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Evaluation of Effective Core Potentials and Basis Sets for the Prediction of the Geometries of Alkyltin Halides

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A systematic comparison of the optimized geometries of five organotin compounds, $Cl_nSn(CH_3)_{4-n}$, $n = 0-4$, with the available gas-phase electron diffraction results is reported. All optimizations were carried out with the B3LYP density functional method. Comparison of 10 basis sets and three effective core potentials leads to the conclusion that the combination of the SDB-aug-cc-pVTZ basis set and the LANL2 effective core potential for tin, together with the 6-31G(d,p) basis set for the other atoms, is recommended for the prediction of the geometries of organotin compounds.

Introduction

Interest in studying heavy-metal inorganic systems by computational methods stems from their importance in materials science as well as in industrial and biological catalysis. Furthermore, recent advances in computer technology have facilitated the use of reliable theoretical methods to study chemical systems involving heavy main group elements and transition metals. Of particular interest to us are tin-containing compounds, specifically stannylene acetals, which are frequently used as synthetic intermediates.[1,2] A variety of tin-containing systems has recently been examined computationally, ranging from small organotin systems such as halogenated tin derivatives[3,4] to large biological organotin systems such as Sn−DNA systems,[5] using a diverse range of methods. Examples of the computational methods used in recent studies include semiempirical (PM3),[5,6] Hartree−Fock,[7,8] perturbation theory (MP2, MP4),[3,4,9] coupled-cluster (CCSD),[3,4,9] and density functional theory (DFT).[3,4,10,11] Furthermore, an assortment of basis sets has been used to describe tin, including small Pople basis sets (STO-3G, 3-21G)[10] and larger correlation consistent (cc-pVDZ, aug-cc-pVTZ)[9,12] basis sets.

In addition, several effective core potentials (ECP) and their respective basis sets have been employed.[11−13] Effective core potentials are frequently used to describe heavy atoms in electronic structure calculations because they reduce the computational effort involved and they can be designed to account for the relativistic effects, a necessary requirement to obtain good agreement with experimental data. Most computational studies on organotin systems have used DFT and a selection of effective core potentials. Despite the extensive literature available to us at the outset of our research, it was not clear which combination of effective core potential and basis set is most appropriate for the study of organotin compounds.

In this systematic study, five organotin compounds are examined with 10 basis sets and three effective core potentials to determine the most appropriate method for future study. In particular, we want to identify the best combination of basis set and effective core potential for the prediction of the geometries of tin-containing compounds. For this purpose, the optimized bond lengths and angles of $SnCl_4$ (**1**), Cl_3SnCH_3 (**2**), $Cl_2Sn(CH_3)_2$ (**3**), $ClSn(CH_3)_3$ (**4**), and $Sn(CH_3)_4$ (**5**) are compared with gas-phase electron diffraction experimental data.

Computational Methods

Gas-phase geometry optimizations and frequency calculations of all five molecules were performed with the B3LYP hybrid density functional by use of the Gaussian 03 program suite.[14] The B3LYP functional implemented in Gaussian 03 is a combination of Becke's three-parameter hybrid exchange functional (B3)[15,16] and the correlation functional of Lee, Yang and Parr.[17] There are, of course, many other possible choices for the exchange and correlation potentials in DFT calculations. We have chosen to use B3LYP in view of its widespread use in current computational studies. The 6-31G(d,p) basis set was used for C, Cl, and H, whereas various combinations of basis sets and effective core potentials were used to describe tin. Forty-six electrons were assigned to the core of tin, whereas the remaining four (valence-shell) electrons were explicitly included in the full quantum chemical calculation. Although it would be desirable to use small-core potentials,[18,19] in view of a small advantage,[12] we have used large-core potentials in the interest of computational efficiency. This choice should have a small effect (about 1 mÅ and 1.4 kcal/mol) on the results.[12] Frequency analyses were used to confirm that all optimized structures correspond to mimima (no imaginary frequencies) on the potential energy surfaces. Bond lengths (*r*) are reported in ångstroms and bond angles (∠) in degrees.

The basis sets included in our study, in increasing size, are LANL2MB,[20] SBKJC_VDZ,[21] MWB,[22] LANL2DZ,[20] LANL2-DZdp,[23] CRENBL,[24] SDB-cc-pVTZ,[25] SDB-aug-cc-pVTZ,[25] SDB-cc-pVQZ,[25] and SDB-aug-cc-pVQZ.[25] The effective core potentials selected for evaluation were SBKJC,[26] SDB,[22] and LANL2.[20] Only these ECPs were used because the MWB and four SDB basis sets all use the SDB ECP, and all LANL2 basis sets use the same LANL2 ECP. It should be noted that the CRENBL ECP was used only in tandem with the CRENBL basis set, because when paired with other basis sets the geometry optimizations failed to converge. However, optimized geometries were obtained with the CRENBL basis set and all other ECPs. The basis sets and effective core potentials[27,28] used to describe tin are discussed further in the following sections.

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TABLE 1: Experimental Geometries of $Cl_nSn(CH_3)_{4-n}$, Obtained from Gas-Phase Electron Diffraction Data (r in Å, ∠ in Degrees)

molecule	r(Sn,C)	r(Sn,Cl)	r(C,H)	∠(Cl,Sn,C)	∠(Cl,Sn,Cl)	∠(C,Sn,C)	∠(Sn,C,H)
$SnCl_4$[a]		2.280			109.5		
Cl_3SnCH_3[b]	2.104	2.304	1.100	113.9	104.7		107.5
$Cl_2Sn(CH_3)_2$[c]	2.108	2.327	1.113	109.8	107.5	not reported	not reported
$ClSn(CH_3)_3$[b]	2.106	2.351	1.125	103.2		114.9	113.4
$Sn(CH_3)_4$[d]	2.143		1.117			109.5	112.0

[a] Reference 38. [b] Reference 39. [c] Reference 40. [d] Reference 41.

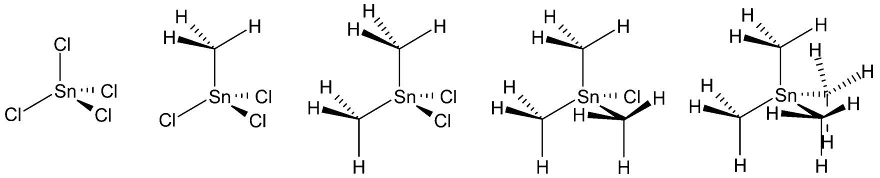

Figure 1. Optimized conformations of $Cl_nSn(CH_3)_{4-n}$, $n = 0-4$.

In addition, all-electron energy calculations were performed where tin is described with the 3-21G(d,p) basis set. Although this basis set has been used to describe tin previously,[10] it should be noted that these all-electron calculations are not relativistic, and do not employ effective core potentials.

Basis Sets and Effective Core Potentials

Using effective core potentials to describe Sn involves separation of the valence electrons and core electrons, and replacement of the latter with an energy potential, often termed a *pseudopotential*. The basis sets that describe the valence electrons differ in the number, size, and types of basis functions used, and each ECP has a corresponding basis set that is unique in the manner in which it was derived and parametrized. Similarly, each ECP differs in how the pseudopotential was developed and constructed.

The individual LANL2 Sn basis sets are unique; however, all are based upon those developed by Hay and Wadt at the Los Alamos National Laboratory (LANL).[20] All of these basis sets use the LANL2 ECP[20] as the default effective core potential. LANL2MB is a minimal basis set, whereas LANL2DZ is a double-ζ basis set. The LANL2DZdp basis set uses the double-ζ basis set of Hay and Wadt[20] together with diffuse p-functions and five d-type polarization functions, from Sunderlin and co-workers.[29] Again, the default ECP associated with these basis sets is also the LANL2 ECP.[20] This ECP is one of three that was tested in this study, and it was paired with all the basis sets mentioned in the previous section.

The effective core potential developed by Stevens, Basch, Krauss, Jasien and Cundari is referred to as the SBKJC ECP.[21] The associated basis set is the SBKJC_VDZ basis set,[30] which is a double-ζ basis set that is designed to replace all but the outermost electrons.[21]

Both the MWB basis set and its ECP, the Stuttgart−Dresden−Bonn (SDB) ECP, were developed by Dolg and co-workers.[22] The MWB basis set is often referred to as the Stuttgart Relativistic Large Core basis set (Stuttgart RLC).

The correlation consistent SDB basis sets examined in this study are SDB-cc-pVnZ (n = T, Q) and SDB-aug-cc-pVnZ (n = T, Q). These four basis sets were developed by Martin and Sundermann[25] and were optimized for use with the aforementioned large-core SDB relativistic pseudopotential.[22] The resulting basis sets are triple- and quadruple-split basis sets, with the option of an augmented (aug) basis set which includes diffuse functions. It should be noted that the SDB basis sets are considerably larger than the other basis sets in this study. Specifically, the largest basis set is the SDB-aug-cc-pVQZ, which has a (15s,11p,4d,3f,2g) → [5s,5p,4d,3f,2g] contraction. This basis set includes 79 contracted Gaussians on tin.

The last basis set tested in this study is the CRENBL[24] basis set. La John and co-workers[24] developed this basis set for Sn by refining methods previously developed by Pitzer and co-workers.[31,32] The CRENBL ECP is often deemed "shape consistent" because the shape of the atomic orbitals in the valence region is retained.

Experimental Geometries

To assess the ability of various combinations of effective core potentials and basis sets to accurately predict the geometries of tin compounds, the optimized bond lengths (r) and bond angles (∠) were compared with the gas-phase electron diffraction data shown in Table 1. As expected, the five molecules exhibit four-coordinate, tetrahedral tin centers. Structures obtained via X-ray diffraction were not used in this study because the solid-state and gas-phase geometries of $Cl_nSn(CH_3)_{4-n}$ are different. Specifically, the solid-state structures contain tin atoms with higher coordination than the four-coordinate tetrahedral geometry observed in the gas phase. For example, the X-ray structure of $Cl_2Sn(CH_3)_2$[33] contains a distorted octrahedral Sn center. Similarly, $Sn(CH_3)_4$ also distorts slightly around the Sn center in the solid, likely due to crystal packing.[34] $ClSn(CH_3)_3$ also has coordination discrepancies between the gas phase[35] and solid state, with the solid $ClSn(CH_3)_3$ existing as a chlorine-bridged linear polymer with the tin atom adopting a five-coordinate, distorted trigonal bipyramidal geometry.[36]

Calculated Geometries

In agreement with the gas-phase experimental results, optimization of the structures of the five molecules leads to four-coordinate, tetrahedral tin centers with the conformations shown in Figure 1. $SnCl_4$ and $Sn(CH_3)_4$ have T_d symmetry, $ClSn(CH_3)_3$ and Cl_3SnCH_3 are C_{3v}, and $Cl_2Sn(CH_3)_2$ has C_{2v} symmetry. For the sake of brevity, the optimized structures are not reported, but rather we use a statistical approach to assess the various combinations of basis sets and effective core potentials. Complete details for the optimized geometries of every combination of basis set and effective core potential are available in the Supporting Information.

Standard Deviations

To compare the calculated bond lengths (r_c) and bond angles (∠$_c$) with the corresponding experimental values (r_e and ∠$_e$),

TABLE 2: Standard Deviations in Bond Lengths (s_r) and Bond Angles ($s_\angle$) of the Organotin Compounds

basis set	ECP	s_r	$s_\angle$
all-electron DFT		0.042	2.2
LANL2MB	LANL2	0.035	2.0
LANL2MB	SDB	0.030	2.1
LANL2MB	SBKJC	0.042	2.0
MWB	SDB	0.049	2.0
MWB	LANL2	0.024	2.0
MWB	SBKJC	0.030	2.0
SBKJC_VDZ	SBKJC	0.034	2.0
SBKJC_VDZ	LANL2	0.028	2.0
SBKJC_VDZ	SDB	0.077	2.0
LANL2DZ	LANL2	0.026	2.0
LANL2DZ	SDB	0.065	2.0
LANL2DZ	SBKJC	0.032	2.0
LANL2DZdp	LANL2	0.023	2.0
LANL2DZdp	SDB	0.059	3.2
LANL2DZdp	SBKJC	0.029	1.9
SDB-cc-pVTZ	SDB	0.038	1.9
SDB-cc-pVTZ	LANL2	0.017	2.0
SDB-cc-pVTZ	SBKJC	0.019	2.0
CRENBL	CRENBL	0.061	2.0
CRENBL	LANL2	0.022	2.0
CRENBL	SDB	0.042	2.0
CRENBL	SBKJC	0.026	2.0
SDB-aug-cc-pVTZ	SDB	0.033	1.9
SDB-aug-cc-pVTZ	LANL2	0.015	2.0
SDB-aug-cc-pVTZ	SBKJC	0.018	1.9
SDB-cc-pVQZ	SDB	0.030	1.9
SDB-cc-pVQZ	LANL2	0.015	2.0
SDB-cc-pVQZ	SBKJC	0.016	1.9
SDB-aug-cc-pVQZ	SDB	0.030	1.9
SDB-aug-cc-pVQZ	LANL2	0.015	2.0
SDB-aug-cc-pVQZ	SBKJC	0.016	1.9

we have computed the standard deviations in bond lengths (s_r) and bond angles ($s_\angle$) as defined in eqs 1 and 2, respectively,

$$s_r = \sqrt{\frac{\sum_{i=1}^{n}(r_{ci} - r_e)^2}{(n_r - 1)}} \tag{1}$$

$$s_\angle = \sqrt{\frac{\sum_{i=1}^{n}(\angle_{ci} - \angle_e)^2}{(n_\angle - 1)}} \tag{2}$$

Table 2 lists the standard deviations in bond lengths and bond angles for all combinations of basis sets and effective core potentials included in this study. The basis sets are ordered in terms of increasing size, and within each set the effective core potentials are listed in an arbitrary order. The all-electron calculation with the 3-21G(d,p) basis set on tin employs the smallest number of basis functions. The MWB, SBKJC_VDZ and LANL2DZ basis sets include the same number of basis functions. The SDB-aug-cc-pVQZ basis set is the largest included in this study.

Bond Lengths and Bond Angles

As shown in Table 2, the standard deviations for bond angles range from 1.9 to 3.2°, although the majority of the values are clustered around 1.9−2.0°. This difference is too small to provide a basis for choosing one method over another. This conclusion is not surprising given that the five molecules involve a four-coordinate tin that is either tetrahedral or nearly tetrahedral. For this reason, our choice of a practical computational method is based on the results obtained for bond lengths.

The standard deviations for bond lengths range from 0.015 to 0.077 Å, with most between 0.015 and 0.050 Å. The standard deviations show a general tendency to decrease as the size of the basis set increases. Density functional methods with the 6-31G(d,p) basis set typically yield bond lengths within 0.010−0.020 Å of the experimental values for small organic molecules.[37] It is clear from Table 2 that similar accuracy is obtainable with the larger basis sets used in this study.

With the larger basis sets included in this study, the smallest deviations are obtained with the LANL2 effective core potential, whereas the largest deviations are obtained with the SDB effective core potential. There are significant time savings with the SDB-aug-cc-pVTZ-LANL2 (30%) and SDB-cc-pVQZ-LANL2 (50%) methods relative to the SDB-aug-cc-pVQZ-LANL2 method. Therefore, we conclude that the SDB-aug-cc-pVTZ basis set and LANL2 effective core potential provides the best compromise between computational efficiency and the accuracy of the optimized structures.

Conclusion

The ability of various combinations of basis sets and effective core potentials to reproduce gas-phase electron diffraction geometries of small organotin molecules ($Cl_nSn(CH_3)_{4-n}$) has been determined, in terms of the standard deviations between the calculated and experimental values of the bond lengths and angles. It was concluded, on the basis of computational efficiency and the s_r and $s_\angle$ values, that the B3LYP method with the SDB-aug-cc-pVTZ basis set and LANL2 effective core potential on tin, together with the 6-31G(d,p) basis set for the other atoms, is recommended for the prediction of the geometries of organotin systems. This level of theory will be used in our future studies of organotin systems.

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Supporting Information Available: Archive entries for the geometry optimizations and frequency calculations of the five $Cl_nSn(CH_3)_{4-n}$ molecules (Figure 1) are available free of charge via the Internet at http://pubs.acs.org.

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