

# Parameters for Force Field Calculations of Compounds Containing Tetrahedral Tin

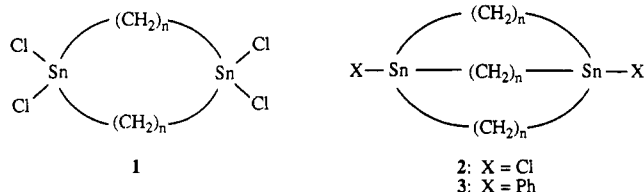
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Force field parameters for use in MM2 modeling programs for compounds containing tetrahedral tin atoms bonded to hydrogen,  $sp^2$  carbon,  $sp^3$  carbon, and chlorine have been developed. Calculated lengths and angles of  $MeSnH_3$ ,  $EtSnH_3$ ,  $Me_2SnH_2$ ,  $Me_3SnH$ ,  $Me_4Sn$ , and  $Me_3SnCl$  are in good agreement with reported values determined by microwave or electron diffraction spectroscopy, and the calculated structure of  $ClSnH_3$  agreed with that deduced from IR data and ab initio calculations. A comparison of the calculated structural features of  $(c-C_6H_{11})_3SnCl$  with those determined by X-ray crystallography suggested that a slight Lewis acid-base interaction occurs in the solid state. The calculated and X-ray crystal structures of  $Ph_3SnCl$ ,  $sec-BuSnPh_3$ , and (1-adamantyl)diphenylmethyltin were in reasonable agreement, but poor results were obtained for  $Ph_2Sn$  and  $(o-tolyl)_4Sn$ . Calculated and X-ray crystal structures for the series of cyclic oligomers  $(Ph_2Sn(CH_2)_n)_n$  ( $n = 1, 2, 4$ ) are reported. The X-ray structure of the  $n = 4$  compound is included in this paper; the crystals were monoclinic, space group  $P2_1/n$ , with  $a = 13.240$  (2) Å,  $b = 15.929$  (3) Å,  $c = 14.906$  (3) Å,  $\beta = 109.20$  (1)°,  $V = 2968.8$  Å<sup>3</sup>, and  $Z = 2$ , and the structure was refined to  $R = 0.036$  and  $R_w = 0.045$  for 3626 data with  $F_o^2 > 3\sigma(F_o^2)$ . The force field parameter set accurately reproduces the energy difference between the axial and equatorial conformations of (trimethylstannyl)cyclohexane.

Molecular mechanics calculations have become a widely applied and powerful tool in the stereochemical investigations of organic molecules,<sup>1</sup> but applications to organometallic compounds have been limited. Recently MM2 parameter sets have been developed for silicon, phosphorus, selenium, and tellurium compounds, lithium enolates, and organocobalt complexes,<sup>2a-f</sup> and the AMBER force field has been successfully applied to model crown ether-cation interactions.<sup>2g</sup> On the basis of our investigations of the anion binding behavior of Lewis acidic organotin macrocyclic (1) and macrobicyclic hosts (2),<sup>3</sup> we wished to



a:  $n = 4$ ; b:  $n = 5$ ; c:  $n = 6$ ; d:  $n = 7$ ; e:  $n = 8$ ; f:  $n = 9$ ; g:  $n = 10$ ; h:  $n = 12$

use molecular mechanics to model organostannanes. Molecular calculations involving tin were reported in 1972 by Ouellette, who parameterized an early MM1-like force field and performed pioneering calculations on some simple organostannanes and other group 14 compounds.<sup>4</sup> We report here an updated and extended MM2 parameter set for tetrahedral tin that includes tin bonds to hydrogen,  $sp^3$  carbon,  $sp^2$  carbon, and chlorine. The parameter set

successfully models simple tetravalent stannanes and correctly calculates the energy difference between the axial and equatorial conformations of (trimethylstannyl)cyclohexane. Reasonable agreement between calculated and crystal structures of larger organostannanes was generally found, although crystal-packing forces apparently resulted in significant differences between calculated gas-phase and solid-state structures in several cases. In the following paper, we have applied the parameter set for modeling macrobicyclic organostannanes.

## Force Field Parameters

**Tin Halides and Tetrahedral versus Trigonal-Bipyramidal Tin Atoms.** At the outset, we should note that one faces a special problem in attempting to develop force field parameters for a heavy atom such as tin bonded to a halogen. Tin halides are Lewis acids that are well-known to form expanded valence structures in bonding with donor molecules or ions. Depending on the strength of the interaction between tin and the donor, the geometry at tin can vary from a slightly distorted tetrahedron to a trigonal bipyramid. Given the complexity of the possible bonding patterns of stannate structures, we have attempted here to treat only tetravalent tin species.

With the above constraint, Sn-Cl bonds still presented a problem. In the solid state at 130 K,  $Me_3SnCl$  is a chlorine-bridged polymer containing nearly trigonal-bipyramidal tin atoms,<sup>5a</sup> and the X-ray crystal structure information is clearly not appropriate for our parameter set. Indeed, most X-ray crystal structures of tin halides are not appropriate for our purposes because the tin atoms act as Lewis acids. However, electron diffraction studies of  $Me_3SnCl$  in the gas phase, where the possibility of association is minimal, reveal that the structure is still that of a distorted tetrahedron with a Cl-Sn-C bond angle of 103.2°. Additional evidence for the inherent flattening of the chlorotrialkyltin unit comes from a comparison of the crystal structures of the chloromacrocyclics **2b-g** and

(1) (a) Allinger, N. L. *J. Am. Chem. Soc.* 1977, 99, 8127-8134. (b) Eliel, E.; Allinger, N. L.; Angyal, S. J.; Morrison, G. A. *Conformational Analysis*; Interscience: New York, 1965. (c) Burkert, U.; Allinger, N. L. *Molecular Mechanics*; American Chemical Society: Washington, DC, 1982.

(2) (a) Frierson, M. R.; Imam, M. R.; Zalkow, V. B.; Allinger, N. L. *J. Org. Chem.* 1988, 53, 5248-5258. (b) Unwalla, R. J.; Profeta, S.; Cartledge, F. K. *J. Org. Chem.* 1988, 53, 5658-5663. (c) Bowen, J. P.; Allinger, N. L. *J. Org. Chem.* 1987, 52, 2937-2938. (d) Allinger, N. L.; Allinger, J. A.; Yan, L. Q. *J. Mol. Struct.* 1989, 201, 363-369. (e) Spears, G. W.; Caulfield, C. E.; Still, W. C. *J. Org. Chem.* 1987, 52, 1226-1231. (f) Endicott, J. F.; Kumar, K.; Schwartz, C. L.; Perkovic, M. W.; Lin, W.-K. *J. Am. Chem. Soc.* 1989, 111, 7411-7420. (g) Kollman, P. A.; Merz, K. M., Jr. *Acc. Chem. Res.* 1990, 23, 246-252.

(3) (a) Blanda, M. T.; Horner, J. H.; Newcomb, M. *J. Org. Chem.* 1989, 54, 4626-4636. (b) Newcomb, M.; Horner, J. H.; Blanda, M. T.; Squatrito, P. J. *J. Am. Chem. Soc.* 1989, 111, 6294-6301. (c) Newcomb, M.; Blanda, M. T.; Azuma, A.; Delord, T. J. *J. Chem. Soc., Chem. Commun.* 1984, 1159-1160. (d) Azuma, Y.; Newcomb, M. *Organometallics* 1984, 3, 9-14.

(4) Ouellette, R. J. *J. Am. Chem. Soc.* 1972, 94, 7674-7679

(5) (a) Lefferts, J. L.; Molloy, K. C.; Hossian, M. B.; Van der Helm, D.; Zuckerman, J. J. *J. Organomet. Chem.* 1982, 240, 349-361. (b) Calogero, S.; Ganis, P.; Peruzzo, V.; Tagliavini, G. *J. Organomet. Chem.* 1979, 179, 145-152.

(6) (a) Beagley, B.; McAloon, K.; Freeman, J. M. *Acta Crystallogr., Sect. B: Struct. Sci.* 1974, B30, 444-449. (b) Fujii, H.; Kimura, M. *Bull. Chem. Soc. Jpn.* 1970, 43, 1933-1939. (c) Fujii, H.; Kimura, M. *Bull. Chem. Soc. Jpn.* 1971, 44, 2643-2647.

the phenyl macrobicycles **3b,e,g**.<sup>7</sup> In **2b-g** the average of all of the Cl-Sn-C angles is 101.5 (17)°, while in the phenyl macrobicycles the average of all Ph-Sn-C angles is 105.9 (18)°. The difference between these averages is three times as large as the standard deviations and appears to be real. Thus, we conclude that a flattening of the R<sub>3</sub>Sn group in a trialkyltin chloride is an inherent property of these compounds and one for which the force field parameter set must account.

**Stretching Parameters.** Ouellette originally estimated the tin-carbon (sp<sup>3</sup>) and the tin-hydrogen parameters as 2.124 and 2.229 mdyn/Å, respectively, on the basis of the normal-coordinate analysis of methylstannane.<sup>8a</sup> Since that time, normal-coordinate analyses have been completed on a number of simple organostannanes, yielding values for the Sn-C(sp<sup>3</sup>) stretching constant ranging from 2.10 to 2.34 mdyn/Å and for the Sn-H stretching constant ranging from 1.99 to 2.24 mdyn/Å.<sup>8b-f</sup> Ab initio calculations for stannane, methylstannane, and distannane have also been reported.<sup>8g,j,k</sup> On the basis of these experimental and theoretical values, Sn-C(sp<sup>3</sup>) and Sn-H stretching parameters of 2.15 and 2.25 mdyn/Å were respectively selected.

Because some of the macrocyclic and macrobicyclic organostannanes we wished to model have chlorine or phenyl ring attached to tin, we have developed parameters to model these structural features. Normal-coordinate analyses of trimethylstannyl chloride and methyltrichlorostannane have been reported to give values of 1.90 and 2.11 mdyn/Å, respectively, for the Sn-Cl stretching constant.<sup>8c,e</sup> An ab initio calculation by Schneider on chlorostannane gave a value for Sn-Cl stretching of 2.298 mdyn/Å.<sup>8l</sup> On the basis of these values, we selected 2.1 mdyn/Å for the Sn-Cl stretching parameter.

The selection of values for Sn-C(sp<sup>2</sup>) presented a problem because no experimental valence force field parameters for a simple olefinic organostannane are available. However, normal-coordinate analyses of (trimethylstannyl)acetylene<sup>9a</sup> and of some aromatic organostannanes<sup>9b</sup> have been reported. The work of Höfler, who used a simplified normal-coordinate analysis to compare aromatic hydrocarbons, silanes, germanes, and stannanes,<sup>9b</sup> served as a guide in the selection of bending and stretching parameters. A value of 2.30 mdyn/Å for the Sn-C(sp<sup>2</sup>) stretching parameter was selected.

Equilibrium bond lengths for a number of organostannanes are available from X-ray diffraction,<sup>3b,5b,10</sup> electron diffraction,<sup>6,11</sup> and microwave<sup>8d,12</sup> studies. From

Table I. MM2 Parameters for Tin<sup>a</sup>

Stretching Parameters					
MM2 atom types		K <sub>s</sub> , mdyn/Å	l <sub>0</sub> , Å		
C(3)	Sn	2.15	2.14		
C(2)	Sn	2.30	2.14		
H	Sn	2.25	1.70		
Cl	Sn	2.10	2.38		
Bending Parameters					
MM2 atom types			type <sup>b</sup>	K <sub>θ</sub> , mdyn/rad <sup>2</sup>	θ <sub>0</sub> , deg
C(3)	C(3)	Sn		0.40	109.0
C(2)	C(2)	Sn		0.45	120.0
H	C(3)	Sn	1	0.30	107.5
			2	0.30	109.5
			3	0.30	111.0
C(3)	Sn	C(3)	1	0.28	105.0
			2	0.28	105.0
			3	0.28	104.0
C(2)	Sn	C(2)		0.28	104.0
C(3)	Sn	C(2)		0.28	104.0
H	Sn	H		0.20	109.0
C(3)	Sn	H	1	0.26	108.0
			2	0.26	107.0
			3	0.26	109.0
C(3)	Sn	Cl		0.43	98.0
C(2)	Sn	Cl		0.43	101.0
H	Sn	Cl		0.40	104.0
Torsion Parameters <sup>c</sup>					
MM2 atom types				V <sub>3</sub> , kcal/mol	
C(3)	Sn	C(3)	C(3)	0.066	
C(3)	Sn	C(3)	H	0.066	
C(3)	Sn	C(2)	C(2)	0.066	
C(2)	Sn	C(3)	C(3)	0.066	
C(2)	Sn	C(2)	C(2)	0.066	
C(2)	Sn	C(3)	H	0.066	
H	Sn	C(3)	C(3)	0.24	
H	Sn	C(3)	H	0.066	
C(3)	C(3)	C(3)	Sn	0.50	
H	C(3)	C(3)	Sn	0.10	
Cl	Sn	C(3)	C(3)	0.066	
Cl	Sn	C(2)	C(2)	0.066	
Cl	Sn	C(3)	H	0.066	
van der Waals Parameters					
atom	r, Å		ε		
Sn	2.33		0.60		

<sup>a</sup>C(3) and C(2) refer to sp<sup>3</sup>- and sp<sup>2</sup>-hybridized carbons, respectively. <sup>b</sup>Type refers to the substitution pattern at the central atom Y: type 1, X-R<sub>2</sub>Y-Z; type 2, X-RHY-Z; type 3, X-H<sub>2</sub>Y-Z. <sup>c</sup>The V<sub>1</sub> and V<sub>2</sub> terms were set to zero.

(7) The crystal structures of **2c** and **2e** have been reported.<sup>3b</sup> The structures of **2b,d,f,g** and **3b,e,f** are reported in the following paper.

(8) (a) Kimmel, H.; Dillard, C. R. *Spectrochim. Acta* 1968, 24A, 909-919. (b) Imai, Y.; Aida, K. *Bull. Chem. Soc. Jpn.* 1982, 55, 999-1002. (c) Imai, Y.; Aida, K.; Sohma, K.-I.; Watari, F. *Polyhedron* 1982, 1, 397-403. (d) Durig, J. R.; Li, Y. S.; Sullivan, J. F.; Church, J. S.; Bradely, C. B. *J. Chem. Phys.* 1983, 78, 1046-1058. (e) Soliman, M. S.; Khattab, M. A.; El-Kourashy, A. G. *Bull. Soc. Chim. Belg.* 1985, 94, 87-91. (f) Watari, F. *Spectrochim. Acta* 1978, 34A, 1239-1244. (g) Pouchan, C.; Lespes, G.; Dargelos, A. *J. Phys. Chem.* 1988, 92, 28-33. (h) Pierce, L. *J. Chem. Phys.* 1961, 34, 498-506. (i) Thomas, E. C.; Laurie, V. W. *J. Chem. Phys.* 1969, 50, 3512-3515. (j) Fernández Sanz, J.; Márquez, A.; Pouchan, C. *Chem. Phys.* 1989, 130, 451-456. (k) Fernández Sanz, J.; Márquez, A. *J. Phys. Chem.* 1989, 93, 7328-7333. (l) Schneider, W.; Thiel, W. *J. Chem. Phys.* 1987, 86, 923-936. (m) Bürger, H.; Betzel, M.; Schultz, P. *J. Mol. Spectrosc.* 1987, 121, 218-235.

(9) (a) Belyakov, A. V.; Bogoradovskii, E. T.; Zavgorodnii, V. S.; Apal'kova, G. M.; Nikitin, V. S.; Khaikin, L. S. *J. Mol. Struct.* 1983, 98, 27-38. (b) Höfler, F. *Monatsh. Chem.* 1976, 107, 705-719.

(10) (a) Belsky, V. K.; Simonenko, A. A.; Reikhsfeld, V. O.; Saratov, I. E. *J. Organomet. Chem.* 1983, 244, 125-128. (b) Tse, J. S.; Lee, F. L.; Gabe, E. J. *Acta Crystallogr.* 1986, C42, 1876-1878. (c) Barrans, Y.; Pereyre, M.; Rham, A. *J. Organomet. Chem.* 1977, 125, 173-177. (d) Frampton, C. S.; Roberts, R. M. G.; Silver, J. *J. Organomet. Chem.* 1985, 297, 273-279.

the X-ray data, carbon-tin bond lengths involving both sp<sup>2</sup> and sp<sup>3</sup> carbon appear to average 2.14 Å, and, therefore, this value was selected for both Sn-C(sp<sup>2</sup>) and Sn-C(sp<sup>3</sup>). The experimental bond lengths for Sn-C derived from microwave spectroscopy studies are well within the scatter of values found in diffraction studies, and no correction of the microwave data was warranted.

Experimental tin-chlorine bond lengths decrease as the number of chlorines attached to tin increases (SnCl<sub>4</sub>, 2.28 Å; MeSnCl<sub>3</sub>, 2.304 Å; Me<sub>2</sub>SnCl<sub>2</sub>, 2.327 Å; Me<sub>3</sub>SnCl, 2.35 Å).<sup>6</sup> We have chosen the Sn-Cl length to match the X-ray crystallographic data for the chloro macrobicycles **2b-g** (average 2.38 (1) Å),<sup>7</sup> even though this value is somewhat longer than the gas-phase value for Me<sub>3</sub>SnCl.<sup>6a</sup> The bond

(11) Nagashima, M.; Fujii, H.; Kimura, M. *Bull. Chem. Soc. Jpn.* 1973, 46, 3708-3711.

(12) Durig, J. R.; Whang, C. M.; Attia, G. M.; Li, Y. S. *J. Mol. Spectrosc.* 1984, 108, 240-248.

stretching parameters and bond length parameters are summarized in Table I.

**Bending Parameters.** Spectroscopic bending force constants decrease as one proceeds down group 14. Spectroscopic bending constants derived experimentally from normal-coordinate analyses of vibrational spectra and theoretically from *ab initio* calculations were compared for carbon, silicon, and tin. Silicon bending constants show a relatively small reduction relative to carbon, typically 5–15%, and bending constants involving tin as the central atom are typically 20–50% smaller than the corresponding values for carbon.<sup>13</sup> In the MM2 parameter set for silicon developed by Allinger,<sup>2a</sup> bending parameters involving silicon as the central atom are actually slightly larger than those for carbon. For example, the  $C(sp^3)\text{-Si-C}(sp^3)$  value is 0.48 mdyne/rad<sup>2</sup>, while the  $C(sp^3)\text{-C}(sp^3)\text{-C}(sp^3)$  value is 0.45 mdyne/rad<sup>2</sup>. However, the large decrease in spectroscopic bending force constants for bond involving tin required that we reduce the H-Sn-H,  $C(sp^3)\text{-Sn-C}(sp^3)$ , and H-Sn-C( $sp^3$ ) bending parameters; values of 0.20, 0.28 and 0.26 mdyne/rad<sup>2</sup> were respectively selected. The corresponding parameters for C( $sp^2$ ) have tentatively been set equal to the C( $sp^3$ ) values.

A notable feature of the equilibrium bond angles ( $\theta_0$ ) in Table I is the small values required when tin was the central atom in a triad not containing hydrogen. The  $C(sp^3)\text{-Sn-C}(sp^3)$  values of  $\theta_0 = 105^\circ$  (types 1 and 2) and  $104^\circ$  (type 3) were required to reproduce the small observed bond angles in  $Me_2SnH_2$  ( $104.8^\circ$ ) and  $Me_3SnH$  ( $107.5^\circ$ ). In order to permit the C-Sn-C bond angles in  $Me_3SnCl$  to expand to the observed value ( $114.9^\circ$ ), the bending force parameter for Cl-Sn-C was made significantly greater than that for C-Sn-C. The larger value for Cl-Sn-C relative to C-Sn-C is not out of line with other parameters in MM2; for example, the C-C-Cl bending constant is significantly larger than the C-C-C bending value (0.56 and 0.45 mdyne/rad<sup>2</sup>, respectively).

The Cl-Sn-H bending parameters were based on the experimental<sup>8m</sup> and *ab initio* calculated<sup>8l</sup> structures of  $ClSnH_3$ . The  $H_3Sn$  group in  $ClSnH_3$  is flattened relative to the corresponding group in  $ClCH_3$  in much the same way as the  $R_3Sn$  group in a monochlorotin compound is flattened; this results in a reduction of approximately  $3^\circ$  for the Cl-Sn-H bond angle relative to Cl-Cl-H.

The development of the C-C-Sn and H-C-Sn parameters was influenced by the desire to reproduce the *A* value of the trimethylstannyl group, which has been determined by two groups to be 0.94 and 1.06 kcal/mol.<sup>15</sup> As discussed below, the final set of parameters gives a reasonable value for the energy difference between axial and equatorial (trimethylstannyl)cyclohexane. The final set of bending parameters is included in Table I.

**Stretch-Bend Parameters.** We have not included stretch-bend parameters due to the lack of any suitable experimental structures that would serve as models. These parameters are primarily used to account for the bond stretching that accompanies bond angle reduction in small-ring compounds, and the omission of the parameter should have a negligible effect on the structures considered here.

(13) The H-M-H bending parameter was estimated from a comparison of the bending force constants in  $MH_4$  and  $CH_3MH_3$  ( $M = C, Si, Sn$ ).<sup>8d,14</sup>

(14) (a) Pulay, P.; Fogarasi, G.; Pang, F.; Boggs, J. E. *J. Am. Chem. Soc.* **1979**, *101*, 2550–2560. (b) Komornicki, A. *J. Am. Chem. Soc.* **1984**, *106*, 3114–3118.

(15) (a) Moder, T. I.; Hsu, C. C. K.; Jensen, F. R. *J. Org. Chem.* **1980**, *45*, 1008–1010. (b) Kitching, W.; Doddrell, D.; Grutzner, J. B. *J. Organomet. Chem.* **1976**, *107*, C5–C10. (c) Kitching, W.; Olszowy, H. A.; Harvey, K. *J. Org. Chem.* **1982**, *47*, 1893–1904.

**Torsional Parameters.** Torsional parameters present a problem in that several important experimental numbers such as the rotational barriers in methylethylstannane and *n*-propylstannanes have not been measured. However, accurate rotational barriers for methylstannane<sup>12</sup> and tetramethylstannane<sup>16</sup> are known, as are estimates of the lower limits of both the  $CH_3$  and  $SnH_3$  torsion barriers in ethylstannane.<sup>8d</sup> Due to the length of the carbon-tin bond, it is a safe assumption that rotational barriers involving tin as one of the central atoms are due only to torsional strain, and this simplifies greatly the relationship between experimental rotation barriers and the values in the parameter set.

The rotational barrier of methylstannane was originally determined as 0.65 kcal/mol<sup>8a</sup> but was later revised downward to 0.595 kcal/mol.<sup>12</sup> With the assumption that this barrier is due only to torsional strain, the  $V_3$  torsional parameter for the H-C-Sn-H unit was set to 0.066 kcal/mol (one-ninth of the observed barrier).

Another experimental rotational value that is known well is the barrier to methyl rotation in tetramethylstannane,<sup>16</sup> which provides an estimate of the C-Sn-C-H torsion parameter. In crystalline tetramethylstannane, tetrahedral symmetry is reduced to  $C_3$  symmetry, resulting in two different rotational barriers of 0.45 and 0.81 kcal/mol for the two types of methyl groups present. The barrier in liquid or gaseous tetramethylstannane is likely to lie between the two limiting crystalline phase values, which puts the value in the general vicinity of the value determined for methylstannane. Thus,  $V_3$  for the C-Sn-C-H torsion was also set to 0.066 kcal/mol.

The third experimental barrier that is relevant here is the  $SnH_3$  rotation barrier in ethylstannane, for which Durig has determined a lower limit of 1.12 kcal/mol.<sup>8d</sup> From this value for the rotation barrier and the H-Sn-C-H torsion value determined above, one obtains a minimum for the H-Sn-C-C torsion parameter of 0.24 kcal/mol. The dramatic increase in the H-Sn-C-C torsion parameter relative to those for H-Sn-C-H and C-Sn-C-H has an analogy in the corresponding parameters in the silane parameter set developed by Allinger.<sup>2a</sup>

The Sn-C-C-H and Sn-C-C-C torsion parameters are difficult to determine because these terms typically make up only a fraction of the rotation barrier in the molecules in which they occur and relatively large changes in these torsion terms result in small changes in calculated rotation barriers. As an example, a change in the Sn-C-C-H  $V_3$  torsion term from 0.0 to 0.2 kcal/mol resulted in an increase of the calculated methyl rotation barrier in ethylstannane from 2.6 to 3.2 kcal/mol. One should realize that even large relative errors in such small torsion barriers are likely to produce insignificant errors in the total energy of the MM2 calculation.

The lower limit for the methyl torsion in ethylstannane was estimated by Durig to be 2.12 kcal/mol,<sup>8d</sup> and our calculations are thus consistent with the barrier being somewhat larger than this minimum value. We have tentatively set the Sn-C-C-H torsion to 0.1 kcal/mol, which results in a calculated methyl rotation barrier of 2.9 kcal/mol for  $EtSnH_3$ . In analogy to the silane force field,<sup>2a</sup> the C-C-C-Sn parameter was made significantly larger than the H-C-C-Sn value.

Torsion barriers for simple chlorostannanes apparently have not been reported. In the absence of experimental data, we have set the  $V_3$  torsion values for groups con-

(16) Durig, J. R.; Craven, S. M.; Bragin, J. *J. Chem. Phys.* **1970**, *52*, 2046–2052. (e) Prager, M.; Dupr e, K.-H.; M uller-Warmath, W. *Z. Phys. B: Condens. Matter* **1983**, *51*, 309–318.

taining Sn-Cl equal to those for the analogous Sn-C groups. As with the silane parameter set,<sup>2a</sup> the  $V_1$  and  $V_2$  torsional terms involving tin were set to zero.

**van der Waals Parameters.** The selection of these parameters was influenced by our desire to reproduce the  $A$  value for (trimethylstannyl)cyclohexane, 1.0–1.1 kcal/mol.<sup>15</sup> When Ouellette's value<sup>4</sup> for the van der Waals radius of tin (2.40 Å) and an  $\epsilon$  value of about 0.3 were used with the above parameters to calculate the energy difference between the axial and equatorial conformers, an  $A$  value of about 1.4 kcal/mol was obtained. This value could be decreased by reducing  $\theta_0$  for Sn-C-H, but reduction beyond 107° appeared to be unreasonable for the tetrahedral carbon atom. Accordingly, the van der Waals radius for tin was reduced to 2.33 Å and  $\epsilon$  was increased to 0.60. These parameters resulted in a calculated  $A$  value of 1.14 kcal/mol.

We emphasize that our bias for fitting the single experimental  $A$  value could have given poor van der Waals parameters. The tin atom is relatively small (the radius of Te has been set at 2.40 Å for MM2 calculations)<sup>2d</sup> and quite soft ( $\epsilon$  for C, Si, and Te are 0.044,<sup>1</sup> 0.147<sup>2a</sup> and 0.368,<sup>2d</sup> respectively). Unfortunately, we have no other structures with which to test our values directly.

### Structure Modeling Results

Table II contains the results of modeling calculations on a variety of simple tin-containing compounds whose structures are known. Some of the highlights of the calculations and special requirements for the parameterization set are presented in this section. For large molecules where comparisons are made to crystal structures, crystal-packing forces are expected to deform the molecule from its optimum gas-phase structure. Because the force constants for stretching and bending involving tin are about half the values of those of carbon analogues, the structural features involving a tin atom are expected to be more susceptible to such deformation than those involving only carbon atoms. Thus, we have focused on tin-containing features in Table II; the calculated C-C bond lengths and C-C-C angles typically reproduced the experimental crystal structure values with more precision than the features involving tin atoms.

**Simple Stannanes.** The MM2 parameters developed in this work give results that are in close agreement with the experimental bond lengths and angles for MeSnH<sub>3</sub> determined by Durig<sup>3d</sup> and with the theoretical structure calculated by Pouchan using *ab initio* methods.<sup>8g</sup> In terms of stretching and bending energies, the molecule is seen to be strain free in both eclipsed and staggered conformations.

The microwave structure of ethylstannane has been determined by Durig.<sup>8d</sup> The key structural feature of interest is the C-C-Sn angle, which was determined to be 112.6°. The value of 113.9° calculated originally by Ouellette<sup>4</sup> without the benefit of knowledge of the experimental value was thus somewhat too large. The experimental value for the C-C-Sn angle of EtSnH<sub>3</sub> is essentially the same as the C-C-C angle in propane (112.4°).<sup>17</sup>

The structures of Me<sub>2</sub>SnH<sub>2</sub> and Me<sub>3</sub>SnH were determined by electron diffraction.<sup>6a</sup> The C-Sn-C angle of 104.8° observed for Me<sub>2</sub>SnH<sub>2</sub> is distinctly smaller than the almost tetrahedral angles observed for the analogous group 14 compounds Me<sub>2</sub>SiH<sub>2</sub> and Me<sub>2</sub>GeH<sub>2</sub>.<sup>8h,i</sup> In order to calculate the C-Sn-C bond angle correctly, it was necessary

to decrease  $\theta_0$  for the C-Sn-C bond angle to 105°. The observed C-Sn-C bond angle in Me<sub>3</sub>SnH was also accurately reproduced with this equilibrium bond angle.

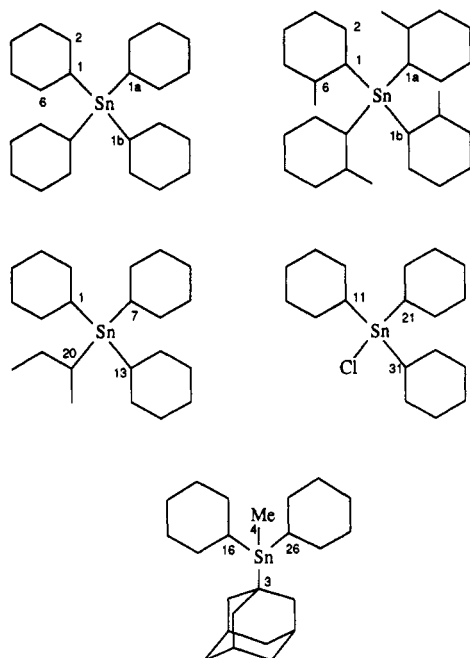
**Trialkyltin Chlorides.** As noted above, the gas-phase structure of Me<sub>3</sub>SnCl shows that the molecule is a distorted tetrahedron.<sup>6a</sup> The substitution of Cl (in Me<sub>3</sub>SnCl) for H (in Me<sub>3</sub>SnH) results in an increase in the C-Sn-C bond angles of about 7°, and the X-Sn-C bond angles are reduced by about 5° when X is Cl rather than H. The bond angles of Me<sub>3</sub>SnCl were accurately reproduced by maintaining a small equilibrium bond angle for C(sp<sup>3</sup>)-Sn-Cl and a bending force constant for this triad that was significantly greater than that of C(sp<sup>3</sup>)-Sn-C(sp<sup>3</sup>).

The X-ray crystal structure of (c-C<sub>6</sub>H<sub>11</sub>)<sub>3</sub>SnCl also shows a flattened-tetrahedral geometry around tin with an average Cl-Sn-C angle of 101.6° and an Sn-Cl bond length of 2.40 Å.<sup>5b</sup> The authors of the crystal structure report strongly assert that the structure is not significantly distorted by intermolecular association. However, the molecular orientation of this compound in the solid state has the chlorine of one molecule directly "behind" the Sn-Cl bond of another molecule at a distance of 3.31 Å, the proper orientation for a Lewis acid-base interaction. The bond length in (c-C<sub>6</sub>H<sub>11</sub>)<sub>3</sub>SnCl of 2.40 Å is 0.05 Å longer than the electron diffraction value for the Sn-Cl bond length in Me<sub>3</sub>SnCl determined in the gas-phase study.<sup>6a</sup> In the chloro macrobicycles **2b-g**, where intermolecular association is precluded by the bicyclic structures, the observed Sn-Cl bond lengths vary from 2.353 to 2.398 Å with a mean value of 2.38 (1) Å.<sup>7</sup> Further, in the chloride complex of bicyclic host **2e** (a complex containing both a stannate and a stannane),<sup>3b</sup> where solid-state <sup>119</sup>Sn NMR spectroscopy indicated a slight interaction between the stannane tin atom and the encapsulated chloride, the Sn-Cl distances for the stannane tin atom (2.415 (5) and 3.388 (5) Å) are very similar to those in the crystal structure of (c-C<sub>6</sub>H<sub>11</sub>)<sub>3</sub>SnCl. Therefore, one might surmise that a weak intermolecular interaction occurs in the crystal of (c-C<sub>6</sub>H<sub>11</sub>)<sub>3</sub>SnCl.

The MM2 modeling results for (c-C<sub>6</sub>H<sub>11</sub>)<sub>3</sub>SnCl also suggest a slight Lewis acid-base interaction in the solid state. As can be seen in Table II, the X-ray crystal structure of (c-C<sub>6</sub>H<sub>11</sub>)<sub>3</sub>SnCl and the calculated structure differ significantly. In the crystal structure, (c-C<sub>6</sub>H<sub>11</sub>)<sub>3</sub>SnCl has C<sub>s</sub> symmetry due to crystal-packing forces, whereas the MM2 structure has C<sub>3</sub> symmetry. The molecule is significantly flatter in the solid state than is calculated; i.e., the calculated Cl-Sn-C bond angles are about 2° larger than the observed values, and two of the C-Sn-C bond angles in the crystal structure are about 5° larger than the calculated C-Sn-C bond angle. The effects of crystal-packing forces are unknown, and they might be the origin of some of the differences between the experimental and calculated structures of this molecule, but it would appear to be reasonable to conclude that intermolecular association in the solid state could be involved. Of course, given the choice between selecting force field parameters consistent with the gas-phase structure of Me<sub>3</sub>SnCl or those consistent with the solid-state structure of (c-C<sub>6</sub>H<sub>11</sub>)<sub>3</sub>SnCl, the values that correctly predict the gas-phase structure were desired.

**Aromatic Organostannanes.** As a test of the parameters involving the Sn-C(sp<sup>2</sup>) bond, we initially examined tetraphenyltin and tetra-*o*-tolyltin (Figure 1). In the crystalline state, both of these compounds adopt S<sub>4</sub> symmetry.<sup>10a</sup> MM2 successfully reproduced the S<sub>4</sub> symmetry of both molecules, but in neither case were the bond angles around tin satisfactorily calculated. For Ph<sub>4</sub>Sn the ex-

(17) Lide, D. R. *J. Chem. Phys.* 1960, 33, 1514–1518.



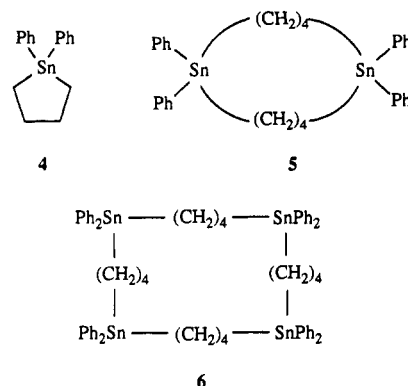
**Figure 1.** Numbering systems for aryl-containing tin compounds. The numbering follows that given in the crystal structure reports.

perimental bond angles for C(1)–Sn–C(1a) and C(1)–Sn–C(1b) of 108.6 (1) and 111.2 (2) $^{\circ}$ ,<sup>10a</sup> respectively, were both calculated as 109.5 $^{\circ}$ . For (*o*-tolyl)<sub>4</sub>Sn the calculated C(1)–Sn–C(1b) angle was compressed to 106.9 $^{\circ}$  from its experimental value of 112.6 (3) $^{\circ}$ , and the calculated C(1)–Sn–C(1a) angle was increased to 110.7 $^{\circ}$  from the experimental value of 107.9 (1) $^{\circ}$ . The experimental and calculated aryl dihedral angles, C(2)–C(1)–Sn–C(1a), differed by 22 $^{\circ}$  in the case of Ph<sub>4</sub>Sn and 2 $^{\circ}$  in the case of (*o*-tolyl)<sub>4</sub>Sn.

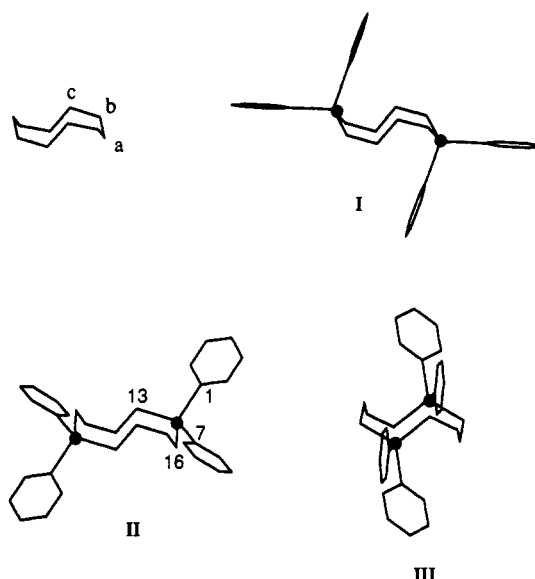
Better results were achieved in calculations of the structures of the triaryltin compounds *sec*-butyltriphenylstannane and chlorotriphenylstannane (Figure 1). In both cases most of the bond and torsion angles were reproduced satisfactorily. Unlike (*c*-C<sub>6</sub>H<sub>11</sub>)<sub>3</sub>SnCl discussed above, Ph<sub>3</sub>SnCl does not show any effects of intermolecular association; the shortest Sn–Cl intermolecular contact is reported to be 5.847 (2) Å.<sup>10b</sup> Therefore, the crystal structure of this molecule was appropriate for use in the parameterization.

The structure of (1-adamantyl)diphenylmethyltin (Figure 1) also was calculated. The precision in the crystal structure is somewhat poorer in this case than for most of the other structures, but the Sn–C bond to the adamantyl group is clearly longer than other Sn–C bonds considered here. The MM2 calculated structure accurately reproduced this long bond.

**Cyclic Organostannanes.** Calculations were also performed on the oligomeric series of cyclic stannanes 4–6 (Figure 2). The crystal structure of 1,1-diphenyl-1-stannacyclopentane (4) reveals that this molecule exists in a twisted conformation of C<sub>2</sub> symmetry with an endocyclic C–Sn–C angle of 95 $^{\circ}$  and a Ph–Sn–Ph angle of 120 $^{\circ}$ .<sup>18</sup> MM2 successfully reproduced the C<sub>2</sub> symmetry, but the calculated C–Sn–C and Ph–Sn–Ph angles of 87.1 and 115.6 $^{\circ}$ , respectively, differed significantly from the experimental values. It should be noted, however, that the crystal structure was refined only to an *R* value of 16%, a level of refinement that only reveals the general features



**Figure 2.** Cyclic oligomers: 1,1-dimethyl-1-stannacyclopentane (4), 1,1,6,6-tetraphenyl-1,6-distannacyclodecane (5), and 1,1,6,6,11,11,16,16-octaphenyl-1,6,11,16-tetrastannacycloicosane (6).



**Figure 3.** Boat–chair–boat conformation of cyclodecane and MM2 minimized structures for the three conformations of compound 5 resulting from replacement of methylenes a–c in cyclodecane with diphenylstanna groups. The numbering system for conformation II is that used for the structure reported in ref 18.

of the structure;<sup>18</sup> therefore, the standard deviations for the angles, while not reported, are likely to be quite large.

Calculations of the structure of the cyclic dimer 5 provide the first test of the behavior of the parameter set in a compound approaching macrocyclic dimensions. Cyclodecane and derivatives therefrom have been shown to prefer a boat–chair–boat conformation which contains three nonequivalent types of methylene groups, designated a–c in Figure 3. As discussed by Davies in his analysis of the crystal structure of 5, by replacement of pairs of opposing methylene units with diphenylstanna units, three potential structures (I–III in Figure 3) of 5 can be envisioned.<sup>18</sup> MM2 calculations have been completed on these three conformers for comparison with the crystal structure of 5 (Table IV).

In the solid state, conformation II is the preferred structure of 5.<sup>18</sup> This appears to be reasonable, because simple inspection of models suggests that substitution of methylene units of type b with the more sterically demanding Ph<sub>2</sub>Sn groups will result in the smallest increase in steric interactions for the molecule.<sup>18</sup> The MM2 calculations, however, indicate that this is not the case; conformation I is lower in energy than II by 1.8 kcal/mol.

(18) Davies, A. G.; Tse, M.-W.; Kennedy, J. D.; McFarlane, W.; Pyne, G. S. *J. Chem. Soc., Perkin Trans. 2* 1981, 369–375.

Table II. Bond Lengths and Angles of Organostannanes<sup>a</sup>

compd	bond	exptl	calcd	angle	exptl	calcd
MeSnH <sub>3</sub> <sup>b</sup>	Sn-C	2.140 (1)	2.140	C-Sn-H	109.36 (3)	109.3
	Sn-H	1.708 (1)	1.700	Sn-C-H	110.36 (4)	110.40
EtSnH <sub>3</sub> <sup>c</sup>	Sn-C	2.143 (3)	2.148	C-Sn-H	109.5 (1)	109.2
	Sn-H		1.700	C-C-Sn	112.6 (9)	112.7
	C-C	1.552 (25)	1.532			
Me <sub>2</sub> SnH <sub>2</sub> <sup>d</sup>	Sn-C	2.150 (3)	2.140	C-Sn-C	104.8 (5)	105.5
	Sn-H	1.680 (15)	1.699	C-Sn-H	108.0 (15)	109.5
				Sn-C-H	111.7 (5)	110.3
Me <sub>3</sub> SnH <sup>d</sup>	Sn-C	2.147 (4)	2.139	C-Sn-C	107.5 (6)	107.4
	Sn-H	1.705 (67)	1.699	C-Sn-H	111.5 (20)	111.5
				Sn-C-H	111.6 (7)	110.3
Me <sub>4</sub> Sn <sup>e</sup>	Sn-C	2.144 (3)	2.139	Sn-C-H	112.0 (16)	110.5
Me <sub>3</sub> SnCl <sup>d</sup>	Sn-C	2.106 (6)	2.140	C-Sn-C	114.9 (16)	114.9
	Sn-Cl	2.351 (7)	2.379	Cl-Sn-C	103.2 (6)	103.2
				Sn-C-H	113.4 (14)	110.6
(c-C <sub>6</sub> H <sub>11</sub> ) <sub>3</sub> SnCl <sup>f</sup>	Sn-Cl	2.407 (5)	2.380	Cl-Sn-C	101.90 (5)	104.2
	Sn-C	2.162 (20)	2.161	Cl-Sn-C <sup>g</sup>	101.40 (5)	104.2
	Sn-C <sup>g</sup>	2.065 (22)	2.161	C-Sn-C	119.00 (5)	114.2
				C-Sn-C <sup>g</sup>	115.00 (6)	114.2
ClSnH <sub>3</sub> <sup>h</sup>	Sn-Cl	2.328	2.380	Cl-Sn-H	105.5	105.7
	Sn-H	1.696	1.700	H-Sn-H	113.1	113.0
Ph <sub>4</sub> Sn <sup>i</sup>	Sn-C	2.139 (4)	2.150	C(1)-Sn-C(1a)	108.6 (1)	109.5
				C(1)-Sn-C(1b)	111.2 (2)	109.5
				Sn-C(1)-C(2)	120.9 (3)	120.1
				Sn-C(1)-C(6)	121.5 (3)	120.2
(o-tolyl) <sub>4</sub> Sn <sup>i</sup>	Sn-C	2.152 (5)	2.161	C(1)-Sn-C(1a)	107.9 (1)	110.7
				C(1)-Sn-C(1b)	112.6 (3)	107.0
				Sn-C(1)-C(2)	117.5 (4)	117.6
				Sn-C(1)-C(6)	124.4 (4)	122.6
sec-BuSnPh <sub>3</sub> <sup>j,k</sup>	Sn-C(1)	2.16 (1), 2.13 (2)	2.150	C(1)-Sn-C(7)	107.26 (5), 106.08 (5)	108.7
	Sn-C(7)	2.15 (1), 2.16 (1)	2.151	C(1)-Sn-C(13)	107.13 (5), 110.96 (5)	109.2
	Sn-C(13)	2.17 (1), 2.16 (1)	2.151	C(1)-Sn-C(20)	108.27 (5), 108.69 (6)	108.6
	Sn-C(20)	2.23 (2), 2.20 (2)	2.159	C(7)-Sn-C(13)	108.94 (6), 106.14 (5)	110.7
				C(7)-Sn-C(20)	113.57 (5), 109.47 (6)	110.0
Ph <sub>3</sub> SnCl <sup>h,l</sup>	Sn-Cl	2.362 (1), 2.369 (1)	2.378	C(13)-Sn-C(20)	111.38 (5), 115.09 (6)	109.6
	Sn-C(11)	2.117 (3), 2.117 (3)	2.150	Cl-Sn-C(11)	105.85 (12), 106.74 (12)	105.4
	Sn-C(21)	2.124 (3), 2.123 (3)	2.150	Cl-Sn-C(21)	105.08 (11), 103.39 (12)	105.4
	Sn-C(31)	2.126 (3), 2.120 (3)	2.150	Cl-Sn-C(31)	104.18 (12), 104.45 (12)	105.4
				C(11)-Sn-C(21)	117.11 (14), 114.18 (14)	112.5
				C(11)-Sn-C(31)	109.83 (14), 110.94 (14)	112.5
				C(21)-Sn-C(31)	112.90 (15), 115.91 (15)	112.5
(ad)Sn(Ph) <sub>2</sub> CH <sub>3</sub> <sup>m</sup>	Sn-C(3)	2.175 (9)	2.174	C(16)-Sn-C(26)	109.8 (4)	112.0
	Sn-C(4)	2.163 (10)	2.139	C(16)-Sn-C(3)	113.1 (3)	109.1
	Sn-C(16)	2.139 (10)	2.151	C(16)-Sn-C(4)	106.8 (5)	108.8
	Sn-C(26)	2.144 (10)	2.151	C(26)-Sn-C(3)	108.5 (4)	109.5
				C(26)-Sn-C(4)	109.2 (5)	109.5
			C(3)-Sn-C(4)	109.4 (5)	108.0	

<sup>a</sup> Bond lengths in Å; bond angles in degrees. The numbering systems for the aryl-containing compounds are the same as those used in the crystal structure reports; see Figure 1. <sup>b</sup> Structure by microwave spectroscopy.<sup>12</sup> <sup>c</sup> Structure by microwave spectroscopy.<sup>8d</sup> <sup>d</sup> Structure by electron diffraction.<sup>8a</sup> <sup>e</sup> Structure by electron diffraction.<sup>11</sup> <sup>f</sup> Structure by X-ray crystallography.<sup>5b</sup> <sup>g</sup> Two bonds (angles) have this value in the crystal structure. <sup>h</sup> Structure by rotovibrational analysis of IR spectrum<sup>8m</sup> and ab initio calculation.<sup>8l</sup> <sup>i</sup> Structure by X-ray crystallography.<sup>10a</sup> <sup>j</sup> Structure by X-ray crystallography. <sup>k</sup> Two molecules per asymmetric unit. <sup>l</sup> Structure by X-ray crystallography.<sup>10b</sup> <sup>m</sup> (1-Adamantyl)diphenylmethyltin; structure by X-ray crystallography.<sup>10d</sup>

This results mainly from relief of van der Waals interactions in I relative to II. Conformation III is calculated to be highest in energy due to large increases in bending and torsion energies that raise the total energy to a value 4.8 kcal/mol greater than that of I. The preference of molecule 5 in the solid state for what is calculated to be a slightly higher energy conformation may well be due to packing forces within the crystal that are not accounted for by MM2.

Some of the features of the crystal structure 5 and the calculated structure for conformation II are presented in Table III. There is very good agreement between the two structures; the largest Sn-C bond length deviation is 0.02 Å, and the largest deviation in an angle containing tin in the triad is 2.1°. The MM2 reproduction of the transan-

nular Sn-Sn distance to within about 2% of the observed value is especially gratifying.

We have obtained the crystal structure of 1,1,6,6,11,11,16,16-octaphenyl-1,6,11,16-tetrastannaeicosane (6), which contains four diphenylstanna units in a 20-membered ring. An ORTEP drawing of the molecule is shown in Figure 4. As one might anticipate for a large and relatively unconstrained macrocycle, the crystal structure of 6 was not the minimum-energy structure found in MM2 modeling. In the crystal structure of 6, there is a strong eclipsing interaction (the C(4)-Sn(2)-C(8a)-C(7a) dihedral angle is 1.3°) that rapidly relaxed in unrestricted MM2 modeling. However, when the crystal structure coordinates were employed as a starting point for the MM2 structure and the eclipsed dihedral angle and its symme-

Table III. Comparison of Experimental and Calculated Structural Features of Cyclic Organostannanes 4-6<sup>a</sup>

compd	feature	exptl	calcd
4 <sup>b</sup>	C-Sn-C	95	87.1
	Ph-Sn-Ph	120	115.6
	Sn-C-C	115	104.3
5 <sup>b,c</sup>	Sn-C(1)	2.150 (9)	2.149
	Sn-C(7)	2.131 (6)	2.151
	Sn-C(13)	2.155 (7)	2.151
	Sn-C(16)	2.167 (8)	2.152
	Sn-Sn(a)	5.46	5.58
	C(1)-Sn-C(7)	108.2 (3)	109.9
	C(1)-Sn-C(13)	107.5 (3)	108.6
	C(1)-Sn-C(16)	110.1 (3)	108.3
	C(7)-Sn-C(13)	111.0 (3)	109.8
	C(7)-Sn-C(16)	106.6 (3)	108.7
	C(13)-Sn-C(16)	113.3 (3)	111.5
	Sn-C(13)-C(14)	114.8 (4)	113.2
	Sn-C(16)-C(15)	117.1 (5)	116.4
	Sn-C(13)-C(14)-C(15)	160.5	162.8
	C(13)-C(14)-C(15)-C(16)	-68.3	-66.7
	C(14)-C(15)-C(16)-Sn(a)	-63.7	-66.7
6 <sup>d</sup>	Sn(1)-C(1)	2.137 (6)	2.145
	Sn(1)-C(5)	2.142 (6)	2.145
	Sn(1)-C(9)	2.137 (5)	2.152
	Sn(1)-C(15)	2.142 (6)	2.152
	Sn(2)-C(4)	2.149 (5)	2.151
	Sn(2)-C(8)	2.145 (5)	2.148
	Sn(2)-C(21)	2.149 (5)	2.150
	Sn(2)-C(27)	2.142 (5)	2.150
	Sn(1)-Sn(2)	7.548	7.551
	Sn(1)-Sn(1a)	9.982	9.867
	Sn(1)-Sn(2a)	6.424	6.447
	Sn(2)-Sn(2a)	9.845	9.989
	C(1)-Sn(1)-C(5)	110.4 (3)	109.5
	C(1)-Sn(1)-C(9)	106.3 (2)	109.2
	C(1)-Sn(1)-C(15)	110.0 (2)	111.6
	C(5)-Sn(1)-C(9)	109.5 (2)	108.4
	C(5)-Sn(1)-C(15)	110.7 (2)	109.0
	C(9)-Sn(1)-C(15)	110.0 (2)	109.2
	C(4)-Sn(2)-C(8)	115.6 (2)	113.6
	C(4)-Sn(2)-C(21)	107.5 (2)	106.1
	C(4)-Sn(2)-C(27)	105.4 (2)	108.7
	C(8)-Sn(2)-C(21)	110.8 (2)	110.6
	C(8)-Sn(2)-C(27)	108.7 (2)	107.9
	C(21)-Sn(2)-C(27)	108.5 (2)	110.0
	Sn(1)-C(1)-C(2)	115.9 (4)	114.2
	Sn(1)-C(5)-C(6)	116.6 (5)	112.4
	Sn(2)-C(8)-C(7)	116.1 (4)	114.9
	Sn(2)-C(4)-C(3)	111.5 (4)	111.1
	Sn(1)-C(1)-C(2)-C(3)	179.1	-178.0
	C(1)-C(2)-C(3)-C(4)	-175.7	-176.7
	C(2)-C(3)-C(4)-Sn(2)	178.1	-178.0
	Sn(1)-C(5)-C(6)-C(7)	-176.4	-176.6
	C(5)-C(6)-C(7)-C(8)	173.5	179.8
	C(6)-C(7)-C(8)-Sn(2)	71.8	75.6
C(1)-Sn(1)-C(5)-C(6)	-110.7	-121.7	
C(5)-Sn(1)-C(1)-C(2)	67.7	63.9	
C(4)-Sn(2)-C(8a)-C(7a)	-1.3	-1.5 <sup>e</sup>	
C(8)-Sn(2)-C(4)-C(3)	-174.9	-169.4	

<sup>a</sup>Bond lengths in Å; bond angles in degrees. <sup>b</sup>Structure by X-ray crystallography;<sup>18</sup> see Figure 3 for atom numbering. <sup>c</sup>Calculated results for conformation II of compound 5. <sup>d</sup>Structure by X-ray crystallography (this work); see Figure 4 for atom numbering. <sup>e</sup>This dihedral angle was constrained in the modeling.

try-equivalent angle were constrained, the MM2 minimized structure was in quite good agreement with the crystal structure (Table III). For example, the differences in the experimental and calculated values for the Sn-Sn distances averaged less than 1%. When the dihedral angle constraints were removed, this minimized constrained structure was found to be not even a local minimum.

**Energies of (Trimethylstannyl)cyclohexane Conformers.** An important test of any MM2 parameterization is its ability to predict the conformational preference of

Table IV. Comparison of Calculated MM2 Energies for Conformers I-III of 5

MM2 energy <sup>a</sup>	conformer		
	I	II	III
total	11.7	13.50	16.5
stretch	0.93	0.93	0.91
bend	6.19	5.47	8.55
stretch-bend	0.33	0.33	0.40
torsion	1.36	2.55	4.80
van der Waals	2.89	4.23	1.84

<sup>a</sup>Energies in kcal/mol.

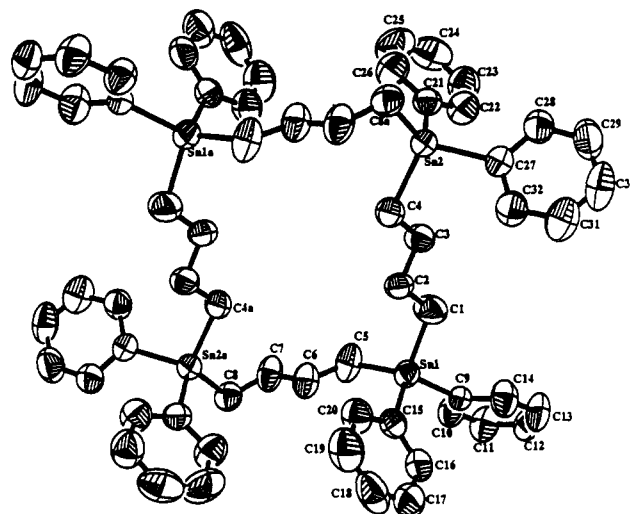
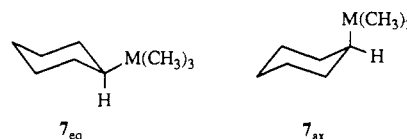


Figure 4. ORTEP drawing of compound 6 at the 50% probability level.

a substituent on a cyclohexane ring. The energy difference between axial and equatorial substituted conformers (i.e.  $\tau_{ax}$  and  $\tau_{eq}$ ) is due mainly to a mixture of bending and van



der Waals interactions that severely test the parameter set under development. NMR studies, primarily by Kitching, have estimated the *A* values of the trimethylsilyl, trimethylgermyl, trimethylstannyl, and trimethylplumbyl groups to be 2.4-2.6, 2.1, 1.06, and 0.67 kcal/mol, respectively.<sup>15b,c</sup> The isostructural *tert*-butyl group has an estimated *A* value of approximately 5.0 kcal/mol.<sup>1b,2a</sup> This steady decrease in the *A* values of the (CH<sub>3</sub>)<sub>3</sub>M unit (where M = C, Si, Ge, Sn, and Pb) is due to the steady increase in the C-M bond lengths and the resulting reduction in 1,3-diaxial van der Waals interactions in the axial conformers.

MM2 calculations on axial and equatorial *tert*-butylcyclohexane and (trimethylsilyl)cyclohexane were reported by Allinger, but a breakdown of the various energetic interactions (stretch, bend, torsion, etc.) was not given.<sup>2a</sup> In Table V are presented the results of MM2 calculations for (trimethylstannyl)cyclohexane, (trimethylsilyl)cyclohexane, and *tert*-butylcyclohexane. In both the stannyl and silyl compounds, there is complete relief of repulsive van der Waals interactions in both the axial and equatorial conformers. In axial (trimethylstannyl)cyclohexane, the van der Waals term has become distinctly negative (-0.38 kcal/mol), indicating that the 1,3-diaxial interaction is now attractive rather than repulsive. In both the stannyl and silyl compounds, the bending terms provide the major



**Table V. Comparison of Calculated MM2 Energies for Axial and Equatorial *tert*-Butylcyclohexane, (Trimethylsilyl)cyclohexane, and (Trimethylstannyl)cyclohexane**

structure	MM2 energy <sup>b</sup>	M = C	M = Si <sup>a</sup>	M = Sn
7 <sub>eq</sub>	total	13.31	4.30	4.09
	stretch	1.38	0.50	0.41
	bend	1.97	0.93	1.33
	stretch-bend	0.30	0.02	0.12
	torsion	3.73	3.08	2.15
	van der Waals	5.92	-0.21	0.10
	7 <sub>ax</sub>	total	18.31	6.78
stretch		1.50	0.52	0.43
bend		4.32	2.48	2.43
stretch-bend		0.43	0.10	0.17
torsion		5.46	3.87	2.58
van der Waals		6.60	-0.19	-0.38

<sup>a</sup> Calculated with the silicon parameters reported in ref 2a.  
<sup>b</sup> Energies in kcal/mol.

source of the energy difference between axial and equatorial conformers, accounting for about two-thirds of the difference in each case. The remainder of the difference results from the torsional term. Equatorial (trimethylstannyl)cyclohexane is calculated to be favored over the axial conformer by 1.14 kcal/mol, in good agreement with the reported experimental values of 0.94 and 1.06 kcal/mol.<sup>15a,b</sup>

### Conclusion

The force field parameter set for compounds containing tetravalent tin developed in this work reproduced experimental gas-phase structures of simple stannanes including chlorostannane and trimethylchlorostannane. Reasonable agreement was found between calculated and solid-state structures, especially when one realizes that crystal-packing forces can be important in the solid state. Differences between the calculated and crystal structures of (*c*-C<sub>6</sub>H<sub>11</sub>)<sub>3</sub>SnCl suggested that slight association in the solid state exists, a conclusion that is supported by other evidence, and this type of comparison might prove to be important for revealing Lewis acid-base interactions in other solids. The parameter set reproduces the energy difference between the axial and equatorial conformers of (trimethylstannyl)cyclohexane with reasonable accuracy.

Some of the parameters in the set were estimated due to insufficient experimental data, and errors were almost certainly introduced in the approximations. The van der Waals terms are especially suspect. Nevertheless, the results suggest that reasonably accurate MM2 calculations of structures and energies of compounds containing tetravalent tin bonded to H, C, or Cl can now be obtained. In fact, structural calculations of macrobicyclic host **2** and their precursors **3** were found to be in generally good agreement, as we report in the following paper. Of course, more precise experimental data, especially for bending and torsion in simple stannanes, would be expected to improve the parameter set.

### Experimental Section

**Computations.** Calculations were performed on the program MACROMODEL<sup>19</sup> (versions 2.0 and 3.0) on a DEC Microvax II computer and the program PCMODEL<sup>20</sup> (versions 88.0 and 89.0) on an IBM-compatible personal computer. Tin parameters were

(19) Mohamadi, F.; Richards, N. G. J.; Guida, W. C.; Liskamp, R.; Lipton, M.; Caufield, C.; Chang, G.; Hendrickson, T.; Still, W. C. *J. Comput. Chem.* **1990**, *11*, 440-467.

(20) Supplied by Serena Software, P.O. Box 3076, Bloomington, IN 47402-3076.

**Table VI. Summary of Crystal Data for **6****

formula	C <sub>64</sub> H <sub>72</sub> Sn <sub>4</sub>
mol wt	1316.05
cryst syst	monoclinic
<i>a</i> , Å	13.240 (2)
<i>b</i> , Å	15.929 (3)
<i>c</i> , Å	14.906 (3)
$\beta$ , deg	109.20 (1)
<i>V</i> , Å <sup>3</sup>	2968.8
space group	<i>P</i> 2 <sub>1</sub> / <i>n</i> (No. 14)
<i>Z</i>	2
density, g/cm <sup>3</sup>	1.47
<i>F</i> (000)	1312
instrument	Enraf-Nonius CAD4
monochromator	graphite cryst, incident beam
radiation	Mo K $\alpha$ ( $\lambda$ = 0.71073 Å)
scan type	$\omega$ - $\theta$
scan rate, deg/min	2-20 (in $\omega$ )
max $2\theta$ , deg	55
$\mu$ , cm <sup>-1</sup>	17.1
temp, °C	23 $\pm$ 1
no. of unique data	6802
no. of obsd data, $F_o^2 > 3\sigma(F_o^2)$	3626
no. of variables	307
<i>R</i> , <i>R</i> <sub>w</sub> <sup>a</sup>	0.036, 0.045
largest peak in final diff map, e/Å <sup>3</sup>	0.75
goodness of fit	1.15

$$^a R = \sum ||F_o| - |F_c|| / \sum |F_o|; R_w = (\sum w(|F_o| - |F_c|) / \sum w F_o^2)^{1/2}.$$

**Table VII. Atomic Coordinates and Isotropic Thermal Parameters for **6****

atom	<i>x</i>	<i>y</i>	<i>z</i>	<i>B</i> (eq), Å <sup>2</sup>
Sn(1)	0.32594 (3)	0.06671 (3)	0.24193 (2)	4.849 (9)
Sn(2)	0.86544 (3)	0.09585 (3)	0.17451 (2)	4.620 (8)
C(1)	0.4951 (5)	0.0698 (5)	0.2713 (4)	7.1 (2)
C(2)	0.5322 (4)	0.0736 (3)	0.1853 (4)	5.1 (1)
C(3)	0.6538 (4)	0.0771 (4)	0.2125 (4)	5.4 (1)
C(4)	0.6940 (4)	0.0875 (4)	0.1289 (4)	5.5 (1)
C(5)	0.2610 (6)	-0.0492 (4)	0.1747 (4)	7.3 (2)
C(6)	0.1935 (5)	-0.0445 (4)	0.0742 (4)	6.7 (2)
C(7)	0.1453 (5)	-0.1296 (4)	0.0343 (4)	6.7 (2)
C(8)	0.0671 (4)	-0.1216 (4)	-0.0648 (4)	6.0 (1)
C(9)	0.3012 (4)	0.0756 (3)	0.3762 (3)	4.4 (1)
C(10)	0.2351 (4)	0.0212 (4)	0.4022 (4)	6.3 (2)
C(11)	0.2249 (5)	0.0265 (5)	0.4909 (4)	7.4 (2)
C(12)	0.2795 (5)	0.0852 (4)	0.5551 (4)	6.6 (2)
C(13)	0.3451 (6)	0.1386 (5)	0.5315 (4)	7.7 (2)
C(14)	0.3558 (5)	0.1336 (4)	0.4424 (4)	7.3 (2)
C(15)	0.2526 (4)	0.1712 (4)	0.1542 (4)	5.1 (1)
C(16)	0.2008 (5)	0.2332 (4)	0.1857 (4)	6.8 (2)
C(17)	0.1529 (6)	0.3006 (5)	0.1269 (5)	8.9 (2)
C(18)	0.1579 (6)	0.3051 (5)	0.0383 (5)	9.7 (2)
C(19)	0.2089 (6)	0.2455 (5)	0.0056 (5)	8.8 (2)
C(20)	0.2562 (5)	0.1788 (4)	0.0629 (4)	6.7 (2)
C(21)	0.9284 (4)	-0.0191 (3)	0.2468 (4)	5.0 (1)
C(22)	0.9393 (5)	-0.0304 (4)	0.3403 (4)	6.5 (2)
C(23)	0.9761 (6)	-0.1043 (5)	0.3854 (5)	7.8 (2)
C(24)	1.0064 (6)	-0.1683 (4)	0.3403 (6)	8.9 (2)
C(25)	0.9960 (6)	-0.1590 (4)	0.2463 (6)	9.5 (2)
C(26)	0.9565 (5)	-0.0847 (4)	0.1999 (5)	7.3 (2)
C(27)	0.9064 (4)	0.1963 (3)	0.2755 (3)	4.9 (1)
C(28)	1.0059 (5)	0.1997 (4)	0.3468 (4)	6.3 (2)
C(29)	1.0305 (6)	0.2663 (5)	0.4101 (5)	7.9 (2)
C(30)	0.9607 (6)	0.3298 (4)	0.4041 (4)	8.2 (2)
C(31)	0.8633 (6)	0.3277 (4)	0.3348 (5)	7.7 (2)
C(32)	0.8368 (5)	0.2623 (4)	0.2704 (4)	6.2 (2)

entered for atom Z<sub>0</sub> in MACROMODEL and atom 32 in PCMODEL.

PCMODEL (version 89.0) often encountered floating point math errors and ceased running when the initial geometry of the structure differed greatly from a chemically reasonable structure. PCMODEL (version 89.0) also had a tendency to minimize some simple organostannanes as high-energy, nontetrahedral structures. Neither of the above problems was encountered with PCMODEL (version 88.0) or with MACROMODEL. In the minimizations of Ph<sub>4</sub>Sn and (*o*-tolyl)<sub>4</sub>Sn, it was noted that PCMODEL (version 89.0) tended



**Table VIII. Selected Distances and Angles for 6**

Distances (Å)			
Sn(1)–C(1)	2.137 (6)	Sn(1)–C(5)	2.142 (6)
Sn(1)–C(9)	2.137 (5)	Sn(1)–C(15)	2.142 (6)
Sn(2)–C(4)	2.149 (5)	Sn(2)–C(8)	2.145 (5)
Sn(2)–C(21)	2.149 (5)	Sn(2)–C(27)	2.142 (5)
C(1)–C(2)	1.516 (7)	C(2)–C(3)	1.527 (8)
C(3)–C(4)	1.516 (7)	C(5)–C(6)	1.473 (8)
C(6)–C(7)	1.532 (8)	C(7)–C(8)	1.504 (9)
Angles (deg)			
C(1)–Sn(1)–C(5)	110.4 (3)	C(1)–Sn(1)–C(9)	106.3 (2)
C(1)–Sn(1)–C(15)	110.0 (2)	C(5)–Sn(1)–C(9)	109.5 (2)
C(5)–Sn(1)–C(15)	110.7 (2)	C(9)–Sn(1)–C(15)	110.0 (2)
C(4)–Sn(2)–C(8)	115.6 (2)	C(4)–Sn(2)–C(21)	107.5 (2)
C(4)–Sn(2)–C(27)	105.4 (2)	C(8)–Sn(2)–C(21)	110.8 (2)
C(8)–Sn(2)–C(27)	108.7 (2)	C(21)–Sn(2)–C(27)	108.5 (2)
Sn(1)–C(1)–C(2)	115.9 (4)	C(1)–C(2)–C(3)	112.6 (5)
C(2)–C(3)–C(4)	114.2 (5)	Sn(2)–C(4)–C(3)	111.5 (4)
Sn(1)–C(5)–C(6)	116.6 (5)	C(5)–C(6)–C(7)	112.7 (6)
C(6)–C(7)–C(8)	111.8 (6)	Sn(2)–C(8)–C(7)	116.1 (4)
Sn(1)–C(9)–C(10)	122.0 (4)	Sn(1)–C(9)–C(14)	120.8 (4)
Torsion Angles (deg)			
C(5)–Sn(1)–C(1)–C(2)	67.7		
Sn(1)–C(1)–C(2)–C(3)	179.1		
C(8a)–Sn(2)–C(4)–C(3)	-174.9		
Sn(2)–C(4)–C(3)–C(2)	178.1		
C(5)–C(6)–C(7)–C(8)	173.6		
C(1)–Sn(1)–C(5)–C(6)	-110.7		
Sn(1)–C(5)–C(6)–C(7)	-176.4		
C(4)–Sn(2)–C(8a)–C(7a)	-1.3		
C(1)–C(2)–C(3)–C(4)	-175.7		
Sn(2)–C(8)–C(7)–C(6)	71.8		

to converge before a true minimum was reached; no calculations of aryltin compounds were attempted on PCMODEL (version 88.0) due to its limited ability to handle  $\pi$ -systems. Except for the cases noted here, no significant differences were observed between the results of calculations performed with MACROMODEL and PCMODEL.

**Crystal Structure of 6.** The preparation of compound 6 has been described.<sup>3d</sup> The sample was recrystallized from hexane-ether and had mp 107.5–108 °C (uncorrected). Cell constants

and an orientation matrix for data collection were obtained from least-squares refinement with use of the setting angles of 25 reflections in the range  $2 < \theta < 13^\circ$ . During data collection, as a check on crystal and electronic stability, three representative reflections were measured every 41 min. A total loss in intensity of 3.4% was observed. A linear decay correction and Lorentz and polarization corrections were applied to the data. No absorption correction was made. From the systematic absences  $0k0$  ( $k \neq 2n$ ) and  $h0l$  ( $h + l \neq 2n$ ) and from subsequent least-squares refinement, the space group was determined to be  $P2_1/n$  (No. 14). The structure was solved by direct methods. Non-hydrogen atoms were refined anisotropically. Hydrogen atoms were located and added to the structure factor calculations, but their positions were not refined. The structure was refined in full-matrix least squares, where the function minimized was  $\sum w(|F_o| - |F_c|)^2$  and the weight  $w$  is defined as  $4F_o/\sigma^2(F_o^2)$ . Plots of  $\sum w(|F_o| - |F_c|)^2$  versus  $|F_o|$ , reflection order in data collection,  $(\sin \theta)/\lambda$ , and various classes of indices showed no unusual trends. The scattering factors and anomalous dispersion terms were taken from literature values.<sup>21</sup> Crystallographic data and details of data collection are given in Table VI. Atomic coordinates of all non-hydrogen atoms are reported in Table VII, and selected distances and angles are given in Table VIII. All crystallographic calculations were performed on a PDP-11/60 based TEXRAY<sup>22</sup> system.

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**Supplementary Material Available:** Tables of hydrogen atom positional parameters and bond lengths, bond angles, and anisotropic thermal parameters for the non-hydrogen atoms of compound 6 (4 pages). Ordering information is given on any current masthead page.

(21) *International Tables for X-Ray Crystallography*; Kynoch Press: Birmingham, U.K., 1974; Vol. IV.

(22) TEXRAY is a trademark of Molecular Structure Corp. (1982).