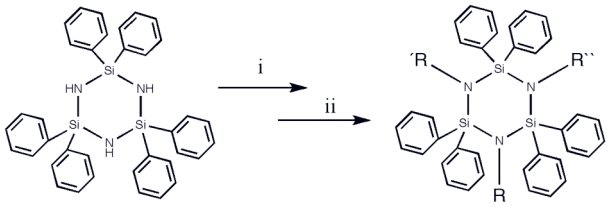
DFT Calculations on Hexaphenylcyclotrisilazanes – a Structural Discussion

Amra Suljanovic[1], Roland C. Fischer, and Michaela Flock

[1]*Anorganische Chemie, TU Graz, Stremayerg. 16, A-8010 Graz, Austria*
E-mail: amra.suljanovic@tugraz.at

Although polysilazanes are known for quite a long time, they still remain in the focus of attention. [1], [2] In the last few years their application as ceramic precursors has been discovered especially in the field of high temperature or dielectric coatings. [3] We recently became interested in the chemistry of hexaphenylcyclotrisilazanes, as a molecular precursor for potential applications in material science.

It is clear that various substituents on the six membered ring (see scheme below) play a crucial role on the polymer properties, especially the thermal behavior. Similar Si-N ring systems have been analyzed in the past, but they contain smaller methyl substituents at the silicon atoms.[4] In contrast to our hexaphenyl substituted ring, which is stable under reaction conditions, the studied methyl derivatives frequently undergo rearrangement reactions when further derivatized.
Moreover, the six membered silicon rings usually appear in three conformations (chair, boat and twist) but for the currently studied SiN-rings the structure is different. Crystallographic data show more or less planar ring geometries.
Additional DFT calculations (mPW1PW91/6-311G*) have been made to gain a deeper insight and to assist the interpretation of the structural properties. According to the generated data, the Si-N ring conformation changes with different substituents. NMR shifts and NBO analysis aid the interpretation of the measured data.



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	R	R`	R``
7	H	H	$SiMe_2H$
8	H	$SiMe_2H$	$SiMe_2H$
9	$SiMe_2H$	$SiMe_2H$	$SiMe_2H$
10	Me	Me	Me

	R	R`	R``
2	H	H	Li
3	H	Li	Li
4	Li	Li	Li
5	H	H	K
6	H	K	K

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