

The molecular structure of a germacyclobutane by gas electron diffraction and ab initio molecular orbital calculations¹

Arne Haaland^{a,*}, Svein Samdal^a, Tor G. Strand^a, Maxim A. Tafipolsky^a,
Hans Vidar Volden^a, Bartholomeus J.J. van de Heistee^b, Otto S. Akkerman^b,
Friedrich Bickelhaupt

^a Department of Chemistry, University of Oslo, Box 1033 Blindern, N-0315 Oslo, Norway

^b Vakgroep Organische Chemie, Vrije Universiteit, De Boelelaan 1083, 1081 HV Amsterdam, Netherlands

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Abstract

The molecular structure of 1,1,3,3-tetramethylgermacyclobutane has been determined by gas electron diffraction supplemented by ab initio calculations at the HF/6-31G* and MP2/6-31G* levels. Structure refinement of a C_s model with the differences between symmetry inequivalent Ge–C and C–C bond distances fixed at the HF values yielded the bond distances Ge–C = 197.5(3) and C–C = 156.7(2) pm (endocyclic) and Ge–C = 195.9(3) and C–C = 152.9(2) pm (exocyclic). The endocyclic valence angles are $\angle CGeC = 75.3(2)^\circ$, $\angle GeCC = 89.5(2)^\circ$ and $\angle CCC = 100.7(3)^\circ$. The exocyclic $\angle CGeC = 108.8(8)^\circ$. The central ring is non-planar with a puckering angle of $24(2)^\circ$, the barrier to planarity is estimated to be $V_o = 4.2(8) \text{ kJ mol}^{-1}$. Optimisation of the structure of 1,1-dimethylgermacyclopropane at the HF/6-31G* level yields $\angle CGeC$ valence angles of 47.5° (endocyclic) and 116.2° (exocyclic). © 1997 Elsevier Science S.A.

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1. Introduction

The synthesis of 1,1,3,3-tetramethylgermacyclobutane was reported by Bickelhaupt and coworkers in 1984 [1]. We now report the molecular structure as determined by gas electron diffraction (GED) and ab initio molecular orbital calculations at the HF/6-31G* and MP2/6-31G* levels. As far as we know, this represents the first structure determination of a germacyclobutane.

2. Computational

Ab initio calculations were carried out with the GAUSSIAN 94 program system with a standard 6-31G*

basis [2]. The geometry of 1,1,3,3-tetramethylgermacyclobutane was first optimised at the Hartree–Fock (HF) level under the assumption that the molecular symmetry is C_s . The resulting molecular structure is shown in Fig. 1; bond distances, valence angles and dihedral angles are listed in Table 1. The molecular force field was calculated, the force constants were scaled by a factor of 0.81, and root-mean-square ‘framework’ vibrational amplitudes l calculated with the program ASYM40 [4]. The contributions from the ring puckering mode (73 cm^{-1}) were excluded. Optimisation of a molecular model of C_{2v} symmetry, i.e. a model with a planar GeC_3 ring, yielded an energy 3.0 kJ mol^{-1} higher than the C_s model.

Optimisation of the C_s model at the MP2/6-31G* level yielded optimal structure parameters listed in the third column of Table 1.

Structure optimisation of a C_{2v} model of 1,1-dimethylgermacyclopropane was carried out at the HF level.

* Corresponding author.

¹ Dedicated to the memory of Professor Yu.T. Struchkov in recognition of his contributions to structural chemistry.

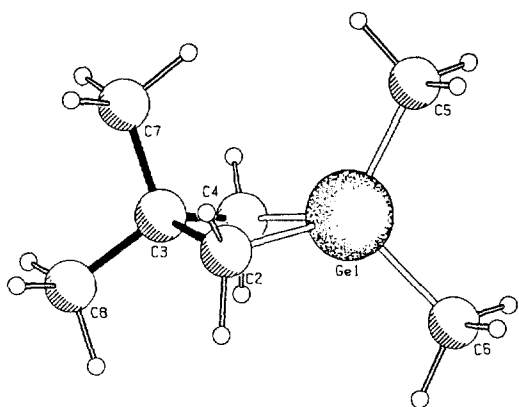


Fig. 1. Molecular model (PLUTON [3]) of 1,1,3,3-tetramethylgermacyclobutane, symmetry C_{2v} .

3. GED

The sample was synthesised as previously described [1]. GED data were recorded with a Balzers Eldigraph KDG-2 unit [5] with a conventional metal inlet system at about 25 °C. Exposures were made at nozzle to photographic plate distances of about 50 and 25 cm. Six plates from each set were photometered on a modified Joyce–Loebl microdensitometer and the data processed with a program system written by Strand and coworkers [6]. Atomic scattering factors were taken from Ref. [7]. Backgrounds were drawn as least squares adjusted eighth degree polynomials to the difference between total experimental and calculated molecular intensities. The

Table 1
Structure parameters of 1,1,3,3-tetramethylgermacyclobutane^a

	HF/6-31G [*]	MP2/6-31G [*]	GED		
	r_e/\angle_e (pm/deg)	l (pm)	r_e/\angle_e (pm/deg)	r_a/\angle_a (pm/deg)	l (pm)
<i>Bond distances</i>					
Ge–C(2)	196.4	5.3	196.1	197.5(3)	6.0(2) ^c
Ge–C(5,6)	194.8, 194.7	5.3, 5.3	193.9, 193.7	195.9, 195.8(3)	6.0(2) ^c
C(2)–C(3)	157.0	5.5	156.1	156.7(2)	6.0(2) ^d
C(3)–C(7,8)	153.3, 152.9	5.2, 5.2	152.6, 152.2	153.0, 152.7(2)	5.7(2) ^d
C–H(mean)	108.3	7.1	109.3	111.1(2)	8.7(2)
<i>Nonbonded distances</i>					
Ge ··· C(3)	251	5.6	250	251.0(15)	[5.6]
Ge ··· C(7)	336	8.9	329	331.2(16)	[8.9]
Ge ··· C(8)	381	7.3	382	383.5(16)	[11.0] ^e
Ge ··· H(Me)	254	12.1	254	258.0(9)	[12.1]
C(2) ··· C(4)	242	6.6	241	241.3(6)	[6.4]
C(7) ··· C(8)	250	7.4	249	250.3(15)	[7.4]
C(2) ··· C(7)	254	7.6	252	253.5(6)	[7.6]
C(2) ··· C(5,6)	335, 333	11.6, 11.1	335, 332	337.3, 334.9(6)	[11.6, 11.1]
C(5) ··· C(6)	318	11.1	315	318.5(17)	[11.1]
C(5) ··· C(7)	398	10.8	385	388(4)	[10.8]
C(5) ··· C(8)	534	11.1	530	534(4)	[11.1]
C(6) ··· C(7)	522	11.2	515	520(4)	[11.2]
C(6) ··· C(8)	501	9.0	507	501(4)	[9.0]
<i>Valence angles</i>					
C(2)GeC(4)	76.1		75.8	75.3(2)	
C(2)GeC(5,6)	117.7, 116.4		118.1, 116.6	118.1, 116.8(3)	
C(5)GeC(6)	109.4		108.8	108.8(8)	
GeC(2)C(3)	89.7		89.2	89.5(2)	
C(2)C(3)C(4)	101.0		100.9	100.7(3)	
C(2)C(3)C(7,8)	109.9, 113.1		109.6, 113.3	109.9, 113.1(3)	
C(7)C(3)C(8)	109.5		109.8	109.9(10)	
GeC(5)H	110.4		109.9	111.4(8)	
C(3)C(7)H	110.9		110.5	[110.9]	
<i>Puckering angle $\phi = C(4)GeC(2)–C(2)C(3)C(4)$</i>					
	20		24	24(2)	
<i>Barrier to planarity (kJ mol⁻¹)</i>					
	3.0			4.2(8)	
<i>R-factors^b</i>			0.032 (50 cm); 0.039 (25 cm); 0.035 (total)		

^a Estimated standard deviations in parentheses in units of the last digit.

^b $R = [\sum W(I_{obs} - I_{calc})^2 / \sum W(I_{obs})^2]^{1/2}$.

^{c,d} These amplitudes were refined with constant difference.

^e This amplitude was adjusted by stepwise variation, then fixed.

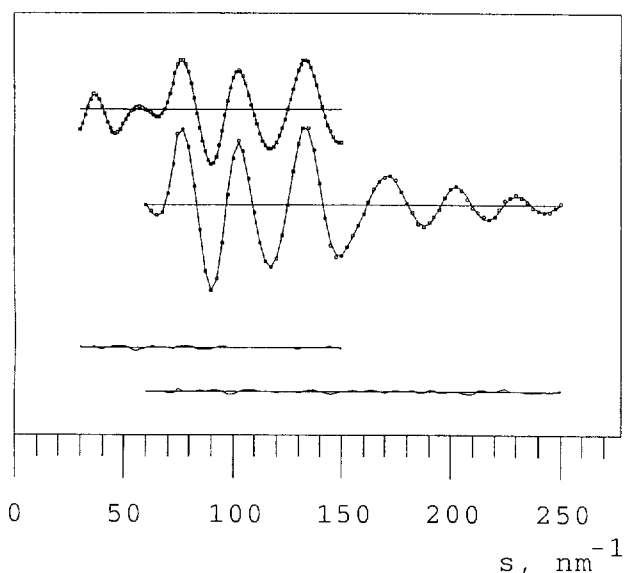


Fig. 2. Experimental (dots) and calculated (lines) modified molecular intensity curves for 1,1,3,3-tetramethylgermacyclobutane. The vertical scale is arbitrary. Below: difference curves.

resulting modified molecular intensity curves are shown in Fig. 2.

4. Structure refinement

Structure refinements were carried out with the program KCED26 [8] and were based on a molecular model of C_s symmetry. See Fig. 1. Determination of the structure of the GeC_7 framework requires the determination of three different Ge–C bond distances, three different C–C bond distances, three different $\angle CGeC$ valence angles, two different $\angle CCC$ valence angles and (at least) one parameter determining the conformation of the ring. The C_s model was, therefore, further constrained by making the following assumptions:

(i) the differences between the three symmetry inequivalent Ge–C distances were fixed at the HF values;

(ii) the differences between the three symmetry inequivalent C–C bond distances were fixed at the HF values;

(iii) the difference between the valence angles $\angle C(2)GeC(5)$ and $\angle C(2)GeC(6)$ was constrained to the HF value;

(iv) the difference between the valence angles $\angle C(2)C(3)C(7)$ and $\angle C(2)C(3)C(8)$ was constrained to the HF value;

(v) all $\angle CCH$ valence angles were fixed at the HF values.

The ring conformation was described by the puckering angle ϕ , defined as the angle between the planes $C(2)GeC(4)$ and $C(2)C(3)C(4)$. The equilibrium puckering angle was denoted by ϕ_e and the barrier to planarity

by V_0 . The potential energy was assumed to have the form

$$V(\phi) - V_0 = -k_2\phi^2 + k_4\phi^4$$

where $k_4 = V_0/\phi_e^4$ and $k_2 = 2V_0/\phi_e^2$.

The gas was modelled as a mixture of pseudo-conformers with ϕ ranging from 0 to 35° in steps of 7°, and the mole fraction of each pseudo-conformer was assumed proportional to the Boltzmann factor $\exp[-V(\phi)/RT]$. Vibrational amplitudes were assumed to be independent of ϕ .

5. Results and discussion

Least squares refinements of the mean Ge–C, C–C and C–H bond distances, the endocyclic valence angle $\angle C(2)GeC(4)$, the mean of the exocyclic angles $\angle C(2)GeC(5)$ and $\angle C(2)GeC(6)$, the mean of the exocyclic angles $\angle C(2)C(3)C(7)$ and $\angle C(2)C(3)C(8)$, and finally a mean $\angle GeCH(Me)$ angle, the equilibrium ring puckering angle ϕ_e , the barrier to planarity V_0 , mean r.m.s. vibrational amplitudes l of C–H, C–C and Ge–C bond distances converged to the values listed in Table 1. As refinements were carried out with diagonal weight matrices, the e.s.d.s have been doubled to reflect the added uncertainty due to data correlation [9] and further expanded to include an estimated scale uncertainty of 0.1%. Experimental and calculated intensity curves are compared in Fig. 2, and experimental and calculated radial distribution curves in Fig. 3. We find the agreement satisfactory.

The agreement between structure parameters obtained by experimentally by GED or by calculations at

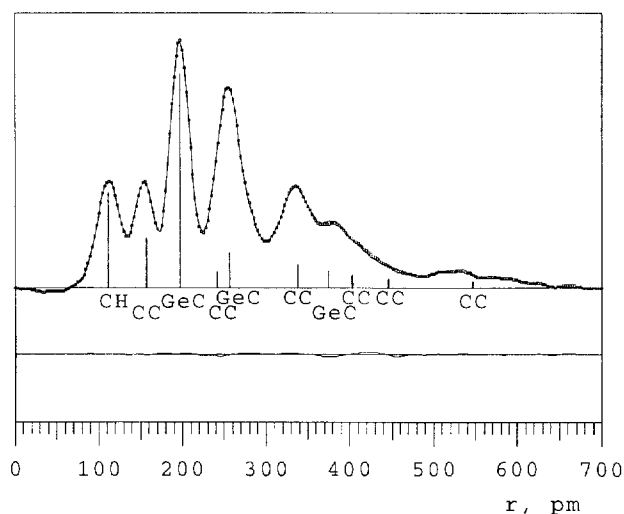


Fig. 3. Experimental (dots) and calculated (line) radial distribution curves for 1,1,3,3-tetramethylgermacyclobutane. The vertical scale is arbitrary. Below: difference curves. Artificial damping constant $k = 25 \text{ pm}^2$.

the HF or MP2 level (see Table 1) is generally good. The discussion which follows is based on the experimental values, since these are accompanied by error estimates.

The endocyclic Ge–C bond distances appear to be elongated by some 3 pm relative to tetramethylgermane, 194.5(3) pm, [10] and the endocyclic C–C bond by some 2 pm relative to neo-pentane, 153.7(3) pm [11]. The exocyclic bond distances are normal.

The central GeC_3 ring is significantly non-planar, the angle between the $\text{C}(2)\text{GeC}(4)$ and $\text{C}(2)\text{C}(3)\text{C}(4)$ planes is $\phi_e = 24(2)^\circ$, while the barrier to planarity is estimated as $4.2(8) \text{ kJ mol}^{-1}$. The puckering angle in cyclobutane is $\phi_e = 28(2)^\circ$, while the barrier to planarity is $6.10(4) \text{ J mol}^{-1}$ [12]. The estimated puckering angle in silacyclobutane is $34(2)^\circ$ [13].

In Fig. 4 we compare the endocyclic valence angles in cyclopentane, cyclobutane and cyclopropane with the valence angles at Si or Ge in sila- or germa-analogues. Here we have also included the valence angle in 1,1-dimethylgermacyclopropane obtained by structure optimisation at the HF/6-31G* level. The thermodynamic stability of cycloalkanes decreases with decreasing ring size along the series $(\text{CH}_2)_6 > (\text{CH}_2)_5 > (\text{CH}_2)_4 > (\text{CH}_2)_3$; while cyclohexane is believed to be essentially strain-free, the strain per CH_2 unit has been estimated as 6 kJ mol^{-1} in cyclopentane, 29 kJ mol^{-1} in cyclobutane and 39 kJ mol^{-1} in cyclopropane [19]. The stabilities of the analogues sila-, germa-, and stanna-cycles of

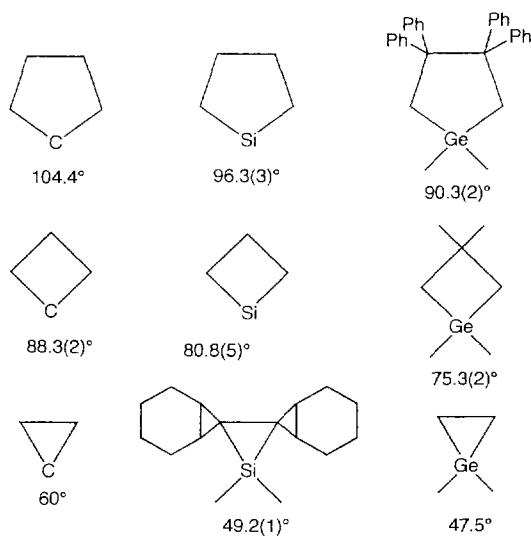


Fig. 4. Endocyclic $\angle\text{CCC}$ valence angles in cyclopentane (the quoted angle is an average value; during pseudorotation of the ring individual $\angle\text{CCC}$ angles vary between 102 and 107° , see Ref. [14]), cyclobutane [12] and cyclopropane [15], all determined by GED. Endocyclic $\angle\text{CSiC}$ or $\angle\text{CGeC}$ angles in silacyclopentane [16] and silacyclobutane [13] by GED, in a substituted silacyclopentane by X-ray crystallography (XRC), [17] in a substituted germacyclopentane by XRC, [18] in 1,1,3,3-tetramethylgermacyclobutane by GED (this work) and in 1,1-dimethylgermacyclopropane by HF MO calculations (this work).

composition $\text{H}_2\text{E}(\text{CH}_2)_n$, where $n = 2, 3$ or 4 , also appear to decrease with decreasing size of the ring ($4 > 3 > 2$) as well as with increasing size of the hetero atom ($\text{C} > \text{Si} > \text{Ge} > \text{Sn}$). As indicated in Fig. 4, the observed trends are readily rationalised in terms of increasing angle strain.

Since the endocyclic $\angle\text{CGeC}$ angle is more than 30° smaller than tetrahedral, we were surprised that the exocyclic $\angle\text{CGeC} = 108.8(8)^\circ$ angle is not significantly larger than tetrahedral, as one would expect on the basis of a simple hybridisation model. Even in 1,1-dimethylgermacyclopropane, where the endocyclic $\angle\text{CGeC}$ angle is calculated to be 47.5° , the exocyclic $\angle\text{CGeC}$ angle is calculated to be no more than 116.2° ! The optimal C–C bond distance is 155.0 pm ; the endocyclic Ge–C bond distance is 192.4 pm ; the exocyclic Ge–C 194.1 pm .

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