Inorg. Chem. **1998,** *37,* 2223−2226

Calculation of the Structural, Energetic, and Spectral Properties of Alumoxane and Aluminosilicate “Drum” Molecules

J. A. Tossell

Department of Chemistry and Biochemistry, University of Maryland, College Park, Maryland 20742

Received May 30, 1997

In aluminosilicate cage compounds Al−O−Al linkages are usually not found, in accord with the “Al avoidance” rule. In some cases Al−O−Al linkages can be stabilized by forming additional bonds to the bridging O atom. This can occur through direct coordination of cations or by the fusing of aluminosilicate rings to create “drum”-like molecules. We have calculated the structures, energetics, and NMR and vibrational spectra for several such aluminosilicate drum-like molecules and for related alumoxanes, as well as for analogous silicate molecules. Calculations on $Si_2Al_4O_6H_8$, $Al_6O_6H_6$, $Si_4Al_4O_8H_{12}$, $Si_6O_9H_6$, $Si_8O_{12}H_8$, $Si_4Al_4O_{12}H_8^{4-}$, and $Si_4Al_4O_{12}H_8Na_4$ reproduce the experimental structures (where available) and the observed trends in Si NMR shieldings. In the double 3-ring and double 4-ring (D3R and D4R) silicate cages $Si_6O_9H_6$ and $Si_8O_{12}H_8$ the Si atoms are shielded compared to their monomeric units, with a significantly greater shielding for the D4R compared to the D3R. The Si_4,Al_4 D4R bare anion has about the same Si shielding as $Si_8O_{12}H_8$, while the neutral $Si_4Al_4O_{12}H_8Na_4$ shows a 13 ppm deshielding. These trends in Si NMR shieldings are in accord with those observed in both the molecules and in aluminosilicate minerals. On the other hand, the fused or “drum”-like D3R and D4R rings show Si atoms and Al atoms which are calculated to be *deshielded* with respect to their corresponding monomers, in accord with experiment. We also reproduce the difference in frequency of the most intense IR absorptions for the various double-ring molecules. While silicate D4R cages are considerably more stable than corresponding D3R, the stabilities of the D3R molecule $Al_6O_6H_6$ and the hypothetical D4R symmetry $Al_8O_8H_8$ are quite similar. Calculated gas-phase proton affinities for $Si_6O_9H_6$, $Si_2Al_4O_6H_8$, and $Al_6O_6H_6$ are similar, although protonation causes cage breaking for $Si_2Al_4O_6H_8$ and $Al_6O_6H_6$. For a drum-like D4R of composition $Si_4Al_4O_8H_{12}$, which is calculated to be stable with respect to $Si_2Al_4O_6H_8$ and $Si_4O_4H_8$, we present a calculated structure as well as NMR properties.

Introduction

Roesky and co-workers and others have recently reported the synthesis of soluble aluminosilicate compounds with framework structures much like those in aluminosilicate minerals.[1−3] Such compounds are interesting for a number of reasons. First, they make it possible to establish whether the principles determining structural stability are the same in molecular and mineral aluminosilicates. Second, they allow the use of solution spectroscopic methods to characterize what are, in some sense, fragments of mineral structures. Third, they may be suitable as precursors for the sol−gel synthesis of minerals such as zeolites, including those with structures never before seen.

An important aspect of the structure of these aluminosilicates is their distribution of Al and Si. In aluminosilicate minerals at ambient temperature, tetrahedrally coordinated Al atoms generally do not share polyhedral corners with each other, that is, Al−O−Al linkages do not exist. This is often formulated as the “Al avoidance rule” or “Loewenstein’s rule”.[4] Nonetheless, in crystalline aluminosilicates at high temperature and in aluminosilicate glasses, such Al−O−Al linkages do exist in limited amounts.[5] Recent studies from our group have elucidated the molecular basis of the Al avoidance rule, semiquantitatively reproducing the energies of different Al,Si arrangements in ring[6] and cube[7] aluminosilicates and suggesting methods for stabilizing structures which violate the rule.[8,9] Essentially, we find that the underbonded O atoms in Al−O−Al linkages can be stabilized by preferentially bonding counterions such as alkalis or alkaline earths to them. Inspection of the “drum”-like molecules synthesized in Roesky’s group indicates a different way in which underbonded O atoms can be saturated and Al−O−Al linkages thereby stabilized. These drum molecules, such as $Si_2Al_4O_6R_8$, contain 3-rings “fused” by the creation of three-coordinate O atoms, that is, O atoms bonded to two Al atoms and one Si. Such O atoms are in fact slightly overbonded using the normal criteria, since their Pauling bond strength sum[10] is slightly greater than 2. The alumoxanes,[11] such as $Al_6O_6R_6$, are related to $Si_2Al_4O_6R_8$ by the substitution of an Al for a Si−H group. In $Al_6O_6R_6$ each O is bonded to three Al^{IV} atoms and so receives a Pauling bond strength sum of 2.25. Our models for these species, $Si_2Al_4O_6H_8$ and $Al_6O_6H_6$ (in which alkyl groups are replaced by H atoms), are shown in Figure 1.

---

(1) Montero, M. L.; Uson, I.; Roesky, H. W. *Angew. Chem., Int. Ed. Engl.* **1994**, *33*, 2103.

(2) Montero, M. L.; Voigt, A.; Teichert, M.; Uson, I.; Roesky, H. W. *Angew. Chem., Int. Ed. Engl.* **1995**, *34*, 2504.

(3) Voigt, A.; Murugavel, R.; Ritter, U.; Roesky, H. W. *J. Organomet. Chem.* **1996**, *521*, 279.

(4) Loewenstein, W. *Am. Mineral.* **1954**, *39*, 62.

(5) Navrotsky, A.; Peraudeau, G.; McMillan, P.; Coutures, J.-P. *Geochim. Cosmochim. Acta* **1982**, *46*, 2039.

(6) Tossell, J. A. *Am. Mineral.* **1993**, *78*, 911.

(7) Tossell, J. A. *J. Phys. Chem.* **1996**, *100*, 14828.

(8) Tossell, J. A. In *Tailor-Made Silicon-Oxygen Compounds: From Molecules to Materials*; Corriu, R., Jutzi, P., Eds.; Vieweg: Wiesbaden, 1996; pp 31−45.

(9) Tossell, J. A.; Saghi-Szabo, G. *Geochim. Cosmochim. Acta* **1997**, *61*, 1171.

(10) Pauling, L. *J. Am. Chem. Soc.* **1929**, *51*, 1010.

(11) Mason, M. R.; Smith, J. M.; Bott, S. G.; Barron, A. R. *J. Am. Chem. Soc.* **1993**, *115*, 4971.

S0020-1669(97)00674-5 CCC: $15.00

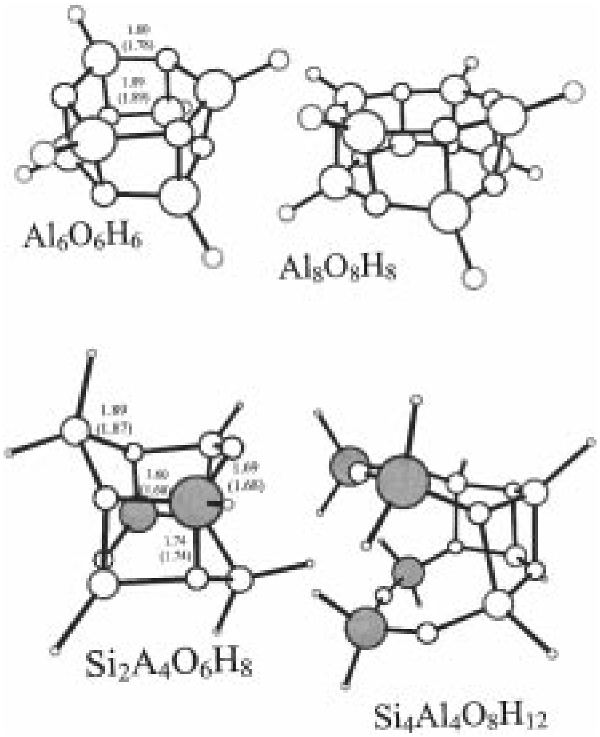

Figure 1. Calculated geometries for $Si_2Al_4O_6H_8$, $Al_6O_6H_6$, and $Si_4Al_4O_8H_{12}$. For $Si_2Al_4O_6H_8$ and $Al_6O_6H_6$, experimental bond distances for alkyl-substituted species (refs 1 and 11) are given in parentheses. The atoms in order of decreasing size are Si, Al, O, and H. The Si atoms are shown as solid circles.

Computational Methods

We evaluated structures and stabilities of the molecules at the 6-31G* Hartree−Fock level[12] using the GAMESS[13] and GAUSSIAN94[14] programs. Molecular geometries are generally given accurately at this level, with a tendency to underestimate bond lengths by a few hundredths of an angstrom.[12] For all the molecules except $Si_4Al_4O_8H_{12}$, the largest and least symmetric, we also evaluated the Hessian matrix and the vibrational frequencies, all of which were positive, indicating that we had found at least local energy minima. Establishing that the structures found correspond to the global minimum is more difficult, but our starting geometries always differed substantially from the optimized geometries so that we were sampling a reasonable portion of the energy surface, and we did not bias our results by using experimental geometries to start the optimizations. The most problematic species from the point of view of energy minimization is the D4R drum molecule $Si_4Al_4O_{12}H_8$, but this is also perhaps the most interesting since no such molecule has yet been synthesized. NMR shieldings were then calculated using the GIAO method[15] at the 6-31G* SCF level using GAUSSIAN94. Calculated 6-31G* SCF vibrational frequencies were scaled by the standard factor 0.893.[16] To convert from calculated electric field gradients in atomic units to nuclear quadrupole coupling constants (NQCC) in MHz, we used the Hartree−Fock level value[17] for the nuclear quadrupole moment of ^{17}O.

Results and Discussion

Calculated bond distances for $Si_2Al_4O_6H_8$ and $Al_6O_6H_6$ are compared with experimental values for the corresponding alkyl group terminated compounds in Figure 1. We collect calculated Si, Al, and O NMR shieldings in Table 1 and calculated electric field gradients at O and Si−O−M stretching vibrational energies in Table 2. Table 3 contains energies calculated at the 6-31G* SCF level for some relevant reactions.

Table 1. Calculated NMR Shieldings for Monomers and for Oligomers (Obtained at the 6-31G* SCF Level Using the GIAO Method as Implemented in GAUSSIAN94)

molecule	σ(Si)	σ(Al)	σ(O)
H_2O			334.3
$HSi(OH)_3$	492.4		300.0
$HAl(OH)_3^-$		541.9	314.8
$HAl(OH)_2$		520.0	305.3
$Si_4O_6H_4$ (D2R)	481.9		228.4
$Si_6O_9H_6$ (D3R)	506.9		256.5
$Si_8O_{12}H_8$ (D4R)	516.5		257.8
$Si_4Al_4O_{12}H_8^{4-}$ (D4R)	516.3	577.3	256.5
$Si_4Al_4O_{12}H_8Na_4$ (D4R)	503.4	559.4	258.0, 252.9
$Si_2Al_4O_6H_8$ (drum D3R)	485.2	523.1(2H, 2O)	243.2 (III)
		545.1(1H, 3O)	259.4 (II)
$Al_6O_6H_6$ (drum D3R)		536.8	251.1
$Al_8O_8H_8$ (drum D4R)		543.8	248.1
$Si_4Al_4O_8H_{12}$ (drum D4R)	480.5−484.5	548.7−555.4	242.7−276.6

Table 2. Other Properties of $Si_6O_9H_6$, $Si_8O_{12}H_8$, $Si_2Al_4O_6H_8$, and $Al_6O_6H_6$ Calculated at the 6-31G* SCF Level

molecule	scaled frequency of most intense IR mode (cm^{-1})	^{17}O NQCC (MHz)
$Si_6O_9H_6$	1047	4.88
$Si_8O_{12}H_8$	1082	4.57
$Si_2Al_4O_6H_8$	1005	3.40 (O^{II})
		3.23 (O^{III})
$Al_6O_6H_6$	787	2.85

Table 3. Calculated Reaction Energies at the 6-31G* SCF Level (in kcal/mol)

reaction	Δ*E*
(1) $6HSi(OH)_3 \rightarrow Si_6O_9H_6 + 9H_2O$	−27.1
(2) $8HSi(OH)_3 \rightarrow Si_8O_{12}H_8 + 12\ H_2O$	−55.7
(3) $6HAl(OH)_2 \rightarrow Al_6O_6H_6 + 6H_2O$	−157.0
(4) $8HAl(OH)_2 \rightarrow Al_8O_8H_8 + 8H_2O$	−205.3
(5) $2HSi(OH)_3 + 2HAl(OH)_2 + 2H_2AlOH \rightarrow Si_2Al_4O_6H_8 + 6H_2O$	−110.6
(6) $4H_2Si(OH)_2 + 4HAl(OH)_2 \rightarrow Si_4Al_4O_8H_{12} + 8H_2O$	−147.1
(7) $Si_2Al_4O_6H_8 + 4\ H_2O \rightarrow 2SiAl_2O_5H_8$	−16.0
(8) $Si_6O_9H_6 + 3\ H_2O \rightarrow 2Si_3O_6H_6$	+13.4
(9) $2Si_2Al_4O_6H_8 + Si_4O_4H_8 \rightarrow 2Si_4Al_4O_8H_{12}$	−40.1
(10) $Si_6O_9H_6 + H^+ \rightarrow Si_6O_9H_7^+$	−189.5
(11) $Al_6O_6H_6 + H^+ \rightarrow Al_6O_6H_7^+$	−198.6
(12) $Si_2Al_4O_6H_8 + H^+ \rightarrow Si_2Al_4O_6H_9^+$	−191.5

Clearly the calculated structures of $Al_6O_6H_6$ and $Si_2Al_4O_6H_8$ (Figure 1) compare well with experiment. Also shown are our calculated structures for the hypothetical (or at least not yet synthesized) drum-like D4R molecule $Si_4Al_4O_8H_{12}$ and for the D4R alumoxane $Al_8O_8H_8$ (a lower symmetry $Al_8O_8R_8$ structure has been characterized[11b]). $Si_2Al_4O6H_8$ may be described as a dimer of $SiAl_2O_3H_4$, fused by the creation of 3-coordinate O atoms. Similarly we can fuse two S4R molecules of composition $Si_2Al_2O_4H_6$ with an Al,Al,Si,Si distribution around the ring to produce the fused or drum-like D4R molecule $Si_4Al_4O_8H_{12}$. Since Si,Al 4-rings are in general more stable than 3-rings, such a drum-like D4R molecule should be stable compared to $Si_2Al_4O_6H_8$. The change in energy at the 6-31G* SCF level for formation of 2 mol of $Si_4Al_4O_8H_{12}$ from 2 mol of $Si_2Al_4O_6H_8$ and 1 mol of $Si_4O_4H_8$ is indeed −40.1 kcal. On the other hand, the D3R cage in $Si_2Al_4O_6H_8$ is completely closed, while in $Si_4Al_4O_8H_{12}$ one side is open, which could make the compound

---

(12) Hehre, W. J.; Radom, L.; Schleyer, P. v. R.; Pople, J. A. *Ab Initio Molecular Orbital Theory*; Wiley; New York, 1986.

(13) Schmidt, M. W.; et al. *J. Comput. Chem.* **1993**, *14*, 1347.

(14) Frisch, M. J.; et al. *GAUSSIAN94*, Rev. B.3; Gaussian, Inc.: Pittsburgh, PA, 1994.

(15) Wolinski, K.; Hinton, J. F.; Pulay, P. *J. Am. Chem. Soc.* **1990**, *112*, 8251.

(16) Pople, J. A.; Scott, A. P.; Wong, M. W.; Radom, L. *Isr. J. Chem.* **1993**, *33*, 345.

(17) Schaefer, H. F.; Klemm, R. A.; Harris, F. E. *Phys. Rev.* **1968**, *176*, 49.

more susceptible to hydrolysis. However, some such open cage structures are known, for example, $Si_6O_7R_6(OH)_4$, which basically consists of two S4R units sharing an edge.[18]

The calculated Si NMR shieldings in Table 1 show the right trends compared to the corresponding monomers.[3,21] Condensing the silicate monomer $HSi(OH)_3$ to a double-ring structure increases the calculated shielding by about 15 ppm for the D3R case and 25 ppm for the D4R. Similar increases in Si NMR shieldings have been calculated for the formation of single 3- and 4-rings from $H_2Si(OH)_2$ monomers and have been shown to be in good agreement with experimental data.[19] For unstrained rings (4-rings or larger) the shielding increase appears to be generally about 8−9 ppm for every Si−O−H group converted to Si−O−Si. For strained rings, for example, either single or double 3-rings, the shielding is lower. For example, as discussed in ref 19b, the S3R $[(CH_3)_2SiO]_3$ is deshielded by about 10 ppm compared to the S4R $[(CH_3)_2SiO]_4$. For the hypothetical D2R, $Si_4O_6H_4$ (D_{2h} symmetry), the calculated shielding is actually smaller than that in the monomer. However, Earley[20] has established (and we confirm) that the most stable isomer of $Si_4O_6H_4$ is actually a cage of T_d symmetry. The increase in the Si NMR shielding in the aluminosilicate cage compounds of ref 3 compared to their corresponding monomers (the “coordination shift”, $\Delta\sigma(SiO_3)$ as defined in ref 3) is observed to be about 13−18 ppm for species of the Si_4Al_4... type, to be compared with our calculated differences of 24 and 11 ppm for $Si_4Al_4O_{12}H_8{}^{4-}$ and $Si_4Al_4O_{12}H_8Na_4$, respectively, versus the monomer $HSi(OH)_3$. When half the Si atoms of $Si_8O_{12}H_8$ are replaced by Al atoms to form the anion $Si_4Al_4O_{12}H_8{}^{4-}$ the calculated Si shielding is almost unchanged compared to $Si_8O_{12}H_8$ (516.5 vs 516.3 ppm), but when this anion is charge-compensated by the addition four Na^+ atoms, the Si shielding is reduced to 503.4 ppm. Experimentally the Si NMR shifts of the Si_4Al_4... anionic species in ref 3 cluster around −80 ppm, while the Si NMR shift of $Si_8O_{12}H_8$ is about −83 ppm, so that the shielding difference between them is small. But when a Si is replaced by an Al,alkali combination, a substantial deshielding is seen experimentally in minerals,[21] on the order of 5 ppm for each Al second-nearest neighbor to the Si. Since each Si in $Si_4Al_4O_{12}H_8Na_4$ has three Al second-nearest neighbors, this would suggest a deshielding of about 15 ppm compared to $Si_8O_{12}H_8$, while our calculations give a deshielding of 13 ppm.

On the other hand, in the drum-like D3R and D4R molecules $Si_2Al_4O_6H_8$ and $Si_4Al_4O_8H_{12}$, the Si is *deshielded* compared to the corresponding monomer, $HSi(OH)_3$. The calculated deshielding for $Si_2Al_4O_6H_8$ compared to $HSi(OH)_3$ is about 7 ppm, while the experimental deshielding is smaller, from near 0 to 2 ppm for the various Si_2Al_4... drum-like species in ref 3. This deshielding is perhaps not too surprising for $Si_2Al_4O_6H_8$, in which each Si is part of a Si,Al 2-ring. Such 2-ring geometries are expected to be deshielded, as in the D2R $Si_4O_6H_4$. But for the D4R drum molecule $Si_4Al_4O_8H_{12}$, explaining the deshielding is harder, since all four Si atoms are at the edges of 4-rings. Such deshielding thus seems to be a general characteristic of these drum molecules. Some interesting trends are also seen in the calculated Al NMR shieldings, although comparable experimental data is lacking. The Al atoms in $Si_4Al_4O_{12}H_8{}^{4-}$ and $Si_4Al_4O_{12}H_8Na_4$ are shielded compared to the monomer $HAl(OH)_3{}^-$ while that in $Al_6O_6H_6$ is deshielded by a few parts per million. The Al shielding is calculated to be about 7 ppm higher in $Al_8O_8H_8$ than in $Al_6O_6H_6$. These shielding trends for Al are thus very much like those for Si, as expected.

These compounds can also be characterized in terms of other properties, such as their IR and Raman spectra and their electric field gradients or nuclear quadrupole coupling constants at O. As noted by Voight et al.,[3] the most intense IR absorption in these aluminosilicate molecules is invariably an asymmetric Si−O−M stretch and is a useful diagnostic tool. Our calculated (scaled) frequencies for this vibration are 1082 and 1005 cm^{-1} for $Si_8O_{12}H_8$ and $Si2Al_4O_6H_8$, respectively. The experimental value[22] for $Si_8O_{12}H_8$ is 1141 cm^{-1}, and the values for Si_2Al_4-type drum molecules[3] range from 1066 to 1047 cm^{-1}. The calculated value of 4.57 MHz for the ^{17}O NQCC of $Si_8O_{12}H_8$ is in good agreement with the experimental value[23] of 4.9 ± 0.5 MHz. In $Si_2Al_4O_6H_8$ each O is bonded either to one Si and one Al (O^{II}) or to one Si and two Al (O^{III}). Both types of O atoms have NQCC values considerably lower than that for the Si−O−Si type O atoms in $Si_6O_9H_6$ and $Si_8O_{12}H_8$. In $Al_6O_6H_6$ and $Al_8O_8H_8$ each O is bonded to three Al atoms and the NQCCs are even lower. In general, replacement of Si by Al reduces the NQCC at O.[24]

Reaction energies are given fairly accurately at the 6-31G* Hartree−Fock SCF level for isodesmic reactions, in which the total number of each type of bond is identical in reactants and products.[12] Results are usually also quite good if the bond types are similar, although not identical. For example, we calculate the enthalpy change for forming the S4R $Si_4O_4H_8$ and four H_2O molecules from four molecules of $H_2Si(OH)_2$ to be −33.1 kcal/mol at the 6-31G* SCF level and −33.5 kcal/mol at the correlated Møller−Plesset second-order (MP2) perturbation theory[12] level (using the HF geometries). This suggests that correlation effects on O−H and O−Si bonds are quite similar. Unfortunately, for the double-ring compounds considered here, studies at the MP2 level were not computationally feasible, but we expect our reaction energies calculated at the HF SCF level to be little changed by MP2 corrections, by analogy with the S4R formation reaction discussed above. In Table 3, the first six reactions are for the formation of D3R and D4R oligomers from the corresponding monomers. In accord with the results of Earley and with experiment, the stability of the all-Si D4R is greater than that of the D3R. For the alumoxanes the situation is somewhat different. First, using the Al^{III} species $HAl(OH)_2$ as the monomeric unit, the energies for double-ring formation are much more higly exothermic than in the Si case. Of course this arises mainly from the increased coordination number of Al in the double rings. On a per monomer basis the D3R is also slightly more stable than the D4R. This is consistent with the fact that the drum-like D4R $Al_8O_8H_8$ has apparently never been synthesized, although a lower symmetry structure has been obtained. Equations 5 and 6 (Table 3) are formation reactions for the $Si_2Al_4O_6H_8$ molecule, which has been synthesized (with alkyl groups in place of H), and for our hypothetical $Si_4Al_4O_8H_{12}$ molecule. The calculated exothermicities per Al or Si atom are very similar for the formation reactions of these two molecules, suggesting that they have similar stabilities and that

---

(18) Hambley, T. W.; Maschmeyer, T.; Masters, A. F. *Appl. Organomet. Chem.* **1992**, *6*, 253.

(19) (a) Tossell, J. A. *J. Noncryst. Solids* **1990**, *120*, 13. (b) Tossell, J. A. *Chem. Mater.* **1994**, *6*, 239.

(20) Earley, C. W. *J. Phys. Chem.* **1994**, *98*, 8693.

(21) (a) Engelhardt, G.; Michel, D, *High-resolution Solid-state NMR of Silicates and Zeolites*; Wiley: New York, 1987. (b) Bertling, K.; Marsmann, H. C. *Phys. Chem. Miner.* **1988**, *16*, 295.

(22) Bartsch, M.; Bornhauser, P.; Calzaferri, G.; Imhof, R. *J. Phys. Chem.* **1994**, *98*, 2817.

(23) Kowalewski, J.; Nilsson, T.; Tornroos, K. W. *J.Chem. Soc., Dalton Trans.* **1996**, 1597.

(24) Dirken, P. J.; Kohn, S. C.; Smith, M. E.; van Eck, E. R. H. *Chem. Phys. Lett.* **1997**, *266*, 568.

$Si_4Al_4O_8H_{12}$ is therefore a reasonable synthetic target. Equations 7 and 8 are for the hydrolysis of the drum-like and normal D3R to give two single rings. This process is favorable enthalpically for the $Si_2Al_4O_6H_8$ drum molecule but unfavorable for $Si_6O_9H_6$. The last three equations in Table 3 are for the protonation of O atoms in the various D3R cages. In each case we started the geometry optimization with the proton rather far from the molecule and with no symmetry constraints, so as to obtain the lowest energy isomer possible. The calculated gas-phase proton affinity is quite large and of about the same magnitude for $Si_6O_9H_6$, $Al_6O_6H_6$, and $Si_2Al_4O_6H_8$. An important difference between these three reactions, however, is the effect of protonation on the cage. For both $Al_6O_6H_6$ and $Si_2Al_4O_6H_8$, protonation of the three-coordinate O breaks the cage, producing an O bonded to two tetrahedrally coordinated atoms and one proton and a three-coordinate Al bonded to only one O. In $Si_6O_9H_7^+$ the D3R cage remains intact. The hydration products $Si_6O_9H_7^+$ and the isomer of $Si_2Al_4O_6H_9^+$ formed by protonation of three-coordinate O are shown in Figure 2.

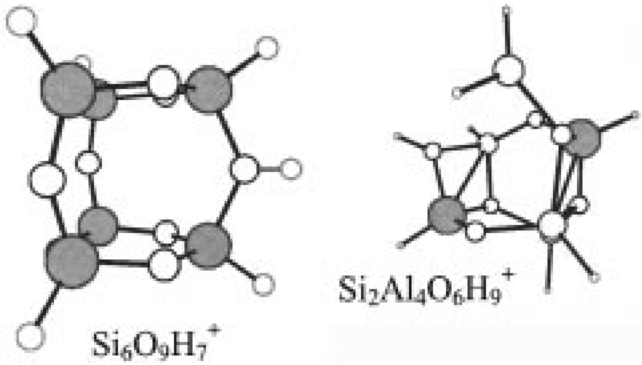

Figure 2. Calculated geometries for the lowest energy isomers of $Si_6O_9H_7^+$ and $Si_2Al_4O_6H_9^+$. The atoms in order of decreasing size are Si, Al, O, and H. The Si atoms are shown as solid circles.

Conclusions

Ab initio calculations at the 6-31G* SCF level satisfactorily reproduce the structures of alumoxane and aluminosilicate drum molecules and the experimental trends in their Si NMR shieldings compared to the monomers. Trends in the frequency of the most intense Si−O−M IR stretching vibration are also in accord with experiment. The formation of drum-like molecules by fusing of single rings may be seen as another way of creating O atoms with Pauling bond strength sums of 2.0 or more from Al−O−Al linkages. A structure has been calculated for a hypothetical drum-like D4R molecule, $Si_4Al_4O_8H_{12}$, which is found to be stable compared to $Si_2Al_4O_6H_8$ and $Si_4O_4H_8$. In this molecule the Si has about the same NMR shielding as in $Si_2Al_4O_6H_8$.

Acknowledgment. This work was supported by DOE Grant DE-FG02-94ER14467.

IC970674J