Co–CN ligand arrangements, respectively. This order directly parallels the expected trend in trans interaction.

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Conformational Analysis. XVIII.[1] Force Field Calculations of Conformational Equilibria of Group IV Organometallic Compounds

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Abstract: Force field calculations of two conformations of CH_3MH_3, two of $(CH_3)_2MH_2$, two of $(CH_3)_3MH$, three of $CH_3CH_2MH_3$, four of $CH_3CH_2CH_2MH_3$, four of $CH_3MH_2CH_2CH_3$, two of $(CH_3)_2MHCH_2CH_3$, two of $(CH_3)_2MHCH(CH_3)_2$, four of $(CH_3CH_2)_2MH_2$, and two of $C_6H_{11}MH_3$ for two series of compounds where M is germanium and tin have been done. Comparisons are made with the previously reported silicon analogs. The parameters for the force field functions are chosen so that the calculated structures and torsional barriers of CH_3MH_3, $(CH_3)_2MH_2$, and $(CH_3)_3MH$ are consistent with the available microwave data. The remaining calculated structures and conformational energies await experimental tests. The conformations of germanium and tin compounds are predicted to be controlled by hydrogen–hydrogen nonbonded attractive terms and thus join silicon compounds in manifesting unique conformational properties in contrast to those of hydrocarbons.

It was reported in a recent paper[2] from this laboratory that force field calculations of the conformational energies of organosilicon compounds successfully predict their conformational properties as determined by nmr spectroscopy. This paper illustrated that the conformational concepts based on carbon compounds are not directly comparable to their silicon analogs. Attractive van der Waals interactions stabilize the gauche conformation of 2-silabutane with respect to the anti conformation. Other compounds containing the 2-silabutane structural unit such as 2-methyl-2-silabutane, 2,3-dimethyl-2-silabutane, and 3-silapentane exhibit the same ordering of conformational energies. In view of the successful extension of force field calculations to hydrocarbons containing silicon as a heteroatom, it was logical to consider the organogermanes and organostannanes. Lead compounds containing lead–hydrogen bonds are sufficiently unstable to have precluded the determination of the necessary physical properties with which to parameterize the force field equations. Accordingly, lead compounds are excluded from this study.

Force Field Calculations

The classical model used in this study involves the calculation of the strain energy, E_s, of the conformation which is defined as the sum of energy terms given in eq 1. The individual terms are the energies associated with bond stretching, bond angle deformations, bond torsions, and nonbonded interactions. The force field can be viewed as two harmonic potentials involving bonded atoms and two nonbonded potentials.

$$E_s = E_r + E_\theta + E_\phi + E_{nb} \qquad (1)$$

The harmonic potentials are given by eq 2 and 3. For each bond or bond angle, the l_0 and θ_0 values are selected to represent "strain free" values. The individual force constants k_r and k_θ are calculated or estimated from normal coordinate analysis of the infrared and Raman spectra of representative molecules.

$$E_r = \sum {}^1/_2 k_r(l - l_0)^2 \qquad (2)$$

$$E_\theta = \sum {}^1/_2 k_\theta(\theta - \theta_0)^2 \qquad (3)$$

The torsional potential is given by eq 4 for the threefold barrier involved in the molecules of interest. The dihedral angle is given by ϕ and the barrier height by k_ϕ.

$$E_\phi = \sum {}^1/_2 k_\phi(1 + \cos 3\phi) \qquad (4)$$

The Hill function given in eq 5 is used to account for the attractive and repulsive van der Waals forces.

$$E_{nb} = \sum \epsilon\{-2.25\alpha^{-6} + 8.28 \times 10^5 \exp(-\alpha/0.0736)\} \qquad (5)$$

Energy minimization was achieved by utilizing the method of Boyd.[3] When the root-mean-square deviation of the coordinate position was less than 0.002 Å the iterative process was terminated.

Two additional programs were placed prior to the minimization method in order to decrease the labor of preparing the input data. A molecule builder program calculates the coordinates of the molecules and

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[1] This research was supported by Grants GP-9231 and GP-33423 from the National Science Foundation.

[2] Conformational Analysis. XV: R. J. Ouellette, D. Baron, J. Stolfo, A. Rosenblum, and P. Weber, *Tetrahedron*, 28, 2163 (1972).

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arranges the structures in the desired initial geometries. The second program is an atom and parameter inclusion matrix which selects all of the appropriate combinations of atoms and the related parameters for the proper potential functions. All intermediate data from the two programs were directly accessible on disc. An IBM 370 was used for the calculations. The total times for the molecule builder, atom inclusion matrix, and minimization steps for the molecules discussed in in this report varied from 9 to 40 sec. These times represent an efficient approach to the problem of calculating the steric energy of molecules.

The parameters chosen for carbon and hydrogen structural units are those of Allinger,[4] and are listed in Table I. Nonbonded interactions between atoms bonded to a common atom were not included. Rather than use the complete set of early parameters, the choice was made to adopt k_0(X–C–C–Y) = 0.5 kcal/mol suggested in more recent calculations.[5]

Table I. Parameters for the Calculation of Molecular Geometries and Conformational Energies

	H	C	Si	Ge	Sn
		van der Waals Constants			
r	1.45	1.65	2.15	2.25	2.40
ϵ	0.100	0.040	0.310	0.350	0.600
		Bond Stretching Constants			
l_0(C–M)		1.513	1.870	1.950	2.143
k(C–M)		4.50	2.97	2.700	2.124
l_0(M–H)		1.094	1.485	1.530	1.700
k(M–H)		4.80	2.78	2.570	2.229
		Angle Bending Constants			
θ_0(H–M–H)		110.9	108.2	109.0	109.5
k(H–M–H)		0.3194	0.236	0.216	0.132
θ_0(H–M–C)		108.6	109.5	109.5	109.5
k(H–M–C)		0.5486	0.403	0.352	0.227
θ_0(H–C–M)		108.6	110.0	109.5	109.5
k(H–C–M)		0.5486	0.476	0.449	0.390
θ_0(C–C–M)		109.8	112.0	110.2	110.2
k(C–C–M)		0.7986	0.684	0.640	0.560
θ_0(C–M–C)		109.8	110.5	110.0	109.5
k(C–M–C)		0.7986	0.570	0.490	0.320
		Torsional Constants			
X–C–M–Y		0.50	0.50	0.38	0.22

Force constants for C–M and H–M stretching as well as H–M–H bending where M is silicon are available from normal coordinate analysis of methylsilane[6] and silane.[7] The force constant for C–Si–C bending is estimated.[8] The C–M and H–M stretching force constants and the H–M–H bending constants for M equal to germanium and tin are available from normal coordinate analysis of methylgermane[9] and methylstannane.[10] By analogy with the ordering of the bending force constants involving carbon as the central atom, the H–M–C bending force is set at a value between those of H–M–H and C–M–C. The C–C–M and H–C–M bending force constants are chosen to be less than the C–C–C and H–C–C values in order to reflect the effect of the ease of deforming an angle when another member of group IV is substituted for carbon.

In order to fit the torsional barrier for silaethane,[11] the torsional parameter k_0(H–C–Si–H) is set at 0.5 kcal/mol. The k_0(X–C–Si–Y) for X and Y equal to the other combinations of hydrogen and carbon have been assigned identical values as has been done for k_0(X–C–C–Y).[5] These reproduce the barriers of silaethane, 2-silapropane,[12] and 2-methyl-2-silapropane.[11]

For k_0(H–C–Ge–H) a value of 0.38 kcal/mol is chosen to fit the barrier of methylgermane.[13] Setting all k_0(X–C–Ge–Y) equal to the same value seems a reasonable choice. The barrier for dimethylgermane[14] is reproduced with these values. For k_0(H–C–Sn–H) a value of 0.22 kcal/mol is chosen to fit the barrier for methylstannane.[15] The other k_0(X–C–Sn–Y) terms are also set to the same value although there is no experimental verification of the validity of this choice.

Energy and Structures

Each structural type for the various group IV elements is described under a separate heading. Calculated structures of the simpler compounds are listed in Table II. The component energies obtained are given in Table III for the minimized structure for the four simplest compounds. The symbols E_r, E_θ, E_ϕ, E_{nb}, and E_s refer to the energies associated with stretching, bending, torsional, nonbonded, and total steric energies, respectively. The E_s values for all compounds are given in Table IV for ease of comparison.

CH_3MH_3. The force field parameters chosen lead to calculated structures for the staggered conformation of the CH_3MH_3 compounds which agree with the observed structures for M = Si,[16] Ge,[13] and Sn.[17] In the eclipsed conformations it is predicted that there is little change in structure and the slight distortions which do occur decrease in the series silicon > germanium > tin.

In terms of E_r and E_θ the molecules are strain free in both staggered and eclipsed conformations. The E_{nb} terms dominate the conformational energies of the staggered conformations and are negative. Since the silicon compounds contain gauche H–H interactions at the minimum of the chosen van der Waals curve the E_{nb} terms become less negative for the germanium and tin compounds as the bond distances increase.

As indicated in the section describing the force field calculations, the E_ϕ term is chosen to fit the torsional barrier. However, since conformational equilibria

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Table II. Calculated and Observed Structures of Group IV Organometallic Compounds

		CH_3MH_3			$(CH_3)_2MH_2$			$(CH_3)_3MH$			$CH_3CH_2MH_3$		
		Si	Ge	Sn	Si	Ge	Sn	Si	Ge	Sn	Si	Ge	Sn
M–H	Obsd	1.484	1.529	1.700	1.483			1.489					
	Calcd	1.487	1.529	1.697	1.484	1.529	1.698	1.484	1.528	1.698	1.485	1.529	1.699
	Eclpd	1.481	1.530	1.697	1.484	1.529	1.699	1.484	1.529	1.700	1.485	1.530	1.699
M–C	Obsd	1.867	1.945	2.143	1.876	1.950		1.868					
	Calcd	1.868	1.948	2.140	1.868	1.947	2.140	1.867	1.946	2.139	1.882	1.960	2.158
	Eclpd	1.871	1.949	2.141	1.866	1.948	2.139	1.868	1.947	2.139	1.884	1.962	2.139
H–M–H	Obsd	108.7	109.2	109.5	107.8								
	Calcd	109.5	109.3	109.4	108.7	109.4	110.2				109.2	109.5	110.0
	Eclpd	108.3	109.2	109.3	109.9	109.2	110.3				108.8	109.3	109.9
C–M–C	Obsd				111.0	110.0		110.2					
	Calcd				110.0	109.5	109.0	109.7	109.0	108.9	113.6[a]	113.7[a]	113.9[a]
	Eclpd				111.2	109.6	109.1	110.0	109.1	109.6	113.8	113.8	113.9
H–M–C	Obsd	110.2			109.5			108.8					
	Calcd	109.4	109.6	109.6	109.5	109.5	109.4	109.0	110.0	110.0	109.7	109.4	109.0
	Eclpd	110.6	109.7	109.6	109.6	109.0	109.3	108.8	109.9	109.3	110.1	109.6	109.0

[a] These values are for the C–C–M bond angle.

Table III. Calculated Component Energies of Group IV Organometallic Compounds

		Staggered			Eclipsed (C–M)			Eclipsed (C–C)		
		Si	Ge	Sn	Si	Ge	Sn	Si	Ge	Sn
CH_3MH_3	E_r	0.01	0.00	0.00	0.01	0.00	0.00			
	E_θ	0.08	0.04	0.03	0.09	0.04	0.03			
	E_ϕ	0.00	0.00	0.00	1.50	1.14	0.66			
	E_{nb}	−0.87	−0.80	−0.57	−0.72	−0.73	−0.57			
	E_s	−0.78	−0.76	−0.54	0.88	0.45	0.12			
$(CH_3)_2MH_2$	E_r	0.00	0.01	0.01	0.01	0.01	0.01			
	E_θ	0.11	0.08	0.06	0.12	0.08	0.06			
	E_ϕ	0.00	0.00	0.00	1.50	1.14	0.66			
	E_{nb}	−1.97	−1.81	−1.28	−1.83	−1.74	−1.29			
	E_s	−1.86	−1.72	−1.21	−0.20	−0.51	−0.56			
$(CH_3)_3MH$	E_r	0.01	0.01	0.01	0.02	0.01	0.01			
	E_θ	0.19	0.13	0.10	0.20	0.12	0.10			
	E_ϕ	0.00	0.00	0.00	1.50	1.14	0.66			
	E_{nb}	−3.33	−3.02	−2.10	−3.19	−2.95	−2.13			
	E_s	−3.13	−2.88	−1.98	−1.47	−1.69	−1.36			
$CH_3CH_2MH_3$	E_r	0.16	0.26	0.32	0.17	0.28	0.32	0.40	0.59	0.71
	E_θ	0.40	0.41	0.43	0.41	0.41	0.43	1.01	1.06	1.10
	E_ϕ	0.00	0.00	0.00	1.50	1.05	0.66	1.50	1.51	1.50
	E_{nb}	−0.36	−0.17	0.00	−0.25	−0.12	−0.01	1.07	1.21	1.40
	E_s	0.20	0.50	0.75	1.83	1.61	1.40	3.98	4.37	4.73

Table IV. Conformational Energies

		Si	Ge	Sn
CH_3MH_3	Stgd	−0.78	−0.76	−0.54
	Eclpd	0.88	0.45	0.12
$(CH_3)_2MH_2$	Stgd	−1.86	−1.72	−1.21
	Eclpd	−0.20	−0.51	−0.56
$(CH_3)_3MH$	Stgd	−3.13	−2.88	−1.98
	Eclpd	−1.47	−1.69	−1.36
$C_2H_5MH_3$	Stgd	0.20	0.50	0.75
	(C–C) eclpd	3.98	4.37	4.73
	(C–M) eclpd	1.83	1.61	1.40
$CH_3CH_2MH_2CH_3$	0°	0.66	0.45	0.25
	60°	−1.02	−0.72	−0.23
	120°	0.68	0.65	0.69
	180°	−0.88	−0.51	−0.03
$CH_3CH_2CH_2MH_3$	0°	5.86	6.42	6.72
	60°	0.75	0.98	1.23
	120°	3.85	4.01	4.32
	180°	0.19	0.52	0.56
$CH_3MH_2CH(CH_3)_2$	Sym	−0.49	0.18	0.82
	Asym	−0.30	0.37	0.92
$(CH_3)_2MHCH(CH_3)_2$	Sym	−1.67	−0.98	−0.08
	Asym	−1.86	−1.19	−0.25
$(C_2H_5)_2MH_2$	a,a	0.04	0.79	1.36
	a,g	−0.07	0.61	1.14
	cis(g,g)	0.80	0.78	1.43
	trans(g,g)	−0.37	0.14	1.27
$C_6H_{11}MH_3$	eq	1.14	1.72	1.92
	ax	2.40	2.92	3.17

between conformers possessing staggered arrangements of bonds involve dihedral angles near 60° the E_ϕ term will be near zero and will not affect the E_s term.

$CH_3CH_2MH_3$. There are no microwave data available for the compounds of this class. This is unfortunate because the geometries of these molecules would provide tests for the validity of several of the chosen parameters. Due to the size of M it is predicted that the C–C–M bond angles will be 113.6, 113.7, and 113.9° for silicon, germanium, and tin, respectively. There is thus a widening of the angle with respect to the 112.4° angle in propane.[18] The same trend is shown in the ethyl halides: the C–C–X bond angles are 109.7,[19] 111,[20], 111,[21] and 112°[22] for X = F, Cl, Br, and I, respectively.

The calculated barriers for eclipsing about the carbon–carbon bond are 3.78, 3.87, and 3.98 kcal/mol for silicon, germanium, and tin. In propane the experimental barrier is 3.37[23] kcal/mol. The increased barrier

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energies with increasing size of M and the larger barriers of the members of group IV other than carbon find some analogy in the barriers of the ethyl halides. The barriers are 3.33,[24] 3.68,[20] and 3.68[21] kcal/mol for ethyl fluoride, chloride, and bromide, respectively. The barrier of ethyl iodide is 3.2 ± 0.5 kcal/mol,[24] but a barrier of 3.65 kcal/mol[25] has been estimated using Buckingham and Lennard-Jones potential functions. The similarity of the barriers for M = Si, Ge, and Sn and the definite increase over that for carbon appear to be reasonable. The presence of hydrogens bonded to M may account for the slight increase in the barriers whereas the halogen barriers are more nearly equal. An increase in the C–C–M bond angle averaging approximately 1° is calculated for the eclipsed conformation.

The barriers for eclipsing about a C–M bond are 1.63, 1.11, and 0.65 kcal/mol for silicon, germanium, and tin, respectively. These values are all close to the barrier energies for the CH_3MH_3 compounds. In the eclipsed conformations there is little predicted increase in the C–C–M bond angle.

$CH_3MH_2CH_3$. The geometries of this series of compounds differ from the geometries of the isomeric $CH_3CH_2MH_3$ compounds. By locating the large atom in the interior position, the two methyl groups are moved away from each other and the C–M–C bond angle decreases with increasing size of M. The experimental angles are 111.0 and 109.5° for silicon and germanium, respectively. No data are available for the tin compound. The calculated angles are 110.0, 109.5, and 109.0° for silicon, germanium, and tin, respectively. The nonbonded attractions between hydrogens on the methyl groups are tending to decrease the bond angle below that at the tetrahedral value.

As could have been reasonably expected, the single torsional barriers decrease in the order 1.66, 1.21, and 0.65 kcal/mol for silicon, germanium, and tin, respectively. The experimental barriers are 1.65[16] and 1.18 kcal/mol[14] for silicon and germanium, respectively. There is essentially no difference between the barriers of CH_3MH_3 and $CH_3MH_2CH_3$ excluding the carbon compounds in which the barriers actually increase from 2.93[11] to 3.37 kcal/mol.[23] Again, this implies greater repulsive interaction between the methyl groups in propane than in the other members of the series. The agreement between the experimental and calculated barriers indicates that the setting of a single value for V_0(X–C–M–Y) for each M is correct.

$(CH_3)_3MH$. No data are available for comparison with the calculated structures of this series of compounds for germanium or tin. There is good agreement between the calculated and experimental structures for silicon. It should be noted that the C–M–C bond angles decrease below that of the tetrahedral value for germanium and tin. This phenomenon is the result of the increased number of favorable van der Waals interactions between hydrogen atoms which allows for some bending of the C–M–C angle. There is similar evidence for the operation of the same phenomenon in $(CH_3)_2MH_2$ compounds although less pronounced.

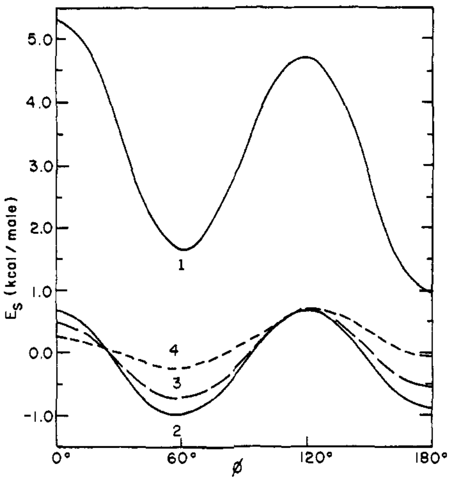

Figure 1. Torsional coordinate for $CH_3CH_2MH_2CH_3$: curve 1, M = C; 2, M = Si; 3, M = Ge; 4, M = Sn.

While the barriers for germanium and tin have not been experimentally determined, the calculated values of 1.66, 1.19, and 0.62 kcal/mol for silicon, germanium, and tin are close to those of the CH_3MH_3 and $(CH_3)_2MH_2$ compounds for which good agreement is obtained.

$CH_3CH_2MH_2CH_3$. In Figure 1 the E_s values of this series of compounds as a function of ϕ are depicted. The most striking feature of the torsional coordinate function is the stability of the gauche conformation over that of the anti conformation. In each case the E_{nb} term involving predominately hydrogen–hydrogen terms contributes strongly to E_s and accounts for the order of stabilities. It was previously shown for silicon that the choice of ϵ is unimportant.[2] The only nonbonded terms involving silicon are those to the C-4 hydrogen atoms. If there were no bond angle differences between the gauche and anti conformations, the E_{nb} terms involving silicon would be equal in the two conformations and therefore would be cancelled. While there are small bond angle changes, the effect on the E_{nb} terms involving silicon accounts for only a 0.01 kcal/mol contribution to the gauche–anti energy difference. In the case of germanium and tin, the difference will be insignificant.

The dihedral angles between methyl groups in this series of compounds are 59.6, 58.9, and 55.7° for silicon, germanium, and tin, respectively. In butane, the calculated dihedral angle is 63.6°,[26] a value which reflects necessary conformational compromises in order to lessen the van der Waals repulsive terms. A bond angle increase from 111.8 to 113.0°[26] is predicted for the anti–gauche butane conversion. For the remaining members of group IV there is essentially no bond angle increase and the torsional angle is predicted to decrease below 60° in the gauche conformation. One set of terminal hydrogen–hydrogen van der Waals interactions is in the minimum of the energy curve for the silicon compound. In the other members of the series the larger bond distances give rise to smaller negative van der Waals contributions, and as a consequence it is energetically advantageous to decrease the torsional angle in order to achieve more attractive van der Waals interactions.

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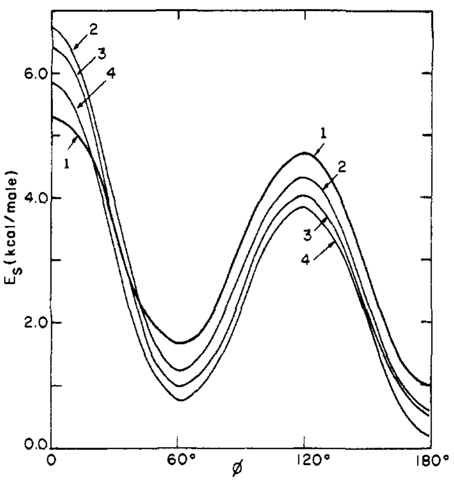

Figure 2. Torsional coordinate for $CH_3CH_2CH_2MH_3$: curve 1, M = C; 2, M = Si; 3, M = Ge; 4, M = Sn.

Another consequence of the above discussion is reflected by the ordering of the energies of the H-CH_3 and CH_3-CH_3 eclipsed conformations. In silicon, the CH_3-CH_3 eclipsed conformation is of slightly lower energy than the H-CH_3 eclipsed conformation. While the difference of only 0.02 kcal/mol by itself would not ordinarily be considered significant, the difference widens to 0.20 and 0.44 kcal/mol, respectively, for germanium and tin. There are hydrogen-hydrogen van der Waals interactions stabilizing the CH_3-CH_3 eclipsed conformation over that of the H-CH_3 eclipsed conformation, which become more favorable as the bond lengths are increased through this series of compounds. While this ordering of energies is interesting, it should not overshadow the significantly different shape of the torsional coordinate function of the members of group IV when compared to carbon. Carbon stands alone as the anomaly with respect to the other members of the periodic family.

The predicted stability of the gauche conformation over that of the anti conformation has been verified for silicon.[2] Experimental tests are awaited for germanium and tin. Taking account of the entropy of mixing[27] due to the two enantiomeric gauche conformations, the ΔG for an anti $\rightleftarrows$ gauche equilibrium should be -0.6 kcal/mol at 25° for both germanium and tin. The mole fraction of the gauche conformation is predicted to be 0.73.

$CH_3CH_2CH_2MH_3$. The order of conformational energies of this series of compounds is exactly like that of butane. The difference between this series of compounds and the isomeric $CH_3MH_2CH_2MH_3$ compounds is related to the long C-M bond and its placement within the molecule. In gauche $CH_3CH_2CH_2MH_3$, the MH_3 and CH_3 groups are in the gauche relationship. A "short" CH_2CH_2 unit separates the CH_3 group from the "large" MH_3 group which is attached to the CH_2CH_2 unit by a "long" bond balancing the effect of the "large" group. In $CH_3MH_2CH_2CH_3$ there are two "long" C-M bonds compared to one in $CH_3CH_2CH_2MH_3$. One of the "long" bonds is in the CH_2MH_2 unit and serves to separate the two CH_3 groups. Furthermore, one CH_3 group is moved out from the CH_2MH_2 unit by a "long" bond.

The dihedral angles between MH_3 and CH_3 groups in the gauche conformation of $CH_3CH_2CH_2MH_3$ are 64.1, 65.5, and 67.9° in the silicon, germanium, and tin compounds, respectively. These values are all larger than the 63.6° for butane. Therefore, while the "large" MH_3 group is balanced to some extent by the long C-M bond, torsional changes are also necessary in the gauche conformation.

The energies of the eclipsed conformations are larger for the various M compounds than for carbon. Previously, the possibility that the ϵ value for silicon might not be realistic was tested. It was shown that a decrease of one-third did not alter the shape of the torsional coordinate. While this possibility was not tested for germanium and tin, it is clear that the fundamental features of the torsional coordinate will not change. Of greater importance is the limitation of the bond bending potential function for large $\Delta\theta$. The calculated C-C-M bond angles in the MH_3-CH_3 eclipsed conformations are 117, 118, and 122° for silicon, germanium, and tin, respectively. It is likely that the calculated energies of the MH_3-CH_3 eclipsed conformation and to a lesser degree the MH_3-H eclipsed conformations are too high and may more closely parallel those of butane due to the aforementioned inadequacy of the angle bending function.

$(CH_3)_2CHMH_2CH_3$. Only the energies of the symmetric and asymmetric conformations are given for this series of compounds. In the symmetric conformation a methyl group is in a gauche position with respect to two methyl groups, whereas there is only one gauche methyl-methyl interaction in the asymmetric conformation. The differences in conformation energies are 0.19, 0.19, and 0.13 kcal/mol for silicon, germanium, and tin, respectively, with the symmetric conformation as the more stable in every case. The operation of attractive van der Waals forces previously discussed for $CH_3MH_2CH_2CH_3$ compounds accounts for this order of stabilities. It is interesting to note that the conformational energy differences between gauche and anti $CH_3MH_2CH_2CH_3$ of 0.14, 0.21, and 0.20 kcal/mol for silicon, germanium, and tin, respectively, are somewhat different than those for $(CH_3)_2CHMH_2CH_3$ compounds. In the former compounds, the dihedral angles between the gauche methyl groups decrease to below 60° in order to achieve stabilization due to attractive van der Waals energy terms. In the symmetric conformation of the latter compound nothing is gained by rotating the CH_3 group toward one of the other two CH_3 groups as this simultaneously moves it away from the second CH_3 group.

While the symmetric conformations of these compounds are predicted to be more stable than the asymmetric conformations, the ΔG for the asym $\rightleftarrows$ sym equilibrium at 25° should be approximately 0.2 and 0.3 kcal/mol for the germanium and tin compounds, respectively, because of an entropy of mixing term which favors the asymmetric conformation.

$(CH_3)_2CHMH(CH_3)_2$. The asymmetric conformations of this series of compounds contain three sets of gauche methyl-methyl interactions compared to two in the symmetric conformations. As in CH_3MH_2-

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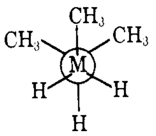
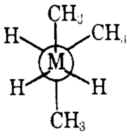
[27] E. L. Eliel, "Stereochemistry of Carbon Compounds," McGraw-Hill, New York, N. Y., 1962, p 214.



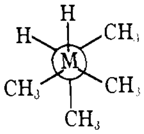
symmetric



asymmetric

CH_2CH_3 and $(CH_3)_2CHMH_2CH_3$ compounds, gauche interactions stabilize the conformations which contain them. The conformational energy differences are 0.19, 0.21, and 0.17 kcal/mol for silicon, germanium, and tin, respectively.

The ΔG for the sym $\rightleftarrows$ asym equilibrium at 25° should be -0.6 kcal/mol for both germanium and tin because of an entropy of mixing term favoring the asymmetric conformation.



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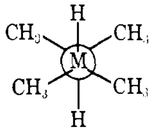

symmetric

$(C_2H_5)_2MH_2$. There are four nonequivalent staggered conformations involved in this series of compounds. From the calculations of simpler compounds which corporate a C–C–M–C skeleton, a gauche conformation is predicted to be more stable than an anti conformation. Therefore, the order of stability trans (gauche–gauche) > gauche–anti > anti–anti is expected. This order is calculated for the silicon and germanium compounds but the gauche–anti conformation is more stable than the trans(gauche–gauche) for tin. This apparent anomaly is the result of the decrease in the dihedral angle of C–C–Sn–C below 60° as previously noted for $CH_3CH_2SnH_2CH_3$. In the latter compound the methyl groups move to a dihedral angle of 55.7 to achieve a more favorable van der Waals energy term. In the trans (gauche–gauche) conformation of $(C_2H_5)_2SnH_2$ such motion by both methyl groups moves them toward methylene groups at a 53° dihedral angle. Although it is impossible to attribute the difference in energy to any single or small group of interactions, the van der Waals stabilization achieved by gauche arrangements simply is not achieved as effectively in this conformation. The E_{nb} terms are -0.20, -0.44, and -0.49 kcal/mol for anti–anti, anti–gauche, and trans(gauche–gauche) conformations, respectively. Accompanying the lack of a significant change in the van der Waals energy for the added gauche interaction is a net increase in energy in the E_r and E terms. The E_r terms are 0.58, 0.58, and 0.42 kcal/mol for the anti–anti, anti–gauche, and trans(gauche–gauche) conformations, respectively. The E_θ terms are 0.98, 0.97, and 1.29 for the same ordering of conformations.

The difference in energy between the trans(gauche–gauche) and cis(gauche–gauche) conformations decreases in the order silicon > germanium > tin. In the cis(gauche–gauche) conformation the two methyl groups which experience net repulsive van der Waals terms are moved apart due to the increase in the C–M bond length. Furthermore, all the force constants and torsional constants decrease allowing the more ready accommodation of the terminal methyl groups near each other.

When experimental data on the conformational equilibria of this series of compounds become available it will be necessary to correct the observed free energies for symmetry and entropy of mixing of the conformers prior to comparing the data with these calculations.

$C_6H_{11}MH_3$. The calculated conformational preferences of SiH_3, GeH_3, and SnH_3 are 1.26, 1.20, and 1.25 kcal/mol, respectively. The values are all significantly lower than the experimental value of 1.7 kcal/mol[28] for CH_3. The smaller conformational preference of MH_3 groups with respect to CH_3 might not have been expected *a priori*. For comparison, the conformational preferences of F, Cl, Br, and I values are 0.276, 0.528, 0.476, and 0.468 kcal/mol,[29] respectively. Furthermore, the conformational preferences of OH and SH are 0.6[30] and 1.20[31] kcal/mol, respectively.

In the axial conformation of methylcyclohexane, the methyl proton directed over the plane of the ring gives rise to strong repulsive nonbonded terms with the axial protons on the 3 and 5 carbon atoms. For the "over the plane" proton in the axial conformation of the $C_6H_{11}MH_3$ compounds, the nonbonded terms are much smaller. The long C–M and M–H bonds increase the distance to the two ring axial protons. This increase is made more dramatic by the ease with which the $H-MH_2-C$ bond angle can increase compared to the $H-CH_2-C$ bond angle. Furthermore, the M–C–H bond angle can decrease and move the axial MH_3 group away from the top of the ring. In methylcyclohexane, the E_{nb} terms are more severe than for $C_6H_{11}MH_3$ and all of the bonding force constants involving carbon are larger than for the other members of group IV.

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