

Ab initio study of the basicity and propensity of siloxanols towards hydrogen bond formation

Marek Cypryk *

Centre of Molecular and Macromolecular Studies of the Polish Academy of Sciences, Sienkiewicza 112, 90-363 Łódź, Poland

Received 19 April 1997

Abstract

Hydrogen bonding of silanols as proton donors to water as a proton acceptor and intramolecular hydrogen bonding in oligosiloxanediols were studied by ab initio molecular orbital methods. The calculated proton affinities and basicities of free and hydrogen-bonded silanols reveal that hydrogen bond, in which silanol group is a H-donor, strongly enhance the basicity of silanol oxygen. Thus, the silanol group in such complex is by 54–113 kJ/mol more basic than the free silanol group. Hydrogen-bonded complexes of this type are predicted to show enhanced reactivity in condensation reactions of silanols. © 1997 Elsevier Science S.A.

Keywords: Silanols; Siloxanols; Hydrogen complex formation; Proton affinity; Basicity; Ab initio calculation

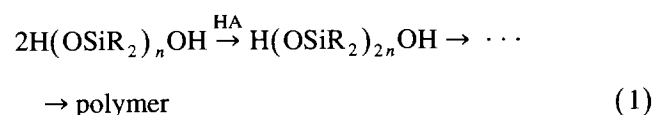
1. Introduction

Silanol functions play an important role in silicon chemistry. They are involved in condensation reactions resulting in siloxane bond formation [1], the most important processes leading to siloxane polymers (silicones) [2–5] and polysilicates [6]. Silanol groups are also important structural fragments of zeolites and silica, as they strongly modify the surface properties of these materials [7,8].

The reactivity and molecular properties of silanols have therefore been extensively studied, both experimentally and theoretically [9–17]. Silanols show ambident acidic and basic character; according to the IR measurements, silanols in solution are stronger acids than the corresponding carbinols, whereas basicities of both classes of compounds are comparable [10]. In the gas phase, trimethylsilanol was reported to be less basic by 42 kJ/mol than the isostructural alcohol, *t*-butanol [18,19]. This result contrasts with calculations, that predict the proton affinities of H₃SiOH and H₃COH to be identical (761 kJ/mol, 181.9 kcal/mol) [20].

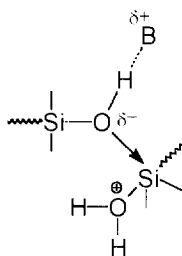
Due to their ambident behaviour, silanols form relatively strong hydrogen bonds acting as donors as well as acceptors of a proton [10–13]. Hydrogen bonds affect to a large extent the acidity and basicity of silanols. For

example, the acidity of silanol groups involved in H-bonds as proton acceptors in hydrated silica gel is greatly enhanced [21]. On the other hand, the hydrogen-bonded complexes of silanols with bases show increased reactivity in reactions of nucleophilic substitution. Thus, silanol–amine adducts are the true reactive species in base-catalysed heterofunctional condensation of silanols with silyl chlorides and silyl acetates [22,23]. There is kinetic evidence that hydrogen aggregates of silanols play also an important role in acid-catalysed polycondensation of silanediols (Eq. (1)), strongly affecting kinetics of the process [24–29].



The mechanism of the condensation (Eq. (1)) involves the cooperation of acid and base in activation of both silanol groups: the one, which plays a role of an electrophile and the other, which acts as a nucleophile. The interaction with a base results in the increased nucleophilicity of oxygen in the latter group (Scheme 1) [26]. If the condensation reaction is carried out in non-basic medium, the role of a base B is played by other silanol groups and by water produced during condensation [26]. However, because of the number and complexity of molecular species formed in such systems, experimental results are difficult to interpret. The

* Corresponding author.



Scheme 1.

methods of theoretical chemistry are therefore very helpful in predicting properties of these species. In most of theoretical investigations, the parent silanol H_3SiOH was used as a model [15,30–34]. The data concerning structure and reactivity of more complex silanol molecules are sparse [15,35,36]. However, in real systems, silanol groups usually appear as fragments of large molecules, like linear polysiloxanes or a silica network, in which their reactivity is affected by geminal siloxane or silanol linkages. In addition, silanol groups are often involved in hydrogen-bonded complexes with each other or with other polar species, like water. It is important to know how these interactions influence the reactivity of silanol groups. In substitution reactions, such as condensation, the crucial factor, determining the reaction mechanism, is the basicity and nucleophilicity of silanols. This paper presents the *ab initio* study of thermodynamics of the hydrogen bond formation by several mono- and bi-functional silanols and siloxanols to water. Thermodynamics of intramolecular hydrogen bonding in model siloxanediols is also reported. Comparison of the calculated proton affinities and basicities of free and complexed silanols shows the influence of the hydrogen bond on the basic properties of silanol group.

2. Theoretical methods

Ab initio calculations have been carried out using standard techniques [37] as implemented in the Gaussian 94 series of programs [38]. Geometry optimizations, harmonic frequencies and zero-point vibrational energies were calculated with the polarized 6-31G* basis set. All structures were identified as true local minima on the energy potential surface by the frequency calculations. The intramolecular vibrational components of the thermal energy were scaled by the usual factor of 0.893 [37]. Single point calculations, which include part of the electron correlation, were performed using the Møller–Plesset perturbation theory up to fourth order (the frozen-core approximation was used) [39–42]. This level of theory, denoted as MP4SDTQ/6-31G*//HF/6-31G*, was used for energy compar-

isons. The energies of the formation of bimolecular complexes were corrected for basis set superposition error (BSSE) using the full counterpoise method [43]. The orbital and bond analyses were performed with both the Mulliken [44,45] and the Natural Bond Orbital (NBO) methods [46,47].

3. Results and discussion

3.1. Geometries

3.1.1. Silanols 1, 2, 3, 4, 5

The following silanols were chosen as models for calculations: the parent silanol H_3SiOH (**1**), silanediol $\text{H}_2\text{Si}(\text{OH})_2$ (**2**), disiloxanol $\text{H}_3\text{SiOSiH}_2\text{OH}$ (**3**), disiloxanediol $\text{HOSiH}_2\text{OSiH}_2\text{OH}$ (**4**) and trisiloxanediol $\text{H}(\text{OSiH}_2)_3\text{OH}$ (**5**). The HF/6-31G* optimized geometries of **1–5** are presented in Fig. 1. For siloxanediols **4** and **5** two geometry minima were calculated: the gauche ‘open-chain’ conformation (**4a** and **5a**) and the ‘cyclic’ conformation involving the intramolecular H-bond between silanol end-groups (**4b** and **5b**).

The geometry of **1** has already been calculated at various levels of theory and the present results are in accord with previous studies [15,20,30–34]. The Si–O bond distance in **1** (C_s symmetry) calculated at HF/6-31G* is 1.647 Å and the SiOH angle is 119°. The electron correlation methods give somewhat longer bonds and slightly smaller angles. Thus, at the MP2/6-31G* level, the Si–O bond length is 1.670 Å and the SiOH angle is 116.5° [34]. The most stable conformation of silanediol **2** is gauche–gauche structure of C_2 symmetry, which is ascribed to the anomeric effect [48,49]. Disiloxanol **3** and the diols **4a** and **5a** also appear in conformations in which the XOSiOX moieties are in gauche–gauche positions (the XOSiO dihedral angles being close to 60°), indicating that the anomeric effect operates in siloxanes as well. ‘Cyclic’ conformations of diols **4b** and **5b** are lower in energy than the ‘open-chain’ structures **4a** and **5a** by 2.1 and 23.0 kJ/mol, respectively, which reflects additional stabilization provided by the intramolecular hydrogen bond. The energy gain on going from **4a** to **4b** is small because the small ring does not allow efficient orbital overlapping and the resulting H-bond is relatively weak.

There is no experimental data concerning the geometry of silanols in the gas phase. On the other hand, many crystal structures of silanols have been published [9]. The comparison of these structures with the gas-phase geometries is therefore the only way to verify theoretical results, although it must be done with caution, since the hydrogen bonds and other intermolecular forces operating in a crystalline network induce some distortions in bonding parameters.

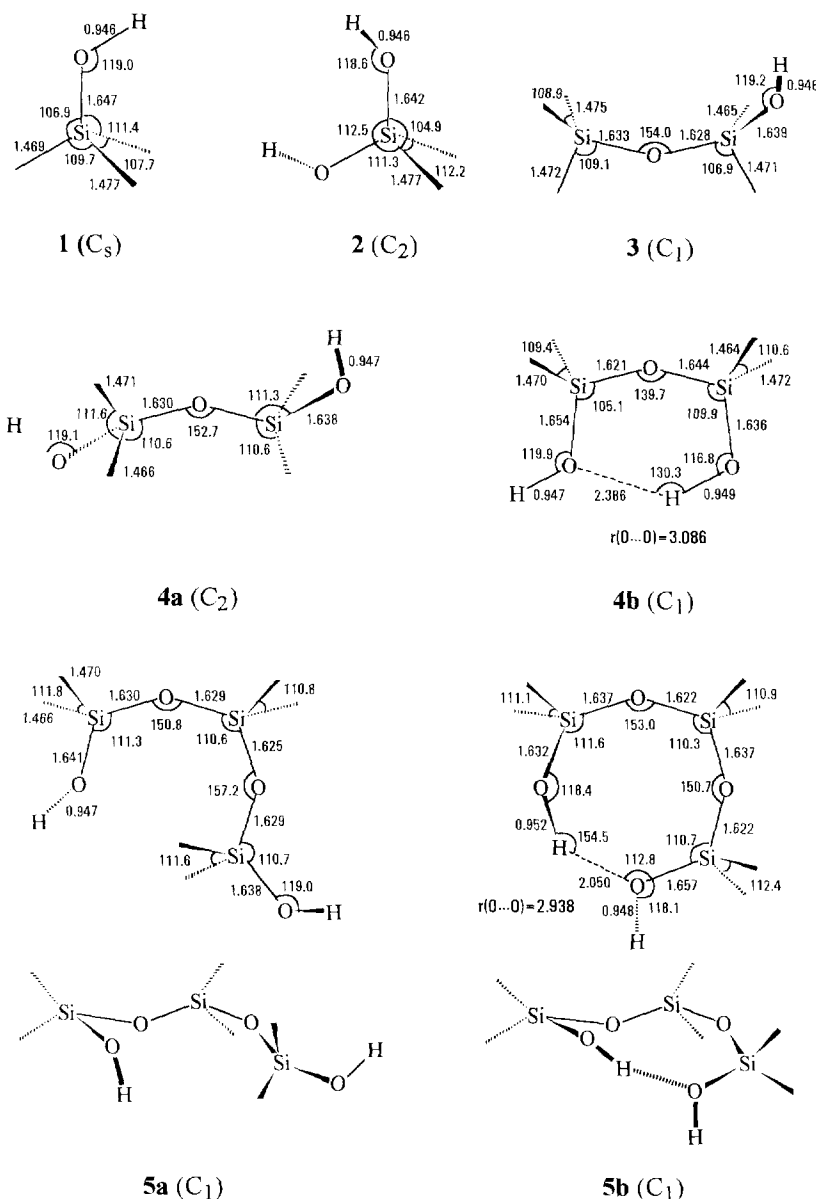


Fig. 1. HF/6-31G* optimized geometries of the model silanols and siloxanols.

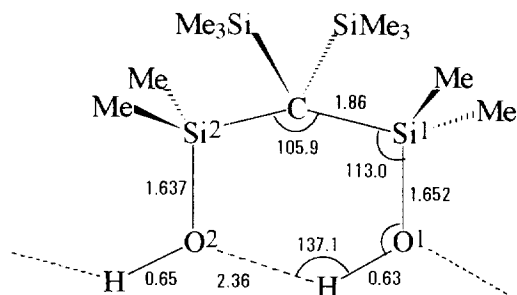
Typical Si–O bond lengths in silanols, according to the many X-ray studies, are in the range of 1.63–1.65 Å [9]. The HF/6-31G* calculated bond distances for **1–5** fall in this range very well (Fig. 1). In particular, geometrical parameters for the ‘open-chain’ conformation of disiloxanediol **4a** are in excellent agreement with those found in an X-ray study for tetramethyldisiloxane-1,3-diol (Table 1) [50]. The calculated SiOSi angle in **4a** is somewhat wider than that measured for tetramethyldisiloxanediol, however, it is well known that SiOSi angles in siloxanes obtained by Hartree–Fock methods are too wide [51]. In the crystal of tetramethyldisiloxanediol intramolecular hydrogen bonds do not occur, because they are not favoured thermodynamically, compared to the intermolecular bonds. However, in gas

phase and in solution their formation is more likely. Intramolecular H-bonds were identified in the crystal structures of sterically hindered silanols. For example,

Table 1
Comparison of some structural parameters calculated (HF/6-31G*) for disiloxanediol **4a** with those measured for H(OSiMe₂)₂OH (bond distances in Å, angles in degrees)

Parameter	4a	H(OSiMe ₂) ₂ OH ^a
$r(\text{Si–OSi})$	1.630	1.624, 1.631
$r(\text{Si–OH})$	1.638	1.640, 1.643
$r(\text{O–H})$	0.947	
$\angle \text{SiOSi}$	152.7	141.4
$\angle \text{OSiO(H)}$	111.3	109.6, 110.0

^a See Ref. [50].



Scheme 2.

the intramolecular hydrogen bonds, which occur in a crystalline network of $(\text{Me}_3\text{Si})_2\text{C}(\text{SiMe}_2\text{OH})_2$ [52] impose the six-membered ring geometry upon this molecule, analogous to that of **4b** (Scheme 2). Except for the O–H bond distances, which are much shorter than those calculated for **4b**, the other molecular parameters of both species are in reasonable agreement. In contrast to **4b**, the $\text{Si}^1\text{--O}^1$ bond in $(\text{Me}_3\text{Si})_2\text{C}(\text{SiMe}_2\text{OH})_2$ is longer than the $\text{Si}^2\text{--O}^2$ bond (Scheme 2). This elongation is caused by the intermolecular hydrogen bond, in which O^1 appears as a proton acceptor. The intermolecular hydrogen bond is presumably stronger than the intramolecular $\text{O}^2 \cdots \text{H}(\text{O}^1)$ bond, thus, its effect on the adjacent $\text{Si}^1\text{--O}^1$ bond elongation is more distinct.

The optimization of the geometry of **5a** was more difficult. Potential energy surface is very flat due to the high flexibility of siloxane chain. The optimization procedure was repeated several times using different starting geometries to find the conformation of the lowest energy. The anomeric effect and steric effects of hydro-

gen substituents are responsible for the optimized 'open-chain' geometry of **5a**, which resembles very closely the 'cyclic' form **5b** (Fig. 1). The distance between both end groups ($\text{Si}^1\text{O}^1\text{H}^1$ and $\text{Si}^2\text{O}^2\text{H}^2$) in **5a** is relatively small ($r(\text{O}^1\text{--Si}^2) = 3.87 \text{ \AA}$). This is one of the reasons for a high cyclization ability of trisiloxanediols, and of oligosiloxanediols in general, in condensation reactions [2–5,26].

3.1.2. Protonated silanols **6**, **7**, **8**, **9**

The optimized geometries of the protonated silanols (**1**, **2**, **3** and **4**) are shown in Fig. 2. The most important geometrical change upon protonation of silanols is the elongation of the Si–O bond (by ca. 0.2 Å). The Si–O bond distance in $\text{H}_3\text{SiOH}_2^+$ (**6**) calculated at HF/6-31G* is 1.859 Å (1.867 Å at MP2/6-31G* [34]), by ca. 0.22 Å longer than in the neutral silanol **1**. The only experimental data for protonated silanols is X-ray structure of *t*-Bu₃SiOH₂⁺, in which the Si–O bond length is 1.779 Å [53]. In contrast to protonated siloxanes [20,51,54], the oxonium centre in protonated silanols is not planar, with the nonplanarity extent of 6°–20°. The Si–H bonds shorten upon protonation by ca. 0.02 Å and the HSiH angles widen by 8°–10°, to ca. 116° (Figs. 1 and 2).

These changes can be explained, according to the Natural Bond Orbital analysis, by the hyperconjugation effects [46,47]. The strongest delocalization interactions in silanol **1**, in terms of the second order perturbation theory [46,47], are those involving electron donation from the oxygen lone pairs to the $\sigma^*(\text{Si--X})$ antibonding orbitals. Thus, the second order energies of the

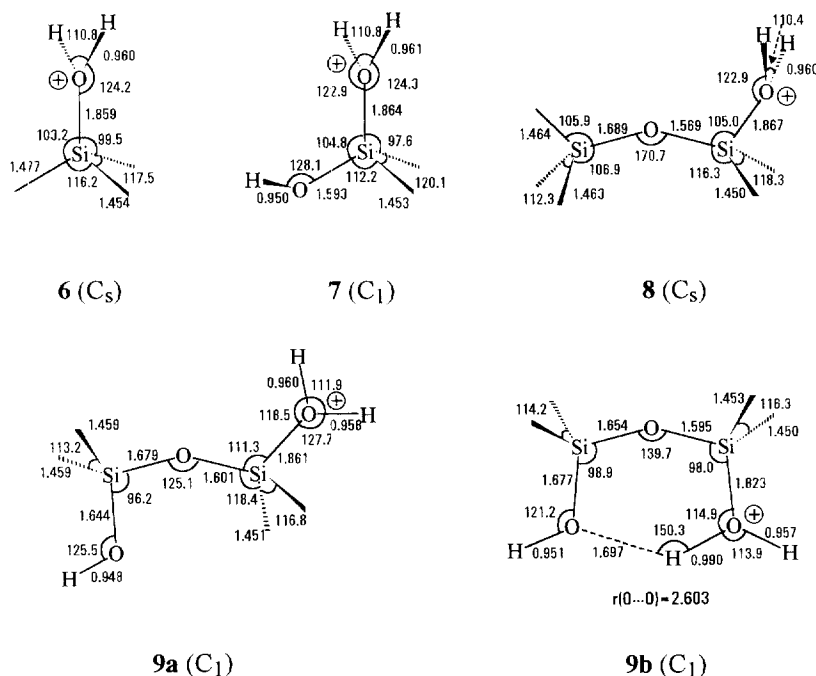
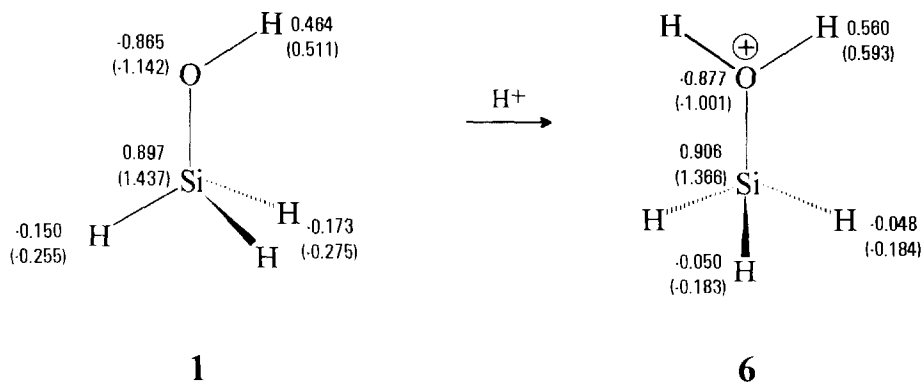


Fig. 2. HF/6-31G* optimized geometries of the protonated silanols and siloxanols.



Scheme 3.

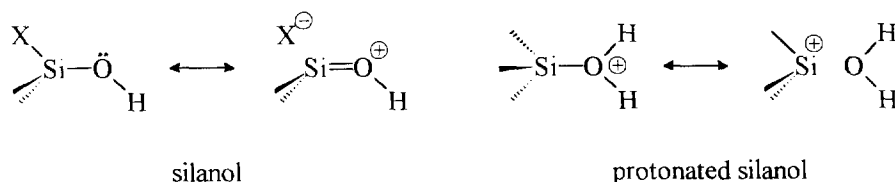
$n_{\pi}(\text{O}) \rightarrow \sigma^*(\text{Si-H})$ interactions between the lone pair occupying the p orbital perpendicular to the symmetry plane of the molecule, with the Si-H antibonds involving two out-of-plane hydrogens are 35.1 kJ/mol each. The energy of $n_{\sigma}(\text{O}) \rightarrow \sigma^*(\text{Si-H})$ interaction between the other oxygen lone pair (sp^2 -hybridized) with the Si-H antibond lying in the symmetry plane is 25.9 kJ/mol. These interactions are partially compensated by slightly weaker $\sigma(\text{Si-H}) \rightarrow \sigma^*(\text{Si-O})$ delocalizations. All delocalization interactions result in additional stabilization of the molecule. Their contribution to the total energy may be calculated by zeroing all orbital interactions and recalculating the energy of the altered Fock matrix [46,47]. Thus, for example, the overall delocalization energy, E_{del} , in **1** is 298.3 kJ/mol.

Direction of electron transfer reverses upon protonation of silanols. Delocalization pattern becomes strongly asymmetric, with domination of the interactions donating electrons to the oxonium centre. Thus, the strongest delocalizations in protonated silanol **6** are the $\sigma(\text{Si-H}) \rightarrow \sigma^*(\text{Si-O})$ interactions (the corresponding second-order energies are ca. 43.1 kJ/mol for each interaction). The other delocalizations are much weaker. The positive charge induces polarization of a siloxanol chain, reflected in changes of charge distribution over the molecule. The atomic charges according to Mulliken analysis (bare numbers) and to Natural Population Analysis (numbers in parentheses) for **1** and **6** are presented in Scheme 3. Both methods show that the charge is largely transferred from silicon ligands (hydrogens in this case) to the oxonium centre. The total delocalization energy decreases; it was calculated for **6** to be

226.4 kJ/mol, by 71 kJ/mol less than in the corresponding neutral silanol **1**.

The strongest delocalizations in siloxanols are geminal $n(\text{O}) \rightarrow \sigma^*(\text{Si-O}')$ interactions. For example, according to the NBO method, the second order energies of the $n_{\sigma}(\text{O}) \rightarrow \sigma^*(\text{Si-O}')$ and $n_{\sigma}(\text{O}') \rightarrow \sigma^*(\text{Si-O})$ interactions in disiloxanol **3** are 64 and 55.2 kJ/mol, respectively (where O = silanol oxygen, O' = siloxane oxygen). The $n_{\pi}(\text{O}) \rightarrow \sigma^*(\text{Si-H})$ and $\sigma(\text{Si-H}) \rightarrow \sigma^*(\text{Si-O})$ interactions are much weaker, ranging from 16.7 to 35.6 kJ/mol. In the protonated disiloxanol **8** the electron donation to the oxonium centre strongly dominates. Thus, the energies of the $n_{\sigma}(\text{O}') \rightarrow \sigma^*(\text{Si-O})$ and $\sigma(\text{Si-H}) \rightarrow \sigma^*(\text{Si-O})$ interactions increase upon protonation to 106.3 and 42.3 kJ/mol, respectively. The total delocalization energy decreases by 49 kJ/mol (from 807.9 to 758.6 kJ/mol) upon protonation of **3**. The corresponding change in delocalization energy upon protonation of silanediol **2** is only 31 kJ/mol. Thus, the loss of the delocalization energy upon protonation of siloxanol and silanediol is smaller than upon protonation of **1**, because of the strong electron donating properties of oxygen compared to hydrogen.

Due to extensive delocalization onto the Si-O antibond in the oxonium centre, the Si-O(H_2) bond becomes longer and weaker than in neutral silanols. The adjacent silyl group gains partial character of a silylium cation, which is reflected by shortening of the Si-H bonds and by widening of the HSiH angles. This effect, analogous to that observed upon protonation and silylation of siloxanes [54], may be illustrated by the resonance structures in Scheme 4.



Scheme 4.

3.1.3. Hydrogen-bonded complexes of silanols **10**, **11**, **12**, **13**

The HF/6-31G* optimized geometries of the complexes involving silanols **1**, **2**, **3** and **4** with water as a H-acceptor are shown in Fig. 3. Hydrogen-bonded complexes of silanols with water acting as a H-donor are not the subject of this study. According to previous calculations, they are weaker and the basicity of the silanol group in these complexes is expected to be highly reduced [55,56].

The optimized geometries of the complexes involving silanols having two oxygen atoms in the molecule (**2**, **3** and **4**) have cyclic structure with two hydrogen bonds, in which water is also a proton donor to the other oxygen atom in silanol molecule (Fig. 3). Present calculations confirm the results obtained previously for the complexes **11** and **12** by the MINI-1 method, although the bond lengths obtained using the 6-31G* basis set are slightly different [15].

Typical hydrogen bond lengths H...O found in crystalline silanols are in the range of 1.9–2.2 Å, and the O...O distances are between 2.6 and 2.9 Å [9]. The bond distances calculated in this study fit very well in this range. The calculated OH...O angles in **10** and **13** are 160°–163° (compared to ca. 160–170° in crystals

[9]). The OH...O angle in **5b** is by only few degrees smaller (154.4°). The corresponding angles in **4b**, **11** and **12** are smaller because of constraints imposed by the geometry of small rings. The changes in silanol geometries upon formation of adducts follow the general rules defined earlier [57]. Thus, the (Si)O–H... bond becomes longer than in free silanols by ca. 0.006–0.01 Å and the Si–OH... bond shortens by 0.008–0.013 Å. More distant bonds in siloxane chain show an alternate elongation–shortening pattern (structures **12** and **13** in Fig. 3), in accord with Gutmann rules [57]. The SiOH angle decreases by ca. 3° upon H-bond formation.

These changes reflect alteration of the electron density in silanols as a result of hydrogen bond formation. In particular, stronger delocalization of electrons from the silanol oxygen in the H-bonded group to the Si–X antibonding orbitals (X = H or siloxane oxygen) causes shortening and strengthening of the Si–O(H) bond. This is supported by population analysis, which shows that the net atomic charge on silanol oxygen increases (i.e., becomes more negative). Thus, the corresponding Mulliken charge increases on hydration of **1** by 0.042 e (NPA: 0.022 e). The second order energies of the $n_p(\text{O}) \rightarrow \sigma^*(\text{Si}-\text{H})$ interactions increase from 35.1

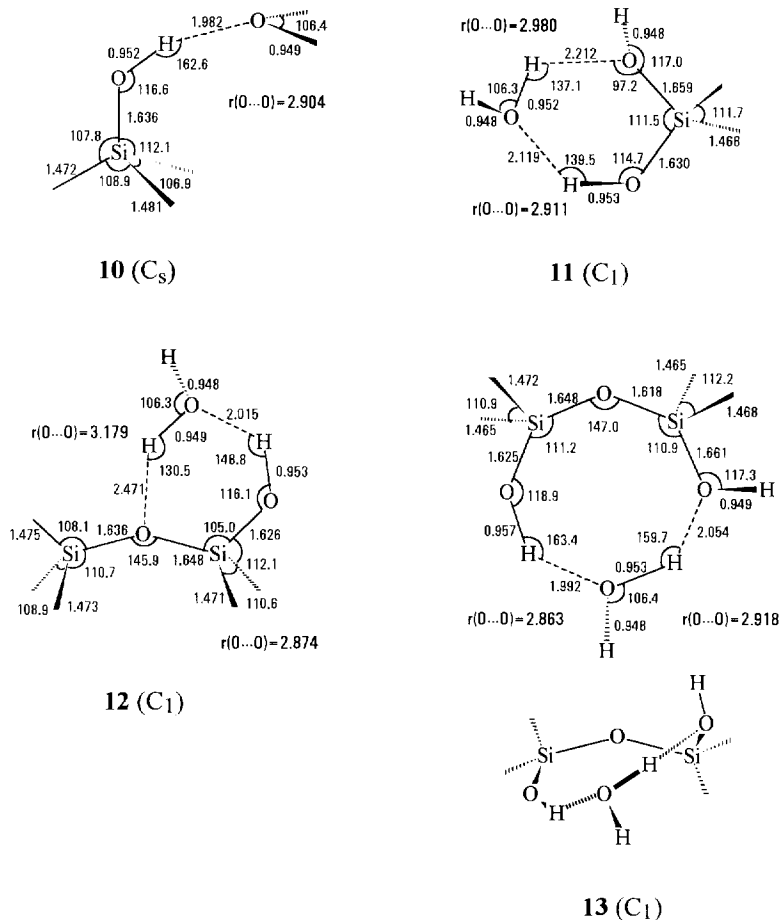
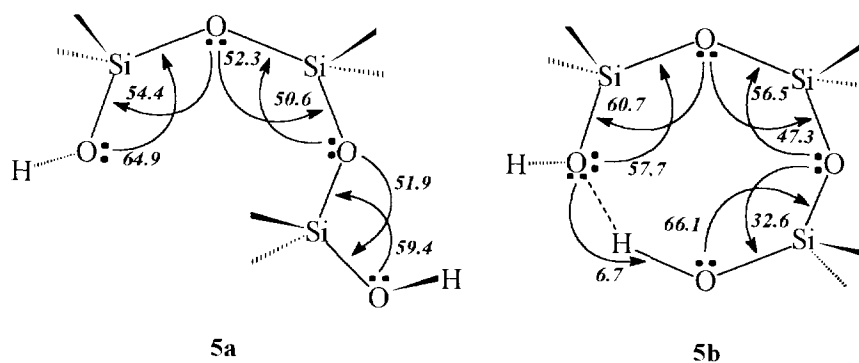


Fig. 3. HF/6-31G* optimized geometries of the hydrogen-bonded complexes of silanols with water.



Scheme 5.

kJ/mol in **1** to 38.9 kJ/mol in **10**. Polarization of the oligosiloxane chain induced by the hydrogen bond can be seen comparing the delocalization schemes for **5a** and **5b** (Scheme 5). The numbers at arrows in Scheme 5 represent the second order perturbation energies (kJ/mol) of the geminal $n_{\pi}(\text{O}) \rightarrow \sigma^*(\text{Si}-\text{O}')$ delocalizations. The second order energy of the $n_{\pi}(\text{O}) \rightarrow \sigma^*(\text{H}-\text{O}')$ interaction (28.0 kJ/mol) corresponding to the H-bond in **5b** is also shown for comparison. Electron transfer from the silanol group involved as a H-

donor in the hydrogen bond in **5b** is more extensive than the transfer in the opposite direction.

3.1.4. Protonated complexes of silanols **14**, **15**, **16**, **17**

The HF/6-31G* geometries of the protonated complexes of silanols are shown in Fig. 4. Hydrogen bond in the protonated silanol complexes is, as expected, stronger than that in uncharged complexes. The $\text{O} \cdots \text{O}$ distance shortens by ca. 0.35 Å, while the $\text{SiO}-\text{H} \cdots$ bond elongates by 0.04–0.05 Å. The $\text{OH} \cdots \text{O}$ angle

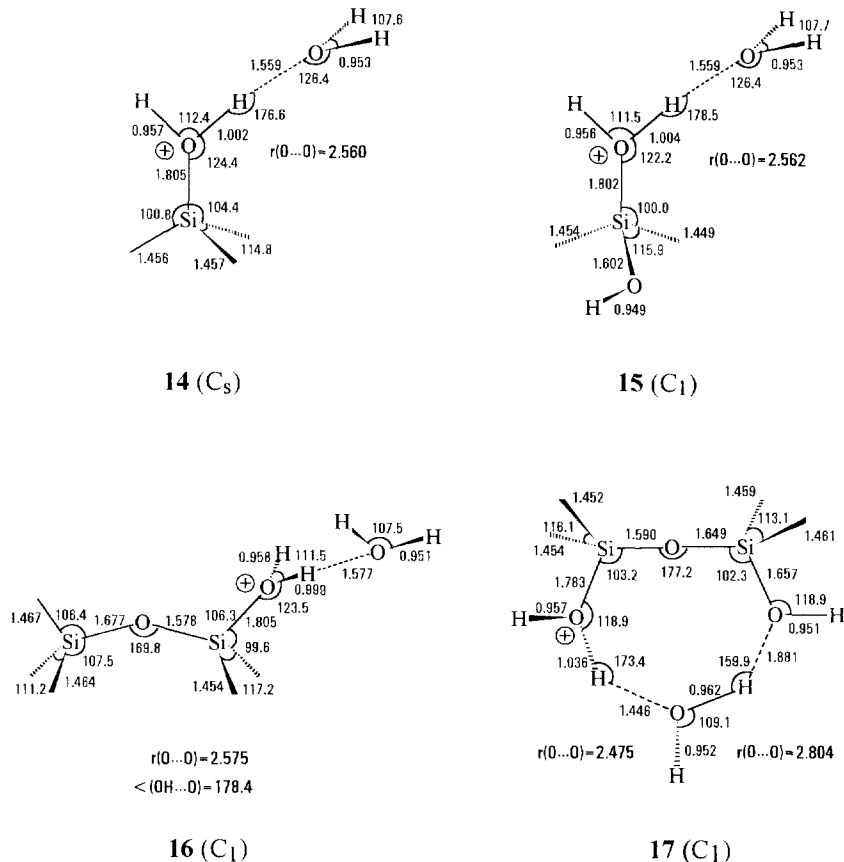


Fig. 4. HF/6-31G* optimized geometries of the protonated silanol–water complexes.

Table 2

The negative of the absolute energies (hartrees) and dipole moments (debyes) of the model silanols and their complexes

Species	–E(HF)	–E(MP2)	–E(MP3)	–E(MP4)	Dipole moment
H ₃ SiOH (1)	366.13040	366.38945	366.40480	366.41586	1.527
H ₂ Si(OH) ₂ (2)	441.04791	441.48648	441.49891	441.51564	1.041
H ₃ SiOSiH ₂ OH (3)	731.17544	731.68649	731.70874	731.73187	1.224
H(OSiH ₂) ₂ OH (4a)	806.09164	806.78206	806.80145	806.83025	2.546
H(OSiH ₂) ₂ OH (4b)	806.09220	806.78283	806.80252	806.83106	3.227
H(OSiH ₂) ₃ OH (5a)	1171.13667	1172.07971	1172.10564	1172.14699	0.507
H(OSiH ₂) ₃ OH (5b)	1171.14266	1172.08838	1172.11433	1172.15568	2.833
H ₃ SiOH ₂ ⁺ (6)	366.43164	366.68721	366.70592	366.71579	
HOSiH ₂ OH ₂ ⁺ (7)	441.35014	441.78590	441.80149	441.81712	
H ₃ SiOSiH ₂ OH ₂ ⁺ (8)	731.48257	731.99066	732.01593	732.03822	
H(OSiH ₂) ₂ OH ₂ ⁺ (9a)	806.40226	807.09054	807.11315	807.14102	
H(OSiH ₂) ₂ OH ₂ ⁺ (9b)	806.41425	807.10402	807.12638	807.15394	
H ₃ SiOH · OH ₂ (10)	442.15224	442.59976	442.62029	442.63627	4.271
H ₂ Si(OH) ₂ · OH ₂ (11)	517.07242	517.70136	517.71880	517.74067	2.244
H ₃ SiOSiH ₂ OH · OH ₂ (12)	807.19714	807.89846	807.92577	807.95411	2.954
H(OSiH ₂) ₂ OH · OH ₂ (13)	882.12129	883.00409	883.02809	883.06235	3.371
H ₃ SiOH ₂ ⁺ · OH ₂ (14)	442.48370	442.93067	442.95354	442.96852	
HOSiH ₂ OH ₂ ⁺ · OH ₂ (15)	517.40152	518.02829	518.04779	518.06880	
H ₃ SiOSiH ₂ OH ₂ ⁺ · OH ₂ (16)	807.53235	808.23117	808.26086	808.28803	
H(OSiH ₂) ₂ OH ₂ ⁺ · OH ₂ (17)	882.45790	883.33967	883.36581	883.39863	

opens up on protonation to 177–179°. The cyclic structure of the complexes of silanediol (11) and siloxanol (12) breaks upon protonation resulting in the ‘open’ structures 15 and 16, respectively. This indicates that the basicity of the oxygen geminal to the oxonium centre is considerably reduced, since its lone pairs are strongly delocalized towards the protonated silanol group. The Mulliken net atomic charge on the oxygen geminal to the oxonium centre becomes less negative on protonation of 11 and 12 by 0.077 and 0.074, respectively. Consequently, the geminal oxygen in protonated adducts 15 and 16 cannot efficiently interact with proton originating from water.

The cyclic geometry of the complex 13 is preserved upon protonation, since its geometry permits effective orbital interaction responsible for the formation of the

additional H-bond. The structure of the resulting ionic complex 17 suggests that the proton transfer from one chain end to the other through hydrogen-bridge should proceed with very low, if any, energy barrier. Analogous mechanism facilitating proton transfer was postulated to play an important role in acidolysis of the siloxane bond [4].

3.2. Energies of hydrogen-bonded complex formation

The bonding energies of silanol–water complexes were calculated as the negative of the enthalpy of reaction represented by Eq. (2). The electronic energies for all calculated species and the dipole moments for neutral species are listed in Table 2. Dipole moments of 1, 2 and 10 are in reasonable accord with previous

Table 3

Standard thermodynamics quantities (kJ/mol) calculated for the hydrogen bond formation by model silanols (reactions 2 and 4)^a

Complex	ΔH^{ob}	ΔS° J/mol K	ΔG^{oc}	K_{eq}
H ₃ SiOH · OH ₂	–30.1 (–19.7)	–87.1	7.7	$4.5 \cdot 10^{-2}$
H ₂ Si(OH) ₂ · OH ₂	–41.0 (–22.6)	–117.9	12.6	$6.3 \cdot 10^{-3}$
H ₃ SiOSiH ₂ OH · OH ₂	–32.2 (–18.8)	–104.7	12.4	$6.7 \cdot 10^{-3}$
H(OSiH ₂) ₂ OH (4b) ^d	–2.1	–15.1	2.4	0.38
H(OSiH ₂) ₂ OH · OH ₂ (13) ^e	–60.2 (–39.3)	–147.2	4.6	0.16
H(OSiH ₂) ₃ OH (5b) ^f	–21.8	–39.2	–9.9	55

^aBased on the MP4/6-31G*//HF/6-31G* energies; the intramolecular frequencies scaled by 0.893.

^bThe values in parentheses are the BSSE-corrected values of the enthalpies.

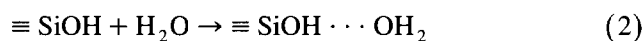
^cThe BSSE-corrected ΔG° values.

^dReaction: 4a → 4b.

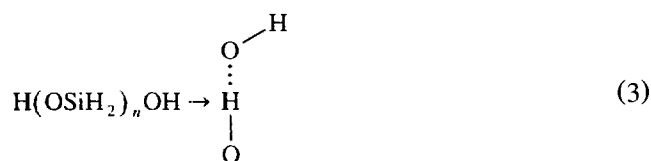
^eReaction: 4a + H₂O → 13.

^fReaction 5a → 5b.

reports [35,56]. The higher values of dipole moments were found for hydrogen adducts.



where $\equiv \text{SiOH} = \mathbf{1}$, $\mathbf{2}$, $\mathbf{3}$ and $\mathbf{4a}$. The enthalpies of the intramolecular hydrogen bond formation in siloxanediols $\mathbf{4b}$ and $\mathbf{5b}$ were calculated in an analogous way (Eq. (3)):



where $n = 2$ or 3 .

For both types of complexes, Gibbs free energies and the corresponding equilibrium constants were estimated, assuming the ideal gas approximation [37]. The calculated thermodynamic quantities are presented in Table 3.

Hydration of the silanol $\mathbf{1}$ was studied at the 6-31G(*), DZP and TZP levels of theory [55,56]. The complex, in which silanol is involved as a proton donor ($\text{H}_3\text{SiOH}-\text{OH}_2$), was calculated at the 6-31G(*) level to be 18 kJ/mol stronger than that with silanol being a H-acceptor (without BSSE correction) [55]. More recent work reports the bonding energies of 25.1 kJ/mol for $\text{H}_3\text{SiOH}-\text{OH}_2$ ($\mathbf{10}$) and 16.7 kJ/mol for $\text{H}_3\text{SiO}(\text{H})-\text{HOH}$ at the DZ(p,d) level (including correction for BSSE) [56]. Energy of complexation tends to decrease with the increasing basis set completeness, while electron correlation methods lead to the increase of the bonding energy [56]. The BSSE corrected MP4/6-31G*//HF/6-31G* enthalpy of complexation is 19.7 kJ/mol for $\mathbf{10}$ (Table 3).

Interaction of silanediol $\mathbf{2}$ with water was studied at the DZP level [35]. The doubly bonded cyclic complex $\mathbf{11}$, in which silanediol appeared in gauche–gauche conformation, was found to be the most stable among various structures examined [35]. Calculations at HF/6-31G* gave slightly different bonding parameters but confirmed the gauche–gauche geometry of the most stable adduct. The bonding energy calculated at the DZP level is 24.7 kJ/mol [35]. At MP4/6-31G*//HF/6-31G* the corresponding energy is 22.6 kJ/mol.

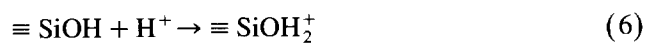
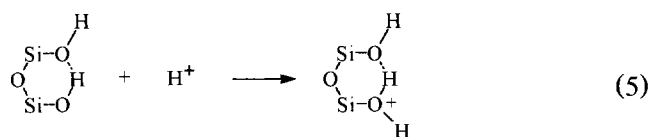
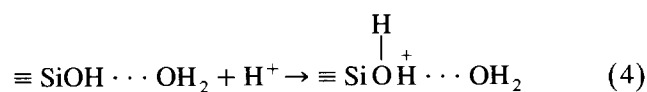
Silanol–water adducts ($\mathbf{10}$ – $\mathbf{13}$) and the intramolecularly bonded trisiloxanediol ($\mathbf{5b}$) show similar enthalpies of formation. The complex $\mathbf{11}$ involving two hydrogen bonds is by 2.9 kJ/mol stronger than $\mathbf{10}$, which has only one H-bond. Although geometry of $\mathbf{12}$ suggests the existence of a second H-bond to siloxane oxygen, the adduct $\mathbf{12}$ is no stronger than $\mathbf{10}$. These data indicate that the contribution of the additional H-bonds in $\mathbf{11}$ and $\mathbf{12}$ to the total binding energy is very small

(or even negligible) and therefore these bonds must be very weak. The main reason for that is the unfavourable geometry of small rings. Moreover, since siloxanes in solution are less basic than silanols [10], the hydrogen bond to the siloxane oxygen is expected to be much weaker than that to silanol oxygen [15]. In contrast, according to calculations, the basicities of silanols and siloxanes in the gas phase are similar (see Section 3.3) [54].

The complex $\mathbf{13}$ is exceptionally strong, since its geometry allows efficient overlap of the interacting orbitals, although probably not optimal, what can be deduced from the fact that no distinct cooperativity effect has been detected. The enthalpy of formation of $\mathbf{13}$ is exactly twice that of $\text{H}_3\text{SiOH} \cdot \text{OH}_2$. The high equilibrium constant of formation of $\mathbf{5b}$ suggests that this species may exist in solution in high concentration. The intramolecular H-bond in disiloxanediol $\mathbf{4b}$ is much weaker, although the calculated equilibrium constant of 0.38 suggests that this complex may exist in solution at considerable concentration.

3.3. Basicity of silanols and their hydrogen-bonded complexes.

The absolute proton affinities (PA) and the basicities of silanols and their hydrogen-bonded complexes were calculated as the negative of the enthalpy and of the free energy, respectively, for reactions represented by Eqs. (4)–(6). The absolute and relative (with respect to $\mathbf{1}$) proton affinities and basicities of the studied species are listed in Table 4.



The only quantitative experimental data concerning the gas phase proton affinities of silanols is the PA for Me_3SiOH , which was deduced from the energy of reaction 7 to be 768.6 kJ/mol (183.7 kcal/mol) [19].



The proton affinity of the parent silanol $\mathbf{1}$ was calculated at various levels of theory. The most accurate values are those obtained using G1 and G2 theories and MP2(full)/6-31G* optimized geometry (G1: $\text{PA}_0 = 741.4$ kJ/mol (177.2 kcal/mol); G2: $\text{PA}_0 = 742.7$ kJ/mol (177.5 kcal/mol) [34], $\text{PA}_{298} = 746.4$ kJ/mol (178.4 kcal/mol) [58]). At the MP4/6-31G*//HF/6-

Table 4

Calculated absolute and relative (H_3SiOH) proton affinities and basicities (kJ/mol) of model silanols and their complexes in standard state (1 atm, 298 K)

Species	PA	Relative PA	ΔG°	Relative basicity
H_3SiOH (1)	761.5	0	728.9	0
$\text{H}_3\text{SiOH}\cdot\text{OH}_2$ (10)	848.1	86.6	815.5	86.6
$(\text{CH}_3)_3\text{SiOH}^a$	768.6	7.1		
$\text{H}_2\text{Si}(\text{OH})_2$ (2)	766.9	5.4	743.5	14.6
$\text{H}_2\text{Si}(\text{OH})_2\cdot\text{OH}_2$ (11)	839.3	77.8	814.2	85.3
$\text{H}_3\text{SiOSiH}_2\text{OH}$ (3)	778.6	17.1	751.9	23.0
$\text{H}_3\text{SiOSiH}_2\text{OH}\cdot\text{OH}_2$ (12)	874.5	113.0	843.9	115.0
$\text{H}(\text{OSiH}_2)_2\text{OH}$ (4a)	791.2	29.7	745.2	16.3
$\text{H}(\text{OSiH}_2)_2\text{OH}$ (4b)	822.6	61.1	787.0	58.1
$\text{H}(\text{OSiH}_2)_2\text{OH}\cdot\text{OH}_2$ (13)	861.5	100.0	836.4	107.5
$\text{H}_3\text{SiOSiH}_3^b$	775.3	13.8	740.1	11.2

^a See Ref. [19].

^b See Ref. [54].

31G* level, the PA_{298} for **1** is 761.5 kJ/mol (182.0 kcal/mol) (Table 4).

The basicity order for uncomplexed silanols is **4a** > **3** > **2** > **1**, although the differences are not large and can be ascribed to the greater polarizability of larger molecules. The relatively strong hyperconjugation effect associated with the presence of the geminal oxygen substituent (OH in **2**, OSi in **3** and **4**) may additionally stabilize protonated siloxanols relative to the parent silanol **1**. The calculated basicities of model silanols and siloxanes are similar [54]. For example, at the MP4/6-31G*//HF/6-31G* level disiloxane is by 9.2 kJ/mol more basic than **1** (Table 4).

The silanol groups involved in the hydrogen bond as proton donors are much stronger bases than the related free species (Table 4). Thus, the complexes **12** and **13** are by 90 kJ/mol more basic than the corresponding disiloxanols **3** and **4a**. The basicity of the cyclic complex **4b** is by 42 kJ/mol higher than that of the open chain conformer, **4a**. The enhanced basicity of hydrogen-bonded complexes of silanols is associated with the increase of electron density on oxygen in the silanol group involved in the H-bond as a proton donor. Such complexes are expected to be more reactive than the free silanols in reactions of the nucleophilic substitution.

Thermodynamic quantities of the above reactions in solution differ from the values calculated for these reactions in the vapour phase, because of the solvation effects [59]. However, in 'inert' solvents, where no strong, specific interactions between solvent and a solute are involved, the solvation effect is usually small [59]. When the species to be compared have similar structure, like, for example, the series of siloxanols or siloxanediols, one may expect that thermodynamic parameters of their solvation are similar and the order of the calculated basicities is preserved on going from vapour to solution.

4. Conclusions

The hydrogen-bonded complexes discussed here are the simplest representatives of a variety of possible structures. Calculated thermodynamic parameters of hydrogen bond formation indicate that these complexes may exist in solution in significant concentration.

The silanol groups involved in the hydrogen bond as H-donors (to water or another SiOH group) show much higher basicity than the corresponding free species. Hydrogen bond in the protonated complexes of silanols is shorter and stronger than in the neutral complexes. The main reason for the enhanced basicity of such complexes is the increase of electron density at the silanol oxygen.

The enhanced basicity of the hydrogen-bonded silanol groups is responsible for a great tendency to formation of polymeric aggregates in solution, particularly at high SiOH concentrations.

Assuming that the nucleophilicity is roughly proportional to the basicity of a given species, the hydrogen-bonded silanol groups are expected to be more reactive towards silicon in nucleophilic substitution reactions, in particular, in condensation.

Oligosiloxanediols form intramolecular end-to-end complexes, which are responsible for their higher reactivity in condensation reactions in 'inert' solvents, compared to monofunctional siloxanols [26].

Acknowledgements

This work was a part of the KBN research project No. 3 T09A 118 08.

References

- [1] M.G. Voronkov, V.P. Mileshekevich, Yu.A. Yuzhelevsky, *The Siloxane Bond*, Plenum Press, New York, 1978.
- [2] W. Noll, *Chemistry and Technology of Silicones*, Academic Press, New York, 1968.
- [3] J.J. Lebrun, H. Porte, in: *Comprehensive Polymer Science* vol. 5, Pergamon Press, Oxford, 1989, Chap. 34, p. 593.
- [4] J. Chojnowski, in: *Siloxane Polymers* Ellis Horwood/PTR, Prentice-Hall, Englewood Cliffs, NJ, 1993, Chap. 1, p. 1.
- [5] J. Chojnowski, in: *Silicon-Containing Polymers*, The Royal Society of Chemistry, Cambridge, UK, 1995, p. 72.
- [6] J.S. Falcone Jr., S.D. Boyce, in: *Encyclopedia of Polymer Science and Engineering*, vol. 15, Wiley-Interscience, New York, 1989, pp. 178–204.
- [7] R.K. Iler, *The Chemistry of Silica*, Wiley, New York, 1979, pp. 622–729.
- [8] C.R.A. Catlow (Ed.), *Modelling of Structure and Reactivity in Zeolites*, Academic Press, London, 1992.
- [9] P.D. Lickiss, *Adv. Inorganic Chem.* 42 (1996) 147, For a review.
- [10] R. West, R.H. Baney, *J. Am. Chem. Soc.* 81 (1959) 6145.
- [11] G.J. Harris, *J. Chem. Soc.* (1963) 5978.
- [12] G.J. Harris, *J. Chem. Soc. B*, (1970) 488, 493.

- [13] J. Chojnowski, S. Chrzczonowicz, *Bull. Acad. Pol. Sci. Ser. Sci. Chem.* 13 (1965) 143.
- [14] L. Wilczek, J. Chojnowski, *Makromol. Chem.* 184 (1983) 77.
- [15] P. Ugliengo, E. Garrone, V.R. Saunders, J. Sauer, *Chem. Rev.* 94 (1994) 2095.
- [16] R. Damrauer, R. Simon, M. Krempp, *J. Am. Chem. Soc.* 113 (1991) 4431.
- [17] M.S. Gordon, R. Damrauer, M. Krempp, *J. Phys. Chem.* 97 (1993) 7820.
- [18] C.G. Pitt, M.M. Bursley, D.A. Chatfield, *J. Chem. Soc., Perkin Trans. 2* (1976) 434.
- [19] J.A. Stone, A.C.M. Wojtyniak, W. Wytenburg, *Can. J. Chem.* 64 (1986) 575.
- [20] M.L. Hendewerk, R. Frey, D.A. Dixon, *J. Phys. Chem.* 87 (1983) 2026.
- [21] C.W. Chronister, R.S. Drago, *J. Am. Chem. Soc.* 115 (1993) 4793.
- [22] S. Rubinsztajn, M. Cypryk, J. Chojnowski, *J. Organometal. Chem.* 367 (1989) 27.
- [23] M. Cypryk, S. Rubinsztajn, J. Chojnowski, *J. Organometal. Chem.* 377 (1989) 197.
- [24] Z. Lasocki, S. Chrzczonowicz, *J. Polym. Sci.* 59 (1962) 259.
- [25] Z. Lasocki, Z. Michalska, *Bull. Acad. Pol. Sci. Ser. Sci. Chim.* 18 (1965) 261, 597.
- [26] J. Chojnowski, S. Rubinsztajn, L. Wilczek, *Macromolecules* 20 (1987) 2345.
- [27] W. Sarich, A. Surkus, D. Lange, E. Popowski, H. Kelling, *Z. Anorg. Allg. Chem.* 581 (1990) 199.
- [28] M. Cypryk, P. Sigwalt, *Macromolecules* 27 (1994) 6245.
- [29] R. Bischoff, P. Sigwalt, *Polymer Intern.* 40 (1996) 99.
- [30] P. Ugliengo, E. Garrone, *J. Mol. Catal.* 54 (1989) 439.
- [31] P. Ugliengo, V.R. Saunders, E. Garrone, *Chem. Phys. Lett.* 169 (1990) 501.
- [32] P. Ugliengo, A. Bleiber, E. Garrone, J. Sauer, A.M. Ferrari, *Chem. Phys. Lett.* 191 (1992) 537.
- [33] J. Sauer, R. Ahlrichs, *J. Chem. Phys.* 93 (1990) 2575.
- [34] L.A. Curtiss, H. Brand, J.B. Nicholas, L.E. Iton, *Chem. Phys. Lett.* 184 (1992) 215.
- [35] E.M. Ferrari, P. Ugliengo, E. Garrone, *J. Chem. Phys.* 97 (1993) 2671.
- [36] J. Sauer, J.-R. Hill, *Chem. Phys. Lett.* 218 (1994) 333.
- [37] W.J. Hehre, L. Radom, P.v.R. Schleyer, J.A. Pople, *Ab Initio Molecular Orbital Theory*, Wiley, New York, 1986.
- [38] M.J. Frisch, G.W. Trucks, H.B. Schlegel, P.M.W. Gill, B.G. Johnson, M.A. Robb, J.R. Cheeseman, T. Keith, G.A. Petersson, J.A. Montgomery, K. Raghavachari, M.A. Al-Laham, V.G. Zakrzewski, J.V. Ortiz, J.B. Foresman, J. Cioslowski, B.B. Stefanov, A. Nanayakkara, M. Challacombe, C.Y. Peng, P.Y. Ayala, W. Chen, M.W. Wong, J.L. Andres, E.S. Replogle, R. Gomperts, R.L. Martin, D.J. Fox, J.S. Binkley, D.J. Defrees, J. Baker, J.P. Stewart, M. Head-Gordon, C. Gonzalez, J.A. Pople, *Gaussian 94, Revision C.2 Gaussian*, Pittsburgh, PA, 1995.
- [39] C. Møller, M.S. Plesset, *Phys. Rev.* 46 (1934) 618.
- [40] J.A. Pople, R. Krishnan, H.B. Schlegel, J.S. Binkley, *Int. J. Quantum Chem. Symp.* 14 (1978) 545.
- [41] R. Krishnan, M.J. Frisch, J.A. Pople, *J. Chem. Phys.* 72 (1980) 4244.
- [42] M.J. Frisch, R. Krishnan, J.A. Pople, *Chem. Phys. Lett.* 75 (1980) 66.
- [43] S.F. Boys, F. Bernardi, *Mol. Phys.* 19 (1970) 553.
- [44] R.S. Mulliken, *J. Chem. Phys.* 23 (1955) 1833.
- [45] R.S. Mulliken, *J. Chem. Phys.* 23 (1955) 1840.
- [46] A.E. Reed, L.A. Curtiss, F. Weinhold, *Chem. Rev.* 88 (1988) 899.
- [47] E.D. Glendening, A.E. Reed, J.E. Carpenter, F. Weinhold, *NBO Version 3.1*.
- [48] Y. Apeloig, A. Stanger, *J. Organometal. Chem.* 346 (1988) 305.
- [49] A.E. Reed, C. Schade, P.v.R. Schleyer, P.V. Kamath, J. Chandrasekhar, *J. Chem. Soc., Chem. Commun.*, (1988) 67.
- [50] P.D. Lickiss, A.D. Redhouse, R.J. Thompson, W.A. Stańczyk, K. Rózga, *J. Organometal. Chem.* 453 (1993) 13.
- [51] S. Shambayati, J.F. Blake, S.G. Wierschke, W.L. Jorgensen, S.L. Schreiber, *J. Am. Chem. Soc.* 112 (1990) 697.
- [52] N.H. Buttrus, C. Eaborn, P.B. Hitchcock, P.D. Lickiss, A.D. Taylor, *J. Organometal. Chem.* 309 (1986) 25.
- [53] Z. Xie, R. Bau, C.A. Reed, *J. Chem. Soc. Chem Commun.*, (1994) 2519.
- [54] Y. Apeloig, M. Cypryk, submitted.
- [55] B.C. Chakoumakos, G.V. Gibbs, *J. Phys. Chem.* 90 (1986) 906.
- [56] P. Ugliengo, V.R. Saunders, E. Garrone, *J. Phys. Chem.* 94 (1990) 2260.
- [57] V. Gutmann, *The Donor–Acceptor Approach to Molecular Interactions*, Plenum Press, New York, 1978.
- [58] D.J. Lucas, L.A. Curtiss, J.A. Pople, *J. Chem. Phys.* 99 (6697) (1993).
- [59] S.N. Vinogradov, R.H. Linnell, *Hydrogen Bonding*, Van Nostrand Reinhold, New York, 1970.