

Bicyclo[1.1.0]tetragermane and Bicyclo[2.2.0]hexagermane; An *Ab Initio* Study of Bicyclic Germanium Compounds

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By means of *ab initio* calculations, it is predicted that bicyclo[1.1.0]tetragermane exhibits a strong bond-stretch isomerism, whereas bicyclo[2.2.0]hexagermane adopts a normal structure with the four-membered rings fused.

There has been considerable recent interest in the preparation and characterization of the heavier atom analogues of bicycloalkanes. In the last three years derivatives of bicyclo[1.1.0]tetrasilane¹ and bicyclo[2.2.0]hexasilane² have been synthesized, and their X-ray structures have been

determined.^{3,4} We report here the first *ab initio* calculations on bicyclo[1.1.0]tetragermane (**1**) and bicyclo[2.2.0]hexagermane (**2**), in continuance of our recent comparative study of the corresponding silicon compounds.⁵ Geometries were fully optimized at the Hartree-Fock (HF) level with the split-

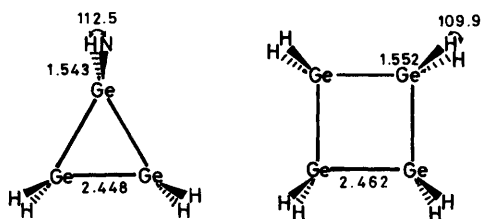
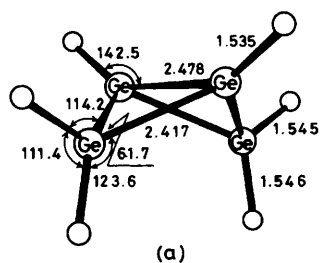
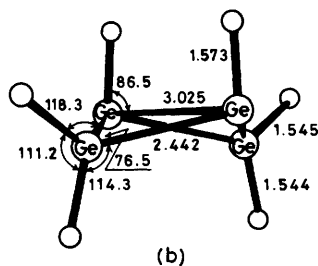


Figure 1. Optimized geometries of cyclotrigermane (D_{3h}) and cyclotetragermane (D_{4h}) (in Å and degrees). The total energies are -6200.02939 and -8266.77912 a.u., respectively. No puckered D_{2d} form of cyclotetragermane was favoured, in contrast with C_4H_4 and Si_4H_4 .



(a)



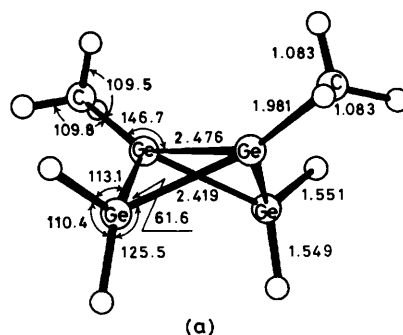
(b)

Figure 2. Optimized geometries of two isomers (a) and (b) of (1) (C_{2v}) (in Å and degrees). The inter-flap angles and total energies are 118.3° and -8265.56420 a.u. for (a) and 143.6° and -8265.58888 a.u. for (b).

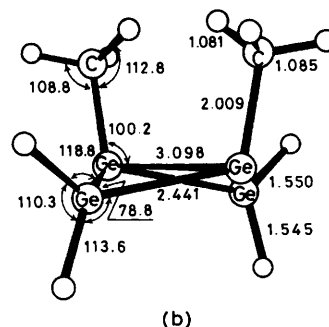
valence 3-21G(*) basis set augmented by a set of d polarization functions (exponent 0.246) on Ge.⁶ For comparison, calculations were performed for the monocyclic germanium compounds, cyclotrigermane and cyclotetragermane, at the same theoretical level; these results are shown in Figure 1.

As Figure 2 shows, two distinctly different structures, (a) and (b), were located for (1), as for the silicon analogue.^{5,7-9} Both have C_{2v} symmetry. The peripheral Ge-Ge bond lengths in (a) and (b) are rather shorter than the Ge-Ge bond lengths in the three-membered ring of cyclotrigermane (Figure 1). The central Ge-Ge bridge bond (2.478 Å) in (a) is only 0.03 Å longer than the Ge-Ge bonds in cyclotrigermane. In sharp contrast, the central Ge-Ge bond in (b) is stretched to 3.025 Å and has some singlet diradical character. The stretching of ca. 0.5 Å is similar to that calculated recently for the corresponding silicon compound.^{5,7-9} However, the energy difference (15.5 kcal mol⁻¹) favouring (b) over (a) is twice or three times larger in (1) than the corresponding HF/3-21G(*) value of 6 kcal mol⁻¹ for the silicon compound,⁷ suggesting the greater stability of the 'bond-stretch' isomer of the germanium compound.

The important geometrical differences between (a) and (b) lie not only in the central bond lengths, but also in the Ge-Ge-H angles at the bridgehead positions [142.5° (a) vs. 86.5° (b)]. The much smaller Ge-Ge-H angles in (b) enforce a



(a)



(b)

Figure 3. Optimized geometries of two C_{2v} isomers (a) and (b) after methyl substitution (in Å and degrees). The inter-flap angles and total energies are 115.7° and -8343.23491 a.u. for (a) and 147.7° and -8343.24983 a.u. for (b).

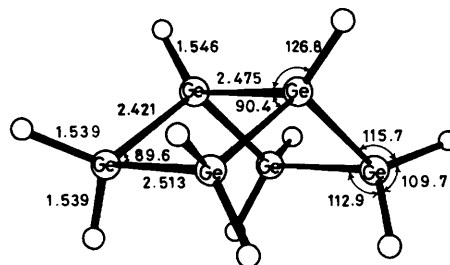
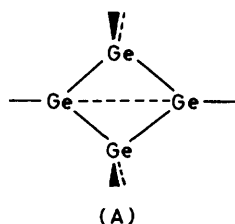


Figure 4. Optimized geometries of (2) (C_{2v}) (in Å and degrees). The inter-flap angle and total energy are 107.1° and -12398.34469 a.u. Because of the size of the molecule, d polarization functions are included only on the bridgehead Ge atoms.

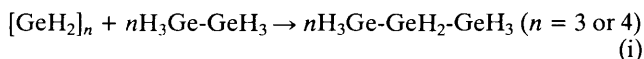
close approach of the two H atoms attached to the bridgeheads. It has recently been shown in the silicon compounds that methyl substitution at the bridgehead positions leads to a 'bond-short' normal isomer for steric and electronic reasons.^{7,9} Thus the two H atoms on the bridgeheads in (1) are replaced by methyl groups. As Figure 3 shows, however, two isomers were located and the bond-stretch isomer was calculated to be 9.4 kcal mol⁻¹ more stable even in 1,3-dimethylbicyclo[1.1.0]tetragermane.[†] It is noteworthy that the methyl substitution has no significant effect on the central Ge-Ge bonds of the two isomers.[‡]

[†] In a preliminary study, we have found that a similar ineffectiveness of methyl substitution results in the corresponding silicon compound, contrary to recent findings.^{7,9} This apparent discrepancy for the silicon compound is due to the fact that no geometry optimization was carried out in the previous studies.^{7,9}

[‡] In silicon compounds the same was also true for more bulky groups, though the bond-stretch isomers became gradually less stable.



As shown in Figures 2 and 3, the inter-flap angles between the fused three-membered rings are much larger in the bond-stretch isomers: 118.3° (a) vs. 143.6° (b) in (1) and 115.7° (a) vs. 147.7° (b) in the methyl substituted (1). This suggests that the bond stretch isomers may be viewed as a four-membered monocyclic ring with a weak transannular bond [see (A)]: germanium has a tendency to prefer four-membered over three-membered rings.



To confirm this view, we calculated the strain energies of cyclotrigermane $[\text{GeH}_2]_3$ and cyclotetragermane $[\text{GeH}_2]_4$ by use of the so-called homodesmotic reactions (i).¹⁰ The values obtained were 44.6 and 13.5 kcal mol⁻¹ for cyclotrigermane and cyclotetragermane, respectively. The strain energy difference of 31 kcal mol⁻¹ is larger than the value of 22 kcal mol⁻¹ between cyclotrisilane (39 kcal mol⁻¹) and cyclotetrasilane (17 kcal mol⁻¹).¹¹ This indicates that the difference in strain energy between four-membered rings and three-membered rings is significantly greater in germanium compounds than in silicon compounds; this forms an interesting contrast with the fact that these ring sizes are almost equally strained (ca. 27 kcal mol⁻¹) in carbon compounds.¹² It appears that germanium three-membered rings are most strained, and germanium four-membered rings are least strained.

As expected from this property of germanium, only a normal structure was located for (2), consisting of four-membered rings. As Figure 4 shows, the central and peripheral Ge-Ge bond lengths in (2) compare favourably with those in the four-membered ring of cyclotetragermane (Figure 1).

In conclusion, the high strain in three-membered germanium rings (and the relatively weak Ge-Ge bonds as compared with C-C bonds) leads to bond-stretch isomerism in (1). On the other hand, compound (2) with its less strained four-membered rings fused, has a normal structure. As in silicon chemistry,¹⁻⁴ both structures (1) and (2) present interesting synthetic targets.

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