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NMR Spectra of Organogermanium Compounds. X.[1] Syntheses, ^{13}C and ^{73}Ge NMR Spectra and Molecular Mechanics Calculations of Germacyclopentanes and Germacyclopentenes

Yoshito Takeuchi,* Katsumi Tanaka, and Toshie Harazono
Department of Chemistry, The College of Arts and Sciences,
The University of Tokyo, Komaba, Meguro-ku, Tokyo 153
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Germacyclopentane, its 1-methyl, and 1,1-dimethyl derivatives together with some germacyclopentenes were prepared and their ^{13}C and ^{73}Ge NMR spectra were determined. Molecular mechanics calculations of germacyclopentanes indicate that the symmetric twist form is the most stable in contrast to cyclopentane where the envelop and twist forms have much the same energy. Though both ^{13}C and ^{73}Ge chemical shifts are less sensitive to the stereochemistry of the methyl group as compared with the corresponding germacyclohexanes, the spectroscopic results can be explained in terms of the structures as depicted by molecular mechanics calculations.

In the previous communications we have reported the preparation and structural study of 1-methyl-[2], 1-phenyl-[3] and 1-*t*-butyl-germacyclohexanes[1] (**GC**) based on ^{13}C and ^{73}Ge chemical shifts, molecular mechanics calculations (MM2) and molecular orbital calculations (MNDO). It was found that the conformational energy of a methyl or a phenyl group bonded to germanium is essentially zero while that of a *t*-butyl group is ca. 1.3 kcal mol^{-1} in a sharp contrast with the case of corresponding cyclohexanes (**C**).

This very small conformational energy is due to the flattening of **GC** ring around germanium atom as well as the extended C–Ge bond length, both of which will reduce the repulsion between the axial substituent on germanium and the C-3, 5 methylene moieties.[2] In this connection it will be interesting to see the structural features of germacyclopentanes (**GP**) which have hitherto never been described.

It is well established that cyclopentane (**1CP**) is a free pseudorotator and the an envelop (hereafter abbreviated as **E**) and a twist-boat (hereafter abbreviated as **T**) form have an identical energy.[4] Alkylcyclopentanes are not any more a free pseudorotator, and in the case of methylcyclopentane (**2CP**) the most stable form is the one with the methyl group at the tip of envelop. The energy difference between **E** and **T** is, however, essentially zero.

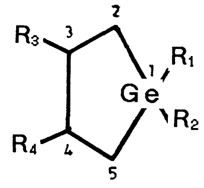
This feature of cyclopentanes (**CP**) will make the stereochemical significance of equatorial and axial orientations of the substituent nearly identical. This can most simply be exemplified by the ^{13}C chemical shifts of *trans*-1,3-dimethylcyclohexane and -cyclopentane. In both compounds one of the two methyl groups is necessarily axial (or pseudo-axial), which will be expected to make averaged chemical shifts to highfield than those of corresponding 1,3-*cis* isomers. In the case of dimethylcyclopentanes the chemical shifts difference between *trans*- and *cis*-isomers is only 0.3 ppm (the former is in the higher field)[5] while the similar difference of dimethylcyclohexanes amounts to 2.35 ppm with the *trans*-isomer in the higher field.[6]

Hence three questions have arisen concerning the stereochemistry of **GP**. One is the determination of the most stable structure of germacyclopentane (**1GP**) or **GP** in general. The second one is to determine the extent of difference between (pseudo)equatorial and (pseudo)axial orientations of the methyl group on germanium in **GP**. The second question is interesting in relation to our previous finding that the two conformers (equatorial and axial) of 1-methylgermacyclohexane (**2GC**) have essentially similar MM2 steric energy with a slight preference to the axial isomer (by ca. 0.2 kcal mol^{-1}).[2] The third one is the possibility that a methyl group or any other substituent bonded to the ring carbon might alter the most stable structure from **T** to something else.

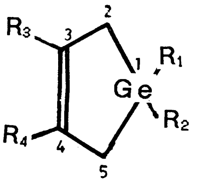
With these in mind we prepared **1GP**, 1-methylgermacyclopentane (**2GP**), and 1,1-dimethylgermacyclopentane (**3GP**). We also attempted to prepare 1,1,3-trimethylgermacyclopentane (**4GP**) and 1,1,3,4-tetramethylgermacyclopentane (**5GP**) without success. Instead, 1,1-dimethyl-3,4-epoxygermacyclopentane (**10GP**) and 1,1-dimethylgermacyclopentan-3-ol (**11GP**) were prepared . Compounds **4GP**, **5GP**, **10GP**, and **11GP** were selected because in these compounds the stereochemical environment of two methyl groups bonded to germanium can be different.

Four germacyclopentenes, 1,1-dimethylgermacyclopent-3-ene (**6GP**), 1,1,3-trimethylgermacyclopent-3-ene (**7GP**), 1,1-diethyl-3-methylgermacyclopent-3-ene (**8GP**), and 1,1,3,4-tetramethylgermacyclopent-3-ene (**9GP**) were prepared. Compounds **7GP** and **9GP** were expected to be the precursor for **4GP** and **5GP**, respectively. The compound **8GP** was chosen to assess the effect of an ethyl group bonded to germanium upon chemical shifts.

We deteremined the ^{13}C and ^{73}Ge NMR spectra of the compounds prepared, and carried out molecular mechanics calculations of **1GP**—**4GP**. For other compounds molecular mechanics calculations were



	R1	R2	R3	R4
1	H	H	H	H
2	Me	H	H	H
3	Me	Me	H	H
4	Me	Me	Me	H
5	Me	Me	Me	Me
10	Me	Me	OH	H
11	Me	Me	—O—	



	R1	R2	R3	R4
6	Me	Me	H	H
7	Me	Me	Me	H
8	Et	Et	Me	H
9	Me	Me	Me	Me

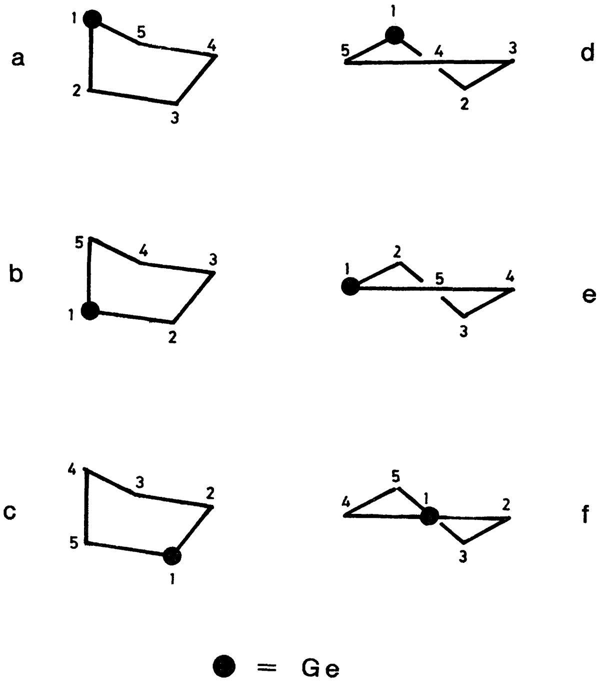


Fig. 1. Input structures for MM2 calculation of germacyclopentane.

impossible because of the lack of parameters.

Results and Discussion

Molecular Mechanics Calculations. Molecular mechanics calculations were carried out for germacyclopentanes **1GP**—**4GP** with the aid of MM2 program[7] to which parameters for germanium as reported by Ouellette[8] were incorporated. The appropriateness of this combination together with the reason why the new germanium parameters reported by Allinger et al.[9] was not employed has already been discussed in our previous paper.[1]

For the input structures for MM2 calculations, **GP** can either be an envelop or a twist and in each structure the germanium atom can have three different positions (a, b, and c for an envelop, and d, e, and f for a twist). In other words, there are six possible input structures for **1GP** (Fig. 1). A similar situation should be involved in the case of **3GP**. In the case of **2GP** the situation is more complicated since for each of the structures a—e, there are two orientations, equatorial (abbreviated as **eq-2GP**) and axial (**ax-2GP**), of the methyl group. For the input structure f, the equatorial and axial structures are degenerated, and hence for **2GP** altogether eleven input structures were considered. For **4GP**, the situation is the same with the case of **2GP**, and eleven input structures were calculated.

The steric energy and its components for each optimized structure are given in Table 1. In MM2 calculations, total steric energies (E_s) are the sum of compression energy (E_c), bending energy (E_b), stretch-bend energy (E_{sb}), torsional energy (E_t) and van der Waals energy which is subdivided into the energy associated with 1,4-interaction ($E_{1,4}$) and that with other interactions (E_{other}). The geometrical parameters for each optimized structures are given in Table 2.

1GP: It is interesting to notice that the input structure **1GP-a** was optimized to an envelop, **E(1GP)**, while the input structure **1GP-b** and **1GP-c** were optimized to a symmetric (in the sence that the germanium nucleus is on the C_2 axis) twist **T(1GP)**. The latter is by ca. 2 kcal mol^{-1} more stable than the former. When the input structure was a twist form, the situation is considerably different, and both **1GP-e** and **1GP-f** were optimized to the same **T**. The input structure **1GP-d** was, however, optimized to a different structure, an unsymmetrical twist **A(1GP)**.

The difference between **T** and **A** is clear when the dihedral angle was compared. In **T** there are two paris of nearly equal dihedral angles while in **A** all five are more or less different. Otherwise, the steric energy of this unsymmetrical species is nearly the same with that of **E(1GP)**.

2GP: The situation is very similar for the case of **1GP**. The most stable structure is again **T(2GP)**, a symmetrical twist. There are two cases (**eq-2GP-a** and **ax-2GP-a**) where the input structures are optimized to **E**. Both envelops have a steric energy about 2 kcal mol^{-1} higher than **T**. The small energy difference between **E** from **eq-2GP-a** and that from **ax-2GP-a** (0.26 kcal mol^{-1}) in favor of the latter is a reminiscence of the situation for equatorial- and axial-1-methylgermacyclohexane (**2GC**).[2]

Two input structures **eq-2GP-c** and **ax-2GP-d** are

Table 1. MM2 Component Steric Energies[a)] of Germacyclopentanes and Corresponding Cyclopentanes (in kcal mol^{-1}: 1 cal=4.18 J)

Compound[b)]	Input[c)]	Output[d)]	E_s	E_c	E_b	E_{sb}	E_t	$E_{1,4}$	E_{other}
1GP	a	E	15.58	0.62	7.43	0.11	6.43	1.41	−0.44
	b,c,e,f	T	13.57	0.40	5.10	−0.01	7.31	1.13	−0.37
	d	A	15.58	0.60	7.21	0.11	6.66	1.44	−0.44
eq-2GP	a	E	14.98	0.65	7.38	0.12	6.68	1.01	−0.86
	b,c,e,f	T	12.80	0.41	5.06	0.00	7.47	0.75	−0.89
	d	A	14.99	0.64	7.21	0.12	6.85	1.04	−0.86
ax-2GP	a	E	14.72	0.65	7.34	0.12	6.70	1.02	−1.12
	b,c,e,f	T	12.80	0.41	5.06	0.00	7.47	0.75	−0.89
	d	A	14.72	0.65	7.31	0.12	6.74	1.02	−1.11
3GP	a	E	13.91	0.68	7.28	0.13	6.92	0.64	−1.74
	b,c,e,f	T	11.81	0.43	5.01	0.00	7.60	0.38	−1.61
	d	A	13.93	0.68	7.18	0.13	7.03	0.65	−1.73
eq-4GP	a,c,d,e,f	eq-T	11.89	0.55	5.11	0.02	7.53	0.94	−2.25
	b	ax-T	13.02	0.62	5.07	0.06	8.58	0.90	−2.21
ax-4GP	b,d	eq-T	11.89	0.55	5.11	0.02	7.53	0.94	−2.25
	c,e,f	ax-T	13.02	0.62	5.07	0.06	8.58	0.90	−2.21
	a	A	14.25	0.82	7.28	0.16	7.00	1.33	−2.34
1CP	a	E	11.41	0.33	2.19	−0.10	6.33	3.16	−0.51
	d	T	11.40	0.33	2.20	−0.10	6.33	3.16	−0.51
eq-2CP	a	E	11.56	0.37	2.43	−0.08	6.23	3.58	−0.98
	b,c	A	11.58	0.38	2.42	−0.07	6.23	3.59	−0.97
ax-2CP	a	E	12.76	0.41	2.19	−0.06	7.43	3.78	−0.98
	b,c	A	11.58	0.38	2.42	−0.07	6.23	3.59	−0.97
3CP	a,b	E	13.00	0.57	2.29	−0.03	7.38	4.13	−1.34
	c	A	12.93	0.68	2.52	−0.05	6.83	4.30	−1.34

a) For difinition of each component steric energies, see text. b) For definition of structures of compounds, see text. c) Input structure: see Fig. 1 for definition. d) Output structure: for definition see text.

optimized to an unsymmetrical twist **A**. These two as well as the optimized structure from an envelop **E(2GP)** have a similar steric energy.

It is interesting to see the conformation of the methyl group bonded to germanium. For optimized **E** structure for **eq-2GP** (which is not the energy minium) the dihedral angles Me–Ge-1–C-2–C-3 (and Me–Ge-1–C-5–C-4) is ca. 155°, which corresponds to 163° for the value of **eq-2CP** (dihedral angle Me–C-1–C-2–C-3). The dihedral angle for optimized *E* structure of **ax-2GP** are 74° while for **ax-2CP** the corresponding values are ca. 82°. Thus, the dihedral angles for **2GP** are generally smaller than those for **2CP**.

The corresponding values for **eq-2GC** (Me–Ge-1–C-2–C-3) and **eq-2C** (Me–C-1–C-2–C-3) are 167° and 180°, respectively, while the corresponding values for **ax-2GC** and **ax-2C** are ca. 69° and 73°, respectively. There is, however, no comparing since both *E* forms of **eq-** and **ax-2GP** are not energy minima. The two dihedral angles for **T** form of **2GP**, 129° and 100°, clearly indicates there is no butane-gauche type interaction between the methyl group and C-3/C-4 methylene moieties in the optimized **T** form.

3GP: An essentially identical situation with the previous case was observed for **3GP**. The most stable structure is a symmetric twist **T(3GP)**. The envelop **E(3GP)**, which is from the input structure **3GP-a**, is 1.8 kcal mol^{-1} higher in energy than **T(3GP)**. An unsymmetrical twist **A(3GP)**, from **3GP-d**, has a similar steric energy with that of **E(3GP)**.

4GP: In order to prove that the most stable structure is in fact **T**, an examination of NMR spectra of such a compound as **4GP** will be helpful. In **T** form the two Ge-1 methyl group remain nearly equivalent regardless of the presence of C-3 methyl group. On the other hand, if **GP** is in **E**, the presence of C-3 methyl will restrain the ring reversal and/or pseudorotation to avoid one of Ge-1 methyl and C-3 methyl will become 1, 3-diaxial. The net effect is that the **GP** ring will remain in **E** in which two Ge-1 methyl groups can be differentiated.

The most stable structure is again **T(4GP)** with an

Table 2. Structures of Germacyclopentanes and Cyclopentanes[a)]

Compound		$r_{1,2}$	$r_{2,3}$	$r_{3,4}$	$r_{4,5}$	$r_{5,1}$	θ_1	θ_2	θ_3	θ_4	θ_5	$\psi_{1,2}$	$\psi_{2,3}$	$\psi_{3,4}$	$\psi_{4,5}$	$\psi_{5,1}$
		nm	nm	nm	nm	nm	°	°	°	°	°	°	°	°	°	°
1GP	E	0.1936	0.1541	0.1555	0.1542	0.1936	88.8	103.8	111.8	112.1	104.1	−38.9	29.7	−1.4	−27.7	38.7
	T	0.1944	0.1541	0.1547	0.1541	0.1945	92.7	104.4	108.1	108.1	104.5	−14.0	38.7	−52.4	38.3	−13.5
	A	0.1936	0.1539	0.1554	0.1544	0.1937	89.2	102.9	111.2	112.5	105.2	−40.2	36.9	−12.7	−18.1	33.6
eq-2GP	E	0.1935	0.1542	0.1556	0.1542	0.1934	89.2	103.6	112.0	112.2	103.9	−38.7	29.6	−1.6	−27.3	37.9
	T	0.1943	0.1541	0.1547	0.1541	0.1944	93.1	104.1	108.1	108.3	104.3	−14.7	39.1	−52.4	37.7	−12.8
	A	0.1935	0.1540	0.1555	0.1544	0.1935	89.5	102.9	111.5	112.6	104.8	−40.0	35.6	−11.0	−19.4	34.2
ax-2GP	E	0.1935	0.1542	0.1555	0.1542	0.1935	89.1	103.7	112.0	112.2	103.8	−38.5	29.0	−0.8	−27.9	38.0
	T	0.1944	0.1541	0.1547	0.1541	0.1943	93.1	104.3	108.2	108.1	104.2	−13.4	38.2	−52.4	38.6	−14.0
	A	0.1935	0.1541	0.1555	0.1543	0.1935	89.2	103.4	111.7	112.3	104.2	−39.1	31.4	−4.2	−25.2	36.9
3GP	E	0.1934	0.1542	0.1556	0.1543	0.1933	89.5	103.5	111.2	112.4	103.7	−38.4	29.4	−1.4	27.1	−37.6
	T	0.1942	0.1541	0.1548	0.1542	0.1942	93.4	104.0	108.2	108.3	104.1	−14.1	38.6	−52.4	38.0	−13.3
	A	0.1934	0.1544	0.1556	0.1544	0.1934	89.7	103.0	111.8	112.6	104.3	−39.3	33.2	−7.5	−22.2	35.4
eq-4GP	eq-T	0.1942	0.1544	0.1550	0.1541	0.1941	93.3	104.4	107.9	108.4	103.9	−13.0	37.3	−52.3	39.0	−14.5
ax-4GP	ax-T	0.1942	0.1545	0.1552	0.1541	0.1941	93.5	105.0	107.8	109.8	104.0	−13.0	36.1	−49.9	37.0	−13.2
	A	0.1934	0.1543	0.1559	0.1544	0.1933	89.7	103.1	111.1	112.6	104.6	−39.7	34.9	−10.3	−19.7	34.2
1CP	E	0.1534	0.1537	0.1541	0.1537	0.1534	102.3	103.9	105.9	106.4	103.9	−40.5	25.1	0.0	−25.1	40.5
	T	0.1540	0.1535	0.1534	0.1535	0.1540	106.3	105.2	102.7	102.8	105.2	−13.4	34.6	−42.6	34.4	−13.0
eq-2CP	E	0.1535	0.1537	0.1541	0.1537	0.1535	102.1	103.9	106.0	106.0	103.9	−40.8	25.5	−0.2	−25.1	40.7
	A	0.1535	0.1534	0.1539	0.1540	0.1537	102.8	102.6	104.8	106.3	105.5	−42.6	36.9	−17.0	−9.4	32.1
ax-2CP	E	0.1537	0.1537	0.1540	0.1537	0.1537	102.0	104.9	106.0	106.1	104.9	−38.8	24.6	−0.6	−23.6	38.4
	A	0.1537	0.1540	0.1539	0.1534	0.1535	102.8	105.6	106.3	104.8	102.6	−42.5	36.9	−17.1	−9.3	32.0
3CP	E	0.1540	0.1537	0.1540	0.1537	0.1540	101.5	105.2	105.9	106.0	105.2	−38.7	24.7	−0.6	−23.7	38.3
	T	0.1547	0.1534	0.1532	0.1535	0.1548	105.1	105.4	102.3	102.8	106.0	−16.9	37.2	−43.0	32.8	−9.9

a) The definition of the structure parameters are as follows: $r_{1,2}$ is the distance between Ge and C-2 in nm, θ_1 is the bond angle C5–Ge–C2 in degrees and $\psi_{1,2}$ is the torsion angle in degrees defined by the C5–Ge–C2–C3. The other parameters are defined analogously.

equatorial methyl at C-3, similar to previous examples. It must be pointed out that **T(4GP)** with an axial C-3 methyl group can be an energy minimum though the steric energy is by more than 1 kcal mol^{-1} larger than the former. The asymmetric twist **A(4GP)** has much higher energy and cannot contribute to the structure.

The values of component energies indicate that the stability of **T** form is to be ascribed to the low E_b term, which is ca. 2.2 kcal mol^{-1} smaller as compared with **E** or **A**. The E_t term of **T** is generally slightly larger than these for **E** and **A**. The E_c and $E_{1,4}$ terms of **T** are slightly but consistently smaller than those for **E** and **A**; the sum is, however, smaller than the gain in E_b.

The difference in steric energy between **E** and **T** may be reflected in the geometrical parameters given in Table 2. Firstly, in the high energy structure (**E** and **A**) of **GP**, the bond angle θ_1 (C5–Ge–C2)(ca. 89°) is always by ca. 4° smaller than that of low energy structures (**T**:93°). This smaller bond angle in **E** and **A** seems to couple with a very small (0.001 nm) but consistent decrease of bond length $r_{1,2}$ and $r_{5,1}$. These two effects associated with germanium in **E** should cause an increase in the E_b term. It must be pointed out such a difference in bond angle also exists for **E** and **T** forms of **CP**.

Another point to be considered is the average flattening. The sum of five dihedral angle is a measure of ring flattening. In **GP** the sum for **E** is less than that for **T** by more than 20° while for **CP** the difference is only ca. 7°. Excessive flattening should increase the steric energy of the system and for this reason the **T** form is the most stable among possible conformers.

Preparation of Germacyclopentanes. The preparation of **1GP—3GP** was carried out in a similar manner that used in the preparation of corresponding germacyclohexanes.[10]

The preparation of **4GP** and **5GP** was attemped, starting from isoprene (2-methyl-1,3-butadiene) and 2,3-dimethyl-1,3-butadiene, respectively, and germanium(II) iodide (GeI_2). 1,1-Diiodo-3-methyl- and 1,1-diiodo-3,4-dimethylgermacyclopent-3-ene initially formed were converted to **7GP** and **9GP**, respectively with the aid of methylmagnesium iodide (MeMgI). **7GP** and **9GP** were hydrogenated with H_2/Ni (50 atm) but the desired **4GP** and **5GP** could not be isolated.

Instead we decided to prepare **10GP** and **11GP** because the possible precursor **6GP** can relatively easily be obtained from butadiene and trichlorogermane ($HGeCl_3$), and a subsequent treatment with MeMgI. **6GP** was treated with *m*-perbenzoic acid to give **10GP** which was treated with lithium aluminum hydride (LAH) to afford **11GP**.

^{73}Ge Chemical Shifts. In Table 3, ^{13}C and ^{73}Ge chemical shifts of germacylopentanes and germacyclopentenes are listed. The values in parentheses are those of the corresponding **GC**.

The chemical shifts of three compounds **1GP—3GP** indicate that the effect of a methyl group is similar in magnitude as that in **GC**. Thus the span is ca. 140 ppm for **GP** and ca. 120 ppm for **GC**. In **GP**, however, the resonances are considerably in lower

Table 3. ^{73}Ge$^{a)}$ and ^{13}C$^{b)}$ NMR Chemical Shifts of Germacyclopentanes, Germacyclopentenes, and Germacyclohexanes$^{c)}$

Compounds	Ge-1	C-2	C-3	C-4	C-5	Me-1	Me-3
1GP	−101.1 (−130.3)	13.22 (9.32)	29.20 (26.78)	29.20 (26.78)	13.22 (9.32)		
2GP	−27.4 (−65.6)	11.86 (12.61)	28.60 (26.09)	28.60 (26.09)	11.86 (12.61)	−5.20 (−6.55)	
3GP	40.0 (−11.3)	14.45 (15.33)	28.65 (28.65)	28.65 (25.90)	14.45 (15.33)	−2.38 (−3.77)	
6GP	37.0	21.78	134.03	134.03	21.78	0.27	
7GP	44.6	23.88	139.76	125.67	20.41	−2.16	22.63
8GP	70.9	20.77	141.12	127.04	17.30	7.20 (CH_2) 10.19 (Me)	23.67
9GP	9.7	27.08	130.71	130.71	27.08	−2.38	19.59
10GP		16.96	58.01	58.01	16.96	−0.22 −1.89	
11GP		24.22	74.44	36.13	10.89	−1.44 −1.84	

a) In ppm relative to external $GeMe_4$ (δ=0). b) In ppm relative to internal $SiMe_4$ (δ=0). c) Values in pharentheses are corresponding germacyclohexanes. Data taken from Ref. 2.

field. This low field shift is most likely due to the reduced bond angle θ_1. A similar effect was reported for ^{29}Si chemical shifts of 1,1-dimethylsilacyclohexane (−1.0 ppm) and 1,1-dimethylsilacyclopentane (16.8 ppm).[11]

The correlation between ^{73}Ge chemical shifts and those of ^{29}Si was reported as below.[12]

$$\delta(^{73}\text{Ge}) = 3.32\delta(^{29}\text{Si}) + 39.9$$

Thus, the ^{73}Ge shift difference between **3GP** and **3GC** is expected to be about 59 ppm based on the above correlation. The observed difference, 51.3 ppm, is not very far from the prediction, indicating that the correlation is, though empirical, quite general.

^{73}Ge chemical shifts of **GP** (**6GP**—**9GP**) are puzzling. In view of a very small chemical shift difference between 1,1-dimethylgermacyclohexane (**3GC**; −11.3 ppm) and 1,1,3-trimethylgermacyclohexane (**4GC**; −12.2 ppm), similarly small differences are expected for the chemical shifts of three compounds, **6GP**, **7GP**, and **9GP** since the effect of a pseudo-equatorial methyl group at C-3 should not be large. In fact, the difference between **6GP** and **7GP** is 7.6 ppm, a rather unexpectedly large value. Furthermore, the shift for **9GP** is considerably in high field.

The only possible explanation is the change of most stable structure in **9GP**. According to molecular mechanics calculations, the most stable conformation of cyclopentene is an envelop with nearly planar double bond moiety.[13,14] The *cis*-dimethyl substituents will suffer from a strong repulsion, and the deviation from the planarity will be increased. One of the methyl group will be bent to the direction opposite to the flap while the other to direction of flap. The latter methyl is expected to induce a substantial high field shift induced by the steric interaction with 1,1-dimethyl moiety. Lack of the relevant parameters inhibit us from carrying out molecular mechanics calculations to prove this explanation.

^{73}Ge chemical shift of **8GP** is also puzzling. Since the shift for tetraethylgermane is 17.8 ppm relative to tetramethylgermane (δ=0), a large difference of 26.3 ppm between **7GP** and **8GP** is unexpected. Here the deviation of germanium from tetrahedral structure seem to be involved though more extensive data should be accumulated before a concrete conclusion can be drawn.

^{13}C Chemical Shifts. The assignment of ^{13}C signals is more or less straightforward, based on the comparison with the data for **GC** and on the number of attached proton(s) as indicated by the INEPT experiment.

There is one anomaly in ^{13}C chemical shifts of C-2, 5. In **GC** C-2 exhibits a low field shift as the number of methyl group bonded to germanium increases. This is also the case with methylcyclohexanes.[6] In **GP**, however, the resonance of C-2 of **2GP** is in the highest field among three compounds investigated. We do not have any explanation for this anomaly.

The chemical shift difference between two methyls of **10GP** and **11GP** is informative. In **11GP** the difference is very small even compared with that of 1,1,3-trimethylgermacyclohexane (2.30 ppm).[15] This is consistent with a symmetric twist **T** structure where the effect of pseudo-equatorial substituent to two methyl groups on germanium is very similar. The fact that the epoxide **10GP** shows a larger difference (1.66 ppm) might indicate that in the particular compound the germacyclopentane ring is not **T**. On the other hand, the epoxide ring cannot be coplanar with the ring, to make the stereochemical enviroment of two methyls somewhat different.

In conclusion, it can be assumed that the optimized structure of the germacyclopentane ring is a symmetric twist **T** regardless of the number and orientation of methyl group(s) bonded to germanium. This makes a sharp contrast to the cyclopentane ring, essentially a free rotator, where an envelop and a twist boat has much the same steric energy.

Most of the ^{73}Ge and ^{13}C NMR data are accounted for in terms of the symmetric twist structure of **GP**. How to explain some anomaly remains, however, to be solved in future.

Experimental

Infrared spectra were obtained with a JASCO A102 grating infrared spectrophotometer as a liquid film. The ^{1}H NMR spectra were recorded with a Varian EM-390 spectrometer as $CDCl_3$ solution containing a small amount of tetramethylsilane (TMS) as the internal standard.

The ^{73}Ge NMR spectra were recorded as solutions in $CDCl_3$ (1 : 1 v/v) on a JEOL FX-90Q spectrometer equipped with an NM-IT 10LF low-frequency insert, operating at 3.10 MHz, in a 10 mm tube at 30 °C. Typical measurement conditions were as follows: pulse width, 150 μs (90°); spectral width, 2000 Hz; number of scans, 5000; pulse delay, 100 ms; data points, 4096. The ^{13}C NMR spectra were determined for the same solutions on the same instrument at 22.50 MHz. Typical measurement conditions were as follows: pulse width, 13 μs (40°); spectral width, 2000 Hz; number of scans, 500; pulse delay, 1 s; data points, 4096. The combined results are given in Table 3.

Molecular Mechanics Calculations. The program used was Allinger's MM2(85).[7] Since in MM2(85) the parameters for germanium are not available, we installed the parameters reported by Ouellette[8] in MM2(85). For the sake of comparison, calculations were also carried out for the corresponding cyclopentanes (**1CP**—**4CP**) and the results were also included in Tables 1 and 2.

Preparation of Germacyclopentane and Germacyclopentane Derivatives (1GP—11GP). Some of organogermanium compounds are sensitive to air and moisture, and elemental analyses are not necessarily feasible. The purity was in most cases monitored by a combination of gas chromatography, mass and NMR spectra.

Preparation of **1GP—3GP** was carried out, with some modification, according to the literature.[10] Thus, the reaction between the bis-Grignard reagent of 1,4-dibromobutane and tetrachlorogermane afforded 1,1-dichlorogermacyclopentane, which was treated with LAH to give **1GP** and with methylmagnesium iodide (MeMgI) to give **3GP**.

1-Methylgermacyclopentane (2GP): 1,1-Dichlorogermacyclopentane was treated with phenylmagnesium bromide to give 1,1-diphenylgermacyclopentane, which was monobrominated, and treated with methylmagnesium bromide. The resultant 1-methyl-1-phenylgermacyclopentane was successively treated with bromine and LAH to afford the desired **2GP**.

1,1-Dimethylgermacyclopent-3-ene (6GP): An ether solution of trichlorogermane (25.1 g, 0.10 mol) was cooled to −78 °C, to which butadiene (30 ml) was added in one portion. The mixture was stirred for 14 h while the temperature was gradually raised to the room temperature. By usual work-up, 1,1-dichlorogermacyclopent-3-ene (11.6 g, 42%) was obtained, bp 65 °C/15 mmHg (1 mmHg=133.322 Pa). The dichloro compound was treated with MeMgI to afford 1,1-dimethylgermacyclopent-3-ene (**6GP**) (4.87 g, 53%), bp 113 °C/766 mmHg. IR (neat) 1607 (C=C).

1,1,3-Trimethylgermacyclopent-3-ene (7GP): GeI_2 (20.0 g, 61.2 mmol) and isoprene (4.5 g, 66.2 mmol) were placed in a sealed tube, which was heated at 60 °C for 4 h. to give viscous, orange-colored 1, 1-diiodo-3-methylgermacyclopent-3-ene. Since this unsaturated compound was found unstable and hence employed in the next step without isolation nor purification. MeMgI was prepared from MeI (52.1 g; 367 mmol) and Mg (8.92 g, 367 mmol) in diethyl ether (200 ml) under argon. The ether solution of the Grignard reagent was cooled to −45 °C to which the diiodide solution (70 ml) was added and the mixture was gradually brought to room temperature. Under ice-cooling the mixture was treated with HCl (2 mol dm^{-3}), and the organic layer was separated, dried with $CaCl_2$. The ether layer was removed and the residue was distilled under a reduced pressure to give 1,1,3-trimethylgermacyclopent-3-ene (**7GP**) (6.51 g, 62%), bp 70—72 °C/35 mmHg (lit,[16] bp 139 °C/741 mmHg).

Found: C, 49.42; H, 8.09%. Calcd for $C_7H_{14}Ge$; C, 49.23; H, 8.26%.

1,1-Diethyl-3-methylgermacyclopent-3-ene (8GP): GeI_2 (5.88 g, 18 mmol) and isoprene (3.12 g, 46 mmol) were placed in a sealed tube, which was heated at 60 °C for 3 h. to give viscous, orange-colored 1,1-diiodo-3-methylgermacyclopent-3-ene. Ethylmagnesium iodide (150 mmol) was prepared in ether (150 ml) was prepared to which the ether solution (70 ml) of above diiodide was dropwise added at −30 °C, stirred for 2 h and kept at room temperature overnight. Under ice-cooling the mixture was treated with saturated aqueous solution of NH_4Cl, and the organic layer was separated, dried with $CaCl_2$. The ether layer was removed and the residue was distilled under a reduced pressure to give **8GP** (2.42 g, 68%), bp 82 °C/58 mmHg. IR (neat) 1635 (C=C).

1,1,3,4-Tetramethylgermacycloent-3-ene (9GP): GeI_2 (16.6 g, 50.8 mmol) and 2,3-dimethylbutadiene (4.3 g, 52.4 mmol) were mixed and gradually heated under a steam of Ar to 50 °C when the reaction was initiated to give an yellow solution. The mixture was further kept at 110 °C for 2 h to complete the reaction. The crude diiodide was dissolved in ether (100 ml), to which MeMgI (200 mmol) in ether (150 ml) was dropwise added under reflux. Refluxing was further continued for 2 h and hydrolyzed with aqueous saturated NH_4Cl solution under ice cooling. The ether layer was washed with water, dried over $CaCl_2$, and the ether was removed. The residue was distilled in vacuo to afford **9GP** (6.93 g, 74%), bp 88 °C/45 mmHg.

1,1-Dimethyl-3,4-epoxygermacyclopentane (10GP): **6GP** (18.9 g, 0.12 mol) was treated with *m*-chloroperbenzoic acid (22.9 g, 0.13 mol) in dichloromethane under ice cooling. Stirring was continued for 2.5 h, and *m*-chlorobenzoic acid was filtered off. The organic layer was successively treated with aqueous sodium hydrogensulfite, sodium carbonate, and ammonium chloride, and dried with magnesium sulfate. By distillation, **10GP** was obtained (13.8 g, 66%), bp 68—70 °C/45 mmHg.

1,1-Dimethylgermacyclopentan-3-ol (11GP): **10GP** (118 g, 68 mmol) was dropwise added to LAH (1.3 g, 34 mmol) in diethyl ether (100 ml) in a stream of argon. After refluxed for 3 h, the mixture was decomposed with aqueous HCl (2 mol dm^{-3}) under ice cooling. The organic layer was washed, dried with magnesium sulfate, and distilled to afford **11GP** (9.6 g, 81%), bp 83 °C/15 mmHg. IR (neat) 3330 (O–H).

Attempted Preparation of 1,1,3-Trimethylgermacyclopentane (4GP): **7GP** (5.39 g, 31.6 mmol) was dissolved in absolute ethanol (100 ml) to which Raney Ni (W-1) (2.0 g) was added and hydrogenated (110 °C, H_2 pressure 50 kg cm^{-2}) for 5 h. After the completion of reaction, the solvent was removed and the residue was distilled in vacuo, preparative gas chromatography. The NMR spectrum indicated that the sample contains at least three inseparable components.

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