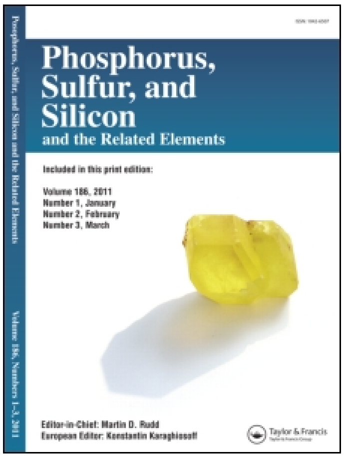

Phosphorus, Sulfur, and Silicon and the Related Elements
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713618290

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To cite this Article Jaschke, Bettina , Klingebiel, Uwe and Gellermann, Eike(2001) 'Effects of Fluorine on Cyclosilazanes and Cyclic Silylhydrazines', Phosphorus, Sulfur, and Silicon and the Related Elements, 168: 1, 129 — 134

To link to this Article: DOI: 10.1080/10426500108546542

URL: http://dx.doi.org/10.1080/10426500108546542

Phosphorus Sulfur and Silicon, 2001, Vol. 168, pp. 129-134
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Effects of Fluorine on Cyclosilazanes and Cyclic Silylhydrazines

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Compared with organic-substituted cyclosilazanes only a few Si-N ring systems with inorganic substituents are known. They differ very much in molecular structure and reaction behaviour. We succeeded in the synthesis of the first (F_2SiN-) cyclodi- and cyclotrisilazanes. Standard molecular orbital ab initio calculations for several cyclosilazanes were carried out for the parent cyclodisilazane, the tetrafluoro-substituted cyclodisilazane, the disilyl-substituted cyclodisilazane, and the disilyl-, tetrafluoro-substituted cyclodisilazane in order to provide a rationalisation for the very short Si···Si distance in the isolated cyclodisilazanes.

Keywords: Cyclosilazanes; Silylhydrazines; Ab initio calculations; X-ray structures

It was found that replacement of all hydrogen atoms bonded to silicon by fluorine atoms leads to a very large thermodynamic stabilization of the cyclosilazane skeleton. The stabilization effect of the exocyclic silyl substituent is also substantial.

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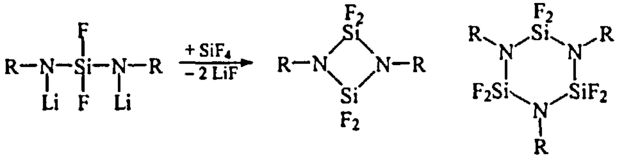
RESULTS

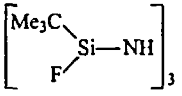
Relative to organic substituted cyclosilazanes only a few (Si-N) ring systems with inorganic substituents are known.[1-3] The ammonolysis of SiF_4 stops at the ammonia adduct $SiF_4 \cdot 2\ NH_3$ and SiF_4 does not react with the less basic silylamines, but with silylamides fluorinated Si–N ring compounds are obtained.



Cyclosilazanes bearing organic substituents and Si-N ring systems in which some or all of the substituents are inorganic differ very much in their reactivity and molecular structures, e.g.

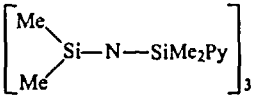
Cyclotrisilazanes

planar



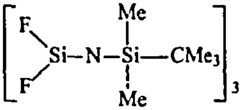
Si—N: 169 pm
Si—F: 160 pm

tub



Me_2Si—N: 177 pm
PySi—N: 172 pm

twist

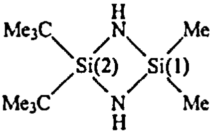


F_2Si—N: 169 pm
Me_2Si—N: 179 pm

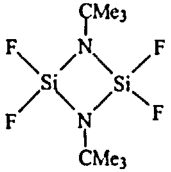
Cyclotrisilazanes are found to be planar to have tub or twist conformation. Rings with hydrogen bonded to the N-atoms are planar. Rings with bulky silyl groups bonded to the N-atoms have a tub conformation and rings with fluorine atoms bonded to the endocyclic silicon atoms have a twist conformation. Due to the electron with drawing effect of the fluorine atoms the endocyclic Si-N bonds are shorter than the exocyclic ones. The opposite is found in cyclotrisilazanes bearing organic substituents.

Cyclodisilazanes with organic substituents at the ring silicon atom have the following common structural properties: — the rings are planar; — the endocyclic Si–N–Si angles are larger while the N–Si–N angles are smaller than 90°; — the endocyclic Si–N bonds are longer than the exocyclic Si–N bonds.

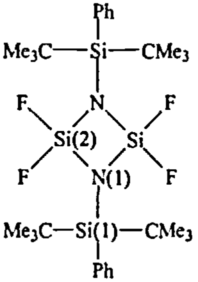
Cyclodisilazanes bearing silyl groups at the nitrogen and fluorine substituents at the ring silicon atoms play the opposite structural features to their organic substituted counterparts. Now the Si–N–Si angles are smaller while the N–Si–N angles are larger than 90°C, and the observed endocyclic Si–N bonds are shorter than the exocyclic ones. This brings the ring silicon atoms into close proximity. The shortest transannular Si···Si distances, very close to that of a normal Si–Si single bond (235 pm), are found in these compounds, e.g.



Si(1)–N : 173.8 pm
Si(2)–N : 174.8 pm
Si(1)–N–Si(2) : 92.5 °

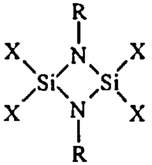


Si–N : 170.6 pm
Si–N–Si : 90.0°
Si···Si : 241.3 pm



Si(1)–N(1) : 178.3 pm
Si(2)–N(1) : 170.1 pm
Si(2)–N(1)–Si(2a) : 88.4°
Si(2)···Si(2a) : 237.6 pm

Ab initio calculations were carried out by Thomas Müller and Yitzhak Apeloig in order to see if they could reproduce the experimental X-ray structures and provide a rationalisation for the very short Si···Si distance in the isolated molecules.



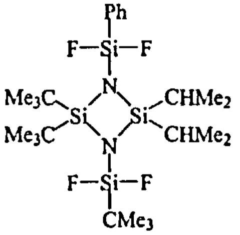
calculated (R = SiH_3)				
X	Si-N_{endo} [pm]	Si-N_{exo} [pm]	Si-N-Si [°]	Si···Si [pm]
H	174.6	172.4	91.3	249.7
F	171.8	174.5	89.8	242.5

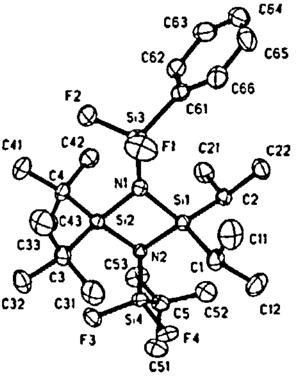
X-ray (R = $Si(CMe_3)_2Me$				
X	Si-N_{endo} [pm]	Si-N_{exo} [pm]	Si-N-Si [°]	Si···Si [pm]
H	174.0	173.3	89.7	244.7
F	170.1	176.8	88.3	237.8

The following main conclusions can be drawn from this combined experimental and theortical study regarding the structures of cyclosilazanes.[1]

1. The major shortening of the Si···Si distance is a result of the combined effects of the substituents, of the four fluorine atoms and the two silyl groups.
2. There are no bonding interactions between the ring silicon atoms.

In compounds with exocyclicly bonded SiF_2 groups the exocyclic Si–N bonds are shorter than the endocyclic ones and the N-atoms often have no planar environment, e.g.

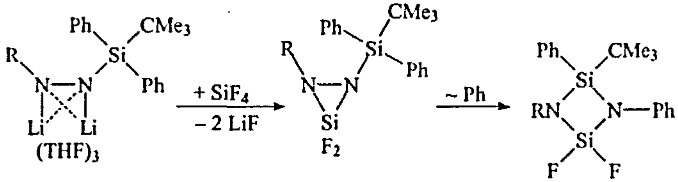




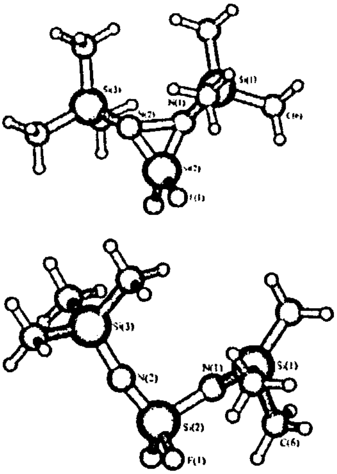
Si(1)–N(1): 176.0 pm
Si(1)–N(1)–Si(2): 92.15°
N(1)–N(2) / N(2)–Si(4): 166.4°

Si(3)–N(1): 168.1 pm
Σ N(2) pyramidal: 355.15°
N(2)–N(1) / N(1)–Si(3): 176.4°

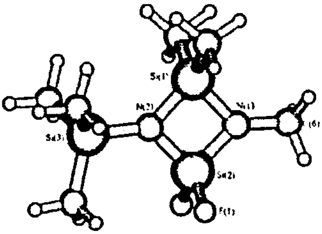
In attempts to prepare a three membered F_2SiN_2 – ring system, we recently found the first examples of a reductive insertion of a silyl group into the nitrogen-nitrogen single-bond accompanied by migration of an organyl or a hydrogen atom group from silicon to a nitrogen atom,[4] e.g.



The (F_2Si–N–) bonds of the four-membered ring 169.2 and 170.4 pm are relatively short. In order to understand the formation of the four membered ring from the three membered ring in an unimolecular isomerisation process, quantum chemical calculations were carried out[4] with the three-membered $F_2Si(NSiMe_3)_2$ ring.



N-N	173.6 pm
F_2Si-N	168.4 pm
Me_3Si-N	173.9 pm
N-SiF_2-N	62.1 °
N-N-$SiMe_3$	114.5 °



N-CH_3	145.4 pm
Me_2Si-NCH_3	177.7 pm
Me_2Si-$NSiMe_3$	177.0 pm
F_2Si-NCH_3	171.0 pm
F_2Si-$NSiMe_3$	172.1 pm
N-$SiMe_3$	175.4 pm
N-$SiMe_2$-N	86.9 °
N-SiF_2-N	90.7 °

It was found that the $SiMe_3$ groups are tilt out of the SiN_2 plane with a dihedral angle of 115.8°. The N-atoms show sp^3 hybridisation. The four-membered ring is planar with a sum of angles around the N atoms of 360°.

Taking into account that the substituents of the calculated and isolated rings are different, the calculated geometry of the ring agrees nicely with the structure of rings characterised by X-ray diffraction. The energetic difference between the three- and four-membered ring is calculated to be 74.7 kcal/mol. The unimolecular rearrangement starts with cleavage of the N-N-bond followed by the fission of the Si-C and the simultaneous formation of the C-N bond, a methyl group transfer. In the third and last step the $SiMe_2$ moiety swings inward and recombines with the unsaturated nitrogen atom. Measured from the reactant side the saddle point has a barrier height of 34.2 kcal/mol under experimental conditions, this energy is provided by heating and additionally through the exothermicity of the reaction.[4]

ACKNOWLEDGMENTS

Support of this work by the Fonds der Chemischen Industrie is gratefully acknowledged.

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