

The Molecular Structure of Hexamethyldigermene Determined by Gas-Phase Electron Diffraction with Theoretical Calculations for $(\text{CH}_3)_3\text{M}-\text{M}(\text{CH}_3)_3$ Where $\text{M} = \text{C}, \text{Si},$ and Ge

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Gas-phase electron diffraction (GED) data together with results from ab initio molecular orbital calculations (HF and MP2/6-311+G(d,p)) have been used to determine the structure of hexamethyldigermene ($(\text{CH}_3)_3\text{Ge}-\text{Ge}(\text{CH}_3)_3$). The equilibrium symmetry is D_{3d} , but the molecule has a very low-frequency, large-amplitude, torsional mode (ϕCGeGeC) that lowers the thermal average symmetry. The effect of this large-amplitude mode on the interatomic distances was described by a dynamic model which consisted of a set of pseudoconformers spaced at even intervals. The amount of each pseudoconformer was obtained from the ab initio calculations (HF/6-311+G(d,p)). The results for the principal distances (r_a) and angles (\angle_{h1}) obtained from the combined GED/ab initio (with estimated 1σ uncertainties) are $r(\text{Ge}-\text{Ge}) = 2.417(2)$ Å, $r(\text{Ge}-\text{C}) = 1.956(1)$ Å, $r(\text{C}-\text{H}) = 1.097(5)$ Å, $\angle\text{GeGeC} = 110.5(2)^\circ$, and $\angle\text{GeCH} = 108.8(6)^\circ$. Theoretical calculations were performed for the related molecules ($(\text{CH}_3)_3\text{Si}-\text{Si}(\text{CH}_3)_3$ and $(\text{CH}_3)_3\text{C}-\text{C}(\text{CH}_3)_3$).

Introduction

Structural studies on the series of gaseous molecules $(\text{CH}_3)_3\text{M}-\text{M}(\text{CH}_3)_3$ ($\text{M} = \text{C},^1 \text{Si},^2 \text{Ge},$ or Sn^3) allow an investigation of the influence of the nature of M upon the structure of the molecules and, in particular, the barrier to rotation about the $\text{M}-\text{M}$ vector. However a full comparison has not been made to date primarily because no gas-phase structural data for $(\text{CH}_3)_3\text{Ge}-\text{Ge}(\text{CH}_3)_3$ have yet been reported. A gas-phase electron diffraction study of $(\text{CH}_3)_3\text{Ge}-\text{Ge}(\text{CH}_3)_3$ supported by a series of theoretical calculations has been undertaken. Additionally the results of ab initio calculations for the molecules $(\text{CH}_3)_3\text{C}-\text{C}(\text{CH}_3)_3$ and $(\text{CH}_3)_3\text{Si}-\text{Si}(\text{CH}_3)_3$ have been carried out to underpin the structural studies determined by gas-phase electron diffraction.

Experimental Section

Gas-Phase Electron Diffraction Data Collection. Samples of hexamethyldigermene were obtained from the Aldrich Chemical Co. and used without further purification. Electron diffraction data were obtained at two different camera distances with an accelerating voltage of 42 kV using the apparatus at the University of Reading. Scattering intensities were recorded on digital image plates and measured using a Fuji BAS1800II image plate system. The electron wavelength was determined by calibration with benzene vapor. Experimental parameters, namely, temperatures, nozzle-to-plate distances, correlation parameters, final scaling factors, and electron wavelengths are listed in Table 1. Data reduction was performed using standard routines⁴ using published scattering factors.⁵ Data analysis was carried out using the program “ed@ed”.⁶ The experimental intensity curves are shown in Figure 1. Radial distribution (RD) curves for the final models of the molecule are presented in Figure 2.

TABLE 1: Experimental Parameters for Hexamethyldigermene

nozzle to plate distance/mm	494.89	244.40
nozzle temperature/ $^\circ\text{C}$	23	23
nominal electron wavelength/Å	0.058378	0.058378
data interval/ Å^{-1}	0.25	0.25
no. of plates	2	2
$s_{\text{min}}/\text{Å}^{-1}$	3	8
$s_{\text{max}}/\text{Å}^{-1}$	10	26
$s_{w1}/\text{Å}^{-1}$	4	8.5
$s_{w2}/\text{Å}^{-1}$	9	25
correlation parameter	0.286	0.3313
scale factor ^a	0.541(9)	0.844(23)

^a Values in parentheses are the estimated standard deviations.

Theoretical Calculations. $(\text{CH}_3)_3\text{Ge}-\text{Ge}(\text{CH}_3)_3$. Ab initio calculations using Gaussian03⁷ were performed to determine the structure of $(\text{CH}_3)_3\text{Ge}-\text{Ge}(\text{CH}_3)_3$ using Hartree–Fock (HF) and Møller–Plesset levels (MP2) of theory and with the 6-311+G(d,p) basis sets. The MP2 calculations were carried out both with and without the inclusion of core electrons. In addition a DFT calculation was performed using B3LYP. The torsional potential for the CGeGeC angle was calculated using HF/6-311+G(d,p) (see Figure 3). The results for the structure optimizations are shown in Table 2.

Calculated vibrational data were needed to convert the r_a distances obtained from the electron diffraction model to obtain a set of geometrically consistent distances (r_{h1}). Ab initio frequency calculations (HF/6-311+G(d,p)) provided theoretical force fields for the molecular vibrations. Vibrational parameters from this force field were obtained using the program SHRINK.^{8,9} The force constants for the distances were scaled by 0.9 as is common.

$(\text{CH}_3)_3\text{C}-\text{C}(\text{CH}_3)_3$ and $(\text{CH}_3)_3\text{Si}-\text{Si}(\text{CH}_3)_3$. The structures of $(\text{CH}_3)_3\text{C}-\text{C}(\text{CH}_3)_3$ and $(\text{CH}_3)_3\text{Si}-\text{Si}(\text{CH}_3)_3$ were determined some years ago,^{1,2} by gas-phase electron diffraction, but no theoretical calculations were performed. As such calculations are known to assist in the interpretation of gas-phase electron

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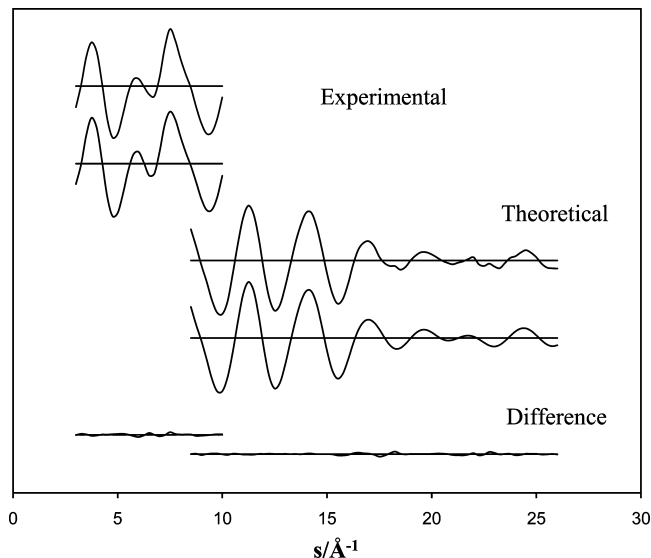


Figure 1. Experimental intensity curves, $s^4 I_t(s)$, for hexamethyldigermane, together with theoretical curves calculated from the final model and difference curves. Difference curves are experimental minus theoretical.

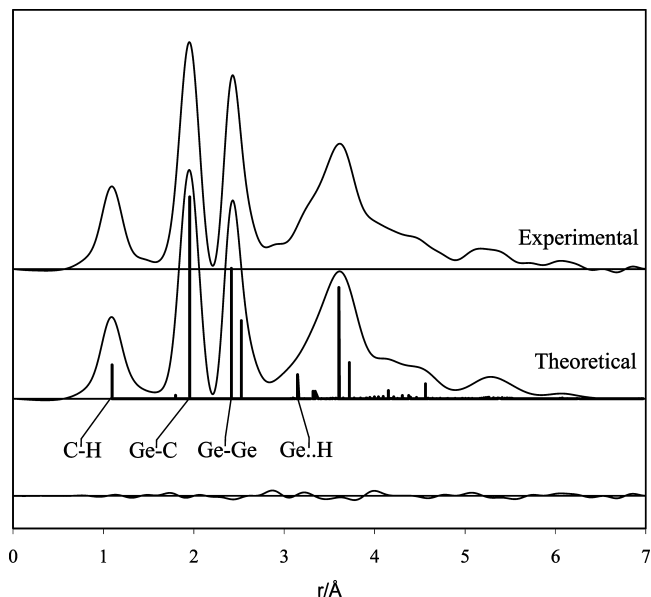


Figure 2. Radial distribution curves for hexamethyldigermane. The experimental curve was calculated from the composite of the two average intensity curves with the use of theoretical data for the region $0 \leq s/\text{Å}^{-1} \leq 2.75$ and $B/\text{Å}^2 = 0.002$. The difference curve is experimental minus theoretical. The vertical lines indicate important interatomic distances and have lengths proportional to the distance weights.

diffraction data, it was decided to execute theoretical calculations (MP2/6-311+G(d,p)) on these molecules in an identical manner to that used for our study of $(\text{CH}_3)_3\text{Ge}-\text{Ge}(\text{CH}_3)_3$ vide supra. The most relevant parameters obtained by calculations are recorded in Table 4 together with the comparable results for $(\text{CH}_3)_3\text{Ge}-\text{Ge}(\text{CH}_3)_3$. The variations of the potential energies with the change of CCCC and CSiSiC torsion angles are shown in Figure 3.

Analysis of the Gas-Phase Electron Diffraction Data. The calculations performed predicted a low frequency (approximately 20 cm^{-1}) for the CGeGeC torsional mode, and the barrier for the torsion was calculated to be 3.3 kJ mol^{-1} . To compensate for this low-frequency torsional motion a dynamic model

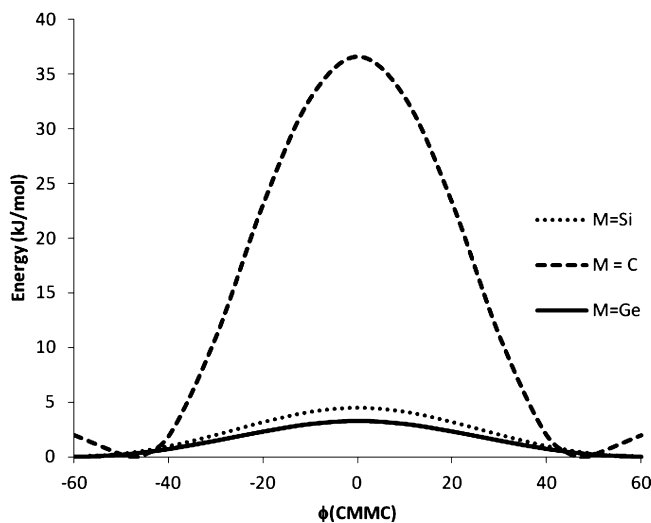


Figure 3. Torsional potential for the CMMC torsional angle for $(\text{CH}_3)_3\text{M}-\text{M}(\text{CH}_3)_3$ where $\text{M} = \text{C}, \text{Si},$ and Ge obtained by ab initio calculations (HF/6-311+G(d,p)).

TABLE 2: Results from ab Initio (6-311+G(d,p) Basis Set) and DFT Calculations for Hexamethyldigermane^a

	HF	MP2 ^b	MP2(Full) ^c	B3LYP
$r(\text{Ge}-\text{Ge})$	2.479	2.457	2.427	2.468
$r(\text{Ge}-\text{C})$	1.977	1.973	1.961	1.985
$r(\text{C}-\text{H})$	1.086	1.094	1.093	1.092
$r(\text{C}-\text{H})$	1.087	1.095	1.094	1.093
$r(\text{C}-\text{H})$	1.086	1.094	1.093	1.092
$\angle\text{GeGeC}$	110.7	110.6	110.6	110.9
$\angle\text{CGeC}$	108.2	108.3	108.3	108.0
$\angle\text{GeCH}$	111.1	110.8	110.8	110.9
$\angle\text{GeCH}$	110.2	110.0	110.1	109.9
$\angle\text{GeCH}$	111.1	110.8	110.8	110.9
$\angle\text{HCH}$	108.1	108.3	108.4	108.3
$\angle\text{HCH}$	108.2	108.4	108.4	108.4
$\angle\text{HCH}$	108.1	108.3	108.4	108.3
ϕCGeGeC	60	60	60	60
ϕCGeGeC	-60	-60	-60	-60
ϕCGeGeC	-180	180	180	180
ϕCGeCH	-61	-61	-61	-61
ϕCGeCH	59	59	59	58
ϕCGeCH	178	178	178	178
ϕGeGeCH	60	60	60	60
ϕGeGeCH	180	180	180	180
ϕGeGeCH	-60	-60	-60	-60

^a Distances are in angstroms and angles are in degrees. ^b Core electrons not included in the correlation calculation. ^c Core electrons included in the correlation calculation.

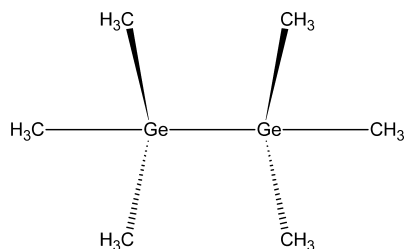
consisting of a set of seven “pseudoconformers” with values of the torsion angle CGeGeC from 60 to 0° at 10° intervals was adopted to describe the molecule. At 60° the $\text{C}_3\text{Ge}-\text{GeC}_3$ fragment has D_{3d} symmetry. Ab initio calculations using HF/6-311+G(d,p) were performed to determine the proportion of each pseudoconformer to include in the model used in the refinement of the electron diffraction data. The pseudoconformers were treated as distinct molecules undergoing the usual framework vibrations, except for the torsional motion.

Each pseudoconformer was defined with identical structural parameters as the theoretical calculations (HF/6-311+G(d,p)) indicated that these parameters are independent of the CGeGeC torsion. The following structural parameters were used: $r(\text{Ge}-\text{Ge})$, $r(\text{Ge}-\text{C})$, $r(\text{C}-\text{H})$, $\angle\text{GeGeC}$, $\angle\text{GeCH}$, ϕCGeGeC , ϕHCGeGe . In this model the $\text{Ge}(\text{CH}_3)_3$ units were assumed to have C_{3v} symmetry.

TABLE 3: Structural Parameters Obtained from Electron Diffraction (GED) Refinements and Theoretical Calculations (6-311+G(d,p) basis set) for Hexamethyldigermene

parameter ^a	GED						ab initio/DFT r_d/\angle_c			
	r_{hl}/\angle_{hl}	r_a	σ	l_{exp}	σ	l_{theo}	HF	MP2	MP2(Full) ^b	B3LYP
$r(\text{Ge}-\text{Ge})$	2.417	2.416	(2)	0.060	(2)	0.055	2.479	2.457	2.427	2.468
$r(\text{Ge}-\text{C})$	1.956	1.954	(1)	0.060	(3)	0.051	1.977	1.973	1.961	1.985
$r(\text{C}-\text{H})$	1.097	1.087	(5)	0.075		0.075	1.087	1.095	1.094	1.093
$\angle\text{GeGeC}$	110.5		(2)				110.7	110.6	110.6	110.9
$\angle\text{GeCH}$	108.8		(6)				110.8	110.6	110.5	110.6

^a Distances are in angstroms and angles are in degrees. Uncertainties are given as 1σ . ^b Core electrons included in the correlation calculation.

**Figure 4.** Hexamethyldigermene.

The independent parameters were unrestrained in the refinement of the electron diffraction data. Values for the dependent parameters from the final refinement are given in Table 3. Intensity curves calculated for the final model are shown in Figure 1, together with experimental and difference curves. Figure 2 contains the corresponding RD curves. In the refinements only two correlations factors were larger than 50 ($r(\text{C}-\text{H})/\angle\text{GeCH} = 51$ and $l(\text{Ge}-\text{Ge})/l(\text{Ge}-\text{C}) = 57$).

Results and Discussion

The structural parameters obtained from the analysis of the electron diffraction data for $(\text{CH}_3)_3\text{Ge}-\text{Ge}(\text{CH}_3)_3$ are recorded in Table 3, and the molecule is depicted in Figure 4. From Table 3 it can be seen that the values obtained experimentally for the Ge-Ge and Ge-C distances are in reasonable agreement with those obtained by the full MP2 treatment. Indeed the only parameter for which full agreement is not obtained is the Ge-C-H angle. The other theoretical treatments predict slightly longer Ge-Ge and Ge-C distances than those obtained experimentally (see Table 3).

From ab initio calculations (HF/6-311+G(d,p)) the barrier to rotation about the Ge-Ge bond was found to be 3.3 kJ mol^{-1} , which suggests there is close to free rotation about this bond with the minimum being when the $\text{C}_3\text{Ge}-\text{Ge}-\text{C}_3$ core has D_{3d} symmetry. In the refinement of the gas-phase electron diffraction data, a number of pseudoconformers were used in which the values of all the parameters were identical except for the value assigned to the C-Ge-Ge-C torsional angle. The values chosen for the torsion angles spanned the range 60° (where the $\text{C}_3\text{Ge}-\text{Ge}-\text{C}_3$ fragment has D_{3d} symmetry) to 0° (where it has D_{3h} symmetry). It was impossible to determine the value of the torsional potential from the experimental data, and therefore the values of percentages of the different conformers used in the refinements were set at those obtained from the ab initio calculations (HF/6-311+G(d,p)).

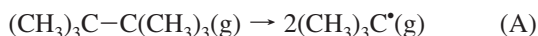
In Table 4 are recorded key structural data obtained for $(\text{CH}_3)_3\text{Ge}-\text{Ge}(\text{CH}_3)_3$ together with comparable data for $(\text{CH}_3)_3\text{M}-\text{M}(\text{CH}_3)_3$, $\text{H}_3\text{M}-\text{MH}_3$, and $(\text{CH}_3)_4\text{M}$ where $\text{M} = \text{C}$, Si , Ge , and Sn . The Ge-C distance ($1.954(1) \text{ \AA}$) is comparable to the value observed in $(\text{CH}_3)_4\text{Ge}^{10}$ ($1.945(3) \text{ \AA}$) while the Ge-Ge distance ($2.416(2) \text{ \AA}$) is slightly longer than the Ge-Ge distance found in $\text{H}_3\text{Ge}-\text{GeH}_3$ ($2.403(3) \text{ \AA}$).¹¹ A similar situation was observed in $(\text{CH}_3)_3\text{Si}-\text{Si}(\text{CH}_3)_3$ where the Si-Si distance² is $2.340(9) \text{ \AA}$ while that in $\text{H}_3\text{Si}-\text{SiH}_3$ ¹² is $2.331(6) \text{ \AA}$. In contrast the central C-C bond ($1.582(10) \text{ \AA}$) in $(\text{CH}_3)_3\text{C}-\text{C}(\text{CH}_3)_3$ ¹ is significantly longer than that reported for ethane ($1.532(6) \text{ \AA}$).¹³ In reporting the long value, Bartell et al. state¹ it appears unrealistically large. The theoretical calculations reported here support the long C-C bond (see Table 4). Additional support for the long bond is provided by thermochemical evidence. The enthalpies of formation of gaseous

TABLE 4: Comparison of Important Structural Parameters^b for Me_6Me_2 ($\text{M} = \text{C}$, Si , Ge , and Sn), H_6M_2 ($\text{M} = \text{C}$, Si , and Ge) and Me_4M ($\text{M} = \text{C}$, Si , Ge , and Sn) Obtained by Electron Diffraction and ab Initio Calculations (MP2(Full)/6-311+G(d,p))

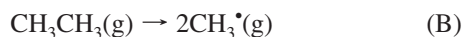
M	$r(\text{M}-\text{M})$		$r(\text{M}-\text{C})$		$\angle\text{MMC}$		$\angle\text{CMC}$		ref	
	GED	ab initio ^a	GED	ab initio ^a	GED	ab initio ^a	GED	ab initio ^a		
$(\text{CH}_3)_3\text{M}-\text{M}(\text{CH}_3)_3$										
C (r_g)	1.582(10)	1.570	1.542(2)	1.538	111.0(3)	111.2	111.0(3)	107.7	1	
Si (r_g)	2.340(9)	2.349	1.877(3)	1.887	108.4(4)	110.2	110.5(4)	108.7	2	
Ge (r_a)	2.416(2)	2.427	1.954(1)	1.961	110.5(2)	110.6	108.8(2)	108.3	This work	
Sn (r_a)	2.776(3)		2.165(3)		111.9(4)				3	
$\text{H}_3\text{M}-\text{MH}_3$										
C (r_g)	1.532(6)								13	
Si (r_g)	2.331(6)								12	
Ge (r_g)	2.403(3)								11	
$(\text{CH}_3)_4\text{M}$										
C (r_g)			1.537(3)						16	
Si (r_g)			1.875(2)						2	
Ge (r_g)			1.945(3)						10	
Sn (r_g)			2.144(3)						17	

^a The ab initio results are from this study. ^b Distances are in angstroms and angles are in degrees.

ethane and $(\text{CH}_3)_3\text{C}-\text{C}(\text{CH}_3)_3$ are known¹⁴ as are the enthalpies of formation of the gaseous radicals CH_3^\bullet and $(\text{CH}_3)_3\text{C}^\bullet$ ¹⁵ and thus the enthalpies of reactions A and B can be calculated from which it can be seen that the longer C–C bond in $(\text{CH}_3)_3\text{C}-\text{C}(\text{CH}_3)_3$ is considerably weaker (46 kJ mol⁻¹) than the comparable bond in ethane.



$$\Delta H^\theta = 328.8 \text{ kJ mol}^{-1}$$



$$\Delta H^\theta = 374.9 \text{ kJ mol}^{-1}$$

The lengthening of the C–C bond and consequent reduction in bond strength in $(\text{CH}_3)_3\text{C}-\text{C}(\text{CH}_3)_3$, in comparison to the values for ethane, acts to minimize the nonbonded interactions ($\text{H}\cdots\text{H}$) that span the C–C bond. To effect the bond lengthening and bond weakening that is observed, there must remain in the molecule some stronger repulsive interactions that are not present in $(\text{CH}_3)_3\text{Ge}-\text{Ge}(\text{CH}_3)_3$. Experimental structural evidence for nonbonded $\text{H}\cdots\text{H}$ repulsive interactions is difficult to obtain as the positions of H atoms are not determined very accurately by gas-phase electron diffraction. From the theoretical calculations, values for the $\text{H}\cdots\text{H}$ distances in both molecules were obtained. For $(\text{CH}_3)_3\text{Ge}-\text{Ge}(\text{CH}_3)_3$ all the $\text{H}\cdots\text{H}$ nonbonded distances that span the Ge–Ge bond are longer than those within the $(\text{CH}_3)_3\text{Ge}$ groups. However, for $(\text{CH}_3)_3\text{C}-\text{C}(\text{CH}_3)_3$ a considerable number of the nonbonded $\text{H}\cdots\text{H}$ distances that span the long central C–C bond are shorter than those within the $(\text{CH}_3)_3\text{C}$ fragments and these short distances will make a large contribution to nonbonded repulsive interaction. The nonbonded $\text{C}\cdots\text{C}$ distances can be determined experimentally. In $(\text{CH}_3)_3\text{C}-\text{C}(\text{CH}_3)_3$ the majority of the $\text{C}\cdots\text{C}$ distances across the central C–C bond are only 0.5 Å greater than the $\text{C}\cdots\text{C}$ distances within a $(\text{CH}_3)_3\text{C}$ group whereas in $(\text{CH}_3)_3\text{Ge}-\text{Ge}(\text{CH}_3)_3$ the comparable difference is 1.0 Å, thus providing further evidence for residual additional repulsive interactions in $(\text{CH}_3)_3\text{C}-\text{C}(\text{CH}_3)_3$.

The torsional potential for the three molecules ($(\text{CH}_3)_3\text{M}-\text{M}(\text{CH}_3)_3$, M = C, Si, and Ge) were calculated by ab initio calculations (HF/6-311+G(d,p)) and are given in Figure 3. Both $(\text{CH}_3)_3\text{Ge}-\text{Ge}(\text{CH}_3)_3$ and $(\text{CH}_3)_3\text{Si}-\text{Si}(\text{CH}_3)_3$ have low torsional barriers (3.3 and 4.5 kJ mol⁻¹, respectively) with their potential minima when the core has D_{3d} symmetry. In contrast $(\text{CH}_3)_3\text{C}-\text{C}(\text{CH}_3)_3$ exhibits very different behavior. It has a large torsional barrier of 36.6 kJ mol⁻¹ and has a minimum when the $\text{C}_3-\text{C}-\text{C}_3$ fragment is rotated 13.5° from the D_{3d} conformation. Bartell et al.¹ in their analysis of the electron diffraction data for $(\text{CH}_3)_3\text{C}-\text{C}(\text{CH}_3)_3$ used a 5° deviation of

the central core from D_{3d} symmetry but suggested that the deviation could be as large as 13°. The theoretical calculations reported here are in agreement with published experimental results¹ which show that $(\text{CH}_3)_3\text{C}-\text{C}(\text{CH}_3)_3$ possesses an unusually bound C–C bond and derivation from D_{3d} symmetry. This is in contrast to those of $(\text{CH}_3)_3\text{Si}-\text{Si}(\text{CH}_3)_3$ ² and $(\text{CH}_3)_3\text{Ge}-\text{Ge}(\text{CH}_3)_3$ which have D_{3d} symmetry, lower torsional barriers, and expected Ge–Ge and Si–Si bond lengths.

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