From experimentel chemistry to in-silico chemistry

Selected topics of computational NMR spectroscopy of carbocations

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Carbocations are important reactive intermediates in Organic Chemistry. Many chemical reactions in polar media as well as biochemical transformations proceed via positively charged ionic intermediates, i.e. carbocations. These are only local (not global) minima on the energy surface with very short lifetimes (may be a millionth of a second or less).

We elucidate structure and electronic stabilization modes of new and unusual carbocations which some have been discussed controversially for many years. Using matrix co-condensation techniques we prepare long-lived carbocations with the aid of superacids at low temperatures in solution. These are characterized experimentally using high field ^{1}H, ^{13}C and ^{29}Si NMR spectroscopy. The experiments are accompanied by high level ab initio molecular orbital calculation of the molecular geometry and charge distribution as well as magnetic properties such as NMR chemical shifts and spin-spin coupling constants.

We describe here the experimental and computational characterization of the first β-silyl-stabilized simple alkyl cation and the first characterization of a static γ-silyl-substituted bicyclobutonium ion.

1 The β-silyl effect in tert.-butyl cation

The low temperature ^{13}C NMR spectrum of the β-triisopropylsilyl substituted t-butyl cation prepared from the corresponding silyl substituted Alkene precursor under very carefully controlled experimental conditions is shown in Fig. 1.

Quantum chemical calculations with wave function methods including electron correlation were performed for β-silyl substituted tert.-butyl cations with various silyl groups. The calculations reveal the geometrical distortions accompanying β-silyl hyperconjugative stabilization (Fig. 2). Visualization of NBO calculations show the formation of a 2-electron 3-center bond thus confirm the stabilization by the β-silyl group (Fig. 3). MP2 ab initio calculation of NMR chemical shifts for a $Si(CH_3)_3$-substituted model structure are in accord with the experimental chemical shifts for the $Si(ipr)_3$ substituted cation (Fig. 4).

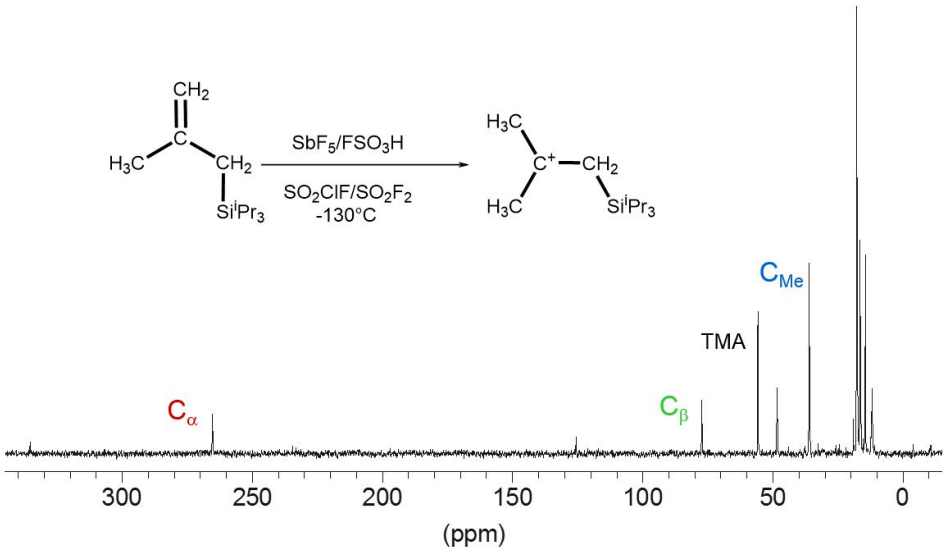

Figure 1: 100 MHz ^{13}C NMR, SO_2ClF/SO_2F_2, -130° , ref. TMA= 55.65 ppm.

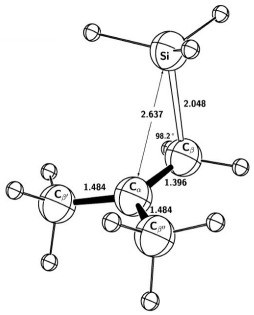

Figure 2: Hyperconjugational distortion of β-SiH_3 substituted t-butyl cation.

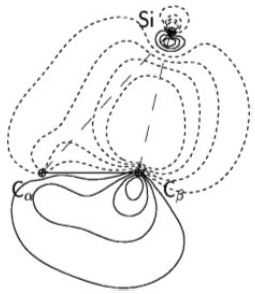

Figure 3: NBO-Analysis showing the natural localized molecular orbital (NLMO) of the 2e3c bond.

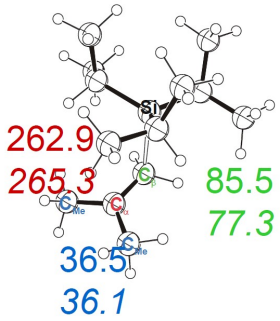

Figure 4: Experimental (italic) ^{13}C NMR chemical shifts of Si(ipr)$_3$-substituted t-butyl cation and calculated (regular) chemical shifts of $Si(CH_3)_3$-substituted t-butyl cation.

2 From hyperconjugational distortion to hypercoordination (bridging)

The $C_4H_7^+$ system has been investigated for many years. The flat potential energy surface leads to a fast threefold degenerate interconversion of the bicyclobutonium ion with the isomeric cyclopropylmethyl cation (Fig. 5). Only averaged chemical shifts could be observed even at the lowest temperatures in solution. Early quantum chemical calculations were not decisive.

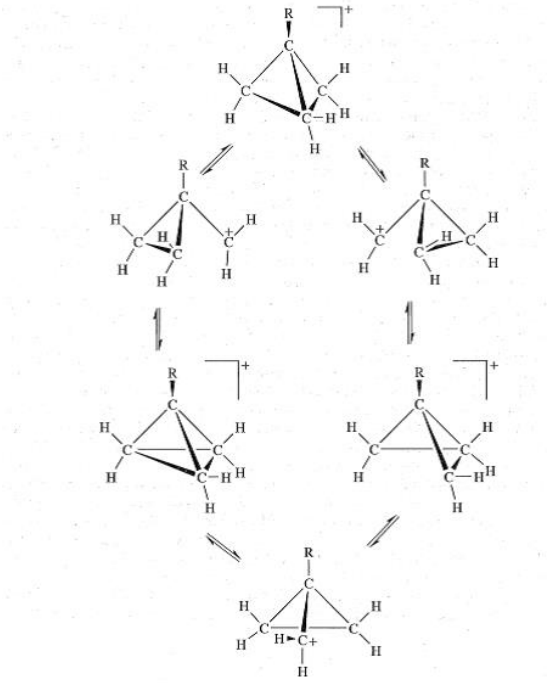

Figure 5: Threefold degenerate rearrangement of $C_4H_7^+$ cations.

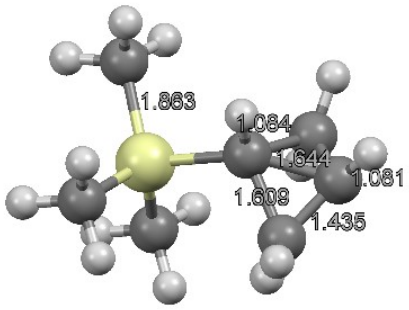

Figure 6: γ-silyl substituted bicyclobutonium ion.

We have applied the silyl effect to generate the first static bicyclobutonium ion in solution. Fig. 6 shows the preferred bridged bicyclobutonium structure of the γ-silyl substituted $C_4H_6R^+$ (R= $Si(CH_3)_3$) cation. A comparison of experimental and calculated ^{13}C NMR chemical shifts shows excellent agreement (Fig. 7).

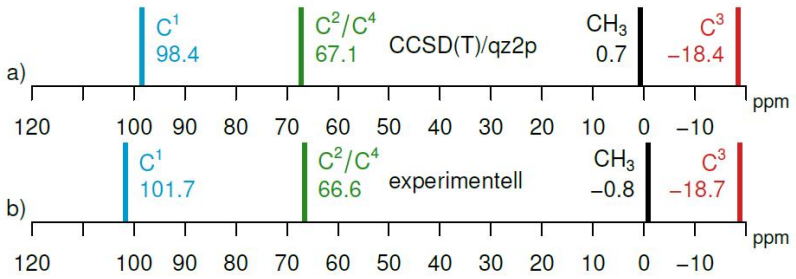

Figure 7: Comparison of experimental and calculated NMR chemical shifts of γ-silyl substituted bicyclobutonium ion

The experimental (J = 5,5 Hz) and calculated (5,9 Hz) vicinal J_{H1H3} spin spin coupling constant (Fig. 8) as well as the calculated J_{C1C3} spin spin coupling constant and coupling deformation density calculations are in accord with bridged structure of the silyl substituted bicyclobutonium ion. NBO calculations indicate an occupied NLMO for the bridging bond (Fig. 9) and a vacant orbital at Silicon in accord with the VB-description of the γsilyl effect.

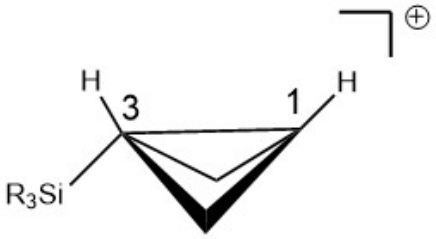

Figure 8: Transannular $^3J_{H,H}$ spin spin coupling in silyl substituted bicyclobutonium ion.

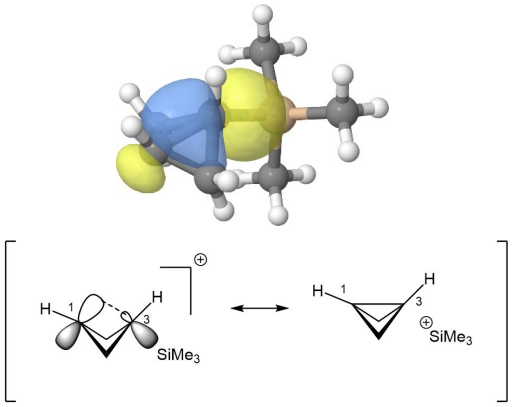

Figure 9: NLMO of the bridging bond in 3-$SiCH_3)_3$ substituted bicyclobutonium ion.

Acknowledgements

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References

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