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Note

Absorption, electrochemical, theoretical, and ^{73}Ge NMR spectral characterization of the germanium *neo*-pentane analogue $(Me_3Ge)_4Ge$

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The germanium-based *neo*-pentane analogue $(Me_3Ge)_4Ge$ has been characterized by UV/visible spectroscopy, cyclic voltammetry, and ^{73}Ge NMR spectroscopy as well as by density functional theory (DFT) calculations. The absorption maximum for $(Me_3Ge)_4Ge$ is blue-shifted relative to those for other related branched oligogermanes $(Ph_3Ge)_3GeH$ and $(Ph_3Ge)_3GePh$, and this species is also the most difficult to oxidize among these three compounds. DFT calculations indicate the HOMO of $(Me_3Ge)_4Ge$ is stabilized relative to those for both tetragermanes by ca. 0.5 eV and therefore the theoretical and experimental results are in agreement. The ^{73}Ge NMR spectrum of $(Me_3Ge)_4Ge$ exhibits two resonances and the feature corresponding to the central formally zero-valent germanium atom is shifted far upfield and was observed at δ −339 ppm.

1. Introduction

Reports of branched oligogermanes have been until recently uncommon [1–5]. The preparation of $(Ph_3Ge)_3GeH$ (**1**) and $(Ph_3Ge)_3GeMe$ was first reported in 1963 [6], and the compounds $(PhCl_2Ge)_3GePh$ [7] and $(PhX_2Ge)_3GePh$ (X = Me, MeO, MeS, Me_2N, Et_2P) [8] were reported in the early 1970s. In light of the successful use of the hydrogermolysis reaction for the stepwise synthesis of linear oligogermanes, we have used this method for the synthesis of the branched oligogermanes $(Ph_3Ge)_3GeH$ (**1**) [4,5] and $(Ph_3Ge)_3GePh$ (**2**) [2]. The former compound was converted into the halide-substituted branched oligogermanes $(Ph_3Ge)_3GeX$ (X = Cl, Br, I) but neither the hydride **1** nor the amide $(Ph_3Ge)_3GeNMe_2$ that was obtained from $(Ph_3Ge)_3GeCl$ could be employed for the synthesis of the *neo*-pentane analogue $(Ph_3Ge)_4Ge$ via the hydrogermolysis reaction due to the steric effects of the four triphenylgermyl- groups [4,5]. However, the reaction of Me_3GeCl with $GeBr_4$ in the presence of lithium metal was recently shown to provide the *neo*-pentyl analogue $(Me_3Ge)_4Ge$ (**3**), which could be further converted into a variety of other branched oligogermane species [3]. The synthesis of **3** was also reported in 1968 using $GeCl_4$ rather than $GeBr_4$ [9].

We have probed the electronic properties of both linear and branched oligogermanes using cyclic voltammetry and UV/visible spectroscopy and have also coupled these investigations with density functional theory (DFT) calculations [4,5,10,11]. We wish to report here the characterization of **3** using these methods as well as the details of its ^{73}Ge NMR spectrum.

2. Results and discussion

The synthesis of **3** was recently reported by Marschner *et al.* (Scheme 1) and was characterized by UV/visible and NMR (^{1}H and ^{13}C) spectroscopy, mass spectrometry, and elemental analysis. Compound **3** exhibits a λ_{max} at 212 nm ($\varepsilon = 3.3 \times 10^4$ L mol^{-1} cm^{-1}) [3] that is considerably blue-shifted relative to those for **1** and **2** that were observed at 251 [4,5] and 256 nm [2] (respectively). A similar trend was observed among the related branched oligosilanes $(Ph_3Si)_3SiH$, $(PhMe_2Si)_3SiPh$ and $(Me_3Si)_4Si$, where $(Ph_3Si)_3SiH$ and $(PhMe_2Si)_3SiPh$ exhibit a λ_{max} values at 240 and 243 nm (respectively) in their UV/visible spectra, both of which are significantly red-shifted relative to that for $(Me_3Si)_4Si$ observed at 210 nm [12]. In order to investigate the reason for the high-energy absorption of **3** we prepared this material by the method of Marschner *et al.* according to Scheme 1 [3], and we further characterized this material using cyclic voltammetry, DFT calculations, and ^{73}Ge NMR spectroscopy such that the attributes of **3** could be fully compared with those of **1** and **2**.

The cyclic voltammogram of **3** in CH_2Cl_2 solvent is shown in Fig. 1 and exhibits one irreversible oxidation wave at 2090 ± 2 mV (Table 1). The oxidation potential for **3** is more positive than those for **1** (1921 ± 8 mV) and **2** (1435 ± 14 mV) and is more also positive

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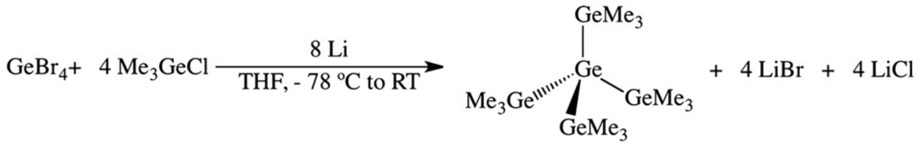

3, 45 %

Scheme 1. Synthesis of the neo-pentane analogue $(Me_3Ge)_4Ge$ (**3**) [3].

than those for all three of the halide-substituted branched oligogermanes $(Ph_3Ge)_3GeX$ (X = Cl, $E_{ox} = 1668 \pm 11$ mV; X = Br, $E_{ox} = 1656 \pm 14$ mV; X = I, $E_{ox} = 1643 \pm 16$ mV). This indicates that **3** is the most difficult species among these six compounds to oxidize, suggesting that the HOMO of **3** is more stabilized than those of the other five branched oligogermanes, and this assumption is consistent with the results of DFT calculations (*vide infra*). Linear oligogermanes that are completely devoid of aryl substituents or have aryl substituents attached only to the terminal germanium atoms typically exhibit only one irreversible oxidation wave [10,13,14], while those having aryl substituents at the internal germanium atoms exhibit $n - 1$ oxidation waves, where n is equal to the number of germanium atoms bonded together in the chain [11]. However, all of the branched oligogermanes we have analyzed using this method also exhibit one irreversible oxidation wave, even if aryl substituents are present [4,5].

Compound **3** was analyzed by density functional theory using the 6−311 + G(d,p)6−31G* basis set and all structures were computed without any enforced symmetries. The results of DFT calculations on compound **3** are shown in Table 1 along with the corresponding data for **1** and **2**. The HOMO energy for **3** is −6.529 eV and is stabilized by ca. 0.5 eV versus those for **1** and **2**, while the energy for the LUMO in each of these three molecules are similar. The calculated value for the absorption with the highest oscillator strength is 206 nm (48,470 eV), and the major contributions to this peak are the electronic transitions between the HOMO-1 → LUMO+5 (24%), HOMO-1 → LUMO+6 (12%), and the HOMO → LUMO+4 (27%) molecular orbitals.

Molecular orbital diagrams for the HOMO, the LUMO, and the LUMO+4 of **3** are shown in Fig. 2. The LUMO+4, LUMO+5, and LUMO+6 are very similar in energy and shape and are antibonding orbitals that are each formed from different p-orbitals located on the central germanium atom of **3** interacting in p-type fashion with the four peripheral Me_3Ge-groups. Similarly, the HOMO, HOMO-1, and HOMO-2 are all very similar in energy and involve p-type bonding interactions with the peripheral Me_3Ge-groups. The LUMO in **3** is distributed over the entire molecule and is primarily composed of the central 4s orbital on the central germanium atom and the 2s orbitals of the methyl carbon atoms. The 4s orbitals of the peripheral germanium atoms have little contribution to the LUMO. The calculated and experimental λ_{max} values for **3** are in excellent agreement, and the stabilization of the HOMO in **3** results in the blue shift of the absorption maximum relative to those for **1** and **2**. In addition, compound **3** is more difficult to oxidize than the branched tetragermanes **1** and **2** and this is expected due to the fact that the HOMO in **3** is stabilized relative to those in both **1** and **2**. Thus, conjugation between the germanium-based orbitals and the π^*-system of aryl substituents has a significant effect on the energy of the frontier orbitals in these oligogermanes. In the absence of aryl groups, the HOMO in these branched oligogermanes becomes stabilized resulting in a significant blue shift of the λ_{max} versus that observed when aryl substituents are present.

We have characterized a number of oligogermanes using ^{73}Ge NMR spectroscopy and have found a general trend in chemical shift values relative to Me_4Ge at δ 0 ppm, where triorganosubstituted germanium atoms R_3*Ge*-exhibit resonances between δ −30

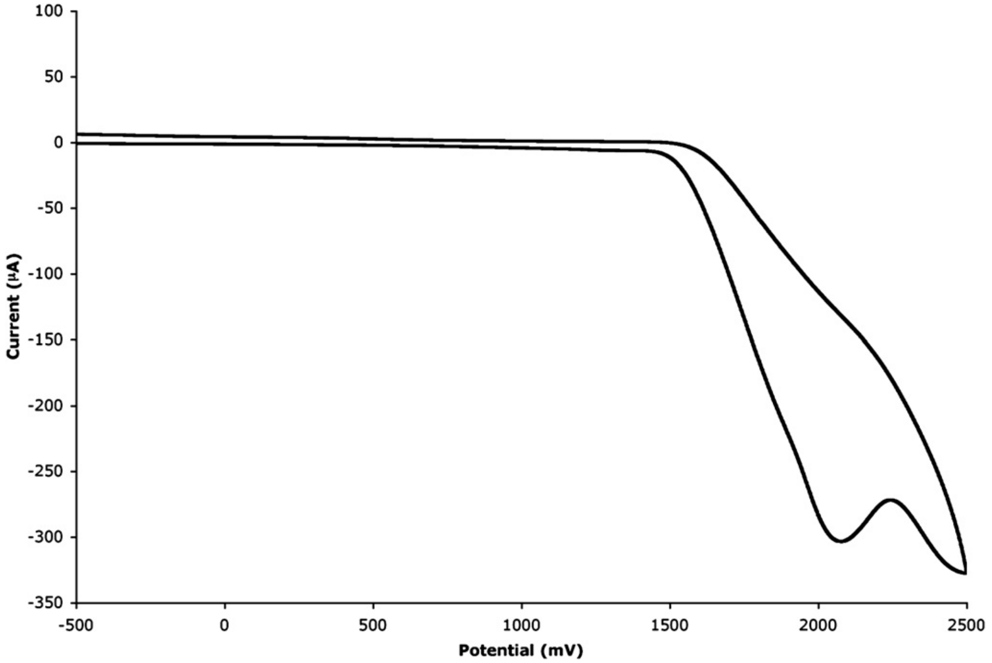

Fig. 1. Cyclic voltammogram of $(Me_3Ge)_4Ge$ (**3**) in CH_2Cl_2.