

Force field parameters for aminoorganosilanes



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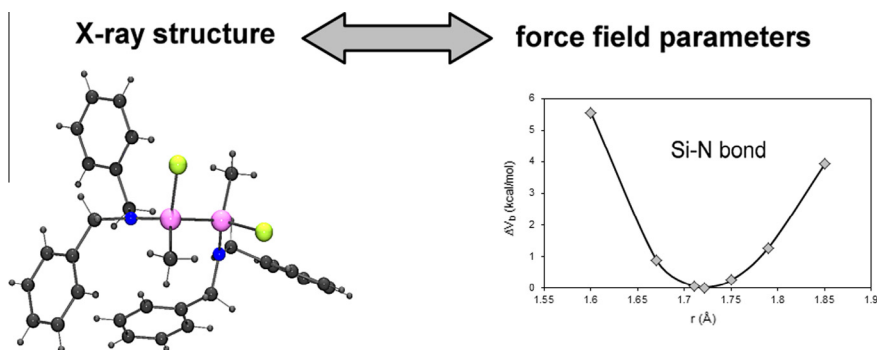
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HIGHLIGHTS

- Two new aminoorganosilanes have been synthesized.
- The X-ray structure of one disilane was determined.
- Quantum chemical calculations were performed on model complexes with Si–N bonds.
- MMX force field parameters have been derived and tested on X-ray structures.

GRAPHICAL ABSTRACT



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ABSTRACT

Force field parameters for new compound classes are an important prerequisite for the fast and reliable modeling of these compounds with commercial available modeling software. The development of MMX force field parameters for aminoorganosilanes is described in this work. Combined efforts have been undertaken including synthesis, structural characterization of suitable compounds, and quantum chemical calculation with a systematic set of model compounds. 1,2-Dibenzylamino-1,2-dichloro-dimethyldisilane has been synthesized and characterized by X-ray structure analysis. It is possible to calculate bond lengths and angles of this and other aminosilanes with the new force field parameters.

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Introduction

There is a practical interest in aminosilanes resulting from their potential application possibilities. They are valuable source materials for the silicon nitride synthesis and allow access to high performance silicon based ceramics [1,2]. Furthermore, organosilanes play an important role as building blocks for multifunctional polysilanes [3] and crosslinked silazane polymers [4].

Our intention was to synthesize crystalline aminoorganosilanes and develop Si–N MMX force field parameters for the modeling

program PCModel [5]. This will enable us to obtain fast information on demand about structures and conformational preferences of these compounds, even for oligomeric and polymeric derivatives.

For that purpose, we undertook a combined approach of experiment and theory. First, we will report about the synthesis and characterization of a new aminoorganosilane including X-ray structural characterization. The second part deals with the simulation of aminoorganosilane structures in order to derive Si–N force constants from high level *ab initio* calculations. For the binding interaction potentials (the bond potential V_b , the angle potential V_a and the torsion potential V_{tor}) new Si–N force constants were calculated. The accuracy of the new MMX force field parameters was verified by modeling aminoorganosilanes within the program

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PCModel and comparison of the calculated geometric parameters with available X-ray structures from the CSD database and synthesized compounds. This paper continues our previous work on the development of Force Field Parameters [6].

Synthesis and characterization of benzyldisilane

Crystalline aminoorganosilanes are accessible by reaction of chloroorganosilanes with secondary amines with flat aromatic substituents as we have learned from the successful synthesis of crystalline *N*-methylanilinoorganosilanes [7]. Another organylamine which should suit the requirements as substituent for obtaining crystalline aminoorganosilanes is dibenzylamine. Some derivatives have been synthesized and a X-ray structure of a representative example was determined. Starting from 1,1,2,2-tetrachlorodimethyldisilane (**1**) two different products are obtained. The reaction of 1,1,2,2-tetrachlorodimethyldisilane with dibenzylamine and triethylamine in molar ratio 1:1:1 gave a mixture of Cl(NBz₂)MeSi–SiMeCl₂ (**2**) and Cl(NBz₂)MeSi–SiMe(NBz₂)Cl (**3**). The reaction of 1,1,2,2-tetrachlorodimethyldisilane with an excess of dibenzylamine gave exclusively Cl(NBz₂)MeSi–SiMe(NBz₂)Cl (**3**) see Scheme 1. It was not possible to introduce three or four dibenzylamino groups into the disilane using this method. We were able to obtain single crystals of **3** which were suitable for X-ray structure analysis. This demonstrates the possibility to obtain crystalline aminosilanes also with dibenzylamine. The geometric parameters are summarized in Table 1 and the crystallographic data in the experimental section.

Compound **3** crystalizes in the triclinic space group P-1 with two crystallographic independent molecules in the unit cell (Fig. 1). The Si–Si bond length with 2.345 Å is comparable to similar compounds [8–11]. The Si–Cl and Si–C bond lengths are well within the sum of the covalent radii [12]. In contrast to that the Si–N bonds are shorter than expected (1.699–1.701 Å). The sum of covalent radii of silicon and nitrogen is 1.91 Å [12]. This hints to a partial double bond character of the Si–N bonds. The silicon atoms are in distorted tetrahedral geometry with bond angles between 99.48° and 116.15°. The overall conformation of both crystallographic independent molecules is staggered with the chlorine atoms in synclinal position. The benzyl groups are folded at the CH₂-group as one would expect and the phenyl groups bound thereon adopt suitable conformations to allow favorable crystal packing.

MMX force field parameterization

There are two ways to extend a force field with new parameters – out of experimental data (geometries of X-ray structures) or out of quantum chemical calculations (optimized geometries). Just a few structures of aminoorganosilanes were published so far. That

Table 1

Bond lengths (in Å) and bond angles (in °) from the X-ray structure analysis of dibenzylaminoorganosilane (**3**).

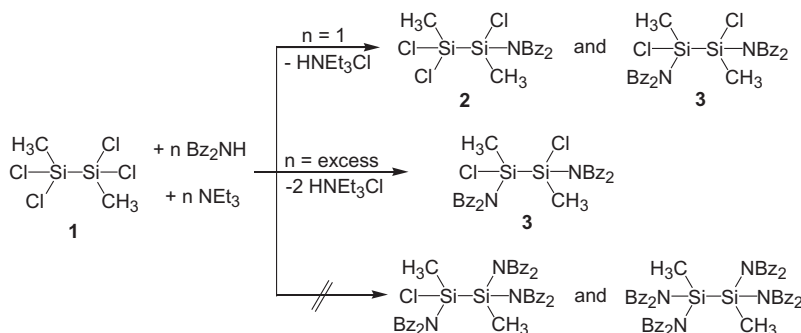
Molecule 1		Molecule 2	
Si(1)–Si(2)	2.345(1)	Si(3)–Si(4)	2.348(1)
Si(1)–Cl(1)	2.093(1)	Si(3)–Cl(3)	2.087(1)
Si(2)–Cl(2)	2.115(1)	Si(4)–Cl(4)	2.114(1)
Si(1)–N(1)	1.701(2)	Si(3)–N(3)	1.701(3)
Si(2)–N(2)	1.700(2)	Si(4)–N(4)	1.699(2)
Si(1)–C(1)	1.853(3)	Si(3)–C(31)	1.862(4)
Si(2)–C(2)	1.863(3)	Si(4)–C(32)	1.876(3)
N(1)–Si(1)–C(1)	110.4(2)	N(3)–Si(3)–C(31)	110.1(2)
N(1)–Si(1)–Cl(1)	111.66(9)	N(3)–Si(3)–Cl(3)	111.7(1)
C(1)–Si(1)–Cl(1)	106.2(2)	C(31)–Si(3)–Cl(3)	107.1(2)
N(1)–Si(1)–Si(2)	114.89(9)	N(3)–Si(3)–Si(4)	116.15(9)
C(1)–Si(1)–Si(2)	112.9(1)	C(31)–Si(3)–Si(4)	111.6(1)
Cl(1)–Si(1)–Si(2)	100.02(5)	Cl(3)–Si(3)–Si(4)	99.48(6)
N(2)–Si(2)–C(2)	112.1(1)	N(4)–Si(4)–C(32)	111.5(1)
N(2)–Si(2)–Cl(2)	111.02(8)	N(4)–Si(4)–Cl(4)	111.06(8)
C(2)–Si(2)–Cl(2)	103.3(1)	C(32)–Si(4)–Cl(4)	104.1(1)
N(2)–Si(2)–Si(1)	112.37(8)	N(4)–Si(4)–Si(3)	113.29(8)
C(2)–Si(2)–Si(1)	114.2(1)	C(32)–Si(4)–Si(3)	114.3(1)
Cl(2)–Si(2)–Si(1)	103.03(4)	Cl(4)–Si(4)–Si(3)	101.70(4)
Cl(1)–Si(1)–Si(2)–C(2)	–40.5(1)	Cl(3)–Si(3)–Si(4)–Cl(4)	–71.14(6)

means, the necessary geometries for the parameterization must be derived from quantum chemical calculations of Si–N compounds. Afterwards, the crystal structures can be used to verify the calculated new force constants by comparing their modeled structure with the X-ray structure. The parameterization is a four-step procedure consisting of the model compound design, the quantum chemical calculations, the potential calculations with the derivation of the parameters and the evaluation of the force constants [13]. Following this procedure the development of force field parameters for binding potentials (V_b , V_a , V_{tor}) will be explained.

Model compounds

First of all model compounds have to be designed which contain the structural feature of interest, in this case the Si–N bond. Furthermore Si–C, Si–Cl and Si–Si bonds have to be present in the model compounds, since we need angle and torsion potentials which include these atoms, as well. According to already existing aminoorganosilanes, which mostly are alkylaminodisilanes, chloromethylaminodisilanes with 0–4 chloro and amino substituents were composed (Table 2). The dimethylamino group was chosen because methyl groups are easier to calculate quantum mechanically than phenyl rings.

The R- and S-isomers have the same energy and for simplicity mainly the R-isomers are considered. Furthermore, the model set



Scheme 1. Syntheses of dibenzylaminodisilanes from 1,1,2,2-tetrachlorodimethyldisilane (**1**).

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