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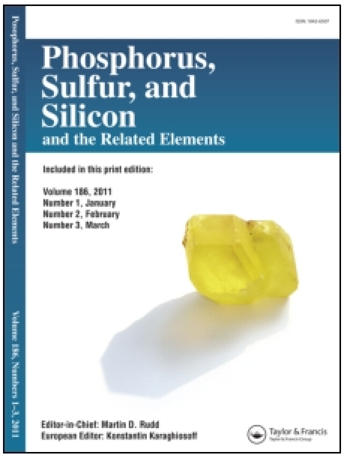

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Group 14 Homologues of Hydrocarbons

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Experimental values of geometric parameters are compared with the results of theoretical calculations for saturated (alkane-like) compounds containing Si, Ge, Sn, and Pb, in addition to hydrogen and carbon. The objective is to evaluate the accuracy and efficiency of computational methods for general use in theoretical studies of saturated group 14 homologues. In this paper we report bond lengths obtained using MMFF (Merck Molecular Force Field) and the semiempirical PM3 method. Both procedures are found to provide useful, but only fair rectifications of experimental bond length data.

Keywords: hydrocarbon analogues; group 14; MMFF; PM3

INTRODUCTION

The study of group 14 elements has been of major interest since the 19th century.[1] The compounds of interest in the present study are those in which one or more carbon atoms of a saturated hydrocarbon are replaced by third period and higher group 14 elements. Many compounds of this type have been synthesized, often by adding phenyl or methyl groups to the group 14 atoms to maintain their molecular stability. A large number of novel saturated group 14 compounds have been synthesized in the University of Texas at El Paso laboratories.[2,3]

Compounds of the group 14 elements have also been the subject of many theoretical studies.[4,5] A large number of these studies focus on relative stabilities and predictions of the energies of molecules containing group 14 elements. There has been little mention in the literature of how various theoretical and computational methods perform when estimating the geometries of such molecules.

Experimental techniques used to examine geometries of group 14 molecules include x-ray, neutron and electron diffraction, and EXAFS. The results of such experiments are compared with their theoretically determined counterparts in this paper. Several methods are under investigation, including molecular mechanics, semiempirical and *ab intio* quantum chemical calculations, and the use of density functional theory (DFT). The results for the least costly procedures, molecular mechanics and semiempirical calculations, are given below.

COMPUTATIONAL METHODS

Traditional molecular mechanics methods, such as MM2[6] or MM3[7] cannot be applied to an arbitrary set of saturated group 14 molecules, due to a lack of parameters for the heavier elements of the group. The newer method developed by Allinger, *et al.*, MM4,[8] also lacks such parameters. However, the MERCK molecular force-field (MMFF) recently developed by Halgren,[9] does allow the examination of the entire series of saturated group 14 compounds. Therefore we tested this method first, as it was the cheapest method available in terms of computational demands.

MMFF differs from the popular MM2, MM3, and MM4 molecular mechanics methods in that it does not use experimental data for the core force field parameters. Instead, the results of high level *ab initio* calculations are used for this purpose, which allows for the addition of parameters for neutral and charged groups where experimental data is insufficient or nonexistent. MMFF was also developed and parameterized principally to handle systems of biochemical interest. However, the force field parameters for atoms not in the core are generated from carefully calibrated empirical rules based on covalent radii, electronegativities and other atomic properties. These rules allow the calculation of geometric results for compounds containing elements with atomic numbers up to 102.

From the generally available semiempirical methods, MNDO and PM3 are parameterized for all of the group 14 elements.[10] The AM1 method is not parameterized for germanium, tin, or lead. The majority of recent applications of semiempirical methods use the PM3 protocol, and PM3 is also used for the results which are reported here.

RESULTS FOR BENCHMARK STRUCTURES

Experimental and calculated bond lengths for saturated group 14 methane homologues (MH_4, M = C, Si, Ge, Sn, Pb), and for the permethylated derivatives (neopentanes), are listed in TABLE 1, and TABLE 2 contains the corresponding results for C-M bonds of ethane derivatives (CH_3-MH_3). Each calculation takes less than a fraction of a second (MMFF) or a few seconds (PM3) on either IBM or SGI workstations.

Bond	Expt.	MMFF	PM3	Bond	Expt.	MMFF	PM3
C-H	1.093[a]	1.092	1.087	C-CH_3	1.539[a]	1.535	1.527
Si-H	1.49[a]	1.485	1.488	Si-CH_3	1.875[b]	1.875	1.890
Ge-H	1.54[a]	1.493	1.505	Ge-CH_3	1.98[c]	1.927	1.960
Sn-H	1.72[a]	1.682	1.702	Sn-CH_3	2.18[c,d]	2.145	2.145
Pb-H		1.753	1.694	Pb-CH_3	2.20[e]	2.191	2.186

[a] Reference 11. [b] Reference 12. [c] Reference 13. [d] Reference 14. [e] Reference 15.

TABLE 1 Bond lengths in Group 14 methane homologues (Å).

Bond	Expt.[a]	MMFF	PM3	Bond	Expt.[a]	MMFF	PM3
C-C	1.539	1.512	1.504	C-H	1.086	1.094	1.098
Si-C	1.875	1.844	1.864	Si-H	1.481	1.485	1.493
Ge-C	1.980	1.925	1.955	Ge-H	1.527	1.493	1.506
Sn-C	2.143	2.145	2.186	Sn-H	1.701	1.681	1.701
Pb-C	2.238	2.192	2.204	Pb-H		1.753	1.692

[a] Reference 5.

TABLE 2 Bond lengths in Group 14 ethane homologues (Å).

Plots of the calculated bond lengths versus experiment are shown in FIGURE 1 for the MMFF calculated values and in FIGURE 2 for the PM3 results. The experimental data are derived from electron diffraction, microwave, or neutron diffraction studies. Both methods give fair correlations of the experimental data. The statistical parameters of the fits to least squares lines are: MMFF mean dev. 0.033, the max. dev. 0.055 and corr. coeff. 0.994; for PM3, the values were 0.038, 0.043 and 0.992. The largest deviations for either method are over the limits expected for theoretical predictions of bond lengths for closed shell systems without transition metal atoms.

DISCUSSION

From TABLE 1 and TABLE 2, for the MMFF method, problems with calculating bond lengths seem to be primarily associated with the longer bonds involving the higher atomic number group 14 elements. This is certainly understandable given the fact that MMFF is not parameterized for Ge, Sn,, and Pb, except through very general rules based on element covalent radii and electronegatives. Actually, the performance of MMFF turns out to be quite acceptable as a semiquantitative first approximation model for the shapes and geometries of the systems under discussion. The very short calculation times associated with a molecular mechanics method are also advantageous. For these reasons, its use is recommended as a first step in modeling the group 14 saturated hydrocarbon homologues. The accuracy of MMFF models for other types of main group element compounds is under investigation.

In the PM3 results, the overall agreement of calculated and experimental bond lengths is also fairly good. However, the calculated values for Pb-H bonds are insensibly anomalous in not demonstrating the expected monotonic increase in length compared to the calculated Sn-H bonds. We have not been able to identify the source of this anomaly, which must, of course, lie in the parameterization of PM3 in

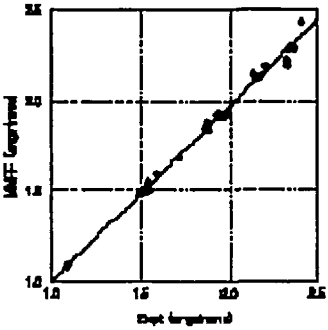

FIGURE 1 MMFF calculated bond lengths versus experiment

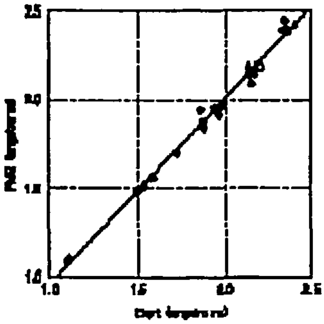

FIGURE 2 PM3 calculated bond lengths versus experiment

the software used in our laboratory.[10] Our overall judgment is that there are no advantages in using PM3 as a first step in modeling these group 14 compounds compared to the MMFF method. Neither method seems to be completely free of deficiencies that might lead to difficulties in estimating bond lengths and nonbonded interactions in more complicated larger molecules.

These theoretical methods were applied to calculate the molecular structures of two larger group 14 derivatives whose X-ray crystal structures have been recently determined.[3(a),3(b)] These two molecules, $\mathrm{Me_3Ge\text{-}SnPh_3}$ and $\mathrm{Ph_3Ge\text{-}SnMe_3}$, were initially shown to have central Ge-Si bonds that differed in length by over 0.6 Å depending on the relative sites of the trimethyl and triphenyl substituents. A later experimental study of the same molecule indicated that there was little difference in the two bond lengths. [3(b)] The two sets of experimental results are listed with the MMFF and PM3 calculated bond lengths in TABLE 3 below.

Compound	Bond	Expt.^{a}	Expt.^{b}	MMFF	PM3
$\mathrm{Me_3GeSnPh_3}$	Ge-Sn	2.599	2.602	2.310	2.456
	C(sp^3)-Ge	1.963	1.943	1.923	1.954
	C(sp^2)-Sn	2.155	2.154	2.113	2.092
$\mathrm{Ph_3GeSnMe_3}$	Ge-Sn	2.652	2.611	2.325	2.476
	C(sp^2)-Ge	1.931	1.957	1.906	1.916
	C(sp^3)-Sn	2.167	2.137	2.144	2.141

^{a}Reference 3(a). ^{b}Reference 3(b).

TABLE 3 Bond lengths in $\mathrm{Me_3Ge\text{-}SnPh_3}$ and $\mathrm{Ph_3Ge\text{-}SnMe_3}$ (fi)

From this table, one notes that calculated Sn-Ge bond lengths are somewhat different from those determined experimentally, perhaps in agreement with our pessimism about the calculations outlined above. However, both methods do get the overall approximate C_3 shapes of the molecules correctly, and both methods calculate C-C bond lengths (not given in TABLE 3) in good agreement with experiment. Furthermore, C-Ge and C-Sn bond lengths are modeled successfully, and the size of the difference in the Sn-Ge bond lengths from the second, presumably more accurate, experiment is in very good agreement with the magnitude of the difference calculated by both MMFF and PM3 methods.

Ab initio HF and DFT methods are presently under investigation to determine if they would be more accurate for calculation of group 14 molecule geometries. The common basis sets, including those in the Gaussian, Inc. suite of programs, are not formulated for lead, and only STO-3G and 3-21G(*) have the capability to handle germanium and tin. Since our investigation is meant to comprise the structures of saturated hydrocarbon homologues that may include any of the group 14 elements, these restrictions have led us to examine the group of basis sets developed at Los Alamos laboratories, commonly referred to as the LA-series of basis sets.[16,17] All of the LA basis sets use effective core potentials (ECP) for the heavier group 14 atoms and some of them use an ECP for silicon as well. The results of several preliminary calculations led us to choose the LACVP** basis set combined with the B3PW91 and B3LYP density functional methods for a full evaluation, and the results of this work will be reported in due course. We are greatly encouraged by the results obtained so far.

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