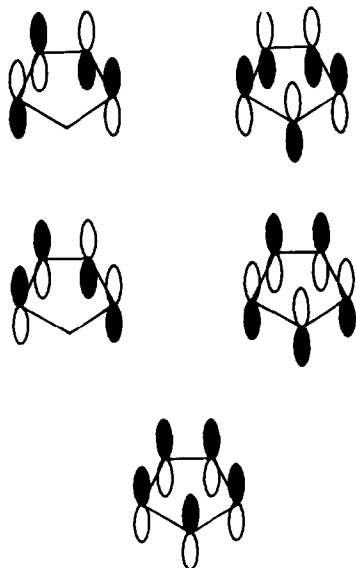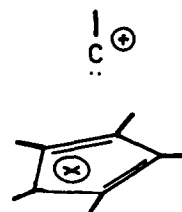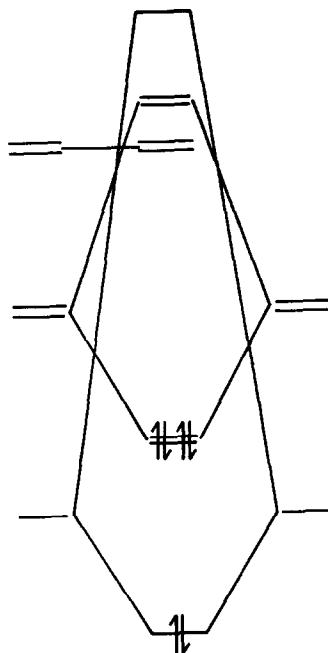
18   19   20
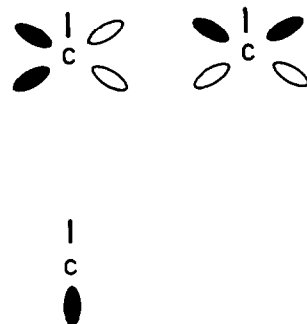
Professor W.C. Nieuwpoort and drs. H.T. Jonkman are presently engaged in an ab initio quantum mechanical calculation of the various structures of the parent $(CH)_6^{2\oplus}$ cation. Preliminary data show that structure 3 in indeed an energy minimum (see accompanying paper). The authors thank professors W.C. Nieuwpoort and P. v. R. Schleyer for a stimulating discussion.

Footnotes and references:

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5. PMR chemical shifts are measured with methylene chloride as internal standard, taken as $\delta = 5.30$ ppm downfield from TMS.

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