hexyltin Complexes. Dicyclohexyltin oxide is insoluble in all solvents and stable up to high temperature (>220 °C). Such properties suggest that the coordinative association is preserved in the dicyclohexyltin oxide, as in the structure of dimethyltin oxide[1]. On the other hand, dicyclohexyltin sulfide is soluble in common organic solvents such as benzene, acetone, chloroform and dimethyl sulfoxide, and is a colorless crystalline solid with sharp melting point (193–194 °C). In particular, cryoscopic measurement in benzene indicates that dicyclohexyltin sulfide is trimeric. The IR bands of the complexes relevant to their molecular structures listed in Table 4 show the expected values.

Among the stretching modes, ν(Sn–C) band is known to depend on the structure[18,19]. The red shift of the ν(Sn–C) mode of $Cy_2Sn(S_2CNMe_2)_2$ compared to that of dicyclohexyltin oxide and dicyclohexyltin sulfide may be ascribed to decrease of Lewis acidity of the tin atom by hexa-coordination.

The physical and chemical properties of dicyclohexyltin (IV) complexes are in accordance with those of dimethyltin complexes in the solid state and in solution.

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Tl – Tl Interactions in Tl Dimer Investigated by Relativistic and Nonrelativistic EHT Calculations

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Interactions between Tl atoms for the Tl dimer are studied by relativistic and nonrelativistic EHT methods. Relativistic bond weakening for the Tl dimer is qualitatively explained by comparing orbital energies from relativistic and nonrelativistic calculations. It is also shown that significant overlap exists, especially for 6p orbitals, at the internuclear distance larger than 4 Å, implying that Tl – Tl interaction is not just the electrostatic interaction in the recently discovered dimeric thallacarborane.

Introduction

Diatomic Tl_2 is one of the favorite molecules in elucidating relativistic bond weakening because the inclusion of spin-orbit effects results in substantial decrease of calculated dissociation energies.[1-3] Bond weakening for Tl_2 ground state is attributed to the requirement to form a hybrid of $6p_{1/2}$ and $6p_{3/2}$ atomic spinors in order to produce an analog of bonding σ molecular orbital. The hybridization costs energy

since the atomic Tl is in $^2P_{1/2}$ ground state which is essentially the configuration of one $6p_{1/2}$ open shell electron. From the above argument, we may expect that this weakening might be expainable in the orbital interaction level.

In this report, we employ simple EHT method[4] to study relativistic effects. We utilize existing programs for the relativistic[5] and nonrelativistic[4] EHT calculations.

Most previous calculations on Tl_2 are based upon relativistic effective core potentials.[1,2] The results from the pre-

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Table 1. Orbital Exponents, ζ, and Coulomb Parameters, H_{ii}, for REX and EHT Calculations of Tl[a]

	6s		6p (or 6p₃/₂)		6p₁/₂	
	ζ	H_{ii}	ζ	H_{ii}	ζ	H_{ii}
RP	2.52018	−12.22322	1.62002	−4.80409	1.84836	−5.75136
ARP	2.5202	−12.22	1.6961	−5.12		
NRP	2.1908	−9.83	1.6555	−5.24		
EXP	2.3034	−11.60	1.5966	−5.80		

[a]H_{ii}'s are in eV and scaling constant for H_{ij} is 1.75.

sent EHT calculations are not as quantitative as other calculations, but will be easier to interprete in terms of orbital interactions. In addition, informations regarding unoccupied orbitals, which is usually not reliable in SCF type calculations, are also useful in EHT calculations.

The interaction between Tl atoms is also interesting from another point of view. One of the newly synthesized metal carborane complexes[6] has dimeric structure with Tl–Tl distance of about 4 Å. Although Tl(1) is the formal charge for this thallium dicarballide, and there are some experimental evidences of bonding interactions between Tl and B atoms for this complex,[6] we might gain some insight about the bonding characteristics from the study of Tl₂.

Calculations and Results

Four different types of EHT parameters, shown in Table 1, are used in the calculations, one set in the relativistic EHT (REX)[5] calculations and the remaining three in the conventional EHT[4] calculations. Parameters for REX were obtained from atomic Dirac–Fock calculations by Pyykko *et al.*[5] and denoted as relativistic parameters (RP). When the spin–orbit splittings are eliminated by averaging RP, it is possible to generate parameters that contain all other relativistic effects except the spin–orbit effects. These averaged relativistic parameters (ARP) can be used in the conventional EHT calculations. In order to estimate relativistic effects, it is necessary to have corresponding nonrelativisitic parameters. This can be done by generating parameters from results of the nonrelativistic atomic calculations. Nonrelativistic parameters (NRP) in Table 1 are obtained from atomic HF calculations also by Pyykko *et al.*[5] and presumably of the same quality as RP in representing atomic properties expected from HF calculations. The last set of parameters is from the experimental atomic data,[7] which should contain all the relativistic effects and other additional effects such as electron correlation effects. These parameters are denoted as experimental parameters (EXP) in Table 1. In EXP, spin–orbit splittings are not included.

REX calculations are performed with RP and EHT ones with ARP, NRP and EXP at various internuclear distances from 3.0 Å to 6.0 Å. Since parameters for 5d orbitals are readily available, calculations with RP, ARP and NRP were carried out for dsp-valence shell as well as for the sp-valence. The influence of the 5d shell, which is completely filled, on molecular orbitals formed by 6s and 6p valence orbitals is negligible and the results from dsp-valence calculation are not reported.

Orbital energies at internuclear separations of 3.0, 4.0,

Table 2. Orbital Energies (in eV) and Total Overlap between two Tl Atoms (TO) for Several Internuclear Distances of Tl₂ from REX and EHT Calculations

	6sσ	6sσ*	6pσ	6pπ	TO
RP–REX					
3.0 Å	−13.36	−11.31	−5.64	−6.23	0.793
4.0 Å	−12.44	−12.05	−6.14	−5.82	0.395
5.0 Å	−12.24	−12.20	−5.92	−5.71	0.142
6.0 Å	−12.22	−12.22	−5.78	−5.73	0.020
ARP–EHT					
3.0 Å	−13.43	−11.59	−4.79	−5.93	0.945
4.0 Å	−12.46	−12.08	−5.86	−5.46	0.527
5.0 Å	−12.24	−12.20	−5.63	−5.22	0.275
6.0 Å	−12.22	−12.22	−5.30	−5.14	0.093
NRP–EHT					
3.0 Å	−11.33	−9.12	−5.01	−6.12	1.160
4.0 Å	−10.34	−9.54	−5.91	−5.62	0.579
5.0 Å	−9.92	−9.76	−5.79	−5.36	0.306
6.0 Å	−9.84	−9.82	−5.46	−5.27	0.111
EXP–EHT					
3.0 Å	−13.17	−10.93	−5.25	−6.84	1.186
4.0 Å	−12.06	−11.39	−6.56	−6.28	0.594
5.0 Å	−11.67	−11.56	−6.51	−5.96	0.350
6.0 Å	−11.61	−11.60	−6.11	−5.84	0.142

5.0, and 6.0 Å are summarized in Table 2 for $6s\sigma$, $6s\sigma^*$, $6p\sigma$ and $6p\pi$ orbitals from EHT calculations and corresponding molecular spinors from REX calculations. It is noted that the gerade and ungerade symmetries are omitted here for the sake of simplicity. In REX calculations, $6p\pi$ orbital is no longer degenerate and only the lower energy component $6p\pi_{1/2}$ is shown in Table 2. There are six valence electrons in Tl₂ and three orbitals with the lowest orbital energies are expected to be filled at each internuclear distance. In Table 2, all EHT calculations show the similar orbital interaction patterns. One interesting point is that $6p\sigma$ and $6p\pi$ orbitals cross between 3 Å and 4 Å because $6p$ orbitals from one Tl atom begin to make antibonding overlap with the tail part of the $6p$ orbitals from the other Tl atom. This type of energy level crossing also occurs for the molecule of light atoms[8] like B₂. Since the equilibrium bond lengths for Tl₂ calculated by other methods are in the range of 3.0–5.0 Å, $6p\sigma$–$6p\pi$ crossing should be properly accounted for any accurate description of the Tl₂ potential energy surface. The ground state of Tl₂ is a $^3\Sigma^-$ state from $(6p\pi)^2$ configuration in the $\Lambda\Sigma$-coupling case and a 0_u^- state from $(6p\sigma_{1/2})(6p\pi_{1/2})$ configuration in the $\omega\omega$-coupling case according to the effective core potential calculations.[1,2]

In all cases, orbital energies for $6s\sigma$ and $6s\sigma^*$ behave as weakly bonding and antibonding orbitals, respectively. Calculation reveals that mixing between $6s$ and $6p$ orbitals is insignificant even at 4.0 Å. Substantial mixing of $6s$ and $6p$ exist at 3 Å, but this short distance is not of the primary interest here. At the distance of 4 Å, which is the value close to the equilibrium bond length of the $^1\Sigma_g^+$ state from $(6p\sigma)^2$ configuration in the previous calculation,[2] the $^1\Sigma_g^+$ state is lower in energy than the $^3\Sigma_g^-$ state. This is expected from orbital energies in Table 2 and also the result of more elaborate cal-

culation by Christiansen and Pitzer.[2] For this $^1\Sigma_g^+$ state, bond energy can be reasonably estimated by comparing $6p\sigma$ orbital energy at 4 Å with $6p$ orbital energy of Tl atom. The energy differences between these two orbitals for $6p\sigma$ orbital at 4 Å are 0.38eV, 0.74eV, 0.67eV and 0.76eV for RP-REX, ARP-EHT, NRP-EHT and EXP-EHT calculations, respectively. Of course, these energy differences are not exact molecular binding energies due to obvious reasons associated with EHT models, but can be used in the study of the trend and the magnitude of relativistic effects. The difference between RP-REX and ARP-EHT is mainly due to the spin-orbit effect and we may conclude that spin-orbit effect is responsible for destabilization of the Tl_2 molecule by about 0.36eV. The order of magnitude for Tl_2 bond weakening is in resonable agreement with that calculated by more accurate methods.[2] Rest of the relativistic effects other than the spin-orbit effect are shown as the difference between ARP- and NRP-EHT values and amount to less than 0.1 eV. Comparison of ARP-EHT value with EXP-EHT one indicates that both calculations predict essentially similar molecular structure although orbital energies for individual molecular orbitals differ by 0.5-1.0eV. Similar analysis can be applied to the molecular bindings at shorter internuclear distances and dissociation energy for the $^3\Sigma_g^-$ state and the same trend for spin-orbit and other relativistic effects is expected. However, we omit the discussion of the $^3\Sigma_g^-$ state because of the complicated nature of two-orbital ($6p\sigma$ and $6p\pi$) interplay which is very sensitive to the relative spacing between two molecular orbitals.

Total overlap population between two Tl atoms is also shown in Table 2. At 4 Å, the interatomic Tl-Tl distance found in a recently synthesized thallacarborane,[6] there are fair amounts of overlap populations for all calculations. The bond order is smaller than 1 but large enough to be considered as bonding interaction. Inspite of reduction in bonding interaction due to spin-orbit effect in case of RP-REX case, the measure of the overlap population reaches 0.4 as shown in Table 2. In the thallium carbollide complex, Tl atoms have formal charges of +1 and many other atoms, especially B atoms in carborane cages, probably participate in bonding

with Tl atoms.[6] Charge of +1 will certainly reduce the electron densities of $6p$ electrons and produce much weaker bonding interaction between Tl atoms than that expected from the present calculations. On the other hand, additional coordination may introduce or encourage promotion of electrons from $6s$ to $6p$ orbitals. As a result, we conclude that there are fair amount of orbital overlaps and possibly some bonding interactions in addition to the electrostatic interaction, which should be repulsive, present in the dimeric thallacarbollide. Furthermore, we expect that any systems containing Tl or Tl(I) species with the Tl-Tl distance near 4 Å have orbital interactions between two Tl atoms. This orbital interaction will become insignificant for Tl(III) species.

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