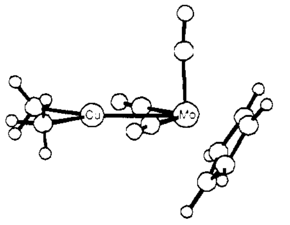
plex.[11] Although the authors acknowledged the existence of a short metal–metal bond distance, their EHMO study failed to account for its presence. Their study concluded that the metal fragments were held together by a combination of relatively weak Ni–W and C–Ni interactions. Our calculations show that while this is true for the Cu–Mo analogue, **4**, the Ni complex contains the strong interactions characteristic of the Rh complex, **5**. The MO diagram from the EH study illustrated that the Ni fragment orbitals were sufficiently destabilized to allow the interaction of the Ni 3d orbitals with the "t_{2g}" set of the tungsten fragment (similar to the Rh 4d/Mo "t_{2g}" set interaction seen in Figure 5 although to a more limited extent). The key interaction that is present in both complexes is the metal–metal interaction of π symmetry. The additional electron present in the Ni complex singly occupies the metal–metal π antibonding orbital 27a′ which therefore only partially cancels the corresponding bonding interaction. Taken together with the interaction of σ symmetry (an interaction not shown in the EHMO diagram) the total direct metal–metal interaction possesses a bond order of roughly 1.5, which is clearly a significant interaction. Strong back donation of electron density to the bridging carbonyls further contributes to the short metal–metal bond distance that is observed in the complex.

(tmed)CuMo(CO)$_3$(η^5-C$_5$H$_5$). On the basis of the bonding descriptions presented so far, we might now ask what would be expected from the interaction of a $Mo(CO)_3(\eta^5\text{-}C_5H_5)^-$ fragment with $Cu(tmed)^+$, a fragment less sterically bulky than $M(PPh_3)_2^+$. The most obvious expectation might be that the Cu, N, N plane would approach the Mo fragment in the plane of two carbonyl ligands, **14**, to take advantage of the destabilized Cu–N antibonding HOMO and interact with the virtual carbonyl π^* orbitals.



14

The crystal structure reported by Doyle and Eriksen,[10] **6**, shows instead that the Cu fragment approaches Mo from below the plane containing the two carbonyls such that the final geometry of the Mo fragment resembles the four-legged piano stool. The Cu–Mo bond distance of 2.59 Å is substantially shorter than that found in $(PPh_3)_2CuMo(CO)_3(\eta^5\text{-}C_5H_5)$, **4**. Our calculations suggest that if steric effects are not taken into account, the most favorable geometry is the coplanar orientation, **14**. In this geometry the overlap of the Cu–L antibonding orbital with the bridging CO π^* orbitals is much larger than that in the four-legged piano stool geometry (0.121 vs 0.086) allowing twice as much electron density to be transferred from the copper fragment to the carbonyls. The steric effects of the tmed group, however, are significant and the complex is forced to swing the tmed group down below the plane of the bridging carbonyls. The back donation to the carbonyls in **6** is too small (it is similar in magnitude to that seen in **4**) to be a significant factor in the short Cu–Mo bond distance. The short Cu–Mo bond distance is instead the result of the lower energy Cu sp_z hybrid interacting with the Mo t_{2g} set. The change from phosphines to amines coordinated to Cu changes the relative amount of Cu 4s and 4p character in the hybrid from one-third 4s and two-thirds 4p to two-thirds 4s and one-third 4p, respectively. The greater 4s character in the amine-coordinated Cu sp_z hybrid is responsible for the lower energy of this orbital, the greater interaction with the Mo t_{2g} set, and hence the short metal–metal bond.

Conclusion

We have shown that heterobimetallic carbonyl complexes with coordinatively unsaturated late transition metal centers—centers not normally thought of as good electron density donors—are capable of donating electron density back to the virtual carbonyl π^* orbitals of an adjacent metal center. For the molecules studied in this work, the back donation was accompanied by a dative metal–metal interaction involving the transfer of electron density from the coordinatively saturated fragment to the LUMO of unsaturated fragment.

Acknowledgment. The authors thank the Robert A. Welch Foundation (Grant No. A-648) and the National Science Foundation (Grant No. CHE 86-19420) for their support.

The Silanoic Acid Dimer $(HSiOOH)_2$: A Simple Molecular System Incorporating Two Very Strong Hydrogen Bonds

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Contribution CCQC No. 29 from the Center for Computational Quantum Chemistry, School of Chemical Sciences, University of Georgia, Athens, Georgia 30602. *Received June 21, 1988*

Abstract: Ab initio molecular electronic structure theory has been used to predict and characterize the remarkable species $(HSiOOH)_2$. The dissociation energy to two silanoic acid monomers is predicted to be D_0 = 25 kcal/mol, twice that observed for the well-characterized valence isoelectronic formic acid dimer. Fundamental vibrational frequencies allowed in the infrared spectrum are predicted as follows: ν(O–H) = 2905 cm^{-1}, ν(Si=O) = 1229 cm^{-1}, and ν(Si–O) = 955 cm^{-1}. By avoiding formal double bonds to silicon, a much lower energy cyclic isomer of the silanoic acid dimer may be found, and this structure is also theoretically characterized.

An important new direction in chemistry for the past decade or more has been the exploration of molecules in which one or more carbon atoms from a hydrocarbon compound has been replaced by silicon. One such obvious example is silanoic acid, HSiOOH, the silicon analogue of formic acid, HCOOH. The silanoic acid molecule was first observed in the laboratory by Withnall and Andrews,[1,2] using the technique of matrix isolation infrared spectroscopy. The observations of Withnall and Andrews were bolstered by the ab initio quantum mechanical predictions

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[†] Robert S. Mulliken Graduate Fellow.

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0002-7863/89/1511-1569$01.50/0

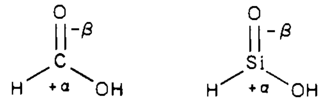
of Dixon and Gole[3] for silanoic acid.

Subsequently, Wlodek, Fox, and Bohm[4] have apparently made the second experimental observation of silanoic acid. With the selected-ion flow tube (SIFT) technique they formed $SiH_3O_2^+$ ions, from which proton transfer to a molecule M or recombination with electrons appears to lead to the neutral silanoic acid. Very recently, kinetic studies by Chu, Beach, Estes, and Jasinski[5] have provided further evidence of the possible importance of silanoic acid. In their studies of the reaction

$$SiH_2 + O_2 \rightarrow \text{products} \qquad (1)$$

the Jasinski group concludes[5] that an adduct is involved and that silanoic acid is the most plausible candidate. In the more practical realm of solution chemistry, Eaborn and co-workers[6] have recently provided convincing evidence for CH_3SiOO^-, a derivative of silanoic acid.

The analogy between formic acid and silanoic acid leads to an intriguing new possibility when one considers the polarity of the two molecules:



(2)

Simple qualitative ideas argue that carbon is significantly more electronegative than silicon. In Pauling's 1970 freshman text, he gives 2.5 and 1.8 for the electronegativities of carbon and silicon. This difference of 0.7 in electronegativities is substantial when one realizes that the full range of Pauling's electronegativity scale is from 0.7 (cesium) to 4.0 (fluorine).

The experimental dipole moment of formic acid is 1.41 D.[7] The electronegativity argument suggests that the positive charge α on the silicon (2) in silanoic acid should be greater than the analogous charge α on the carbon atom in formic acid. This should mean that the dipole moment of silanoic acid will be significantly larger than that of formic acid. Here, we have predicted the dipole moment of silanoic acid using ab initio self-consistent-field (SCF) theory. Three basis sets have been used: (a) minimum basis set (MBS), specifically STO-3G,[8] (b) double-ζ (DZ),[9] and (c) double-ζ plus polarization (DZ+P).[10] The predicted silanoic acid dipole moments are 2.48 (MBS), 3.83 (DZ), and 3.39 (DZ+P) D. It is clear that the dipole moment of silanoic acid is more than twice as large as that of formic acid.

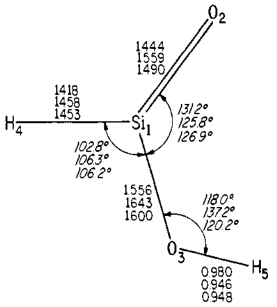
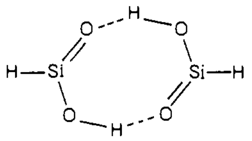


Figure 1. Predicted equilibrium geometries for the silanoic acid monomer. Bond distances are given in angstroms. Three levels of self-consistent-field (SCF) theory are given for each geometrical parameter. The top entry is from minimum basis set [MBS + d(Si)] SCF theory, the middle from double-ζ (DZ) SCF theory, and the bottom from double-ζ plus polarization (DZ+P) SCF theory.

The magnitude of the dipole moment of silanoic acid has implications for the stability of the silanoic acid dimer. In turn, the silanoic acid dimer



(3)

is of interest in light of the great scientific importance of the formic acid dimer. It is not an exaggeration to state that the formic acid dimer is more fully characterized than any other molecular system incorporating two hydrogen bonds. The latter statement is supported by an abundance of experimental[11-34] and theoretical[35-54] papers. If one accepts the thesis that hydrogen bonding may be qualitatively explained in terms of classical electrostatic ideas,[55]

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then the binding energy of the silanoic acid dimer should be greater than that of the formic acid dimer.

A larger binding energy for the silanoic acid dimer would be significant, since the formic acid dimer, with a dissociation energy[22,27,32-34] $D_0 \sim 12$ kcal/mol, is already strongly bound for a hydrogen-bonded system. In fact Bauer and co-workers[33] note that in the gas phase at 300 and 310 K the ratios of formic acid dimer to monomer are 1.1 and 1.6, respectively, for densities $n = 10^{-7}$ mol/cm^3. That is, under these conditions the dimer is the more abundant species. Under similar conditions to those explored by Bauer,[33] the silanoic acid dimer might be vastly more abundant than the monomer, assuming that neither is highly reactive.

The purpose of this research, then, is to pursue the simple qualitative prediction that the silanoic acid dimer might contain two uniquely strong hydrogen bonds. Although the present work is entirely theoretical, it is hoped that experimental studies will follow in the near future.

Theoretical Details

From the outset, this research attempted to employ theoretical methods analogous to those used in the recent formic acid dimer study of Chang, Yamaguchi, Miller, and C.Y.M.S.[53] All theoretical predictions were made at the ab initio self-consistent-field (SCF) level of theory. Following C.Y.M.S. and as anticipated by our introductory remarks on the dipole moment of silanoic acid, three basis sets of contracted Gaussian functions were used:

(a) Minimum basis set [MBS + d(Si)]. This set includes one 1s function on each hydrogen atom, 1s, 2s, $2p_x$, $2p_y$, and $2p_z$ functions on each oxygen atom, and 1s, 2s, $2p_x$, $2p_y$, $2p_z$, 3s, $3p_x$, $3p_y$, and $3p_z$ functions on each silicon atom. Actually, the minimum basis set is slightly extended in this work to include a set of six d-like functions ($\zeta = 1.0$) on silicon. For the silanoic acid dimer $(HSiOOH)_2$, the MBS + d(Si) includes 54 contracted Gaussian functions. The particular functions chosen were the standard STO-3G basis sets of Pople and co-workers.[8] The Si atom d function is a linear combination of three primitive Gaussians ($\alpha = 1.6014, 0.5021, 0.1956$; $c = 0.16866, 0.58480, 0.40568$).

(b) Double-ζ (DZ) basis set. These are the DZ sets of Huzinaga and Dunning.[9] For hydrogen the (4s/2s) set[9] is scaled by a factor of 1.2; i.e., all primitive Gaussian orbital exponents are multiplied by $(1.2)^2 = 1.44$. For oxygen the technical designation[10] is O(9s5p/4s2p). For silicon, the (11s7p/6s4p) basis of Dunning and Hay[56] was chosen to complement the H and O basis sets. The DZ basis set includes 84 contracted Gaussian functions for $(HSiOOH)_2$.

(c) Double-ζ plus polarization (DZ+P) basis set. In this set, polarization functions were added to all atoms. Orbital exponents were chosen as $\alpha_p(H) = 0.75$, $\alpha_d(O) = 0.85$, and $\alpha_d(Si) = 0.50$. All six components of the d-like functions (x^2, y^2, xy, xz, and yz multiplied by $e^{-\alpha r^2}$) were included in this basis set. For the silanoic acid dimer, the DZ+P basis thus includes 132 contracted Gaussian functions.

Molecular Structures

The three theoretical equilibrium geometries for the silanoic acid monomer are seen in Figure 1. Our most reliable (DZ+P) structure for the monomer is very similar to the earlier DZ+P SCF structure of Dixon and Gole.[3] The latter authors used slightly different polarization function orbital exponents and report an equilibrium total energy of −439.896 44, very close to the $E = -439.90028$ found in the present research. We defer to Dixon and Gole's discussion of the monomer structure.[3]

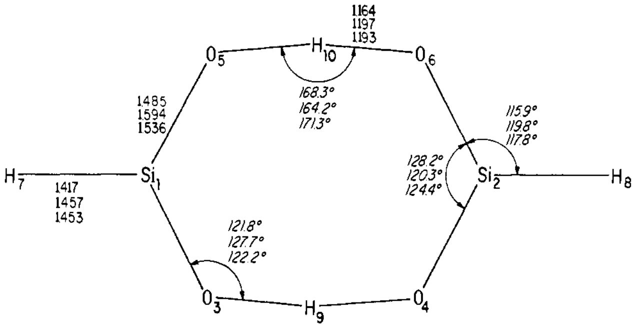

Figure 2. D_{2h} stationary point geometries for the silanoic acid dimer. All bond distances are in angstroms. For each geometrical parameter the top, middle, and bottom entries refer to MBS + d(Si) SCF, DZ SCF, and DZ+P SCF levels of theory, respectively. As discussed in the text, these structures are in fact the transition state for the double proton transfer, and this reality is reflected at the two higher levels of theory. However, MBS + d(Si) SCF theory incorrectly predicts that this structure is the equilibrium geometry for the silanoic acid dimer.

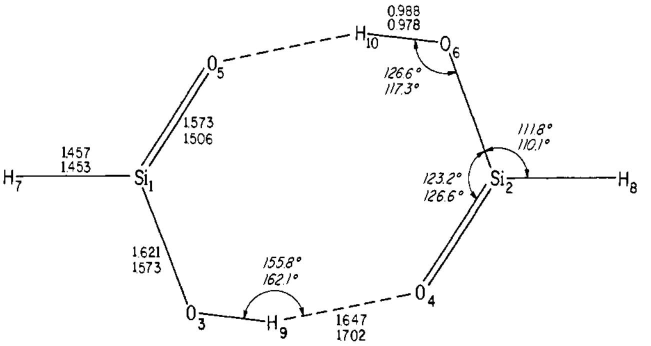

Figure 3. Predicted equilibrium geometries for the silanoic acid dimer. Bond distances are given in angstroms. The upper entry for each geometrical parameter was obtained from DZ SCF theory and the lower entry from DZ+P SCF theory. Note in the text that at the MBS + d(Si) SCF level of theory there is *no* equilibrium geometry in this region of conformation space.

The early stages of this research yielded a startling theoretical result. At the MBS + d(Si) SCF level of theory, the equilibrium structure of the silanoic acid dimer had D_{2h} symmetry. That is, the structure known for formic acid dimer to be the transition state for double proton transfer is in fact the silanoic acid equilibrium geometry (MBS + d(Si) SCF). If true, this would have been indicative of a completely new type of chemical bond, unlike any of the multitude of known carboxylic acid dimers. The MBS + d(Si) SCF equilibrium geometry for $(HSiOOH)_2$ is seen in Figure 2.

However, the two more complete basis sets (DZ SCF, DZ+P SCF) show that MBS+ d(Si) SCF theory is misleading with respect to the structure of the silanoic acid dimer. In fact, the structure depicted in Figure 2 is the transition state for double proton transfer. (The aberrant behavior of MBS + d(Si) SCF is not altogether surprising, yet it is disappointing, since this simple level of theory has been successful in earlier studies of a range of hydrogen-bonding situations. Most analogously, for the formic acid dimer C.Y.M.S. found MBS SCF theory to do an excellent job of reproducing the much more reliable DZ+P SCF predictions.[53] Clearly, these results suggest some caution in the future use of MBS + d(Si) SCF theory for the study of similar hydrogen-bonded systems.)

The appearance of the spurious MBS + d(Si) SCF D_{2h} equilibrium geometry, however incorrect for $(HSiOOH)_2$, does spur one on to some possible speculations. Perhaps one might yet find a true D_{2h} minimum for a related dimer. Ge and Sn have the same Pauling electronegativities[6] as Si, so the dimers $(HGeOOH)_2$ and $HSnOOH)_2$ are obvious candidates. Other ways of rearranging the charge distribution would include $(HCOSH)_2$, $(HCSOH)_2$,

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Table I. Summary of Total Energies (hartrees) and Relative Energies (kcal/mol) for the Silanoic Acid Monomer and Dimer

	MBS + d(Si)	DZ	DZ+P
monomer	-434.62486	-439.76001	-439.90028
D_{2h} dimer	-869.32175[a]	-879.55817	-879.82794
C_{2h} dimer		-879.57036	-879.84415
D_e for dimerizn	45.2	31.6	27.4
ZPVE corrn	-1.4	-2.8	-2.1
D_0 for dimerizn	43.8	28.8	25.2
barrier height		7.6	10.2

[a] For MBS + d(Si), D_{2h} is a minimum.

$(HSiOSH)_2$, and $(HSiSOH)_2$, all of the above involving the substitution of a sulfur atom for one of the oxygen atoms. Yet other possibilities might include species such as $(FSiOOH)_2$, $(HOSiOOH)_2$, and $(LiSiOOH)_2$. A qualitative theoretical sweep of such possible structures might be highly informative. Preliminary results indicate that the dimerization energy of (FSiOOH) is about the same as that of the parent silanoic acid, while that of (LiSiOOH) may be less.

The true equilibrium geometry of the silanoic acid dimer must be qualitatively similar to the DZ SCF and DZ+P SCF predictions seen in Figure 3. We first discuss the structural changes within the HSiOOH moiety upon dimerization. There is no shift (to within 0.001 Å, DZ+P SCF) between the monomer and dimer Si-H distances. The O-H distance increases by 0.030 Å upon dimerization. The Si-O single-bond distance decreases by 0.027 Å, while the Si=O double-bond distance increases by 0.016 Å. Overall, the difference between silicon-oxygen single- and double-bond distances is 0.110 Å for the monomer but only 0.067 Å for the dimer. Clearly, there is a shift toward a measure of "conjugation" for the dimer. The O—Si=O bond angle changes by only 0.3° (DZ+P SCF) in going from monomer to dimer, but the monomer H-O-Si angle is decreased by 2.9° upon dimerization.

In comparing the silanoic acid and formic acid dimers, the most sensitive and yet most analogous comparisons ought to be for the H···O hydrogen-bonded distances. These two distances are 1.702 Å for silanoic acid 1.818 Å for the formic acid dimer,[53] both at the DZ+P SCF level of theory. The shorter hydrogen-bonding distance for the silanoic acid dimer is consistent with our original hypothesis that it should contain stronger hydrogen bonds than does the formic acid dimer. Another direct comparison is the O-H···O hydrogen-bonding angles. These angles are 162.1° for the silanoic acid dimer but only 172.7° for the formic acid dimer. For comparison for the D_{2h} transition states the DZ+P SCF dimer method predicts O-H-O angles of 179.3° (formic acid) and 171.3° (silanoic acid dimer).

Dissociation Energy of Silanoic Acid. Table I is a summary of the predicted energetics for the silanoic acid dimer. The minimum basis set results are virtually meaningless, since MBS SCF theory predicts a qualitatively wrong equilibrium geometry, as discussed in the previous section. This is regrettable, since MBS SCF theory does a reasonable job of predicting the energetics for the formic acid dimerization.[53]

The DZ SCF and DZ+P SCF dimerization energies D_e are 31.6 and 27.4 kcal, respectively, for $(HSiOOH)_2$. The larger hydrogen bond energies for the less complete DZ basis set are typical. The analogous DZ SCF and DZ+P SCF predictions for formic acid are 19.3 and 14.3 kcal, respectively. Thus, the motivating hypothesis for this study is confirmed.

Within the harmonic approximation, the zero-point vibrational energies (ZPVE) of monomer and dimer have been evaluated; as expected, the dimer (with six additional vibrational degrees of freedom) has a greater ZPVE than does two monomers. These differences

$$\Delta\mathrm{ZPVE} = 2\mathrm{ZPVE(monomer)} - \mathrm{ZPVE(dimer)} \qquad (4)$$

are -2.8 kcal (DZ) and -2.1 kcal (DZ+P). Therefore, the predicted dimerization energies D_0 (including zero-point vibrational energies) are 28.8 kcal (DZ) and 25.2 kcal (DZ+P). For comparison the analogous formic acid predictions are 16.8 kcal (DZ) and 12.3 kcal (DZ+P).[53] The reliability of the DZ+P SCF predictions for formic acid is confirmed by the experimental D_0 values, which fall in the range 13 ± 2 kcal.[22,27,32-34]

Table II. Harmonic Vibrational Frequencies (cm^{-1}) and IR Intensities (km/mol) for the HSiOOH Monomer

		DZ		DZ+P		
		freq	int	freq	int	assignt
A′	ω_1	4203	236	4181	193	O—H
	ω_2	2428	76	2459	74	Si—H
	ω_3	1216	188	1395	247	Si=O
	ω_4	962	84	998	57	Si—O
	ω_5	913	95	985	196	H—Si—O
	ω_6	681	269	867	109	H—O—Si
	ω_7	342	108	371	106	O—Si=O
A″	ω_8	614	2	674	65	H—Si—O oop
	ω_9	518	469	522	261	H—O—Si oop

Table III. Comparison of Theoretical and Experimental[1,2] (in Parentheses) Vibrational Frequencies for Isotopic Variants of the Silanoic Acid Monomer[a]

	$HSi^{16}O^{16}OH$	$HSi^{18}O^{18}OH$	$DSi^{16}O^{16}OD$	$D^{18}O^{18}OD$
ν(Si=O)	1395 (1249)	1350 (1211)	1387 (1245)	1342 (1210)
ν(Si—O)	998	960	976 (891)	938 (866)

[a] All theoretical predictions are harmonic vibrational frequencies ω determined with the DZ+P SCF method. The experimental frequencies are the anharmonic fundamentals ν.

The ab initio prediction that the dimerization energy D_0 should be about twice as large for silanoic acid (25.2 kcal) as for formic acid (12.3 kcal) should be qualitatively solid. Thus, following the analysis of Borchardt, Caballero, and Bauer[33] for formic acid, the abundance of silanoic acid dimer should far outweigh that of the silanoic acid monomer even at low densities. The two hydrogen bonds in silanoic acid dimer are seen to be very strong, with an average hydrogen bond energy of 12.6 kcal/mol. This may be compared with that of the classic water dimer hydrogen bond, where the dissociation energy is of the order of 4 kcal/mol.[57]

Infrared Spectra. As noted in the introduction, the silanoic acid monomer was first observed via matrix isolation infrared spectroscopy by Withnall and Andrews.[1,2] It would not be surprising to see $(HSiOOH)_2$ first observed by the same technique. Therefore, having established the extraordinary strength of the two hydrogen bonds in the silanoic acid dimer, the most important theoretical step toward the identification of this dimer is the prediction of vibrational frequencies.

The silanoic acid monomer results are summarized in Table II. The second highest intensity (247 km/mol) is predicted for the Si=O stretch, and the Si=O stretch is the only fundamental identified by Withnall and Andrews.[1,2] This correspondence supports an increasing number of reports[58] that ab initio IR intensities can be very helpful in understanding which features of the IR spectra are present and which are absent.

By examining three other isotopic variants of HSiOOH (^{18}O, H; ^{16}O, D; ^{18},o, D), Withnall and Andrews[1,2] were able to identify a total of six IR fundamentals. Given the quadratic force constants, it is a trivial matter to predict harmonic vibrational frequencies for isotopically substituted molecules, and this is done in Table III. The DZ+P SCF harmonic frequencies for the Si=O stretch lie above the observed fundamentals by 11.7% (^{16}O, H), 11.5% (^{18}O, H), 11.4% (^{16}O, D), and 10.9% (^{18}O, D). For the two observed Si-O single-bond stretching frequencies the analogous differences are 9.5% (^{16}O, D) and 8.3% (^{18}O, D).

Table IV gives predicted IR spectral parameters for the silanoic acid dimer. The assignment of fundamental vibrational frequencies follows that of C.Y.M.S.[53] The A_g and B_g modes $\nu_1 - \nu_{12}$ have identically zero infrared intensities within the double harmonic approximation to the vibrational problem and will not

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(57) Curtiss, L. A.; Fruip, D. J.; Blander, M. *J. Chem. Phys.* **1973**, *71*, 2703.

(58) See, for example: Lee, T. J.; Bunge, A.; Schaefer, H. F. *J. Am. Chem. Soc.* **1985**, *107*, 137.

Table IV. Harmonic Vibrational Frequencies (cm^{-1}) and IR Intensities (km/mol) for the Equilibrium Structure of the Silanoic Acid Dimer

		DZ		DZ+P		
		freq	int	freq	int	assignt
A_g	ω_1	3342	0	3519	0	O—H
	ω_2	2430	0	2460	0	Si—H
	ω_3	1175	0	1339	0	Si=O
	ω_4	1323	0	1232	0	H—O—Si
	ω_5	972	0	1060	0	Si=O
	ω_6	889	0	949	0	H—Si—O
	ω_7	397	0	429	0	O—Si=O
	ω_8	218	0	195	0	O···O
	ω_9	122	0	132	0	O—H···O ip
B_g	ω_{10}	1163	0	1004	0	δ(O—H) oop
	ω_{11}	617	0	670	0	δ(Si—H) oop
	ω_{12}	161	0	166	0	O—H···O oop
A_u	ω_{13}	1184	606	1026	302	δ(O—H) oop
	ω_{14}	626	261	680	276	δ(Si—H) oop
	ω_{15}	142	56	136	28	O—H···O oop
	ω_{16}	96	1	85	2	twist about Si—H bond
B_u	ω_{17}	3424	2972	3582	2790	O—H
	ω_{18}	2427	201	2457	201	Si—H
	ω_{19}	1216	636	1373	614	Si=O
	ω_{20}	1281	698	1197	484	H—O—Si
	ω_{21}	950	241	1046	284	Si—O
	ω_{22}	904	31	961	23	H—Si—O
	ω_{23}	391	200	424	163	O—Si=O
	ω_{24}	284	111	261	106	O—H···O ip

be observed in any conventional IR experiment. Among the remaining fundamentals $\nu_{13} - \nu_{24}$ the asymmetric O–H stretching frequency ν_{17} is by far the most likely to be observed, with a theoretical IR intensity of 2790 km/mol (DZ+P SCF). The comparable mode of the formic acid dimer also has the highest IR intensity, but smaller, namely I = 1575 km/mol.

While the strongest IR intensity for $(HSiOOH)_2$ is stronger than that for $(HCOOH)_2$, this situation is reversed for the second strongest. Specifically, the Si=O stretch is predicted to have I = 614 km/mol, while the C=O stretch for the formic acid dimer has I = 1188 km/mol (DZ+P SCF). The third highest ab initio IR intensity occurs for ω_{20}, the H–O–Si bending mode, for which I = 484 km/mol. In contrast, the H–O–C bending mode for the formic acid dimer is predicted to have weak IR intensity, I = 75 km/mol (DZ+P SCF). The fourth highest IR intensity predicted for $(HSiOOH)_2$ differs even more sharply from that for $(HCOOH)_2$. For the former, $I[\omega_{13}(a_u)]$ = 302 km/mol, while for the latter I_{13} = 0.4 km/mol. The fifth highest intensity is predicted to be that for the Si–O single-bond stretch.

It is worth noting that the $(HSiOOH)_2$ IR intensities are radically different from those of the monomer. The O–H stretch intensity is 14 times more intense for the dimer than the monomer while the Si=O double-bond stretch is only twice as intense for the dimer. The Si–O single-bond stretch is 5 times more intense for the dimer than for the monomer.

It is abundantly well-established that DZ+P SCF harmonic vibrational frequencies lie on the order of 10% above the observed fundamentals.[59,60] Thus, we know that the frequency predictions seen in Table IV will be too high. We must ask ourselves whether one can go about scientifically predicting the true fundamentals. We suspect that the answer to this question is a qualified yes.

The dominant feature in the $(HSiOOH)_2$ IR spectrum should be the asymmetric O–H stretch. For the formic acid dimer DZ+P SCF theory predicts ω_{17} = 3835 cm^{-1}, while ν_{17}(experiment) = 3110 cm^{-1}. In the silanoic acid dimer, this O–H stretch prediction is reduced to 3582 cm^{-1} (DZ+P SCF), but the correction factor of 1.233 will probably still be valid. If this is true, the O–H stretch in $(HSiOOH)_2$ should occur at 2905 cm^{-1}. In principle, one might also predict the dimer O–H fundamental by its predicted shift with respect to the HSiOOH monomer; unfortunately, the monomer O–H stretch for silanoic acid has not yet been observed.

Table V. Dimer–Monomer Vibrational Frequency Shifts (cm^{-1}) for the Allowed Fundamentals of $(HSiOOH)_2$[a]

		DZ SCF	DZ+P SCF	
A_u	ω_{13}	+666	+504	δ(O—H) oop
	ω_{14}	+12	+6	δ(Si—H) oop
B_u	ω_{17}	−779	−599	O—H
	ω_{18}	−1	−2	Si—H
	ω_{19}	0	−22	Si=O
	ω_{20}	+600	+330	H—O—Si
	ω_{21}	−12	+48	Si—O
	ω_{22}	−9	−24	H—Si—O
	ω_{23}	+49	+53	O—Si=O

[a] All theoretical predictions were made at the DZ+P SCF level of theory. For modes 15, 16, and 24 of the dimer, there are no comparable monomer normal vibrations.

Table VI. Vibrational Frequencies (cm^{-1}) and IR Intensities (km/mol) of D_{2h} Stationary Point for $(HSiOOH)_2$

		DZ		DZ+P		
		freq	int	freq	int	assignt
A_g	ω_1	2433	0	2464	0	Si—H
	ω_2	1743	0	1580	0	H—O—Si
	ω_3	1104	0	1175	0	Si—O
	ω_4	602	0	646	0	O—H
	ω_5	327	0	346	0	H—Si—O
B_{1g}	ω_6	1180	0	1341	0	Si—O
	ω_7	928	0	982	0	H—Si—O
	ω_8	150	0	144	0	H—O—Si
	ω_9	1399i	0	1466i	0	O—H
B_{2g}	ω_{10}	624	0	673	0	δ(Si—H) oop
	ω_{11}	198	0	212	0	wag (SiO_2)
B_{3g}	ω_{12}	1506	0	1407	0	δ(O—H) oop
A_u	ω_{13}	121	0	101	0	twist (SiO_2)
B_{1u}	ω_{14}	1531	611	1433	284	δ(O—H) oop
	ω_{15}	635	262	683	265	δ(Si—H) oop
	ω_{16}	171	71	173	36	wag (SiO_2)
B_{2u}	ω_{17}	1686	571	1535	534	H—O—Si
	ω_{18}	1235	331	1355	350	Si—O
	ω_{19}	915	135	973	109	H—Si—O
	ω_{20}	572	36	598	22	O—H
B_{2u}	ω_{21}	2432	90	2463	92	Si—H
	ω_{22}	1006	901	1096	176	Si—O
	ω_{23}	550	6770	532	3381	H—Si—O
	ω_{24}	330	2905	147	7527	O—H

Since the dimer–monomer shifts are of inherent interest for silanoic acid, these are given in Table V. Since the Si=O double-bond stretch has been observed for the monomer at 1249 cm^{-1}, one can use the appropriate shift to make a quantitative prediction of ν_{19} for $(HSiOOH)_2$. The prediction from theory is that ν(Si=O) shifts very little from monomer to dimer, namely −22 cm^{-1} (DZ+P SCF). As noted above, the DZ+P SCF prediction for the monomer Si=O harmonic frequency lies 11.7% higher than the observed fundamental in the matrix isolation experiments of Withnall and Andrews.[1,2] Using this same correction, we expect the dimer Si=O stretch to be shifted downward by 20 cm^{-1} with respect to the monomer. That is, the Si=O stretching fundamental for $(HSiOOH)_2$ is predicted to lie at 1249 − 20 = 1229 cm^{-1}.

A partial check on the above semiempirical estimation scheme is provided by the comparison between theoretical and experimental frequencies for the $DSi^{16}O^{16}OD$ monomer. There the DZ+P SCF harmonic Si=O stretch (1387 cm^{-1}) lies 11.4% above the observed fundamental (1245 cm^{-1}). This correction factor does not change our prediction that the Si=O stretching frequency for the dimer should lie 20 cm^{-1} below that for the HSiOOH monomer.

It should also be possible to make a reasonable quantitative estimate of the Si–O single-bond stretch for the dimer from the observed fundamental[1,2] ν = 891 cm^{-1} for the monomer $DSi^{16}O^{16}OD$. At the DZ+P SCF level of theory the harmonic

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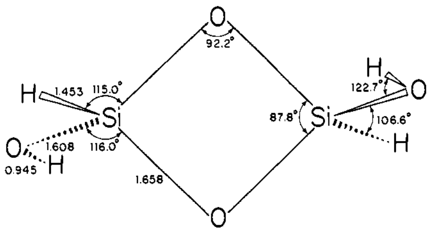


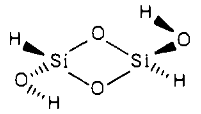
Figure 4. Predicted equilibrium geometry (DZ+P SCF theory) for the substituted cyclobutane-like isomer of the silanoic acid dimer. Bond distances are given in angstroms. The H-O-Si-H torsional angle is 180°.

frequency for this mode is predicted to be 976 cm^{-1}. Thus, the theoretical harmonic Si-O stretch lies 9.5% above the observed fundamental. The DZ+P SCF monomer-dimer shift for the Si-O stretch is small, namely +48 cm^{-1}. When the correction factor of 9.5% is applied, the monomer-dimer shift is reduced to 44 cm^{-1}. And thus ν_{21}(Si-O) is predicted to be 891 + 44 = 935 for $(DSi^{16}O^{16}OD)_2$. For $(HSi^{16}O^{16}OH)_2$, one should directly apply the 9.5% correction to the dimer prediction ω_{21}(DZ+P SCF) = 1046 cm^{-1}. Thus, one predicts ν_{21}(Si-O) = 955 cm^{-1}.

Table VI gives the DZ and DZ+P harmonic vibrational analyses for the transition state for double proton transfer within $(HSiOOH)_2$. The principal purpose of this table is to demonstrate conclusively that the D_{2h} stationary point is a true transition state, with one and only one imaginary vibrational frequency. This imaginary frequency ω_9 is predicted to be substantial, 1399i cm^{-1} with DZ SCF and 1466i cm^{-1} with DZ+P SCF.

An imaginary vibrational frequency of such high absolute value should be indicative of a sizable barrier for double proton transfer. This is, of course, confirmed in Table I, where the predicted barriers are 7.6 kcal (DZ SCF) and 10.2 kcal (DZ+P SCF). These barriers for two-proton transfer are significantly less than those (14.2 kcal/mol, DZ SCF; 15.6 kcal/mol, DZ+P SCF) predicted at the same level of theory for the formic acid dimer. Also consistent is the fact that the predicted imaginary vibrational frequency for $(HCOOH)_2$ is larger (1663i cm^{-1}, DZ SCF; 1695i cm^{-1}, DZ+P SCF).

Lower Energy Cyclic Isomer of $(HSiOOH)_2$. It has been known for at least three decades that multiple bonds to silicon are not readily made.[61,62] In particular, when alternative singly bonded silicon isomers can be conceived, the latter are usually energetically favored.[63] Therefore, one is motivated to find an isomer of the silanoic acid dimer that removes the two formal Si=O double bonds. Michl[64] suggested to us the following $(HSiOOH)_2$ isomer:



(5)

Michl's initial suggestion was that the four-membered ring (eq 5) should lie at least 50 kcal/mol below the silanoic acid dimer (eq 3).[64] The stationary point geometry for the trans form of the four-membered ring (eq 5) was optimized at the DZ+P SCF level of theory and is seen in Figure 4. As shown in Table VII, this *trans*-cyclobutane-related structure is a true minimum, predicted (DZ+P SCF) to lie 118.2 kcal/mol (115.3 kcal after ZPVE correction) below two separated HSiOOH monomers. Alternatively, the cyclobutane-like trans structure lies 90.9 kcal/mol below the $(HSiOOH)_2$ structure incorporating two hydrogen bonds. Thus, the qualitative prediction by Michl[64] is confirmed by quantitative ab initio theory.

Given the enormous energetic disadvantage of the two-hydrogen-bond structure with respect to the cyclobutane-related isomer, we question whether the former should be observed at all. There are several aspects to this question. First, if the dimer is trapped in the two-hydrogen-bond structure (i.e., some third body carries away the excess energy, assuming the dimer was formed by the collision of two monomers), the molecule will be trapped. In other words, the only likely reaction mechanism leading from structure (eq 5) to the lower energy structure (eq 3) involves the complete breakage of both hydrogen bonds. Further, there should be no barrier for the dimerization to the formic acid-like structure.

Table VII. Theoretical Predictions (DZ+P SCF) of Harmonic Vibrational Frequencies (cm^{-1}) for the Cyclobutane-Related Isomer of $H_4O_4Si_2$, Depicted in Figure 4[a]

A_g	4216	O—H
	2459	Si—H
	1077	Si—O
	987	H—Si—O_r
	940	Si—O_r
	841	H—O—Si
	583	ring deformn
	308	O_r—Si—O
B_u	4215 (316)	O—H
	2456 (251)	Si—H
	1045 (717)	Si—O
	973 (269)	H—Si—O_r
	921 (532)	Si—O_r
	829 (242)	H—O—Si
	499 (158)	O_r—Si—O
	128 (4)	ring puckering
A_u	1022 (599)	Si—O_r
	782 (11)	H—Si—O_r
	338 (267)	H—Si—O—H torsion
	161 (58)	O_r—Si—O
B_g	886	H—Si—O_r
	719	Si—O_r
	393	O_r—Si—O
	207	H—Si—O—H torsion

[a] The total energy at the equilibrium geometry is −879.988 97 hartrees. Infrared intensities are given in kilometers per mole in parentheses. In the characterization of vibrational frequencies, the subscript r implies that an oxygen atom is part of the central four-membered ring.

The question arises as to whether there should be a barrier to the formation of the cyclobutane-related dimer (eq 5) from two silanoic acid monomers. This is a more difficult question, since the electronic structure of the four-membered ring is quite different from that of two silanoic acid monomers. It is at least possible that there might be a barrier for dimerization to the cyclobutane structure. If such were the case, it might be possible to preferentially populate the higher energy two-hydrogen-bond structure.

The four-membered ring structure is sufficiently stable energetically that it may well be produced via mechanisms not involving the silanoic acid monomer. In this light the vibrational frequencies in Table VII may be helpful in identifying this $H_4O_4Si_2$ isomer. Without repeating the above analysis for the two-hydrogen-bond structure, it may be stated that the same frequency scaling principles should be applicable.

Concluding Remarks

The results presented and discussed here are a tiny fraction of what could be readily produced from the present study. Specifically, we have only considered the infrared spectra of the $HSi^{16}O^{16}OH$ dimer. For the formic acid dimer, extensive experimental infrared and Raman data are available for *four* isotopic variants. Our assumption has been that Raman intensities (which were qualitatively nicely reproduced for the formic acid dimer[53]) would be superfluous for the yet to be observed silanoic acid dimer. We hope that the present report is sufficient to stimulate an earnest search for the IR spectrum of both $(HSiOOH)_2$ and its energetically lower cyclobutane-like isomer. Should isotopic data become available or appear impending, we will be happy to generate the corresponding ab initio predictions.

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(62) Mulliken, R. S. *J. Am. Chem. Soc.* **1950**, *72*, 4493.
(63) See, for example: Schaefer, H. F. *Acc. Chem. Res.* **1982**, *15*, 283.
(64) Michl, J., personal communication.