Structure Elucidation

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Donor-Stabilized 1,3-Disila-2,4-diazacyclobutadiene with a Nonbonded Si···Si Distance Compressed to a Si=Si Double Bond Length

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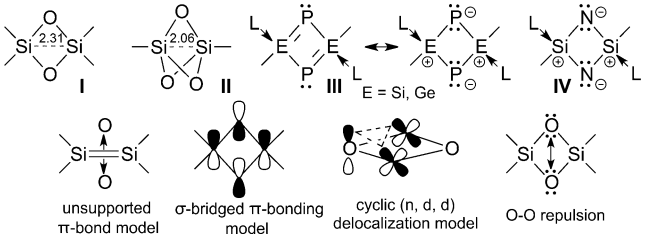
Abstract: *A donor-stabilized 1,3-disila-2,4-diazacyclobutadiene presents an exceptionally short nonbonded Si···Si distance (2.23 Å), which is as short as that of Si=Si bonds (2.15–2.23 Å). Theoretical investigations indicate that there is no bond between the two silicon atoms, and that the unusual geometry can be related to a significant coulomb repulsion between the two ring nitrogen atoms. This chemical pressure phenomenon could provide an alternative and superior way of squeezing out van der Waals space in highly strained structures, as compared to the classical physical methods.*

Two atoms approaching within a distance shorter than the sum of van der Waals radii, without bonding interactions, results in significant repulsion. High pressure can force molecules to approach each other, thus violating the van der Waals space.[1] Such high compression of molecules, which leads to intermolecular overlaps of molecular orbitals, induces, in some cases, unique physical phenomena such as metallization of neutral molecules (i.e., O_2 at 95 GPa, SiH_4 at 91 GPa, N_2O predicted above 177 GPa).[2–5] Endohedral confinement of atoms within small cage compounds also leads to unusual nonbonded structures with short internuclear distances.[6] Indeed, two atoms of He in C_{60} were predicted to exist as weakly bonded van der Waals complexes, $He_2@C_{60}$ (see Figure 3 a),[7] and a smaller hydrocarbon cage, $C_{20}H_{20}$, can force two He atoms to a high-energy structure in which the He···He distance is two times smaller than the van der Waals radius of helium.[8] However under these conditions, in any case, nonbonded interatomic distances never approached a length as short as that of a covalent single bond.

An exception is the nonbonded Si···Si dihedral distance (2.31 Å) found in the 1,3-diosiloxane **I**, and it is even shorter



than Si–Si covalent bonds (2.36 Å).[9–11] Computational calculations have predicted an even shorter Si···Si distance (2.06 Å) for the related bicyclic molecule **II**.[12] The electronic origin of the exceptionally short nonbonded distances, called a "phantom bond", has been the subject of many experimental and theoretical investigations[13] and several models with particular orbital interactions [unsupported π-bond model,[14,15] σ-bridged π-bonding model,[16] and cyclic (n,d,d) delocalization model[17]] have been proposed to explain the unusual geometry of 1,3-disiloxanes. Alternatively, the ring deformation resulting from the elongation of the O···O diagonal distance arising from the electrostatic repulsion was also considered.[1a] Several related four-membered cyclic compounds (**III**) are also known to deform to diamond-shaped patterns for the same reason,[18–20] although they do not exhibit a diagonal distance shorter than a covalent single bond.[15a,21] In spite of these theoretical studies, none of them are supported by experimental evidence. The lack of available molecules, other than 1,3-disiloxanes, has limited further discussion. Here we report the synthesis of the phosphine-stabilized 1,3-disila-2,4-diazacyclobutadiene **2** (see Scheme 1; of type **IV** as shown above), presenting a diagonal Si···Si distance which falls within the range of Si=Si bond lengths.

Recently, we reported the synthesis of the first persistent phosphine-stabilized silyne by photolysis of the corresponding diazomethane derivative.[22] By analogy, we considered the synthesis of the silylene-substituted azide **3** as a potential precursor of the elusive silanitrile species [R-SiN] (Scheme 1).[23,24] We thus carried out the reaction of the phosphine-stabilized chlorosilylene **1** with sodium azide in the

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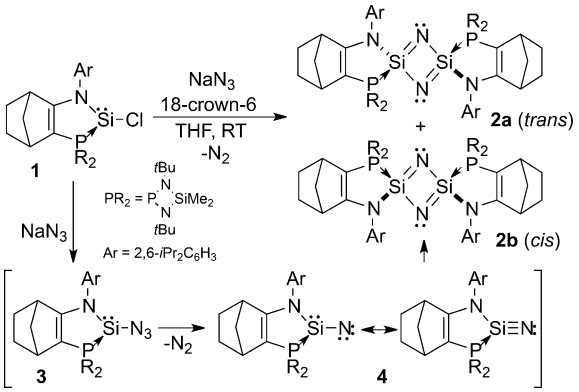


Scheme 1. Synthesis of the 1,3-disila-2,4-diazacyclobutadiene **2**. THF = tetrahydrofuran.

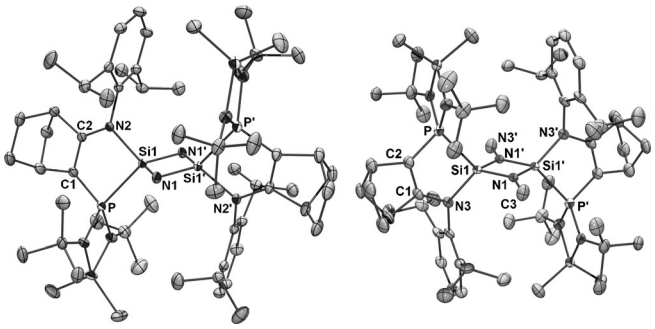


Figure 1. Molecular structures of **2a** (left) and **6** (right). Hydrogen atoms are omitted for clarity. Thermal ellipsoids shown at 30% probability. Selected bond lengths [Å] and angles [°]: **2a**: Si1–Si1′ 2.23502(17), N1–N1′ 2.6055(5), Si1–N1 1.7114(2), Si1–N1′ 1.7213(2), Si1–P 2.39855(11), Si1–N2 1.8305(2); Si1-N1-Si1′ 81.247(11), N1-Si1-N1′ 98.756(11), Selected torsion angles [°]: P-Si1-Si1′-P′ 180, N3-Si1-Si1′-N3′ 180; **6:** Si1-Si1′ 2.518(2), N1-N1′ 2.368(4), Si1-N1 1.730(2), Si1-P 2.366(2), Si1-N1-Si1′ 93.51(11), N1-Si1-N1′ 86.49(11).

presence of a catalytic amount of dibenzo-18-crown-6 (5 mol%) at room temperature. However the reaction does not afford the expected azide **3**, but leads to the formation of the 1,3-diaza-2,4-disilacyclobutadienes **2**, in which the unsaturated four-membered ring is intramolecularly stabilized by the two phosphine ligands. The heterocycle **2**, was obtained as a mixture of *trans*- and *cis*-isomers (**2a**/**2b** = 1.8:1) as indicated by the presence of two singlets in the ^{31}P NMR spectrum at $\delta = 45.8$ and 38.8 ppm, respectively. The isomer ratio is temperature dependent, and after heating a toluene solution of **2a,b** at 60 °C for 12 hours, the ratio is 50:50, and in agreement with a reversible isomerization. The derivative **2** corresponds to the dimer of the desired silanitrile **4**, which is probably formed after decomposition of **3**, as indicated by the gas evolution observed during the reaction. In the ^{29}Si NMR spectrum, the resonances corresponding to the silicon atoms stabilized by the two phosphine ligands appear at relatively low-field, compared to related donor-stabilized silaimines ($\delta = -48$ to -67 ppm),[25–27] as a doublet of doublets for the *trans*-isomer **2a** ($\delta = -25.3$ ppm; $J_{SiP} = 89.8$ and 26.1 Hz) and as a pseudo-triplet for the *cis*-isomer **2b** ($\delta = -24.1$ ppm; $J_{SiP} = 53.8$ Hz).

The two isomers of **2** were isolated by selective crystallization in different solvents (**2a** in C_6D_6, and **2b** in THF). The X-ray diffraction analysis of both isomers revealed similar structural geometries with an essentially planar central four-membered ring ($\Sigma° = 360.0°$ for **2a**, and 359.9° for **2b**), which is strongly deformed to form diamond-shaped patterns with acute Si-N-Si angles [**2a**: 81.427(11)°, **2b**: 81.28(7)°] (Figure 1).[28] The Si–N bond lengths of the central four-membered ring [**2a**: 1.7114(2) and 1.7213(2) Å, **2b**: 1.7096(16) and 1.7147(16) Å] are intermediate between single (1.76–1.80 Å) and double bonds (1.58 Å),[29–33] thus suggesting some π-delocalization. Indeed, they are much shorter than the exocyclic Si1–N2 bonds [**2a**: 1.8305(2) Å, **2b**: 1.8242(17) Å]. However, theoretical calculations indicate a non-aromatic character for **2** [NICS (0.75) = −4.84 ppm]. This low value may be due to local diamagnetic phenomena and **2** can actually be considered to be slightly antiaromatic.[34] The Si1–P bond distances are only slightly longer than those observed for phosphine-stabilized silylenes (2.31–2.35 Å),[35,36] thus suggesting a strong coordination of the phosphine ligands on the Si^{IV} atoms. Of particular interest, both isomers of **2** present exceptionally short Si1···Si1′ diagonal distances [**2a**: 2.23502(17) Å, **2b**: 2.2303(10) Å], which are significantly shorter than those observed for tetramesityl-1,3-disiloxanes (2.31–2.39 Å),[9–11] and are within the range expected for Si=Si bonds (2.15–2.23 Å).[37]

Experimental electron density distribution analysis using accurate single-crystal X-ray diffraction data provides strong experimental evidence for the absence of any diagonal Si–Si bond. On the static model map (Figure 2a), the bonding electrons of the Si–N and Si–P bonds were clearly observed around the bonds. The densities of the cyclic Si–N bonds spread throughout the four-membered ring, which may result from a convolution of electron densities of the cyclic Si–N bonds and the back-lobe σ-lone pairs on N1 and N1′. Indeed, the corresponding front-lobe σ-lone pairs of the N atoms were clearly observed at the opposite side on the outside of the SiNSiN ring. The n_π lone pairs on N1 and N1′ were also found on the SiNSiN ring plane but their density is low because of the considerable π-delocalization to the adjacent Si atoms (Figure S4b). Of particular interest, there is only little electron density between the diagonal Si atoms. Furthermore, the AIM analysis on the experimental electron density characterized the topological property at the center of the four-membered ring as a ring [(3, +1)] critical point with the small density (0.57 e Å^{-3}) and small positive Laplacian density (3.6 e Å^{-5}) values. These observations on the electron density distribution analysis strongly indicate the absence of a Si–Si bond (Figure 2b). These experimental results were supported by the DFT calculations performed on **2a** at the B3LYP/6-31G* level of theory.[38–41] Indeed, calculations[42] reproduce well the geometry of **2a** with a Si–Si distance of 2.22 Å (experimental value: 2.23 Å) and also show the positive Laplacian electron density[43] (Figure 2b) as well as ring (3, +1) critical point [not bond (3,−1) critical point][44–46] between the two Si atoms (Figure 2d). Analysis of the Kohn–Sham MOs revealed similar features to those found for the simpler system $(H_2Si\text{-}N)_2^{2-}$ and are associated with the interaction of two separated $H_2Si\cdots SiH_2$ and $N^-\cdots N^-$ units within D_{2h}

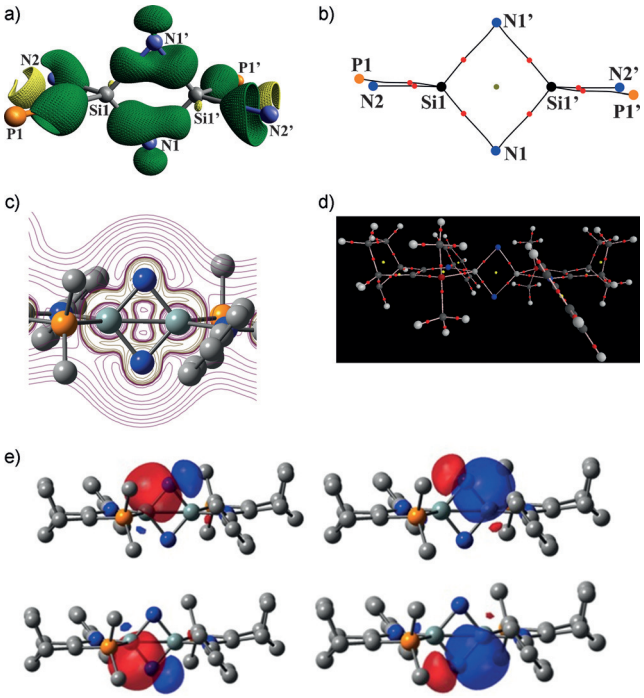


Figure 2. a) Isosurface plot of the static model map around the SiNSiN four-membered ring of **2a**, drawn at ± 0.15 e Å^{-3}, afforded by X-ray electron density distribution analysis. Green and yellow surfaces denote positive (electron rich) and negative (electron deficient) regions, respectively. b) Bond paths (black solid lines), and bond (red dots) and ring (green dot) critical points around the SiNSiN four-membered ring of **2a** based on the X-ray electron density distribution analysis. c) Representation of the Laplacian of electron density along the plane determined by the Si-N-Si-N atoms of **2a**. d) Bond critical points of **2a**. Red and yellow dots represent bond and ring critical points. Notice the ring critical point at the center of the four membered ring. e) Localized natural orbitals involving Si—N covalent bonds of the four-membered ring in **2a**.

symmetry. In particular, the HOMO-7 MO of this simple system is similar to the a_{2u} canonical MO of cyclobutadiene and closely resembles the HOMO described by Bertrand et al. for a singlet biradical $(HB\text{-}PH_2)_2$,[47] thus indicating the absence of MOs associated with direct Si—Si bonding (see the Supporting Information). Actually, the interaction diagram of this model system indicates that the MOs are not associated with Si···Si interactions because of a strong overlap of the $2a_g$, $1b_{2g,u}$, and $1b_{3g,u}$ fragments[14] with $2\sigma_g$ and $\pi_{gs,y}$ and $\pi_{ux,y}$ ensembles associated to the $N^-\cdots N^-$ moiety (see Figure S1 in the Supporting Information). In addition, the natural bond orbital (NBO) analysis of the DFT wave function showed four localized NBOs, with no bonding interaction between both silicon atoms (Figure 2e).

The remaining question is the origin of this short Si···Si distance despite the lack of bonding between both atoms. As there is no endohedral confinement of atoms induced by an external rigid structure (Figure 3a), we can consider the strong electrostatic repulsion between the negatively charged nitrogen atoms in the four-membered ring. Assuming a rhomboidal pseudo-D_{2h}-symmetry for **2**, any given Si···Si distance determines the corresponding N–N distance for a fixed Si—N

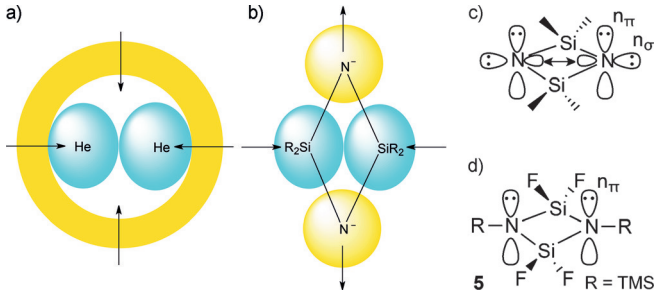


Figure 3. Two possible ways of constraining a pair of nonbonding atoms at distances shorter than the sum of their van der Waals radii: a) endohedral confinement; b) electrostatic repulsion between two atoms perpendicular to the A–A axis (this work); c) repulsion between two in-plane nitrogen lone pairs (n_σ); d) the cyclodisilazane **5**.

bond distance (Figure 3b). In addition to the highly accumulated negative charge on the nitrogen atoms resulting from strongly polarized $Si^{\sigma+}$–$N^{\sigma-}$ bonds, the σ-bond-type arrangement of two in-plane nonbonding orbitals on the nitrogen atoms (n_σ), which was actually observed by experimental analysis (Figure 2a), should lead to a significant repulsion (Figure 3c). Indeed, the cyclodisilazane **5**, with only on-plane nonbonding orbitals (n_π) on the two nitrogen atoms, present an essentially square geometry (Si-N-Si: 88.4°, N-Si-N: 91.6°, Si-Si: 2.376 Å),[48] thus suggesting the absence of such a strong N–N repulsion (Figure 3d).

The van der Waals terms were calculated by means of Buckingham–Hill equations[49] for the N···N and Si···Si terms (see the Supporting Information). We computed different, nonbonding energies (ΔE_{nb}) versus Si–Si distance ($R_{Si,Si}$) curves, depending upon the different charges assigned for the endocyclic nitrogen atoms (q_N; Figure 4). As postulated, the nonbonding energies increase as the charges of the nitrogen atoms are higher. However, the energy minima associated with these profiles correspond to lower values of the Si···Si distance. Thus, for a q_N charge value of −1.6 a.u. (the value calculated for **2a**), the energy minimum is obtained at $R_{SiSi} =$

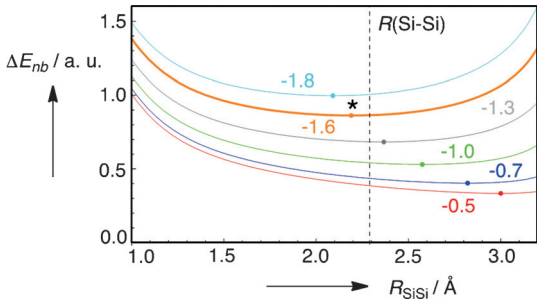
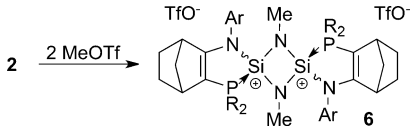


Figure 4. Nonbonding energies, ΔE_{nb}, computed for different Si–Si distances R_{SiSi} (see the Supporting Information for details). The different curves have been obtained with different atomic charges for the nitrogen atom of **2a**. The values of these charges (in a.u.) are indicated close to the curves and in different colors. The points correspond to the minimum of each curve. The asterisk indicates the experimental Si–Si distance found in **2a**. The dashed line highlights the limit of the Si···Si distance associated with regular Si—Si and Si=Si covalent bonds.

2.20 Å, a value very close to the computed Si···Si distance as well as the experimentally observed one. Therefore, we can conclude that the Coulombic repulsion between these nitrogen atoms shrinks the Si···Si distance to values even shorter than those found for a classical covalent bond (2.33 Å), with a Coulomb compression similar to that shown in Figure 3b, thus explaining the unique structure of **2**.

Electronically strained **2** presents a strongly nucleophilic character and immediately reacts with 2 equivalents of methyl triflate at room temperature to afford the dicationic *N*,*N*′-dimethyl-cyclodisilazane **6** (Scheme 2). The heterocycle **6** was isolated as highly moisture sensitive colorless crystals (68%).



Scheme 2. The reaction of **2** with MeOTf. Tf = trifluoromethanesulfonyl.

The derivative **6** is almost completely insoluble in classical organic solvents, and all attempts to solubilize it in chlorinated solvents resulted in its fast decomposition. Therefore, we have not been able to characterize **6** by NMR spectroscopy. However, the structure of **6** was unambiguously established by single-crystal X-ray diffraction analysis. As expected, the methylation of the two ring nitrogen atoms of **2** greatly release the chemical pressure, thus leading to significantly shortened N1···N1′ [2.368(4) Å] and elongated Si1···Si1′ [2.518(2) Å] interatomic distances in **6** relative to those in **2a** [N1···N1′: 2.6055(5) Å, Si1···Si1′: 2.23502(17) Å] (Figure 1). The Si1···Si1′ distance is now much longer than those of Si–Si bonds (2.35–2.38 Å).

In conclusion, we have synthesized and fully characterized, a phosphine-stabilized 1,3-disila-2,4-diazacyclobutadiene by dimerization of the corresponding transient silanitrile. Of special interest, this hetero-cyclobutadiene presents an exceptionally short nonbonded Si···Si distance (2.23 Å) which is as short as Si=Si bonds (2.15–2.23 Å). Theoretical investigations and experimental X-ray electron density distribution analysis indicated that there is no bond between the two silicon atoms, and that the unusual geometry of **2** can be related to a significant Coulombic repulsion between the two negatively charged ring nitrogen atoms. This chemical pressure on nonbonding atoms should provide a way of squeezing out van der Waals space in highly strained structures, as opposed to classical methods based on physical confinement.

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Keywords: density functional calculations · reactive intermediates · silicon · small ring systems · structure elucidation

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