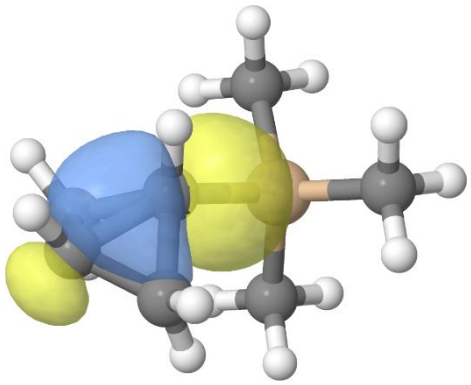
Quantum Chemical Calculation of $J_{(Si,C)}$ Nuclear Spin-Spin Coupling Constants. A Tool for Investigation of Silicon Carbon Hyperconjugation and Hypercoordination in Carbocations

Martin Holzschuh, Christoph Freudenberger, Philipp Huber, Hans-Ullrich Siehl
University Ulm – Institute of Organic Chemistry I, Albert-Einstein-Allee 11, 89069 Ulm
ullrich.siehl@uni-ulm.de

Nuclear spin-spin coupling arises through interaction of the nuclei with the spin or angular momentum of the intervening electrons in a magnetic field. Thus spin-spin coupling constants are dependent on the bonding, i.e. the electron density between the nuclei. [1,2]

$J_{(Si,C)}$-coupling constants in selected silyl-substituted carbocations[3] and structurally similar model compounds were calculated in order to explore the effect of delocalisation of electron density arising from hyperconjugation and hypercoordination on the magnitude of silicon-carbon spin-spin coupling constants.[4]

The variation of $J_{(Si,C)}$-spin-spin coupling constants can be correlated with structural parameters, such as Si-C-bond lengths, NBO-charges and localized molecular orbitals (NLMOs).



CCSD/cc-pVTZ calculated C^1C^3 NLMO of
endo-3-trimethylsilylbicyclobutonium cation

1. Ramsey, N. F.; Purcell, E. M. *Phys. Rev.* **1952**, *85* (1), 143–144.
2. Ramsey, N. F. *Phys. Rev.* **1953**, *91* (2), 303–307.
3. leading references: Siehl, H.-U.; Müller, T. In *The Chemistry of Organic Silicon Compounds*; Rappoport, Z., Apeloig, Y., Eds.; Wiley & Sons, Ltd.: Chichester, UK, **1998**; Vol. 2, pp 595–701. Siehl, H.-U. In *Recent Developments in Carbocation and Onium Ion Chemistry*; Laali, K. K., Ed.; ACS Washington, DC, **2007**; pp 1–31.
4. Holzschuh, M.; Freudenberger, C.; Huber, P.; Siehl, H.-U. submitted.