5474 *J. Phys. Chem. A* **2004,** *108,* 5474−5478

Molecular Structures of Trimethylchlorogermane, $(CH_3)_3GeCl$, and Trimethylbromogermane, $(CH_3)_3GeBr$, Obtained by Gas-Phase Electron Diffraction and Theoretical Calculations

Kirsten Aarset*,† and Elizabeth M. Page‡

Faculty of Engineering, Oslo University College, Postboks 4 St. Olavs plass N-0130 Oslo, Norway, and School of Chemistry, University of Reading, Whiteknights Park, Reading, RG6 6AD, UK

Received: February 27, 2004

The structures of trimethylchlorogermane ($(CH_3)_3GeCl$) and trimethylbromogermane ($(CH_3)_3GeBr$) have been determined by gas-phase electron diffraction (GED), augmented by the results from ab initio calculations employing second-order Møller−Plesset (MP2) level of theory and the 6-311+G(d) basis set. All the electrons were included in the correlation calculation. The results from the ab initio calculations indicated that these molecules have C_{3v} symmetry, and models with this symmetry were used in the electron diffraction analysis. The results for the principal distances (r_g) and angles ($\angle_\alpha$) from the combined GED/ab initio study of trimethylchlorogermane (with estimated 2σ uncertainties) are: r(Ge−C) = 1.950(4) Å, r(Ge−Cl) = 2.173(4) Å, r(C−H) = 1.090(9) Å, ∠CGeC = 112.7(7)°, ∠CGeCl = 106.0(8)°, ∠GeCH = 107.8(12)°. The results for the principal distances (r_g) and angles ($\angle_\alpha$) from the combined GED/ab initio study of trimethylbromogermane (with estimated 2σ uncertainties) are: r(Ge−C) = 1.952(7) Å, r(Ge−Br) = 2.325(4) Å, r(C−H) = 1.140(28) Å, ∠CGeC = 114.2(11)°, ∠CGeBr = 104.2(13)°, ∠GeCH = 106.9(43)°. Local C_{3v} symmetry and staggered conformation were assumed for the methyl groups.

Introduction

From reports in the literature it is apparent that the Ge−X and Ge−C bond lengths in $(CH_3)_{4-n}GeX_n$ (X = F, Cl, or Br and n = 0−4, except n = 1 for X = F) show a systematic decrease with increase in the value of n.[1−9] However, the data for the monohalo species trimethylchlorogermane and trimethylbromogermane are only partial in nature and are provided by microwave studies.[2,5] It was therefore decided to carry out full structural determinations on the molecules $(CH_3)_3GeX$ (X = Cl, Br) by gas-phase electron diffraction supported by theoretical calculations. An analogous trend in decreasing Ge−X bond length with increasing value of n has been observed for the M−Cl bond in the series of compounds $(CH_3)_{4-n}MCl_n$. (M = Si or C and n = 0−4).[10−17]

Experimental Section

Samples of trimethylchlorogermane and trimethylbromogermane (98% purity) were obtained from the Aldrich Chemical Co. and used without further purification. Electron diffraction data were obtained with the electron diffraction apparatus at the University of Reading using Kodak Electron Image plates. The optical densities were measured using a commercial AGFA II scanner.[18,19] Information about the experimental conditions for all data sets used in the present investigation is given in Table 1. The experimental intensity curves are shown in Figure 1. The data are available as Supporting Information. Radial distribution (RD) curves (Figures 2 and 3 for trimethylchlorogermane and trimethylbromogermane, respectively) were calculated in the usual way by Fourier transformation of the functions $I'_m(s) = Z_xZ_{Ge}(A_xA_{Ge})^{-1}sI_m(s)\exp(-Bs^2)$ (x = Cl or Br) with $B = 0.0020$ Å^2 and where $A = s^2F$ and F is the absolute value of the complex scattering amplitudes. The scattering amplitudes and phases were taken from tables.[20]

TABLE 1: Experimental Conditions for Data Collection for $(CH_3)_3GeCl$ and $(CH_3)_3GeBr$

	$(CH_3)_3GeCl$	$(CH_3)_3GeBr$
temperature, °C	20	20
no. long camera plates (LC, ca. 50 cm)[a]	5	3
no. short camera plates (SC, ca. 25 cm)[a]	3	2
s_{min}/Å^{-1}, LC[b]	3.00	3.00
s_{max}/Å^{-1}, LC[b]	12.50	13.50
s_{min}/Å^{-1}, SC[b]	8.00	9.75
s_{max}/Å^{-1}, SC[b]	26.75	27.00
Δs/Å^{-1}	0.25	0.25
nominal electron wavelength/Å	0.058561	0.058561
calibration substance	benzene	benzene

[a] The plates for $(CH_3)_3GeCl$ were traced twice (for one of the plates only once trace was used in the refinements) and the plates for $(CH_3)_3GeBr$ were traced three times. [b] $s = 4\pi\lambda^{-1}\sin\theta$ and 2θ is the scattering angle.

Theoretical Calculations

To aid in the elucidation of the structures of trimethylchlorogermane and trimethylbromogermane, theoretical calculations using GAUSSIAN 94[21] (ab initio and DFT calculations) were performed. The influences of change in the nature of the basis set and level of theory were studied by performing several calculations for each molecule. All the calculations were performed using the 6-311G basis set with different numbers of diffuse and polarization functions (see Table 2). The MP2 calculations were performed both with the core electrons included and excluded from the correlation calculations. To

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* Corresponding author.

† Oslo University College.

‡ University of Reading.

10.1021/jp040181h CCC: $27.50

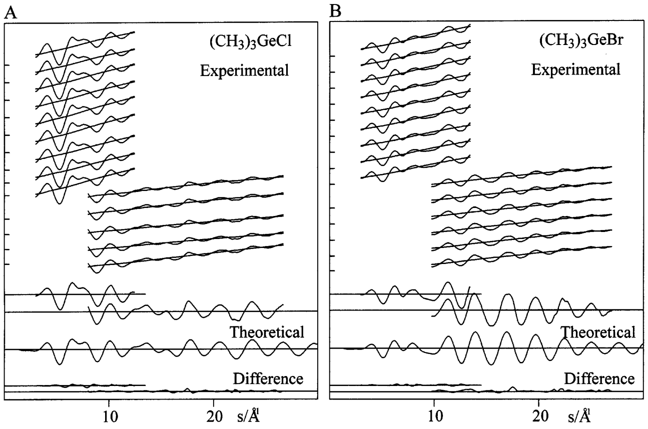

Figure 1. Experimental intensity curves, $s^4I_t(s)$, for (A) trimethylchlorogermane (B) trimethylbromogermane. Each plate is shown magnified 5× with respect to the final backgrounds on which they are superimposed.

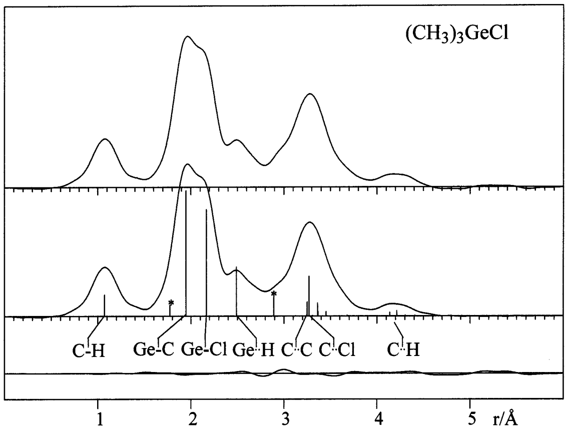

Figure 2. Radial distribution curves for trimethylchlorogermane. The experimental curve was calculated from the composite of the two average intensity curves with the use of theoretical data for the region $0 \leq s/Å^{-1} \leq 2.50$ and $B/Å^2 = 0.002$. The difference curve is experimental minus theoretical. The vertical lines indicate important interatomic distances and have lengths proportional to the distance weights. The asterisk indicates the distances from the impurity (CCl_4).

perform the electron diffraction refinements, vibrational parameters (l = root-mean-square amplitudes of vibration, K = perpendicular amplitude corrections, δr = centrifugal distortions) are also needed, and these were calculated with the force field obtained in the HF/6-311+G(d) calculations (scaled by a factor of 0.9 for bend and 0.8 for stretch), using ASYM40.[22] The torsions of the methyl groups were excluded when calculating the vibrational parameters because they gave unreasonably high perpendicular amplitude corrections.

Analysis of the Structures

The theoretical calculations performed indicate that both trimethylchlorogermane and trimethylbromogermane possess C_3-GeX moieties with C_{3v} symmetry. Our findings are in accord with the results of spectroscopic studies[2,5] on these molecules.

The molecules trimethylchlorogermane and trimethylbromogermane are depicted in Figure 4, which contains the atom numbering scheme. Since the theoretical calculations indicated that trimethylchlorogermane and trimethylbromogermane have cores with C_{3v} symmetry, models with this symmetry were adopted in the analyses of the electron diffraction data. Such models can be defined by the following parameters (X = Cl or Br): r(Ge−C), r(Ge-X), r(C−H), ∠CGeX, ∠GeCH. Local C_{3v} symmetry and a staggered conformation were assumed for the methyl groups. The theoretical calculations also indicated only minor derivations from C_{3v} symmetry for the methyl groups (see Table 2).

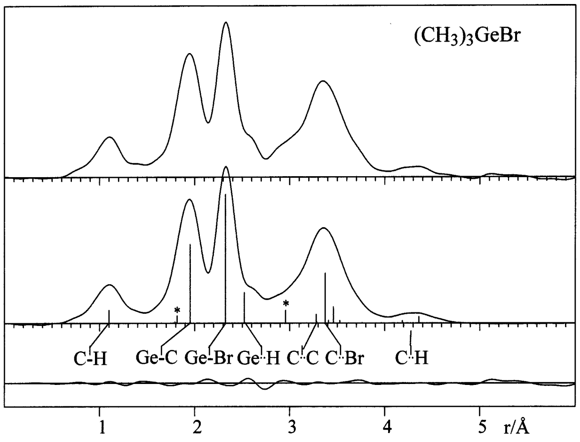

Figure 3. Radial distribution curves for trimethylbromogermane. The experimental curve was calculated from the composite of the two average intensity curves with the use of theoretical data for the region $0 \leq s/Å^{-1} \leq 2.50$ and $B/Å^2 = 0.002$. Difference curve is experimental minus theoretical. The vertical lines indicate important interatomic distances and have lengths proportional to the distance weights. The asterisk indicates the distances from the impurity (CCl_4).

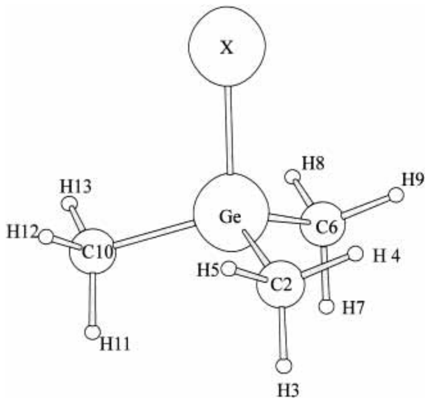

Figure 4. Diagram showing the numbering scheme of $(CH_3)_3GeX$ (X = Cl or Br).

The electron diffraction refinements were carried out by the least-squares method,[23] adjusting a theoretical $sI_m(s)$ curve simultaneously to the two average intensity curves (one from each camera distance) using a unit weight matrix. The geometries were calculated on the basis of r_α parameters. These were converted to the r_a type required by the scattering intensity formula by using values of centrifugal distortion (δr), perpendicular amplitude corrections (K), and root-mean-square amplitudes of vibration (l).[24]

Results from preliminary refinements using the model described above suggested the presence of more than one compound in the diffracted samples. The main discrepancies between the experimental and theoretical RD curves appeared at around 1.8 and 2.9 Å for both molecules. Neither $(CH_3)_3GeCl$ nor $(CH_3)_3GeBr$ possesses distances with this length. A possible explanation for the additional distances in the RD curves is the presence of minor amounts of CCl_4 in samples of both compounds. The compounds were purchased from Aldrich Chemical Co. and, while their mode of synthesis is not known, use of the equilibrium reaction given below in the presence of

TABLE 2: Results from Theoretical Calculations for $(CH_3)_3GeCl$ and $(CH_3)_3GeBr$[a]

	r(Ge-X)	r(Ge−C)	r(C−H_4)	r(C−H_3)	∠CGeX	∠CGeC	∠GeCH_4	∠GeCH_3	∠H_4CH_5	∠H_4CH_3
$(CH_3)_3GeCl$										
B3LYP/6-311+G(d)	2.224	1.962	1.091	1.094	105.5	113.1	110.4	110.3	108.5	108.6
HF/6-311G(d)	2.206	1.952	1.084	1.086	105.8	112.9	110.7	110.4	108.2	108.3
HF/6-311G(d,p)	2.206	1.951	1.084	1.087	105.8	112.9	110.5	110.1	108.5	108.6
HF/6-311+G	2.268	1.939	1.081	1.084	105.1	113.5	110.9	110.5	108.1	108.2
HF/6-311+G(d)	2.207	1.952	1.084	1.086	105.7	112.9	110.7	110.5	108.3	108.3
HF/6-311+G(d,p)	2.207	1.952	1.085	1.087	105.8	112.9	110.4	110.2	108.5	108.6
HF/6-311++G(d,p)	2.207	1.952	1.084	1.087	105.8	112.9	110.4	110.2	108.5	108.6
MP2/6-311+G(d)[b]	2.194	1.950	1.092	1.094	105.8	112.9	110.5	110.6	108.3	108.4
MP2/6-311+G(d)[c]	2.188	1.939	1.092	1.093	105.8	112.9	110.5	110.6	108.4	108.5
MP3/6-311+G(d)[b]	2.197	1.951	1.093	1.095	105.8	112.9	110.6	110.7	108.3	108.4
$(CH_3)_3GeBr$										
B3LYP/6-311+G(d)	2.379	1.964	1.091	1.094	106.1	112.6	110.5	110.2	108.5	108.6
HF/6-311G(d)	2.365	1.954	1.083	1.086	106.2	112.6	110.8	110.2	108.3	108.3
HF/6-311G(d,p)	2.366	1.953	1.084	1.087	106.2	112.6	110.6	109.9	108.6	108.6
HF/6-311+G	2.420	1.940	1.081	1.084	105.4	113.2	110.9	110.4	108.1	108.2
HF/6-311+G(d)	2.366	1.954	1.084	1.086	106.1	112.6	110.8	110.2	108.3	108.3
HF/6-311+G(d,p)	2.367	1.953	1.084	1.087	106.1	112.6	110.5	109.9	108.6	108.6
HF/6-311++G(d,p)	2.367	1.953	1.084	1.087	106.1	112.6	110.5	109.9	108.6	108.6
MP2/6-311+G(d)[b]	2.354	1.952	1.092	1.094	106.1	112.6	110.5	110.3	108.4	108.5
MP2/6-311+G(d)[c]	2.345	1.941	1.092	1.094	106.0	112.7	110.5	110.3	108.4	108.5

[a] Distances (r) are in Ångstrøms and angles (∠) are in degrees. [b] All core electrons excluded in the correlation calculations. [c] All electrons included in the correlation calculations.

TABLE 3: Structural Parameters for $(CH_3)_3GeCl$ and $(CH_3)_3GeBr$

parameters[a]	$(CH_3)_3GeCl$		$(CH_3)_3GeBr$	
	electron diffraction	ab initio[b]	electron diffraction	ab initio[b]
	r_α/$\angle_\alpha$	r_e/$\angle_e$	r_α/$\angle_\alpha$	r_e/$\angle_e$
r(Ge−X)	2.172 (4)	2.188	2.324 (4)	2.345
r(Ge−C)	1.947 (4)	1.939	1.949 (7)	1.941
$r(C-H)_{ave}$	1.083 (9)	1.092	1.126 (28)	1.092
∠CGeX	106.0 (8)	105.8	104.2 (13)	106.0
$\angle GeCH_{ave}$	107.8 (12)	110.5	106.9 (43)	110.4

	r_g/$\angle_\alpha$	$l_{refined}$	r_e	$l_{calculated}$	r_g/$\angle_\alpha$	$l_{refined}$	r_e	$l_{calculated}$
r(Ge−X)	2.173 (4)	0.058 (4)	2.188	0.056	2.325 (4)	0.045 (7)	2.345	0.056
r(Ge−C)	1.950 (4)	0.052 (6)	1.939	0.054	1.952 (7)	0.042 (15)	1.941	0.054
$r(C-H)_{ave}$	1.090 (9)	0.066 (9)	1.092	0.080	1.140 (28)	[0.080]	1.092	0.080
r(C···C)	3.244 (16)	[0.114]	3.233	0.114	3.275 (24)	[0.114]	3.232	0.114
r(C···X)	3.293 (16)	0.101 (12)	3.294	0.115	3.379 (30)	[0.117]	3.431	0.117
r(Ge···H_3)	2.508 (15)	0.100[c] (15)	2.539	0.120	2.525 (6)	[0.122]	2.537	0.122
r(Ge···H_4)	2.508 (15)	0.100[c] (15)	2.536	0.120	2.525 (6)	[0.120]	2.538	0.120
r(C_2···H_7)	3.452 (31)	[0.191]	3.487	0.191	3.509 (83)	[0.190]	3.479	0.191
r(C_2···H_8)	4.148 (16)	[0.124]	4.164	0.124	4.197 (46)	[0.124]	4.165	0.124
r(C_2···H_9)	3.377 (20)	[0.194]	3.408	0.194	3.392 (74)	[0.194]	3.409	0.194
∠CGeC	112.7 (7)		112.9		114.2 (11)		112.7	

[a] Distances (r) and amplitudes (l) are in Ångstrøms and angles (∠) are in degrees. Parenthesized values are 2σ and include estimates of uncertainties in voltage/nozzle height and of correlation in experimental data. Values in square brackets were kept constant at the calculated values. [b] MP2(with all electrons included in the correlation calculations) level of theory and 6-311+G(d) basis set used. [c] Refined as a group.

a chlorinated alkane as solvent is a likely route:

$$3(CH_3)_4Ge + GeCl_4 \rightarrow 4(CH_3)_3GeCl$$

The chlorinated solvents CCl_4, $CHCl_3$, and CH_2Cl_2 all possess C−Cl bonds and Cl···Cl interactions that would lead to peaks in the radial distribution curves at 1.77 and 2.89 Å, respectively. Mass spectrometry confirmed the presence of CCl_4 in the samples of $(CH_3)_3GeX$ (X = Cl and Br).

Refinements were therefore attempted upon models which consisted mainly of $(CH_3)_3GeX$ (X = Cl or Br) with small amounts carbon tetrachloride. The amount of CCl_4 was refined while the structural parameters were kept at the values obtained in an earlier study.[4] The amount of CCl_4 refined to 4 (2) % and 12 (5) % for $(CH_3)_3GeCl$ and $(CH_3)_3GeBr$, respectively.

It was possible to refine all the independent bond distances and angles for both molecules. The amplitudes associated with bond distances were all refined, except for the one associated with r(C−H) in $(CH_3)_3GeBr$. The amplitudes that could not be refined were constrained at the values obtained from the ASYM40 calculations.

A joint analysis of the electron diffraction data and the moment of inertia obtained by microwave spectroscopy[2,5] was attempted for both molecules. However, the uncertainties in the structure parameters were not reduced at all in the joint analysis. The results for the joint analysis are therefore not reported. The results for the structure parameters obtained by these two methods are compared.

Results from the final refinements for trimethylchlorogermane and trimethylbromogermane are given in Table 3. Intensity curves calculated for the final models are shown in Figure 1, together with experimental and difference curves. Figures 2 and

TABLE 4: Correlation Matrix (×100) for Parameters Refined in the Final Least-Squares Refinements for $(CH_3)_3GeCl$

		σ_{LS}[a]	r_1	r_2	r_3	$\angle_4$	$\angle_5$	l_6	l_7	l_8	l_9	l_{10}	α
1	r(Ge−C)	0.0008	100	44	13	−38	−38	11	−26	−30	−6	16	−14
2	r(Ge−Cl)	0.0037		100	9	−29	−5	57	−45	10	8	18	14
3	r(C−H)	0.0040			100	−4	−37	4	−7	−7	−7	2	3
4	∠CGeCl	0.0025				100	6	−6	5	8	−1	−25	24
5	∠GeCH	0.1790					100	−13	−5	16	−2	−11	−14
6	l(Ge−C)	0.0015						100	−21	44	27	29	29
7	l(Ge···H)	0.0045							100	8	6	6	−6
8	l(Ge−Cl)	0.0029								100	24	21	5
9	l(C−H)	0.0028									100	12	4
10	l(Ge···C)	0.0039										100	−10
11	α(CCl_4)	0.0068											100

[a] Standard deviations from least-squares refinements. Distances (r) and amplitudes (l) are in Ångstroms, angles (∠) in degrees.

TABLE 5: Correlation Matrix (×100) for Parameters Refined in the Final Least-Squares Refinements for $(CH_3)_3GeBr$

		σ_{LS}[a]	r_1	r_2	r_3	$\angle_4$	$\angle_5$	l_6	l_7	α
1	r(Ge−C)	0.0023	100	−14	4	−12	1	31	42	−7
2	r(Ge−Br)	0.0011		100	−2	−20	19	−24	−21	−13
3	r(C−H)	0.0102			100	9	−33	3	−1	0
4	∠CGeBr	0.4795				100	−15	8	0	20
5	∠GeCH	1.5067					100	31	41	−5
6	l(Ge−C)	0.0053						100	78	40
7	l(Ge−Cl)	0.0025							100	19
8	α(CCl_4)	0.0182								100

[a] Standard deviations from least-squares refinements. Distances (r) and amplitudes (l) are in Ångstroms, angles (∠) in degrees.

TABLE 6: Comparison of Structure Parameters for $(CH_3)_{4-n}GeBr_n$ and $(CH_3)_{4-n}GeCl_n$ (n = 0, 1, 2, 3,4)

	r_g(Ge−C)	r_g(Ge-X)	$\angle_\alpha$(CGeX)	$\angle_\alpha$(CGeC)	ref
$GeCl_4$		2.112 (1)			4
$(CH_3)GeCl_3$	1.893 (10)	2.132 (3)	112.3 (9)		3
$(CH_3)_2GeCl_2$	1.928 (6)	2.143 (4)	108 (2)	121 (4)	3
$(CH_3)_3GeCl$	1.950 (4)	2.173 (4)	106.0 (8)	112.7 (7)	this work
$(CH_3)_3GeCl$[a]	1.940 (3)	2.170 (1)	105.9 (1)		2
$(CH_3)_4Ge$	1.958 (4)			109.47[b]	1
$GeBr_4$		2.272 (1)			7
$(CH_3)GeBr_3$	1.889 (32)	2.276 (2)	111.6 (3)		6
$(CH_3)_2GeBr_2$	1.911 (12)	2.303 (2)	107 (3)	124 (7)	6
$(CH_3)_3GeBr$	1.952 (7)	2.325 (4)	104.2 (13)	114.2 (11)	this work
$(CH_3)_3GeBr$[a]	1.936 (6)	2.323 (1)	106.3 (1)	112.4(1)	5
GeF_4		1.67 (3)			9
$(CH_3)GeF_3$	1.904 (9)	1.714 (2)	113.2 (6)		8
$(CH_3)_2GeF_2$	1.928 (2)	1.739 (3)	107.3 (7)	121.0(35)	8

[a] The distances are given as r_s and angles as $\angle_o$. [b] Assumed.

3 contain the corresponding RD curves, and the correlation matrices for the refined parameters are given in Tables 4 and 5.

Discussion

Models assuming a C_{3v} symmetry for these title molecules and with a small amount of CCl_4 impurity (4% and 12% for $(CH_3)_3GeCl$ and $(CH_3)_3GeBr$, respectively) gave an excellent agreement with the electron diffraction data. All the parameters for the bond distances, bond angles, and amplitudes associated with the bond distances, except for the amplitude associated with the C−H distance in $(CH_3)_3GeBr$, were refined; thus the geometries of these molecules were well determined from the electron diffraction data. Including CCl_4 in the theoretical models had no significant effect on the structure parameters, but including CCl_4 improved the fit between experimental and theoretical intensity curves dramatically.

In Table 2 the results from the theoretical calculations for these molecules are given. The structure parameters obtained by ab initio calculations show only small variations with different numbers of diffuse and polarization functions on the 6-311G basis set. The variation in some of the structure parameters is somewhat larger when the level of theory is changed. Of special interest are the Ge−C and the Ge−X distances. Both distances change slightly on changing the level of theory from HF to MP2 (core electrons excluded from the correlation calculations). The distances estimated in the MP2 calculations are also dependent on the orbitals included in the correlation calculations. It can be seen from Table 2 that the distances calculated excluding all the core electrons from the correlation calculation are somewhat longer than when the core electrons are included. This observation has been made previously for molecules containing germanium.[25,26]

From Table 3 it can be seen that the values for the Ge-X bond length obtained in the ab initio calculations (MP2/6-311+G(d)) are longer than those found experimentally. The Ge−C bond length was calculated to be shorter than that found experimentally. Some of the refined angles differ by up to 2 degrees from the calculated values, but in these cases the uncertainties on the refined angles are relatively large.

It can be seen from Table 6 that the Ge−C and Ge−X (X = Cl or Br) bond lengths obtained from electron diffraction are somewhat longer than those found in microwave investigations carried out on these molecules.[2,5] However, since the results from the microwave investigation are given as r_s and the electron diffraction results as r_g, the agreement is relatively good. The important structure parameters for $(CH_3)_3GeCl$ and $(CH_3)_3GeBr$ are compared with those obtained for $(CH_3)_{4-n}GeX_n$ (X = F, Cl, or Br and $n = 0-4$, except $n = 1$ for X = F)[1−9] in Table 6. For F-, Cl-, and Br-substituted germanium compounds, the Ge−C and Ge−X distances increase as the numbers of F, Cl, or Br atoms decrease. This finding was also observed for the silicon compounds, $(CH_3)_{4-n}SiCl_n$[10−13]($n = 0-4$), and similar changes were reported for the carbon analogues $(CH_3)_{4-n}CCl_n$[14−17] ($n = 0-4$). The trend can be rationalized by the dual effects of "crowding" of the methyl groups and/or the increasing positive charge on the C, Ge, or Si atoms that results from the increasing degree of halogenation in the molecules. As can be seen from Table 6, the observed decrease in the Ge−C bond length does not depend on the halogen attatched to the Ge atom.

Acknowledgment. This work has received support from The Research Council of Norway (Program for Supercomputing) through a grant of computing time and a travel grant from Oslo University College (K.Aa).

Supporting Information Available: Tables giving total scattered intensities, molecular intensities, and Cartesian coordinates from the final electron diffraction refinements for trimethylchlorogermane and trimethylbromogermane. This material is available free of charge via the Internet at http://pubs.acs.org.

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