

Scaled Hartree-Fock Force Field Calculations for Organothallium Compounds: Normal-Mode Analysis for TlCH_3 , $\text{Tl}(\text{CH}_3)_2^+$, $\text{Tl}(\text{CH}_3)_3$, $\text{Tl}(\text{CH}_3)_2\text{Br}$, and $\text{Tl}(\text{CH}_3)_4^-$

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In a recent paper we presented Hartree-Fock (HF) calculations for aliphatic organothallium compounds. The diagonal HF force constants obtained from a Fletcher-Powell geometry optimization are now used for a normal-mode analysis of TlCH_3 , $\text{Tl}(\text{CH}_3)_2^+$, $\text{Tl}(\text{CH}_3)_3$, $\text{Tl}(\text{CH}_3)_2\text{Br}$, and $\text{Tl}(\text{CH}_3)_4^-$. In order to calculate frequencies comparable to experimental values, the HF force field has been scaled by using scaling factors obtained from experimental infrared and Raman measurements on $\text{Tl}(\text{CH}_3)_2^+$ and TlBr . The vibrational spectra of $\text{Tl}(\text{CH}_3)_2^+$ were remeasured (infrared and Raman) in order to obtain an accurate force field. Predictions are made for the vibrational spectrum of the as yet undetected TlCH_3 molecule. Experimental infrared and Raman results for $\text{Tl}(\text{CH}_3)_3$ compare reasonably well with our calculated frequencies (experimental $\nu_{\text{sym}}(\text{Tl}-\text{C}) = 450 \text{ cm}^{-1}$, $\nu_{\text{asym}}(\text{Tl}-\text{C}) = 465 \text{ cm}^{-1}$, $\nu_{\text{sym}}(\text{C}-\text{H}) = 2917 \text{ cm}^{-1}$, $\nu_{\text{asym}}(\text{C}-\text{H}) = 3020 \text{ cm}^{-1}$; scaled HF $\nu_{\text{sym}}(\text{Tl}-\text{C}) = 488 \text{ cm}^{-1}$, $\nu_{\text{asym}}(\text{Tl}-\text{C}) = 514 \text{ cm}^{-1}$, $\nu_{\text{sym}}(\text{C}-\text{H}) = 2892 \text{ cm}^{-1}$, $\nu_{\text{asym}}(\text{C}-\text{H}) = 2999 \text{ cm}^{-1}$). Relativistic and correlation effects are analyzed for the vibrational frequencies of $\text{Tl}(\text{CH}_3)_2^+$.

1. Introduction

Currently, accurate theoretical vibrational frequencies can only be obtained for small molecules containing light atoms. This requires very time consuming ab initio quantum-chemical methods that must include electron correlation by CI (configuration interaction) or other techniques.¹ For larger molecules containing heavy atoms, there are a number of difficulties that must be overcome before such calculations can be carried out. (i) The accurate calculation of the correlation energy is necessary to achieve reasonable force fields but is very costly in computer time and disk space. (ii) The analytical calculation of the second-derivative matrix of the total energy,³ required to obtain a complete force field, is also very time consuming and is not yet practical. (iii) Often the harmonic force field approximation is not sufficient to obtain accurate frequencies. (iv) For very large molecules or very heavy atoms (more than about 100 electrons) the SCF procedure itself begins to be time consuming, and a direct SCF procedure has to be used to avoid large amounts of two-electron integral storage. (v) Relativistic effects must be included in calculations on heavy elements.² For example, the molecule $\text{Tl}(\text{CH}_3)_2\text{Br}$ contains 10 atoms and 134 electrons. Using a sufficiently large basis set with diffuse functions for correlation and a gradient procedure for geometry optimization, including correlation by a CI procedure with only double substitutions and a suitably limited active space, would not be practical with the computer and program codes currently available. There is therefore a need for appropriate approximations to compute vibrational frequencies of good quality for larger molecules.

The number of electrons involved can be reduced by using the pseudopotential method, which can also include relativistic effects if the pseudopotential parameters are adjusted to Dirac-Fock (DF) atomic data.⁴ Such methods yield results that are nearly as accurate as all-electron calculations and have in the past been used for a large number of molecules.⁵ For example, with a [Pt] core for Tl^6 and an [Ar 3d¹⁰] core for Br,⁷ $\text{Tl}(\text{CH}_3)_2\text{Br}$ has been

reduced to a 28-valence-electron system.⁸ However, even when sufficiently large basis sets are used for all atoms, including pseudopotentials, a CI procedure is still too time consuming.

It is well-known that the Hartree-Fock (HF) procedure usually yields good results for the molecular structures of relatively stable molecules. This is not the case for force fields, since HF is not able to describe the dissociation behavior satisfactorily. Hence, HF often systematically overestimates the force field for organic molecules.⁹ Meyer, Pulay, Blom, and Altona suggested a scaling of the HF force field set.¹⁰ In this procedure the set of diagonal force constants k_{ii} are scaled by coefficients c_i and off-diagonal terms k_{ij} by $(c_i c_j)^{1/2}$ to give the best agreement between calculated and observed vibrational frequencies for a set of reference molecules. These scaling factors are used to adjust the force fields calculated for similar molecules for which experimental data are not available. The basis sets must remain unchanged in this procedure. Relativistic, correlation, and anharmonicity effects will be accounted for in the scaling procedure. Good results have been obtained for organic molecules with this method.¹⁰

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Table I. Vibrational Frequencies for $\text{Tl}(\text{CH}_3)_2^+$ (cm^{-1})^a

irrep	active	exptl	f_1	f_2	RHF	NRHF	main coord
A1'	Ra	2920	2921	2889	3194	3189	C-H str
		1176	1179	1271	1422	1409	H-C-H bend
		486	486	478	507	486	Tl-C str
A2''	IR	2923	2922	2889	3194	3189	C-H str
		1180	1181	1275	1422	1410	H-C-H bend
		547	545	534	543	520	Tl-C str
E'	IR, Ra	3020	3010	3009	3326	3317	C-H str
		1460	1463	1442	1561	1551	H-C-H bend
		803	803	753	880	837	Tl-C-H bend
		160	159	159	140	125	C-Tl-C bend

^aThe point group used is D_{3h} . Experimental vibrational frequencies are from this work and ref 12. f_1 values are best-fit frequencies obtained from force constants (including off-diagonal force constants); f_2 values are calculated as for f_1 but exclude off-diagonal force constants (SHF).

In a previous paper⁸ we reported relativistic HF calculations for a series of aliphatic organothallium compounds. In this paper we present a normal-mode vibrational analysis for this series of molecules (TlCH_3 , $\text{Tl}(\text{CH}_3)_2^+$, $\text{Tl}(\text{CH}_3)_3$, $\text{Tl}(\text{CH}_3)_2\text{Br}$, and $\text{Tl}(\text{CH}_3)_4^-$). In order to compute frequencies comparable with experimentally determined values, scaling factors obtained from infrared (IR) and Raman (Ra) measurements of the reference molecules TlBr ¹¹ and $\text{Tl}(\text{CH}_3)_2$ ⁺¹² have been used. The experimental diagonal force fields were determined from the measured frequencies. The scaling factors f_s were calculated by using the equation $f_s = k^{\text{exptl}}/k^{\text{HF}}$. HF vibrational frequency analyses for large organometallic compounds containing heavy metals have not been reported extensively in the past, and it is of considerable interest to investigate the effects of relativity and correlation for such compounds. The method used is described briefly in the next section. The results are presented and discussed in section 3. A summary is given in section 4.

2. Experimental and Computational Details

The nonrelativistic and relativistic pseudopotentials and basis sets used for the SCF calculations are described in detail in previously published papers.⁶⁻⁸ The geometries have been optimized by using a Fletcher-Powell procedure,¹³ from which numerical force constants have been obtained.¹⁴ In order to obtain the fundamental frequencies, we developed a symmetry-adapted normal-coordinate analysis program¹⁵ that determines the vibrational frequencies for each irreducible representation of the molecular point group by using Wilson's GF-matrix method.¹⁶

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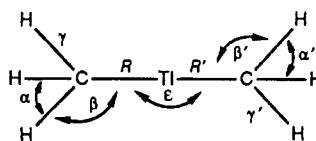
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Table II. Nonrelativistic (k^{NR}), Relativistic (k^{R}), and Experimental (k^{exptl}) Diagonal Force Constants (mdyn/Å) and Scaling Factors f_s^{R} and f_s^{C} for the Molecules TlBr and $\text{Tl}(\text{CH}_3)_2^+$

	Q	k^{NR}	k^{R}	k^{exptl}	f_s^{R}	f_s^{C}
Stretch						
Tl-Br	R''	1.310	1.207	1.261	0.921	1.044
Tl-C	R	2.155	2.354	2.204	1.092	0.936
C-H	r	5.860	5.888	4.817	1.005	0.818
Bend						
C-Tl-C	ϵ	0.067	0.084	0.109	1.264	1.290
(Tl,H)-C-H	α, β	0.461	0.503		1.091	
Tl-C-H	β	0.204	0.234	0.170	1.147	0.726
H-C-H	α	0.520	0.520	0.446		0.858

^aThe geometry and internal coordinates of $\text{Tl}(\text{CH}_3)_2^+$ and the combined bending mode (Tl,H)-C-H are described in the text. The experimental force constant for TlBr is from ref 11, and that for $\text{Tl}(\text{CH}_3)_2^+$ is from this work (see text).

Figure 1. Internal coordinates of $\text{Tl}(\text{CH}_3)_2^+$.

The experimental vibrational spectrum of $\text{Tl}(\text{CH}_3)_2^+$ was reported incompletely;¹² hence, we remeasured this molecule using solid $\text{Tl}(\text{CH}_3)_2\text{Br}$, prepared by literature methods.¹⁷ $\text{Tl}(\text{CH}_3)_2\text{Br}$ has been shown to consist of discrete $\text{Tl}(\text{CH}_3)_2^+$ and Br^- ions in the solid state.¹² The infrared spectrum of solid $\text{Tl}(\text{CH}_3)_2^+\text{Br}^-$ was recorded at ca. 298 K as a KBr disk (4000–400 cm^{-1}) or as a petroleum jelly mull between Polythene plates (400–50 cm^{-1}) on a Digilab FTS-60 Fourier transform infrared spectrometer. The Raman spectrum was recorded at ca. 298 K with the sample enclosed in a glass capillary by using a Jasco R-300 Raman spectrometer with a Coherent CR-4 argon ion laser (514.5-nm line). The experimental frequencies are collected in Table I.

3. Results and Discussion

The calculated nonrelativistic and relativistic diagonal harmonic HF force constants together with the experimental values for the molecules TlBr and $\text{Tl}(\text{CH}_3)_2^+$ are given in Table II. From these we obtain the relativistic and correlation scaling factors $f_s^{\text{R}} = k^{\text{R}}/k^{\text{NR}}$ and $f_s^{\text{C}} = k^{\text{exptl}}/k^{\text{R}}$, also listed in Table II. k^{NR} is the force constant from a nonrelativistic HF calculation (NRHF), k^{R} is obtained from a relativistic HF calculation (RHF) by using spin-orbit averaged relativistic force constants, and k^{exptl} is obtained by a fit procedure with measured vibrational frequencies (SHF).^{11,12} In order to accurately fit the initial force constants to the experimental frequencies, it was necessary to include off-diagonal elements in the \mathbf{F} matrix.

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Table III. Calculated Relativistic (R) and Scaled (S) Force Constants (mdyn/Å) for the Molecules TlCH₃ (I), Tl(CH₃)₃ (II), Tl(CH₃)₂Br (III) and Tl(CH₃)₄⁻ (IV)

	I		II		III		IV	
	R	S	R	S	R	S	R	S
	Stretch							
Tl-Br					1.577	1.646		
Tl-C	1.422	1.331	2.346	2.196	2.441	2.285	1.938	1.814
C-H	5.754	4.707	5.868	4.800	5.882	4.811	5.935	4.855
	Bend							
Tl-C-H	0.144	0.105	0.186	0.135	0.216	0.157	0.157	0.114

The values used are as follows (in mdyn/Å): -0.100 (RR'), -0.016 (rr), -0.075 (Rr), 0.006 ($r\alpha$), 0.129 ($r\beta$), 0.089 ($r\beta'$), 0.08 ($R\beta$), -0.03 ($\beta\beta$), -0.02 ($\alpha\beta$). The definition of the internal coordinates is given in Figure 1. These are the same as the values previously published for Hg(CH₃)₂¹⁸ with the exception of that of RR' , which has been changed slightly to improve the agreement with experiment. The frequencies obtained with use of the F matrix given in Table II are in excellent agreement with experiment, with errors less than 10 cm⁻¹ in the calculated frequencies. For the frequency analyses of TlCH₃, Tl(CH₃)₃, Tl(CH₃)₂Br, and Tl(CH₃)₄⁻ we omitted the off-diagonal force constants. This is justified for two reasons. First, the errors produced by the scaling method are larger than the changes in frequencies due to off-diagonal force constants, and second, off-diagonal force constants are difficult to obtain from HF calculations as an analytical form of the second-derivative energy matrix, for the nonlocal pseudopotentials have not been available to our group.⁸

It is evident that relativistic effects should be included to obtain reasonable HF force constants for molecules that contain heavy elements such as thallium. For example, the relativistic contributions to the Tl-Br and the Tl-C stretching force constant are much larger than the corresponding correlation effects (Table I). Relativistic effects are only important for the vibrational modes of molecular moieties that include at least one heavy atom (Br or Tl). Thus, for the C-H stretching and H-C-H bending modes relativistic effects are minor and can be neglected. For the Tl-C and Tl-Br bond stretching force constants, relativistic and correlation effects are opposite in sense. In gold chemistry,¹⁹ for example, it is well-known that a relativistic bond contraction implies an increase in k ,² even if the dissociation energy decreases relativistically. This is not the case for the Tl-Br bond, where relativistic effects result in a decrease in the force constant. The reason for this is probably the small decrease (0.06 Å) in the Tl-Br bond distance²⁰ resulting from a small relativistic Tl(6p) contraction⁶ and the relatively large relativistic Tl-Br bond destabilization, e.g. $D_e(\text{NR}) - D_e(\text{R}) = 0.78$ eV.²⁰ The largest scaling factor obtained for a bond stretch is that for the C-H bond vibration. It is well-known from previous HF calculations that C-H stretching frequencies are significantly overestimated within the HF approximation.

The calculated relativistic and scaled force constants⁸ of the molecules TlCH₃, Tl(CH₃)₃, Tl(CH₃)₂Br and Tl(CH₃)₄⁻ are listed in Table III. The scaling factors of Table I were used. The H-C-H bending mode is not expected to change significantly for different thallium-containing compounds; thus, we used the H-C-H bending value obtained for Tl(CH₃)₂⁺ for all the compounds. We should also point out two other facts concerning our definition of the internal coordinates in the HF geometry

Table IV. Calculated Vibrational Frequencies for TlCH₃ (cm⁻¹)^a

irrep	SHF	RHF	main coord
A ₁	2364	3167	C-H str
	1223	1353	H-C-H bend
	397	411	Tl-C str
E	2969	3283	C-H str
	1412	1527	H-C-H bend
	604	706	Tl-C-H bend

^aThe point group used is C_{3v}. The irrep's are IR and Raman active.

optimization procedure.⁸ First, the Tl-C bond lengths have been optimized simultaneously. For example, we defined the C-Tl-C force constant by the potential energy expression $V = 0.5k(R + R')$, where R and R' are the changes in the Tl-C distances. We used $\alpha = R + R'$ with $R = R'$ as the variational parameter in the Fletcher-Powell geometry optimization.¹³ This is related to a symmetric C-Tl-C bond stretching vibration. The force constant $1/2 \partial^2 E / \partial \alpha^2$ is assumed to be approximately $\partial^2 E / \partial R^2$, which is justified given the relatively small magnitude of the off-diagonal force constant $\partial^2 E / \partial R \partial R'$ (vide supra). Second, the Tl-C-H bending vibration includes an H-C-H bending component and the total force constant obtained is a sum of both, indicated as (Tl,H)-C-H in Table I. We therefore corrected our HF values⁸ by subtracting the H-C-H bending force constant given in Table I. Harmonic frequency analyses for TlCH₃, Tl(CH₃)₃, Tl(CH₃)₂Br, and Tl(CH₃)₄⁻ were performed with use of the scaled and corrected diagonal force field. The vibrational frequencies for these molecules will be discussed below.

σ -Bonded organothallium(I) compounds have never been isolated,²¹ and possible reasons for this have been discussed.⁸ However, it was suggested that such compounds might be stable in the gas phase and could be observed by matrix isolation spectroscopic methods.⁸ The calculated frequencies for the simplest such compound, TlCH₃, are given in Table IV. The Tl-C stretching and Tl-C-H bending frequencies are quite low compared to the frequencies of other Tl compounds (Tables V-VII). Methyl rocking vibrations usually absorb between 700 and 950 cm⁻¹ and depend strongly on the nature of the M-C σ -bond (M = any metal).¹⁶ For example, the CH₃ rocking vibrations in the alkyl group 1 compounds occur below 500 cm⁻¹,^{22,23} which reflects a more ionic M-C σ -bond. The symmetric CH₃ rocking frequency in TlCH₃ of 604 cm⁻¹ suggests a weak covalent Tl-C σ -bond.

Tl(CH₃)₃ was first prepared by Gilman and Jones in 1946.²⁴ Since then, many organothallium(III) compounds have been prepared,²¹ but there has been some discussion in the past whether or not the TlC₃ moiety in Tl(CH₃)₃ has

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Table V. Experimental²³ and Calculated Vibrational Frequencies for Tl(CH₃)₃ (cm⁻¹)^a

irrep		sym ^b	active		exptl	SHF	RHF	main coord
C _{3v}	D _{3h}		D _{3h}	C _{3v}				
A1	A2''	a	IR	IR, Ra	3020	2999	3316	C-H str
	A1'	s	Ra		2917	2892	3197	C-H str
	A2''	a	IR		1395	1419	1535	H-C-H bend
	A1'	s	Ra		1141	1269	1409	H-C-H bend
	A2''	a	IR		697	675	790	Tl-C-H bend
	A1'	s	Ra		445	488	506	Tl-C str
A2			2999	3315	C-H str
			1406	1518	H-C-H bend
			2999	3316	C-H str
E	E'	a	IR, Ra	IR, Ra	3020	2999	3316	C-H str
	E''	a	Ra		2984	2999	3316	C-H str
	E'	s	IR, Ra		2930	2892	3197	C-H str
	E''	a	Ra		1429	1419	1535	H-C-H bend
	E'	a	IR, Ra		1395	1419	1535	H-C-H bend
	E'	s	IR, Ra		1150	1269	1409	H-C-H bend
	E'	s	IR, Ra		754	674	789	Tl-C-H bend
	E''	a	Ra		656	673	788	Tl-C-H bend
	E'	s	IR, Ra		462	514	533	Tl-C str

^aThe point groups used are C_{3v} and D_{3h}. ^bs = symmetric and a = asymmetric (in the local symmetry of the CH₃ group).

Table VI. Calculated Vibrational Frequencies for Tl(CH₃)₂Br (cm⁻¹)^a

irrep	active	SHF	RHF	main coord
A1	IR, Ra	3002	3318	C-H str
		2899	3205	C-H str
		1522	1530	H-C-H bend
		1384	1468	H-C-H bend
		724	844	Tl-C-H bend
		504	521	Tl-C str
		222	217	Tl-Br str
		138	138	C-Tl-Br bend
A2	Ra	3002	3318	C-H str
		1522	1530	H-C-H bend
		722	842	Tl-C-H bend
		531	549	Tl-C str
B1	IR, Ra	3002	3318	C-H str
		2899	3205	C-H str
		1522	1530	H-C-H bend
		1384	1468	H-C-H bend
		723	843	Tl-C-H bend
		531	549	Tl-C str
		163	163	C-Tl-Br bend

^aThe point group used is C_{2v}.

Table VII. Calculated Vibrational Frequencies for Tl(CH₃)₄⁻ (cm⁻¹)^a

irrep	active	SHF	RHF	main coord
A1	Ra	2908	3215	C-H str
		1295	1362	H-C-H bend
		446	461	Tl-C str
E	Ra	3017	3335	C-H str
		1527	1532	H-C-H bend
		620	726	Tl-C-H bend
F2	IR, Ra	2959	3272	C-H str
		1350	1361	H-C-H bend
		641	744	Tl-C-H bend
		471	494	Tl-C str

^aThe point group used in T_d.

a planar arrangement. A recent gas-phase study by Leites et al.²⁵ suggests a nonplanar structure, but we have shown theoretically⁸ that Tl(CH₃)₃ is expected to exhibit a planar TlC₃ structure. In addition, unpublished IR and Ra studies on trimethyl group 13 compounds carried out by Johnson and Downs²³ give strong evidence for a planar TlC₃ arrangement. Since the vibrational analysis of this compound has not been published and discussed in detail in the past, it was interesting for us to perform a frequency

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analysis using scaled HF force constants as described above. The results are given in Table V together with those of Johnson and Downs.²³ Our calculated results agree quite well with experimental results, and this demonstrates the utility of the scaling method.

Most of the stable organothallium compounds are of the type R₂TlX.²¹ Many are well-known to be salts of the type R₂Tl⁺X⁻. Tl(CH₃)₂Br has not been studied in detail,²¹ but it has been shown from X-ray measurements by Hausen and co-workers²⁶ that the solid-state structure is similar to that of Tl(CH₃)₂Cl, which contains discrete Cl⁻ and linear Tl(CH₃)₂⁺ ions. However, in the gas phase the structure must be molecular Tl(CH₃)₂Br units. The molecule has not been studied in the vapor phase, and solutions of this compound are difficult to obtain since Tl(CH₃)₂Br is very insoluble in common solvents. Reasons for this are given in ref 8. The calculated frequencies of Tl(CH₃)₂Br are listed in Table VI. The only measured Tl-Br stretching frequency in organothallium(III) compounds is that of PhTlBr₂ with a value of 206 cm⁻¹,²⁷ which compares very well with our calculated value of 222 cm⁻¹.

LiTl(CH₃)₄ can be prepared from the reaction between LiCH₃ and Tl(CH₃)₃.²⁸ This compound is reported to be a light-sensitive salt, which is more reactive than LiTiH₄.^{28,29} With the exception of NMR measurements by Weibel and Oliver,³⁰ Tl(CH₃)₄⁻ or related species have not been studied in detail by spectroscopy. Theoretical work suggested (ref 8 and references contained therein) that MTl(CH₃)₄ (M = Cs, Tl) should be more stable than the known lithium salt (M = Li). Our calculated frequencies are listed in Table VII. The irreducible representation F1, which is not Raman or infrared active within the selection rules of an ideal harmonic oscillator, is not listed in the table since the frequency analysis produces the same frequency values as shown for the representation E.

4. Summary

Vibrational spectra for several organothallium compounds have been obtained with use of scaled HF frequencies. The scaling factors have been calculated from

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experimentally determined vibrational spectra of $\text{Tl}(\text{CH}_3)_2^+$ and TlBr . The calculated frequencies for $\text{Tl}(\text{CH}_3)_3$ are in good agreement with the measurements of Johnson and Downs. The vibrational spectra for the as yet unmeasured gas-phase structures of TlCH_3 , $\text{Tl}(\text{CH}_3)_2\text{Br}$, and $\text{Tl}(\text{CH}_3)_4^-$ are predicted. Scaled HF frequencies may have deviations up to 10% compared to experiment but are certainly useful for the prediction of infrared and Raman data for organometallic compounds and the assignment of spectral bands, which would nor-

mally require the preparation of isotopically substituted molecules.

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AM1 Parameters for Aluminum

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AM1 has been parametrized for aluminum. Calculations are reported for a number of molecules containing aluminum. The results are better than those given by the MNDO or PM3 models. The technique used by Stewart to parametrize PM3 is criticized.

Introduction

Aluminum is an important element, in both chemistry and chemical technology. Organoaluminum compounds in particular have proved of major interest and value as catalysts and in organic synthesis. There is therefore a clear need for a theoretical treatment of aluminum compounds that could be used in conjunction with experiment to interpret their chemical behavior. As usual,¹ ab initio procedures are of limited value in this connection because of the computing time required by those of adequate accuracy.

This need has been met in organic chemistry by the parametric ("semiempirical") methods developed by our group, i.e., MINDO/3,² MNDO,³ and AM1,⁴ AM1 being the latest and most effective. Tests⁵ have shown AM1 to give results comparable with those from ab initio methods that require thousands of times more computing time, and the calculations can be carried out very easily, comprehensive easy-to-use computer programs being freely available (AMPAC⁶). However, while MNDO parameters for aluminum have been available⁷ for some time now and have proved useful,⁸ the errors in the MNDO heats of formation (ΔH_f°) tend to be rather large. Furthermore, MNDO suffers from well-known deficiencies that have been overcome⁴ in AM1.

We therefore decided to parametrize AM1 for aluminum. Here we report our results. In the meantime, Stewart has described⁹ a new version of AM1 that he terms PM3 and that contains parameters for aluminum. Various points concerning this are discussed below.

Procedure

The techniques used here to optimize the parameters in semiempirical treatments have been described in detail.¹⁰ However, some further comment seems appropriate in view of two recent papers by Stewart^{9,11} describing a procedure that he claims to be simpler and more effective

than the one developed by our group.

Optimization of parameters involves minimization of an error function (SSQ) consisting of a sum of the squares of the weighted errors in various properties of a selected *basis set* of molecules. In our approach, the basis set consists of a limited number of molecules and properties, chosen to provide a balanced sample of the various known types. The weighting factors and the properties and molecules in the basis set are determined by trial, the choice being based on the chemical acceptability of the results for as many additional molecules and properties as the available data will allow. A further problem is the fact that the *parameter hypersurface*, defining SSQ as a function of the parameters, has numerous minima. The minimum reached in a given optimization depends on the initial values assumed for the parameters. Since there is no way to tell whether or not a given minimum is the optimum one and since there is no systematic way to escape from one minimum to another, parametrization can involve an enormous amount of computation.

Stewart, on the other hand, claims^{9,11} that optimum results can be obtained by a single minimization if enough molecules and properties are included in the basis set. According to this view, parametrization can be made

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