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NMR Spectra of Organogermanium Compounds. Part XII.[1]
^{73}Ge and ^{13}C NMR Spectra and Molecular Mechanics Calculations of 3-Germabicyclo[3.1.0]hexanes and Related Compounds

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^{73}Ge and ^{13}C NMR spectra of several 3-germabicyclo[3.1.0]hexanes (GBCH) were determined. The results are consistent with the structure as predicted by molecular mechanics calculations. Thus, GBCH prefer the boat form as bicyclo[3.1.0]hexanes (BCH) do. GBCH finally assumes the chair form by excessive substitution.

In the field of conformational analysis the bicyclo[3.1.0]hexane ring system (BCH) has remained as one of the most interesting target. This is partly due to the fact that the bicyclic system is related to a class of natural product, thujane(1-isopropyl-4-methylbicyclo[3.1.0]hexane) and its derivatives. BCH has widely been investigated by several means. Thus, Hildebrandt et al.[2] reported the zero-point average structure of BCH as determined by electron diffraction and microwave spectroscopy. They observed the well-documented preference of boat conformation with the flap angle of φ= 70.6° and α=25.2° for the cyclopropane and cyclopentane moieties, respectively (Fig. 1). Another interesting feature is a distinctly short C1–C5 distance of 1.454 Å.[2]

An X-ray diffraction study of a solid derivative of BCH, N'-isopropylidenebicyclo[3.1.0]hexane-6-exo-carbohydrazide was attempted by Morris et al.[3] The flap angles φ and α were found to be 69.48° and 29.79°, respectively, while the C1–C5 distance was 1.474 Å in a good agreement with the spectroscopic results.

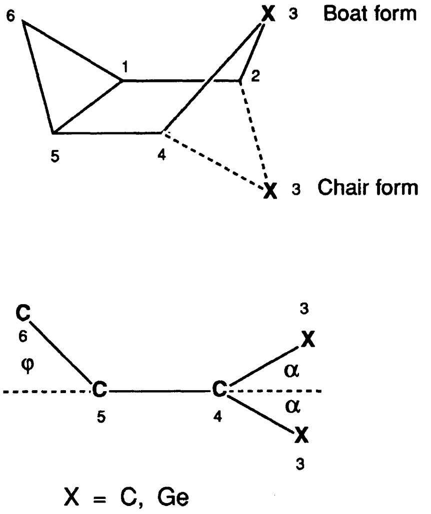

Fig. 1. Conformation of Bicyclo[3.1.0]hexane and 3-Germabicyclo[3.1.0]hexane.

The preferred boat conformation of bicyclo[3.1.0]hexane (**6C**) skeleton was observed to persist in such systems as 6-oxabicyclo[3.1.0]hexane (**7C**) or 6-thiabicyclo[3.1.0]hexane.

The five-membered ring is, however, flexible, and an early X-ray study of 3,3-diethyl-6,6-diphenyl-1-azabicyclo[3.1.0]hexane revealed the chair conformation, which certainly is due to the presence of bulky endo substituent at C3.[4] A similar conclusion was drawn from the kinetic and spectroscopic study of 3-substituted BCH.[5]

In our extensive investigation on the structure of germacycloalkanes, one of the most interesting findings is the flattening of germacyclohexane (**1G**) around germanium. This effect causes the difference between axial and equatorial environment much less significant as compared with the case in cyclohexane (**1C**). Thus, the conformational energy of a methyl group of 1-methylgermacyclohexane (**2G**) is 0.2 kcal in favor of the axial conformer,[6] which is in a sharp contrast with the well-documented conformational energy of a methyl group in methylcyclohexane (**2C**).[7]

The effect of germanium is also remarkable in five-membered rings. We proposed that for germacyclopentane (**4G**), the symmetric (as regard to the position of germanium) twist form is the most stable in contrast to cyclopentane (**4C**) where the envelop and twist forms have much the same energy.[8] Thus, the comparative study of carbocycles vs. germacycles has so far been effective in elucidating the fundamental feature of stereochemistry of organogermanium compounds.

In respect to preference of a boat form in BCH, the structure of 3-germabicyclo[3.1.0]hexane (**6G**) will be particularly interesting. Thus, the prolonged C–Ge bond length will reduce the bowsprit-flagpole type interaction in the boat form and further favor the boat form **b-6G**, while a bulky endo 3-substituent will disfavor the boat form of 3-germabicyclo[3.1.0]hexane ring system (GBCH). It will be interesting to find out the steric requirement for preferred boat conformation for BCH and GBCH, respectively. In this study we describe the structure of **6G** and other GBCH based on the molecular mechanics calculations (MM2) and examine their

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^{73}Ge and ^{13}C NMR spectra in the light of the calculated structure. MM2 calculations were carried out for a variety of BCH and GBCH for comparison. The structures of compounds discussed in this paper are listed below (Chart 1).

Results and Discussion

Steric Energy Based on Molecular Mechanics Calculations. The steric energy and its component energies for a variety of BCH and GBCH are listed 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}), tortional energy (E_t), van der Waals energy, which is subdivided into the energy associated with 1,4-interaction ($E_{1,4}$) and that with other interaction (E_{other}), and dipole/dipole interaction energy (E_{di}).

It was reported that **b-6C** is favored by 2.5 kcal over the chair form of **c-6C**.[9] Our calculations (MM2) give a similar difference (2.59 kcal). Most of the difference is originated from the difference in E_t (2.43 kcal) which has long been accepted for the preference of **b-6C** over **c-6C** because of minimized eclipsing effect.

Cyclohexanes and Germacyclohexanes

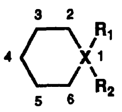
Compound	X	R_1	R_2
1C	C	H	H
2C	C	Me	H
3C	C	Me	Me
1G	Ge	H	H
2G	Ge	Me	H
3G	Ge	Me	Me

Cyclopentanes and Germacyclopentanes

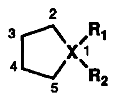
Compound	X	R_1	R_2
4C	C	H	H
5C	C	Me	Me
4G	Ge	H	H
5G	Ge	Me	Me

Bicyclo[3.1.0]hexanes and 3-Germabicyclo[3.1.0]hexanes

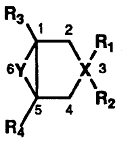
Compound	X	Y	R_1	R_2	R_3	R_4
6C	C	C	H	H	H	H
7C	C	O	H	H	H	H
8C	C	C	Me	Me	H	H
9C	C	C	Et	Et	H	H
10C	C	C	Et	Et	Me	H
11C	C	C	Et	Et	Me	Me
12C	C	C	Ph	Ph	H	H
13C	C	O	Me	Me	H	H
14C	C	O	Ph	Ph	H	H
6G	Ge	C	H	H	H	H
7G	Ge	O	H	H	H	H
8G	Ge	C	Me	Me	H	H
9G	Ge	C	Et	Et	H	H
10G	Ge	C	Et	Et	Me	H
11G	Ge	C	Et	Et	Me	Me
12G	Ge	C	Ph	Ph	H	H
13G	Ge	O	Me	Me	H	H
14G	Ge	O	Ph	Ph	H	H



X=C 1C-3C
X=Ge 1G-3G



4C.5C
4G,5G



6C-14C
6G-14G

Chart 1.

It is expected that an endo-methyl group in 3,3-dimethylbicyclo[3.1.0]hexane (**8C**) will increase the steric energy of boat form of BCH to a considerable extent. In fact the steric energy of the chair form of **c-8C** is now by 1.05 kcal mol^{-1} smaller than that of **b-8C**. It is indicated that **c-8C** has considerably larger E_b (ca. 0.7 kcal). The increase is compensated by the combination of favorable E_t (0.89 kcal) and E_{sb} (0.23 kcal).

For 3,3-diethylbicyclo[3.1.0]hexane (**9C**), the steric energy difference between **b-9C** and **c-9C** further increases in favor of the latter which is now close to ca. 3 kcal mol^{-1}. The difference further increases for 3,3-diethyl-1-methylbicyclo[3.1.0]hexane (**10C**) and 3,3-diethyl-1,5-dimethylbicyclo[3.1.0]hexane (**11C**). A methyl group at C-1(5) position seems to disfavor the boat form.

The results of molecular mechanics calculations for BCH can be dependable in view of the previous results.[9] On the other hand, the reliability of MM2 calculations of GBCH exclusively depends on whether the parameters necessary to treat germylcyclopropane moiety are appropriate or not. These parameters are not included in the set proposed by Ouellette[10] nor that by Allinger.[11] The strategy taken by us to overcome this situation will be described in the Experimental section.

The preference of the boat form is also indicated for GBCH. Thus, the difference of steric energy between **b-6G** and **c-6G** is 1.49 kcal mol^{-1} which is ca. 1 kcal less than that for **6C**. This smaller difference in total steric energy is partly due to the 1,4-interaction term ($E_{1,4}$). As is expected, $E_{1,4}$ for **c-6G** is smaller by 0.31 kcal than that for **b-6G** while that for **c-6C** is larger than that for **b-6C** by 0.21 kcal. The difference in the tortion term between **b-6G** and **c-6G** is as large as 2.59 kcal mol^{-1}, which is very close to that observed for **6C**.

As expected, the boat form is preferable also for 3,3-dimethyl-3-germabicyclo[3.1.0]hexane (**8G**) and 3,3-diethyl-3-germabicyclo[3.1.0]hexane (**9G**) though the difference is smaller as the number and size of the substituent increase. The steric energy for the boat and chair forms of 3,3-diethyl-1-methyl-3-germabicyclo[3.1.0]hexane (**b-10G** and **c-10G**) is nearly equal, and finally, the chair is preferable for 3,3-diethyl-1,5-dimethyl-3-germabicyclo[3.1.0]hexane (**11G**) by 0.38 kcal mol^{-1}. The difference is small in comparison with the preference of **c-11C** over **b-11C** which is as large as 3 kcal mol^{-1}. The result is significant since this calculation is supported by NMR data described later.

Structure Based on Molecular Mechanics Calculations. The optimized structure of all BCH and GBCH is symmetric with essentially planar C1–C2–C4–C5 moiety. There is a possibility that the cyclopentane/germacyclopentane moiety is a twist form. Input structures for **6C** and **6G** with a twist five-membered ring ended in **c-6C** and **b-6G**, respectively, to indicate that the five-membered ring is forced to be symmetric in BCH and GBCH. The structural parameters of BCH

Table 1. MM2 Component Steric Energies[a)] of Bicyclo[3.1.0]hexanes and 3-Germabicyclo[3.1.0]hexanes (in kcal mol^{-1} : 1 cal=4.18 J)

Compound[b)]	E_s	E_c	E_b	E_{sb}	E_t	$E_{1,4}$	E_{other}	E_{di}
b-6C	17.58	0.53	6.32	−0.43	9.42	1.95	−0.23	0.03
c-6C	20.17	0.55	6.53	−0.50	11.85	2.16	−0.44	0.03
b-8C	22.16	0.92	6.43	−0.27	12.66	3.00	−0.59	0.03
c-8C	21.11	0.85	7.16	−0.50	11.87	3.09	−1.39	0.03
b-9C	30.91	1.64	9.63	−0.07	14.55	4.64	0.48	0.03
c-9C	28.06	1.37	9.68	−0.39	13.80	5.05	−1.49	0.03
b-10C	35.09	2.27	10.46	−0.01	15.92	5.68	0.73	0.03
c-10C	30.12	1.72	10.57	−0.39	14.05	5.68	−1.55	0.03
b-11C	31.49	1.76	8.62	0.03	16.49	5.08	−0.57	0.08
c-11C	28.47	1.48	8.65	−0.18	15.86	5.40	−2.81	0.08
b-6G	19.03	0.65	8.01	−0.32	9.98	0.62	0.06	0.03
c-6G	20.52	0.73	7.75	−0.35	12.44	0.31	−0.39	0.02
b-8G	19.01	0.68	7.68	−0.31	12.35	−0.26	−1.16	0.02
c-8G	19.49	0.84	8.48	−0.38	12.68	−0.45	−1.69	0.02
b-9G	21.07	0.76	8.43	−0.25	12.82	1.54	−2.26	0.03
c-9G	21.46	0.91	9.45	−0.33	12.86	1.37	−2.82	0.02
b-10G	20.73	0.80	7.45	−0.20	13.70	1.84	−2.90	0.04
c-10G	20.57	0.94	8.84	−0.27	13.22	1.66	−3.87	0.04
b-11G	21.47	0.97	7.20	−0.13	14.62	2.08	−3.35	0.08
c-11G	21.08	1.14	8.65	−0.17	13.95	1.88	−4.46	0.08

a) For definition of each component steric energies, see text. b) For definition of abbreviation of compounds, see text.

Table 2. Structures of Bicyclo[3.1.0]hexanes and 3-Germabicyclo[3.1.0]hexanes[a)]

Compound	r_{12} (r_{45})	r_{23} (r_{34})	r_{15}	r_{16} (r_{56})	θ_{512} (θ_{154})	θ_{123} (θ_{543})	θ_{234}	θ_{615} (θ_{651})	θ_{165}	φ_{6123} φ_{6543}	φ_{1234} φ_{5432}	φ_{2154}	φ_{5123} φ_{2154}
	Å	Å	Å	Å	deg	deg	deg	deg	deg	deg	deg	deg	deg
b-6C	1.524	1.540	1.511	1.511	107.3	106.3	103.5	60.0	60.0	46.1	29.4	0.0	18.6
c-6C	1.525	1.539	1.517	1.510	107.3	104.6	104.0	59.8	60.3	85.4	33.7	0.0	20.9
b-8C	1.523	1.548	1.509	1.510	107.7	108.9	103.5	60.0	60.0	53.3	18.1	0.0	11.6
c-8C	1.525	1.545	1.518	1.509	106.9	104.7	102.3	59.8	60.4	77.1	36.3	0.0	22.8
b-9C	1.525	1.563	1.507	1.508	107.2	110.1	101.3	60.0	59.9	52.4	18.6	0.4	12.5
c-9C	1.525	1.547	1.518	1.509	106.5	104.8	100.1	59.8	60.4	90.0	39.7	0.8	25.9
b-10C	1.522	1.551	1.505	1.508	107.8	110.1	101.5	60.3	60.0	53.9	17.9	0.5	11.4
	1.524	1.564		1.513	106.9	110.2		60.0		52.3	18.3		12.3
c-10C	1.524	1.547	1.515	1.509	107.0	105.5	100.7	60.0	60.2	87.7	36.5	0.5	23.1
	1.525	1.557		1.512	106.4	105.5		59.8		87.9	37.0		23.9
b-11C	1.524	1.563	1.505	1.510	107.4	110.0	101.5	60.1	59.8	52.1	18.2	0.2	12.0
c-11C	1.525	1.558	1.515	1.511	106.6	106.0	101.0	59.9	60.2	85.9	35.0	1.1	21.6
b-6G	1.530	1.943	1.523	1.514	114.6	106.7	92.1	59.8	60.4	52.1	20.7	0.0	15.6
c-6G	1.530	1.940	1.529	1.511	115.1	103.7	93.5	59.6	60.8	86.8	26.4	0.0	19.6
b-8G	1.530	1.941	1.524	1.513	114.9	106.7	92.9	59.8	60.5	53.6	37.5	0.0	13.2
c-8G	1.531	1.938	1.532	1.511	114.8	102.4	93.3	59.5	60.9	89.9	30.8	0.0	22.8
b-9G	1.530	1.942	1.524	1.513	114.9	107.0	92.7	59.8	60.5	55.3	16.7	0.0	12.5
c-9G	1.531	1.938	1.532	1.511	114.6	102.5	92.8	59.6	60.9	90.4	31.5	0.0	23.4
b-10G	1.530	1.942	1.522	1.512	115.7	106.6	92.9	59.9	60.4	55.8	16.4	0.1	12.5
	1.530	1.943		1.515	114.6	107.0		59.7		55.3	16.5		12.4
c-10G	1.530	1.938	1.531	1.510	115.1	102.0	92.8	59.7	60.8	91.4	32.3	0.0	23.9
	1.531	1.939		1.514	114.3	102.3		59.5		90.9	32.4		23.4
b-11G	1.531	1.941	1.525	1.514	114.8	107.1	92.7	59.8	60.5	55.2	17.0	0.2	12.7
c-11G	1.532	1.936	1.534	1.512	114.5	102.3	92.6	59.5	60.9	91.5	32.9	0.3	24.4

a) The difinition of the structural parameters are as follows: r_{12} is the distance between atom 1 and atom 2 in Å, θ_{123} is the bond angle atom 1–atom 2–atom 3 in degrees and φ_{1234} is the tortion angle in degrees defined by the atom 1–atom 2–atom 3–atom 4.

and GBCH estimated by MM2 calculations are listed in Table 2.

The bond length and bond angle for a variety of BCH are quite similar for all compounds investigated regardless of the type and number of the substituents or whether the ring is a chair or a boat. The short C1–C5 bond length previously reported for BCH is not reproduced by MM2 calculations. Much the same is true for GBCH. For BCH the length is in the range of 1.505—1.518 Å and for GBCH it is 1.523—1.534 Å, which is not very far from the normal C–C bond length.

The dihedral angles as conventionally defined or the flap angles φ and α as defined in Fig. 1, which can be variable depending on the size of the ring substituent(s), have been accepted as one of the characteristics of BCH. The flap angles φ and α for BCH and GBCH estimated from the MM2 optimized structure are summarized in Table 3. In Table 3, data for **4C**, 1,1-dimethylcyclopentane (symmetric form; **5C**), **4G** and 1,1-dimethylgermacyclopentane (symmetric form; **5G**) are included for the sake of reference for α.

One flap angle φ is not sensitive to substitution at C3-(Ge3) or C1(5) whether the compound is in a boat or in a chair conformation. φ is generally larger for GBCH where the bowsprit–flagpole interaction is smaller. The difference between BCH and GBCH is ca 4—5° both for a boat or a chair.

The other flap angle α of **5C** is smaller than that of **4C** by 7.4° to indicate that α is sensitive to *gem*-dimethyl substitution at C1 (for definition, see the structures) while these of **4G** and **5G** are essentially identical to indicate that the germacyclopentanes are not sensitive to the same substitution. A similarly large change in α takes place in the boat form of BCH. Thus, the *gem*-dimethyl substitution at C3 substantially reduces α, from 29.6° (**b-6C**) to 18.0° (**b-8C**). This substantial flattening will accompany the corresponding increase of total steric energy of **8C**, making **c-8C** more stable than **b-8C**. The same debate can be applied to the **9C–11C** pair. On the other hand, the *gem*-dimethyl substitution at C3 will not change α to any significant extent for the chair form.

In contrast to this, as is indicated by the **b-6G–b-8G** pair, the *gem*-dimethyl substitution reduces α of GBCH in a boat form only by 3° to indicate the bowsprit–flagpole interaction is not very large in the boat form of GBCH. Interestingly, in the chair forms of both BCH and GBCH, the *gem*-dimethyl substitution does not cause essentially any change of α to indicate that the substitution does not cause steric hindrance here.

Rees and Whittaker[12] estimated the flap angles of a variety of thujanes and proposed that 1-methyl group will distort the five membered ring because of the interaction between the 1-methyl group and C2 hydrogen atoms. According to our calculation the five-membered rings of all of BCH and GBCH are not seriously distorted.

The flap angle α is generally susceptible to substitution at C3 and can be a good measure of conformation of BCH and GBCH. The available data are in a good agreement with the prediction by MM2 calculations.

^{13}C NMR Spectra. ^{13}C and ^{73}Ge NMR chemical shifts of BCH and GBCH are listed in Table 4.

No ^{13}C NMR data are available for **8C–11C** and hence it is impossible to compare these with the corresponding **8G–11G**. The assignment for **8G**, **9G**, and **11G** was based on the off-resonance decoupling and J-modulated spin-echo technique.

The most characteristic feature of ^{13}C resonances of **6C**[12] is the high field signals of cyclopropyl carbon nuclei (C6 at δ=5.8 and C1,5 at δ=16.7). It will be interesting to compare the data for **6G** with these of **6C**. The preparation of **6G** was, however, difficult because of the labile Ge–H bonds. Hence, the C6 chemical shift of **6G** is estimated as below.

It is reported that the C6 resonances of 3-methyl-*cis*-bicyclo[3.1.0]hexan-3-ol and 3-ethyl-*cis*-bicyclo-[3.1.0]hexan-3-ol are δ=11.9 and 11.6, respectively.[12] In aliphatic systems the effects of substituents on remote carbon nuclei do not depend on the nature of substituents to any significant extent.[13] Hence the two compounds can be used as the model of the effect of *gem*-dimethyl or *gem*-diethyl substitution on C6 shifts of **8G** and **9G**. The observed C6 resonance of **8G** (and **9G**; δ=13.12) is very close to the values of the model compounds to indicate that the high field shift of carbon nuclei of cyclopropane moiety also prevails in GBCH.

Much the same is true for C1,5. The C1,5 chemical shifts of the two model compounds are 17.2 and 17.0, respectively which are close to the values for **8G** (δ=18.62) and **9G** (δ=18.50).

The effect of Me1 on C6 resonance as estimated from previous examples is ca. 6 ppm to downfield. Hence the signal at 20.37 (for **10G**) was assigned to C6. The signal of **10G** at δ=20.09 was assigned to C2 based on the chemical shift and splitting pattern at off-resonance decoupling condition. The C6 resonance of **11G** at δ=26.27, by ca. 6 ppm downfield further is in line with this assignment.

The Me1,5 resonance of **11G** is 3.45 ppm upfield as compared with Me1,5 resonance of **10G**. In **11G** the two methyl groups are syn-clinal and are susceptible to γ-effect. It must be pointed out, however, that if **11G** assumes a chair as is indicated by MM2, an interaction will be involved between Ge3 moiety and Me1,5 which seems the case as far as ^{73}Ge resonance is concerned. The carbon shift is not straightforward in this regard. A piece of observation which may favor the chair form of **11G** is a small but distinct upfield shift of side-chain methylene resonance as compared with these of **9G** and **10G** which is again due to the 1,3-diaxial type interaction with C1,5 methyl groups.

The data for 3,3-diphenyl-3-germabicyclo[3.1.0]hex-

Table 3. Flap Angles[a)] of Bicyclo[3.1.0]hexanes and 3-Germabicyclo[3.1.0]hexanes

Molecule	φ	α	Molecule	φ	α
4C	—	46.0			
5C	—	38.6			
b-6C	67.2	29.6	**c-6C**	67.3	34.2
	70.6	25.2[b)]			
	63.0	38.0[c)]			
b-8C	66.0	18.0	**c-8C**	66.9	36.8
b-9C	64.9	18.2	**c-9C**	66.2	39.8
b-10C	65.0	17.8	**c-10C**	66.6	37.0
b-11C	64.8	17.9	**c-11C**	66.7	35.5
4G	—	40.3			
5G	—	40.7			
b-6G	69.5	21.8	**c-6G**	71.9	33.4
b-8G	69.5	18.5	**c-8G**	71.5	33.4
b-9G	69.5	17.7	**c-9G**	71.3	33.4
b-10G	69.6	17.4	**c-10G**	71.0	35.1
b-11G	69.2	18.0	**c-11G**	70.6	35.5

a) In degree (°). For definition, see Fig. 1. b) Experimental data (Ref. 2 electron diffraction) c) Experimental data (microwave spectroscopy) taken from R. L. Cook and T. B. Malloy, Jr., *J. Am. Chem. Soc.*, **96**, 1703 (1974).

Table 4. ^{73}Ge[a)] and ^{13}C[b)] NMR Chemical Shifts of Bicyclo[3.1.0]hexane and 3-Germabicyclo[3.1.0]hexanes

Compound	X3	C1	C2	C4	C5	C6	Me1 (Me5)	Me3	Et-3		Ph			
									CH_2	CH_3	ipso-	*o*-	*m*-	*p*-
	(^{13}C)													
6C[c)]	20.2	16.7	27.6	27.6	16.9	5.8								
	(^{73}Ge)													
8G	57	18.62	17.36	17.36	18.62	13.12		−0.75						
								0.61						
9G	76	18.50	13.26	13.26	18.50	13.12			6.93	9.59				
									8.25	10.03				
10G	82	25.97	20.09	15.09	26.84	20.37	27.08		7.04	9.59				
									8.15	9.97				
11G	46	29.42	22.98	22.98	29.42	26.27	23.20		6.63	9.63				
									7.51	9.99				
12G	d)	18.41	15.88	15.88	18.41	12.61					137.73	134.99	128.62	129.17
											137.73	134.96	128.86	129.56
13G[e)]	d)	58.01	16.96	16.96	58.01			−0.22						
								−1.89						
14G	d)	58.87	16.60	16.60	58.87						137.73	134.79	128.62	129.43
											137.73	134.96	128.86	129.56

a) In ppm relative to external $GeMe_4$ (δ=0). b) In ppm relative to internal $SiMe_4$ (δ=0). c) Data taken from Ref. 12 d) The signal could not be observed. e) Data taken from Ref. 8.

ane (**12G**) are very similar to those for **8G**. The ^{13}C chemical shifts of 3,3-dimethyl-3-germa-6-oxabicyclo[3.1.0]hexane (**13G**) and 3,3-diphenyl-3-germa-6-oxabicyclo[3.1.0]hexane (**14G**) are consistent with the structure. The chemical shift difference, small but distinct, of *endo* and *exo* methyl moiety (1.67 ppm) is interesting. The corresponding difference for two methyls of **8G** is 1.36 ppm and both cases indicate the presence of the bowsprit–flagpole interaction. The chemical shift difference of two methyls of 1,1-dimethyl-1-germacyclopentan-3-ol is only 0.4 ppm.[8)]

So far, C-13 chemical shifts of GBCH are not inconsistent with the prediction by MM2 to the effect that only **11G** has a chair form.

^{73}Ge NMR Spectra. In view of the general difficulty to observe ^{73}Ge signals, and particularly in view of fairly large molecular weights, it is rather surprising that we could observe ^{73}Ge resonances of **8G**–**11G** though the half-widths are a little larger than those of **1G**–**5G**. We have observed that the ^{73}Ge chemical shifts of *gem*-dimethylgermyl moiety are sensitive to ring size. Thus that of **3G** (−13.7 ppm relative to $GeMe_4$)[14)] and **5G** (40.0 ppm relative to $GeMe_4$)[8)] differs by 53.7 ppm.

For accessing the effect of adjoining cyclopropane ring, and its relative orientation to the germacyclopentane moiety (i.e., boat or chair) upon ^{73}Ge chemical shifts of GBCH, the shift for 1,1-dimethylgermacyclopentane (**5G**) (δ=40) and that for 1,1-dimethylgermacyclopent-3-ene (δ=37) will be the reference. From the chemical shift for **8G** (δ=57), it is assumed that the effect of fused (possibly *cis*-fused) cyclopropane is ca. 17 ppm. The effect of 3-ethyl groups causes an additional downfield shift of 19 ppm (**9G**; δ=76). This is a reasonable value in view of the shifts for 1,1,3-trimethyl-1-germacyclopent-3-ene (δ=44.6) and 1,1-diethyl-3-methyl-1-germacyclopent-3-ene (δ=70.9).[8)] The shift (δ=82) observed for **10G** is along this line, and compounds **8G**–**10G** seem to have the same (thus boat) structure.

The shift (δ=46) observed for **11G** is anomalous since a similar shift with that of **10G** is expected. The only possible explanation is that the compound has a chair structure where the γ-effect is expected because of the interaction between germanium moiety and two methyl groups at C1,5.

In conclusion, MM2 calculations indicate that GBCH remains boat until excessive substitution disfavors the boat form. This is in a sharp contrast to the case of BCH where an *endo*-substituent at C3 makes the chair more favorable. The NMR data are in agreement with the above argument. It must be pointed out that the discussion is not conclusive, and that a more direct experimental determination of the structure of **8G** and **11G** should be attempted. Research along this line is being carried out in this laboratory.

Experimental

Molecular Mechanics Calculations. Molecular mechanics calculations were carried out with the aid of MM2 program. Two proposed parameter sets for germanium, one by Ouellette[10)] and the other by Allinger[11)] were compared. Since the relative magnitude of steric energies is not changed, and so we used Ouellette's parameters as was the case with our previous study.

The set lacks some parameters required for the germylcyclopropane moiety. The tortional parameters required are: Ge–C–Cc–Cc, Ge–C–Cc–H, C–Ge–C–Cc, H–Ge–C–Cc, and Ge–C–Cc–C unit where Cc stands for a cyclopropyl carbon atom. We assumed that both V_1 and V_2 of these are zero and V_3 are equal to the corresponding value for the compounds without germanium. Thus, V_3 of C–Ge–C–Cc term is equal to that of C–C–C–Cc. Another parameter to be added is Cc–C–Ge term, which was assumed equal to Cc–C–C.

We have attempted several calculations with slightly changed additional parameters mentioned above. It was found that the relative magnitude of steric energy and its components do not change with different parameters to indicate that the discussion based on MM2 calculations with our parameters is acceptable as far as relative magnitude rather than the absolute value is discussed.

NMR Spectra. 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.

Preparation of 3-Germabicyclo[3.1.0]hexane and Related Compounds. The preparation of 3-germabicyclo[3.1.0]hexanes were previously reported.[15)]

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