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Article

How to Make the Ionic Si−O Bond More Covalent and the Si−O−Si Linkage a Better Acceptor for Hydrogen Bonding[†]

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Variation of a bond angle can tune the reactivity of a chemical compound. To exemplify this concept, the nature of the siloxane linkage (Si−O−Si), the most abundant chemical bond in the earth's crust, was examined using theoretical calculations on the molecular model compounds $H_3SiOSiH_3$, $(H_3Si)_2O\cdots HOH$, and $(H_3Si)_2O\cdots HOSiH_3$ and high-resolution synchrotron X-ray diffraction experiments on 5-dimethylhydroxysilyl-1,3-dihydro-1,1,3,3-tetramethyl-2,1,3-benzoxadisilole (**1**), a molecular compound that gives rise to the formation of very rare intermolecular hydrogen bonds between the silanol groups and the siloxane linkages. For theoretical calculations and experiment, electronic descriptors were derived from a topological analysis of the electron density (ED) distribution and the electron localization function (ELF). The topological analysis of an experimentally obtained ELF is a newly developed methodology. These descriptors reveal that the Si−O bond character and the basicity of the siloxane linkage strongly depend on the Si−O−Si angle. While the ionic bond character is dominant for Si−O bonds, covalent bond contributions become more significant and the basicity increases when the Si−O−Si angle is reduced from linearity to values near the tetrahedral angle. Thus, the existence of the exceptional intermolecular hydrogen bond observed for **1** can be explained by its very small strained Si−O−Si angle that adopts nearly a tetrahedral angle.

Introduction

The Si−O bond is the most common chemical bond in the earth's crust owing to the high affinity of oxygen for silicon and the high natural abundance of these elements. Ubiquitous minerals, such as quartz, crystobalite, tridymit, feldspars, natural and unnatural zeolites, as well as man-made silica materials, such as mesoporous silica (e.g., MCM-41, SBA-15), comprise a high content of siloxane linkages (Si−O−Si) and a rare number of silanol groups (Si−O−H) on the surface.[1] Important industrial applications of zeolites and mesoporous silica involve, for instance, their use as heterogeneous catalyst supports and as selective molecular adsorbents.[1] The surface of the silica materials is able to bind polar molecules, such as water, alcohols, or amines, through SiO−H···A (A = acceptor molecules) hydrogen bonding at the exterior silanol sites. The basicity of the more abundant siloxane linkages situated at the surface is generally considered too low to bind polar molecules, for example, through $RO-H\cdots O(SiO\text{-}_3)_2$ and $R_2N-H\cdots O(SiO\text{-}_3)_2$ hydrogen bonding (R = hydrogen, alkyl and aryl groups).[1] Only for the high-pressure silica modifications stishovite and coesite, evidence for hydrogen bonding under extreme conditions (>5 GPa and >1000 °C) has been obtained from IR spectroscopy.[2] Despite its significance, there is still a vivid controversy on the correct description of the Si−O bond character in silica materials. Some authors regard the Si−O bond as

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[†] Dedicated to Professor Dietmar Seyferth on the occasion of his 80th birthday.

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(1) (a) Iler, R. K. *The Chemistry of Silica*, Wiley: New York, 1979. (b) Beall, G. J. In *SILICA. Reviews in Mineralogy*; Heaney, P. J., Prewitt, C. T, Gibbs, G. V., Eds.; American Mineralogist: Washington, DC, 1994; p 606.

(2) (a) Koch-Müller, M.; Fei, Y.; Hauri, E.; Liu, Z. *Phys. Chem. Miner.* **2001**, *28*, 693. (b) Gibbs, G. V.; Cox, D. F.; Ross, N. L. *Phys. Chem. Miner.* **2004**, *31*, 232.

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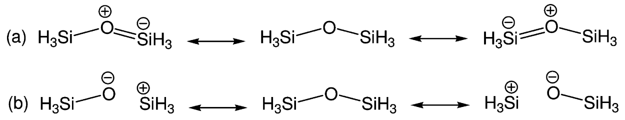
Scheme 1. Lewis Formula Representations of (a) the Obsolete Back-Bonding Model and (b) the Ionic Bond Model Discussed for the Siloxane Linkage in $H_3SiOSiH_3$



"very ionic",[3,4] others emphasize a still "substantial covalent character",[3,5] while again others describe it as a "mixture of covalent and strong ionic bonding".[3,6] Therefore, the Si−O bond is also referred to as "the elusive bond".[7]

Linear and branched silicones, the most important class of organometallic polymers used in the chemical industry, also contain the siloxane linkage (Si−O−Si) in their backbones.[8] The material properties of silicones are governed by the inherently low basicity of the siloxane linkage and its inability to form hydrogen bonds with polar molecules such as water. Silicone polymers containing Me_2SiO units are highly hydrophobic and frequently find applications as water repellents.[8] By contrast, the ether linkage (C−O−C) possesses a considerably higher basicity, which is reflected in its pronounced hydrophilicity. Many ethers, such as tetrahydrofuran and crown ethers, are highly miscible with (or soluble in) water owing to their ability to form hydrogen bonds of the type $HO{-}H\cdots O(CX_3)_2$ (X = hydrogen, alkyl, aryl).

Disiloxane $H_3SiOSiH_3$, the simplest molecule containing the siloxane linkage (Si−O−Si), has been used as a model compound to study the nature of the Si−O bond. A historic explanation for the low basicity still found in some textbooks involves the obsolete back-bonding models (a) of the type $p(O)\rightarrow d(Si)$ or more recently, of the type $n(O)\rightarrow\sigma^*(Si{-}X)$ (Scheme 1). These back-bonding models were also held responsible for the observation of very large Si−O−Si angles in siloxanes, which typically fall in the range between 135 and 180°. However, both back-bonding models have now been discarded in favor of an ionic bond model (b), which attributes the large Si−O−Si angles to the electronegativity difference of the elements (Scheme 1).[9]

Previously, several relationships between the Si−O bond length, the Si−O−Si angle (θ), Si and O Mulliken charges, and degree of Si−O bond ionicity have been proposed.[9,10] It has been even suggested that the Si−O−Si angles can be used as a direct measure of the Si−O bond character, as an increase of the angle leads to greater charges at the silicon and oxygen atoms, which increases the Si−O bond ionicity.[3,11] However, given that the ionic bond model is operative, the low basicity is counterintuitive to the high electron density (ED) and the negative charge situated at the oxygen atom, the two properties that are usually associated with a good acceptor for hydrogen bonding.[12] In fact, there are literally thousands of well-defined molecular compounds having siloxane bonds, only three of which serve as acceptors for hydrogen bonds.[13−15] In these compounds (discussed below in more detail), the siloxane linkages are incorporated into strained ring systems and the donor of the hydrogen bond is a silanol group. To the best of our knowledge, no explanation for these exceptional cases of hydrogen bonding has yet been put forward. Hydrogen-bonding in molecular organosilanols has been extensively investigated by the concepts of supramolecular chemistry.[16] In the vast majority of organosilanols that also contain a siloxane linkage (more than 80 entries in the CCDC database[17]), the silanol sites are both the donor and the acceptor of the hydrogen bonds.

Herein, we investigate the Si−O bond ionicity and basicity depending on the Si−O−Si angle using state-of-the-art quantum chemical ab initio calculations on the model compounds $H_3SiOSiH_3$, $(H_3Si)_2O\cdots HOH$, and $(H_3Si)_2O\cdots HOSiH_3$, whereby H_2O and H_3SiOH act as model hydrogen bond donors. We will provide evidence that the basicity of the siloxane linkage can be dramatically improved by decreasing the Si−O−Si angle, which can be rationalized on the basis of the electronic descriptors resulting from an analysis of the ED[18] and electron localization function (ELF).[19] To verify the conclusions drawn from the ab initio calculations, we report on the synthesis and high-resolved single-crystal synchrotron X-ray diffraction data of a novel molecular organosilanol also containing a very strained

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(3) Gibbs, G. V.; Rosso, K. M.; Teter, D. M.; Boisen, M. B.; Bukowinski, M. S. T. *J. Mol. Struct.* **1999**, *485*−*486*, 13.

(4) (a) Kudo, T.; Nagase, S. *J. Am. Chem. Soc.* **1985**, *107*, 2589. (b) Gordon, M. S.; Packwood, T. J.; Carroll, M. T.; Boatz, J. A. *J. Phys. Chem.* **1991**, *95*, 4332. (c) Cohen, R. E. In *SILICA. Reviews in Mineralogy*; Heaney, P. J., Prewitt, C. T., Gibbs, G. V., Eds.; American Mineralogist: Washington, DC, 1994; p 369.

(5) (a) Coppens, P. *X-ray Charge Densities and Chemical Bonding*; Oxford University Press: Oxford, U.K., 1997; p 253. (b) Tsirelson, V. G.; Evdokimova, O. A.; Belokoneva, E. L.; Urusov, V. S. *Phys. Chem. Miner.* **1990**, *17*, 275. (c) Teppen, B. J.; Miller, D. M.; Newton, S. Q.; Schäfer, L. *J. Phys. Chem.* **1994**, *98*, 12454.

(6) Binggeli, N.; Troullier, N.; Martin, J. L.; Chelikowsky, J. R. *Phys. Rev.* **1991**, *B44*, 4771.

(7) Gibbs, G. V.; Downs, J. W.; Boisen, J. *Rev. Mineral.* **1994**, *29*, 331.

(8) (a) Noll, W. *Chemistry and Technology of the Silicones*; Academic Press: New York, 1968. (b) Clarson, S. J.; Semlyen, J. A. *Siloxane Polymers*; Prentice Hall: Englewood Cliffs, NJ, 1993. (c) Manners, I. *Angew. Chem., Int. Ed.* **1996**, *35*, 1603.

(9) (a) Oberhammer, H.; Boggs, J. E. *J. Am. Chem. Soc.* **1980**, *102*, 7241. (b) Gillespie, R. J.; Johnson, S. A. *Inorg. Chem.* **1997**, *36*, 3031.

(10) (a) Nicholas, J. B.; Winans, R. E.; Harrison, R. J.; Iton, L. E.; Curtiss, L. A.; Hopfinger, A. J. *J. Phys. Chem.* **1992**, *96*, 7958. (b) Hill, R. J.; Gibbs, G. V. *Acta Crystallogr.* **1979**, *B35*, 25.

(11) Jackson, M. D.; Gibbs, G. V. *J. Phys. Chem.* **1988**, *92*, 540.

(12) Shambayati, S.; Blake, J. F.; Wierschke, S. G.; Jorgensen, W. L.; Schreiber, S. L. *J. Am. Chem. Soc.* **1990**, *112*, 697.

(13) Eaborn, C.; Hitchcock, P. B.; Lickiss, P. D. *J. Organomet. Chem.* **1984**, *264*, 119.

(14) Gusev, A. I.; Los', M. G.; Varazhkin, Y. M.; Morgunova, M. M.; Zhinkin, D. Y. *J. Struct. Chem.* **1976**, *17*, 329.

(15) Spielberger, A.; Gspaltl, P.; Siegl, H.; Hengge, E.; Gruber, K. *J. Organomet. Chem.* **1995**, *499*, 241.

(16) (a) Lickiss, P. D. *Adv. Inorg. Chem.* **1995**, *42*, 147. (b) Chandrasekhar, V.; Boomishankar, R.; Nagendran, S. *Chem. Rev.* **2004**, *104*, 5847. (c) Lickiss, P. Polysilanols. In *The Chemistry of Organic Silicon Compounds*; Rappoport, Z., Apeloig, Y., Eds.; John Wiley: Chichester, 2001; Chapter 12, p 695. (d) Beckmann, J.; Jänicke, S. L. *Eur. J. Inorg. Chem.* **2006**, *17*, 3351.

(17) Cambridge Structural Database (CSD) Version 5.29, release January, 2008.

(18) (a) Bader, R. F. W. *Atoms in Molecules A Quantum Theory*; Clarendon Press: Oxford, U.K., 1995. (b) Koritsanszky, T. S.; Coppens, P. *Chem. Rev.* **2001**, *101*, 1583. (c) Coppens, P. *Angew. Chem., Int. Ed.* **2005**, *44*, 6810.

(19) (a) Becke, A. D.; Edgecombe, K. E. *J. Chem. Phys.* **1990**, *92*, 5397. (b) Kohout, M.; Savin, A. *Int. J. Quantum Chem.* **1996**, *60*, 875. (c) Savin, A.; Flad, H.-J.; Flad, J.; Preuss, H.; von Schnering, H. *Angew. Chem., Int. Ed.* **1992**, *31*, 185.

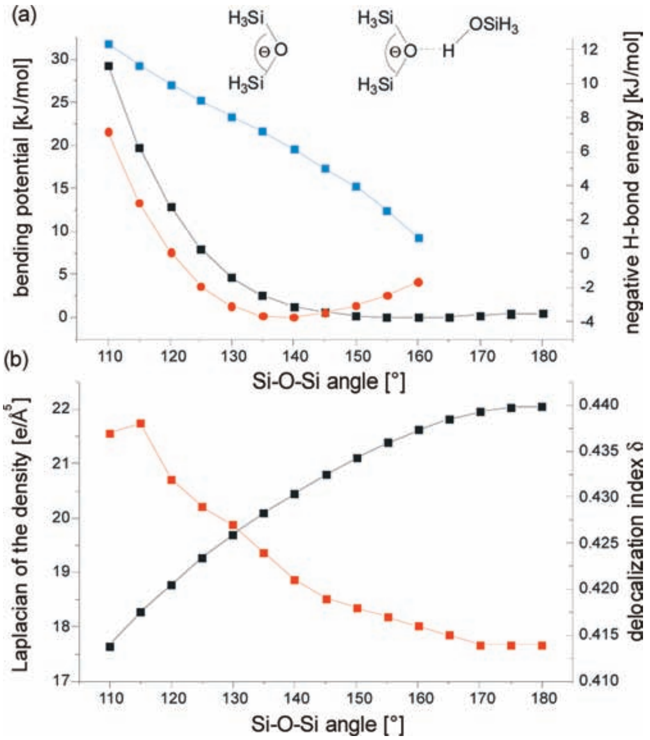

Figure 1. (a) Bending potential energy curve of the Si−O bond of $H_3SiOSiH_3$ (black) and $(H_3Si)_2O{\cdots}HOSiH_3$ (red) and the negative hydrogen bond energy curve of $(H_3Si)_2O{\cdots}HOSiH_3$ (blue); (b) Laplacian of the ED at the Si−O bond critical point of $H_3SiOSiH_3$ (black) and delocalization index δ(Si,O) of the Si−O bond of $H_3SiOSiH_3$ (red).

siloxane linkage incorporated into a five-membered ring system, which gives rise to the formation of a new intermolecular hydrogen bond between a silanol group and a siloxane linkage.

Results and Discussion

Angular Dependence of Ionicity and Basicity. Relaxed potential energy surface (PES) scans for the model compounds $H_3SiOSiH_3$, $(H_3Si)_2O{\cdots}HOH$, and $(H_3Si)_2O{\cdots}HOSiH_3$ were carried out at the B3LYP/cc-pVTZ level of theory, to analyze the electronic situation in the siloxane linkage at Si−O−Si angles between 110 and 180° within 5° intervals. The PES scan of $(H_3Si)_2O{\cdots}HOH$ was difficult and only for Si−O−Si angles of 110 and 115° convergence was reached easily. The hydrogen bond energies associated with these complexes are $E_{HB} = -3.6$ and -2.7 kJ/mol, respectively. For larger Si−O−Si angles, the convergence criteria were not reached because of the flat PES, which is consistent with the observation that hydrogen bonds of the type HO−H$\cdots$O$(SiX_3)_2$ (X = oxygen, alkyl, aryl) are not formed.[1,14] For $(H_3Si)_2O{\cdots}HOSiH_3$, the PES scan provided reasonable complexes up to Si−O−Si angles of 160°. The angular dependence of the hydrogen bond energy is shown in Figure 1a (blue curve). The basicity of the siloxane linkage can be improved strongly by decreasing the Si−O−Si angle. Thus, the strongest hydrogen bond with $E_{HB} = -12.5$ kJ/mol is found for the smallest Si−O−Si angle considered (110°). At a Si−O−Si angle of 140°, the hydrogen bond is already half as strong ($E_{HB} = -6.2$ kJ/mol). An approximate extrapolation of the curve leads to $E_{HB} = 0$ for Si−O−Si = 163° explaining why no optimized structure exists for larger angles. Hydrogen bonding is therefore not feasible for siloxanes having Si−O−Si angles larger than 163°, which is the case for most known siloxanes.[12,17] For Si−O−Si angles smaller than 163° hydrogen bonding is generally possible; however, in almost all organosilanols that also contain a siloxane linkage, the silanol sites themselves are better acceptors for hydrogen bonding than the siloxane linkage.[16] For the model complex $H_3SiOH{\cdots}O(H)SiH_3$, E_{HB} is -14.5 kJ/mol.[20] The comparison of different acceptors, for example, water, ether, and methanol, in model complexes of the type A$\cdots$$HOSiH_3$ reveals that the hydrogen bond is still stronger ($E_{HB} = -15$ to -21 kJ/mol) than that in $(H_3Si)_2O{\cdots}HOSiH_3$ even if small Si−O−Si angles are considered.[20] Nonetheless, for strained siloxane linkages with Si−O−Si angles smaller than about 135° the hydrogen bond energy may be large enough to be chemically significant.

Figure 1a also shows the bending potential energy curves for $H_3SiOSiH_3$ (black curve) and $(H_3Si)_2O{\cdots}HOSiH_3$ (red curve), which are consistent with the fact that most siloxanes contain large Si−O−Si angles between approximately 135° and 180°. The barrier to linearization from the minimum angle position (Si−O−Si = 151.4° obtained by relaxed optimization of $H_3SiOSiH_3$ at the same level of theory) is only 0.5 kJ/mol, which is in agreement with earlier calculations at different levels of theory.[10,21] For Si−O−Si angles smaller than 135°, both curves suggest that the siloxane linkages are strained. The barrier to decrease the Si−O−Si angle to 110°, that is, the angle that yields the strongest hydrogen bond, is 29.3 kJ/mol. The energy required to bend the Si−O−Si angle to values significantly smaller than 135° is too high to be compensated by the energy gain associated with the formation of hydrogen bonds. Consequently, the design of a hydrogen bond complex involving a Si−O−Si acceptor group requires a very small siloxane angle best incorporated into a strained ring system (see below).

There are several parameters (e.g., charges of Si and O, Laplacian at the bond critical point (bcp)) that show a correlation with the Si−O bond length.[9,10] For both, $H_3SiOSiH_3$ and $(H_3Si)_2O{\cdots}HOSiH_3$, with increasing Si−O−Si angle the bond lengths decrease because of larger Coulomb interactions as can be seen from increasing Bader charge separation (see Supporting Information). The positive Laplacian of the ED ($\nabla^2\rho = 17.5 - 22.0$ e/Å^5) at the Si−O bond critical points of $H_3SiOSiH_3$ is depicted in Figure 1b (black curve) and shows that the siloxane bond is highly ionic over the whole range from 110 to 180°. However, the fact that the Laplacian of the ED adopts smaller values when the Si−O−Si angle decreases also suggests that the degree of ionicity is reduced. The absolute values of the Laplacian of the ED at the bcp are often misleading, especially for closed shell interactions and strongly polarized bonds where the slope of the density along the bond path is steep.[22] Therefore,

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(20) Beckmann, J.; Grabowsky, S. *J. Phys. Chem.* **2007**, *A111*, 2011.
(21) Ernst, C. A.; Allred, A. L.; Ratner, M. A.; Newton, M. D.; Gibbs, G. V.; Moskowitz, J. W.; Topiol, S. *Chem. Phys. Lett.* **1981**, *81*, 424.
(22) Henn, J.; Ilge, D.; Leusser, D.; Stalke, D.; Engels, B. *J. Phys. Chem.* **2004**, *A108*, 9442.

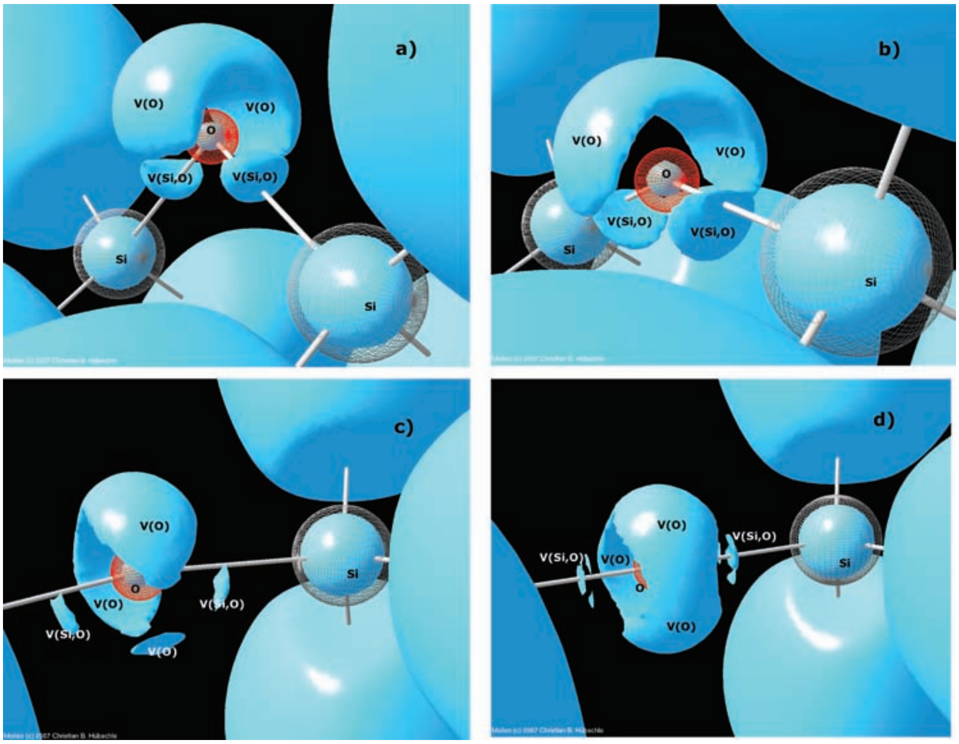

Figure 2. ELF isosurface representations at an ELF value of 0.842 calculated for $H_3SiOSiH_3$ at angles of (a) 110°, (b) 155°, (c) 165° and (d) 180°. The location of the valence basin attractors (V(O) for monosynaptic valence basins = lone pairs, V(Si,O) for disynaptic valence basins = Si−O bonds) under the isosurface are plotted additionally.

the delocalization index δ(Si,O) of the Si−O bond was also studied, which provides the number of electron pairs delocalized between two atoms and is presumably the most unambiguous parameter to reveal the bond character.[23] The angular dependence of the delocalization index δ(Si,O) is shown in Figure 1b (red curve). For all Si−O−Si angles, the δ(Si,O) values are smaller than the formal Si−O bond order, which is consistent with a highly ionic bond character.[23] Nevertheless, the delocalization index δ(Si,O) is larger for small Si−O−Si angles, which confirms the idea that a strained siloxane linkage is slightly more covalent.

In an effort to obtain the spatial arrangement of the electrons and the electron populations of the lone pairs and Si−O bonds, an analysis of the ELF was performed.[24] The ELF separates the ED into spatial regions which correspond to the chemical image of electron pairs and thus makes it possible to assign spatial regions of density localization to bonding effects like lone pairs and bonds.[19] An ELF isosurface representation of $H_3SiOSiH_3$ at four representative angles is shown in Figure 2. Between Si−O−Si angles of 110 and 160° (Figures 2a,b), the space comprising the oxygen lone pairs is located above the oxygen atom in the typical shape of a cashew nut as found for oxygen in most bonding situations.[19] Between Si−O−Si angles of 165 and 180° (Figures 2c,d), the space of the oxygen lone pairs is extended toward the lower side of the oxygen atom leading to a perfect torus around the oxygen atom at 180°. As an additional information, the location of the valence basin attractors (V(O) for monosynaptic valence basins = lone pairs, V(Si,O) for disynaptic valence basins = Si−O bonds) under the isosurface are plotted in Figure 2. Between Si−O−Si angles of 110 and 160°, there are two ELF attractors for the lone pairs V(O) while between Si−O−Si angles of 165 and 180°, there are three ELF attractors distributed at the same distances around the oxygen atom. The expansion of the space of the lone pairs from a localized position above the oxygen atom at small Si−O−Si angles to perfect delocalization around the oxygen for 180° provides a straightforward explanation for the fact that hydrogen bonding is only possible at strained Si−O−Si linkages.

According to the catastrophe theory applied to the ELF, a chemical process is always characterized by a change of the number and position of critical points (attractors and saddle points) in the ELF topology.[25] The appearance of a new attractor in the ELF topology between 160 and 165° coincides with the fact that the hydrogen bond energy drops to zero between 160 and 165° (Figure 1a). Therefore, it can be concluded that $H_3SiOSiH_3$ undergoes a chemical process (as defined by the catastrophe theory) between these Si−O−Si angles that involves a reorientation of the electrons around the oxygen atoms. The basins of the two Si−O bonds (V(Si,O)) have a rather small volume that decreases from V = 3.8 to 0.8 Å^3 when going from 110 to 180°. Interestingly, the positions of the attractors of the bond basins coincide with the bond axis at 110°, but shift to a position outside the bond axis for higher angles (Figure 2). The position of the attractor can be used to define the extent of

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[23] (a) Bader, R. F. W.; Stephens, M. E. *J. Am. Chem. Soc.* **1975**, *97*, 7391. (b) Macchi, P.; Sironi, A. *Coord. Chem. Rev.* **2003**, *238−239*, 383.

[24] Gibbs, G. V.; Cox, D. F.; Ross, N. L.; Crawford, T. D.; Downs, R. T.; Burt, J. B. *J. Phys. Chem.* **2005**, *A109*, 10022.

[25] Krokidis, X.; Noury, S.; Silvi, B. *J. Phys. Chem.* **1997**, *A101*, 7277.

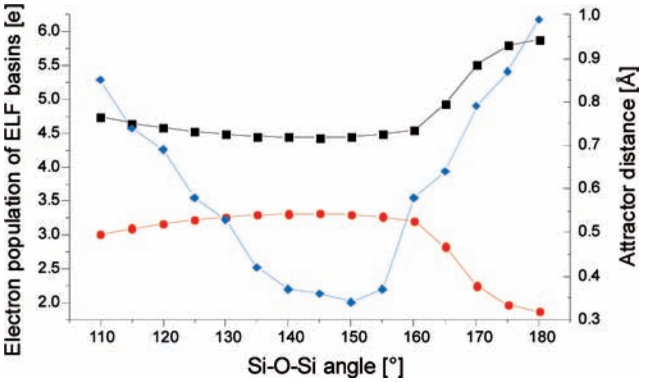


Figure 3. Electron population of lone pairs at the oxygen atom (black curve) and the two Si−O bonds (red) as well as distance between two neighbored ELF attractors of oxygen lone pairs (blue) for model compound $H_3SiOSiH_3$.

polarity of a chemical bond, that is, an ionic formulation is suitable if the attractor is no longer on the straight connectivity line.[26,27] This clearly indicates that the Si−O bond has a significant covalent contribution at small Si−O−Si angles (polar covalency[26]) and becomes more and more solely ionic when the siloxane angle increases.

The electron populations were obtained by integration of the ED within the ELF basins and are shown in Figure 3. The electronic situation of the bonds (red curve) and lone pairs (black curve) changes dramatically between 160 and 165°, which is consistent with the proposed reorientation of the electrons and the event of a chemical process according to the catastrophe theory. The Si−O bonds lose approximately 1.5 e when the Si−O−Si angle increases from 160 to 180° and thus become substantially more electron deficient. In turn, the lone pairs gain approximately 1.5 e and become electron richer. However, despite the electron gain of the lone pairs the basicity of the oxygen atom does not increase because of the unfavorable spatial distribution discussed above. In the region below 160° where hydrogen bonding is generally possible, the curves are quite flat. Interestingly, the distance of the lone pair attractors to each other (blues curve in Figure 3) reaches a minimum value of 0.34 Å at 150°, which coincides with the Si−O−Si angle determined for $H_3SiOSiH_3$ (151.4°) by the full geometry optimization and the minimum of the bending potential energy curve (Figure 1a).

The relaxed PES scan for $(H_3Si)_2O\cdots HOSiH_3$ provided very similar ELF results for Si−O−Si angles between 110 and 160°. There is no change in the populations of the basins, which confirms that no charge transfer occurs between the two molecules in the hydrogen bonded complex. The ELF isosurface representation of $(H_3Si)_2O\cdots HOSiH_3$ at a Si−O−Si angle of 125° is shown in Figure 4. Within the ELF topology, O···H hydrogen bond contacts reveal no attractors but are defined by a common boundary of a protonated monosynaptic valence basin (V(O,H)) with a lone pair valence basin (V(O)) of another molecule or functional group.[28] This requirement is fulfilled for $(H_3Si)_2O\cdots HOSiH_3$ as a nearly symmetrical contact exists between V(O,H) and both V(O) of the oxygen atom (Figure 4). The two lone pair basins V(O) of the siloxane oxygen atom as well as the bond basin V(O,Si) and lone pair basins V(O) in the silanol group can be distinguished by the color code, which represents the volume of the basins.

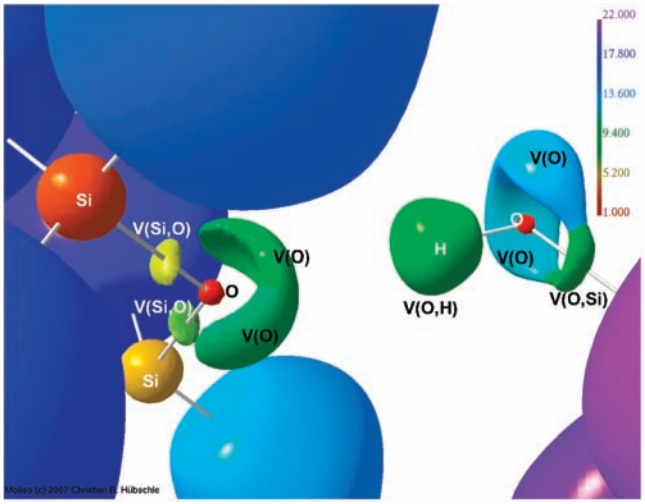
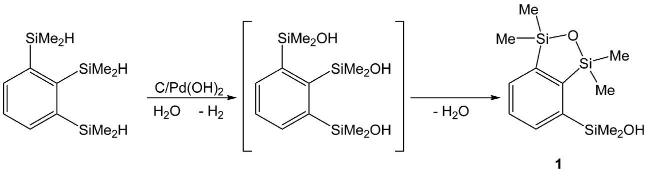


Figure 4. ELF isosurface representation at an ELF value of 0.850 of $(H_3Si)_2O\cdots HOSiH_3$ at a Si−O−Si angle of 125°. Color code representing the volumes of the basins on a linear scale.

Scheme 2. Synthesis of 5-Dimethylhydroxysilyl-1,3-dihydro-1,1,3,3-tetramethyl-2,1,3-benzoxadisilole (**1**)



Experimental Validation. In an effort to verify the hypothesis that the basicity can be improved by reducing the Si−O−Si angle closer to values usually adopted by ether molecules (values around the tetrahedral angle), we turned our attention to a novel organosilanol having a strained siloxane linkage, namely 5-dimethylhydroxysilyl-1,3-dihydro-1,1,3,3-tetramethyl-2,1,3-benzoxadisilole (**1**). A benzoxadisilole was selected as acceptor for the reason that this compound class usually possesses the smallest Si−O−Si angles known. Compound **1** was prepared by the catalytic oxidation of 1,2,3-tris(dimethylsilyl)benzene using Pearlman's catalyst ($C/Pd(OH)_2$) initially giving rise to the formation of the intermediate 1,2,3-tris(hydroxydimethylsilyl)benzene, which spontaneously underwent self-condensation (Scheme 2). Compound **1** comprises a strained siloxane linkage incorporated into a five-membered ring structure (as acceptor) and a silanol group (as donor of the hydrogen bond). Compound **1** was characterized by multinuclear NMR spectroscopy (see Experimental Section) and IR spectroscopy. In CCl_4, the IR spectrum of **1** gives rise to a sharp band at 3688 cm^{-1}, which was assigned to the OH-stretching vibration of the free silanol group. In the solid state, the IR spectrum of **1** reveals a broad intense band at 3423 cm^{-1}.

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(26) Savin, A.; Nesper, R.; Wengert, S.; Fässler, T. F. *Angew. Chem., Int. Ed.* **1997**, *36*, 1808.
(27) Silvi, B.; Savin, A. *Nature (London)* **1994**, *371*, 683.
(28) Alikhani, M. E.; Fuster, F.; Silvi, B. *J. Struct. Chem.* **2005**, *16*, 203.

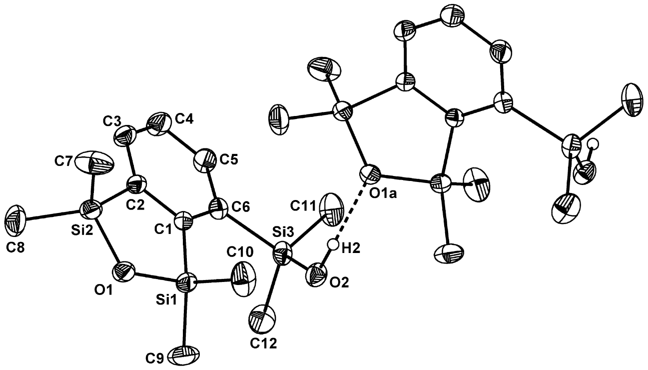

Figure 5. Crystal and molecular structure of **1** with displacement ellipsoids at 240 K (50% probability level). Hydrogen atoms were omitted for clarity (except for H2 of the hydrogen bond).

The red-shift of the OH-stretching vibration of $\Delta\tilde{\nu}$ (OH) = 265 cm^{-1} is indicative for hydrogen bonding.[29]

The synchrotron X-ray diffraction experiment indeed confirmed that **1** possesses a strained siloxane linkage (Si−O−Si angle 116.4(1)°) that is involved in intermolecular $\mathrm{Si_2O\cdots H{-}OSi}$ hydrogen bonding (Figure 5). Selected bond parameters are collected in Chart 1. From the geometric and IR parameters, it can be concluded that the hydrogen bond in **1** is of medium strength according to the definition by Jeffrey and Steiner.[30] An examination of the CCDC database[17] revealed that besides **1**, only three (from more than 80 relevant entries) other silanols undergo intermolecular hydrogen bond formation with siloxane linkages present, as evidenced by intermolecular O···O distances shorter than 3.0 Å. Two of these compounds, namely, $\mathrm{HOMe_2SiX(SiMe_2O)_2SiMe_2}$ (**2**, X = N;[13] **3**, X = CH[14]), are structurally related and comprise siloxane linkages (Si−O−Si angles 133.0 and 134.4(2)°, respectively) incorporated into six-membered ring structures. The third compound is an intermolecular complex (**4**) between 1,6-dihydroxydodecamethylcyclohexasilane and two dodecaoxasilanorbornane molecules having siloxane linkages (Si−O−Si angle 116.21(9)°) incorporated into a bicyclic [2.2.1] ring structure.[15] Unfortunately, neither for **2**, **3**, nor for **4** were the IR red shifts of the OH-stretching vibrations determined. Consistent with our theoretical prediction, compounds **1**−**4** have unusually small Si−O−Si angles (below 135°), which explains their ability to serve as hydrogen bond acceptors.

To complement experimental findings by theoretical results, we have also calculated appropriate model compounds of **1**−**3**, namely, $\mathrm{H_2Si(OSiH_2)_2O\cdots HOSiH_3}$, and $\mathrm{C_6H_4(H_2Si)_2O\cdots HOSiH_3}$ (Chart 1), to estimate hydrogen bond energies E_{HB} and the red-shift of the OH-stretching vibration $\Delta\tilde{\nu}$ (OH) and to compare these values to those obtained by the PES scans of $\mathrm{(H_3Si)_2O\cdots HOSiH_3}$. This comparison shows that $\mathrm{C_6H_4(H_2Si)_2O\cdots HOSiH_3}$, the model complex of **1**, forms a significantly stronger $\mathrm{Si_2O\cdots H{-}OSi}$ hydrogen bond than $\mathrm{H_2Si(OSiH_2)_2O\cdots HOSiH_3}$, the model complex of **2** and **3**, which is consistent with the angular dependence of the hydrogen bond strength derived from the PES scans (see Figure 1 and Supporting Information).

The multipolar modeling[31] of the experimental structure factors of **1** gave access to the electron-density distribution, and a subsequent atoms-in-molecules (AIM)[18] analysis yielded bond and atomic properties. Figure 6 shows the static deformation density and Laplacian distribution in the bicyclic fragment and in the plane of the hydrogen bond and shows the difference between homopolar covalent bonds (C−C), heteropolar covalent bonds (Si−C), and ionic bonds (Si−O). The maximum of the deformation density (increase of density in relation to the independent atom model (IAM)) is observed in the middle of C−C bonds. For Si−C bonds, there are two kinds of maxima: the smaller ones are situated at the silicon atoms and the larger ones are located at carbon atoms (Figure 6a). For the Si−O bonds there are only maxima situated at the oxygen atoms. In the Laplacian map there is one valence shell charge concentration (VSCC) at each carbon atom of the C−C bond forming the typically saddle shaped region of a homopolar covalent bond (Figure 6c). There is one VSCC at the carbon atom but none at the silicon atom for the Si−C bond; however, there is a pronounced deformation of the Laplacian toward the silicon atom. Finally, there is one large VSCC at the oxygen atom that is not deformed toward the silicon atom for the Si−O bond so that silicon and oxygen atoms nearly retain the spherical form of ions. The deformation of the oxygen lone pair toward the hydrogen atom is consistent with the formation of the hydrogen bond (Figures 6b and 6d).

The bond properties for the siloxane linkage (density at the bcps: Si1−O1 = 0.86(2) e/Å^3, Si2−O1 = 0.90(2) e/Å^3, Laplacian at the bcps: Si1−O1 = 16.7(1) and Si2−O1 = 18.3(1) e/Å^5) confirm that the Si−O bonds have mainly ionic bond character. The values are very close to values calculated for $\mathrm{H_3SiOSiH_3}$ at the appropriate Si−O−Si angle (see Figure 1 and Supporting Information). The bond properties of the Si−O bond in the silanol group are similar ($\rho(bcp_{Si3\text{-}O2}) = 0.97(2)$ e/Å^3 and $\nabla^2\rho(bcp_{Si3\text{-}O2}) = 19.6(1)$ e/Å^5). The density at the bcps for heteropolar covalent Si−C bonds is not higher ($\rho(bcp_{Si-C}) = 0.80$ e/Å^3 at an average over eight Si−C bonds, see Supporting Information) but the value of the Laplacian is significantly smaller ($\nabla^2\rho(bcp_{Si-C}) = 6.0$ e/Å^5 at an average over eight Si−C bonds, see Supporting Information). In contrast to this, the homopolar covalent C−C bonds exhibit a much larger value of the density at the bcps and a large negative Laplacian value ($\rho(bcp_{C-C}) = 2.14$ e/Å^3 and $\nabla^2\rho(bcp_{C-C}) = -19.7$ e/Å^5 at an average over six C−C bonds, see Supporting Information). According to the criteria given by Koch and Popelier, the bond properties of the hydrogen bond O2−H2···O1 ($\rho(bcp_{H2\cdots O1}) = 0.16(3)$ e/Å^3 and $\nabla^2\rho(bcp_{H2\cdots O1}) = 2.7(1)$ e/Å^5) classify the hydrogen bond as being strong.[32] The atomic properties reveal a large charge separation in the siloxane and silanol moiety as it was previously found for Si−O bonds.[33] The Si atoms of the siloxane linkage (Si1 and Si2) have large charges of

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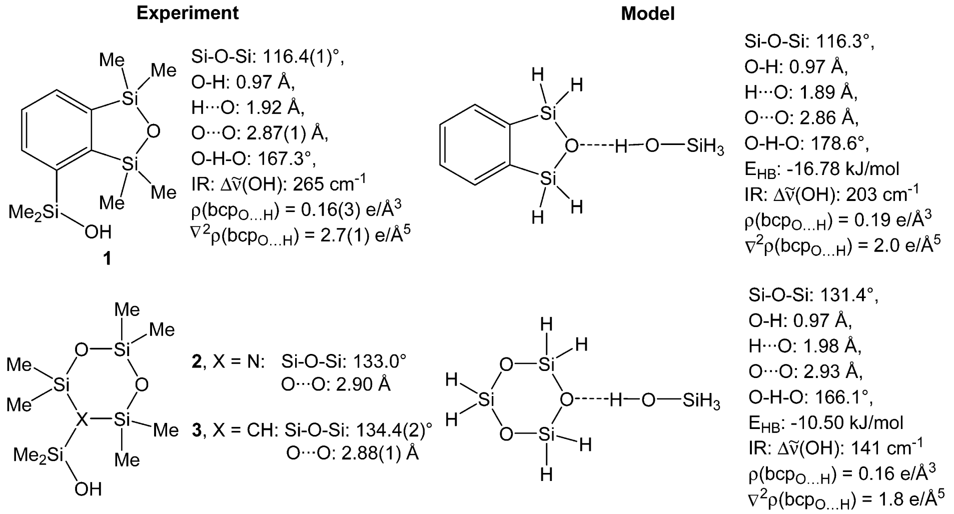
(29) West, R.; Baney, R. H. *J. Am. Chem. Soc.* **1959**, *81*, 6145.

(30) (a) Jeffrey, G. A. *An Introduction to Hydrogen Bonding*; Oxford University Press: Oxford, U.K., 1997. (b) Steiner, T. *Angew. Chem.* **2002**, *114*, 50.

(31) Hansen, N. K.; Coppens, P. *Acta Crystallogr.* **1978**, *A34*, 909.

Chart 1. Structural, Spectroscopic, and Topological Parameters of Experimental (**1**−**3**) and Calculated Hydrogen Bonded Complexes between Silanols and Siloxanes



Si-O-Si: 116.4(1)°,
O-H: 0.97 Å,
H···O: 1.92 Å,
O···O: 2.87(1) Å,
O-H-O: 167.3°,
IR: $\Delta\tilde{\nu}$(OH): 265 cm^{-1}
$\rho(bcp_{O...H})$ = 0.16(3) e/$Å^3$
$\nabla^2\rho(bcp_{O...H})$ = 2.7(1) e/$Å^5$

Si-O-Si: 116.3°,
O-H: 0.97 Å,
H···O: 1.89 Å,
O···O: 2.86 Å,
O-H-O: 178.6°,
E_{HB}: -16.78 kJ/mol
IR: $\Delta\tilde{\nu}$(OH): 203 cm^{-1}
$\rho(bcp_{O...H})$ = 0.19 e/$Å^3$
$\nabla^2\rho(bcp_{O...H})$ = 2.0 e/$Å^5$

2, X = N: Si-O-Si: 133.0°
O···O: 2.90 Å

3, X = CH: Si-O-Si: 134.4(2)°
O···O: 2.88(1) Å

Si-O-Si: 131.4°,
O-H: 0.97 Å,
H···O: 1.98 Å,
O···O: 2.93 Å,
O-H-O: 166.1°,
E_{HB}: -10.50 kJ/mol
IR: $\Delta\tilde{\nu}$(OH): 141 cm^{-1}
$\rho(bcp_{O...H})$ = 0.16 e/$Å^3$
$\nabla^2\rho(bcp_{O...H})$ = 1.8 e/$Å^5$

2.50 e and small total volumes of 5.8 $Å^3$, that are again very similar to those of the silanol group (Q_{tot} = 2.46 e and V_{tot} = 6.0 $Å^3$). The oxygen atom of the siloxane bond (O1) reveals the values Q_{tot} = −1.23 e and V_{tot} = 15.6 $Å^3$, whereas the oyxgen atom of the silanol group (O2) adopts the values Q_{tot} = −1.61 e and V_{tot} = 21.5 $Å^3$.

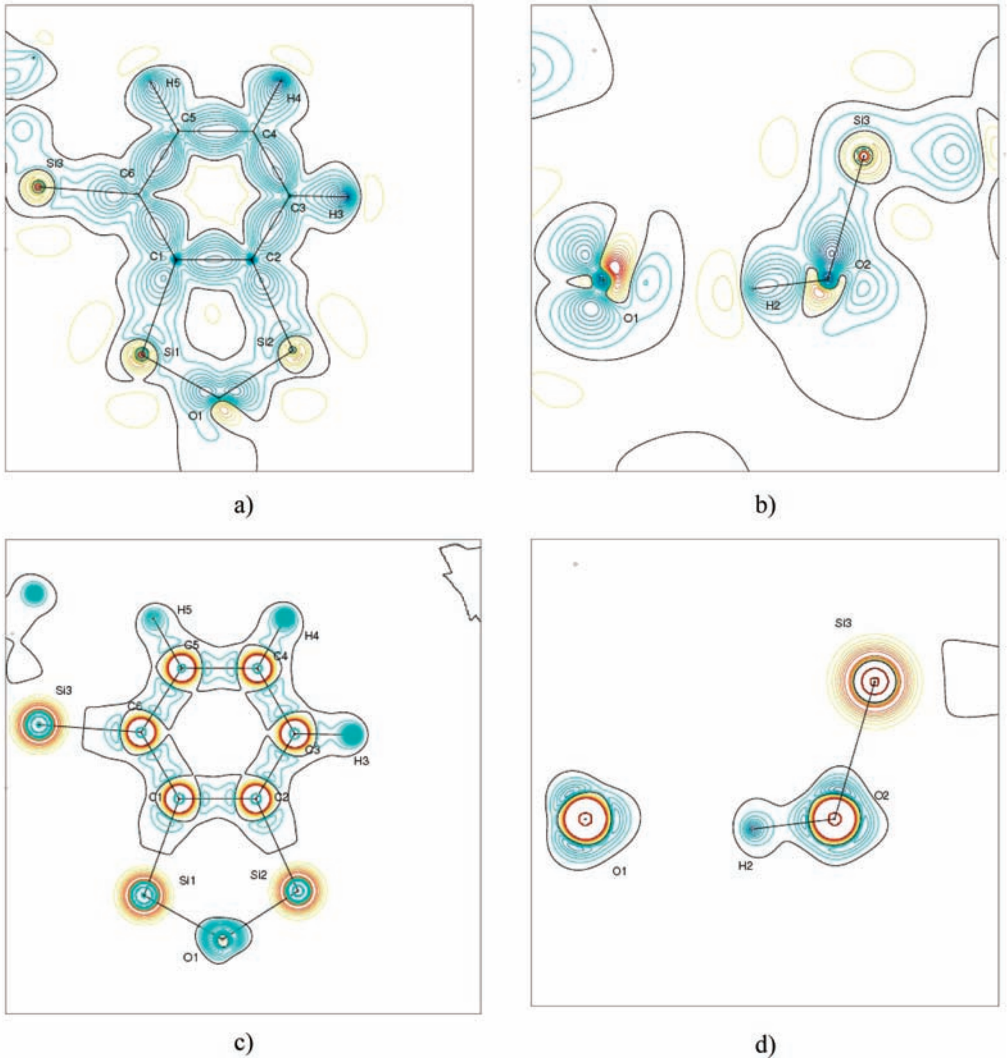


Figure 6. Static deformation density map (a) in the plane of the bicyclic fragment, (b) in the plane of the hydrogen bond (contour intervals = 0.1 e/$Å^3$, blue = positive, red = negative, black = zero); Laplacian distribution map (c) in the plane of the bicyclic fragment, (d) in the plane of the hydrogen bond (contour intervals = 25 e/$Å^5$, blue = negative, red = positive, black = zero); derived from X-ray diffraction experiment of **1**.

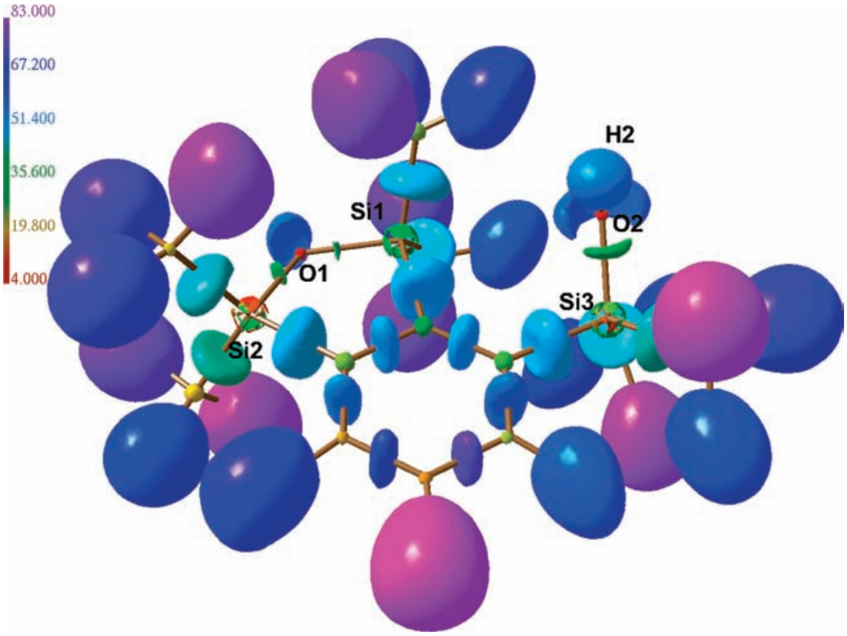


Figure 7. Experimentally obtained ELF isosurface of 0.86 for **1**, color code representing the volumes of the basins on a linear scale.

As the ELF cannot be calculated from the experimental ED satisfactorily, the constrained wave function fitting approach of Jayatilaka et al.[34] was applied to obtain the ELF from experimental structure factors at the CHF/cc-pVDZ level of theory (CHF = constrained Hartree−Fock). The obtained ELF isosurface of 0.86 for **1** is shown in Figure 7. With these data, a topological analysis of the experimental ELF was carried out according to the method published only recently.[35] Most interestingly, there is only one ELF basin for the lone pair electrons of the oxygen atom being the acceptor of the hydrogen bond that is populated with 4.50 e, which at first suggests that the putative two lone pairs have merged upon hydrogen bond formation. To investigate this hypothesis, single point calculations (HF/cc-pVDZ and B3LYP/cc-pVTZ) were performed on a single molecule and a hydrogen bonded dimer of **1** in the gas phase using the experimental geometry of the crystal structure. In both cases, only one ELF basin was observed for the four non-bonding electrons expected for the oxygen atom of the siloxane linkage. This apparently suggests that the hydrogen bond is not the reason for the merger of the two lone pairs; however, the merger might be the reason for the exceptionally strong hydrogen bond. As the experimental ELF contains all information of the crystal field including electrostatic interactions, the lone pair of the O atom $V(O)_{silox}$ is populated more and the Si−O bonds $V(Si,O)_{silox}$ (sum of both Si−O bonds) are populated less than in the single point calculations. However, the general agreement between the experimental and theoretical ELF topology is very good (experiment, i.e., CHF/cc-pVDZ: $N(V(O)_{silox}) = 4.50$ e, $N(V(Si,O)_{silox}) = 3.30$ e, $N(V(O)_{silanol}) = 4.23$ e, $N(V(Si,O)_{silanol}) = 1.81$ e; theory HF/cc-pVDZ: $N(V(O)_{silox}) = 4.20$ e, $N(V(Si,O)_{silox}) = 3.60$ e, $N(V(O)_{silanol}) = 4.33$ e, $N(V(Si,O)_{silanol}) = 1.73$ e; theory B3LYP/cc-pVTZ: $N(V(O)_{silox}) = 4.32$ e, $N(V(Si,O)_{silox}) = 3.45$ e, $N(V(O)_{silanol}) = 4.47$ e, $N(V(Si,O)_{silanol}) = 1.69$ e).

Conclusion

A combined theoretical and experimental study of the Si−O−Si linkage in siloxanes was performed. Quantum chemical ab initio calculations on the model compounds $H_3SiOSiH_3$, $(H_3Si)_2O\cdots HOH$, and $(H_3Si)_2O\cdots HOSiH_3$ as well as high-resolved single-crystal synchrotron X-ray diffraction experiments on the siloxanol **1**, which is involved in intermolecular $Si_2O\cdots H{-}OSi$ hydrogen bonding, yielded the geometry, the ED distribution, and the ELF. The results are consistent with the ionic bond model of the Si−O bond; however, covalent bond contributions become more significant when the Si−O−Si angle is reduced to extremely small values near the tetrahedral angle. The basicity of unstrained siloxane linkages is negligible; however, when the Si−O−Si angle is reduced to very small values, the same linkage is able to act as hydrogen bond acceptor. In this manner, fine-tuning of the bond reactivity is possible by variation of the Si−O−Si angle. Our results suggest that strained siloxane linkages possessing small Si−O−Si angles may be useful for the design of new silicon based crown ethers and related ligands.

Experimental and Computational Details

Synthesis of 5-Dimethylhydroxysilyl-1,3-dihydro-1,1,3,3-tetramethyl-2,1,3-benzoxadisilole (1). A solution of 1,2,3-tris(dimethylsilyl)benzene[36] (1.00 g, 3.95 mmol) in THF (20 mL) was

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[32] Koch, U.; Popelier, P. L. A. *J. Phys. Chem.* **1995**, *99*, 9747.

[33] Kocher, N.; Henn, J.; Gostevskii, B.; Kost, D.; Kalikhman, I.; Engels, B.; Stalke, D. *J. Am. Chem. Soc.* **2004**, *126*, 5563.

[34] (a) Jayatilaka, D.; Grimwood, D. J. *Acta Crystallogr.* **2001**, *A57*, 76. (b) Grimwood, D. J.; Bytheway, I.; Jayatilaka, D. *J. Comput. Chem.* **2003**, *24*, 470. (c) Jayatilaka, D.; Grimwood, D. J. *Acta Crystallogr.* **2004**, *A60*, 111.

[35] Hübschle, C. B.; Dittrich, B.; Grabowsky, S.; Messerschmidt, M.; Luger, P. *Acta Crystallogr.* **2008**, *B64*, 363.

[36] Beckmann, J.; Hesse, M. *Z. Anorg. Allg. Chem.* **2007**, *633*, 1233.

slowly added to a suspension of Pearlman's catalyst C/Pd$(OH)_2$ (25 mg) in THF (90 mL) and water (10 mL). After the evolution of hydrogen gas had ceased (approximately 2 h), the catalyst was filtered off, and the solvent evaporated under reduced pressure. CH_2Cl_2 (20 mL) was added, and the solution dried over Na_2SO_4, whereby last traces of the catalyst were absorbed. The solvent was removed to give a crude solid material that was recrystallized from hexane to give **1** as colorless crystals (800 mg, 2.83 mmol, 80%; mp. 99−101 °C).

^{1}H NMR ($CDCl_3$): $\delta = 7.60$ (m, 2H), 7.41 (t, 1H), 2.23 (s, 1H), 0.49 (s, 6H), 0.42 (s, 6H), 0.38 (s, 6H). ^{13}C NMR ($CDCl_3$): $\delta =$ 153.6, 148.3, 143.9, 134.4, 131.9, 127.6, 2.3, 1.8, 1.0. ^{29}Si NMR ($CDCl_3$): $\delta = 16.3$, 14.3, 7.9. CP MAS ^{29}Si NMR: $\delta = 16.6$, 14.1, 5.3. IR $\tilde{\nu}$(OH): 3423 cm^{-1} (KBr), 3688 and 3444 cm^{-1} (NaCl, CCl_4). Calc. for $C_{12}H_{22}O_2Si_3$ (282.57): C 51.01, H 7.85; Found C 50.92, H 7.96.

Crystallography. The data set for **1** was measured at the synchrotron beamline F1 of HASYLAB/ DESY in Hamburg at 240 K with a wavelength $\lambda = 0.560$ Å. A total of 208742 reflections were measured from which 14536 were unique to a resolution of 1.04 Å^{-1}. For the monoclinic space group $P2_1/n$, an overall completeness of data of 96.3% could be reached (Table 1). It was not possible to further cool down the sample because of severe problems with phase transitions. As the molecular structure is very rigid, atomic motions were sufficiently small (see Figure 5). Conventional spherical refinement was carried out by the program SHELXL[37] to establish the starting positional and displacement parameters (anisotropic for non-hydrogen atoms, isotropic for hydrogen atoms) for the aspherical refinement steps. For aspherical refinement, the Hansen-Coppens multipole formalism[31] as implemented in the program XD2006[38] was used. The chemically most reasonable density model including local site symmetries and chemical constraints was applied (see Supporting Information). C−H and O−H distances were fixed to average values obtained from neutron diffraction analyses.[39] For the silicon atoms, a non-standard entry in the scattering table was introduced (2 3.0628 2 3.0628 4 3.0628 6 3.0628 8 3.0628). All non-hydrogen atoms were treated up to the hexadecapole level of expansion, while bond-directed dipoles and quadrupoles were introduced for all hydrogen atoms. The expansion-contraction parameter κ was refined independently for all non-constrained atoms in the synchrotron data sets, but fixed to 1.13 for hydrogen atoms. κ' values were fixed to default values for all atoms (0.85 for Si, 1.00 for O and C, 1.29 for H).[40] Analysis of the obtained ED distribution was carried out using the XDPROP program of the XD2006 suite.[38] From the experimental structure factors, an experimental wave function (CHF/cc-pVDZ) and subsequently experimental ELF were determined by means of constrained wave function fitting using the program platform TONTO.[41] Topological analysis of experimental ELF was performed with Basin.[42] CCDC-723174 contains the supplementary crystallographic data for this paper. This data can be obtained free of charge from the Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

Table 1. Crystallographic and Refinement Details of **1**

chemical formula	$C_{12}H_{22}O_2Si_3$
M(g/mol)	282.57
crystal system	monoclinic
space group	$P2_1/n$
Z	4
a (Å)	8.922(2)
b (Å)	16.700(3)
c (Å)	11.151(2)
α (deg)	90.0
β (deg)	103.59(3)
γ (deg)	90.0
V (Å^3)	1615.0(6)
ρ (g/cm^3)	1.162
F(000)	608
μ (mm^{-1})	0.15
crystal size (mm$^{>3}$)	0.4 × 0.4 × 0.3
color	colorless
T (K)	240
λ (Å)	0.560
(sin θ_{max})/(λ)(Å^{-1})	1.04
max 2θ (deg)	71.0
no. of collected reflections	208742
no. of unique reflections	14536
no. of observed reflections ($I > 2\sigma$)	5899
completeness (%)	96.3
R_{int} (%)	2.88
spherical refinement:	
$R(F)$ (%)	4.20
$wR(F^2)$ (%)	14.95
GoF	0.90
multipole refinement:	
ratio reflections/parameters	19.66
$R(F)/R(F^2)$ (%)	2.85/3.07
$wR(F)/wR(F^2)$ (%)	2.63/5.19
GoF	1.01
max residual density (e/Å^3)	0.20
min residual density (e/Å^3)	−0.21
mean residual density (e/Å^3)	0.02
constrained wave function fitting:	
Λ	0.60
χ^2	0.93
$wR(F)$ (%)	4.27
GoF	0.97

Computational Methodology. Full geometry optimizations were carried out for the model compounds $H_3SiOSiH_3$, $(H_3Si)_2\cdots HOSiH_3$, $H_2Si(OSiH_2)_2O\cdots HOSiH_3$, and $C_6H_4(H_2Si)_2O\cdots HOSiH_3$ at the B3LYP/cc-pVTZ level of theory using the program GAUSSIAN 03.[43] Relaxed PES scans of the model compounds $H_3SiOSiH_3$, $(H_3Si)_2O\cdots HOH$, and $(H_3Si)_2O\cdots HOSiH_3$ were carried out at the same level at Si−O−Si angles between 110° and 180° with 5° intervals. The corresponding hydrogen bond energies were calculated by the difference of the scaled[44] zero-point vibrational energy corrected molecular energies of $(H_3Si)_2O\cdots HOSiH_3$ and $H_3SiOSiH_3$/SiH_3OH; additionally, basis set superposition error was corrected by the counterpoise procedure.[45] Topological bond and atomic parameters according to Bader were derived from the GAUSSIAN wave function output using the program MORPHY98,[46] while the delocalization index was calculated with AIM2000.[47] The ELF was calculated from the GAUSSIAN checkpoint file using the program DGrid[42] and was topologically analyzed using Basin.[42]

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(37) *SHELXL*: Sheldrick, G. M. *Acta Crystallogr.* **2008**, *A64*, 112.

(38) Volkov, A.; Macchi, P.; Farrugia, L. J.; Gatti, C.; Mallinson, P.; Richter, T.; Koritsanszky, T. *XD2006 - A Computer Program for Multipole Refinement, Topological Analysis of Charge Densities and Evaluation of Intermolecular Energies from Experimental or Theoretical Structure Factors*, revision 5.42; State University of New York at Buffalo: Buffalo, NY, 2006.

(39) Allen, F. H.; Kennard, O.; Watson, D. G.; Brammer, L.; Orpen, A. G.; Taylor, R. *International Tables for X-ray Crystallography*; Kluwer, C., Ed.; Academic Publishers: Amsterdam, Netherlands, 1992; Vol. *C*, Chapter 9.5, p 685.

(40) Volkov, A.; Abramov, Y. A.; Coppens, P. *Acta Crystallogr.* **2001**, *A57*, 272.

(41) Jayatilaka, D.; Grimwood, D. J. *TONTO - A Fortran Based Object-Oriented System for Quantum Chemistry and Crystallography*; University of Western Australia: Perth, Australia, 2007.

(42) Kohout, M. *DGrid and Basin*, version 4.2; Max-Planck-Institut für Chemische Physik fester Stoffe: Dresden, Germany, 2007.

(43) Frisch, M. J. et al. *GAUSSIAN 03*, Revision B.04; Gaussian, Inc.: Pittsburgh, PA, 2003.

(44) Bachrach, S. M.; Hayes, J. M.; Dao, T.; Mynar, J. L. *Theor. Chem. Acc.* **2002**, *107*, 266.

Supporting Information Available: For model compound $H_3SiOSiH_3$ for all Si−O−Si angles between 110 and 180° from PES scan: Si−O bond distances, density values of Si−O bcps, Laplacian values of Si−O bcps, delocalization indices of Si−O bonds, Si/O atomic charges and atomic volumes, total and relative molecular energies, sum of electron populations and volumes of ELF basins allocated to oxygen lone pairs and Si−O bonds, numbers and distances of ELF attractors. For model compound $(H_3Si)_2O\cdots HOSiH_3$ for all Si−O−Si angles between 110 and 160° from PES scan: Si−O bond distances in siloxane, donor···acceptor distances H···O, O−H distances in silanol, Si−O distances in silanol, O−H···O angles, density and Laplacian values of $Si-O_{siloxane}$ and O···H bcps, $n(O_{siloxane}) \rightarrow \sigma^*(O-H_{silanol})$ delocalization energies, hydrogen bond energies, Si/O atomic charges and atomic volumes of siloxane, Si/O/H atomic charges and atomic volumes of silanol, total and relative molecular energies, sum of electron populations and volumes of ELF basins allocated to oxygen lone pairs and Si−O bonds, numbers and distances of ELF attractors. Experimental section: Applied local site symmetries, constraints and κ values, all bond lengths and angles of **1**, residual density maps, density, Laplacian and ellipticity values of all bond and ring critical points of **1**, atomic charges and atomic volumes of all atoms of **1**. X-ray crystallographic data for **1** (CIF). This material is available free of charge via the Internet at http://pubs.acs.org.

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(45) Boys, S. F.; Bernardi, F. *Mol. Phys.* **1970**, *19*, 553.

(46) Popelier, P. L. A.; Bone, R. G. A. *MORPHY-98, A Topological Analysis Program*; see: (a) Popelier, P. L. A.; Bone, R. G. A. *Mol. Phys.* **1996**, *87*, 1169. (b) Popelier, P. L. A.; Bone, R. G. A. *Comput. Phys. Commun.* **1996**, *93*, 212.

(47) *AIM2000 - A Program to Analyse and Visualise Atoms in Molecules*; Biegler-König, F.; Schönbohm, J.; Bayles, D. *J. Comput. Chem.* **2001**, *22*, 549.