Molecular Structure of 2,2,5,5-Tetramethyl-1,3-diselena-2-germacyclohexane. Evidence for Symmetrical Twist-boat Conformation

Shuji Tomoda,*[a] Masakatsu Shimoda,[a] Mitsuru Sanami,[a] Yoshito Takeuchi,*[a] and Yoichi Iitaka[b]

[a] *Department of Chemistry, College of Arts & Sciences, The University of Tokyo, Komaba, Meguro-ku, Tokyo 153, Japan*

[b] *Faculty of Pharmaceutical Sciences, The University of Tokyo, Hongo, Bunyo-ku, Tokyo 112, Japan*

An *X*-ray crystallographic analysis and dynamic ^{1}H n.m.r. study have shown that the title compound exists in a symmetrical 2,5-twist-boat conformation both in the solid state and in solution; an unusually high barrier for interconversion between the two enantiotopic conformational isomers (32.4 kJ/mol) has been measured.

Conformational effects in heteroatom-substituted systems have been the subject of intense investigation by both experimental[1] and theoretical[2] chemists. In particular, systems having the X–C–Y moiety (X and Y heteroatoms) in a six-membered ring have been thoroughly studied in view of the anomeric effect.[1a] Most systems exist exclusively or predominantly in the chair conformation[3] and are limited to those containing second- and/or third-row heteroatoms as X and Y, with a few exceptions.[4] We present herein an unprecedented example of a six-membered ring having an Se–Ge–Se segment which adopts an exclusive twist-boat conformation both in the solid state and in solution.

During our investigation of the direct spectral observation of dimethylgermylene (dimethylgermanediyl)[5] we required the title compound (**1**), which contains three consecutive fourth-row heteroatoms (Se–Ge–Se), as a precursor. *X*-Ray crystallographic analysis of (**1**) reveals that the six-membered ring has an unusual symmetrical geometry as shown in Figure 1.† While the bond angles and distances of (**1**) are not significantly different from those observed for ordinary organoselenogermanes,[6] the torsion angle between the two planes which make up the six-membered ring [Se(1)–Ge(2)–Se(3) and C(4)–C(5)–C(6)] is approximately 45°, indicating that (**1**) possesses a C_2 symmetry axis along the line connecting the two atoms Ge(2) and C(5). The highly symmetrical 2,5-twist-boat conformation of (**1**) in the solid state is surprising because the intramolecular non-bonded distances between selenium and methylene carbon (*ca.* 3.21 Å) are

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† *Crystal data*: $C_7H_{16}Se_2Ge$: triclinic, space group $P\bar{1}$; $T = 298$ K; $a = 10.525(5)$, $b = 9.169(5)$, $c = 6.598(3)$ Å, $\alpha = 106.71(5)$, $\beta = 103.50(5)$, $\gamma = 97.435(5)°$, $Z = 2$; $\lambda = 0.71069$ Å; μ(Mo-K_α) = 120.0 cm^{-1}. ω–2θ scan; $6 \leqslant 2\theta \leqslant 60°$; 2650 reflections, $R = 0.149$. Atomic co-ordinates, bond lengths and angles, and thermal parameters have been deposited at the Cambridge Crstallographic Data Centre. See Notice to Authors, Issue No. 1.

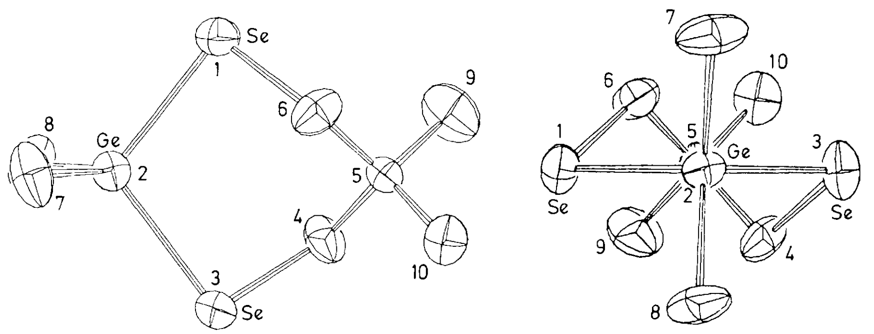

Figure 1. ORTEP plot of the molecular structure of 2,2,5,5-tetramethyl-1,3-diselena-2-germacyclohexane (**1**) (hydrogens are omitted). Atoms are shown by 30% probability ellipsoids. Bond distances (Å): Ge(2)–Se(1) 2.349; Ge(2)–Se(3) 2.352; Ge(2)–C(7) 1.953; Ge(2)–C(8) 1.967; Se(1)–C(6) 1.941; Se(3)–C(4) 2.003; bond angles (°): Se(1)–Ge(2)–Se(3) 103.2; C(7)–Ge(2)–C(8) 111.5; Se(1)–Ge(2)–C(7) 108.6; Se(1)–Ge(2)–C(8) 112.1; Ge(2)–Se(1)–C(6) 92.4; Se(1)–C(6)–C(5) 116.2; C(4)–C(5)–C(6) 109.9.

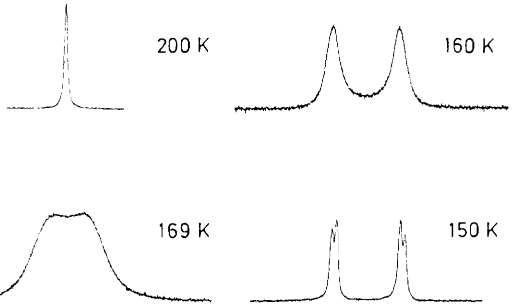

Figure 2. Variable temperature ^{1}H n.m.r. spectra of (**1**) in $CFCl_3$/$CDCl_3$ (1 : 1) at 500 MHz.

much less than the sum of the usual van der Waals radii of carbon (1.7 Å) and selenium (1.9 Å). These non-bonded atoms are clearly in contact with each other, which may suggest attractive interactions due to the hypervalent nature of selenium.[7,8] 1,3-Diaxial interactions, which would cause major destabilization of the hypothetical chair conformation,‡ between the axial methyl at Ge(2) and the axial methylene protons (3.53 Å for chair and 3.86 Å for twist-boat) may be somewhat relieved on going from the chair to the twist-boat (**1**), but may not be significant even in the chair because of appreciably elongated bond distances (2.35 Å for Ge–Se, 1.95—1.97 Å for Ge–C, and 1.94—2.00 Å for Se–C). The marginally distorted bond angles around the sp^3-hybridized germanium atom may be indicative of the absence of *gem*-dialkyl effects,[3] which would contribute to destabilization of the chair form of (**1**).

It has been reported that six-membered cyclic compounds having a twist-boat structure in the solid state exist as a mixture of chair and twist-boat conformational isomers in solution[3] owing to significant intermolecular interactions in the solid state. In order to confirm that an intramolecular interaction is responsible for the twist-boat structure of (**1**), the conformational behaviour of (**1**) was studied in solution.

The ^{1}H n.m.r. spectrum of (**1**) in $CFCl_3$/CD_2Cl_2 (1 : 1) at 500 MHz shows temperature dependent behaviour for only the methylene resonance (Figure 2). This signal (δ 2.55) broadens at about 200 K and reaches the coalescence point at 170 K. Further cooling causes collapse of the broad singlet into two broad singlet absorptions (160 K; Δv 175.7 Hz), which upon further cooling (150 K) collapse into a set of doublets with a splitting of 11.6 Hz, a typical geminal methylene coupling constant. During this process the methyl resonances (δ 1.03 and 1.11) remain unaffected and no extra resonances are observed. In addition, the ^{77}Se (δ −153.3 relative to external Me_2Se) and ^{13}C n.m.r. spectra (δ 6.8, 25.6, 30.9, 34.5) do not show any changes with temperature (down to 173 K) owing to chemical exchange. The ^{1}H n.m.r. spectrum at 150 K is consistent only with a single preferred conformation of (**1**) which is a symmetrical twist-boat form possessing a C_2 symmetry axis (2,5-twisted form), exactly as observed in the *X*-ray diffraction analysis. The barrier for interconversion between the two enantiotopic twist-boat conformational isomers ($\Delta G^‡$) is 32.4 kJ/mol (7.74 kcal/mol) at T_c 170 K.§ The conformational barrier for (**1**) in solution is much greater than calculated for the interconversion between the two twist-boat conformations of cyclohexane (0~7.5 kJ/mol),[9] but is of similar magnitude to the experimental values for macrocyclic hydrocarbons (*ca.* 30 kJ/mol).[10]

The anomalously high barrier between the two enantiotopic twist-boat conformers for (**1**) is remarkable since considerable reduction of *syn*-eclipsing repulsive interactions in the transition state for pseudo-rotation in (**1**) due to longer Ge–Se, C–Ge, and C–Se bonds would, *a priori*, be expected. The 'rabbit-ear' effect[1a] of the selenium lone pairs may be substantially attenuated in the hypothetical chair conformation. The results for (**1**) are in sharp contrast to the non-germanium containing analogue, 1,3-diselenacyclohexane, which adopts a pure chair conformation in solution as revealed by a variable temperature ^{1}H n.m.r. study [$\Delta G^‡$ (178 K) 34.3 kJ/mol].[4]

Whether or not such anomalous behaviour of fourth-row heteroatoms is due to so-called 'heavy heteroatom effects,' such as hypervalency,[8] needs further investigation. This is now being studied.

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‡ The Cartesian co-ordinates of a hypothetical chair conformation of compound (**1**) were generated by a computer-assisted molecular modelling system using the *X*-ray data of (**1**).

§ The rate constant (k_r 390.36 s^{-1} at 170 K) was calculated by the equation $k_r = \pi (\Delta\nu)/\sqrt{2}$ ($\Delta\nu$ 175.72 Hz); $\Delta G^‡$ was calculated using the Eyring equation; $k_r = kT/h \cdot \exp(-\Delta G^‡/RT)$.

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