for non-hydrogen atoms brought refinement to convergence at $R = \sum||F_0| - |F_c||/\sum|F_0| = 0.052$ and $R_w = [\sum w||F_0| - |F_c||^2/\sum|F_0|^2]^{1/2} = 0.061$. The least-squares weighting that was used was $w^{1/2} = 1$ for $|F_0| \leq 46.0$ and $w^{1/2} = 46.0/|F_0|$ for $|F_0| \geq 46.0$. The atomic scattering factors for the non-hydrogen atoms were those from Cromer and Waber;[22] those for hydrogen atoms were from Stewart.[23] Anomalous dispersion factors for the Rh atoms were from ref 24. All calculations were performed on a VAX 8650 computer or a μVAX-II.

There are two, very similar, independent molecules in the asymmetric unit. The atomic coordinates are recorded in Table III, and bond lengths and angles are given in Table IV.

Acknowledgment. We acknowledge support of this work from an Atlantic Richfield Foundation Grant of Research Corp., the National Science Foundation (CHE-8704933), and the donors of the Petroleum Research Fund, administered by the American Chemical Society. Crystallographic calculations were aided by NSF Instrumentation Grant CHE-8700787. The Johnson Matthey Co. is gratefully acknowledged for generous loans of rhodium trichloride.

Registry No. **3**, 14523-22-9; **4**, 12081-16-2; **5**, 85288-96-6; **6**, 87156-72-7; **7**, 18903-55-4; **8**, 55831-89-5; **9**, 116669-56-8; **10**, 17945-72-1; **11**, 116669-57-9; **12**, 116669-58-0; **13**, 116669-59-1; **14**, 116669-60-4; **15**, 116669-61-5; **16**, 85288-95-5; **17**, 28031-49-4; **18**, 116669-62-6; **19**, 116698-91-0; **20**, 116698-92-1; **21**, 116698-93-2; **22**, 116698-94-3; **23**, 116698-95-4; **24**, 116698-96-5; **25**, 116698-97-6; **26** (isomer 1), 116699-08-2; **26** (isomer 2), 116836-58-9; **27** (isomer 1), 116699-09-3; **27** (isomer 2), 116781-94-3; **28** (isomer 1), 116836-57-8; **28** (isomer 2), 116699-10-6; **29**, 116698-98-7; **30**, 116781-92-1; **31**, 116698-99-8; **32**, 116699-00-4; **33** ($n = 1$, R_1 = Me, R_2 = H), 116699-01-5; **33** ($R_1 = R_2$ = H, $n = 3$), 116699-02-6; **33** (R_1 = H, R_2 = $(CH_2)_4$–, $n = 1$), 116699-03-7; **33** ($R_1 = R_2$ = Me, $n = 1$), 116699-07-1; **34**, 116669-63-7; **37**, 116599-60-1; **38**, 116699-04-8; **39**, 116699-05-9; **40**, 116781-93-2; **41**, 116724-43-7; **42**, 116724-44-8; **43**, 116747-04-7; **44**, 116699-06-0; $RhCl_3$, 10049-07-7.

Supplementary Material Available: Listings of anisotropic thermal parameters for non-hydrogen atoms and refined hydrogen atom positional parameters (3 pages); a listing of observed and calculated structure factors (10 pages). Ordering information is given on any current masthead page.

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Interesting Bonding between the Inverted Germanium Atoms in Pentagerma[1.1.1]propellane and Derivatives. A Theoretical Study

Shigeru Nagase* and Takako Kudo

Department of Chemistry, Faculty of Education, Yokohama National University, Yokohama 240, Japan

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The unique Ge–Ge central bonding in the title compounds are characterized by means of ab initio calculations and a π-complex model. It is found that electron-accepting substituents at the peripheral positions have an important effect on the bond lengths. Especially interesting is the trioxa substitution which leads to an unusual bond shortening.

Among strained compounds, [1.1.1]propellane having three three-membered rings fused to a common carbon–carbon bond is a most intriguing species because of its unusual structure with "inverted" tetrahedral configurations at the bridgehead carbon atoms;[1] the nature of the interesting interbridgehead C–C bonding has repeatedly been debated.[2] The structures and properties of the silicon analogues have been investigated in the last year.[3–6] We report now several interesting features of the germanium analogues pentagerma[1.1.1]propellane (1) and its derivatives by means of ab initio calculations. Our primary concern is on the characterization of the central Ge–Ge bridge bonding between the inverted tetracoordinate germanium atoms because of growing interest. Geometries were fully optimized at the Hartree–Fock (HF) level with the split-valence d-polarized 3-21G(d) and 3-21G(2d) basis sets.[7,8] For uniform comparison, all values cited here are

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(2) For example, see: (a) Stohrer, W.-D.; Hoffmann, R. *J. Am. Chem. Soc.* **1972**, *94*, 779. (b) Newton, M. D.; Schulman, J. M. *J. Am. Chem. Soc.* **1972**, *94*, 773. (c) Wiberg, K. B. *J. Am. Chem. Soc.* **1983**, *105*, 1227. (d) Jackson, J. E.; Allen, L. C. *J. Am. Chem. Soc.* **1984**, *106*, 591. (e) Epiotis, N. D. *J. Am. Chem. Soc.* **1984**, *106*, 3170. (f) Honegger, Ev.; Huber, H.; Heilbronner, E.; Dailey, W. P.; Wiberg, K. B. *J. Am. Chem. Soc.* **1985**, *107*, 7172. (g) Hedberg, L.; Hedberg, K. *J. Am. Chem. Soc.* **1985**, *107*, 7257. (h) Wiberg, K. B.; Dailey, W. P.; Walker, F. H.; Waddell, S. T.; Crocker, L. S.; Newton, M. *J. Am. Chem. Soc.* **1985**, *107*, 7247. (i) Politzer, P.; Jayasuriya, *J. Mol. Struct.* (*Theochem.*) **1986**, *135*, 245. (j) Pierini, A. B.; Peale, H. F.; Medrano, J. A. *J. Mol. Struct.* (*Theochem.*) **1986**, *148*, 109. (k) Messmer, R. P.; Schultz, P. A. *J. Am. Chem. Soc.* **1986**, *108*, 7407. (l) Wiberg, K. B.; Bader, R. W. F.; Lau, C. D. H. *J. Am. Chem. Soc.* **1987**, *109*, 985, 1001. (m) Feller, D.; Davidson, E. R. *J. Am. Chem. Soc.* **1987**, *109*, 4133.

(3) Nagase, S.; Kudo, T. *Organometallics* **1987**, *6*, 2456.

(4) Schleyer, P. v. R.; Janoschek, R. *Angew. Chem., Int. Ed. Engl.* **1987**, *26*, 1267.

(5) Schoeller, W. W.; Dabisch, T.; Busch, T. *Inorg. Chem.* **1987**, *26*, 4383.

(6) For the silicon analogues of polyhedral strained compounds such as tetrahedrane, prismane, and cubane, see: (a) Nagase, S.; Nakano, M.; Kudo, T. *J. Chem. Soc., Chem. Commun.* **1987**, 60. (b) Nagase, S.; Nakano, M. *Angew. Chem., Int. Ed. Engl.* **1988**, *27*, 1081.

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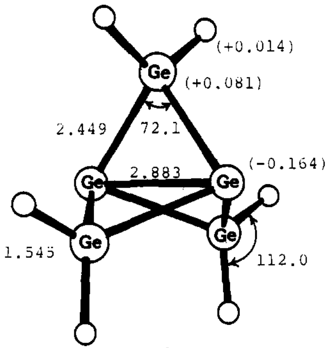

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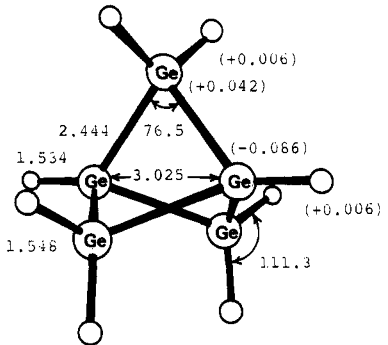
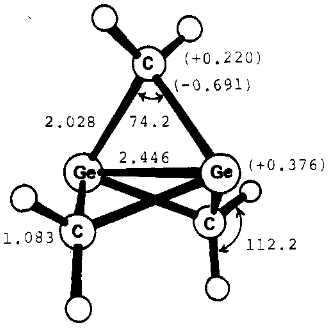


2

Figure 1. HF/3-21G(d) optimized geometries (in Å and deg) and gross atomic charges (in parentheses) of 1 and 2 with D_{3h} symmetry. The total energies are −10331.18358 (1) and −10332.34089 (2) au.

those at the HF/3-21G(d) level unless otherwise mentioned.

Figure 1 shows the optimized geometry of 1. The peripheral Ge–Ge bond lengths (2.449 Å) compare favorably with the Ge–Ge bond lengths (2.448 Å) in the three-membered ring of cyclotrigermane.[9] However, the central Ge–Ge bond is stretched by ca. 0.44 Å to have a long bond length of 2.883 Å;[10,11] this contrasts with the fact that [1.1.1]propellane has a normal central bond length.[1,2] For comparison, also shown in Figure 1 is the optimized structure of bicyclo[1.1.1]pentagermane (2) which lacks a formal interbridgehead bond. The central bond length (2.883 Å) in 1 is rather close to the nonbonded Ge–Ge separation (3.025 Å) in 2. It appears that the central bond stretching in 1 is due to relatively weak Ge–Ge bonds (compared with C–C bonds)[12] and high strain in the germanium three-membered rings: the strain energy of cyclotrigermane (44.6 kcal/mol) is ca. 18 kcal/mol larger than that of cyclopropane.[9,13,14]



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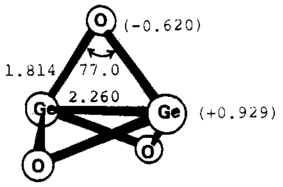

4

Figure 2. HF/3-21G(d) optimized geometries (in Å and deg) and gross atomic charges (in parentheses) of 3 and 4 with D_{3h} symmetry. The total energies are −4247.53727 (3) and −4354.48746 (4) au. The HF/3-21G(2d) optimized geometry of 4 (total energy = −4354.79555 au) are GeGe = 2.247 Å, GeO = 1.811 Å, and ∠GeOGe = 76.7°.

In an attempt to design a short Ge–Ge bridge bond, it is instructive to view 1 as resulting from a donor–acceptor interaction between GeGe and three GeH_2 units. In 1 the GeGe part carries a large amount of negative charge (−0.164 e on each Ge atom despite the electropositive character of Ge), as shown in Figure 1. This indicates that GeGe and GeH_2 participate in 1 as a poor and a good donor, respectively. The dominant electron donation into the antibonding π^* vacant orbital of the original GeGe unit should be responsible for the stretching of the Ge–Ge bond. In addition, the orbital expansion resulting from the dense electron clouds around the bridgeheads enhances the bond stretching.

If these views are correct, electron-accepting substituents at the peripheral positions should suppress significantly the stretching of the central Ge–Ge bond. As an attempt, the peripheral GeH_2 groups in 1 were all replaced by CH_2 groups because carbon is electronegative to germanium. As Figure 2 shows, the substitution converts the charges on the bridgehead Ge atoms from −0.164 e (negative) to +0.376 e (positive) as a result of the increased electron donation from GeGe to three CH_2 units and the decreased back electron donation into the π^* orbital of GeGe. As expected from the decreased repulsive character in the interbridgehead region, the central Ge–Ge bond length is shortened to 2.446 Å in 1,3-digerma[1.1.1]propellane (3).

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(8) The 3-21G(d) and 3-21G(2d) basis sets include a set of d polarization functions (exponents 0.8 for C and O^{7b} and 0.246 for Ge^{7d}) and double sets of d polarization functions (exponents 0.4 and 1.6 for C and O and 0.108 and 0.382 for Ge^{7d}), respectively.

(9) Nagase, S.; Nakano, M. *J. Chem. Soc., Chem. Commun.* **1988**, 1077.

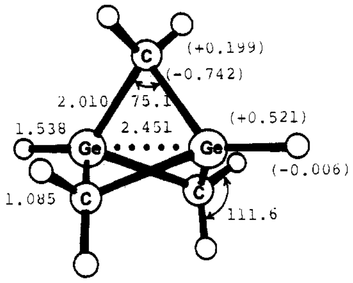
(10) No second minimum with a short central Ge–Ge bond could be located for 1, as also in pentasila[1.1.1]propellane.[3,4] This provides an interesting contrast with the fact that both bond stretch and bond short isomers are located in bicyclo[1.1.0]tetragermane.[9] For the bond stretch isomerism in bicyclo[1.1.0]tetrasilane, see: (a) Schleyer, P. v. R.; Sax, A. F.; Kalcher, J.; Janoschek, R. *Angew. Chem., Int. Ed. Engl.* **1987**, *26*, 364. (b) Dabisch, T.; Schoeller, W. W. *J. Chem. Soc., Chem. Commun.* **1986**, 896 and ref 5. (c) Nagase, S.; Kudo, T. *J. Chem. Soc., Chem. Commun.* **1988**, 54. For the "two-bond" stretch isomer in tetrasilatetrahedrane, see ref 6b.

(11) Because of the bond stretching (i.e., the decrease in the HOMO–LUMO energy gap), it was calculated that the restricted HF solution becomes unstable with respect to the broken-symmetry unrestricted HF solution. This suggests that the central Ge–Ge bond has some singlet diradical character and a multideterminant treatment may be essential for a more correct description of the diradical character. Upon inclusion of electron correlation the bond stretching will be further enhanced by admixture of the LUMO (the antibonding MO of the central Ge–Ge bond) into the HOMO (the bonding MO of the central Ge–Ge bond), as seen in pentasila[1.1.1]propellane.[4]

(12) Rochow, E. G.; Abel, E. W. *The Chemistry of Germanium, Tin, and Lead*; Pergamon: Oxford, 1975. Glockling, F. *The Chemistry of Germanium*; Academic: New York, 1969.

(13) In contrast, cyclotetragermane is much less strained than cyclobutane.[9] Thus, it is expected that octagerma[2.2.2]propellane with three four-membered rings fused possesses a normal central bond length, as does octasila[2.2.2]propellane.[3] The effect is already demonstrated for the normal central bonds in bicyclo[2.2.0]hexagermane[9] and bicyclo[2.2.0]hexasilane[10c] containing only four-membered rings.

(14) The same trend is also seen in three-membered and four-membered silicon rings: cyclotrisilane is more strained than cyclopropane while cyclotetrasilane is less strained than cyclobutane.[6a,10a] For the preliminary comparison in strain between germanium and silicon rings, see ref 9.



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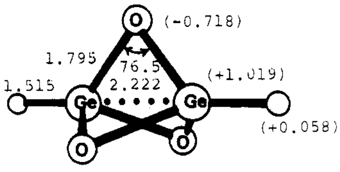

6

Figure 3. HF/3-21G(d) optimized geometries (in Å and deg) and gross atomic charges (in parentheses) of **5** and **6** with D_{3h} symmetry. The total energies are −4248.708 69 (**5**) and −4355.715 54 (**6**) au. The HF/3-21G(2d) optimized geometry of **6** (total energy = −4356.023 59 au) are GeGe = 2.212 Å, GeO = 1.793 Å, GeH = 1.502 Å, and ∠GeOGe = 76.2°.

This clearly suggests that the greater the accepting capacity of peripheral groups, the shorter the central Ge–Ge bond.

Thus, we have next replaced the CH_2 groups in **3** by more electronegative oxygen atoms. The great electronegativity difference between oxygen and germanium leads to the predominance of a π(GeGe) → O forward donation over a O → π*(GeGe) back-donation and makes the bridgehead Ge atoms more positively charged to +0.929 e, followed by significant orbital contraction around the bridgeheads.

The predominance of the forward donation results in forming a π complex between GeGe and O with a T structure;[15,16] a three-center, two-electron bond is created between GeGe and O.[17] On the other hand, little back-donation into the antibonding π* orbital of GeGe and the accompanying orbital contraction around the bridgeheads are suitable for the proximity of the bridgehead Ge atoms. As a consequence, the interbridgehead Ge–Ge bond length becomes as short as 2.260 Å (2.247 Å at the HF/3-21G(2d) level) in 2,4,5-trioxa-1,3-digerma[1.1.1]propellane (**4**),[18] as shown in Figure 2. Noteworthy is that the Ge–Ge bond length in **4** is much shorter than a typical Ge–Ge single bond length (2.443 Å in digermane); it is rather indicative of a Ge–Ge double bond length (2.275 Å in trans-bent digermene),[19] the germaniums in **4** exhibiting formally five valences. To our knowledge, **4** has the shortest Ge–Ge bond length between inverted Ge atoms. It should be noted that no such unusual shortening is expected in the corresponding carbon compound.[3]

An interesting finding is that upon hydrogenation the interbridgehead Ge–Ge length in **3** is essentially constant (see 1,3-digermabicyclo[1.1.1]pentane (**5**) in Figure 3), despite the formal cleavage of the bond. More interesting is the hydrogenation of **4**:[20] the interbridgehead Ge–Ge length becomes even shorter in 2,4,5-trioxabicyclo[1.1.1]-pentagermane (**6**), as shown in Figure 3. As is apparent from the increased positive charges on the bridgehead Ge atoms, these are also explained in terms of the higher π complex character and much decreased back-donation into the π* orbital of the HGeGeH unit: the π* level is higher in HGeGeH (1.74 eV)[21] than in GeGe (1.25 eV). The Ge–Ge distance of 2.222 Å (2.212 Å at HF/3-21G(2d)) in **6** is the shortest separation between formally nonbonded Ge atoms,[22] while the moderate distance (2.560 Å) is seen between the nonbonded Ge atoms in the cyclic dimer $(H_2GeO)_2$ of germanone.[23]

We think that pergerma[1.1.1]propellanes form also interesting synthetic targets upon the replacement of the hydrogens in **1** by proper substituents. A study along this line is in progress.

Acknowledgment. This work was supported in part by a grant from the Ministry of Education, Science, and Culture in Japan. Calculations were carried out at the Computational Room of the Faculty of Education of Yokohama National University and at the Computer Center of the Institute of Molecular Science using the GAUSSIAN 82 program.[24]

Registry No. **1**, 116953-98-1; **2**, 116953-99-2; **3**, 116954-00-8; **4**, 59087-76-2; **5**, 116954-01-9; **6**, 63937-01-9.

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(15) Dewar, M. J. S.; Ford, G. P. *J. Am. Chem. Soc.* **1979**, *101*, 783.

(16) Cremer, D.; Kraka, E. *J. Am. Chem. Soc.* **1985**, *107*, 3800.

(17) For a "σ-bridged π" description of the central bonding in [1.1.1]propellane, see ref 2d. However, note also the arguments in ref 21 and 2m.

(18) It is instructive to note that a similar, but smaller shortening is also seen in the Ge–Ge bond length of digermene oxide H_2GeGeH_2O: GeGe = 2.314 Å, GeO = 1.792 Å, ∠GeOGe = 80.4°, ∠HGeGe = 124.1°, and ∠HGeGeO = 93.8° in C_{2v} symmetry. The GeGe bond length of 2.314 Å is ca. 0.13 Å shorter than those in cyclotrigermane.

(19) For the trans-bent C_{2h} structure of digermene, see: Trinquier, G.; Malrieu, J.-P.; Riviere, P. *J. Am. Chem. Soc.* **1982**, *104*, 4529. Nagase, S.; Kudo, T. *J. Mol. Struct.* (*Theochem*) **1983**, *103*, 35. Goldberg, D. E.; Hitchcock, P. B.; Lapert, M. F.; Thomas, K. M.; Thorne, A. J.; Fjeldberg, T.; Haaland, A.; Schilling, B. E. R. *J. Chem. Soc., Dalton. Trans.* **1986**, 2387 and references cited therein.

(20) The hydrogenation, **4** + H_2 → **6**, is 28.2 kcal/mol exothermic at the MP2/3-21G(d)//HF/3-21G(d) level. It is interesting that the exothermicity does not differ much from the corresponding value of 40.2 kcal/mol for the hydrogenation of trans-bent digermene.

(21) For the present purpose (i.e., as a component part in the donor–acceptor interaction), HGeGeH was optimized in the linear form: GeGe = 2.033 Å and GeH = 1.502 Å. However, note that the linear form of HGeGeH possesses two imaginary frequencies and is not a minimum.

(22) For unusually short bonds in silicon and phosphorus compounds, see: Nagase, S.; Kudo, T.; Kurakake, T. *J. Chem. Soc., Chem. Commun.* **1988**, 1063.

(23) Other optimized geometrical parameters in D_{2h} symmetry are GeO = 1.770 Å, GeH = 1.544 Å, ∠GeOGe = 92.6°, and ∠HGeH = 112.3°.

(24) Binkley, J. S.; Frisch, M. J.; DeFrees, D. J.; Rahgavachari, K.; Whiteside, R. A.; Schlegel, H. B.; Fludre, E. M.; Pople, J. A. Department of Chemistry, Carnegie-Mellon University, Pittsburgh, PA.