

Structure modeling of
Aluminosilsesquioxanes

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Aims

The aims of this research project were:

- a) Optimization of the (known) aluminosilsesquioxane structure of $[\text{HNEt}_3]^+[\{\text{Cy}_7\text{Si}_7\text{O}_9(\text{OSiMe}_3)_2\text{Al}\}]^-$ using empirical (UFF, Dreiding) and semiempirical (MNDO) methods and comparison and evaluation of those methods
- b) Derivation of the as-small-as-possible but as-big-as-necessary model for modelling of the reaction of this silsesquioxane with an olefin, based on structure and HOMO properties
- c) Prediction of the hitherto unknown structure of another aluminosilsesquioxane with the sum formula $[\text{HNEt}_3]^+[\{\text{Cy}_7\text{Si}_7\text{O}_9(\text{H})\text{O}_2\}_2\text{Al}]^-$
- d) Reaction modeling of both silsesquioxanes with an olefin

MNDO [Dewar and Thiel 1977]

The variational principle says that the energy for the exact wave function is lower than the energy for the ground state of any other antisymmetric normalized wave function. So the problem of approximating the wave function is a problem of finding coefficients $c_{i\mu}$ in $\phi_i = \sum_{m} c_{im} X_m$ so that the energy is at a minimum. (ϕ_i are the molecular orbitals and X_i the basis functions).

This leads to a description derived independently and at the same time by Roothan [Roothan 1951] and Hall [Hall 1951], written in matrix form: **FC = SCE**. This is a nonlinear equation as the coefficients $c_{\mu i}$ appear as well in the Fock matrix as in the molecular orbitals and has therefore to be solved iteratively, named the SCF or self-consistent field method. F is the Fock matrix and stands for the average effects of the field of all electrons on each orbitals, S is the overlap matrix and E the energy matrix, where each element ϵ_i is the one-electron energy of a molecular orbital X_i .

In Hartree-Fock (HF) ab-initio calculations all elements of the Fock matrix are calculated using

$$F_{\mu\nu} = H_{\text{core}, \mu\nu} + \sum_{I=1}^K \sum_{s=1}^K P_{Is} [(\mu\nu|\lambda\sigma) - \frac{1}{2}(\mu\lambda|\nu\sigma)],$$
 irrespective of location of the basis

functions ϕ_μ , ϕ_ν , ϕ_λ and ϕ_σ . P is the density matrix and represents the energy of a single electron in the field of bare nuclei and $(\mu\nu|\lambda\sigma)$ are the two-electron repulsion integrals, each electron sees all other electrons as an average distribution.

Most of the computation time in an HF-calculation is required for calculating integrals, so it is an obvious approach to reduce computational effort by neglecting or approximating parts of the integrals. Therefore semi-empirical methods consider

(explicitly) only the valence electrons of the system, the core electrons are subsumed into the nuclear core. In addition, the orthogonality of the employed basis functions simplifies some of the integrals. Common to all semi-empirical methods in that the overlap matrix \mathbf{S} is set equal to the identity matrix \mathbf{I} . The effect is, that the elements that correspond to an overlap between two atomic orbitals on different atoms are set to zero and the Roothaan-Hall equation $\mathbf{FC}=\mathbf{SCE}$ becomes $\mathbf{FC}=\mathbf{CE}$, the standard matrix form.

What is specific to MNDO? MNDO stands for “Modified Neglect of Diatomic Overlap” and is based on NDDO, the “Neglect of Diatomic Differential Overlap” [Pople et. al. 1965]. The basis of NDDO in turn is a method called “CNDO”. CNDO [Pople et. al. 1965], the “Complete Neglect of Differential Overlap”, was the first method to implement the zero-differential overlap approximation, and *neglected all differential overlap*, regardless whether the orbitals are centered on the same or on different atoms.

NDDO, as the next level of approximation, only neglects differential overlap between atomic orbitals on *different* atoms. Thus all two-electron, two-center integrals of the form $(\mu\nu|\lambda\sigma)$ where μ and ν are *on the same atom* and λ and σ are *also on the same atom* are retained.

MNDO differs from NDDO in respect of the definition of the Fock matrix elements. I will describe these differences now more detailed.

The major improvement are the new terms $V_{\mu\mu B}$ and $V_{\mu\nu B}$ in $H_{\text{core}, \mu\mu} = U_{\mu\mu} - \sum_{A \neq B} V_{\mu\mu B}$

and $H_{\text{core}, \mu\nu} = U_{\mu\mu} - \sum_{A \neq B} V_{\mu\nu B}$, which represent two-centre, one-electron attractions

between an electronic distribution $\phi_\mu\phi_\mu$ or $\phi_\mu\phi_\nu$ respectively on atom A and the core of

atom B. These are defined as $V_{\mu\mu B} = -Z_B(\mu_A\mu_A|S_B S_B)$ and $V_{\mu\nu B} = -Z_B(\mu_A\nu_A|S_B S_B)$. Another difference are the core-core repulsion terms with OH and NH being treated separately and a new form for the two-centre, one electron resonance integrals which depend on the overlap $S_{\mu\nu}$ and parameters β_μ and β_ν in $H_{\text{core}, \mu\nu} = \frac{1}{2} S_{\mu\nu} (\mathbf{b}_\mu + \mathbf{b}_\nu)$.

An advantage of MNDO over an earlier semiempirical method, MINDO/3 [Bingham et al. 1975], is the use solely of monoatomic parameters. Almost any element is defined in MNDO. In the original method only an s, p basis set was employed, but versions that are more recent explicitly include d orbitals for heavier elements, although they are of dubious quality.

A problem in MNDO is the overestimation of repulsion between atoms separated by a distance equal to the sum of their Van-der-Waals radii, so hydrogen bonds are not sufficiently modelled. Another problem in MNDO are conjugated systems and sterically crowded molecules, where MNDO energies are too positive and four-membered rings, where the energy is too negative.

Force Fields

When applied to large molecules (i.e. with more than a few hundred atoms) even semiempirical methods are too time consuming to be feasible in a sensible time range.

Thus, although in principle accessible by those methods, a classical model is introduced, where the forces between atoms are only based on simple functions describing a “ball-and-spring” behaviour, e.g. Hooke’s law. This approach reduces the computational costs by about two orders of magnitude (a factor of 100), so even biological systems are accessible, although they consist of thousands of atoms. This area can still be considered as the domain of the non-quantum mechanical approach of force fields.

A “reference” value for bond lengths, angles and torsion angles is defined (derived from experiments) and an energy function of the general form

$$E_{pot}(r_n) = \sum_{bonds} \frac{1}{2} k_i (l_i - l_{i,0})^2 + \sum_{angles} \frac{1}{2} k_i (\Theta_i - \Theta_{i,0})^2 + \sum_{torsion} \frac{1}{2} V_n (1 + \cos(n\mathbf{w} - \mathbf{g})) + \sum_{nonbonded} \mathbf{e}_{ij}$$

can be conceived, where we find (in this order) terms how the energy varies with the bond length, bond angles, torsion angles and interaction between non-bonded atoms. The latter in simple force fields often consists of a Coulomb potential for electrostatic and a Lennard-Jones (6,12) potential for van-der-Waals interactions. In more sophisticated force fields also cross terms, as angle-angle terms etc. are included.

Some force fields have been derived to lead satisfactory results on special groups of molecules, e.g. MM2 (originally) for hydrocarbons [Allinger 1977], SHAPES [Allured et al. 1991] especially for transition metal complexes or AMBER [Weiner et al. 1984] for proteins and nucleic acids.

Here we use the UFF “Universal Force Field” [Rappe et al. 1992] and the Dreiding Force Field [Mayo et al. 1990].

The UFF force field is designed to model the entire periodic table and features a novel treatment of angle bending. The commonly used force fields use an harmonic potential for angle bending, but this approach is misleading when angles approach 180°. Therefore, UFF uses (as the SHAPES force field) a cosine Fourier series

$$E_{ABC}(\vartheta) = K_{ABC} \sum_{n=0}^m C_n \cos J$$

for each angle ABC.

The special reason for using UFF in this case is that the Si-O-Si bond energy changes only very little over a wide range (~120 – 180 °) [Nicholas et al. 1991] and the Fourier expansion in UFF is designed to deal with this particularity.

The Dreiding force field in contrary uses a harmonic cosine form for angle bending and is therefore expected to yield less satisfactory results.

In a geometry optimisation using force fields the energy has to be minimized. A variety of difficulties arise from this question as for example most optimisation algorithms don't allow the energy to rise and so often yield the nearest (and local) instead of the global minimum, that is the aim of the optimization.

Minimization algorithms can be divided into groups that use the derivative of the energy (as e.g. the Newton-Raphson algorithm does) and those who don't (e.g. the simplex algorithm).

All of the algorithms have advantages and disadvantages, dependent on the actual form of the potential energy surface.

An introduction can be found in [Leach 1996].

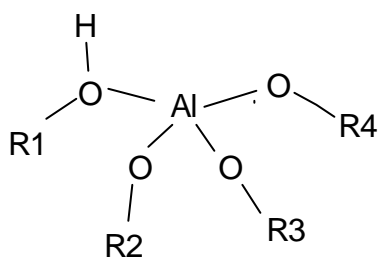
Introduction to Zeolitic Catalysis

Acidic aluminum sites in zeolites play an important role in catalysis as for example in isomerization and cracking of hydrocarbons [Meisel et. al. 1976].

The unique environment of the Brønsted acidic sites controls the overall behavior in Zeolites significantly; one of the consequences is the resulting stereochemistry of the catalysts. In addition, transport mechanisms play an important role since for sterical reasons not every reactant can be transported to the catalytic center and not every product out of the cluster. What makes those studies difficult is the heterogeneity of these systems.

A wide range of reactions between Zeolites and other molecules has been explored with theoretical methods, for example with CO [Bates and Dwyer 1993] or CH₃CN [Meijer et al. 1996]. Since I performed reactions with C-C bonds, I will restrain my description of the catalytic activity of Zeolites to this particular field.

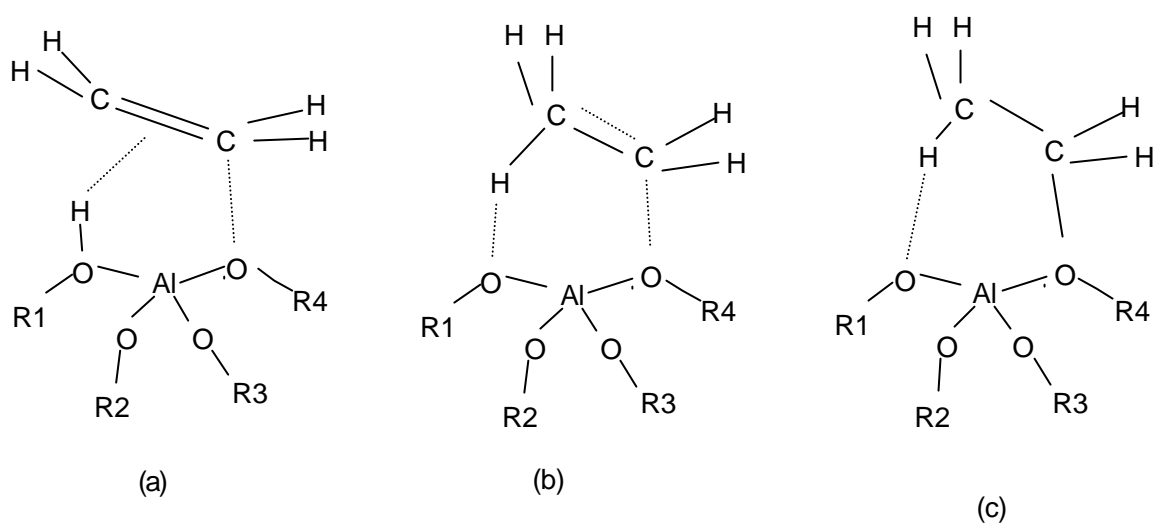
Zeolites have a structure in common where the H next to Al acts as a Brønsted acid and the adjacent oxygens, because of their lone pairs, as Lewis bases.



This particular structure determines the catalytic behaviour to a significant extent. A good review of theoretical aspects of zeolite catalysis can be found in [van Santen and Kramer 1995].

I shall confine my description further to the activation of Olefins; some of the earliest calculations in this area were performed by [Senchenya and Kazansky 1987] and [Pelmenschikov et al. 1987].

The reaction with ethene revealed the following mechanism [Senchenya and Kazansky 1991], based on calculations for a 1T-cluster with the 3-21 G basis set:



The δ -bonded complex is formed (a), stabilized by approximately 30 kJ/mol. As an intermediate, we observe (b), reacting to the σ -bonded complex (c).

We tried to follow this reaction path on a 3T model and on both of our silsesquioxanes.

Experimental

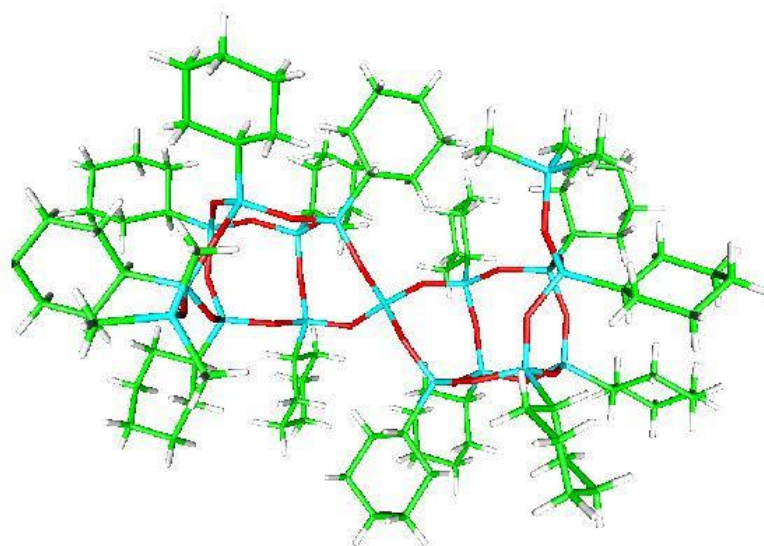
Our first goal is the comparison and evaluation of the UFF, Dreiding and MNDO method with respect to the structure optimization of $[\text{HNEt}_3]^+[\{\text{Cy}_7\text{Si}_7\text{O}_9(\text{OSiMe}_3)_2\}_2\text{Al}]^-$.

The cation was removed in all models because it forms only a separated ion pair with the anion and is expected to have a negligible effect [Edelmann et al 1991]. Therefore, the anion structure obtained from x-ray data was optimized employing all of the mentioned methods. Afterwards the structure of the optimized models was compared with the experimental data.

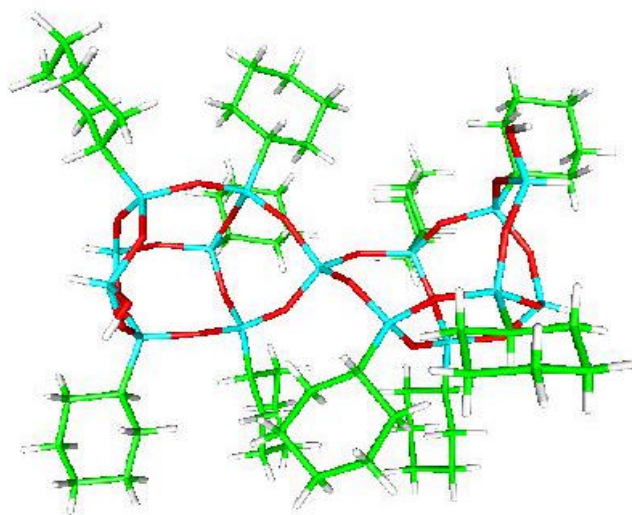
The second aim is to derive the as-small-as-possible but as-big-as-necessary model in respect to both geometry around the central Aluminum and shape and expansion of the HOMO, as this frontier orbital is thought to be very important for catalytic activity. Thus, we successively removed the cyclohexanes and substituted them by hydrogen to observe how those properties change when we simplify the molecule.

The X-ray structure we compare our computed results with can be found in [Edelmann et.al.1999].

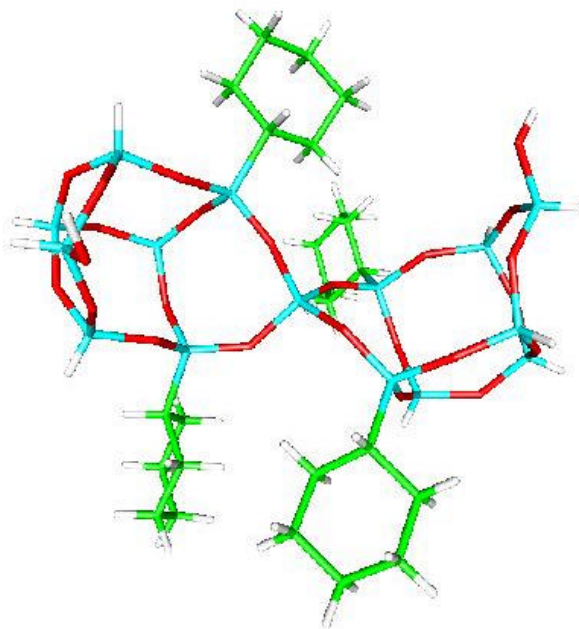
The full anion of the molecule $[\{\text{Cy}_7\text{Si}_7\text{O}_9(\text{OSiMe}_3)_2\}_2\text{Al}]^-$ is as shown below.



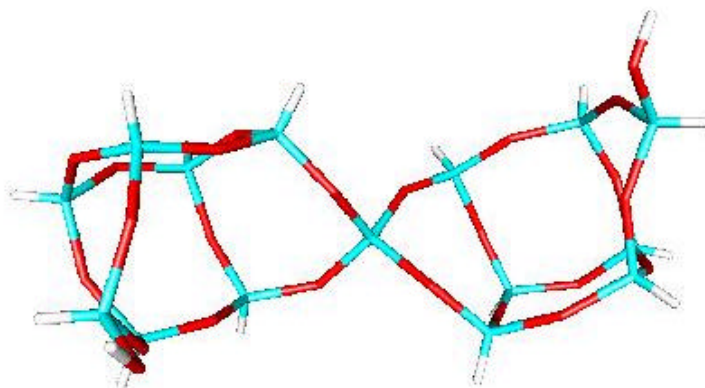
This anion was reduced by removing the four cyclohexanes furthest away from the Aluminum, yielding the so-called layer 3. The SiMe_3 groups were also exchanged by OH yielding a model compound with the formula $[\{\text{Cy}_5\text{Si}_7\text{O}_9\text{H}_2(\text{OH})\text{O}_2\}_2\text{Al}]^-$ and a structure shown below.



From this model we reduced the size by removing the six cyclohexanes separated by one Silicon from the Al in the center, the result is the layer 2 anion with the formula $[\{\text{Cy}_2\text{Si}_7\text{O}_9\text{H}_5(\text{OH})\text{O}_2\}_2\text{Al}]^-$:



Finally we cut the last cyclohexanes from the molecule, yielding layer 1, $[\{\text{Si}_7\text{O}_9\text{H}_7(\text{OH})\text{O}_2\}_2\text{Al}]^-$



All these molecules were optimized using the UFF, Dreiding and MNDO method. For all these layers the HOMO values were computed and isosurfaces were plotted to follow the change in chemical behavior.

Results of optimizations

The bond lengths and angles of the original anion and those of the optimized structures are given in the table 1 (p. 26).

To find a way for measuring the rate of systematic errors we computed an arithmetic mean of the deviations of the bond length and an arithmetic mean of the absolute value of the derivations of the bond lengths. If we then divide the former by the latter, we have a possibility to measure the rate of consistency of the systematic error.

As we can see, the UFF method always overestimates bond lengths by 0.106 to 0.142 Ångstroms with an average of 0.116 Ångstroms within Al-O bond lengths. With respect to O-Si bonds the bond lengths are overestimated by an average of 0.138 Ångstroms, the minimal overestimation is 0.105 Ångstroms and the maximal overestimation 0.160 Ångstroms. The overall average deviation is 0.127 Ångstroms.

As all deviations are within a small range, we can say that UFF gives bond lengths with a systematic error of about +0.13 Ångstroms (100% consistent systematic error, the bond lengths are always overestimated). Therefore, we can expect to transfer this result to other molecules of this class and introduce an amount correction.

To describe the results of the MNDO method, we see that the bond lengths deviate from the experimental values to a much lesser extent. The greatest negative deviations (i.e. underestimation of bond lengths) can be found between layer 1 and the original structure with a deviation between -0.079 Ångstroms (bond a). The greatest overestimation is found between both layer 2 and layer 3 and the original structure

with a deviation of +0.027 Angstroms (bond f). To describe the direction of the deviations, we can say that they are to a lesser extent consistent than those of the UFF method. We derive degrees of consistency of the deviations between 27% and 64%, so we can say that the MNDO method underestimates bond lengths, but not in every case and depending on the type of the bond. Al-O bond lengths are rather underestimated where O-Si bond lengths are rather overestimated.

In table 2 we see the results for the bond angles. We have to distinguish between Al-O-Si angles and O-Al-O bond angles. Both UFF and MNDO yield 100% consistent systematic errors in Al-O-Si angles, UFF yields angles that are underestimated by an average of -27.3 degree. The minimal underestimation amounts to -19.7 degrees whereas the maximal underestimation amounts to -41.2 degrees.

MNDO overestimates bond angles by an average of +14.0 degrees. The minimal overestimation amounts to 1.0 degrees whereas the maximal overestimation has the value of 20.4 degrees.

Thus, none of the methods describes the geometry around the Aluminum correctly, both methods show consistent systematic errors.

The O-Al-O angles are computed with much smaller deviations from the experimental values. Both UFF and MNDO give non-consistent systematic errors (consistent to a degree of 19% respectively 12 %) in a much smaller range than applied to Al-O-Si angles. Where the absolute arithmetic mean of the deviation within Al-O-Si angles was -27.3 degrees (UFF) and 14.0 degrees (MNDO), it is here as small as 3.6 degrees (UFF) and 4.3 degrees (MNDO).

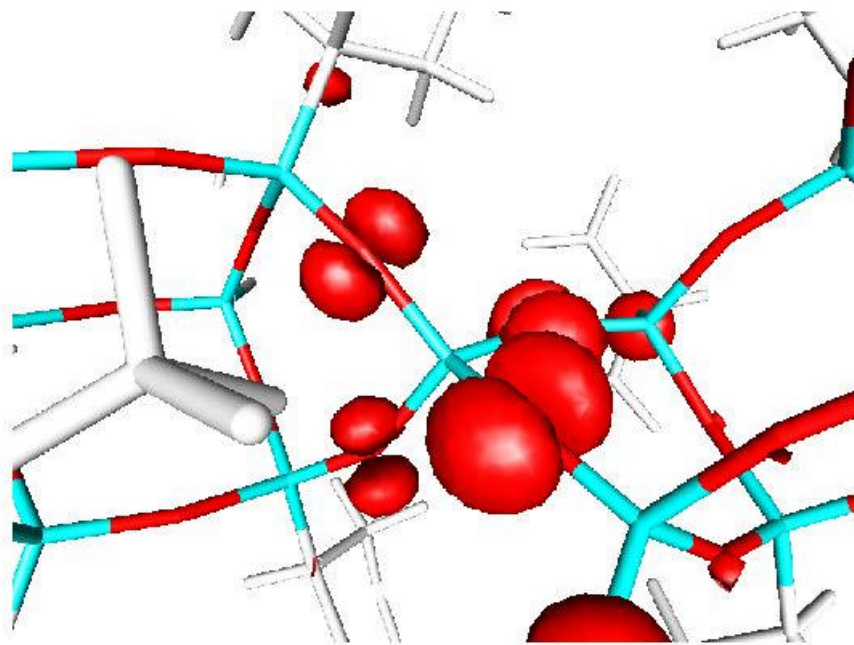
The Dreiding Force Field did not converge in any of the performed optimizations, regardless whether they were started from the original structure or from a structure that has already been optimized with other methods.

Therefore, it could not be applied to this problem. A possible explanation is high sensitivity with regard to the input structure, resulting from the already mentioned treatment of angle bending with a cosine term that can be misleading.

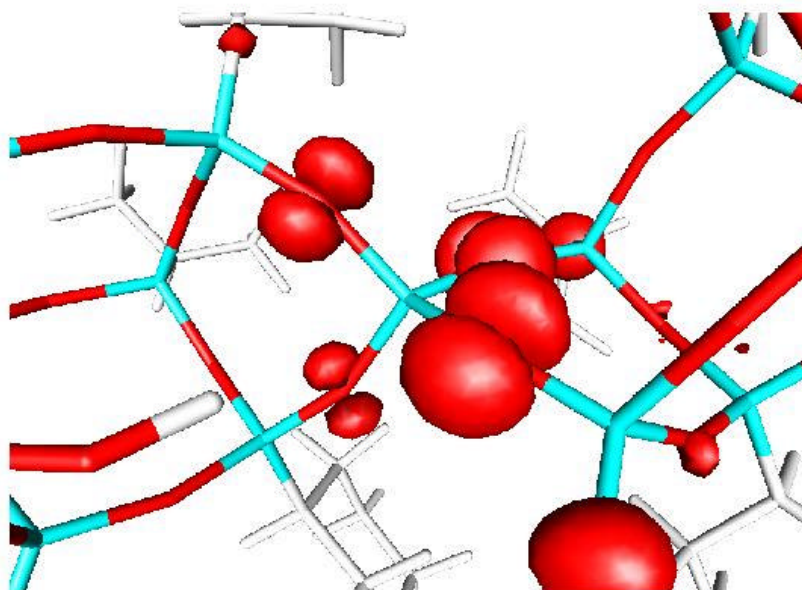
HOMO comparisons

The next step was to compute HOMO values over a 3D grid and plotting isosurfaces at values of $+0.05$ and $-0.05 \text{ e}/\text{\AA}^3$. From the change in shape and expansion as the cyclohexanes were removed we wanted to predict the change in chemical behavior.

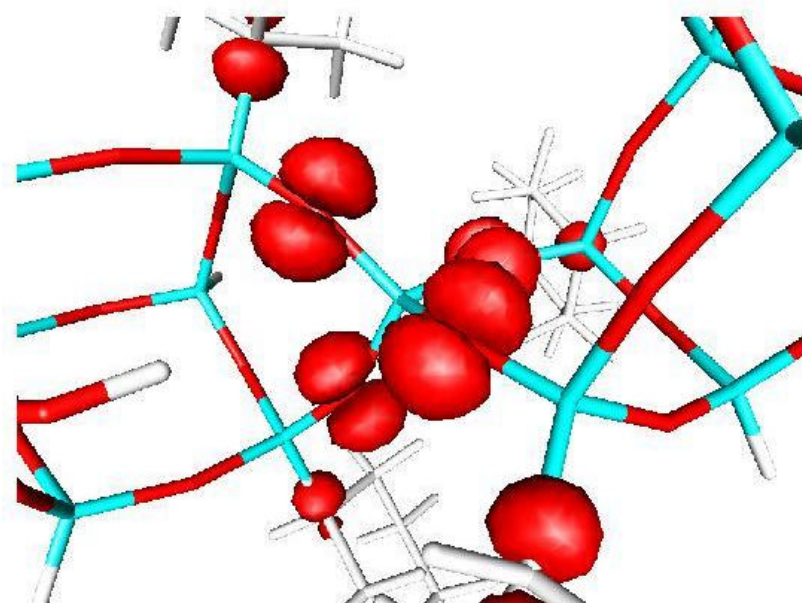
We computed the HOMO of the anion, as no major difference between the HOMO auf the anion and the HOMO of the protonated molecule is expected.



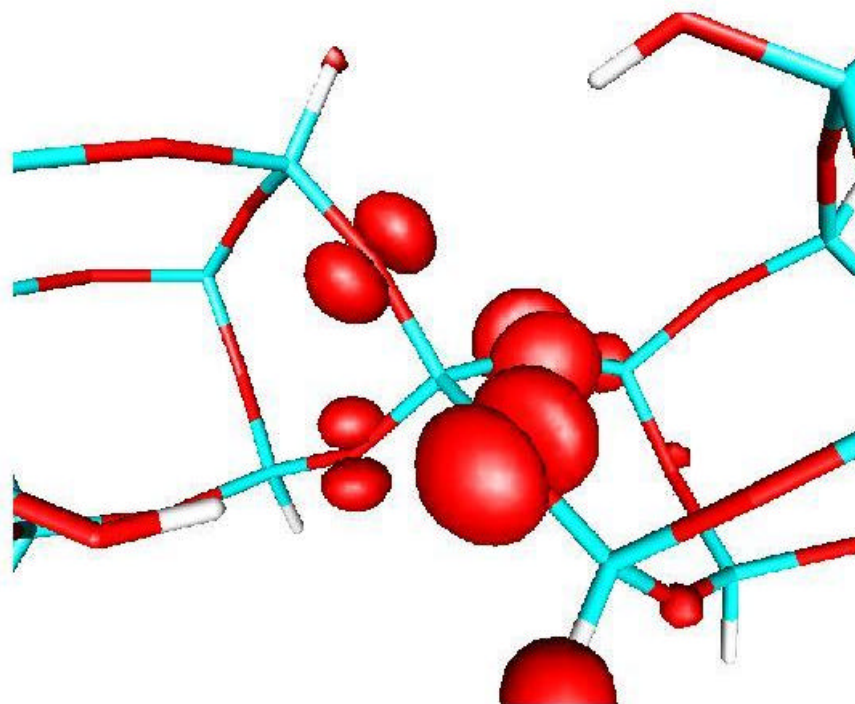
In this figure, we see the isosurfaces of the HOMO frontier orbitals plotted at values of $+0.05$ and $-0.05 \text{ e}/\text{\AA}^3$. We notice that the HOMOs are mainly centered on the oxygens next to the central Aluminum, to a smaller extent on the oxygens separated by one silicon atom from the Aluminum.



In this figure, we see the HOMO of our layer 3, where the four cyclohexanes furthest away from the Aluminum were removed. The perspective is the same as in the figure before; we notice no major change in size or shape of the orbitals. Therefore, we can assume that this model is still accurate enough for a prediction of the catalytic activity.



We again reduced the size of our model, now only the four cyclohexanes closest to the central Aluminum remain. Even in this model, layer 2, we notice no major differences in size and shape of the HOMO orbitals, with regard to the full model.



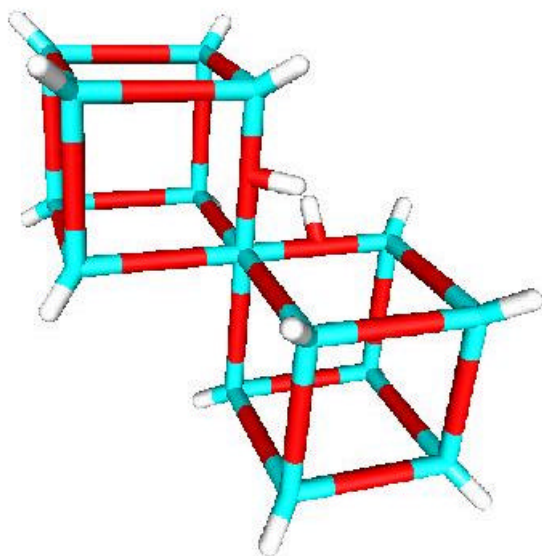
In this picture, we see the HOMO of layer 1, where all cyclohexanes were substituted by hydrogens. Again, we notice no major differences in shape and size of these parts of the orbitals centered on the oxygens. However, we can see an unrealistic size of the HOMO centered on the hydrogen (on the bottom of the picture). Thus, this model can be assumed to be to crude a model for the reaction modeling.

Therefore, because of the HOMO comparison and the geometric comparisons we can state that even layer 2 should be accurate enough to make predictions concerning the catalytic activity. This is an advantage because the computational costs of the later reaction modeling could be efficiently reduced.

Structure prediction of $[\{\text{Cy}_7\text{Si}_7\text{O}_9(\text{OH})\text{O}_2\}_2\text{Al}]^-$

In this step we tried to predict the structure of the anion with the sum formula $[\{\text{Cy}_7\text{Si}_7\text{O}_9(\text{OH})\text{O}_2\}_2\text{Al}]^-$. This structure was at the beginning of our calculations completely unknown, so we had to conceive a sensible input structure for our optimization algorithms.

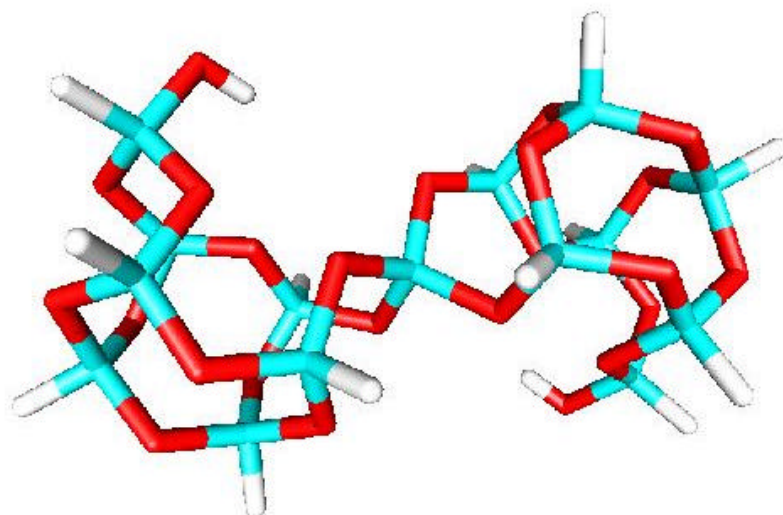
As we compare this sum formula with the one above, we notice that formally spoken the OSiMe_3 groups of the silsesquioxane with the known structure are substituted by the smaller OH groups. Thus, a coordination number of six seems to be possible (Yurii Gun'ko, private conversation), leading to the following input structure.



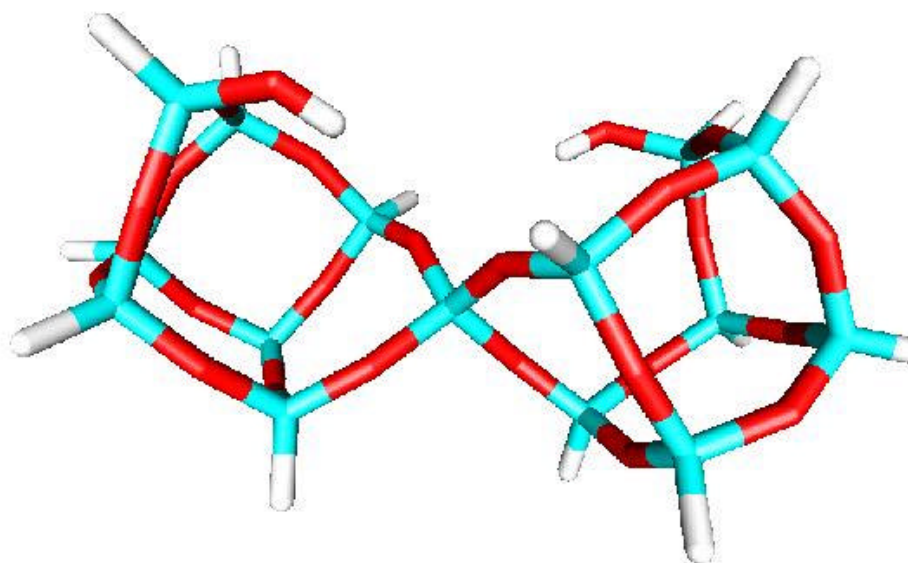
In this structure, all the O-Al and O-Si bonds have an initial length of 1.4 Ångstroms. The hydrogens were initially set on one line with the centers of the cubes and the oxygens in the corners of the cubes with an O-H distance of 1.0 Ångstroms. All intracubic angles have the size of 90 degrees. The hydrogens bonded to the oxygens have been set on one line with the centers of the cubes and the oxygens to which they are bonded. The initial distance was again 1.0 Ångstroms.

This starting point seemed to be sensible, knowing that the multidimensional energy landscape can give misleading results.

This structure was optimized using UFF and MNDO methods, leading to those results:

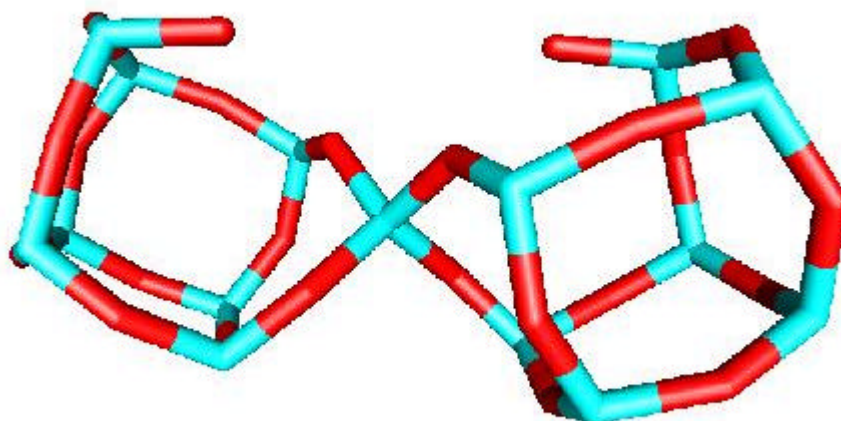


In this figure, we see the UFF optimized structure starting from the cubic input structure.



Here we see the MNDO optimized structure. Obvious are the greater Si-O-Si angles if we compare this structure with the UFF optimized structure.

At this stage, we had two optimized structures; one of them employed a semiempirical method where the other one used force fields. If we look at the structure, we see the most obvious difference in the Si-O-Si and Al-O-Si angles. The Al-O-Si angles all have a size of about 150 degrees when using the MNDO method where they have a size of about 115 degrees when using the Universal Force Field. The next step was to compare the computational results with the later resolved x-ray data.



In this figure, we see the experimental core-structure, derived from x-ray data. If we compare this molecule graphically with our computed models, we notice a better agreement with the MNDO than with the UFF optimized structure. In the next section follows a quantitative analysis of both methods.

Results of structure prediction employing UFF and MNDO

The UFF optimized structure (the guess was the original structure) leads in general to the same results as we found within the optimization of the first silsesquioxane. The deviations with respect to bond lengths are 100% consistent systematic (positive) within UFF

The Al-O bond lengths of the close coordinated oxygens are overestimated by an average of 0.105 Ångstroms, the greatest overestimation amounts to 0.122 Ångstroms whereas the smallest overestimation has the value of 0.073 Ångstroms.

The Al-O bond lengths of the far coordinated oxygens (distances i and j in table 3) are overestimated by an average of 0.421 Ångstroms within a small range, the maximal deviation amounts to 0.429 Ångstroms and the minimal deviation to 0.413 Ångstroms.

The O-Si bond lengths are overestimated by an average of 0.122 Ångstroms with a minimum value of 0.094 Ångstroms and a maximum value of 0.149 Ångstroms.

MNDO applied to the original structure and to our cubic guess leads to quite similar results, what suggests that the energy minimization algorithm found two local minima close to the global minimum.

Bond lengths are in general slightly underestimated, but within x-ray resolution. The errors are not consistent systematic. In both cases MNDO gives a great overestimation of the bond length from Al to the far coordinated oxygens, applied to the cubic structure by an average of 1.17 Ångstroms, applied to the original structure by an average of 0.912 Ångstroms. All other bond lengths are predicted very well within a deviation of 0.04 Ångstroms.

So with respect to bond lengths MNDO predicted the right geometric arrangement of the center of the molecule.

The angle predictions by both methods are within small ranges of the actual value, UFF deviates by an abs. ar. mean of 5.6 degrees; the MNDO deviations are smaller, 2.9 degrees at the cubic input and 3.4 degrees applied to the original structure.

One could think that even UFF gives satisfying results, but a glimpse at the calculated structure compared to the experimental structure shows us that the angles further apart are predicted totally wrong. MNDO gives a much better result.

We can state that we predicted the structure of the unknown aluminosilsesquioxane right, using the MNDO method.

No bond length is predicted with a deviation greater than 0.04 Ångstroms and no angle is predicted wrong more than 2.9 degrees (concerning the near coordinated oxygens). In addition, we predicted the four-fold coordination of the central Aluminum right. We have an error of about one Ångstrom with regard to the bond lengths of the far away coordinated oxygens, but that does not affect the coordination number of the Aluminum.

Reaction modeling

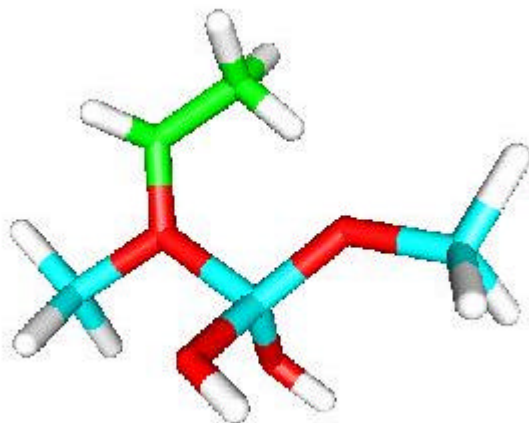
I tried to model the reaction using various methods (MNDO, HF, B3LYP) starting with ethene about 2.5 Ångstroms apart from the acidic hydrogen of the silsesquioxane, as carried out by Senchenya and Kazansky (1991) on a 1T-cluster, employing a 3-21G basis set. An energy minimization was used, as we assumed this part of the reaction to decrease the energy content of the system.

They found that in a first step the π -bond of ethene and the acidic hydrogen of the zeolite form a bond. This result could not be reproduced, with none of the employed methods and with none of various orientations. In all calculations the ethene disappeared from the hydrogen it was assumed to react with; possibly there is an energy barrier that could not be overcome with energy optimization methods.

In a next step, we had to figure out whether the reactants do not react or our used methods were not capable of dealing with this reaction. So we tried to perform the calculations on a 3T cluster and ethene, as for this reaction Senchenya and Kazansky (1991) already revealed a possible reaction path applied to a 1T cluster. The catalytic behavior was assumed not to differ between those molecules.

Therefore, both educts and product have been MNDO and B3LYP (with a 3-21G and 6-31G basis set) optimized and the QST2 transition state search was performed. This method is suggested for more difficult transition states and needs both reactants and products as input data.

In the input structure of the educts, ethene was simply about four Ångstroms apart from the acidic hydrogen; the product structure was the following in case of the 3T cluster.



Even in the case of employing the QST2 method on a 3T duster and ethene, we did not get a sensible transition state. Thus, the results by Senchenya and Kazansky (1991) on a 1T cluster could not be reproduced on a 3T cluster, although the catalytic activity of the 3T cluster was observed experimentally.

We have to assume that the employed methods were not able to deal with this case of reaction modeling

table 1 - silses1 - distances*

Distance	<i>Al- O Bond distances in Angstroms</i>			<i>O-Si-Bond distances in Angstroms</i>				
	a	b	c	d	e	f	g	h
Type of model/method								
Original Structure	1.790	1.732	1.753	1.726	1.612	1.570	1.598	1.593
UFF complete model	1.886	1.821	1.865	1.894	1.717	1.730	1.734	1.743
UFF layer 3	1.880	1.844	1.860	1.889	1.717	1.727	1.723	1.750
UFF layer 2	1.864	1.850	1.870	1.847	1.735	1.724	1.723	1.750
UFF layer 1	1.845	1.851	1.864	1.866	1.727	1.731	1.737	1.725
Original Structure	1.790	1.732	1.753	1.726	1.612	1.570	1.598	1.593
MNDO complete model	1.722	1.725	1.722	1.726	1.602	1.597	1.601	1.598
MNDO layer 3	1.724	1.720	1.725	1.721	1.604	1.597	1.604	1.597
MNDO layer 2	1.718	1.719	1.718	1.719	1.601	1.596	1.601	1.596
MNDO layer 1	1.711	1.716	1.711	1.716	1.597	1.595	1.597	1.595

average difference orig. compared to (all units Angstroms, arithmetic mean)	UFF compl.	UFF layer3	UFF layer2	UFF layer1	MNDO compl.	MNDO layer3	MNDO layer2	MNDO layer1
Al - O - bondlengths	0.116	0.118	0.123	0.106	-0.027	-0.028	-0.032	-0.037
O - Si - bondlengths	0.133	0.136	0.140	0.142	0.006	0.007	0.005	0.003
overall difference	0.125	0.127	0.132	0.124	-0.010	-0.010	-0.013	-0.017

(all units Angstroms, abs. Ar. mean)								
Al - O - bondlengths abs. Ar. Mean	0.116	0.118	0.123	0.106	0.027	0.028	0.032	0.037
O - Si - bondlengths abs. Ar. Mean	0.133	0.136	0.140	0.142	0.011	0.011	0.011	0.011
O - Si - ar. Mean / O-Si - ar.abs mean	100%	100%	100%	100%	55%	64%	45%	27%

(all UFF errors are 100% systematic, the MNDO errors around 50%)

UFF average	
Al - O - bond lengths	0.116
O - Si bond lengths	0.138
overall average deviation	0.127

* bond names are defined in the appendix

table 2 - silses 1 - angles*

Angle	<i>Al - O - Si Bond angles in degrees</i>			<i>O - Al - O Bond angles in degrees</i>						
	a/e	b/f	c/g	d/h	alpha	beta	gamma	delta	epsilon	omega
Type of model/method										
Original Structure	136.1	153.5	138.5	140.0	111.2	111.2	109.9	109.6	111.8	102.8
UFF complete model	109.7	115.1	114.0	120.8	107.1	111.6	113.5	116.5	101.6	107.2
UFF layer 3	115.1	114.8	115.9	117.7	110.1	112.0	113.9	118.6	101.5	101.1
UFF layer 2	113.5	113.6	118.8	112.7	111.8	107.8	114.4	110.2	104.3	108.3
UFF layer 1	111.8	112.3	116.9	111.8	109.3	110.8	113.6	106.5	110.5	105.9
Original Structure	136.1	153.5	138.5	140.0	111.2	111.2	109.9	109.6	111.8	102.8
MNDO complete model	155.7	154.5	155.4	154.8	104.1	110.0	104.0	110.3	110.9	117.6
MNDO layer 3	155.6	158.1	154.0	160.4	105.1	109.7	105.7	110.0	111.1	115.7
MNDO layer 2	155.5	157.4	155.5	157.3	106.2	109.5	106.1	109.5	110.9	114.7
MNDO layer 1	154.9	156.3	155.1	156.4	105.9	110.7	105.9	110.6	109.8	113.9
UFF average angles	112.5	114.0	116.4	115.8	109.6	110.6	113.9	115.3	104.5	105.6
deviation from orig. struct.	-23.6	-39.5	-22.1	-24.1	-1.6	-0.6	4.0	5.7	-7.3	2.8
	(all Al - O - Si angles are underestimated)									
	100 % systematic error				arithmetic mean of der. from orig. struc O- Al O:					0.5
	arithmetic mean:			-27.3	abs. Arithmetic mean:					3.6
					systematic to an extent of					19%
MNDO average angles	155.4	156.6	155.0	157.2	105.3	110.0	105.4	110.1	110.7	115.5
deviation from orig. struct.	19.3	3.1	16.5	17.2	-5.9	-1.2	-4.5	0.5	-1.1	12.7
	(all Al - O - Si angles are overestimated)									
	100% systematic error				arithmetic mean of der. from orig. struc O- Al O:					0.5
	arithmetic mean:			14.0	abs. Arithmetic mean					4.3
					systematic to an extent of					12%

* names of angles are defined in the appendix

table 3 - silses2 - distances & angles

Distance	Al- O Bond distances in Angstroms						O-Si-Bond distances in Angstroms					
	a	b	c	d	l	j	e	f	g	h		
Crystal Structure (original)	1.725	1.749	1.725	1.719	3.662	3.662	1.58	1.627	1.58	1.627		
MNDO; cubic input	1.716	1.711	1.716	1.71	4.832	4.832	1.595	1.597	1.595	1.597		
UFF; orig input	1.847	1.822	1.847	1.822	4.091	4.075	1.728	1.723	1.729	1.721		
MNDO; original input	1.717	1.718	1.718	1.718	4.576	4.571	1.597	1.603	1.597	1.603		
Average difference orig. compared to												
MNDO cubic												
UFF orig												
MNDO orig												
(all units Angstroms, arithmetic mean)												
Al - O - bond lengths (near)	-0.016	0.105	-0.012									
O - Si - bondlengths	-0.008	0.122	-0.007									
Al- O - bond lengths (far)	1.17	0.421	0.912									
Al - O bonds (near), abs. ar. Mean	0.016	0.105	0.012									
O - Si bonds, abs. ar. Mean	0.023	0.122	0.021									
Al - O bonds (far), abs. Ar. Mean	1.17	0.421	0.912									
Al - O (near) ar. Mean / abs. ar. Mean	100%	100%	100%									(MNDO produces non-sy. Errors)
O - Si ar. Mean / abs. ar. Mean (near)	35%	100%	33%									
Al-O (far) ar. Mean / abs. ar. Mean	100%	100%	100%									
Angle	Al - O - Si Bond angles in degrees											
	alpha	beta	gamma	delta	epsilon	omega	ny	my				
Crystal Structure (orig)	108.9	109.9	108.9	109.9	106.7	112.4	84.7	84.7				
MNDO; cubic input	106	110.9	106	110.9	109.2	113.9	78.9	78.9				
UFF; orig input	101.5	113.2	101.1	113.2	112.4	116	96.9	97.5				
MNDO; orig input	104.9	110.4	105	110.3	110.1	116.1	79	78.8				
											ar.	abs.ar.mean
											Mean	
Deviation MNDO, cubic input	-2.9	1	-2.9	1	2.5	1.5	-5.8	-5.8			-1.7	2.9
Deviation UFF, orig. input	-7.4	3.3	-7.8	3.3	5.7	3.6	-5.8	-5.2			-1.2	5.6
Deviation MNDO, orig. input	-4	0.5	-3.9	0.4	3.4	3.7	-5.7	-5.9			-1.4	3.4
bond ang angle names are defined in the appendix												

Summary, Conclusions and further work

We compared the predictive capacities of UFF and Dreiding force fields and MNDO applied to a known and to an unknown aluminosilsesquioxane.

For the optimization of the known structure $[\text{HNEt}_3]^+[\{\text{Cy}_7\text{Si}_7\text{O}_9(\text{OSiMe}_3)\text{O}_2\}_2\text{Al}]^-$ UFF gave consistent systematic errors of significant size, whereas MNDO gave results with a much smaller error and conserved the geometry around the center.

The Dreiding force field did not converge in energy and could therefore not be applied to this problem.

We derived the smallest suitable model for reaction modeling based on HOMO and geometric properties with the formula $[\{\text{Cy}_2\text{Si}_7\text{O}_9\text{H}_5(\text{OH})\text{O}_2\}_2\text{Al}]^-$.

We predicted the structure of the unknown aluminosilsesquioxane $[\{\text{Cy}_7\text{Si}_7\text{O}_9(\text{OH})\text{O}_2\}_2\text{Al}]^-$ right using MNDO, whereas UFF is not applicable. The predicted structure was later confirmed by X-ray data.

None of the employed methods gave good results concerning the modeling of the reaction with ethene.

Further work should be made in the area of reaction modeling, where the reaction mechanism of the 3T cluster with ethene has either to be confirmed or disproved. Thereafter the studied aluminosilsesquioxanes have to be examined again with regard to their catalytic activity.

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Computational Details

All calculations were performed with Gaussian98 on Pentium III – 450 MHz computers under Red Hat Linux. The convergence criteria were used as predefined.

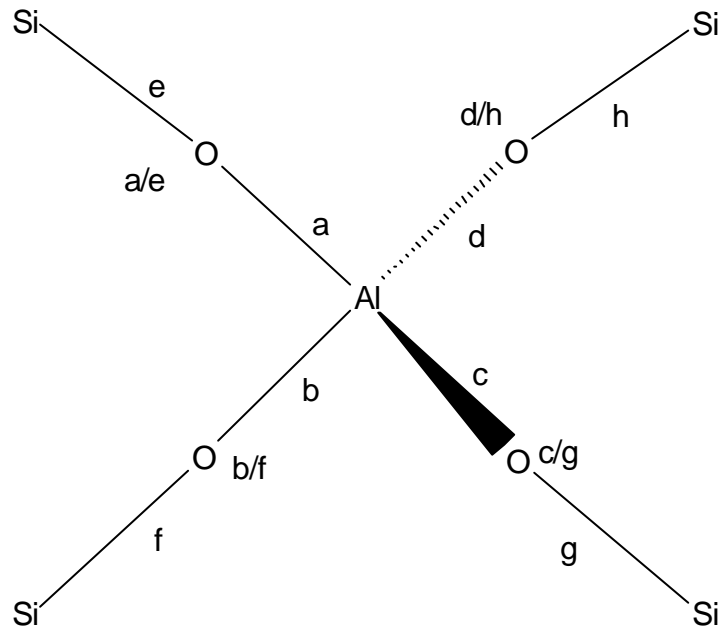
For visualization and measurement of structural properties, we used gOpenMol.

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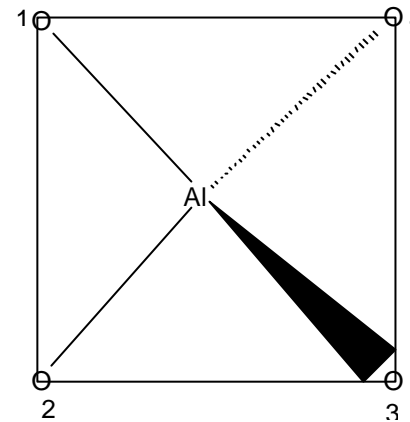
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Definition of bond and angle names

Nomenclature of Al-O / O-Si bonds and Al-O-Si bond angles



Nomenclature of O-Al-O bonds



name of angle is the angle between the following oxygens with Al in the centre

alpha	1 / 2
beta	2 / 3
gamma	3 / 4
delta	1 / 4
epsilon	2 / 4
omega	1 / 3

The smaller of the two angles determines the value.

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Experience

Is

What

You

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If

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What

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Wanted

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