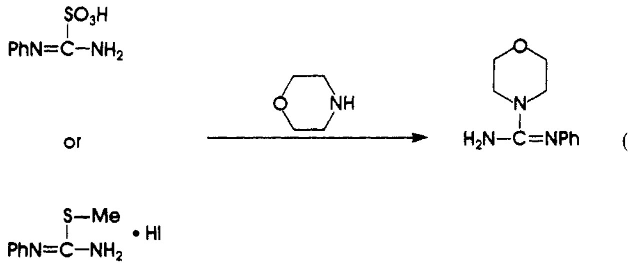
isothiouronium iodide toward morpholine at 35 °C was studied (see eq 3). It was determined that the S-trioxide group was replaced about 15 times faster than the S-methyl group by morpholine.



(3)

This synthetic route is particularly useful for the direct conversion of N-monosubstituted thioureas to di- and trisubstituted guanidines in good overall yield. The key transformation is sulfur activation through oxidation followed by displacement of the oxidized sulfur group by an amine nucleophile (oxidation/displacement). The experimental procedure is facile, no noxious odors are generated, and the isolated intermediate is stable at ambient temperature. The overall reaction time is short and the yields are good.

Currently, we are determining the scope of the reactions of other nucleophiles with oxidized thioureas.

## Experimental Section

Melting points are corrected. Reactions were typically monitored by TLC (silica gel, 90:10 $CHCl_3$/MeOH, oxidation; 95:5:5 MeOH/AcOH/$CHCl_3$, displacement). All reagents and solvents were used without additional purification. Elemental analyses were obtained from Schwarzkopf or Atlantic Laboratories. $^1H$ NMR spectra were obtained on a Varian EM 390 (90 MHz) or a Bruker AM 360 (360.13 MHz) spectrometer with chemical shifts relative to $Me_4Si$. All $^{17}O$ NMR work was done on the Bruker AM 360 (48.8 MHz) with chemical shifts relative to water. Infrared spectra were obtained on a Perkin-Elmer 283 infrared spectrophotometer. All guanidines gave the correct molecular ion peak by chemical ionization mass spectrometry. Mass spectra were obtained on a Finnigan 3300 or a VG 7035 mass spectrometer.

**Synthesis of Sulfonic Acid Derivatives from Thioureas. General Procedure.** A reaction vessel is charged with thiourea (0.013 mol), water (6 mL), sodium chloride (0.005 mol), and sodium molybdate dihydrate (0.0002 mol) and cooled to 0 °C with efficient stirring. Hydrogen peroxide (30%, 0.041 mol) is added dropwise to the cooled suspension at a rate to minimize decomposition (follow the reaction by TLC). In most cases, a temperature of less than 20 °C was maintained during the addition of the first 2 equiv, while the third equivalent was added to maintain the reaction temperature <40 °C. Once the addition is complete (total addition time about 1 h) and the temperature begins falling, the oxidation reaction is over. The product is isolated by cooling the reaction to 10 °C and collecting the solid sulfonic acid by filtration. The sulfonic acid is then washed with a small portion of cold brine.

**Synthesis of Guanidines from Sulfonic Acids. General Procedure.** The sulfonic acid (0.01 mol) prepared above is added to the amine (0.013 mol) in 5 mL of acetonitrile at room temperature. In some cases an exotherm is observed. The reaction is monitored by TLC for disappearance of starting material. In some cases it may be necessary to warm the reaction mixture to reflux to ensure complete reaction. The reaction is worked up by adjusting the pH to the range of 12–14 with 3 N NaOH. In some cases, the desired guanidine may form as a solid precipitate and may then be isolated by filtration. Otherwise, the reaction mixture is extracted rapidly with $CH_2Cl_2$, dried over $Na_2SO_4$, and concentrated. The desired guanidine is obtained in a purity ranging from 80–95%. The guanidine may be further purified by recrystallization from hexane by or formation of an appropriate salt.

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**Registry No.** **1a**, 103-85-5; **1b**, 927-67-3; **1c**, 614-78-8; **1d**, 459-05-2; **2a**, 25343-52-6; **2b**, 25348-90-7; **2c**, 101030-88-0; **2d**, 101010-32-6; **4**, 17813-43-3; **5**, 13636-29-8; **6**, 13636-30-1; **7**, 102-06-7; **8**, 101010-23-5; **9**, 101010-24-6; **10**, 101010-25-7; **11**, 13636-36-7; **12**, 101010-26-8; **13**, 101010-27-9; **14**, 101010-29-1; **15**, 101010-31-5; **16**, 65071-09-2; **17**, 75358-18-8; $NH_2C_4H_9$-*t*, 75-64-9; $NH_2C_4H_9$-*i*, 78-81-9; $NH_2C_4H_9$-*sec*, 13952-84-6; $NH_2Ph$, 62-53-3; 4-$NH_2C_6H_4OMe$, 104-94-9; $NH_2C_6H_{11}$, 108-91-8; 4-$NH_2C_6H_4Cl$, 106-47-8; 2-Me, 4-$MeOC_6H_3NH_2$, 102-50-1; 4-$NH_2C_6H_4NO_2$, 100-01-6; $NH_2C_4H_9$, 109-73-9; pyrrolidine, 123-75-1; morpholine, 110-91-8.

**Supplementary Material Available:** Spectral data and C, H, N analyses (where appropriate) for the guanidines in Table II (3 pages). Ordering information is given on any current masthead page.

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# Structure and Torsional Potential Function of Allylsilane: Results from MM2 and ab Initio Calculations (3-21G(*))

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Allylsilanes are species with substantial synthetic utility,[1] and attempts to model the transition-state stereochemical preferences for allylsilane condensation reactions have appeared.[2] Molecular mechanics methods can greatly aid modeling processes when appropriate parameters are available. Frierson and Allinger[3] have recently reported a silane force field for MM2-82; however, there was no explicit parameter development for dealing with the allylsilane group. We report a set of parameters for MM2-77[4] derived from experimental and ab initio data which permits satisfactory modeling of the structure and conformational energies of allylsilane.

Several experimental investigations examining the structure and conformational preferences of allylsilane have been reported.[5-7] These studies were aimed at deriving a better structural model for allylsilane that would explain observed physical properties, particularly UV and IR spectra.[7] Additionally, there has been a general interest in evaluating the conformational preferences of both XCC=Y and C=CXC systems (X = C, N, O, S, Si; Y = C, O).[7-9] Our interest in allylsilane was derived from MM2 force-field investigations of hyperconjugative effects in fixed rings such as silanorbornenes.[10] Numerous articles have examined the "$\sigma$–$\pi$" conjugation and hyperconjugative effects in silanes, and these have been synopsized in a recent review.[11]

Both electron diffraction (ED)[5] and microwave (MW)[6] studies present results which are consistent with our MM2 and 3-21G(*)[12,13] calculated values for the dihedral angle of the single energy minimum at 103 ± 1°. We also find that the cis conformation ($\omega = 0°$) is now a maximum and should not be populated (barrier height of ~2 kcal/mol above the 103° form). The theoretical and experimental results generally have agreed well (Table I).

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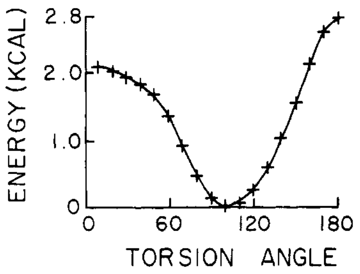

**Figure 1.** Potential function for rotation about C=CCSi calculated with MM2 by using the new parameters herein.

**Table I. Structural Features of Allylsilane (Lengths in Å, Angles in deg; 1 Å = 10 $m^{-10}$)**

| parameter | exp(ED)$^a$ | 3-21G(*)$^b$ | MM2$^c$ |
|---|---|---|---|
| Si–C | 1.875 ± 0.004 | 1.892 | 1.871 |
| C–C | 1.500$^d$ | 1.527 | 1.520 |
| C=C | 1.325 ± 0.004 | 1.320 | 1.340 |
| Si–H | 1.479$^d$ | 1.476 (mean) | 1.485 |
| C–H (mean) | 1.090$^d$ | 1.073 (mean) | 1.102 (mean) |
| Si–C–C | 113.1 ± 0.4 | 111.1 | 110.9 |
| C—c=C | 125.6$^d$ | 124.6 | 123.7 |
| C–Si–H | 108.0$^d$ | 110.1 (mean) | 110.4 (mean) |
| Si–C–H | 109 ± 1.0 | 109.5 (mean) | 108.4 (mean) |
| H–C–H | 105.0$^d$ | 107.9 | 108.1 |
| C=C—H (mean) | 117.0 ± 2.0 | 117.7 | 118.1 |
| $\omega$ | 102 ± 1$^e$; 103.7$^f$ | 103.4 | 102.5 |
| $\mu$ | 0.526$^f$ | 0.573 | 0.760 |

$^a$ Reference 3. $^b$ Full geometry optimization (Berny method), ref 12. $^c$ Using the standard MM2-77 plus the parameters listed in ref 3 except as noted, ref 15. $^d$ Fixed during structure refinement. $^e$ Reference 5. $^f$ Reference 6.

Pople et al.[13] have introduced a flexible and useful medium-sized basis, 3-21G(*), which incorporates d-orbitals on third-row atoms such as silicon. We have also found this basis superior to STO-3G, STO-3G*, or 3-21G in conformational and structural analysis applications.[14] The discrepencies between the 3-21G(*) and experimental structures were not unexpected and were attributable, in part, to assumptions made in the refinement of electron diffraction data.

**Table II. Calculated Relative Energies of Allylsilane Conformers (Dihedral Values in deg; Energies in kcal)**

| C=CCSi | MM2 | 3–21G(*) //MM2$^a$ | 3-21G(*)//3-21G(*)$^a$ | MP3//3-21G(*)$^b$ |
|---|---|---|---|---|
| 0 | 2.09 | 2.11 | 2.25 | 2.04 |
| 60 | 1.34 | 1.26 | 1.29$^c$ | |
| 90 | 0.14 | 0.17 | 0.13$^c$ | |
| 102–104 | 0.0 | 0.0 | 0.0 | 0.0 |
| 120 | 0.24 | 0.35 | 0.27$^c$ | |
| 180 | 2.75 | 3.47 | 3.43 | 3.37 |

$^a$ Designates calculation at 3-21G(*) level on MM2 or 3-21G(*) optimized geometries. $^b$ Single point energy evaluations. $^c$ During these calculations the dihedral angle was constrained to the value given, and all other degrees of freedom were relaxed.

We derived the MM2 torsional parameters[14] for the allylsilane fragment C=CCSi by an analytical fit, with minor manual adjustment, to the relative energies from single-point 3-21G(*) calculations (Table II) by using MM2 optimized geometries. This procedure has proven highly useful in both torsional parameter development and validation.[13,15] We verified the position of the energy minimum and the height of the cis and trans barriers by subsequent full 3-21G(*) geometry optimizations. These are reported in Table I. The torsional potential function obtained with the new MM2 parameters is shown in the figure. While the agreement among most of the dihedral values is quite good, the height of the trans barrier is probably underestimated by MM2. Unlike the situation with the cis barrier in butane-like systems which is systematically overestimated by HF-SCF calculations,[16] the trans conformer of allylsilane should not experience an appreciable lowering of the barrier because of correlation effects.[17] The MP3 calculations shown in Table II confirm this expectation. Thus, the origin of the discrepancy, while partly due to the modest basis set used, probably lies mainly with the molecular mechanical formalism that incompletely compensates for the hyperconjugative stabilization at dihedral values in the vicinity of 90–100°. We found we could not increase the trans barrier without also increasing the cis or shifting the minimum energy dihedral value to 90°, which we did not wish to do. One of us (S.P.) has found that additional higher-order torsional terms ($V_4$,$V_6$) are often necessary to achieve superior fitting to experimental functions and those derived from quantum mechanics. Typical cases involve single bond rotational potentials between $sp^3$ and $sp^2$ atoms. This will be done, most likely, in subsequent force field such as MM3.

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**Registry No.** Allylsilane, 18191-59-8.

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