

spin-orbit coupling constant for Sr_2YMoO_6 ($\zeta_{\text{Mo}}=704 \text{ cm}^{-1}$) is more reduced than that for $\text{Ba}_2\text{ScMoO}_6$ ($\zeta_{\text{Mo}}=950 \text{ cm}^{-1}$), which implies that the (Mo-O) bond for Sr_2YMoO_6 is more covalent than that for $\text{Ba}_2\text{ScMoO}_6$.^{7,11-13} The spin-orbit coupling constant for free Mo^{V} ion is known to be 1030 cm^{-1} .¹⁴ This result could be explained by considering the local structure of the molybdenum site. It is expected that more acidic scandium will reduce (Mo-O) bond covalency because (B-O) bond (B=Sc, Y) competes with (Mo-O) bond by the pathway of 180° .¹⁵ According to Rietveld refinement, the bond distance between molybdenum and oxygen for $\text{Ba}_2\text{ScMoO}_6$ (2.042 (1) Å) is larger than the average value of 1.96 Å for Sr_2YMoO_6 (1.93 (4), 1.96 (4), and 2.00 (4) Å), as shown in Table 2, which supports the magnetic susceptibility fitting result. The trend of orbital reduction factor could be explained by crystal structure. Smaller reduction of κ parameter in Sr_2YMoO_6 ($\kappa=1.00$, $\kappa'=0.75$) than $\text{Ba}_2\text{ScMoO}_6$ ($\kappa=0.86$, $\kappa'=0.55$) implies the fact that distorted crystal structure disturbs effective orbital overlap between molybdenum and oxygen.

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Ab initio Nuclear Shielding Calculations for Some X-Substituted Silatranes Using Gauge-Including Atomic Orbitals

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^{13}C , ^{15}N , and ^{29}Si NMR chemical shifts have been computed for selected X-substituted silatranes (X=Cl, F, H, CH_3) using Gauge-Including Atomic Orbitals (GIAO) at the Hartree-Fock level of theory. The isotropic ^{13}C chemical shifts are largely insensitive to substituent-induced structural changes. In this study, the isotropic ^{13}C chemical shifts between 1-methyl- and 1-hydrogensilatranes by GIAO-SCF calculation at the HF/6-31G level are very similar. But the results of 1-chloro- and 1-fluorosilatranes are about 4 ppm different from the experimental values. In contrast, the isotropic ^{15}N and ^{29}Si chemical shifts and the chemical shielding tensors are quite sensitive to substituent-induced structural changes. These trends are consistent with those of the experiment. The isotropic ^{15}N chemical shift demonstrates a very clear correlation with Si-N distance. But in case of ^{29}Si the correlations are not as clean as for the ^{15}N chemical shift; the calculated variation in the ^{29}Si chemical shift is much larger.

Introduction

The isotropic chemical shift is an immensely useful para-

meter in the determination of chemical structure. This usefulness is largely due to empirical structure/chemical shift correlations. However, the problem of the understanding of the relationship between the chemical shift and molecular structure can be quite difficult. *Ab initio* calculations are

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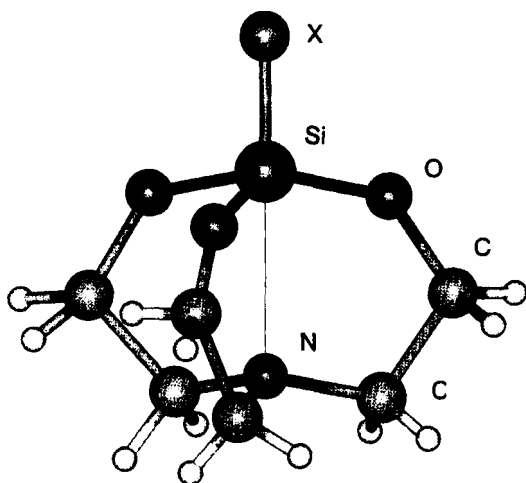


Figure 1. The Structure of X-Substituted Silatrane (X=Cl, F, H, CH₃).

now becoming affordable and accurate enough to be useful in the solution of some of this problem. A comparison of the experimental and theoretical spectra can be very useful in understanding the basic chemical shift-molecular structure relationship.

The interest in silatranes -XSi(OCH₂CH₂)₃N, 1-organyl-2,8,9-trioxa-5-aza-1-silabicyclo [3.3.3] undecanes- is due to their intriguing molecular structure, biological activity, and patterns of chemical reactivity.¹⁻³ The most intriguing aspect of this structure is the existence of and influence of a "transannular bond" between the silicon and nitrogen atoms. The transannular Si-N donor-acceptor bond (Figure 1) makes these molecules especially interesting and challenging for theoretical and experimental studies. All measured Si-N distances⁴⁻⁸ are longer than the sum of the covalent radii (187 pm or 189.5 pm),^{9,10} but shorter than the sum of the appropriate nonbonded radii (269 pm)¹⁰ and much shorter than the sum of van der Waals radii (350 pm).⁹ The Si-N distance is also variable in solution, shortening in polar solvents and lengthening in nonpolar solvents.¹¹ The key structural parameter of silatranes is the Si-N distance. The experimental results and the quantum chemical calculations show that this distance is sensitive to the nature of the substituent on the silicon atom (Table 1).

In this study, in order to correlate the chemical shift interaction with some structure or reactivity parameter we have calculated the chemical shift and the chemical shielding tensors for ¹³C, ²⁹Si, and ¹⁵N nuclei in X-substituted silatranes with particular attention to the transannular bond using the GIAO (Gauge Including Atomic Orbitals) SCF.¹² And as will be demonstrated later, the ¹⁵N and ²⁹Si chemical shifts are susceptible to substituent-induced changes in the length of this transannular bond. Thus, we pay particularly attention to the transannular bond that effects the change of chemical shift.

Computational Methods

All structure optimizations of X-substituted silatranes (X= F, Cl, CH₃, H) were performed with the TURBOMOLE program package¹³ at the 3-21G and 6-31G basis set levels

Table 1. The Geometrical Parameters of X-Substituted Silatranes

X	Basis Set	Distance		Atomic Charge	
		r _{Si-N} (pm)	r _{Si-X} (pm)	Si	N
Cl	3-21G	222.9	217.0	2.071	-0.832
	6-31G	248.3	214.4	2.047	-0.864
	X-Ray	202.3			
F	3-21G	239.1	161.5	2.091	-0.815
	6-31G	249.1	165.3	2.211	-0.866
	ED	232.4 ± 1.4			
H	X-Ray	204.2			
	3-21G	249.6	146.1	1.879	-0.792
	6-31G	264.5	146.5	1.938	-0.837
CH ₃	3-21G	263.3	187.1	2.087	-0.784
	6-31G	273.9	186.8	2.066	-0.830
	ED	245.3			
	X-Ray	217.5			

The experimental values taken from refs. 4-8.

respectively. Chemical shielding calculations were done with the optimized molecular geometries. In all calculations, 3-21G and 6-31G basis sets were employed on all atoms. The semidirect implementation of the coupled Hartree-Fock method using gauge including atomic orbitals (CHF-GIAO) at the SCF level was employed for the calculation of the isotropic ¹³C, ²⁹Si and ¹⁵N NMR shifts and their nuclear shielding constants for silatranes. It uses explicitly field-dependent basis functions as suggested by Ditchfield.¹²

Results and Discussion

We have calculated isotropic NMR shieldings and chemical shifts of ¹³C, ²⁹Si and ¹⁵N for the set of some substituent silatranes. The structural parameter of X-substituted silatranes and the isotropic ¹³C chemical shifts are tabulated in Table 1 and 2, respectively. Experimentally, the OCH₂ carbons of the silatranes framework have isotropic chemical shifts in the neighborhood of 58 ppm and the NCH₂ car-

Table 2. Comparison of Calculated^a and Experimental^b Isotopic ¹³C Chemical Shifts (in ppm) of Selected X-Substituted Silatranes

X	Basis Set	OCH ₂	NCH ₂	α
Cl	3-21G	50.07	45.07	
	6-31G	55.66	48.30	
	Exp	60.10	52.70	
F	3-21G	52.87	52.40	
	6-31G	54.81	48.88	
	Exp	58.50	51.40	
H	3-21G	53.31	50.60	
	6-31G	57.72	53.38	
	Exp	58.2	51.8	
CH ₃	3-21G	53.85	50.11	0.32
	6-31G	58.06	52.80	-0.02
	Exp	58.40	49.20	3.80
TMS				
¹³ C	3-21G	214.65		
	6-31G	208.22		

^a Shifts relative to TMS. ^b Experimental data taken from ref 16.

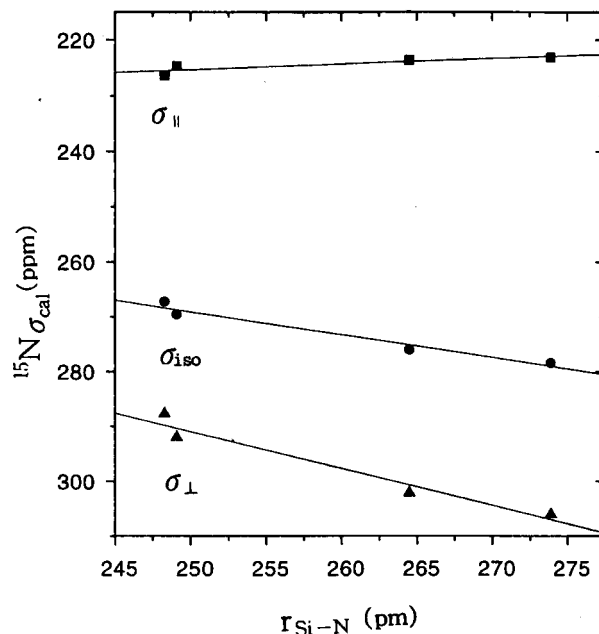
Table 3. The absolute ^{15}N NMR Shielding tensors (in ppm) of Selected X-Substituted Silatranes

X	Basis Set	σ_{\parallel}	σ_{\perp}	$\Delta\sigma^a$	para	diana	σ_{iso}
Cl	3-21G	239.18	279.80	-40.62	-60.09	326.35	266.26
	6-31G	226.31	287.67	-61.36	-65.99	333.21	267.22
F	3-21G	235.75	288.86	-53.11	-55.83	326.99	271.16
	6-31G	224.64	291.99	-67.35	-63.97	333.51	269.54
H	3-21G	234.56	298.34	-63.78	-49.67	326.75	277.08
	6-31G	223.62	302.17	-78.55	-57.66	333.64	275.99
CH_3	3-21G	233.26	303.70	-70.44	-46.49	326.71	280.22
	6-31G	223.14	306.06	-82.92	-55.25	333.67	278.42

^a $\Delta\sigma = \sigma_{\parallel} - \sigma_{\perp}$

bons have isotropic chemical shifts of approximately 51 ppm, as shown in Table 2. These assignments and the peak assignments for the substituents bound to the silicon atom are based upon solution-state ^{13}C NMR studies¹⁴ and variable-field high-resolution solid-state ^{13}C NMR results.¹⁵ Also, all of calculated isotropic chemical shifts for the OCH_2 carbons of the silatranes framework are larger than those of NCH_2 . The isotropic chemical shifts calculated at the HF level using 6-31G basis sets are in agreement with those of solution and solid state ^{13}C NMR studies, particularly of 1-methyl and 1-hydrogensilatranes. Their assignment, therefore, was verified by calculated isotropic ^{13}C chemical shifts, although there were some assignment problems for the ^{13}C spectra in both the solution and solid NMR experiments.^{14,15} As with reported solution-state ^{13}C NMR studies,^{14,15} the isotropic ^{13}C chemical shift of silatranes in the solid-state¹⁶ appears to be nearly independent of the Si-N distances (or substituents). In this study, the isotropic ^{13}C chemical shifts between 1-methyl- and 1-hydrogensilatranes by GIAO-SCF calculation at the HF/6-31G level are very similar. This trend is consistent with that of the experiment. But the results of 1-chloro- and 1-fluorosilatranes are about 4 ppm different from the experimental values as shown in Table 2. The reason for this is that they are strongly correlated molecules composed of electronegative atoms. It is well-known that the shielding tensor is very sensitive to the quality and size of the basis set used^{17,18}. Thus, to make comparison with the experimental values precisely, we need to use larger basis sets including polarization functions. To increase the basis set substantially would have required more computer resource than we had available.

In contrast to the isotropic ^{13}C chemical shift, the isotropic ^{15}N chemical shift demonstrates a very clear correlation with Si-N distance. The ^{15}N NMR shielding tensors of selected X-substituted silatranes, as well as the isotropic ^{15}N chemical shifts, by GIAO-SCF calculation at the HF/3-21G and HF/6-31G levels are given in Table 3. Close inspection of Table 3 reveals the isotropic ^{15}N chemical shift and chemical shielding tensors indeed exhibit modest dependencies on substituent variation. The effect of the substituent on the structure of a silatrane is perhaps most directly seen in Si-N distance. More electronegative substituents give a silatrane geometry with a smaller Si-N distance than those characteristic of silatranes with less electronegative substituents. For the set of silatranes in this study, we can see from Table 3 that, as the Si-N distance decreases, the

**Figure 2.** Correlation curves for some ^{15}N chemical shift parameters vs $r_{\text{Si-N}}$. All of the data were calculated using GIAO at the HF/6-31G level.

absolute isotropic ^{15}N chemical shift decreases, with changes from 278.42 to 267.22 ppm for the methyl and chloro derivatives, respectively. The larger absolute calculated value means more shielding. This trend is consistent with that of experiments.^{16,19}

Since the isotropic shielding, usually observed in the liquid state, is simply the mean of the component of the ^{15}N chemical shift tensor, $\sigma_{\text{iso}} = 1/3(\sigma_{xx} + \sigma_{yy} + \sigma_{zz})$, other combinations or chemical shielding tensors, might be expected to follow different trends. The shielding anisotropy, *i.e.*, the individual tensor components of the shielding tensor, should be even more sensitive to the quality of the quantum-chemical method used than the isotropic shielding constant. Here, we define the shielding anisotropy $\Delta\sigma$ as the difference between the parallel and the orthogonal principle components:¹⁸ ($\Delta\sigma = \sigma_{\parallel} - \sigma_{\perp}$). Changes in $\Delta\sigma$ as well as in the ^{15}N isotropic chemical shifts are due primarily to changes in the value of σ_{\perp} , which varies between 306.06 and 287.67 ppm at the HF/6-31G level, with σ_{\parallel} being fairly constant and exhibiting no easily recognized dependence on substituent. Figure 2 graphically depicts the plots of the various ^{15}N chemical shift parameters (σ_{iso} , σ_{\parallel} , σ_{\perp}) versus Si-N distance. We recognize a very clear correlation for σ_{iso} , σ_{\perp} , σ_{\parallel} . As the Si-N distance decreases, the absolute chemical shielding anisotropy calculated using the GIAO-SCF at the HF/6-31G level changes in magnitude, from -82.92 to -61.36 ppm for the ethyl and chloro derivatives, respectively. Usually, the shielding is split up into the paramagnetic and diamagnetic contributions: $\sigma = \sigma_p + \sigma_d$. The major contribution to isotropic shift is the diamagnetic part as shown in Table 3. But the diamagnetic parts are nearly constant at about 326 ppm and 333 ppm at the HF/3-21G and HF/6-31G level, respectively while the paramagnetic parts clearly show dependences on substituent variation.

The chemical shielding tensor for ^{29}Si yields a more strik-

Table 4. The Absolute ^{29}Si NMR Shielding tensors (in ppm) of Selected X-Substituted Silatranes

X	Basis Set	σ_{\parallel}	σ_{\perp}	$\Delta\sigma^a$	para	diana	σ_{iso}
Cl	3-21G	541.50	564.97	-23.47	-303.63	860.78	557.14
	6-31G	502.94	509.76	-6.82	-358.23	865.71	507.48
F	3-21G	567.34	607.58	-40.24	-266.08	860.25	594.17
	6-31G	518.15	550.92	-32.77	-324.53	863.43	540.00
H	3-21G	558.96	567.52	-8.56	-297.32	862.00	564.67
	6-31G	521.04	516.61	4.43	-348.61	866.70	518.09
CH_3	3-21G	586.89	554.49	32.4	-295.82	861.11	565.29
	6-31G	538.46	480.26	58.2	-366.16	865.82	499.66

$$^a \Delta\sigma = \sigma_{\parallel} - \sigma_{\perp}$$

ing dependence on the substituent variation than that for ^{15}N because the substituent is directly attached to silicon. Although the correlations are not as clean as for the ^{15}N chemical shift, the calculated variation in the ^{29}Si chemical shift is much larger. The principal elements of the ^{29}Si chemical shielding tensors, as well as the isotropic chemical shifts, are given in Table 4. Also, Figure 3 graphically depicts plots of various ^{29}Si chemical parameters versus Si-N distance. The correlations are not as clear as those discussed above for the ^{15}N data. Thus, the substituent effect on the ^{29}Si chemical shift can be viewed as having three types of origins: i) the geometry-structure effect associated with variations in the $\angle\text{OSiO}$ bond angle; ii) the substituent effect due to variations in the N-Si transannular interaction; and iii) the direct substituent effect. This third type of effect is, of course, absent in the ^{15}N case, so one can expect that the interpretation of chemical shift data in terms of the transannular bond should be more difficult for ^{29}Si than for ^{15}N . In addition, 1-chloro- and 1-fluorosilatranes are strongly correlated molecules that have electronegative atoms attached

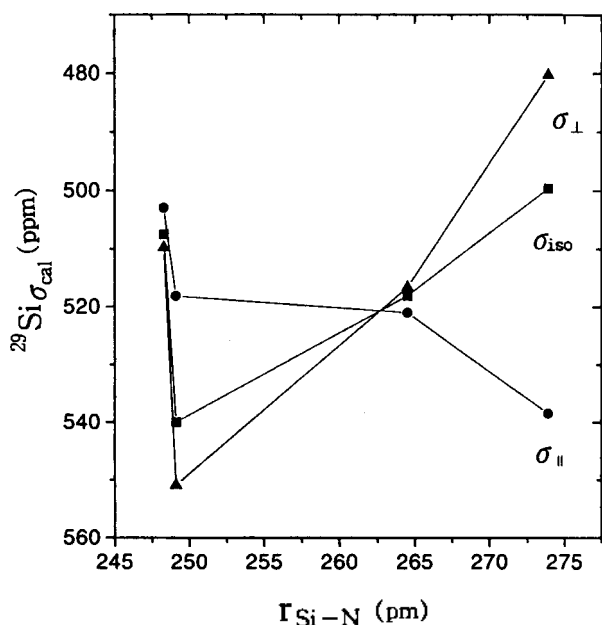


Figure 3. Correlation curves for some ^{29}Si chemical shift parameters vs $r_{\text{Si-N}}$. All of the data were calculated using GIAO at the HF/6-31G level.

directly to silicon. Nevertheless, one can search for correlations between nmr parameters and Si-N distance besides 1-chlorosilatranes in Figure 3. In order to explain the large deviation of 1-chlorosilatranes, we need to consider the influence of a "transannular bond" between the silicon and nitrogen atoms. The shortest Si-N distance known in the solid phase was measured in 1-chlorosilatranes.⁸ This fact is surprising at first sight, because on the basis of the electronegativities of halogen atoms, a shorter Si-N distance is expected in 1-fluorosilatranes than in 1-chlorosilatranes. One possible explanation²⁰ for the opposite experimental results is that the N-Si-X interaction in silatranes may be better modeled by an intramolecular S_N2 reaction, in which the N is approaching the Si and the group on the opposite side is leaving. The chlorine is a better leaving group than the fluorine, and this may explain the shorter Si-N distance. The structural changes of the silatranes skeleton caused by the large Si-N distance changes are shown in Table 1. In the S_N2 reaction model, it is expected that as the N gets closer to the silicon atom, the Si-Cl bond lengths increases. This might be one of the reasons that the isotropic ^{29}Si chemical shift and shielding tensor constants for 1-chlorosilatranes are larger than for 1-fluorosilatranes. In order to interpret for this effect on nmr parameters, we need to adopt larger basis sets than those in this study or the other theory,^{21,22} e.g., GIAO-MP2 and DFT theories because the shielding tensor is very sensitive to the quality and size of the basis set used.^{17,18} 1-chlorosilatranes and 1-fluorosilatranes are strongly correlated molecules composed of electronegative atoms as mentioned previously.

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Reaction of Gas-Phase Atomic Hydrogen with Chemisorbed Hydrogen Atoms on an Iron Surface

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The reaction of gas-phase atomic hydrogen with hydrogen atoms chemisorbed on Fe(110) surface is studied by use of classical trajectory procedures. Flow of energy between the reaction zone and bulk solid phase has been treated in the generalized Langevin equation approach. A London-Eyring-Polanyi-Sato energy surface is used for the reaction zone interaction. Most reactive events are found to occur in strong single-impact collisions on a subpicosecond scale via the Eley-Rideal mechanism. The extent of reaction is large and a major fraction of the available energy goes into the vibrational excitation of H₂, exhibiting a vibrational population inversion. Dissipation of reaction energy to the heat bath can be adequately described using a seven-atom chain with the chain end bound to the rest of solid. The extent of reaction is not sensitive to the variation of surface temperature in the range of T_s=0-300 K in the fixed gas temperature, but it shows a minimum near 1000 K over the T_g=300-2500 K.

Introduction

An understanding of energy transfer among various modes in the interaction system on the surface is a prerequisite for a detailed appreciation of reactive events that follow. Many studies have thus addressed the dynamics of trapping and energy transfer on the surface and the subsequent desorption of the product molecule in gas-surface reactions.¹⁻³ Among others, it may be of special interest to observe direct reactive interactions of gas-phase reactants with atoms or molecules chemisorbed on a metal surface to form a molecule that immediately desorbs from the surface. This so called the Eley-Rideal (ER) mechanism is less common than the Langmuir-Hinshelwood (LH) mechanism in which both reactants are adsorbed and in thermally equilibrium with the surface before the reaction occurs.^{1,4} In the ER mechanism, the difference between the exothermicity of the gas-phase reaction and the heat of chemisorption is large. Thus elucidating the dynamics of intramolecular energy flow in the trapped state formed from an active gas-

phase reactant containing excess energy and the distribution of the excess energy among various motions of the product has been an important problem in gas-surface reactions.⁴⁻²²

Since chemisorption energies for H on a metal surface lie in the range of 2-3 eV,^{23,24} the H-metal surface is an attractive reactive site to produce highly-excited products when the gas reactant to H attraction greatly exceeds this range. Rettner *et al.*^{12,13} studied the reaction of gas phase H (D) with D(H) adsorbed on Cu(111). They showed the translational and internal energy and angular distribution of the HD product representing their sensitivity to the incident energy as well as to which isotope was incident. The spread of the translational energy distribution was found to range from zero to about the maximum available energy that is released in the ER mechanism for this system. Gates and co-workers have examined the reaction between gas phase H (D) and D(H) adsorbed on Si(100) and Si(111), and have suggested the ER mechanism based on kinetics studies and measured activation energies.^{14,15} Kratzer and Brenig¹⁶ performed 2D quantum mechanical calculations for the ER reaction of H atoms incident on H chemisorbed to W. They found that the H₂ product is formed in high vibrational

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