Nuclear Magnetic Resonance Spectra of Organogermanium Compounds. Part 4.[1] Nuclear Magnetic Resonance Spectra and Molecular Mechanics Calculations of Germacyclohexane, Methylgermacyclohexanes, and Dimethylgermacyclohexanes

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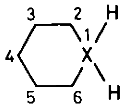
Molecular mechanics calculations in germacyclohexane and methyl-substituted germacyclohexanes reveals that (i) the ring is flattened around the germanium and that (ii) a methyl group on germanium has a slight preference for the axial conformation rather than the equatorial, which is in line with the results for the corresponding silacyclohexanes. The ^{13}C and ^{73}Ge chemical shifts of these germacyclohexanes are consistent with the calculations. Thus, both ^{13}C and ^{73}Ge data indicate that 1-methyl-1-germacyclohexane is a *ca.* 60:40 mixture of axial and equatorial isomers. Attempts to observe directly the two conformers by freezing the inversion on the n.m.r. time scale failed because of the very lower barrier to inversion.

Though the chemistry of organogermanium compounds with tetravalent germanium has been described,[2–4] the structural details of these compounds are much less investigated. We have initiated a study to cast light upon this unexplored field chiefly by n.m.r. (including ^{73}Ge n.m.r.) spectroscopy[1,5,6] and molecular mechanics calculations.



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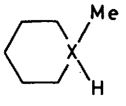

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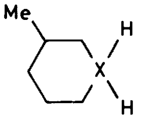

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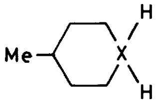

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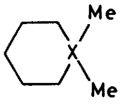

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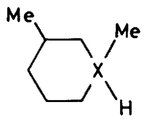

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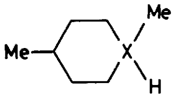


(7)

X = C cyclohexanes (C)
X = Si silacyclohexanes (S)
X = Ge germacyclohexanes (G)

Germacyclohexane (**1G**) is a key compound in organogermanium chemistry and its role is exactly the same as that of cyclohexane (**1C**) in the chemistry of carbocyclic compounds. Crucial features of the chemistry of (**1C**) are associated with the stereochemistry of the ring, *e.g.*, ring reversal and its barrier, 1,3-diaxial interactions or relative stabilities of equatorial and axial conformers of monosubstituted species. Although these are fully documented for (**1C**),[7] the equivalent has not been reported for (**1G**).

The situation is slightly better for silacyclohexane (**1S**) and derivatives. Thus, Ouellette[8] reported molecular mechanics calculations of (**1S**), 1-methyl- (**2S**), 4-methyl- (**4S**), and 1,1-dimethyl-1-silacyclohexane (**5S**), and found that the axial isomer of (**2S**) is slightly more favourable than the equatorial (by 0.20 kcal mol^{-1}), while Jensen and Bushweller[9] attempted to determine the barrier height of ring reversal of (**5S**), which was found in the range of 5.25—5.75 kcal mol^{-1}.

Carleer and Anteunis[10] reported that the conformational energy, *i.e.*, the free energy difference between the axial and equatorial conformers, as determined from the spin–spin coupling constant for the methyl group of (**2S**), is 0.34 kcal mol^{-1} in favour of the axial position, in agreement with the prediction of molecular mechanics calculations.[8]

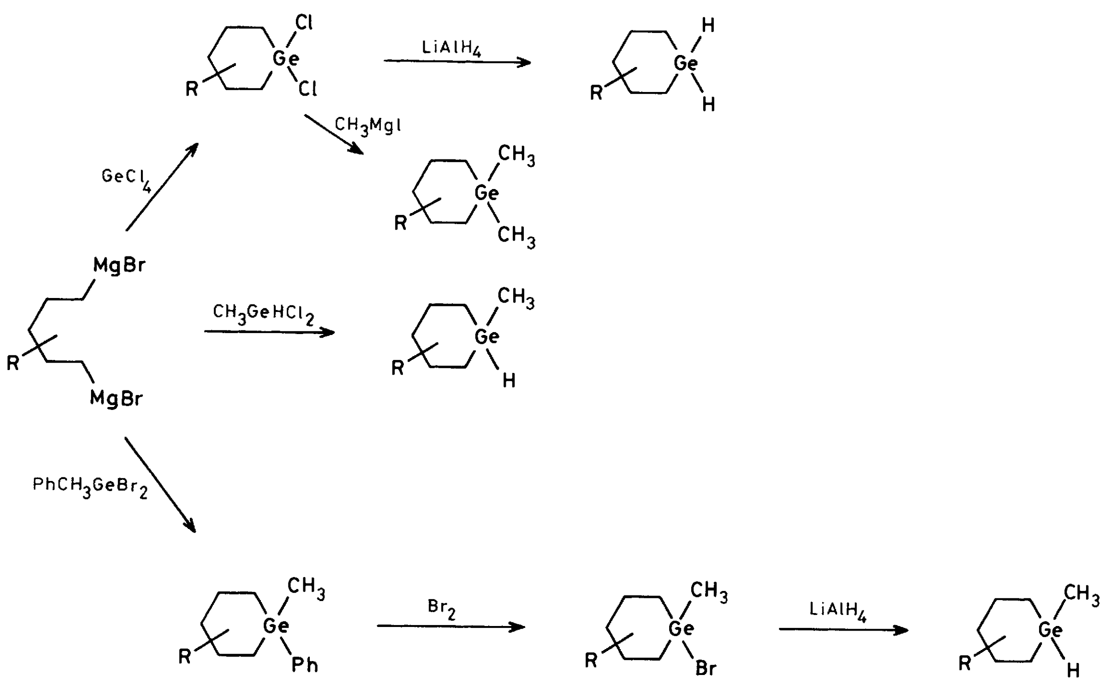
The purpose of this study is to obtain stereochemical information on the hitherto unexplored (**1G**) and its methyl derivatives by means of n.m.r. spectroscopy and molecular mechanics calculations. Combined with the corresponding information for (**1S**) and (**1C**), it is expected to open a new field of chemistry of the heteracyclohexanes of Group IVB elements.

For this purpose (**1G**), 1-, 3-, and 4-methyl-1-germacyclohexane (**2G**)—(**4G**), and 1,1-, 1,3-, and 1,4-dimethyl-1-germacyclohexane (**5G**)—(**7G**) were prepared, and their ^{13}C and ^{73}Ge n.m.r. spectra determined. The n.m.r. data were published in a preliminary account.[1] We also performed molecular mechanics calculations for these germacyclohexanes and related compounds to assess the ring structure and to interpret the n.m.r. data.

Results and Discussion

Preparation of Germacyclohexanes.—To date only compounds (**1G**) and (**5G**) have been described in the literature. Compound (**1G**) was prepared by coupling of the bis-Grignard reagent of 1,5-dibromopentane with tetrachlorogermane to yield 1,1-dichloro-1-germacyclohexane, followed by treatment with lithium aluminium hydride.[11] Compound (**5G**) was obtained by treating the dichlorogermacyclohexane with methylmagnesium iodide.[12]

In a similar manner, compounds (**3G**) and (**4G**) were



R = H or CH$_3$

Scheme. Synthetic route to methylgermacyclohexane derivatives

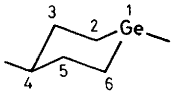
prepared from the bis-Grignard reagents of 2-methyl- and 3-methyl-1,5-dibromopentane, respectively.

It was expected that coupling of the bis-Grignard reagents of appropriate 1,5-dibromopentanes with dichloro(methyl)germane would afford directly the desired 1-methyl-1-germacyclohexanes (**2G**), (**6G**), and (**7G**). It was indeed the case for (**2S**), where the coupling reaction of the bis-Grignard reagent of 1,5-dibromopentane with dichloro(methyl)silane gave (**2S**) in 50% yield.[13] The yield of (**2G**) by this method was, however, low (6%), and for the attempted preparation of (**6G**) and (**7G**) the reaction gave an intractable mixture of germanium-containing species. The ready homolytic cleavage of the Ge–H bond in $MeGeHCl_2$[14] facilitates undesired reactions.

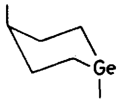
Thus, we employed an alternative approach. Coupling of the bis-Grignard reagent of 1,5-dibromopentane with dibromo(methyl)phenylgermane gave 1-methyl-1-phenyl-1-germacyclohexane (**2GP**). The phenyl group of (**2GP**) was replaced by a bromine atom upon treatment with bromine to yield 1-bromo-1-methyl-1-germacyclohexane (**2GB**). The bromine atom of this compound was replaced by a hydrogen by $LiAlH_4$ treatment to afford the desired (**2G**). The dimethylgermacyclohexanes (**6G**) and (**7G**) were also prepared by this procedure as a mixture of *cis*- and *trans*-isomers.

*Molecular Mechanics Calculations.**—The optimised structures and steric energies of germacyclohexanes (**1G**)—(**7G**) were calculated by the MM2 force field program.[15] Since the parameters for germanium are not supplied in MM2, we used the parameters reported by Ouellette.[16] A chair conformation was assumed, and, for methyl-substituted species, all possible stereoisomers regarding the orientation of the methyl groups(s) were considered. For instance, there are two geometrical isomers for (**7G**), *trans* and *cis*, and for each there are two conformational isomers. Each of these four stereoisomers is designated according to the direction of the two methyl groups, *e.g.*, 1-ax-methyl-4-eq-methyl-1-germacyclohexane is designated as (**7Gae**).

trans

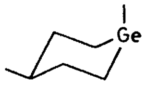


(7Gee)

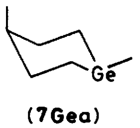


(7Gaa)

cis



(7Gae)



(7Gea)

The structural parameters for selected germacyclohexanes determined by the molecular mechanics calculations are listed in Table 1. Calculations for the corresponding silacyclohexanes and cyclohexanes were also carried out and the results are included in Table 1. Since Ouellette's parameters for silicon and germanium[16] were prepared for an old force field of Allinger[17] (older than MM1) there is some doubt as to the consistency between the results with MM1 or a similar program and those with MM2.

Hence we carried out molecular mechanics calculations on (**1**), (**2**), and (**5**) (S and G altogether) with the MM1 program.[18]

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* Since the steric energy as estimated by molecular mechanics calculations is force-field dependent, it is dangerous to compare values of steric energies for compounds with different number of carbon atoms. In this paper, however, the comparison is always made among stereoisomers with identical number of carbon atoms. It has been well established that in such a case the difference, not the value itself, in the steric energies is a good measure of the difference in the stereochemical environment of each isomer.

Table 1. Structures of germacyclohexanes, silacyclohexanes, and cyclohexanes optimised by the molecular mechanics calculations

		$r_{1,2}$[a]	$r_{2,3}$[a]	$r_{3,4}$[a]	θ_1[b]	θ_2[b]	θ_3[b]	θ_4[b]	$\varphi_{1,2}$[c]	$\varphi_{2,3}$[c]	$\varphi_{3,4}$[c]
(1G)	MM2	0.1947	0.1538	0.1543	101.6	109.9	113.5	114.6	+47.8	−58.2	+66.4
	MM1	0.1950	0.1535	0.1538	103.3	110.6	114.2	114.7	+42.3	−55.2	+67.0
(1S)	MM2	0.1891	0.1537	0.1541	102.0	109.6	113.0	114.2	+50.9	−59.0	+64.5
	MM1	0.1881	0.1533	0.1538	105.7	108.6	113.6	114.6	+47.3	−56.4	+65.8
	Ouellette[8]	0.1864	0.1531	0.1536	104.2	111.6	112.5	113.5	+43.8	−56.0	+64.6
(1C)	MM2	0.1536	0.1536	0.1536	110.9	110.9	110.9	110.9	+56.3	−56.3	+56.3
(2Ge)	MM2	0.1945	0.1538	0.1543	101.8	109.8	113.5	114.7	+47.7	−58.0	+66.4
	MM1	0.1949	0.1535	0.1538	103.4	110.6	114.2	114.7	+42.3	−55.1	+67.0
(2Se)	MM2	0.1877	0.1537	0.1542	102.9	109.5	113.0	114.3	+50.6	−58.5	+64.4
	MM1	0.1879	0.1532	0.1537	105.6	108.8	113.6	114.6	+47.2	−56.4	+65.7
	Ouellette[8]	0.1863	0.1531	0.1536	104.2	111.6	112.5	113.5	+43.7	−55.9	+64.6
(2Ce)	MM2	0.1539	0.1536	0.1535	110.2	111.3	110.9	110.7	+56.1	−56.6	+56.4
(2Ga)	MM2	0.1947	0.1538	0.1543	101.7	109.9	113.5	114.7	+47.5	−57.9	+66.3
	MM1	0.1949	0.1535	0.1538	103.4	110.6	114.2	114.7	+42.2	−55.1	+67.0
(2Sa)	MM2	0.1887	0.1537	0.1542	102.6	109.9	113.1	114.3	+49.6	−58.2	+64.6
	MM1	0.1880	0.1532	0.1537	105.6	109.0	113.0	114.6	+46.5	−56.1	+65.8
	Ouellette[8]	0.1864	0.1531	0.1535	104.3	111.8	112.5	113.5	+42.9	−55.5	+64.8
(2Ca)	MM2	0.1540	0.1536	0.1535	110.2	112.6	110.9	111.0	+53.4	−55.4	+56.1
(5G)	MM2	0.1946	0.1538	0.1543	101.9	109.8	113.5	114.8	+47.5	−57.8	+66.3
	MM1	0.1948	0.1535	0.1538	103.5	110.6	114.2	114.7	+42.2	−55.1	+67.0
(5S)	MM2	0.1870	0.1535	0.1540	104.7	110.0	113.2	113.8	+46.6	−56.7	+65.8
	MM1	0.1877	0.1531	0.1536	105.4	109.3	113.6	114.5	+46.4	−56.1	+65.6
	Ouellette[8]	0.1863	0.1531	0.1535	104.4	111.9	112.5	113.5	+42.8	−55.5	+64.8
(5C)	MM2	0.1545	0.1536	0.1534	109.4	113.4	110.9	110.9	+52.6	−55.4	+56.0

[a] $r_{1,2}$ is the distance between Ge-1 and C-2 in nm. [b] θ_1 is the bond angle C(6)–Ge(1)–C(2) in degrees. [c] $\varphi_{1,2}$ is the torsion angle in degrees defined by the C(6)–Ge(1)–C(2)–C(3) moiety. For the numbering of the atoms, see text. The other torsion angles are defined analogously.

These results are also in Table 1 together with those of Ouellette (S series).[8] It is evident that the Ouellette's results and those with MM1 are essentially identical, while those with MM2 are different from those with the other two force fields. When MM1 is used, the bond angle θ_1 [C(6)–Ge(1)–C(2)] tends to be larger, and the absolute values of the torsion angle $\varphi_{1,2}$ [C(6)–Ge(1)–C(2)–C(3)] and $\varphi_{3,4}$ [C(2)–C(3)–C(4)–C(5)] tend to be smaller than the results obtained with MM2. This tendency is inherent in MM1, and has been reported for cyclohexane.[19]

The optimised structure of **(1G)** by MM1 is very close to that of **(1S)** by MM1 or from ref. 8. When MM2 is used, there is a smooth variation of θ or φ in the order of **(1C)** ⟶ **(1S)** ⟶ **(1G)**. Thus, with MM2 θ_1 is 110.9, 102.0, and 101.6°, respectively, for **(1C)**, **(1S)**, and **(1G)**, while $\varphi_{1,2}$ is $+56.3$, $+50.9$, and $+47.8°$ for the same compounds. The torsion angle $\varphi_{3,4}$ does not, however, vary with the force fields used, and is $+56.3$, 64.5, and $+66.4°$ (MM2), respectively, for the **(1C)**, **(1S)**, and **(1G)**. The fold of the ring is increasingly flattened around the heteroatom, *i.e.*, $\varphi_{1,2}$ as well as $\varphi_{6,1}$ becomes smaller, and increasingly enhanced around C-4, *i.e.*, $\varphi_{3,4}$ as well as $\varphi_{4,5}$ becomes larger in the order **(1C)** ⟶ **(1S)** ⟶ **(1G)**.

Introduction of a methyl group on the germanium atom of germacyclohexanes does not affect the ring structure to any significant extent. Though this is also the case with silacyclohexanes,[8] a fairly large distortion is induced by an axial methyl group in the case of cyclohexanes. The torsion angle $\varphi_{1,2}$ for **(1C)**, **(2Ca)**, and **(5C)** is $+56.3$, $+53.4$, and $+52.6°$, respectively. This change must be caused by a release of strain invoked by an axial methyl group. In contrast, $\varphi_{1,2}$ for **(1G)**, **(2Ga)**, and **(5G)** is essentially unchanged ($+47.8$, $+47.5$, and $+47.5°$, respectively). In sila- and germa-cyclohexanes, owing to the prolonged bond length (Si–C and Ge–C) and the flattened ring structure, the strain caused by an axial methyl group is much less than that in **(1Ca)**.

These observations establish that the optimised structure of **(1G)** [and **(1S)**] by MM2 can be used as a model for all other methyl-substituted germa- (and sila-)cyclohexanes.

Steric Energies.—In Table 2, steric energies of germacyclohexanes calculated by MM2 are listed together with these of corresponding cyclohexanes. In the MM2 calculations, total steric energies (E_s) are the sum of component energies, *i.e.*, 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 that associated with the 1,4-interaction ($E_{1,4}$) and that with other interactions (E_{other}). For **(2)**, **(6)**, and **(7)**, all possible stereoisomers associated with the direction of the methyl groups are taken into consideration.

The most remarkable outcome of the comparison of the **C** and **G** series is the fact that in germacyclohexanes (and in silacyclohexanes[8]) not only an equatorial methyl group on the heteroatom, but also an axial methyl group on the heteroatom induces a modest and similar stabilisation. Thus, **(2Ge)** and **(2Ga)** are lower by 0.89 and 1.11 kcal mol^{-1}, respectively, than **(1G)**. This is in sharp contrast with cyclohexanes, where an equatorial methyl group causes a small destabilisation [**(2Ce)** +0.34 kcal mol^{-1} relative to **(1C)**], and an axial methyl group a very larger destabilisation [**(2Ca)** +2.14 kcal mol^{-1} relative to **(1C)**].

As seen in Table 2, almost all the positive components of the steric energy are larger in methylcyclohexane **(2Ce)** and **(2Ca)** than in cyclohexane **(1C)**, resulting in destabilisation of the former relative to the latter, although the absolute value of the negative component energy E_{other}, *i.e.*, the non-bonded attraction energy, is also larger in the former than in the latter. In methylcyclohexane, the bending energy E_b and the torsional energy E_t are much larger, the other positive component energies are slightly larger, and the non-bonded attraction energy is considerably smaller for the axial **(2Ca)** than for the equatorial conformer **(2Ce)**. The combined effects result in destabilisation of the axial relative to the equatorial conformer.

For germacyclohexanes, on the other hand, the positive component energies except for $E_{1,4}$ are essentially equal for the unsubstituted compound **(1G)** and the methyl-substituted compounds **(2Ge)** and **(2Ga)**. The 1,4-repulsion energy $E_{1,4}$ is

Table 2. Calculated steric energies (E_s) and their components[a] for germacyclohexane, methylgermacyclohexanes, and the corresponding cyclohexanes (in kcal mol^{-1})

Compd.	E_s	E_c	E_b	E_{sb}	E_t	$E_{1,4}$	E_{other}	Compd.	E_s	E_c	E_b	E_{sb}	E_t	$E_{1,4}$	E_{other}
(1G)	5.72	0.40	1.88	0.14	1.29	3.15	−1.14	**(1C)**	6.55	0.34	0.37	0.08	2.16	4.67	−1.06
(2Ge)	4.83	0.41	1.83	0.14	1.33	2.75	−1.63	**(2Ce)**	6.89	0.45	0.47	0.11	2.14	5.20	−1.47
(2Ga)	4.61	0.40	1.85	0.14	1.38	2.73	−1.88	**(2Ca)**	8.69	0.48	0.97	0.15	3.09	5.32	−1.34
(3G)	6.18	1.59	1.94	0.16	1.30	3.80	−1.60								
(4G)	6.30	0.61	2.01	0.17	1.32	3.67	−1.46	**(5C)**	9.27	0.77	1.06	0.16	3.04	5.77	−1.55
(5G)	3.53	0.41	1.81	0.15	1.40	2.35	−2.59	**(6Cee)**	7.21	0.55	0.57	0.13	2.13	5.72	−1.89
(6Gee)	5.28	0.58	1.89	0.16	1.33	3.41	−2.11	**(6Cae)**	9.02	0.59	1.08	0.18	3.08	5.85	−1.76
(6Gae)	5.05	0.58	1.91	0.16	1.38	3.39	−2.37	**(6Caa)**	12.55	0.61	2.52	0.26	4.58	6.28	−1.71
(6Gea)	6.64	0.60	2.63	0.23	1.85	3.30	−1.97								
(6Gaa)	7.37	0.58	2.94	0.24	2.49	3.24	−2.11								
(7Gee)	5.42	0.62	1.98	0.17	1.34	3.27	−1.96	**(7Cee)**	7.22	0.55	0.58	0.13	2.13	5.72	−1.89
(7Gae)	5.18	0.61	1.98	0.17	1.40	3.25	−2.24	**(7Cae)**	10.79	0.61	1.53	0.22	4.08	5.97	−1.62
(7Gea)	6.88	0.51	2.49	0.23	2.21	3.40	−2.06	**(7Caa)**	8.97	1.57	1.08	0.18	3.17	5.84	−1.78
(7Gaa)	6.69	1.61	2.51	0.23	2.26	3.38	−2.30								

[a] For definition of components, see text.

Table 3. ^{73}Ge and ^{13}C SCS of methyl groups in germacyclohexanes and cyclohexanes (in p.p.m.)

		SCS*						
Substituent	Definition	Ge-1	C-1	C-2	C-3	C-4	C-5	C-6
1-Me (eq)	**(6Gee)** − **(3G)**	70.6 (α)		4.20 (β)	0.44 (γ)	0.53 (δ)	0.41 (γ)	3.85 (β)
	(7Gee) − **(4G)**	72.8 (α)		3.74 (β)	0.05 (γ)	0.29 (δ)		
1-Me (ax)	**(6Gae)** − **(3G)**	60.3 (α)		3.11 (β)	−1.21 (γ)	0.36 (δ)	−1.10 (γ)	2.90 (β)
	(7Gae) − **(4G)**	60.9 (α)		2.82 (β)	−1.25 (γ)	0.29 (δ)		
3-Me (eq)	**(3G)** − **(1G)**	0.0 (γ)		8.23 (β)	6.40 (α)	8.04 (β)	−1.07 (γ)	−1.22 (δ)
4-Me (eq)	**(4G)** − **(1G)**	−3.1 (δ)		−1.30 (γ)	7.98 (β)	5.16 (α)		
1-Me (eq)	**(2Ce)** − **(1C)**†		5.65 (α)	8.90 (β)	0.00 (γ)	−0.30 (δ)		
1-Me (ax)	**(2Ca)** − **(1C)**†		1.10 (α)	5.15 (β)	−5.40 (γ)	−0.15 (δ)		
1-Me (obs)	**(2G)** − **(1G)**	65.9 (α)		2.78 (β)	−1.20 (γ)	−0.25 (δ)		

* Letters in parentheses indicates the position of the carbon in question relative to the methyl group. † Estimated statistically from various compounds.

smaller and the non-bonded attraction energy E_{other} is larger in the methyl-substituted compound than in the unsubstituted compound. The combined effects stabilise the former relative to the latter.

In 1-methyl-1-germacyclohexane (**2G**) all the positive component energies including $E_{1,4}$ are essentially equal for the two conformers, and the non-bonded attraction energy E_{other} is larger for the axial (**2Ga**) than for the equatorial conformer (**2Ge**), resulting in stabilisation of the former relative to the latter.

In other words, this stabilisation of the axial relative to the equatorial conformer is ascribed to the stability of the *gauche* conformation over that of the *anti* in the C(Me)–C(1)–Ge(2)–C(3) moiety. The difference (*ca.* −0.2 kcal mol^{-1}) is, however, small, and its may be said that the conformational energy of the methyl group on the heteroatom in 1-methyl-1-germacyclohexane is as small as that of the fluorine atom in cyclohexane, the substituent with the smallest steric energy reported for the cyclohexane series.[20]

The effect on the steric energy caused by a methyl group in germacyclohexanes bonded to a ring carbon atom is essentially identical with that in cyclohexanes. The situation is best exemplified in the case of (**7G**). Of the two conformers for each geometrical isomer, that with an axial methyl group on carbon is much less favourable than its conformer regardless of the orientation of the other methyl group on germanium [*i.e.*, (**7Gae**) over (**7Gea**), and (**7Gee**) over (**7Gaa**)] since the increment in steric energy by an axial methyl group on carbon amounts to *ca.* 1.5 kcal mol^{-1}. In (**6Gaa**), there exists a very unfavourable 1,3-diaxial interaction between the two methyl groups, and this isomer is the least stable of the four isomers of (**6G**). Yet the difference of steric energy between (**6Gaa**) and (**6Gea**) is only 0.73 kcal mol^{-1}, which is in a sharp contrast to the corresponding difference between (**6Caa**) and (**6Cae**) (3.50 kcal mol^{-1}). From the results of the calculations, it is expected that conformational equilibria in (**7Gee**) $\rightleftharpoons$ (**7Gaa**) and (**7Gae**) $\rightleftharpoons$ (**7Gea**) are both nearly completely shifted to the left, *i.e.*, to the conformer with the methyl group on carbon in the equatorial form [(**7Gee**) and (**7Gae**), respectively]. This is in agreement with the ^{13}C and ^{73}Ge n.m.r. data for (**7G**). Thus, as we have previously reported,[1] the chemical shifts of C-4 and the 4-methyl group for *trans*- and *cis*-(**7G**) are essentially identical, while those of C-3 and the 1-methyl group are considerably higher for the *cis*-isomer due to the steric compression effect induced by the quasi-axial methyl group on germanium. This agreement is further supported by the observation that the ^{73}Ge shift for (**7Gae**) is slightly (but in the correct direction) higher than that for (**7Gee**).

The steric energies obtained by MM1 are slightly different from those obtained by MM2. The relative order of magnitude is, however, equal for the two force fields. Thus, by MM1, the steric energies of (**2Ge**) and (**2Ga**) are −1.05 and −1.30 kcal mol^{-1}, respectively, relative to (**1G**), comparable with the corresponding values by MM2, −0.89 and −1.11 kcal mol^{-1}.

Substituent Chemical Shifts (*SCS*) *of Methyl Group.*—Since the ^{13}C SCS is a good measure of combined electronic and steric effects of a substituent, it is interesting to compare the values of

SCS of the methyl group in germacyclohexanes with those in cyclohexanes.[21] In Table 3, the values of SCS of 1- (equatorial and axial), 3- (equatorial), and 4-methyl (equatorial) groups are listed together with those of equatorial and axial methyl groups in cyclohexanes.

SCS for a methyl group on a carbon atom of the germacyclohexane ring can be determined in two ways: one from (**3G**), and the other from (**4G**). The values are somewhat different, but the average values are within + 10% of those for cyclohexane, and the general trend is β-SCS > α-SCS ⩾ γ-SCS ≑ δ-SCS ≑ 0.

SCS for the 1-methyl group in germacyclohexanes can be determined in two ways, one as the chemical shift difference between (**6G**) and (**3G**), and the other as that between (**7G**) and (**4G**). Thus, the difference of ^{13}C chemical shifts between (**6Gae**) and (**3G**) gives one axial-methyl SCS and the difference between (**7Gae**) and (**4G**) gives another SCS. The former value differs slightly from the latter, which is unavoidable because of the difference in substitution of the ring.

These SCS values of the methyl group on germanium are uniformly substantially smaller than those of the methyl groups of cyclohexanes; *e.g.*, the β-SCS of both equatorial and axial 1-methyl groups in germacyclohexanes (3.74, 4.20, 3.85; 2.82, 3.11, and 2.90 p.p.m.) are about half those in cyclohexanes (8.90; 5.15). Furthermore, the γ-SCS value of the axial methyl group is only about a quarter [(−1.25)/(−5.40) = 0.23] of the well documented value for cyclohexane.

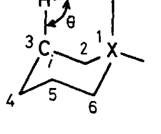
A substantial decrease in the γ-SCS value for the axial methyl group on germanium is anticipated because of the prolonged distance between the axial methyl group on germanium and the axial hydrogens at C-3 and -5. In fact, the distance between the carbon atom of the axial 1-methyl group and the axial hydrogens at C-3 and -5 is 0.292 for (**2Ca**) and 0.324 nm for (**2Ga**). Originally, Grant and Cheney[21] correlated the γ-shift at C-3, -5 with the force vector exerted on the axial hydrogens on C-3 and -5. In calculating the force vector by the equation they proposed, a non-relaxed structure with six genuinely tetrahedral carbons was assumed. Schneider and Weigand[22] showed that this assumption was inadequate because of the sensitivity of non-bonded interactions to small changes in the interproton distance, *i.e.*, the distance between axial hydrogens on C-3 and -5 and the nearest methyl proton. Upon relaxation the interproton distance changes from 0.188 to 0.234 nm.

Schneider and Weigand[22] proposed a revised equation (1) for

$$F = 0.6952 \times 10^{-5}\,(18\varepsilon/r^*)[(r^*/r)^{10} - (r^*/r)^7]\cos\theta \quad (1)$$

the estimation of the shielding force vector F (in dyne) where ε and r^* are constants, 0.004 109 and 3.632 for hydrogen–hydrogen interaction and 0.026 102 and 3.575 for carbon–hydrogen interaction, r represents the distance between the hydrogen attached to C_i and the interacting H (for the equatorial isomer) or C (for axial isomer), and θ is the angle between the force vector and the C_i–H bond. They showed that the relation between the non-bonded interaction term of SCS and the force vector F is simply SCS(non-bonded) = $20F(\times 10^5\ \text{dyne}^{-1})$.

Following their method, we calculated force vectors for (**2Ca**) and (**2Ga**) for their optimised structures. The force vector for (**2Ga**) is -0.11×10^{-5} dyne, which corresponds to γ-SCS(non-bonded) −2.2 p.p.m. The observed γ-SCS is about half this value. The reasons for this discrepancy could be various. Lambert and Vagenas[23] reported a rough dependence of γ-SCS upon torsion angle [in the case of (**2Ca**), the C(Me)–C(1)–C(2)–C(4) angle]. In fact that angle of (**2Ga**) (−69.1°) is different from that of (**2Ca**) (−72.5°) only by 3°, which, according to these authors, accounts for less than 0.2 p.p.m.



X = C or Ge
Y = H or C

It must be pointed out, however, that the ratio of force vector F(**2Ga**) to F(**2Ca**) is *ca.* 1/3, close to the ratio of the observed γ-SCS values. At the present stage, it is reasonable to assume that the γ-SCS in (**2Ga**) is primarily determined by the interproton or carbon–proton distance as previously suggested.[21,22]

Another possible approach is to correlate the γ-shift with the local (at the resonant nuclei) van der Waals energy as calculated by the force field calculations.[24] We are planning to prepare other methylgermacyclohexanes so that this empirical approach can be tested. The possibility of additional effects of germanium cannot, however, be ruled out before the discrepancy is accounted for.

Conformational Equilibrium in 1-*Methyl*-1-*germacyclohexane* (**2G**).—The steric energies of (**2Ge**) and (**2Ga**) predict a small (0.22 kcal mol^{-1}) preference of the latter in the equilibrium (**2Ge**) $\rightleftharpoons$ (**2Ga**). With the rough assumption of equal entropies for the two conformers, the ratio (**2Ga**):(**2Ge**) is *ca.* 0.6:0.4 at ambient temperature. The most straightforward method to determine the ratio experimentally, and hence to confirm the prediction based on the molecular mechanics calculations, is low-temperature n.m.r. spectroscopy where ring reversal is frozen on the n.m.r. time scale.

It was reported,[9] however, that the interconversion barrier for (**5S**) is in the range 5.25—5.75 kcal mol^{-1}, which is too low to allow the observation of freezing out. Judging from the similarity of ring structure of sila- and germa-cyclohexanes, there would not be much chance of direct observation of the freezing of ring reversal for germacyclohexanes. In fact at −150 °C, which is virtually the lowest temperature for solution n.m.r., there is no broadening of the ^{13}C signals of (**5G**).

One possible way of determining the population is the estimation of the ^{13}C and/or ^{73}Ge chemical shifts of (**2Ge**) and (**2Ga**) by some approximate means. The ratio will then be easily estimated since the observed shifts for (**2G**) are the weighted average of those for (**2Ge**) and (**2Ga**).

Thus, the average value of α-SCS of the axial 1-methyl group and that of the equatorial 1-methyl group in 1-methyl-1-germacyclohexanes is 60.6 and 71.7 p.p.m., respectively (Table 3). Since the observed α-SCS of (**2G**) is 65.9 p.p.m., the population x of (**2Ga**) is given by $60.6x + 71.7(1 - x) = 65.9$. The calculated value of x (0.52) qualitatively agrees with the predicted small preference of the axial isomer.

Other convenient signals for this purpose are the ^{13}C resonances of the 1-methyl groups of (**7G**) and (**2G**). The ^{13}C chemical shift of the 1-methyl group observed for (**2G**) (−7.01 p.p.m.) should be again the weighted average of the corresponding shifts of (**6Gae**) (−7.83 p.p.m.) and (**6Gee**) (−5.77 p.p.m.)[1] with the acceptable assumption that the 4-methyl group will not affect the 1-methyl resonance to any significant extent. Accordingly, the population x of (**2Ga**) is given by $-7.83x - 5.77(1 - x) = -7.01$. The calculated value of x (0.60) is again in accord with the molecular mechanics calculations. These observations can now be accepted as experimental confirmation of the fact that the axial isomer of (**2G**) is at least comparable in energy with its equatorial isomer.

Conclusions.—Molecular mechanics calculations as well as ^{13}C and ^{73}Ge n.m.r. spectra indicate a small preference for the axial conformer in the equilibrium (**2Ge**) $\rightleftharpoons$ (**2Ga**), as with the reported case of (**2S**). This preference is ascribed to the stability of the *gauche* conformation over that of *anti* in the C(Me)–C(1)–Ge(2)–C(3) moiety.

It is interesting to introduce a substituent larger than methyl (*e.g.*, t-butyl) on germanium and see whether such a substituent could also be axial. Studies along this line are in progress.

Experimental

I.r. spectra were obtained with a JASCO A102 grating spectrophotometer as a liquid film. ^{1}H N.m.r. spectra were recorded with a Varian EM-390 spectrometer for $CDCl_3$ solutions containing tetramethylsilane as internal standard. ^{73}Ge N.m.r. spectra were recorded for 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, 2 000 Hz; number of scans, 5 000; pulse delay, 100 ms; data points, 4 096. ^{13}C N.m.r. 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, 200 Hz; number of scans, 500; pulse delay, 1 s; data points, 4 096. G.c.–m.s. spectra were obtained on a Hewlett–Packard 5995A instrument controlled by a Hewlett–Packard 9825 desktop computer system with a 25 m (φ 0.2 mm) cross-linked methylsilicone column.

Molecular mechanics calculations were carried out with Allinger's MM1 [18] and MM2 programs.[15] In the preparation of the input data for MM2 as well as MM1 and in the geometrical analysis of optimised structures, the personal-computer graphics program GRIMM was used.[25]

Preparation of Germacyclohexanes.—1,5-Dibromopentane and tetrachlorogermane were commercially available.

*2-Methyl-*1,5*-dibromopentane.* 3-Methylpiperidine and benzoyl chloride were caused to react in aqueous NaOH to give 1*-benzoyl-*3*-methylpiperidine* (86%), b.p. 143—147 °C at 2 mmHg (Found: C, 76.7; H, 8.5; N, 6.6. $C_{13}H_{17}NO$ requires C, 76.8; H, 8.4; N, 6.9%); $\nu_{max.}$(neat) 1 635 cm^{-1} (C=O). The benzoyl derivative was treated with PBr_3–Br_2 to afford the *title compound* (31%), b.p. 135—137 °C at 22 mmHg (Found: C, 29.45; H, 4.6. $C_6H_{12}Br_2$ requires C, 29.5; H, 4.9%).

3-Methyl-1,5-dibromopentane was prepared from 3-methylpentane-1,5-diol and hydrobromic acid in methylene dichloride.[26] Germacyclohexane (**1G**) was prepared from 1,5-dibromopentane.[11]

1*-Methyl-*1*-germacyclohexane* (**2G**). To a solution of dibromo(methyl)phenylgermane[27] (26 mmol) in dry diethyl ether (100 ml) was added the bis-Grignard reagent prepared from 1,5-dibromopentane (26 mmol) and excess of Mg in dry diethyl ether (40 ml) over 2 h under reflux. The mixture was further refluxed for 2 h and then decomposed with cold hydrochloric acid. The ether layer was separated and the aqueous layer was further extracted with ether. The combined extract was washed with water, dried, and evaporated. The residue was distilled with Kugelrohr to yield an oil, 1-methyl-1-phenyl-1-germacyclohexane (**2GP**) (2.71 g, 44%).

A solution of (**2GP**) (9.2 mmol) in 1,2-dibromoethane (30 ml) was caused to react with bromine (9.7 mmol) for 2 h. The solvent was evaporated off and the residue was distilled with Kugelrohr to yield 1-bromo-1-methyl-1-germacyclohexane (**2GB**) (1.56 g, 71%), b.p. 103—107 °C at 15 mmHg. To a solution of $LiAlH_4$ (8.7 mmol) in diethyl ether (30 ml) was added dropwise an ethereal solution of the above bromide (5.1 mmol). After refluxing for 3 h, the mixture was poured into cold water and extracted with diethyl ether. The usual work-up yielded an oil; (**2G**) (0.33 g, 41%) (Found: C, 43.8; H, 8.0. Calc. for $C_6H_{14}Ge$: C, 45.4; H, 8.9%).

The poor analysis seems to be due to contamination by a

Table 4. Physical properties of germacyclohexanes (**1G**)—(**7G**) and their precursors

Compound (Formula)	Yield[a] (%)	Isomer ratio (*cis*:*trans*)	B.p.[b] (°C/mmHg)	ν_H(neat) (cm^{-1})[b] (Ge–H)	δ_H	*m*/*z*[c]
(**1G**) ($C_5H_{12}Ge$)			65—67/150 (120/760)	2 050 (2 044)	3.69 (2 H, m, 1-H)	
(**2GP**) ($C_{12}H_{18}Ge$)	44		95—97/2		0.40 (3 H, s, 1-Me)	
(**2GB**) ($C_6H_{13}BrGe$)	71		103—107/45		0.87 (3 H, s, 1-Me)	
(**2G**) ($C_6H_{14}Ge$)	41		43—46/18	2 030	0.23 (3 H, d, *J* 3 Hz, 1-Me) 3.79 (1 H, m, 1-H)	160.1 (M^+), 145.2 ($M^+ - 15$), 132.2 ($M^+ - 28$)
(**3G**) ($C_6H_{14}Ge$)	11		72—74/55	2 050	3.65 (2 H, m, 1-H)	160.1 (M^+), 132.2 ($M^+ - 28$)
(**4G**) ($C_6H_{14}Ge$)	22		72—75/20	2 050	3.62 (2 H, m, 1-H)	160.1 (M^+), 132.2 ($M^+ - 28$)
(**5G**) ($C_7H_{16}Ge$)	30		93—95/116 (70—85)		0.16 (6 H, s, 1-Me)	
(**6GP**) ($C_{13}H_{20}Ge$)	32	44:56	105—108/2		0.32 (*trans*), 0.42 (*cis*) (3 H, s, 1-Me)	
(**6GB**) ($C_7H_{15}BrGe$)	93		122—127/20		0.85 (*trans*: + *cis*) (3 H, d, *J* 3 Hz, 1-Me)	
(**6G**) ($C_7H_{16}Ge$)	43	34:66	75—78/27	2 040	0.21 (*trans*), 0.23 (*cis*) (3 H, d, *J* 3 Hz, 1-Me)	174.2 (M^+), 159.2 ($M^+ - 15$) 146.2 ($M^+ - 28$)
(**7GP**) ($C_{13}H_{20}Ge$)	39	51:49	102—105/3		0.32 (*cis*), 0.40 (*trans*) (3 H, s, 1-Me)	
(**7GB**) ($C_7H_{15}BrGe$)	83	70:30	92—96/11		0.87 (*cis* + *trans*) (3 H, s, 1-Me)	
(**7G**) ($C_7H_{16}Ge$)	38	58:42	46—48/10	2 040	0.21 (*cis*), 0.23 (*trans*) (3 H, d, *J* 3 Hz, 1-Me)	174.1 (M^+), 159.1 ($M^+ - 15$) 146.1 ($M^+ - 28$)

[a] Yield based on the immediate precursor. [b] Values in parentheses are taken from the literature. [c] Of the peaks due to various isotopomers, only that due to ^{74}Ge is given.

polymerised product. Extensive chromatographic purification was impossible partly because of the small amount of the sample and partly because of gradual decomposition during work-up. The mass spectrum agreed, however, with the formula, m/z 161.1, 160.1, 159.2, 158.2, and 156.2 (M^+). The intensity of these peaks is in accord with the relative abundance of germanium isotopes. We therefore characterise germacyclohexanes by mass spectral rather than the elemental analysis. Table 4 lists m/z values together with other physical and spectroscopic data for germacyclohexanes.

3-Methyl-1-germacyclohexane (**3G**) was prepared from the coupling between 2-methyl-1,5-dibromopentane and $GeCl_4$ and the subsequent reduction of the dichloride with $LiAlH_4$.

4-Methyl-1-germacyclohexane (**4G**) was prepared in a similar manner to (**3G**) from 3-methyl-1,5-dibromopentane.

1,1-Dimethyl-1-germacyclohexane (**5G**) was prepared from 1,1-dichloro-1-germacyclohexane and methylmagnesium iodide (30%).[12]

1,3-*Dimethyl*-1-*germacyclohexane* (**6G**). Reaction of the bis-Grignard reagent of 2-methyl-1,5-dibromopentane with dibromo(methyl)phenylgermane afforded a mixture of *cis*- and *trans*-1,3-dimethyl-1-phenyl-1-germacyclohexane (**6P**) (32%). The *trans*:*cis* ratio was 56:44 based on ^{1}H n.m.r. signal intensities. Treatment of (**6GP**) with bromine afforded 1-bromo-1,3-dimethyl-1-germacyclohexane (**6GB**) (93%). Compound (**6GB**) was converted into (**6G**) by $LiAlH_4$ (43%) as a mixture of *cis*- and *trans*-isomers.

^{73}Ge N.m.r. data were as follows: δ_{Ge} relative to $GeMe_4$ (**6Gee**) (*cis*-isomer) -60.3; (**6Gae**) (*trans*-isomer) -70.9 p.p.m. ^{13}C Data were: δ_C (**6Gee**) (*cis*-isomer) -5.28 (q, 1-Me), 11.95 (t, C-6), 21.75 (t, C-2), 26.12 (t, C-5), 27.60 (q, 3-Me), 31.97 (d, C-3), and 38.43 (t, C-4); (**6Gae**) (*trans*-isomer) -7.58 (q, 1-Me), 11.00 (t, C-6), 20.66 (t, C-2), 24.61 (t, C-5), 27.29 (q, 3-Me), 31.97 (d, C-3), and 38.26 (t, C-4).

1,4-*Dimethyl*-1-*germacyclohexane* (**7G**). The same procedure was employed for the preparation of (**7G**). 1-Phenyl-1,4-dimethyl-1-germacyclohexane (**7GP**) obtained from 3-methyl-1,5-dibromopentane (39%) was brominated to 1-bromo-1,4-dimethyl-1-germacyclohexane (**7GB**) (83%), which was then reduced to (**7G**) by $LiAlH_4$ (38%).

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