be called "classical aromaticity". We can follow our situation best by reference to Figure 5a. Among this group of characteristics, it is $I_{5,6}$ that provides the purest measure of classical aromaticity, closely followed by ΔN (no. 3). The DRE (no. 4) and ${}^{15}N$ (no. 12) have small p_2 loadings but rather more significant p_3 loadings whereas the HSRE (no. 5) is a somewhat more hybrid measure.

(b) The second group is comprised of the magnetic parameters χ_m (no. 9) and Λ (no. 10). These are both marked by *very small* p_1 components but large positive p_2 and large negative p_3 components. Clearly this second group of characteristics includes measurements of "magnetic aromaticity" which is almost completely orthogonal to the "classical aromaticity" measured by characteristics of group (a).

(c) The remaining group of five characteristics all show moderately positive p_1 loading together with negative loadings for both p_2 and p_3 for ΔH_F (calculated or experimental) and positive loadings for both p_2 and p_3 for RC, ΔH_a, and I_1. The characteristics in this third group thus possess elements of both "classical" and "magnetic" aromaticity.

Conclusions. We believe that we have been able to a considerable extent to resolve the apparent impass between classical and magnetic aromaticity and provide a firm basis for the consideration of aromaticity as a quantitative concept. In fact, there are at least two types of aromaticity: the best available measure of classical aromaticity is provided by the Bird $I_{5,6}$ parameter and this parameter correlates well for ΔN and DRE. The second type of aromaticity is magnetic aromaticity, which is measured by χ_m or Λ. These two types, classical and magnetic, of aromaticity are orthogonal. Other aromatic characteristics are influenced by both "classical" and "magnetic" aromaticity to varying extents. Hence, we believe that there are at least two quantitative aromaticity scales. Characteristics that depend on aromaticity can be determined by either or both of these scales. Indeed a case could be made for the existence of *three* types of aromaticity corresponding to the three PC found. At the present time we wish only to claim the existence of at least two types: further work is in hand which it is hoped will further illuminate the nature of the phenomenon of aromaticity. The methods used in this paper are capable of extension to a wide range of other aromatic, antiaromatic, and non-aromatic compounds, ions, and radicals, and to numerous other chemical and physical properties. They offer the potential not only for the understanding and rationalization of known facts but also for the prediction and estimation of unknown properties. Work along these lines is ongoing in our laboratories.

Acknowledgment. We thank a Referee for helpful comments on this paper.

Supplementary Material Available: Predictions of aromatic characteristics for **5**, **6**, **7**, **13**, **14**, **15**, and **16** (65 pages). Ordering information is given on any current masthead page.

Theoretical Studies on the Stability of Tl–C σ-Bonds in Aliphatic Organothallium Compounds

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Abstract: Calculations of the electronic structure and bonding in organothallium compounds (TlR, TlR^+, TlR_2, TlR_2^+, TlR_3, TlR_4^-, TlR_2Br, and TlR′ with R = CH_3, R′ = C_2H_3, or C_2H), in the hydrides (R = H), their dissociation products (CH_3, C_2H_3, C_2H, C_2H_6, and TlBr), and Tl_2 have been carried out. A modified version of Pople's SCF program GAUSSIAN82 has been used, in which the core electrons on the Tl atom are described by a quasi-relativistic [Pt]-core pseudopotential. All bond distances and angles have been optimized with a Fletcher–Powell procedure. SCF–SW–Xα calculations have been carried out to determine the extent of the Tl 5d core orbital participation in the Tl–C bond. Vibrational frequencies have been calculated from the harmonic diagonal SCF valence force field. As a result, the previously undetected molecule $TlCH_3$ is found to be stable with respect to dissociation into Tl and CH_3. The isolated $Tl(CH_3)_3$ molecule is found to possess the expected planar-trigonal (TlC_3) structure. It is explained why organothallium chemistry is mainly the chemistry of Tl(III) in contrast to inorganic thallium chemistry and that Tl–Tl bonds are very weak or do not exist is a relativistic effect.

I. Introduction

In the last 20 years organothallium chemistry has become more and more important in organic synthesis, and experimental studies on structure and bonding have been reported on many organothallium compounds.[1-10] Most of the stable organothallium compounds are of the type R_2TlX (R = alkyl, aryl; X = F, ClO_4, ...). Trialkyl and triaryl compounds are unstable and very reactive; e.g., $TlMe_3$ (Me = CH_3)[11] is reported to be spontaneously inflammable in dry air.[12] In contrast, Me_3M compounds (M = B, Al, Ga, In) are stable.[10] Monoalkyl compounds of the type TlR have never been isolated and the only known structures containing this moiety are of the types $RTlX_2$ and RTlO (X = OAc, CN, Cl, Br, ...).[1,2,10,13] Monoarylthallium compounds are

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only known as stable π-complexes of cyclopentadienide, $Cp^- \leftarrow Tl^+$.[5,14] Also, diorganothallium compounds of the type TlR_2 have not been found[7] and have only been predicted as possible structures in intermediate transition states.[2,15] This may also be the case for the monoalkyl compounds RTl^+ and RTl.[5,10] In contrast, inorganic thallium chemistry shows a preference for Tl(I) compounds, and it is not understood why organothallium chemistry does not. Quantum chemical calculations should give answers to such problems and general insight into the behavior of Tl–C bonds.

Relatively few ab initio calculations on large heavy-atom-containing molecules have been reported previously, due to the long calculation times involved. Moreover, relativistic effects have to be taken into account for heavy elements.[16] Relativistic SCF programs are now under development,[17] but the relativistic treatment of molecules (and atoms) within the Dirac–Fock theory is still at an inchoate stage of development. These difficulties can be partially overcome by using the pseudopotential method[18] in which the core electrons are treated as fixed (frozen-core approximation).[19] This is in agreement with the chemical concept that only valence electrons take part in chemically reacting systems. Moreover, the major relativistic effects can be included in the pseudopotential approximation.[20–23]

Relativistic effects are important in Tl compounds, and some differences from the other main-group III elements can be explained in this way.[24] The relativistic contraction of the Tl 6s orbital is 13%[25] but is negligible for the average of $6p_{1/2}/6p_{3/2}$ orbitals.[26] Hence, relativistic bond contractions are expected where s orbitals participate in the bond.[27] Fine structure (consisting mostly of spin–orbit coupling (SO)) is also important in calculating molecular properties.[22] A p_z orbital, which forms a σ-bond in the z direction, is a mixture of $^1/_3$ $p_{1/2}$ and $^2/_3$ $p_{3/2}$. In the Tl atom, these are split by more than 93 kJ/mol,[28] and it is not clear, without recourse to calculations, whether a pure σ-bond can be achieved or not.[29]

Table I. Contracted Gaussian Basis Sets for Thallium and Bromine for the Nonrelativistic (NRPP) and Relativistic (ARPP) Pseudopotentials[a]

	thallium(NRPP)		thallium(ARPP)		bromine(ARPP)	
	a	f	a	f	a	f
s	1.66856	−0.26467	1.45826	−0.18162	4.32759	0.17671
	1.00802	0.55253	0.723941	0.61017	2.25772	−0.52884
	0.239744	1	0.195627	1	0.407766	0.74593
	0.082597	1	0.066544	1	0.155880	1
	0.041	1	0.041	1		
p	1.57565	−0.02146	1.43752	−0.01126	1.74924	0.17086
	0.810558	0.08788	0.660457	0.11516	0.798846	−0.31148
	0.144387	1	0.137179	1	0.302837	1
	0.044844	1	0.045116	1	0.121408	1
	0.020	1	0.020	1	0.048443	1
d	0.146	1	0.146	1	0.389	1

[a] a, gaussian exponent; f, contraction coefficient.

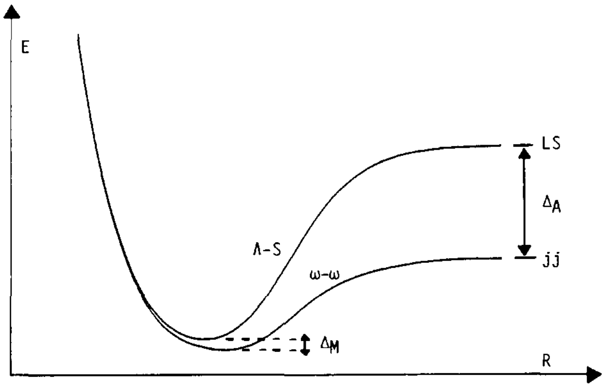

Figure 1. Schematic molecular energy curves for a diatomic molecule in the Λ–S and ω–ω coupling schemes.

We have performed relativistic pseudopotential calculations for the following organothallium compounds: TlR, TlR^+, TlR_2, TlR_2^+, TlR_3, TlR_4^-, TlR_2Br, and TlR′ (R = CH_3, R′ = C_2H_3, C_2H), the corresponding hydrides (R = H), their dissociation products (CH_3, C_2H_3, C_2H, C_2H_6, and TlBr), and Tl_2 to allow discussion of possible Tl–Tl bonds in organothallium compounds. The chemical behavior of the hydrides is very similar to that of the methyl compounds, and therefore it is of interest to compare them. Relativistic effects have been studied with nonrelativistic (NR) and relativistic (R) pseudopotentials for the Tl and Br atom.[26,30] Correlation effects have been taken into account by a SDCI procedure (configuration interaction with single and double excitations only) and a core–valence dipole polarization potential.[26] The participation of Tl 5d core orbitals in the bonding was studied with a SCF-scattered wave-Xα method (SCF-SW-Xα)[31] for $TlMe_2^+$.

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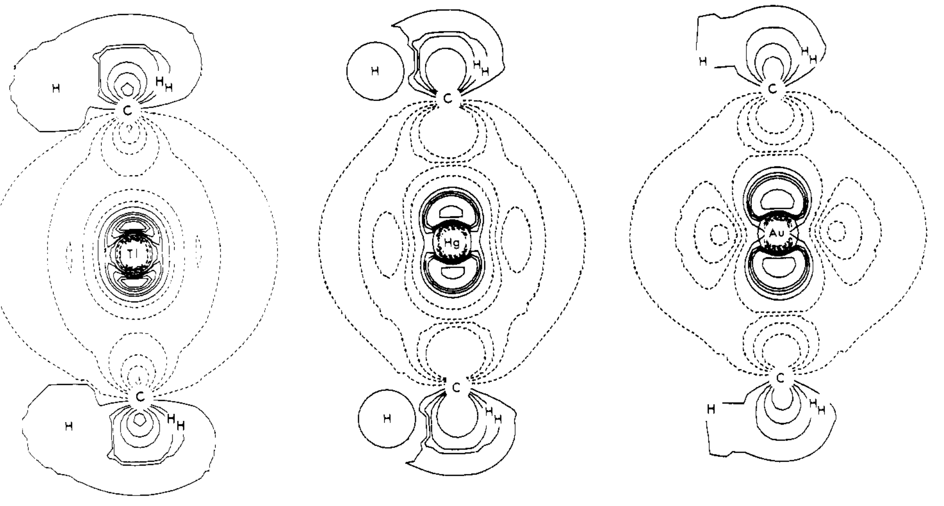

Figure 2. Density contour plot for the $3a_1'$ orbital. From the left to the right: $TlMe_2^+$, $HgMe_2$, $AuMe_2^-$.

II. Method

The pseudopotential parameters for Tl and Br have been reported in previous papers.[26,30] The calculations performed here implement the method of ref 30. The nonrelativistic (NRPP) and spin–orbit-averaged relativistic (ARPP) pseudopotential calculations have been carried out with a modified version of the program package GAUSSIAN82.[32] All bond distances and angles are optimized by a Fletcher–Powell procedure.[32] Our Gaussian basis set for thallium was a contracted (5s/5p/1d)/[4s/4p/1d] and for bromine a (4s/5p/1d)/[2s/4p/1d] basis set (derived by an energy optimization with program PSATOM.[33] The symbol (n)/[m] denotes an n basis set contracted to an m basis set. The Tl and Br polarization functions are taken from Huzinaga et al.[34] The Gaussian exponents and contraction coefficients are listed in Table I. For carbon we used a contracted (9s/5p)/[4s/2p] Dunning basis set[35] extended to [4s/3p/1d] with a p exponent of 0.034 and a d exponent of 0.75 and for hydrogen a contracted (5s)/[2s] Huzinaga basis set[36] extended to [2s/1p] with a p exponent of 1.1. As indicated by a basis set study on TlMe the superposition error is less than 0.8 kJ/mol at the nonrelativistic and relativistic equilibrium geometry and is therefore assumed to be negligible for all the other organothallium compounds. Spin-orbit coupling has been taken into account by a two-component quasi-relativistic pseudopotential (QRPP)[21] for TlMe only, using the program UHREL of Hafner et al.[37] The same basis set is taken as for the spin-averaged case. As a result of our calculation the contribution of spin-orbit coupling to the total energy is found to be small near the region of the equilibrium geometry in the ground state of TlMe. This is true of other results, where σ-bonds in ground states have been calculated.[38] E.g., for TlH we get $\Delta_M = 0.4$ kJ/mol $\ll 62$ kJ/mol $= \Delta_A$ (Figure 1).[26] Hence, to a good approximation we can correct the dissociation energy for spin–orbit coupling by using atomic spin–orbit contributions only.[26,30] Correlation effects have been studied on the molecules TlMe and $TlMe^+$ with a semiempirical pseudopotential ansatz (SEPP) for Tl. Core–valence correlation is described by a dipole polarization potential[26,30] and valence correlation only by a SDCI procedure using a modified version of Davidson's program MELD.[39] For the CI calculations of TlMe and $TlMe^+$ we used an uncontracted (8s/8p/2d) basis set[26,38] with d polarization functions from Huzinaga et al.[34] The CI basis set for the C and H atoms are the same as mentioned above, but uncontracted.

Table II. Molecular Properties of the Hydrides[a]

		TlH^+	TlH	TlH_2^+	TlH_2	TlH_3	TlH_4^-
r_e	NR	1.877	1.925	1.775	1.851	1.837	1.905
r_e	R	3.347	1.883	1.673	1.776	1.739	1.806
Δr_e	R	−1.470	0.042	0.102	0.075	0.098	0.099
α	R			180	119.9	120	109.5
D_e	NR	30	180	112	167	187	202
D_e	R	2	175	69	128	160	178
D_e	SO	2	113	69	97	139	178
ΔD_e	SO	28	67	43	70	48	24
k_e	NR	0.93	1.51	2.22	1.74	1.96	1.90
k_e	R	0.01	1.18	2.55	1.69	2.22	1.81

[a] r_e, Tl–H equilibrium distance in angstroms; α, HTlH angle in degrees; D_e, Tl–H dissociation energy per hydrogen atom in kilojoules per mole (SO correction for Tl, 62 kJ/mol[28]); k_e, Tl–H force constant in millidynes per angstrom; NR, nonrelativistic; R, SO-averaged relativistic; SO, R corrected by atomic SO coupling. $\Delta r_e = r_e(\mathrm{NR}) - r_e(\mathrm{R})$; $\Delta D_e = D_e(\mathrm{NR}) - D_e(\mathrm{SO})$.

Possible errors resulting from the [Pt]-core definition of our Tl pseudopotential in the SCF calculations are d participations from the Tl core (nonspherical core) and deviations from the point charge approximation (core penetration or core overlap). The latter has been considered only for the hydrides and dimers and is described in detail in ref 26 and 38. For the Tl–Me moiety, core penetration effects are very small for distances greater than (or equal to) the ground-state equilibrium distances. E.g., from relativistic calculations of the core Coulomb potential[26] one gets a repulsive core penetration effect of ~1 kJ/mol at 2.2 Å, which will lead to slight increases in Tl–H bond distances of ~0.01 Å and to a lowering of the dissociation energy by ~1 kJ/mol. This is within the accuracy of the pseudopotential method. For studying core d participations we carried out SCF-scattered wave-Xα calculations[31] of the electronic structure of $TlMe_2^+$ (D_{3d}) using the program XASW of Case and Cook.[40] Calculations were also carried out on $HgMe_2$ and $AuMe_2^-$ (isoelectronic with $TlMe_2^+$), by using the geometries given in ref 41 and 42, since the metal atoms in these species have a lower 5d/6s orbital energy separation than Tl[43] and so should show a greater degree of involvement of the metal 5d orbitals in the bonding. The 5d orbital involvement in the bonding occurs mainly in the a_1' orbitals, which involve a significant contribution from the metal $5d_{z^2}$ and 6s and the carbon $2p_z$ orbitals. This effect is most clearly seen in the highest occupied a_1'

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Table III. Molecular Properties of the Aliphatic Organothallium Compounds Calculated with ARPP[a]

	$MeTl^+$	MeTl	Me_2Tl^+	Me_2Tl	Me_3Tl	Me_4Tl^-	Me_2TlBr	C_2H_3Tl	C_2HTl
r_e(TlC)	2.800	2.233	2.089	2.180	2.152	2.221	2.121	2.224	2.219
r_e(CH)	1.076	1.089	1.081	1.085	1.086	1.095	1.083	1.084	1.062
α(TlCH)	98.4	111.2	109.0	110.0	110.9	111.5	111.7		
α(CTlC)			180	121.1	120	109.5	140.0		
D_e(Tl–Me)	−30	121	77	85	117	120	83	156	314
D_e^{SO}(Tl–Me)	−30	59	77	55	97	120	72	94	252
k_e(TlC)	0.11	1.42	2.35	1.88	2.34	1.94	2.44	1.61	1.56
k_e(CH)	6.10	5.75	6.05	5.86	5.87	5.93	5.88	5.84	6.96
$k_e(\alpha$(TlCH))	0.18	0.40	0.50	0.43	0.47	0.41	0.48		

[a] r_e, equilibrium distance in angstroms; α, angle in degrees; D_e, Tl–C dissociation energy per alkyl group in kilojoules per mole; k_e, force constant in millidynes per angstrom; D_e^{SO}, R with atomic SO correction (62 kJ/mol[28]). In the case of Me_2TlBr, the molecules SO correction of TlBr was taken (9 kJ/mol). For the other properties, see text.

orbital, $3a_1'$, which would be pure metal 6s in the absence of bonding. Contours for these orbitals are shown in Figure 2, for $AuMe_2^-$, $HgMe_2$, and $TlMe_2^+$, and these clearly show the decreasing involvement of the metal $5d_{z^2}$ orbital along this series. The outstanding chemical stability of TlR_2^+ compounds has often been explained by Tl(5d) contributions to the Tl–C bond.[1] Figure 2 shows that this is very unlikely.

All pseudopotential calculations were carried out on the high-speed vector machine CRAY1M. The Fletcher–Powell geometry optimization for $TlMe_3$, $TlMe_4^-$, $TlMe_2Br$, and TlC_2H_3 was very time-consuming in CPU time. E.g., for $TlMe_3$ 193 basis functions contracted to 120 were used. This produces between 19 and 23 million (contracted) two-electron integrals depending upon the geometry (the two-electron integral cutoff was set at 10^{-10}),[32] which need 370 Mbyte disk storage in the Raffenetti integral format. The total CPU time for the geometry optimization of $TlMe_3$ was 20 h (per geometry point, 1456-s integral time by 19.7 million two-electron integrals and 2338-s SCF time by 47 cycles using a SCF-convergence threshold of 10^{-8} au; total CPU, 4140 s). In the case of $TlMe_4^-$, we exceeded the available disk space of 450 Mbyte. No direct SCF program was available; hence, we reduced our H basis to (3s)/[2s] as listed in GAUSSIAN82,[32] assuming that this will affect the Tl–C σ-bond only slightly.

III. Results

A. Thallium Hydrides. Some theoretical studies of thallium hydrides (TlH^+, TlH, and TlH_3, (D_{3h})) have been published earlier[23,26] and discussed in detail. Therefore, we shall give only a short outline of our results that are important for discussing the analogous methyl compounds. For our calculations on TlH_2^+ ($D_{\infty h}$), TlH_2 (C_{2v}), TlH_2Br (C_{2v}), and TlH_4^- (T_d), the same basis set is taken as described in ref 26 (uncontracted (7s/7p/2d) for Tl, (5s/2p) for H, and (9s/6p/2d) for Br). The calculated molecular properties are collected in Table II. From the uniform dissociation energy per hydrogen atom we get the stability sequence $TlH_4^- > TlH_3 > TlH > TlH_2 > TlH_2^+ > TlH^+$. Only the most stable, first four thallium hydrides are known experimentally.[1] The expected monovalence of Tl is not observed for the hydrides. The gas-phase SCF hydridization enthalpies may be calculated from the SO-corrected ARPP results (Table II; eq 1–3). The

$$Tl + H \rightarrow TlH \qquad -115\ \text{kJ/mol} \tag{1}$$

$$TlH + H \rightarrow TlH_2 \qquad -81\ \text{kJ/mol} \tag{2}$$

$$TlH_2 + H \rightarrow TlH_3 \qquad -224\ \text{kJ/mol} \tag{3}$$

SDCI energy for step 1 is −197 kJ/mol,[26] which is in excellent agreement with the experimental value of −199 kJ/mol.[44] These energies are not large enough to stabilize the molecules relative to dissociation into Tl_2 and H_2 ($D_e(H_2)$ = 458 kJ/mol,[44] $D_e(Tl_2)$ = 20–50 kJ/mol; see below), and this explains the reported instabilities of such hydrides.[1] TlH_2^+ seems to be stable only in the gas phase. In all other cases $TlH_2^+X^-$ would react to give TlX and H_2. The molecule TlH_4^- is the most stable thallium hydride we have found from our calculations. As an example, $Tl^+TlH_4^-$ is calculated to be stable with respect to dissociation into TlH and TlH_3 by 56 kJ/mol using ARPP. As reported by Strouf and Wold,[45] the stability of $MTlH_4$ compounds would increase from Li to Cs, and we expect, from the ionic radii of Tl^+ and the dissociation energy of TlH, that $TlTlH_4$ would be more stable than $LiTlH_4$ (in kJ/mol):[44] D_e(LiH) = 243, D_e(TlH) = 199, D_e(CsH) = 175. The other "Tl hydrides" $TlMH_4$, (M = B, Al, Ga) of the third main group are all known and isolated.[46] The increase in stability is related to the variation of the M–H dissociation energy from M = Tl to M = B (experimental values in kJ/mol from ref 44): 199 (TlH), 248 (InH), 284 (GaH), 305 (AlH), and 344 (BH).

For the hydrides we get the sequence of Tl–H bond distances $TlH > TlH_4^- > TlH_2 > TlH_3 > TlH_2^+$. This is exactly the sequence we would expect from the simple hybridization model; i.e., the s participation increases from the left to the right. As a result, we get the largest relativistic bond contraction of 0.1 Å in TlH_2^+. The calculated SDCI bond distance of 1.864 Å for TlH is in excellent agreement with the experimental value of 1.870 Å.[44] TlH^+ is a special case because of its low stability.[26]

TlH_2Br is only of theoretical interest as an analogous case to $TlMe_2Br$ because this would dissociate into TlBr and H_2. The calculated molecular properties for TlH_2Br in the trigonal-planar structure using ARPP are as follows: r_e(Tl–H) = 1.720 Å, r_e(Tl–Br) = 2.494 Å, and $\alpha(TlH_2)$ = 132.4°. The resulting Tl–H binding energy is 96 kJ/mol calculated from the dissociation reaction $TlH_2Br \rightarrow TlBr + 2H$. This is comparable to the stability of TlH_2. The Tl–Br binding energy is 250 kJ/mol (SO-corrected for the Br atom; Δ_A = 14 kJ/mol), calculated from the dissociation reaction $TlH_2Br \rightarrow TlH_2 + Br$. We used results from our calculations on TlBr with QRPP: r_e = 2.562 Å (2.618 Å), D_e = 262 kJ/mol (331 kJ/mol), k_e = 1.16 mdyn/Å (1.26 mdyn/Å), and μ_e = 4.91 D (4.49 D); experimental values are in parentheses.[44] The atomic spin–orbit correction has been calculated with the program MCDF[47] as $\Delta_A = \Delta_A^{Tl} + \Delta_A^{Br}$ = 73.5 kJ/mol and is much larger than the molecular stabilization of Δ_M = 8.8 kJ/mol, calculated with program UHREL.[37]

B. Organothallium Compounds. Table III presents the calculated ARPP Tl–C and C–H bond distances, TlCH angles, the corresponding diagonal SCF force constants, and the Tl–Me dissociation energies. Our calculated force constants for the TlCH angle bending vibrations have been derived from the formula (k_e in mdyn/Å, r_e in Å, and $d^2E/d\alpha^2$ in au/rad) given in eq 4. This includes the H–C–H bending mode (50%) as defined in the geometry optimization procedure. Before we discuss the compounds in detail, we first consider the possibility of Tl–Tl bonds in organothallium chemistry.

$$k_e = 4.3595(d^2E/d\alpha^2)_{min} r_e[TlC]^{-1} r_e[CH]^{-1} \tag{4}$$

Theoretical studies on diatomic Tl compounds have been reported and discussed by several authors.[22,23,38,48] The ground state of Tl_2 is probably a weakly bonded O_u^- ($^3\Pi_u$) state with a shallow

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minimum at 3.7 Å. This is also supported by the mass spectroscopic measurements of Balducci et al.[49] (D_e = 20–50 kJ/mol; reinterpreted by Christiansen[23]) as well as of Froben et al.[50] (k_e = 0.4 mdyn/Å). The measurements of this last group also provide evidence that the ground-state dissociation energy of Tl_2 (and In_2), reported in Huber and Herzberg,[44] are overestimated. As pointed out by Christiansen and Pitzer,[48] spin–orbit coupling leads to a nearly total destabilization of Tl_2. Hence, one can get appropriate results only from CI or MCHF methods using ω–ω coupling.

Our calculated values for Tl_2 are quite similar to those of Christiansen and Pitzer[48] and will not be reported here. It is more important to compare the stabilities of the diatomic main-group III compounds for the discussion of Tl–Tl interactions. Dissociation energies are the following (in kJ/mol):[44,48,50–52] B_2 ($^3\Sigma_g^-$), 295; Al_2 ($^3\Sigma_g^-$), 150; Ga_2 ($^3\Pi_u$), 135; In_2, 97; Tl_2 ($O_u^-/^3\Pi_u$), 30. The ground-state symmetries of Ga_2 and In_2 have not been determined yet and require further investigation.[52] This trend in stabilities may explain why no compound with a stable Tl–Tl bond is known either in inorganic or in organometallic chemistry. The only compound postulated to have a stable Tl–Tl bond is $Tl_2Me_6^{2-}$ reported by Wilkie and Oliver.[53] This is analogous to the known species $Ga_2Me_6^{2-}$,[54] but it has probably never been isolated. Reported attempts to prepare $Tl_2R_6^{2-}$ by electrochemical reduction of TlR_3[55] or TlR_2^+[15] were also unsuccessful. Weak Tl–Tl interactions have been found only in vibrational and X-ray measurements of some inorganic Tl(I) compounds.[56] This is in contrast to the other main-group III elements. Metal–metal bonds in compounds of B, Al, and Ga are well-known,[2] and some inorganic compounds with an In–In bond have been isolated.[56,57] Also Tl–M bonds with M ≠ Tl are well-known,[56] and some of these are known to be very stable compounds (e.g., see Weibel and Oliver[58]). From our calculated nonrelativistic SDCI dissociation energy for the $^3\Pi_u$ state of Tl_2 of 93 kJ/mol (compare with the QRPP/CI value of 15 kJ/mol obtained by Christiansen and Pitzer[48]), we conclude that the fact that metal–metal bonds do not exist (or are very weak) in Tl chemistry is due to spin–orbit coupling and to inert pair effects (relativistic 6s contraction[16]), and, hence, this is a pure relativistic effect! We now discuss the calculations on the organothallium compounds in detail.

$TlCH_3^+$. $TlMe^+$ and $TlPh^+$ (Ph = phenyl) have been detected in the mass spectra of $Tl(OOCMe)_3$ and $Tl(OOCPh)_3$,[2,59] but molecular structure data are not available. Alkyl TlR^+ compounds dissociate in the gas phase into the radical $R^\bullet$ and Tl^+. We can therefore neglect SO contributions in $TlMe^+$ at the SCF level.

The obtained NRPP data on $TlMe^+$ are as follows: r_e(TlC) = 2.518 Å, r_e(CH) = 1.078 Å, α(TlCH) = 102.0°, k_e(TlC) = 0.36 mdyn/Å, k_e(CH) = 6.02 mdyn/Å, k_e(α(TlCH)) = 0.28 mdyn/Å, and D_e(Tl–Me) = 37 kJ/mol. We used data from SCF calculations on CH_3 (D_{3h}): r_e(CH) = 1.073 Å, k_e(CH) = 6.09 mdyn/Å, total energy E = −39.573368 au. Compared with ARPP calculations (Table III), we find a relativistic destabilization analogous to that of TlH^+ (Table II). In the relativistic case we get a negative SCF dissociation energy (Table III), the TlCH angle is close to 90°, which is the ideal angle of a nearly noninteracting Tl^+–CH_3 system, and the force constant for C–H stretching is almost equal to that of planar CH_3. This may be explained from the relativistic contraction of the 6s orbital, which lowers the orbital energy and makes it more inert to other bond partners (inert pair effect).[26] A Mulliken population analysis supports this assumption: the Tl orbital population is 1.79 (NR) and 1.99 (R) for the s orbital and 0.28 (NR) and 0.11 (R) for the p orbital. The p population is small, which justifies the neglect of spin–orbit coupling. Electron correlation leads to a stabilization as shown by SDCI/SEPP calculations: r_e(TlC) = 2.362 Å, r_e(CH) = 1.098 Å, α(TlCH) = 99.0°, D_e(Tl–Me) = 62 kJ/mol. Here, we used SDCI data from calculations on CH_3: planar with r_e(CH) = 1.075 Å, k_e(CH) = 5.99 mdyn/Å, total energy E = −39.740000 au, which is in good agreement with experimental results (r_e(CH) = 1.079 Å[60]) or with CI calculations from Siegbahn.[61] $TlMe^+$ is very similar in stability to TlH^+ but should be stable enough to be detected by matrix isolation spectroscopy.

$TlCH_3$. Thallium(I) alkyls (with a Tl–C σ-bond) have never been isolated or detected by spectroscopic methods.[2,6,10] Aliphatic and aromatic TlR compounds may appear to take part in reactions in which TlR_3 compounds are produced from TlX and LiR.[10] Electron impact studies of TlR_3 (R = Me, Ph) gave evidence for TlR,[62] which may also be an intermediate product in the formation of $PhCO_2Tl$ from $TlPh_3$ and CO_2.[10] It is worth noting that MeGa and Me_2Ga have been reported to form stable complexes in liquid ammonia.[63] No such experiments have been done with Tl compounds. Hence, the question arises whether thallium(I) alkyls are stable with respect to dissociation into $Tl^\bullet$ and $R^\bullet$ or not.

From our ARPP calculations (D_e(Tl–Me) = 59 kJ/mol; Table III), we see that TlMe is only weakly bound so that decomposition reactions may easily be possible. Lee suggested three possibilities of decomposition of Tl(I) alkyls:[1,6] (i) polymerization to $(TlR)_x$ analogous to $(TlH)_x$, (ii) decomposition into Tl and TlR_3, and (iii) decomposition into Tl and products of the alkyl group. The first case is unlikely because of the weakness of Tl–Tl bonds discussed above and the small ability for alkyl groups to bridge thallium atoms.[1] Discussing the other two cases in more detail, we first consider results from our nonrelativistic and semiempirical calculations: r_e(TlC) = 2.288 Å, r_e(CH) = 1.089 Å, α(TlCH) = 111.6°, D_e(Tl–Me) = 139 kJ/mol, k_e(TlC) = 1.63 mdyn/Å, k_e(CH) = 5.59 mydn/Å, k_e(α(TlCH)) = 0.40 mdyn/Å with NRPP; r_e(TlC) = 2.177 Å, r_e(CH) = 1.095 Å, α(TlCH) = 111.6°, D_e(Tl–Me) = 169 kJ/mol (corrected for experimental atomic SO coupling by 59 kJ/mol[28]), k_e(TlC) = 1.75 mdyn/Å, k_e(CH) = 5.22 mdyn/Å, k_e(α(TlCH) = 0.40 mdyn/Å with SEPP. The relativistic bond contraction (including SO coupling) is 1.4% (0.05 Å) and is comparable to that of TlH. As expected, there are only slight changes in the C–H distance (<0.001 Å) due to relativistic effects: also, the TlCH bond angle is relatively insensitive ($\Delta_R(\alpha)$ ≅ 0.5°). SO effects influence the geometry only slightly, as indicated by our results with QRPP (r_e(TlC) = 2.257 Å). The dipole moment is calculated to be small on the SDCI level (μ_e = 0.08 D); therefore, relativistic effects are not so important (μ_e^{NR} = 0.32 D, μ_e^R = 0.27 D). Relativistic effects are more important for dissociation energies: the Tl–C bond stability is lowered by 80 to 59 kJ/mol, which is more than 64% of the nonrelativistic energy(!). Compared to this, the molecular SO correction is very small (Δ_M = 2.5 kJ/mol) and therefore negligible, as we would expect for a σ-bond. Comparing the Tl–C dissociation energy and force constant calculated with ARPP with those from $TlMe_3$ we see that TlMe is less stable than $TlMe_3$. This leads to the conclusion that TlMe would react further to form $TlMe_3$ through the following reaction steps (Table III; eq 5 and 6). The total

$$2TlMe \rightarrow TlMe_2 + Tl \qquad +9\ \text{kJ/mol} \qquad (5)$$

$$TlMe_2 + TlMe \rightarrow TlMe_3 + Tl \qquad -122\ \text{kJ/mol} \qquad (6)$$

reaction [(5) + (6)], $3TlMe \rightarrow TlMe_3$, + 2Tl, is then exothermic with ΔU_0^{SCF} = −113 kJ/mol. Correlation effects would probably lead to more negative values of ΔU_0 because of the increasing

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stability of the Tl–C bond from $TlMe$ to $TlMe_3$.

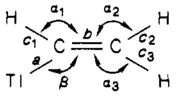
Following the suggestions of Lee,[1,6] we can also consider an alternative reaction path, corresponding to one that occurs in the case of the hydrides (eq 7). This reaction is also exothermic.

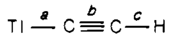
$$2TlMe \rightarrow 2Tl + C_2H_6 \qquad -160\ \text{kJ/mol} \tag{7}$$

However, the activation energy for step 7 would be larger compared to steps 5 and 6 because of steric hindrances and molecular rearrangements of the CH_3 groups. Here, we used results from our SCF calculations on C_2H_6 (experimental values are in parentheses[64]: $r_e(CC) = 1.535$ Å (1.534 Å), $r_e(CH) = 1.086$ Å (1.093 Å), $\alpha(CCH) = 110.0°$ (109.8°), $D_e(H_3C–CH_3) = 275$ kJ/mol ($E = 79.251\,492$ au), $k_e(CC) = 4.51$ mdyn/Å, $k_e(CH) = 5.50$ mdyn/Å, $k_e(\alpha(CCH)) = 0.60$ mdyn/Å. As a consequence of our calculations, we concur with Lee's explanation for the instability of Tl(I) alkyls. However, TlMe could probably be prepared and studied under suitable conditions (e.g., by matrix isolation spectroscopy). We think that one promising way of preparing such compounds would be from mixed hydride–organothallium compounds $RTlH_2$ (e.g., prepared from $RTlX_2$ and MH where X = Hal, ..., M = Li, ...), which would probably react similarly to TlH_3 with loss of H_2 to form RTl.

TlC_2H_3 and TlC_2H. TlC_2H_3 as well as TlC_2H are of interest in the study of Tl–C σ-bond stabilities on differently "hybridized" C atoms. Only compounds of the form R′RTlX, $R'R_2Tl$, or $R_2'RTl$ with R′ = C_2H_3 and C_2H have been isolated. Most reported experimental data for such compounds are vibrational studies and NMR measurements,[2,3] but results on the energetics of Tl–C bond stabilities have not yet been published.

To compare with $TlCH_3$, we have done relativistic as well as nonrelativistic calculations using ARPP and NRPP on TlC_2H_3 and TlC_2H:





The calculated ARPP (NRPP) structural parameters are the following (bond distances in Å, angles in deg, force constants in mdyn/Å): TlC_2H_3, $a = 2.224$ (2.278), $b = 1.337$ (1.339), $c_1 = 1.085$ (1.085), $c_2 = 1.083$ (1.082), $c_3 = 1.084$ (1.084), $\beta = 116.1$ (118.6), $\alpha_1 = 115.7$ (114.8), $\alpha_2 = 123.6$ (123.4), $\alpha_3 = 122.2$ (122.4), $k_a = 1.61$ (1.69), $k_b = 10.26$ (10.23); TlC_2H, $a = 2.219$ (2.257), $b = 1.210$ (1.210), $c = 1.062$ (1.062), $k_a = 1.56$ (1.74), $k_b = 17.66$ (17.75).

We give also our results from all electron calculations on C_2H_3 and C_2H ($C_{\infty v}$): C_2H_3, $b = 1.334$, $c_1 = 1.074$, $c_2 = 1.081$, $c_3 = 1.078$, $\alpha_1 = 134.4$, $\alpha_2 = 121.4$, $\alpha_3 = 121.4$, $k_b = 8.45$, total energy $E = -77.408\,718$ au; C_2H, $b = 1.220$, $c = 1.062$, $k_b = 12.21$, total energy $E = -76.162\,878$ au.

We can now calculate the dissociation energy TlR → Tl + R (ARPP with atomic SO correction, nonrelativistic values in parentheses): TlC_2H_3, $D_e = 94$ kJ/mol (174); TlC_2H, $D_e = 252$ kJ/mol (336). Let us first compare the three different molecules $TlCH_3$, TlC_2H_3, and TlC_2H. As in the aliphatic series the Tl–C, C–H, and C–C bond distances decrease, and the Tl–C bond stability increases from left to right: $TlCH_3 \rightarrow TlC_2H_3 \rightarrow TlC_2H$. This is due to the increasing s character in the Tl–C bond from left to right as indicated also by Maher et al.[65] and Hildenbrand et al.[66] from measured Tl–H spin–spin coupling constants. The relatively large Tl–C_2H dissociation energy is remarkable compared to the other alkyl compounds. In contrast with this, the Tl–C stretching force constant in TlC_2H is smaller than that in TlC_2H_3. This suggests a slight ionic character of the Tl–C bond in TlC_2H, which is also supported from our calculated dipole moments of the system $Tl^{\delta+}R^{\delta-}$ (NRPP values in parentheses): $\mu_e(TlCH_3) = 0.27$ D (0.32), $\mu_e(TlC_2H_3) = 0.49$ D (0.39), $\mu_e(TlC_2H) = 1.18$ D (0.25). Vibrational studies on $RC{\equiv}CTlR_2$ compounds given by Nast et al.[67] also suggest an ionic Tl–C bond. From a normal-coordinate analysis[68] we get a C≡C stretching frequency in TlC_2H of 2191 cm^{-1}. This is in reasonable agreement with the experimentally obtained wavenumbers for $Tl(C_2R)_3$ compounds, which are all about 2068–2138 cm^{-1} depending on the organic substituent R.[67] The relativistic bond length contraction is small in all cases (<0.06 Å) due to the small relativistic Tl(6p) orbital contraction.[26] Hence, changes in C–C and C–H bond length are also small (<0.002 Å) and therefore negligible. Note that the relativistic destabilization of the Tl–C bond is in all three cases about the same, viz. 80 kJ/mol (62 kJ/mol from SO coupling).

$Tl(CH_3)_2$. Ph_2Tl has been postulated as an intermediate product in the reduction of Ph_3Tl.[2] TlR_2 may also occur in the reaction where TlR_3 is formed from TlR (eq 5), as a decomposition product at the electron impact of $TlMe_3$,[69] in the electrochemical reduction of TlR_3[55] or in the pyrolysis of TlR_3.[70]

We have calculated $TlMe_2$ with ARPP (Table III) to have a bent (TlC_2) arrangement with an angle $\alpha(CTlC) = 121.1°$ in the staggered form of the methyl groups. The diagonal harmonic force constant of the (CTlC) bending mode, derived from eq 4, is calculated to be $k_e = 0.10$ mdyn/Å, which is comparable to that of TlH_2 ($k_e(\alpha(HTlH) = 0.14$ mdyn/Å). The calculated dipole moment is 0.25 D. From the dissociation energy of $TlMe_2$ (Table III), we see that this molecule is stable with respect to dissociation into Tl and CH_3, but from the reactions 8–10 (SO-corrected for the Tl atom), we see that $TlMe_2$ is unstable.

$$2TlMe_2 \rightarrow TlMe_3 + TlMe \qquad -132\ \text{kJ/mol} \tag{8}$$

$$3TlMe_2 \rightarrow 2TlMe_3 + Tl \qquad -251\ \text{kJ/mol} \tag{9}$$

$$TlMe_2 \rightarrow C_2H_6 + Tl \qquad -223\ \text{kJ/mol} \tag{10}$$

Such compounds may be only measurable in matrix isolation at low temperatures, e.g. by electron impact of the stable $TlMe_2^+$ or from the thermal decomposition of $TlMe_3$.[70]

$Tl(CH_3)_2^+$. The moiety R_2Tl^+ has been found to be linear in most cases, but in some complexes the CTlC angle is less than 180°, depending on the solvent and anion.[2] We have calculated the linear (CTlC) structure both with NRPP and ARPP. The orientation of the methyl groups has been chosen to be staggered. The ARPP Tl–C bond distance (2.089 Å; Table III) is in very good agreement with the experimental value of 2.097–2.118 Å obtained by crystal structure measurements on different forms of Me_2Tl^+ crown ether complexes (Hughes and Truter[71]). Raman and IR spectra of Me_2Tl^+ compounds give A_1 [$\nu_s(CTlC)$] = 483–507 cm^{-1} and A_2''[$\nu_{as}(CTlC)$] = 535–557 cm^{-1}, depending upon the solvent and anion.[72,73] We obtained by a harmonic frequency analysis[68] for the symmetric stretching mode 509 cm^{-1} and for the asymmetric mode 544 cm^{-1}, which is in very good agreement with experiment.

TlR_2^+ compounds dissociate into Tl^+ and the radical $R^\bullet$. This leads to the assumption that Tl(6s) contributions to the Tl–C σ-bond are more important that in other organothallium compounds. Hence, we expect shorter bond distances and larger relativistic bond contractions. From our NRPP calculations ($r_e(TlC) = 2.190$ Å, $r_e(CH) = 1.083$ Å, $\alpha(TlCH) = 109.7°$, $k_e(TlC) = 2.15$ mdyn/Å, $k_e(CH) = 6.00$ mdyn/Å, $k_e(\alpha(TlCH))$

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= 0.46 mdyn/Å, D_e = 98 kJ/mol per Tl–C bond), we obtain a relativistic bond contraction of 0.101 Å (4.6%), which is small and comparable to that of TlH_2^+ but slightly larger than in all other calculated cases (e.g., 2.4% in TlMe). Also the Tl–C bond distance is the shortest we have found in our calculations. From our results on TlMe we assume that molecular SCF spin–orbit contributions are small. Therefore, the total relativistic reduction in dissociation energy is given by the NRPP/ARPP results, yielding a value of 21 kJ/mol. From our results on $TlMe_2$ we can also give the adiabatic electron affinity of $TlMe_2^+$, which is calculated to be 3.98 eV on the ARPP level.

There is another interesting problem concerning the Tl–C stretching force constant of $TlMe_2^+$. Consider the variation of the k_e(MC) force constant in the series $M^{IIB}Me_2$, $M^{IIIA}Me_2^+$, and $M^{IVA}Me_2^{2+}$, where M represents the metals of the groups IIB, IIIA, and IVA in the periodic table. Usually the k_e(MC) force constants increase from the left to the right, e.g. $CdMe_2 < InMe_2^+ < SnMe_2^{2+}$. This is not the case for the series Hg, Tl, and Pb, where the force constants decrease from the left to the right.[8,74] It has been proposed that a larger core 5d contribution could be the reason.[74] This may be only a partial explanation of the unusually large force constant in the Hg compound (ref 43 and Figure 2). Now, relativistic effects increase the Tl–C force constant from 2.15 to 2.35 mdyn/Å (see above and Table III). Therefore, we conclude that if the decrease in k_e(MC) from Hg to Pb is a relativistic effect, the relativistic increase of the Hg–C stretching force constant in $HgMe_2$ should be very high. There are no data available for relativistic effects on $HgMe_2$, but for the hydrides relativistic effects on force constants have been studied.[38] From the M–C stretching force constants of ref 38 we see indeed a very large relativistic effect for HgH_2 (in mdyn/Å): HgH_2, 2.05 (NR), 2.50 (R); TlH_2^+, 2.22 (NR), 2.55 (R). Therefore, the unusual effects in the force constants of the heavy-element compounds $HgMe_2$, $TlMe_2^+$, and $PbMe_2^{2+}$ may be explained by relativistic effects. It would be interesting to perform nonrelativistic and relativistic calculations for $HgMe_2$.

$Tl(CH_3)_2Br$. Our pseudopotential for Br has been well tested on several other molecules;[30,38] hence, we have chosen $TlMe_2Br$ as a representative of the R_2TlX compounds. The calculated ARPP results are the following: values in Table III and r_e(TlBr) = 2.532 Å, $\alpha(TlC_2)$ = 140.0°, k_e(TlBr) = 1.58 mdyn/Å, $k_e(\alpha\text{-}(CTlBr))$ = 0.15 mdyn/Å, μ_e = 4.43 D. The results for the geometry are quite similar to those of TlH_2Br. The gas-phase structure of $TlMe_2Br$ is unknown, but we can compare with crystal structure measurements on $TlMe_2NCO$ from Chow and Britten.[75] They obtained a Tl–C distance of 21.0 Å, which is in good agreement with our calculated value (2.12 Å). The dissociation energy given in Table III was determined from $TlMe_2Br \rightarrow TlBr + 2Me$ and is comparable to that of $TlMe_2^+$. The Tl–Br bond stability can be calculated from the dissociation $TlMe_2Br \rightarrow TlMe_2 + Br$. In the case of ARPP, corrected by SO coupling of Br (Δ_A = 14 kJ/mol[30]), we get 308 kJ/mol, 46 kJ/mol more than in TlBr. Also, the Tl–Br stretching force constant is larger in $TlMe_2Br$, so the Tl–Br bond is more stable. We can also consider the ionic dissociation, $TlMe_2Br \rightarrow TlMe_2^+ + Br^-$. In this case we get D_e = 575 kJ/mol, which is rather high, and may explain why this is not preferred in solution. The frequency of the Tl–Br stretching mode in R_2TlBr compounds is beyond most spectrometers (the fundamental vibrational frequency of the TlBr molecule is 192 cm^{-1})[44] and no data are available from the literature. Only Tl–C stretching frequencies are available from IR measurements on $(Me_3SiCH_2)_2TlBr$, reported by Kurosawa and co-workers[76] (489 cm^{-1} (ν_s), 520 cm^{-1} (ν_{as})). We obtained from the harmonic relativistic force field 523 cm^{-1} (ν_s) and 551 cm^{-1} (ν_{as}) for the Tl–C stretch and 216 cm^{-1} for the Tl–Br stretch.

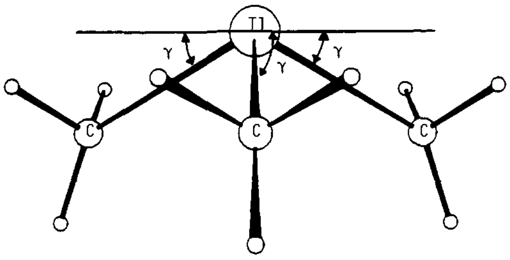

Figure 3.

$Tl(CH_3)_3$. Many organothallium(III) compounds have been prepared,[1,2] but up to now it is not clear whether such compounds prefer a planar (TlC_3) structure or not. A recent gas-phase vibrational study by Leites et al.[77] suggests a nonplanar arrangement for $TlMe_3$ and $TlEt_3$. Crystal structure determination by X-ray diffraction on $TlMe_3$ gives evidence for small distortions due to the interactions with other $TlMe_3$ molecules.[78] Earlier (unpublished) IR and Raman studies by Johnson and Downs[79] are consistent with a monomeric planar skeleton in the vapor phase and in benzene solution. All other trimethyl compounds of the third main group have, in the meantime, been reported to be planar within the accuracy of the experimental method.[80] To clarify the situation for $TlMe_3$, we performed SCF/ARPP calculations for the planar (C_{3v}) as well as for the nonplanar (C_{3v}) (TlC_3) structure (Figure 3).

We first discuss our results for the planar (TlC_3) arrangement (γ = 0°). The ARPP equilibrium geometry (see Table III) is in reasonable agreement with that of Fjeldberg et al.,[81] obtained from gas-phase electron diffraction at temperatures of 30–45 °C (r_e(TlC) = 2.206 (3) Å, r_e(CH) = 1.108 (7) Å, α(TlCH) = 107.5 (9)°. Note that, because of vibrational distortions, the bond distances obtained by Fjeldberg et al. are average rather than equilibrium bond lengths and are therefore likely to be slightly higher than r_e. Price et al. obtained a dissociation energy of 152 kJ/mol from the pyrolysis of $TlMe_3$, assuming the dissociation[70] in eq 11. We have calculated an energy change for this step of

$$TlMe_3 \rightarrow TlMe_2 + Me \qquad (11)$$

181 kJ/mol. CI would increase this value. The next two dissociations $TlMe_2 \rightarrow TlMe + Me$ and $TlMe \rightarrow Tl + Me$ are calculated to have D_e = 50 and 59 kJ/mol, respectively. The estimated value for the overall dissociation (per Me group) is then 98 kJ/mol. Furthermore, it is known from electron impact studies on Me_3M compounds (M = B, Al, Ga, In, Tl)[69] that the M–C bond stability decreases from B to Tl. The measured difference in dissociation energy between $InMe_3$ and $TlMe_3$ by Price et al. is 80 kJ/mol.[70] Fowell and Mortimer obtained for $GaMe_3$ a Ga–C bond stability of 237 ± 2 kJ/mol.[82] Hence, we conclude that the measured value of Price et al. is not due to the dissociation (eq 11) but is a reasonable value for the mean Tl–C bond stability. Further measurements are necessary to obtain accurate Tl–C binding energies. From our previously reported results on HBr[30] (D_e = 264 kJ/mol using QRPP) and from the SCF dissociation energy of CH_4[83] (356 kJ/mol at the HF limit), we obtain, from our calculated dissociation energies for $TlMe_3$ and $TlMe_2Br$, that the reaction

$$TlMe_3 + HBr \rightarrow TlMe_2Br + CH_4 \qquad (12)$$

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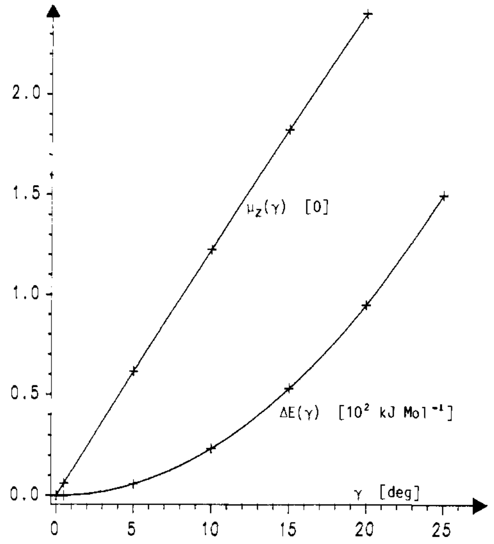

Figure 4. SCF/ARPP potential curve $\Delta E(\gamma)$ and dipole moment behavior $\mu_z(\gamma)$ for the out of plane bending of $TlMe_3$: γ, out of plane angle (see text).

is exothermic with $\Delta U_0^{SCF} = -379$ kJ/mol. This was also found by Lee and Sheldrick, where $TlMe_3$ is reported to react exothermically only with compounds containing an acidic hydrogen, e.g. such as $CHBr_3$ or CH_2Br_2.[84] The reason is the high stability of the C–H as well as the Tl–Br bond relative to the low stability of the Tl–C bond.

The question of whether the CH_3 rotation is free at room temperature or not has sometimes been discussed.[8] Therefore, we have calculated two different methyl group orientations in $TlMe_3$, which we assume to have the lowest and the highest total energy, when all other geometry parameters (bond distances and bond angles) are kept fixed. The structure of lowest energy is assumed to have C_{3h} symmetry. In this case the (TlC_3) skeleton and three H atoms (clockwise or anticlockwise) are in one plane. This arrangement has also the minimum total nuclear–nuclear repulsion (V_{NN}) and the maximum value of the minimum H–H distance between two different Me groups. The difference in electronic energy between both symmetries is $\Delta E(C_{3h}/C_{3v}) = 0.10$ kJ/mol, which is very small and allows free rotation at room temperature.

From the normal-coordinate analysis of $TlMe_3$,[68] we obtain for the Tl–C stretching modes 508 cm^{-1} (ν_s) and 535 cm^{-1} (ν_{as}), respectively. Johnson and Downs obtained from vapor-phase IR and Raman measurements 450 and 465 cm^{-1}.[79] This is in reasonable agreement with our SCF values.

To study the nonplanar (TlC_3) structure, we have varied the angle (see above) in our SCF calculations from 0 to 25° in steps of 5°. We performed also one calculation at $\gamma = 0.5°$ to see if the planar structure describes a minimum in total electronic energy or not. Our results are shown in Figure 4, where the difference in total energy to that of the planar structure and the dipole moment along the C_3 axis are plotted against the angle γ. As a result, the planar (TlC_3) arrangement is observed to have the lowest energy. The energy behavior is almost harmonic (eq 13).

$$\Delta E(\gamma) = 0.236\gamma^2\ (+0.39 \times 10^{-5}\gamma^4)\ \text{(kJ/mol)} \qquad (13)$$

Also the dipole moment almost follows the classical electrostatic behavior for a point charge model (eq 14).

$$\mu_z(\gamma) = 7.06 \sin\gamma\ \text{(D)} \qquad (14)$$

$Tl(CH_3)_4^-$. This compound is reported to be a light-sensitive salt, which is more reactive than $LiTlH_4$.[58,85] No other alkyl compounds of the form $M[TlR_4]$ with $M \neq$ Li and $R \neq$ Me have yet been prepared. Only a few aryl compounds are known.[2] Data for physical properties are not available from the literature (except for NMR measurements by Weibel and Oliver[86]).

As mentioned above, we used in this case a contracted [2s] H basis set for the SCF/ARPP calculations. Hence, the C–H bond distance in $TlMe_4^-$ is probably a bit too large compared with those of the other methyl compounds (Table III). With this smaller basis set the following results for CH_3 have been obtained: r_e(CH) = 1.077 Å, k_e(CH) = 6.26 mdyn/Å, total energy $E = -39.558637$ au. This compares favorably with our results on CH_3 using the larger Huzinaga basis set.[36] The Tl–C bond length is the largest we found in our series, due to the fact that a tetrahedron has a larger p contribution ("sp^3 hybrid"). The Tl–C bond is also the most stable we found. (There is nearly no SO destabilization!) Hence, we would expect that larger cations (Cs^+, Tl^+) would stabilize $MTlR_4$ compounds using the same argument as for the hydrides. If we compare the bond stability of TlH_4^- with $TlMe_4^-$ (Tables II and III), we find that $TlMe_4^-$ is less stable than TlH_4^- with a difference of 58 kJ/mol per Tl–R bond (R = H, Me). Hence, we can concur with the reactivity behavior of both compounds ($TlMe_4^-$ is more reactive than TlH_4^-), as reported by Weibel and Oliver.[85]

IV. Conclusion

The main conclusions of our calculations for the ground states of the organothallium compounds are the following:

(a) Relativistic bond length contractions are small (<6% for the thallium hydrides and <5% for the methylthallium compounds) and dependent on the Tl 6s participation in the Tl–C σ-bond. In both cases we get the sequence in bond length $TlR > TlR_4^- > TlR_2 > TlR_3 > TlR_2^+$ (R = H, Me). In the case of TlH^+ and $TlMe^+$ we get a relativistic expansion (1.5 Å for TlH^+ and 0.3 Å for $TlMe^+$ at the SCF level) due to the low stability of the molecules at the relativistic level.

(b) Spin–orbit coupling effects on dissociation energies can be considered within a good approximation to be the atomic contribution only ($\Delta_M \ll \Delta_A$; Figure 1) as indicated for the hydrides and for $TlCH_3$. This is due to the fact that the ratio of the Tl $6p_{3/2}$ to Tl $6p_{1/2}$ populations is ~2, which implies the formation of a pure σ-bond being destabilized by about $^2/_3$ of the atomic spin–orbit splitting. As a consequence, nonrelativistic coupling schemes hold for SCF ground states at the equilibrium geometry.

(c) The chemical similarity of the methylthallium and hydride thallium compounds has been shown. For the latter the loss of H_2 leads to a shift from left to right in the equilibrium: $TlH_4^- \rightarrow TlH_3 \rightarrow TlH \rightarrow Tl$. This is not the case for the methyl compounds, which are kinetically (but not thermodynamically) stabilized due to larger activation energies for the formation of C_2H_6 rather than H_2. E.g., the instability of TlH_3 in contrast to $TlMe_3$ can be explained in this way.

(d) We can consider two different ways of a dissociation of a Tl–X bond (X are inorganic or organic substituents): a heterolytic dissociation into Tl^+ and X^- (mainly inorganic chemistry) or a homolytic dissociation into $Tl^\bullet$ and $X^\bullet$ (mainly organothallium chemistry). The heterolytic dissociation is not affected by spin–orbit destabilization, whereas, in the case of a homolytic dissociation, spin–orbit coupling destabilizes a Tl–X bond in Tl(I) compounds more than in Tl(III) compounds. There are two reasons; first, the atomic spin–orbit coupling Δ_A contributes only $\Delta_A/3$ per Tl–X bond in TlX_3 if we consider an overall dissociation, and, second, there is nearly no influence of spin–orbit coupling if we consider the dissociation $TlX_3 \rightarrow TlX + X_2$ because of the usually small magnitude of Δ_M. In the case of a Tl–Me bond, spin–orbit coupling reduces the Tl–C bond stability in such a way that it becomes more stable in $TlMe_3$ than in TlMe. This may also explain why organothallium chemistry is preferentially the chemistry of Tl(III). On the other hand, TlX_3 compounds with ionic Tl–X bonds require greater transfer of charge from the Tl(6s) orbital compared with the case of diatomic TlX. This is less true for a covalent bond. Hence, the inert pair effect leads to a shift in stability from Tl(III) to Tl(I) with increasing electronegativity of the ligand X. This explains why Tl^+Cp^- is stable. We therefore

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expect TlR compounds with organic groups R such as CF_3 or $CH(CO_2Me)_2$, which are able to accommodate negative charge to be more stable than those with, e.g., R= CH_3 or Ph.

(e) Tl–Tl bonds are very weak or do not exist because of spin–orbit coupling and inert pair effects. The only reported species with a stable Tl–Tl bond, $Tl_2Me_6^{2-}$, is doubtful in our opinion. The compounds M_2Me_6 (M = Sn, Pb), isoelectronic with $Tl_2Me_6^{2-}$, are known to form stable metal–metal bonds, but they are measured to be less stable than the simple metal dimers M_2.[38,44,56,87] The reason could be an electrostatic repulsion in the $R_3M^{\delta+}{-}^{\delta+}MR_3$ compounds in contrast to M_2. The same argument holds for $Tl_2Me_6^{2-}$, so we expect the Tl–Tl bond to be less stable in $Tl_2Me_6^{2-}$ than in Tl_2; for the latter, the bond stability is assumed to be about 20–50 kJ/mol.

(f) The pseudopotential approximation ([Pt] core for Tl and [$Ar3d^{10}$] core for Br) is accurate enough to provide results that are in good agreement with experiment. The [Pt]-core definition is sufficient for calculations on organothallium compounds. The Tl(5d) participation to Tl–C σ-bonds is found to be small, as indicated by our SCF–SW–Xα results.

There have been few developments in organothallium chemistry during the last decade. Our results suggest that monoalkylthallium compounds could be generated and studied spectroscopically under certain conditions. Vibrational analyses of these compounds using the calculated SCF force field partially listed here will be published soon.

Acknowledgment. P.S. is very grateful to the Alexander von Humboldt-Stiftung for the award of a Feodor–Lynen Fellowship and financial support. Thanks are due to Mrs. Fischer (RUS Computer Center, Universität Stuttgart) for her excellent service in making possible the time-consuming jobs on the CRAY1M. We are also grateful to Dr. U. Wedig (Max-Planck Institut Stuttgart) for changing the program MELD, to Prof. H. Preuss, M. Dolg, G. Igel-Mann, H. Hayd, and K. Vogel (Universität Stuttgart) for their interest and assistance in performing part of these calculations at the University of Stuttgart, to Dr. A. J. Downs (University Oxford) for allowing us to quote results of unpublished work, and to Prof. G. M. Sheldrick (Universität Göttingen) for some helpful suggestions. We also express our gratitude to Prof. M. J. Taylor (University Auckland) and Prof. W. H. E. Schwarz (Universität Siegen) for valuable discussions and for critically reading this paper.

Registry No. TlH, 13763-69-4; TlH_2, 117439-42-6; TlH_3, 82391-14-8; TlH_4^-, 58220-54-5; TlH_2^+, 117470-02-7; $TlCH_3^+$, 117470-03-8; $TlCH_3$, 82391-13-7; TlC_2H_3, 117439-43-7; TlC_2H, 117439-44-8; $Tl(CH_3)_2$, 117439-45-9; $Tl(CH_3)_2^+$, 16785-98-1; $Tl(CH_3)_2Br$, 21648-59-9; $Tl(CH_3)_3$, 3003-15-4; $Tl(CH_3)_4^-$, 117470-04-9.

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Hydrogen Bonding and Proton Transfers Involving the Carboxylate Group

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Received April 18, 1988

Abstract: The complex formed between $HCOO^-$ and HOH is examined by ab initio methods using a 4-31+G* basis set. A number of minima are located in the potential energy surface, the most stable of which is of C_{2v} geometry wherein both protons of HOH participate in H bonds. The barrier impeding proton transfer between OH^- and $HCOO^-$ rises with increasing intermolecular separation for each of the arrangements studied. As the OH^- anion moves toward the C–O axis of $HCOO^-$, the equilibrium position of the bridging proton is shifted toward the former group, paralleling earlier observations for the pair of neutral subunits HCOOH and HOH. On the other hand, $HCOO^-$ and HCOOH behave in different fashion with respect to motions of the hydroxyl group out of the carboxyl plane. These patterns are explained simply on the basis of differing ion–dipole interactions, as are small differences in the optimal geometries and proton-transfer behavior of the various arrangements of the two subunits.

I. Introduction

Since proton transfers comprise perhaps the simplest and most common reaction in chemistry, research into this process has led to a truly enormous body of literature over the years.[1] Most of the early work was limited to study of the reaction in solution, making it difficult to extract properties that are intrinsic to the transfer itself from complications arising from solvent effects. Modern developments have allowed the process to be studied in the gas phase, leading to important advances in our understanding of the phenomenon.[2] Because theoretical calculations are most easily carried out for a given system in isolation, ab initio methods have also made some contributions to this field.[3] The calculations have been especially helpful in providing information that is not readily obtained from experiment, e.g. geometries of short-lived species.

In an effort to achieve a comprehensive understanding of the principles underlying proton-transfer reactions, ab initio methods have been applied systematically in this laboratory to a variety of different systems.[4-7] Calculations of very small and simple

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