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# NMR Spectra of Organogermanium Compounds. IX.[1] NMR Spectra and Molecular Mechanics Calculations of 1-*t*-Butylgermacyclohexanes

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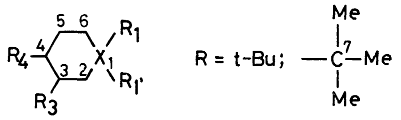
A variety of *t*-butylgermacyclohexanes was prepared and their $^{13}$C and $^{73}$Ge (when possible) NMR spectra were determined. It was estimated that the conformational energy of a *t*-butyl group bonded to germanium is about 1.3 kcal mol$^{-1}$ by NMR data though the molecular mechanics calculations gave variable results depending on the parameter for germanium used; 0.33 kcal mol$^{-1}$ by Allinger's parameter while 1.23 kcal mol$^{-1}$ by Ouellette's parameter. The origin of this discrepancy was discussed. The molecular orbital calculations (MNDO) gave an intermediate value (0.60 kcal mol$^{-1}$).

In the previous communications we have reported the preparation and structural study of 1-methyl-[2] and 1-phenyl-[3] germacyclohexanes based on $^{13}$C and $^{73}$Ge NMR, molecular mechanics calculations (MM2) and molecular orbital calulations (MNDO). It was found that the conformational energy of a methyl group bonded to germanium is as small as ca. −0.2 kcal mol$^{-1}$ (i.e., in favor of the axial conformation; 1 cal=4.184 J)[2] while that of a phenyl group is also small (ca. 0 kcal mol$^{-1}$).[3] As an extension of this investigation, a stereochemical study of germacyclohexanes with a *t*-butyl group bonded to germanium will be of particular interest in relation to that of corresponding *t*-butylcyclohexanes.

Of *t*-butylcyclohexanes, the structure of *cis*-1,4-di-*t*-butylcyclohexane (hereafter abbreviated as *cis*-**10C**: see the structure) was once a target of extensive structural studies by various authors. Thus, it was reported that a cyclohexane ring tends to deform from a chair form to a nonchair when a *t*-butyl group is forced to be axial in a chair form. Evidently by taking a nonchair, the bulky *t*-butyl group can be either equatorial or pseudo-axial.[4—6)]



| | R₁ | R₁′ | R₃ | R₄ |
|---|---|---|---|---|
| **1G** | H | H | H | H |
| **2G** | Me | H | H | H |
| **3G** | H | H | Me | H |
| **4G** | H | H | H | Me |
| **5G** | Me | H | H | Me |
| **6G** | *t*-Bu | H | H | H |
| **7G** | H | H | H | *t*-Bu |
| **8G** | *t*-Bu | H | Me | H |
| **9G** | *t*-Bu | H | H | Me |
| **10G** | *t*-Bu | H | H | *t*-Bu |
| **6G′** | *t*-Bu | Cl | H | H |
| **7G′** | Cl | Cl | H | *t*-Bu |
| **8G′** | *t*-Bu | Cl | Me | H |
| **9G′** | *t*-Bu | Cl | H | Me |
| **10G′** | *t*-Bu | Cl | H | *t*-Bu |

C: Cyclohexane (X=C). G: Germacyclohexane (X=Ge).

Schubert et al.[7] reported that at 110 °C and in the vapor phase *cis*-**10C** exists as a mixture of a chair and a nonchair form with a most probable mixture of about one third chair and two thirds nonchair forms.

Remijnse et al.[8] determined $^1$H NMR sepectra of this compound and based on the values of vicinal coupling constants they concluded that the non-chair (most stable twist) form with two pseudo-equatorial *t*-butyl groups is prevailing in line with the report by van Bekkum et al.[5]

From the advent of molecular mechanics (or force field) calculations, the conformation of *t*-butylcyclohexanes was frequently investigated. van be Graaf et al.[9] concluded from the comparison with available experimental data that both force field proposed by Allinger et al. and by Schleyer et al. gave results which support previous evidences that both *cis*-**10C** and *trans*-1,2-di-*t*-butylcyclohexane exist as conformational mixtures. They also proposed that the best conformational energy for a *t*-butyl group in cyclohexanes is 4.73 kcal mol$^{-1}$. This value was experimentally confirmed by Manoharan and Eliel[10] who analyzed the solution conformation of *cis*-4-*t*-butyl-1-phenyl-*r*-1-(*N*-piperidyl)cyclohexane hydrochloride. An ab initio calculations (STO-3G) was also attempted to indicate that the boat form is most stable for such a compound as *cis*-**10C**.[11]

Thus, all the available experimental and theoretical approaches seem to indicate that an axial *t*-butyl group is extremely unfavorable due to the excessive 1,3-diaxial repulsion between the substituent and the axial hydrogen at C-3,5, and that this repulsion can be relieved by assuming otherwise unfavorable twist-boat or boat form. In other words, 1,3-diaxial interaction between a *t*-butyl group and axial H-3,5 is even larger than the increase of energy associated with a twist-boat.

In this connection it will be interesting to introduce a *t*-butyl group on the germanium atom of a germacyclohexane ring and to assess its conformational energy. Since the conformational energy of a phenyl group is small if bonded to germanium,[3] it is expected that that of a *t*-butyl group is also not very large mostly due to the enhanced C–Ge bond length. In other word, if the conformational energy of a *t*-butyl group is smaller than that associated with a twist-boat, a *t*-butyl group can be axial in germacyclohexanes. Then it can be expected that if a methyl or an even larger *t*-butyl group (an anchoring group) is introduced, the 1-*t*-butyl group may be axial in the *trans*-1,3-disubstituted and *cis*-1,4-disubstituted compounds. If such will be realized, this could be the first example of an axial *t*-butyl group bonded to a flexible cyclic system.

With these prospects in mind, we prepared a variety of 1-*t*-butylgermacyclohexanes, i.e., 1-*t*-butyl- (**6G**), 1-*t*-butyl-3-methyl- (**8G**), 1-*t*-butyl-4-methyl- (**9G**), and 1,4-di-*t*-butyl- (**10G**) germacyclohexanes. For the sake of reference, 4-*t*-butylgermacyclohexane (**7G**) was also prepared.

## Results and Discussion

**$^{13}$C Chemical Shifts.** In the previous studies, the $^{13}$C chemical shifts have extensively been used to assess the stereochemistry of germacyclohexanes. $^{13}$C chemical shifts of C-4 and Me-4 of *cis*-**5G** are essentially identical with those for *trans*-**5G** in which two methyls are necessarily equatorial (i.e., *trans*-**5Gee**). Thus, the conformation of *cis*-**5G** is exclusively 1-axial, 4-equatorial (**5Gae**), and any significant contribution of 1-equatorial, 4-axial (**5Gea**) should be denied since in the latter, the C-4 and Me-4 resonances should appear in a much higher field than those of *trans*-**5Gee**.[12]

Hence, it is expected that $^{13}$C and $^{73}$Ge NMR data are also useful for analyzing the stereochemistry of *t*-butylgermacyclohexanes. In Table 1, the $^{73}$Ge and $^{13}$C chemical shifts of germacyclohexanes **6G**—**10G** are tabulated. For the sake of reference, those for germacyclohexane (**1G**), 1-methyl- (**2G**), 3-methyl- (**3G**), 4-methyl- (**4G**), and 1,4-dimethyl- (**5G**) germacyclohexanes are also included.[2]

The assignment of $^{13}$C signals of *t*-butylgermacyclohexanes is more or less straightforward, based on the comparison with previous results and on the number of attached proton(s) as indicated by the INEPT experiment.

From the intensities of $^{13}$C signals, it was shown that the cis:trans ratio is ca. 1:1 for **8G** and ca. 7:3 for **9G**. The major component of **9G** exhibits its Me-4 signal in a high field (1.69 ppm) as compared with the minor one. This difference can be explained in terms of a contribution of *cis*-**9Gea** with an axial Me-4, or a twist boat form. The latter possibility is excluded in the light of the molecular mechanics calculations (vide infra). This assignment is consistent with other chemical shift values, e.g., C-4 (1.68 ppm higher than that for *trans*-**9G**(**9Gee**). A similar upfield shifts are observed for C-3 (1.45 ppm) and Me-3 (1.28 ppm) signals of one isomer of **8G**. This is again consistent with a contribution of *trans*-**8Gea** in which Me-3 is axial. Thus, a *t*-butyl group bonded to germanium and a methyl group bonded to carbon is conformationally of a comparable size in the sense that the equilibrium between an axial-*t*-butyl, equatorial-methyl isomer and an equatorial-*t*-butyl, axial–methyl isomer is not one-sided.

It seems now possible to make a rough estimation of the equilibrium between two invertmers of *trans*-**8G** and of *cis*-**9G**. If *trans*-**8G** remains, for instance, exclusively in *trans*-**8Gea**, the chemical shift difference at Me-3 between *trans*- and *cis*-**8G** should amount to 4.3 ppm (estimated from **2C**). The observed difference is 1.28 ppm which corresponds to the contribution of ca. 30% of **8Gea**. A similar estimation with other carbon chemical shifts indicates **8Gea** contributes ca. 30% in average. This in turn

Table 1. $^{73}$Ge[a] and $^{13}$C[b] NMR Chemical Shifts of *t*-Butylgermacyclohexanes (**1G**—**10G**)

| Compound | Ge-1 | C-2 | C-3 | C-4 | C-5 | C-6 | Me | *t*-Bu (q) | *t*-Bu (Me) |
|---|---|---|---|---|---|---|---|---|---|
| **1G**[c] | −131.2 | 9.32 | 26.78 | 29.80 | 26.78 | 9.32 | | | |
| **2G**[c] | −65.3 | 12.10 | 25.58 | 29.61 | 25.58 | 12.10 | −7.01 | | |
| **3G**[c] | −131.2 | 17.55 | 33.18 | 37.90 | 25.71 | 8.10 | 27.09 | | |
| **4G**[c] | −134.3 | 8.02 | 34.76 | 34.98 | 34.76 | 8.02 | 23.45 | | |
| *trans*-**5G**[c] | −61.5 | 11.76 | 34.81 | 35.27 | 34.81 | 11.76 | −5.77(1)<br>23.70(4) | | |
| *cis*-**5G**[c] | −73.4 | 10.84 | 33.51 | 35.19 | 33.51 | 10.84 | −7.83(1)<br>23.70(4) | | |
| **6G** | −27.8 | 9.44 | 26.60 | 30.34 | 26.60 | 9.44 | — | 20.79 | 28.68 |
| **7G** | −131.6 | 9.53 | 28.00 | 51.52 | 28.00 | 9.53 | — | 33.47 | 27.84 |
| *trans*-**8G** | −37.5[d] | 17.76 | 32.12 | 37.79 | 24.63 | 8.45 | 26.68 | 21.16 | 29.26 |
| *cis*-**8G** | −37.5[d] | 18.15 | 33.57 | 38.72 | 26.16 | 8.27 | 27.96 | 21.16 | 28.58 |
| *trans*-**9G** | −41.2[e] | 8.38 | 34.96 | 35.84 | 34.96 | 8.38 | 23.74 | 20.17 | 28.30 |
| *cis*-**9G** | −41.2[e] | 7.26 | 33.69 | 34.16 | 33.69 | 7.26 | 22.05 | 21.08 | 28.88 |
| *trans*-**10G** | | 10.01 | 28.38 | 52.54 | 28.38 | 10.01 | — | f)<br>f) | 28.72(1)<br>28.14(4) |
| *cis*-**10G** | | 10.18 | 27.74 | 51.96 | 27.74 | 10.18 | — | 21.65(1)<br>33.76(4) | 29.44(1)<br>27.99(4) |

a) In ppm relative to external $GeMe_4$ ($\delta=0$). b) In ppm relative to internal $SiMe_4$ ($\delta=0$). c) Data taken from Ref. 2a. d, e) Unresolved. f) Unidentified.

corresphonds to the energy difference of ca. 0.5 kcal mol$^{-1}$ between **8Gae** and **8Gea** in favor of the former. If a simple additivity of conformational energy is assumed, this energy difference should correspond to the difference of conformational energy of a methyl group bonded to carbon atom (whether the ring is a cyclohexane or a germacyclohexane will not cause much difference) minus that of a *t*-butyl group bonded to germanium. Thus, the conformational energy of a *t*-butyl group bonded to germanium is ca. 1.3 kcal mol$^{-1}$ (=1.8−0.5 kcal mol$^{-1}$).

It must be added that a much the same conclusion can be drawn as for the conformational energy of a *t*-butyl group from the similar consideration of chemical shifts of **9G**.

Variable temperature study of $^{13}$C NMR spectra of ***9G*** is helpful. Unfortunately, as was the case with other germacyclohexanes,[2] the ring reversal could not be frozen at such a low temperature as −120 °C. Nevertheless, it is evident that C-2,6, C-4, and Me-4 of the major component (cis isomer) showed a much enhanced temperature shifts to lowfield as compared with other carbon nuclei. Thus, these three signals of cis isomer shift to downfield as the temperature lowers from ambient temperature to −120 °C. This can be explained by an increasing contribution of more stable conformer of *cis*-**9G**(**9Gae**) as the temperature lowers. A rough estimation based on the equation $\Delta G° = -RT\ln K$ indicates that the population of more stable isomer (in this case **9Gae**) will increase by ca. 10% as the temperature lowers by 150 °C.

Since in cyclohexanes an axial methyl group will cause an upfield shift of ca. 3.7 ppm at C-2, a 10% increase of **9Gae** conformer will cause a downfield shift of 0.4 ppm at most, which is larger than the observed shift at C-2 (ca. 1 ppm). Considering that, however, an involvement of a *t*-butyl group will make the comparison more difficult (vide infra), the agreement may the regarded reasonable, which in turn supports our discussion.

If the conformational energy of a *t*-butyl group is as large as 1.3 kcal mol$^{-1}$, **6G** should exist mostly in **6Ge**. Hence, the chemical shift difference between **6G** and **1G** should give the substituent chemical shift (SCS) of an equatorial *t*-butyl group in germacyclohexanes. SCS of an equatorial *t*-butyl group can be estimated by use of different compounds, e.g., as the chemical shift difference between *cis*-**8G** (exclusively **8Gee**) and **3G**, or *trans*-**9G** (exclusively **9Gee**) and **4G**, respectively. The estimated values are listed in Table 2 together with the SCS of an equatorial *t*-butyl group in cyclohexanes, i.e., the chemical shift difference between **6C** and **1C**.[13] The SCS values are uniformly small and somewhat scattering, indicating that these values are not very effective as a means of assignment and assessment of stereochemistry of germacyclohexanes in a sharp contrast with the substituent effect of a methyl group.

This situation will make the assignment of $^{13}$C resonances of **10G** isomers more difficult. From the $^{13}$C intensities, the ratio of two isomers is ca. 3 : 1. By subtracting chemical shifts of **7G** from the corresponding shifts of each isomer, two sets of substituent effects of a *t*-butyl group can be estimated and summarized in Table 2. The one (minor component) which gives substituent effects closer to SCS of an equatorial *t*-butyl group is assigned to *trans*-**10G** (necessarily **10Gee**; i.e., the one with and equatorial *t*-butyl group on germanium). It must be admitted that this stereochemical assignment is not free from ambiguity, and an alternative assignment is equally justifiable. This situation, on the other hand, excludes a contribution of a boat or a twist boat form where a large upfield shift should be observed.[13]

**$^{73}$Ge Chemical Shifts.** In the case of 1-methylgermacyclohexanes,[2] the $^{73}$Ge chemical shifts is very sensitive to the stereochemistry of a methyl group bonded to germanium. Thus, that of *cis*-**5G** (**5Gae**) is ca. 12 ppm upfield as compared with that of *trans*-**5G** (**5Gee**). Hence it is possible to estimate the ratio of equatorial and axial isomers of **2G** based on its $^{73}$Ge chemical shifts. It will be interesting to see if 1-*t*-butylgermacyclohexanes are also sensitive to the stereochemistry of the *t*-butyl group and can be a means to distinguish whether the molecule has an axial *t*-butyl group, or a twist form.

Unfortunately, however, due to the enhanced asymmetry of electric field gradient around the

Table 2. Substituent Chemical Shifts (SCS)[a] of an Equatorial *t*-Butyl Group in Germacyclohexanes

| Compds used for estimation | C-2,6 | C-3,5 | C-4 | Others |
|---|---|---|---|---|
| **6G–1G**[b] | +0.12 | −0.18 | +0.54 | |
| *cis*-**8Gee–3Ge** | +0.60(2)<br>+0.17(6) | +0.39(3)<br>+0.45(5) | +0.82 | +0.87 (Me-3) |
| *trans*-**9Gee–4Ge** | +0.36 | +0.20 | +0.86 | +0.29 (Me-4) |
| *trans*-**10Gee–7Ge** | +0.48 | +0.38 | +1.02 | +0.33 (*t*-Bu (q))<br>+0.30 (*t*-Bu (Me)) |
| *cis*-**10G–7Ge**[b] | +0.65 | −0.26 | +0.44 | |
| **6C–1C**[c] | +0.6 | +0.2 | −0.3 | |

a) For definition, see text. b) The conformation of the *t*-butyl group on germanium is not necessarily fully equatorial. c) Data taken from Ref. 12.

germanium nuclei together with the increased molecular weights, the half-width of $^{73}$Ge resonances of **8G** and **9G** was large (ca. 150 Hz or 30 ppm) and could not be resolved. Furthermore, no signal was recorded for **10G** although a reasonable concentration was employed.

Nevertheless, the chemical shift values are very revealing. For **8G** and **9G**, the center of signals are at ca. −38 ppm and −41 ppm, respectively, both are upfield to that of **6G** (−27.8 ppm). Since the substituent effect of Me-3 or Me-4 on $^{73}$Ge shifts is small if any, this upfield shift is accounted for by a contribution of an axial *t*-butyl group.

**Molecular Mechanics Calculations.** In our previous studies on 1-methylgermacyclohexanes,[2b] the conformational energy of a methyl group estimated by NMR chemical shifts are essentially identical with that estimated by molecular mechanics calculations. As has thoroughly been established, the conformational energy of a *t*-butyl group is as large as 4.9 kcal mol$^{-1}$ in cyclohexanes.[10] In germacyclohexanes, our estimation based on NMR chemical shifts of *t*-butylgermacyclohexanes **6G**—**9G** is about 1.3 kcal mol$^{-1}$. It is interesting to estimate the value by means of the molecular mechanics calculation. Another important point to be discussed is the possibility of deforming of *t*-butylgermacyclohexane ring from a chair into a nonchair (e.g., a twist boat).

Table 3. MM2 Component Steric Energies[a] of Germacyclohexanes and Corresponding Cyclohexanes

| Compounds[b,c] | | $E_s$ | $E_c$ | $E_b$ | $E_{sb}$ | $E_t$ | $E_{1,4}$ | $E_{\mathrm{other}}$ |
|---|---|---|---|---|---|---|---|---|
| **1G** | A | 6.11 | 0.38 | 1.68 | 0.14 | 1.24 | 3.69 | −1.02 |
| | O[d] | 5.72 | 0.40 | 1.88 | 0.14 | 1.27 | 3.15 | −1.14 |
| **2Ge** | A | 5.20 | 0.38 | 1.66 | 0.14 | 1.25 | 3.29 | −1.52 |
| | O[d] | 4.83 | 0.41 | 1.83 | 0.14 | 1.33 | 2.75 | −1.63 |
| **2Ga** | A | 4.95 | 0.38 | 1.67 | 0.14 | 1.24 | 3.30 | −1.79 |
| | O[d] | 4.61 | 0.40 | 1.85 | 0.14 | 1.38 | 2.73 | −1.88 |
| **6Ge** | A | 8.79 | 1.05 | 2.19 | 0.17 | 1.20 | 7.70 | −3.51 |
| | O | 7.08 | 0.95 | 2.26 | 0.18 | 1.31 | 6.02 | −3.64 |
| **6Ga** | A | 9.12 | 1.07 | 2.30 | 0.17 | 1.78 | 7.42 | −3.61 |
| | O | 8.31 | 1.01 | 2.04 | 0.18 | 2.32 | 5.64 | −3.48 |
| **9Gee** | A | 9.38 | 1.25 | 2.32 | 0.19 | 1.24 | 8.22 | −3.83 |
| | O | 7.64 | 1.15 | 2.38 | 0.20 | 1.35 | 6.54 | −3.99 |
| **9Gaa** | A | 11.03 | 1.23 | 2.99 | 0.25 | 2.61 | 8.08 | −4.13 |
| | O | 10.33 | 1.20 | 3.29 | 0.27 | 3.24 | 6.28 | −3.96 |
| **9Gea** | A | 10.57 | 1.22 | 2.77 | 0.25 | 2.10 | 8.33 | −4.09 |
| | O | 8.99 | 1.15 | 2.90 | 0.26 | 2.20 | 6.66 | −4.19 |
| **9Gae** | A | 9.68 | 1.26 | 2.44 | 0.20 | 1.81 | 7.93 | −3.96 |
| | O | 8.83 | 1.21 | 2.79 | 0.21 | 2.33 | 6.15 | −3.87 |
| **10Gee** | A | 16.72 | 2.45 | 4.12 | 0.43 | 3.01 | 10.04 | −3.34 |
| **10Gaa** | A | 21.03 | 2.33 | 6.90 | 0.57 | 4.98 | 10.63 | −4.38 |
| **10Gea** | A | 20.27 | 2.36 | 6.66 | 0.58 | 4.45 | 10.88 | −4.66 |
| **10Gae** | A | 16.97 | 2.48 | 4.33 | 0.44 | 3.51 | 9.69 | −3.47 |
| **1GT** | A | 9.94 | 0.42 | 2.52 | 0.17 | 3.30 | 4.48 | −1.23 |
| | O | 11.16 | 0.42 | 2.53 | 0.17 | 5.19 | 4.08 | −1.24 |
| **10GTaa** | A | 19.74 | 2.38 | 4.99 | 0.48 | 5.44 | 11.27 | −4.81 |
| | O | 19.78 | 2.31 | 4.85 | 0.49 | 7.51 | 9.41 | −4.79 |
| **10GTea** | A | 20.01 | 2.37 | 5.06 | 0.48 | 5.42 | 11.33 | −4.65 |
| | O | 20.06 | 2.29 | 4.94 | 0.49 | 7.50 | 9.47 | −4.64 |
| **1C**[d] | | 6.55 | 0.34 | 0.37 | 0.08 | 2.16 | 4.67 | −1.06 |
| **2Ce**[d] | | 6.89 | 0.45 | 0.47 | 0.11 | 2.14 | 5.20 | −1.47 |
| **2Ca**[d] | | 8.69 | 0.48 | 0.97 | 0.15 | 3.09 | 5.32 | −1.34 |
| **6Ce** | | 13.31 | 1.38 | 1.97 | 0.30 | 3.73 | 7.165 | −1.24 |
| **6Ca** | | 18.31 | 1.49 | 4.34 | 0.43 | 5.45 | 7.90 | −1.30 |
| **9Caa** | | 20.48 | 1.62 | 4.94 | 0.50 | 6.48 | 8.52 | −1.58 |
| **9Cea** | | 15.30 | 1.50 | 2.60 | 0.37 | 4.64 | 7.79 | −1.59 |
| **9Cae** | | 18.53 | 1.58 | 4.45 | 0.45 | 5.43 | 8.42 | −1.81 |
| **10Cee** | | 19.90 | 2.35 | 3.63 | 0.51 | 5.31 | 9.66 | −1.55 |
| **10Caa** | | 29.92 | 2.64 | 8.20 | 0.76 | 8.95 | 11.13 | −1.77 |
| **10Cea** | | 24.64 | 2.48 | 5.95 | 0.64 | 7.01 | 10.40 | −1.85 |
| **1CT** | | 11.91 | 0.43 | 0.74 | 0.12 | 5.59 | 5.89 | −0.86 |
| **10CTee** | | 19.74 | 2.38 | 4.99 | 0.48 | 5.44 | 11.26 | −1.85 |
| **10CTaa** | | 25.20 | 2.44 | 4.08 | 0.57 | 9.49 | 11.20 | −2.57 |
| **10CTea** | | 25.47 | 2.41 | 4.27 | 0.57 | 9.34 | 11.26 | −2.52 |

a) For definition of each component steric energies, see text. b) Small letters "e" and "a" represent equatorial and axial, respectively. Thus, **9Gea** is 1-equatorial, 4-axial isomer of **9G**. "T" stands for a twist boat structure. c) A: Allinger model, O: Ouellette model. d) Data taken from Ref. 2b.

It is expected that the conformational energy for a *t*-butyl group will considerably be reduced in germacyclohexanes as compared with that in cyclohexanes. At the same time, the energy difference between a chair form and a twist boat would also be reduced in germacyclohexanes. Then whether such a compound as *cis*-**10G** is a chair form or a twist boat will depend on the relative magnitude of two effects, i.e., a relief of 1,3-diaxial interaction by converting a chair form to a twist boat, and the increase of energy due to nonbonding interaction and other effects such as torsional term associated with a twist boat.

Molecular mechanics calculations were carried out for a variety of *t*-butylgermacyclohexanes using the MM2[14)] program. Parameters for germanium was taken from Allinger's compilations (hereafter Allinger model).[15)] The results are given in Table 3. In Table 3, not only the steric energy but also its component energies are listed for each compound. 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 steric energy difference between axial- and equatorial-**6G** is only 0.33 kcal mol$^{-1}$ in favor of the equatorial isomer. The discrepancy from the estimation based on NMR chemical shifts is significant. If this prediction is correct, a *t*-butyl group on germanium is conformationally much "ligher" not only than a *t*-butyl group on carbon but also than a methyl on carbon. Hence, *trans*-**8G** and *cis*-**9G** should exist exclusively in 1-axial, 3 (or 4)- equatorial form. As described before, this is not consistent with the chemical shifts of Me and the carbon nuclei bonded to Me.

It is interesting to notice that a much higher conformational energy of a *t*-butyl group is calculated if germanium parameters proposed by Ouellette et al.[16)] some years ago (hereafter Ouellette model) are employed. These parameters were used for the calculations of 1-methylgermacyclohexanes[2b)] and 3-methylgermacyclohexanes[17)] with success. The results obtained with Ouellette model are also included in Table 3. The conformational energy of a *t*-butyl group bonded to germanium is 1.23 kcal mol$^{-1}$ in a good agreement with the prediction based on NMR data. The calculation with Allinger model predicts an exclusive contribution of **8Gae** and **9Gae** over **8Gea** and **9Gea**, respectively. With Ouellette model, the steric energy difference between the two invertmers **9Gae** and **9Gea** is only 0.16 kcal mol$^{-1}$, which is consistent with the observations by NMR. With Allinger model the difference amounts to 0.89 kcal mol$^{-1}$.

In order to see why this discrepancy arises, we calculated some other germacyclohexanes with both models. The results are included in Table 3. The conformational energy of a methyl group obtained with Allinger model is $-0.25$ kcal mol$^{-1}$ which is essentially identical with that by Ouellette model ($-0.22$ kcal mol$^{-1}$). Thus, a serious deviation seems to arise only when the steric strain involved in the molecule is excessive.

An examination of each component steric energies indicates that the two models gave much the same results for **2Ge** and **2Ga**. On the contrary, there are a few considerable difference for **6G**. For instance, the difference of bending term $E_b$ (i.e., $E_b$ (ax) $-E_b$ (eq)) is 0.11 kcal mol$^{-1}$ by Allinger model and 0.38 kcal mol$^{-1}$ by Ouellette model, and the difference of torsion term $E_t$ is 0.58 kcal mol$^{-1}$ by Allinger model and 1.01 kcal mol$^{-1}$ by Ouellette model.

This is more clearly shown if the structural parameters listed in Table 4 are compared. Evidently, Allinger model seems to predict much larger flattening of the ring around germanium. Thus, the dihedral

Table 4. Structures of *t*-Butylgermacyclohexanes and *t*-Butylcyclohexanes[a), b)]

| | | $r_{1,2}$ | $r_{2,3}$ | $r_{3,4}$ | $\theta_1$ | $\theta_2$ | $\theta_3$ | $\theta_4$ | $\omega_{1,2}$ | $\omega_{2,3}$ | $\omega_{3,4}$ |
|---|---|---|---|---|---|---|---|---|---|---|---|
| | | nm | nm | nm | ° | ° | ° | ° | ° | ° | ° |
| **1G** | A | 0.1949 | 0.1536 | 0.1541 | 102.8 | 110.7 | 113.8 | 114.2 | 43.2 | 56.1 | 67.5 |
| | O | 0.1947[c)] | 0.1538 | 0.1543 | 101.6 | 109.9 | 113.5 | 114.6 | 47.8 | 58.2 | 66.4 |
| **2Ge** | A | 0.1949 | 0.1538 | 0.1542 | 102.9 | 110.7 | 113.8 | 114.3 | 43.1 | 56.1 | 56.4 |
| | O | 0.1945[c)] | 0.1538 | 0.1543 | 101.8 | 109.8 | 113.5 | 114.7 | 47.7 | 58.0 | 66.4 |
| **2Ga** | A | 0.1949 | 0.1538 | 0.1541 | 102.6 | 110.7 | 113.8 | 114.3 | 43.3 | 56.1 | 67.5 |
| | O | 0.1947[c)] | 0.1538 | 0.1543 | 101.7 | 109.9 | 113.5 | 114.7 | 47.5 | 57.9 | 66.3 |
| **6Ge** | A | 0.1949 | 0.1538 | 0.1542 | 102.9 | 110.5 | 113.8 | 114.3 | 43.6 | 56.2 | 67.5 |
| | O | 0.1947 | 0.1538 | 0.1543 | 101.9 | 109.7 | 113.5 | 114.6 | 47.5 | 58.0 | 66.7 |
| **6Ga** | A | 0.1951 | 0.1538 | 0.1540 | 104.9 | 111.8 | 114.1 | 114.0 | 37.8 | 53.1 | 68.8 |
| | O | 0.1950 | 0.1537 | 0.1542 | 102.5 | 111.2 | 113.6 | 114.4 | 42.4 | 55.9 | 67.5 |
| **6Ce** | | 0.1544 | 0.1537 | 0.1533 | 108.6 | 112.3 | 110.9 | 110.0 | 55.4 | 57.4 | 56.7 |
| **6Ca** | | 0.1546 | 0.1533 | 0.1534 | 108.9 | 114.2 | 110.3 | 110.5 | 51.7 | 51.8 | 54.7 |

a) A; Allinger model, O; Ouellette model. see text. b) The definition of the structural parameters are as follows: $r_{1,2}$ is the distance between Ge-1 and C-2 in nm, $\theta_1$ is the bond angle C-6–Ge-1–C-2 in degrees and $\omega_{1,2}$ is the torsion angle in degrees defined by the C-6–Ge-1–C-2–C-3 moiety. The other parameters are defined analogously. c) Data taken from Ref. 2b.

angle $\omega_{1,2}$ (C-6–Ge-1–C-2–C-3) is estimated to be about 48° by Ouellette model and 43° by Allinger model. For **2Ge** and **2Ga**, as well as **6Ge**, the dihedral angle is essentially identical with that of **1G** whichever models are used. Hence, a flattening of this magnitude is not sufficient to relieve the strain caused by an axial methyl group.

For **6Ga**, both models predict an enhanced flattening: the angle is 42° by Ouellette model and 38° by Allinger model. It seems that the strain caused by an axial *t*-butyl group will more effectively be released in the latter model where the ring around germanium is very flat.

As for the values of parameters for computation are concerned, Allinger model is not very far from Ouellette model except the $V_3$ term of torsion energy. This influences both the dihedral angle and torsion energy as was observed.

It is well established both by experiments and by calculations that the C-1–C-7 bond length of *t*-butylcyclohexane is somewhat prolonged to release the strain. In 4-*t*-butylcyclohexanecarboxylic acid, the length by X-ray crystallography is 0.1550 nm, ca. 0.004 nm longer than the normal bond length.[18] The calculated bond length of Ge–C-7 bond is ca. 0.199 nm, an enhanced length of the same order.

Based on molecular mechanics calculations, van de Graaf et al.[9] has predicted that the position for both an equatorial and an axial *t*-butyl group with respect to the cyclohexane ring differs from perfectly staggered. The deviation from the perfectly staggered along C-1–C-7 amounts to 8.4° for **6Ce** and 20.9° for **6Ca**. In **6G** this deviation is much less than that for **6C**. Thus the deviation is almost null for **6Ge** while it is about 6° for **6Ga** in Allinger model.

All these data seem to indicate that in germacyclohexanes the prolonged C–Ge bond length deduces the repulsion between a *t*-butyl group and the ring to a considerable extent, making the deviation of the ring structure of **6G** from that of **1G** much less than the corresponding deviation between **6C** and **1C**. It seems that the Allinger model tends to give a large relaxation as compared with Ouellette model concerning the twist of a *t*-butyl group.

Next we calculated the steric energy for a twist boat of some germacyclohexanes. The results are also included in Table 3. The differences in the steric energy between a chair **1G** and a twist boat **1G** (abbreviated as **1GT**) is 3.83 kcal mol$^{-1}$ (Allinger model) or 5.44 kcal mol$^{-1}$ (Ouellette model), which is not so much different from the corresponding value between **1CT** and **1C** (5.36 kcal mol$^{-1}$). This value is comparable with the conformational energy of a *t*-butyl group in cyclohexane (4.9 kcal mol$^{-1}$,[10] 5.00 kcal mol$^{-1}$ by our calculation: see Table 3), and hence, according to our estimation (vide infra), is considerably larger than the conformational energy of a *t*-butyl group in germacyclohexanes. Thus, in germacyclohexanes the increment of steric energy associated with the ring deformation cannot be compensated by conversion of a *t*-butyl group from axial to equatorial or to pseudo-axial.

In the case of **10G**, *cis*-**10Gea**, and *trans*-**10Gaa** will be stabilized (0.26 and 1.29 kcal mol$^{-1}$, respectively, in Allinger model) if the ring assumes a twist boat. The gain for *cis*-**10Gea** is, for instance, much less than the steric energy difference from *cis*-**10Gae** (3.04 kcal mol$^{-1}$ in Allinger model and 4.04 kcal mol$^{-1}$ in Ouellette model). Hence the equilibium is shifted to the chair form of *cis*-**10Gae** rather than to **10GTea**. Similarly, **10GTaa** is much higher in energy than **10Gee** in contrast to the case of **10CTaa** which has a comparable energy with **10Cee**.

Thus, in the case of **10G**, in contrast to **10C**, molecular mechanics calculations predict that in germacyclohexanes a twist-boat is not possible, which is in a qualitative agreement with the NMR data. This is another characteristics of germacyclohexanes in contrast to cyclohexanes which tend to convert to a twist boat when two *t*-butyl groups are in unfavorable orientation.

**Molecular Orbital Calculations.** In our previous study on phenylgermacyclohexanes we empolyed MNDO calculations in order to assess the conformational energy of a phenyl group bonded to germanium of germacyclohexane since the lack of parameters for germanium bonded to sp$^2$-hybridized carbons has made molecular mechanics calculations of such compounds impossible.[3] Thus, the difference in heat of formation between equatorial- and axial-phenylgermacyclohexanes is only 0.06 kcal mol$^{-1}$. This unexpectedly small difference was supported by the similarly small difference in heat of formations between **2Ge** and **2Ga** (0.04 kcal mol$^{-1}$).

With these results in mind, we calculated the heat of formation of some *t*-butylgermacyclohexanes by means of MNDO together with the parameter for germanium proposed by Dewar et al.[19] The results are given in Table 5. The difference for **6Ga** and **6Ge** is 0.60 kcal mol$^{-1}$, a value between the two values estimated by MM2 calculations with two different models. Remembering that MNDO has, however, a tendency to overestimate the ring flattening,[20] and hence to underestimate the heat of formation of the axial isomer, the actual conformational energy of a *t*-butyl group should considerably be larger than the calculated value of 0.60 kcal mol$^{-1}$, which supports Ouellette model for *t*-butylgermacyclohexanes.

Nevertheless, the results for **10G** can reproduce the tendency as predicted by MM2 calculations. Thus, the difference in heat of formation between **10Gee** and **10Gaa** (5.14 kcal mol$^{-1}$) corresponds to the difference in conformational energies (4.31 kcal mol$^{-1}$). It is certain that MNDO calculations can be used as a means to estimate the conformational energy of germacyclohexanes in an approximate manner.

Table 5. MNDO Heat of Formation of Germacyclohexanes

| Conformation | Heat of formation | Difference[a,b] |
|---|---|---|
| **2Ga** | −31.29 | |
| **2Ge** | −31.33 | 0.04 (−0.25) |
| **6Ga** | −38.68 | |
| **6Ge** | −39.28 | 0.60 (0.33 or 1.23)[c] |
| **10Gaa** | −27.92 | |
| **10Gee** | −33.06 | 5.14 (4.31) |
| **10Gae** | −31.28 | |
| **10Gea** | −27.83 | −3.45 (−3.30) |

a) The difference is, e.g., defined as the difference in heat of formation between **2Ga** and **2Ge**, i.e., between the one with an axial substituent on germanium and the other with the equatorial. A positive value indicates the equatorial isomer is more stable. b) Values in parentheses are the corresponding difference in MM2 steric energies (Table 2). The sign of figures indicates the same situation as above. c) For explanation, see text.

In conclusion, it seems that the conformational energy of a *t*-butyl group in germacyclohexane is most likely ca. 1.3 kcal mol$^{-1}$, as is indicated by NMR data, which is supported by molecular mechanics calculations with Ouellette model. It will be interesting to estimate the conformational energy of a *t*-butyl group in other heteracyclohexanes, or that of much bulkier groups in germacyclohexanes. Study along this line is under progress in our laboratory.

## 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 solution 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.

**Molecular Mechanics Calculations.** The program used was Allinger's MM2.[14] Since in MM2 the parameters for germanium are not available, we installed the parameters reported by Ouellette[16] and those by Allinger[15] in MM2. Since the former parameters were prepared for the older force field of Allinger[21] (before MM1) based on the experimental values of methylgermane and dimethylgermane, there is some doubt as for the consistency between parameters for germanium and for other atoms. This point was discussed in the previous communication[2b] where it was shown that the use of the combination of MM2 and germanium parameters of Ouellette[16] is acceptable, and this combination is used throughout this investigation.

For the sake of comparison, calculations were also carried out for the corresponding cyclohexanes, and the results were also included in Table 2.

**Molecular Orbital Calculations.** The one in the AMPAC[22] package was used as the computation program. For input geometry of *t*-butylgermacyclohexanes, we used the optimized (by MM2) structures. The computation was carried out by means of micro VAX II with Ultrix-32 ver. 2.0-1 and VAX FORTRAN.

**Preparation of Germacyclohexanes (6G—10G).** The preparation of necessary precursors for **8G** and **9G**, 1,5-dibromo-2-methylpentane and 1,5-dibromo-3-methylpentane were previously described.[2b] Preparation of 1,5-dibromo-3-*t*-butylpentane was carried out according to the literature.[23]

***t*-Butyltrichlorogermane:** Trichlorogermane (113.6 g, 0.635 mol) was dissolved in diethyl ether (500 ml) to which *t*-butyl chloride (58.4 g, 0.635 mol) was added under ice cooling. Stirring was continued for 10 h at room temperature. The solvent was removed under a reduced pressure, and the residual pale yellow oil was recrystallized from pentane to afford very hygroscopic white crystals of the title compound (58 g, 25%).

**1-*t*-Butyl-1-chlorogermacyclohexane (6G′):** 1,5-Dibromopentane (5.4 g, 0.023 mol) was caused to react with Mg (1.91 g, 0.081 mol) in diethyl ether (50 ml) to afford the bis-Grignard reagent, which was added, under the atmosphere of argon and with stirring, to *t*-butyltrichlorogermane (5.61 g, 0.023 mol) in diethyl ether (100 ml) under reflux (inverse Grignard method). Refluxing was continued for 3 h, the resultant solid was filtered, and the ether was evaporated from the remaining oil which was distilled under a reduced pressure to afford **6G′** (3.87 g, 73%).

**1-*t*-Butylgermacyclohexane (6G):** **6G′** (3.87 g, 0.017 mol) was treated with lithium aluminum hydride (LAH; 0.68 g, 0.017 mol) in diethyl ether (30 ml) under argon. After the remaining LAH was decomposed with water, the ether layer was washed with water, dried over CaCl$_2$ and evaporated. The distillation of the residue under a reduced pressure afforded **6G** (1.70 g, 50%). **6G** rapidly polymerizes in air.

**4-*t*-Butyl-1,1-dichlorogermacyclohexane (7G′):** The bis-Grignard reagent of 1,4-dibromo-3-*t*-butylpentane (5.0 g, 0.017 mol) was prepared in tetrahydrofuran (THF, 50 ml) with Mg (0.93 g, 0.038 mol), which was added to tetrachlorogermane (GeCl$_4$; 4.13 g, 0.019 mol) in diethyl ether (120 ml) under argon under reflux. Refluxing was continued for 3 h and the precipitate was rapidly filtered off. The solvent was evaporated under reduced pressure, and the residue was distilled in vacuo to afford **7G′** (1.62 g, 34%).

**4-*t*-Butylgermacyclohexane (7G):** **7G′** (1.62 g, 0.006 mol) and LAH (0.30 g, 0.008 mol) in diethyl ether was refluxed under argon for 1.5 h. The residual LAH was decomposed with water under ice cooling, and the organic layer was washed with water, dried over CaCl$_2$, and evaporated. The residue was distilled in vacuo to afford **7G** (0.62 g, 51%).

**1-*t*-Butyl-3-methyl- (8G) and 1-*t*-Butyl-4-methyl- (9G) ger-**

Table 6. Physical Properties of Germacyclohexanes (**6G**–**10G**) and Their Precursors[a)]

| Compound<br>(Formula) | Yield[a)]<br>% | Isomer ratio<br>cis : trans | Bp $\theta_b$<br>°C/mmHg[c)] | IR (Ge–H)<br>$\nu_H$ (neat) | ¹H NMR<br>$\delta_H$ (90 MHz; $CDCl_3$)[b)] |
|---|---|---|---|---|---|
| **6G**<br>($C_9H_{20}Ge$) | 50 | — | 98—102/20 | 2042 | 1.00 (9H, s, *t*-Bu), 3.58 (1H, m, H-1) |
| **7G**<br>($C_9H_{20}Ge$) | 51 | — | 125/23 | 2050 | 0.83 (9H, s, *t*-Bu), 2.16 (1H, m, H-4),<br>3.41 (2H, m, H-1) |
| **8G**<br>($C_{10}H_{22}Ge$) | 30 | 1 : 1 | 86/14 | 2040 | 0.96 (3H, s, $J$=7 Hz, Me-3)<br>1.10 (9H, s, *t*-Bu), 3.56 (1H, m, H-1) |
| **9G**<br>($C_{10}H_{22}Ge$) | 47 | 7 : 3 | 88/9 | 2038 | 1.03 (3H, d, $J$=6 Hz, Me-4)<br>1.06 (9H, s, *t*-Bu), 3.46 (1H, m, H-1) |
| **10G**<br>($C_{13}H_{28}Ge$) | 12 | 3 : 1 | 106/12 | 2035 | 0.83 (9H, s, *t*-Bu), 1.07 (9H, s, *t*-Bu)<br>3.56 (1H, m, H-1) |
| **6G′**<br>($C_9H_{19}ClGe$) | 73 | — | 72—75/20 | 2050 | |
| **7G′**<br>($C_9H_{18}Cl_2Ge$) | 34 | — | 93—95/116 | — | |
| **8G′**<br>($C_{10}H_{19}ClGe$) | 44 | — | 105—108/2 | — | |
| **9G′**<br>($C_{10}H_{19}ClGe$) | 49 | — | 122—127/20 | — | |
| **10G′**<br>($C_{13}H_{27}ClGe$) | 27 | — | 75—78/27 | 2040 | |

a) Yields based on the immediate precursor. b) Values for the major isomers. c) 1 mmHg≈133.322 Pa.

**macyclohexane:** These compounds were prepared by the reaction between *t*-butyltrichlorogermane and the bis-Grignard reagent of 1,5-dibromo-2-methylpentane, and 1,5-dibromo-3-methylpentane, respectively, via the corresponding 1-*t*-butyl-1-chlorogermacyclohexane **8G′** and **9G′**.

**1,4-di-*t*-Butylgermacyclohexane (10G):** The preparation of this compound was carried out in an essentially indentical procedure employed for the preparation of other germacyclohexanes from 1,5-dibromo-3-*t*-butylpentane and *t*-butyltrichlorogermane via 1-*t*-butyl-1-chloro derivative (**10G′**).

In cases of **6G**, **8G**—**10G**, separation of stereoisomers were unsuccessful partly because of the scarcity of the sample and partly because of the instability of germacyclohexanes with a hydrogen atom bonded to germanium.

The yield and physical properties of the *t*-butylgermacyclohexanes are summarized in Table 6.

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