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Proton Affinities of the Silatranes and Their Analogues

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Ab initio calculations with full geometry optimization have been used to investigate the O and N atom proton affinities and the molecular structures of silatranes ($RSi(OCH_2CH_2)_3N$), as well as the related compounds $RSi(OCH_3)_3$, $RSi(OCH_2)_3CH$, and $RSi(OCH_2CH_2)_3CH$, where R = F, Cl, CH_3, SiH_3, utilizing the 6-31G(d) basis set. It is found that larger electron donor substituents R induce large proton affinities. The silatranes have stronger proton affinities than the other compounds because of the transannular Si−N interaction. For silatranes, only a small difference between the O and N atom proton affinities is found. The silatrane Si−R bond distances are apparently determined by the degree of the anomeric effect in the R−Si−O fragment and transannular Si−N interactions.

Introduction

Pentacoordinated silicon compounds have been of great interest for several decades. In particular, silatranes (Y = O as shown in Figure 1) have been studied extensively since Frye et al. prepared the first compounds in 1961.[1]

The silatrane structure consists of a distorted trigonal bipyramid at Si, with nearly equatorial atoms Y. The axial N is pyramidalized so that its lone pair points to Si. While most chemists have been interested in silatranes because of this geometry and its short transannular Si−N bond distance for some axial substituents R, silatranes are also of interest because of their wide range of biological activities.[2,3] Many researchers, including Voronkov et al., Lukevits et al., Corriu et al., Hencsei, and others, have investigated the silatranes, primarily via structural experiments.[4−13] Additionally, azasilatranes[14−24] (Y = NH, NCH_3) and carbasilatranes[13,25−30] (Y = CH_2) have been reported in

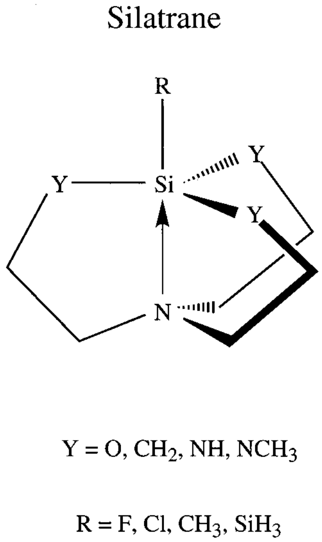

Figure 1. Structures for pentacoordinated silicon compounds.

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many papers. The transannular Si−N bond lengths of carbasilatranes are longer than those in silatranes, while NMR data suggest the transannular Si−N bond in azasilatranes is stronger than that in silatranes.[14]

Most silatrane X-ray structural data show that transannular Si−N bond lengths are in the range of 2.01−2.23 Å.[6−9,12,13] This is somewhat longer than a typical Si−N single-bond distance of 1.7−1.8 Å but much shorter than the sum of the van der Waals radii, 3.5 Å. For this reason silatranes are generally considered to possess a weak transannular Si−N bond. Generally, more electronegative substituents R shorten the Si−N bond lengths, although the Si−N distance is 2.02 Å for R = Cl while it is 2.04 Å for R = F. Therefore, the substituent effect cannot simply be due to electronegativity. Gas-phase structures are known for R = CH_3[31] and R = F,[32] and the Si−N bond lengths in these silatranes are longer than those in the solid state. This indicates the Si−N bond is very deformable if crystal forces can produce such a large change in geometry. Indeed, Schmidt et al. demonstrated this using a simple model.[33]

The early theoretical studies of silatranes were limited to semiempirical methods,[34−38] due to the large size of the molecules. The first *ab initio* calculation[39] was performed using the 3-21G* basis set. Increased computer hardware and the availability of parallel quantum chemistry codes led to the applications of more sophisticated wave functions.[33,40−44] A previous paper by one of us[33] used the 6-31G* basis set to investigate a wide variety of silicon atranes, where R = H, F, OH, NH_2, CH_3, Cl, SH, PH_2, SiH_3, and Y = O, NH, NCH_3, CH_2. The results suggest, in agreement with experiment, that azasilatranes possess the shortest Si−N distances, followed by silatranes and then carbasilatranes. Electronegative groups R generally yield short Si−N bonds, and Cl atoms are the best axial partner for the basal nitrogen.

Silatranes are relatively stable to moisture. In comparison with triethoxysilanes, their analogues, silatranes are more difficult to hydrolyze.[45] However, in the presence of acid, the rate of hydrolytic cleavage of silatranes becomes significantly faster. The first and slowest step of the acidic hydrolysis is protonation at the oxygen with simultaneous nucleophilic attack at the silicon.[46] Recent semiempirical calculations predicted a larger proton affinity at the oxygen atoms in silatranes than in trimethoxysilanes.[47] These calculations also illustrated the necessity of taking the anomeric effects at silicon into account, on the basis of comparison of the structure and properties of silatranes with model compounds containing tetrahedral silicon.[47] In this paper the O atom proton affinities in silatranes and their analogues, $RSi(OCH_3)_3$, $RSi(OCH_2)_3CH$, and $RSi(OCH_2CH_2)_3CH$, are studied, using *ab initio* wave functions to understand the influence of the conformational and anomeric effects and silicon hypervalency on the basicity of these compounds. Substituent effects are investigated for R = F, Cl, CH_3, SiH_3. The N atom proton affinities are also evaluated in this work.

Computational Methods

Restricted Hartree−Fock (RHF) geometry optimizations were performed with the 6-31G* basis set,[48] using the GAMESS electronic structure code.[49] Enthalpic data were determined using Møller−Plesset second-order perturbation theory[50] (MP2) energies at the RHF-optimized geometries. Harmonic zero-point energy and temperature corrections (to 298.15 K) were obtained using the RHF Hessians.

Results and Discussion

The structures of silatranes, $RSi(OCH_2)_3CH$, and $RSi(OCH_2CH_2)_3CH$ possess C_3 symmetry, and those of $RSi(OCH_3)_3$ have C_{3v} symmetry, while all of the protonated compounds have C_1 symmetry.

The Si−R bond length and R−Si−O−C dihedral angle data for the neutral compounds are shown in Tables 1 and 2, respectively. In general, $RSi(OCH_2)_3CH$ possesses the shortest Si−R bond distances, followed by $RSi(OCH_2CH_2)_3CH$, silatranes, and then $RSi(OCH_3)_3$. For

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Table 1. RHF/6-31G(d) Si−R Bond Distances in the Neutral Silicon Compounds[a]

	R = F	R = Cl	R = CH_3	R = SiH_3
$RSi(OCH_2CH_2)_3N$	1.587	2.063	1.862	2.344
$RSi(OCH_3)_3$	1.595	2.077	1.872	2.358
$RSi(OCH_2)_3CH$	1.563	2.013	1.848	2.340
$RSi(OCH_2CH_2)_3CH$	1.576	2.039	1.856	2.342

[a] All distances in angstroms.

Table 2. RHF/6-31G(d) R−Si−O−C Dihedral Angles in the Neutral Silicon Compounds[a]

	R = F	R = Cl	R = CH_3	R = SiH_3
$RSi(OCH_2CH_2)_3N$	150.7	150.0	147.3	148.1
$RSi(OCH_3)_3$	65.2	64.0	79.5	83.8
$RSi(OCH_2)_3CH$	180.0	180.0	180.0	180.0
$RSi(OCH_2CH_2)_3CH$	141.3	141.2	141.0	141.0

[a] All angles in degrees.

Table 3. RHF/6-31G(d) Si−R Bond Distances in the Oxygen-Protonated Silicon Compounds[a]

	R = F	R = Cl	R = CH_3	R = SiH_3
$RSi(OCH_2CH_2)_3N$	1.587	2.057	1.859	2.355
	(0.00)	(0.006)	(0.003)	(−0.011)
$RSi(OCH_3)_3$	1.567	2.013	1.843	2.363
	(0.028)	(0.064)	(0.029)	(−0.005)
$RSi(OCH_2)_3CH$	1.544	1.973	1.833	2.361
	(0.019)	(0.040)	(0.015)	(−0.021)
$RSi(OCH_2CH_2)_3CH$	1.558	1.998	1.839	2.351
	(0.018)	(0.041)	(0.017)	(−0.009)

[a] All distances in angstroms; H^+ attached to one oxygen atom. ΔR values (=R(neutral) − R(cation)) are given in parentheses.

compounds of tetrahedral silicon, the observed sequence of increasing Si−R bond distances can be explained by the corresponding increase in importance of the anomeric interaction between the n(p) oxygen lone pair orbitals and the σ^* orbital of the Si−R bond. This hypothesis is qualitatively confirmed by an analysis of the R−Si−O−C dihedral angles in Table 2. These dihedral angles suggest that the n(p) and σ^*(Si−R) orbitals are orthogonal in $RSi(OCH_2)_3CH$, whereas they are nearly eclipsed in trimethoxysilanes and, to a lesser extent, in $RSi(OCH_2CH_2)_3CH$. Because of conformational similarity, the latter compounds seem to be the best model tetracoordinate organosilanes for elucidation of an influence of the silicon pentacoordination on the structure and properties of silatranes. In particular, the 0.01−0.04 Å elongation of the Si−R bond distances in silatranes as compared to those in $RSi(OCH_2CH_2)_3CH$ (Table 1) reflects a well-known effect for the trigonal-bipyramidal silicon molecules, a weakness of the axial covalent bond by its interaction with the coordination bond.[5,7,8,51]

The values of the Si−R bond distances and dihedral angles R−Si−O−C in protonated compounds are collected in Tables 3 and 4, respectively. Upon oxygen protonation, the silatrane Si−R bond distances change only slightly, by less than 0.01 Å. On the other hand, protonation at oxygen has a much larger effect on the other three types of compounds, with decreases in the Si−R distance of up to 0.065 Å. An exception is R = SiH_3, for which the Si−R distances generally increase upon protonation. This is probably caused by repulsion between the positive charge on Si and the already positively charged SiH_3 group, in contrast with the negatively charged F, Cl, and CH_3 groups. Note also that the largest Si−R bond compression uniformly occurs for the trimethoxysilanes and chloro compounds, presumably because the protonated oxygen of the former compounds does not participate in the strong anomeric effect with the Si−R bond and the Si−Cl bonds of the latter compounds are quite polarizable. Protonation also causes significant conformational changes in the silatranes and trimethoxysilanes, as shown by the dihedral angles in Tables 2 and 4.

Table 4. RHF/6-31G(d) R−Si−O−C Dihedral Angles in the Oxygen-Protonated Silicon Compounds[a]

	R = F	R = Cl	R = CH_3	R = SiH_3
$RSi(OCH_2CH_2)_3N$	169.5[b]	169.5[b]	166.4[b]	164.2[b]
	(−18.8)	(−19.5)	(−19.1)	(−16.1)
	164.3	167	164.4	164.4
	(−13.6)	(−17.0)	(−17.1)	(−16.3)
	180.0	176.8	174.0	171.9
	(−29.3)	(−26.8)	(−26.7)	(−23.8)
$RSi(OCH_3)_3$	88.0[b]	88.0[b]	77.2[b]	95.3[b]
	(−22.8)	(−24.0)	(2.3)	(−11.5)
	39.9	45.7	50.0	49.0
	(25.3)	(18.3)	(29.5)	(34.8)
	53.4	44.2	164.0	57.7
	(11.8)	(19.8)	(−84.5)	(26.1)
$RSi(OCH_2)_3CH$	176.9[b]	177.0[b]	177.9[b]	178.7[b]
	(3.1)	(3.0)	(2.1)	(1.3)
	171.7	173.9	175.0	177.2
	(8.3)	(6.1)	(5.0)	(2.8)
	173.8	176	176.7	177.7
	(6.2)	(4.0)	(3.3)	(2.3)
$RSi(OCH_2CH_2)_3CH$	143.7[b]	143[b]	143.2[b]	142.4[b]
	(−2.4)	(−1.8)	(−2.2)	(−1.4)
	139	141.7	141.0	139.8
	(2.3)	(−0.5)	(0.0)	(1.2)
	146.3	142.2	144.2	145.2
	(−5.0)	(−1.0)	(−3.2)	(−4.2)

[a] All angles in degrees; H^+ attached to one oxygen atom. Δ(angle) values (=angle(neutral) − angle(cation)) are given in parentheses. [b] Including protonated O atoms.

Table 5. Oxygen Proton Affinity for Silicon Compounds[a]

	R = F	R = Cl	R = CH_3	R = SiH_3
$RSi(OCH_2CH_2)_3N$	−205.5	−203.4	−210.0	−207.8
$RSi(OCH_3)_3$	−190.9	−191.0	−203.1	−201.1
$RSi(OCH_2)_3CH$	−185.7	−187.9	−197.2	−197.9
$RSi(OCH_2CH_2)_3CH$	−191.0	−192.0	−200.7	−200.0

[a] All energies in kcal/mol.

The proton affinity data for the molecules of interest are shown in Table 5. When R = CH_3, SiH_3, the O atom proton affinity is about 10 kcal/mol larger than that for R = F, Cl. It seems reasonable that electron-donating R groups yield larger proton affinities, while electron-withdrawing R groups decrease the proton affinity. In general, silatranes have larger proton affinities than the other three types of species, by 7−20 kcal/mol. Mulliken charges on O atoms in the neutral silicon compounds are given in Table 6. For all four types of compounds considered here, these charges are larger for R = CH_3, SiH_3 than those for R = F, Cl. This is consistent with the fact that the corresponding proton affinities are larger. However, the O atom Mulliken charge in the corresponding $RSi(OCH_2CH_2)_3CH$ is more negative than that in each silatrane; therefore, Mulliken charges on

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Table 6. Mulliken Charges on O Atoms in the Neutral Silicon Compounds

	R = F	R = Cl	R = CH_3	R = SiH_3
$RSi(OCH_2CH_2)_3N$	−0.702	−0.697	−0.726	−0.731
$RSi(OCH_3)_3$	−0.689	−0.685	−0.711	−0.714
$RSi(OCH_2)_3CH$	−0.686	−0.679	−0.706	−0.710
$RSi(OCH_2CH_2)_3CH$	−0.716	−0.711	−0.734	−0.738

Table 7. Transannular Si−N Bond Distances in the Silratranes and Their O−Protonated Compounds[a]

	neutral	protonated
$FSi(OCH_2CH_2)_3N$	2.531	2.108
$ClSi(OCH_2CH_2)_3N$	2.555	2.153
$H_3CSi(OCH_2CH_2)_3N$	2.733	2.295
$H_3SiSi(OCH_2CH_2)_3N$	2.702	2.352

[a] All distances in angstroms.

Table 8. Transannular Si−C Bond Distances in $RSi(OCH_2CH_2)_3CH$ and Their Protonated Compounds[a]

	neutral	protonated
$FSi(OCH_2CH_2)_3CH$	3.336	3.381
$ClSi(OCH_2CH_2)_3CH$	3.346	3.422
$H_3CSi(OCH_2CH_2)_3CH$	3.396	3.484
$H_3SiSi(OCH_2CH_2)_3CH$	3.397	3.508

[a] All distances in angstroms.

Table 9. Mulliken Charges on the Si and N Atoms in $RSi(OCH_2CH_2)_3N$ and Their Protonated Compounds

	atom	neutral	protonated
$FSi(OCH_2CH_2)_3N$	Si	1.576	1.593
	N	−0.710	−0.753
$ClSi(OCH_2CH_2)_3N$	Si	1.403	1.427
	N	−0.709	−0.757
$H_3CSi(OCH_2CH_2)_3N$	Si	1.410	1.422
	N	−0.688	−0.747
$H_3SiSi(OCH_2CH_2)_3N$	Si	1.318	1.287
	N	−0.693	−0.743

Table 10. Proton Affinity of the Silatranes[a] **and Si−R Bond Distances in Silatranes by Fixing the Neutral Geometry Except R and Added H**[b]

	proton affinity	Si−R bond dist
$FSi(OCH_2CH_2)_3N$	−179.4	1.577
$ClSi(OCH_2CH_2)_3N$	−180.7	2.037
$H_3CSi(OCH_2CH_2)_3N$	−185.9	1.850
$H_3SiSi(OCH_2CH_2)_3N$	−184.4	2.357

[a] All energies in kcal/mol. [b] All distances in angstroms.

Table 11. Proton Affinity of the Proton Addition to the N Atoms in the Silatranes[a] **and Si−R and Transannular Si−N Bond Distances**[b]

	proton affinity	Si−R bond dist	Si−N bond dist
$FSi(OCH_2CH_2)_3N$	−201.8	1.558 (0.029)	3.330 (−0.799)
$ClSi(OCH_2CH_2)_3N$	−203.0	2.001 (0.062)	3.352 (−0.797)
$H_3CSi(OCH_2CH_2)_3N$	−212.8	1.859 (0.003)	3.395 (−0.662)
$H_3SiSi(OCH_2CH_2)_3N$	−210.8	2.347 (−0.003)	3.409 (−0.707)

[a] All energies in kcal/mol. [b] All distances in angstroms. ΔR values (=R(neutral) − R(cation)) are given in parentheses.

O atoms do not entirely explain the observed proton affinity trend.

The most important structural parameter in silatranes is the transannular Si−N distance. As shown in Table 7, the transannular Si−N bond lengths in the silatranes are shortened considerably upon protonation, by 0.4−0.5 Å. A similar trend has been noted in the neutral and protonated azasilatranes and ascribed to the strengthened interaction in the transannular Si−N bond of the protonated compounds.[15,16] In contrast, proton addition increases the transannular Si−C distances in $RSi(OCH_2CH_2)_3CH$ by 0.05−0.1 Å (see Table 8), because there is no significant transannular Si−C interaction in these neutral and protonated molecules. It is therefore likely that the greater proton affinity in the silatranes is due to the strengthened transannular Si−N interaction.

The analysis of Mulliken charges in the silatranes help to qualitatively understand electrostatic effects, particularly for transannular Si−N bonds. The Mulliken charges on the Si and N atoms in both the neutral and protonated silatranes are given in Table 9. Upon protonation, the N atom charges decrease by 0.04−0.06 electron and the Si charges decrease slightly (become more positive), except for R = SiH_3. Thus, the charge separation increases upon protonation. The decrease in the transannular Si−N bond distances is the smallest for R = SiH_3 (Table 7) due to the Si- - -N electrostatic interaction being smaller than for more electronegative R groups.

To better understand the influence of the transannular Si−N bond on the oxygen atom proton affinity and the Si−R bond distance of the silatranes, the structures of the cationic silatranes obtained by proton addition to an O atom, such that all atoms except R and the added H are fixed at their positions in the neutral structures, have been studied. As shown in Table 10, the magnitudes of these proton affinities obtained by fixing geometries are much smaller than those obtained without geometry constraints, and these Si−R bond distances are shorter than those in the neutral and protonated silatranes. Therefore, relaxation of the transannular bond plays a critical role in determining the proton affinity. Strengthening the transannular Si−N bond upon O-protonation elongates (weakens) the Si−R bond due to the cooperativity effects.

The N atom proton affinities in the silatranes and the corresponding Si−R and transannular Si−N bond distances are shown in Table 11. Comparison of Tables 5 and 11 shows that there is little difference between the O and N atom proton affinities. However, the Si−N bond distances of $[RSi(OCH_2CH_2)_3NH]^+$ are much longer than those of $RSi(OCH_2CH_2)_3N$, and the Si−R bond lengths of the N-protonated compounds are shorter than those in the O-protonated and neutral compounds due to the dramatically decreased transannular Si−N interaction when a proton is added to N. These proton affinity data support the view that O-protonation of silatranes is *kinetically* more favorable than N-protonation, all other factors being the same.[6−8,51] Associated with N-protonation are energy requirements for weakening the Si−N dative bond and for nitrogen inversion. The higher these costs, the smaller will be the difference between the nitrogen and oxygen proton affinities of silatranes. This is consistent with the observed high electrophilicity of the oxygen atoms and inertness of the

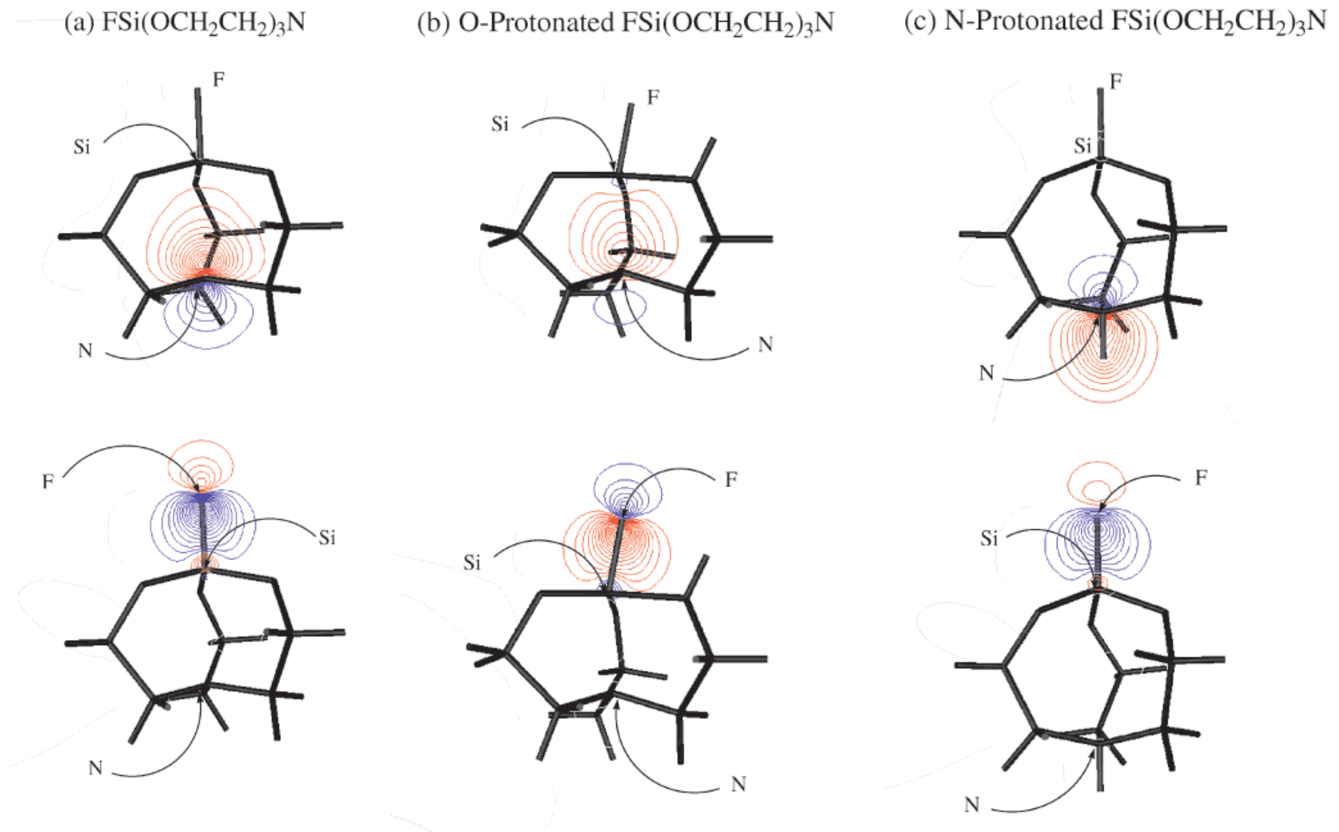

Figure 2. Boys localized orbitals for the R = F (a) silatrane, (b) O-protonated silatrane, and (c) N-protonated silatrane. The top frame shows the N lone pair, while the bottom frame shows the Si−F bond.

nitrogen to a proton or other electrophile attack for most silatranes. It is interesting to note that the silatranyl complex $Os(Si\{OCH_2CH_2\}_3N)Cl(CO)(PPh)_2$, bearing a very strong donor substituent R at the Si and a very long (weak) Si−N bond (3.000 Å), readily undergoes N-alkylation and N-protonation.[52] The calculated trend to increase the difference between the N (Table 11) and O (Table 5) proton affinities with increasing Si−N bond distance in the neutral silatranes (Table 7) is consistent with these experimental data.

A previous paper from one of us[33] used localized orbitals to show that the transannular Si−N interaction is different from that in normal Si−N bonds. The Boys localized orbitals[53] of the silicon atranes and the O-protonated and N-protonated compounds for R = F are shown in Figure 2. A Mulliken population analysis indicates that the lone pair MOs in Figure 2a,c are almost 100% N, while the lone pair MO in Figure 2b is 3% Si and 97% N. This supports the notion that the O-protonated compounds have stronger transannular Si−N bonds than do the neutral silatranes and the N-protonated compounds. These populations also suggest that protonation at O introduces some covalent character into the transannular bond. Thus, the large proton affinity in the silatranes results from the strengthened transannular Si−N bonds in the protonated species. The small but noticeable increase in Si−R distances in silatranes as compared to those in $RSi(OCH_2CH_2)_3CH$ bearing nearly the same n(p), σ^*(Si−R) anomeric effects suggests some covalent character of the Si−N bond even in the neutral silatranes.

Conclusions

The proton affinities of the silicon atranes and their analogues have been investigated as a function of substituents R. When R is an electron donor substituent, the proton affinities of the silatranes and their analogues are large. Silatranes, $RSi(OCH_2CH_2)_3CH$, possess larger proton affinities, compared with $RSi(CH_2CH_2)_3N$, $RSi(OCH_3)_3$, and $RSi(OCH_2)_3CH$. Protonation causes large conformational changes and decreases the transannular Si−N bond lengths for the silatranes. To investigate the reason for the large proton affinities of the silatranes, N atom proton affinities and the Boys localized orbitals have been studied. As a result, it is found that large proton affinities for the silatranes result from the strengthened transannular Si−N interaction for the silatranes upon the O-protonation. The silatrane Si−R bond distances are apparently determined by the degree of the anomeric effect in the R−Si−O fragment and transannular Si−N interactions.

As noted in the Introduction, whereas silatranes are difficult to hydrolyze, the opposite appears to be true for the protonated species. In future work, we will address the hydrolysis mechanisms of silatranes and their protonated analogues.

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