Inorg. Chem. **2005**, *44*, 3007–3009

Inorganic Chemistry
Communication

On the Existence and Stability of Branched Selenium Chains: Isomers of Me_2Se_3 and Et_2Se_3

Ralf Steudel* and Yana Steudel

Institut für Chemie, Technische Universität Berlin, Sekretariat C2, D-16023 Berlin, Germany

Received December 17, 2004

According to ab initio MO calculations at the G2(MP2) level of theory, branched isomers of dialkyl triselenides, R—Se(=Se)—Se—R (**1**; R = Me, Et), are less stable by more than 60 kJ mol^{-1} than the isomeric unbranched chains R—Se—Se—Se—R (**2**). Therefore, species **1** cannot be generated in substantial concentrations under equilibrium conditions at moderate temperatures, as has recently been claimed by Meja and Caruso (*Inorg. Chem.* **2004**, *43*, 7486). Alternatively, the isomeric CH_3—Se—CH_2—Se—Se—Et (**3**) can be considered to explain the reported gas chromatograms and mass spectra previously assigned to Et—Se(=Se)—Se—Et (**1b**). However, the isomerization **2b** → **3** is also endothermic, by $\Delta G^\circ_{298} = 63$ kJ mol^{-1}. The isomeric selenols HSe—C_2H_4—Se—Se—Et (**4**) and CH_3—CH(SeH)—Se—Se—Et (**5**) are also less stable than **2b** (by ca. 56 kJ mol^{-1}), but **4** is another candidate to explain the mass spectrum formerly assigned to **1b**. The calculated structures of **1**–**5** are reported.

In a recent publication, Meja and Caruso reported the first observation of branched selenium chains of composition R_2Se_3 (R = Me, Et).[1] The authors analyzed mixtures of commercial diselenides R_2Se_2 after storage for several months by gas chromatography/time-of-flight mass spectrometry (GC/TOF-MS) and observed signals of di- and triselenides as a result of the following reversible reaction[2]

$$2R_2Se_2 \rightarrow R_2Se + R_2Se_3$$

In addition, small satellite peaks were observed in the gas chromatogram and assigned to branched species of the selenosulfoxide type R—Se(=Se)—Se—R (**1**) because the elemental composition of the molecular ions of these substances was identical to those of the main components R—Se—Se—Se—R (**2**) and the fragmentation pattern under CI (chemical ionization) and EI (electron ionization) conditions seemed to support the connectivity in **1**. The authors did not explain the origin of the branched isomers but considered the isomerization **2** → **1**. Reference was made to older and partly erroneous publications (from 1929 to 1971) on branched sulfur and selenium chains, but the most recent work on such species was not cited. It has repeatedly been demonstrated by high-level ab initio MO calculations that branched sulfur chains R—S(=S)—R (thiosulfoxides; R = H, alkyl) are less stable by ca. 80 kJ mol^{-1} than the unbranched isomers (disulfanes).[3] More sulfur-rich species such as H—S—S—S(=S)—S—S—H are less stable than the isomeric unbranched oligosulfanes H_2S_n by ca. 50 kJ mol^{-1}.[4] In addition, the barrier for isomerization of disulfanes to thiosulfoxides is about 200 kJ mol^{-1}.[3c] Therefore, such open-chain species cannot be observed under equilibrium conditions at moderate temperatures.[5] In a similar fashion, branched selenium chains such as **1** are expected to be too unstable to be formed by thermal isomerization of unbranched selenanes,[6] but exact thermodynamic data are not yet available.

We have performed standard ab initio molecular orbital (MO) calculations[7] at the G2(MP2) level of theory[8] to determine the structures and relative energies of various isomers of R_2Se_3 (R = Me, Et). These structures are shown in Figure 1, and the energies, enthalpies, and Gibbs free energies are listed in Table 1. Selected bond and torsion angles are compiled in Table 2 in the Supporting Information. The considerable energy differences of 60−70 kJ mol^{-1} between the linear triselenides **2** and their branched isomers **1** exclude the formation of the latter under the experimental conditions described by Meja and Caruso. In addition, a

---

* To whom correspondence should be addressed. E-mail: steudel@sulfur-research.de.

(1) Meja, J.; Caruso, J. A. *Inorg. Chem.* **2004**, *43*, 7486−7492.

(2) Such mixtures can also contain higher polyselenanes R_2Se_n (n = 4−8): Potapov, V. A.; Amosova, S. V.; Petrov, P. A. *Sulfur Lett.* **1992**, *15*, 165−168.

(3) (a) Laitinen, R. S.; Pakkanen, T. A.; Steudel, R. *J. Am. Chem. Soc.* **1987**, *109*, 710−714. (b) Bickelhaupt, F. M.; Solà, M.; von Ragué Schleyer, P. *J. Comput. Chem.* **1995**, *16*, 465−477. (c) Steudel, R.; Drozdova, Y.; Miaskiewicz, K.; Hertwig, R. H.; Koch, W. *J. Am. Chem. Soc.* **1997**, *119*, 1990−1996. (d) Gerbaux, P.; Salpin, J.-Y.; Bouchoux, G.; Flammang, R. *Int. J. Mass Spectrom.* **2000**, *195/196*, 239−249. (e) Steudel, R.; Steudel, Y.; Wong, M. W. *Top. Curr. Chem.* **2003**, *230*, 117−134.

(4) Wong, M. W.; Steudel, Y.; Steudel, R. *Chem. Phys. Lett.* **2002**, *364*, 387−392.

(5) Under nonequilibrium conditions, chainlike thiosulfoxides have been observed (see ref 3d).

(6) Homoatomic selenium cations with branched structural units are known: Krebs, B.; Bonmann, S.; Eidenschink, I. *Encyclopedia of Inorganic Chemistry*; King, R. B., Ed.; Wiley: Chichester, U.K., 1994; Vol. 7, p 3667.

10.1021/ic048220r CCC: $30.25

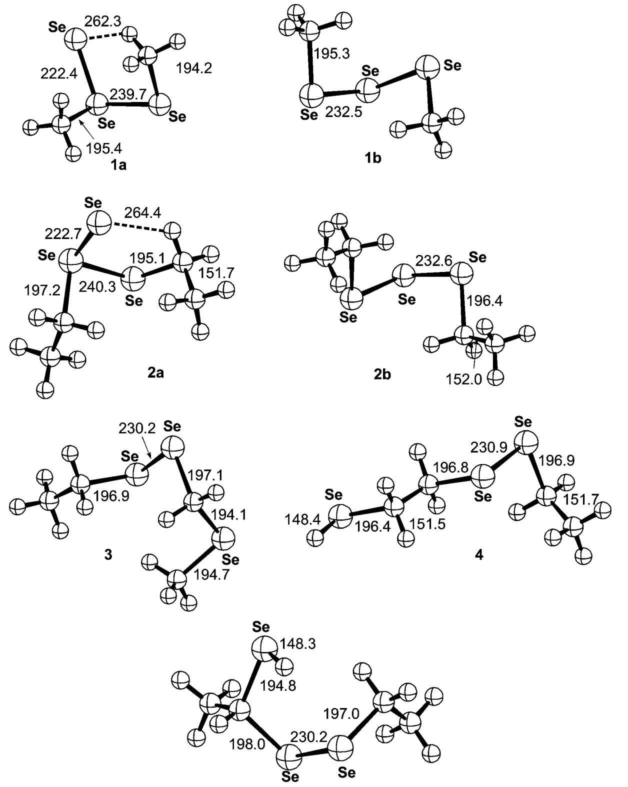

Figure 1. Structures of the isomeric molecules $\mathrm{Me_2Se_3}$ (**1a**,**b**) and $\mathrm{C_4H_{10}Se_3}$ (**2a**,**b**, **3**−**5**) calculated at the MP2(full)/6-31G* level of theory (bond lengths in pm). The global minimum structures **2a**,**b** are of C_2 symmetry; all others are of C_1 symmetry. Several less stable rotamers (based on their ΔG°_{298} data) exist on the potential energy hypersurfaces of **2a**, **2b**, and **3**−**5**.

Table 1. Relative G2(MP2) Energies and Enthalpies (kJ mol^{-1}) of Molecules of Composition $\mathrm{Me_2Se_3}$ (**1a**) and $\mathrm{C_4H_{10}Se_3}$ (**1b**, **3**−**5**) Compared to the Isomeric Linear Triselenides $\mathrm{Me_2Se_3}$ (**2a**) and $\mathrm{Et_2Se_3}$ (**2b**) as References[a]

species	ΔE°_0	ΔH°_{298}	ΔG°_{298}
branched $\mathrm{Me_2Se_3}$ (**1a**)	67.2	66.8	68.3
branched $\mathrm{Et_2Se_3}$ (**1b**)	61.5	61.2	62.9
mono-/diselenide $\mathrm{C_4H_{10}Se_3}$ (**3**)	66.0	66.6	62.9
1-selenol $\mathrm{C_4H_{10}Se_3}$ (**4**)	58.2	58.0	56.1
2-selenol $\mathrm{C_4H_{10}Se_3}$ (**5**)	51.3	50.5	55.1

[a] Absolute energies (E°_0, hartree) at the G2(MP2) level: −7279.59123 (**1a**), −7358.04403 (**1b**), −7279.61683 (**2a**), −7358.06745 (**2b**), −7358.04229 (**3**), −7358.04530 (**4**), −7358.04791 (**5**).

careful analysis of the reported mass spectrum assigned to **1b**[1] shows that the species involved does not contain a $\mathrm{Se_3}$ unit given that no $\mathrm{Se_2^+}$ is eliminated as is typical for **2b** and therefore can be expected for structure **1b** as well. Furthermore, the loss of $\mathrm{CH_2}$, $\mathrm{CH_2Se}$, and $\mathrm{CH_3Se}$[1] indicates the presence of single methyl and/or methylene groups linked to Se rather than to C.

To explain the reported satellite peaks in the GC analysis and the mass spectrum of $\mathrm{Et_2Se_3}$, another type of isomerization of the unbranched triselenides can be considered. The satellite peaks were obeved only if the triselenide contained at least one ethyl group (i.e., for $\mathrm{Et_2Se_3}$ and $\mathrm{MeEtSe_3}$). One could therefore assume the insertion of the central Se atom of the linear triselenide **2b** either into one of the C−C bonds, generating isomer **3**, or into one of the C−H bonds, producing either one of the selenols **4** or **5** shown in Figure 1.

Although isomers **3**−**5** have the same mass as the starting triselenide **2b**, their fragmentation patterns under mass spectrometric conditions would be different. The main fragments observed for the species from the satellite GC peak of $\mathrm{Et_2Se_3}$ are $\mathrm{C_3H_7Se_2^+}$ and $\mathrm{C_2H_5Se_2^+}$ upon CI ionization and $\mathrm{C_3H_8Se_2^+}$, $\mathrm{CH_3Se_2^+}$, and $\mathrm{C_3H_7Se^+}$ under EI conditions.[1] It is evident that most of these ions can easily be formed from the isomer **3** or the selenol **4**, whereas the formation of ions containing the fragment $\mathrm{C_3Se_2}$ from **1b** is difficult to understand without the assumption of a hypothetical internal rearrangement (as proposed in ref 1). Therefore, species **3** or **4** might serve to explain the reported GC diagrams and mass spectra. The expected fragmentation pattern of the isomeric selenol **5** does not match the reported mass spectrum equally well. In particular, the most important route, i.e., the elimination of $\mathrm{CH_{2/3}Se}$, could not be understood with this isomer. Other isomers of $\mathrm{C_4H_{10}Se_3}$ with all selenium atoms separated by carbon atoms can also be excluded.

However, isomers **3**−**5** are all considerably less stable than the linear triselenide. The Gibbs energies for the isomerization of Et−Se−Se−Se−Et (**2b**) to isomer **3** and to the selenoles **4** and **5** were calculated as $\Delta G^\circ_{298} = 55-63$ kJ mol^{-1} (Table 1). Therefore, these endothermic isomerizations can be excluded as spontaneous reactions occurring during the reported experiments. One therefore is tempted to speculate that one of the species **3** or **4** was already present as an impurity in the starting material $\mathrm{Et_2Se_2}$.

Summarizing, we conclude that there is presently no convincing experimental evidence for branched dialkyl triselenides (**1**), and their existence under equilibrium conditions is unlikely given that such species are less stable by more than 60 kJ mol^{-1} (ΔG°_{298} for R = Me, Et) than the isomeric unbranched chains **2**. These findings are also of importance for the structure of liquid and amorphous elemental selenium, for which branched structures have

---

(7) Frisch, M. J.; Trucks, G. W.; Schlegel, H. B.; Scuseria, G. E.; Robb, M. A.; Cheeseman, J. R.; Montgomery, J. A., Jr.; Vreven, T.; Kudin, K. N.; Burant, J. C.; Millam, J. M.; Iyengar, S. S.; Tomasi, J.; Barone, V.; Mennucci, B.; Cossi, M.; Scalmani, G.; Rega, N.; Petersson, G. A.; Nakatsuji, H.; Hada, M.; Ehara, M.; Toyota, K.; Fukuda, R.; Hasegawa, J.; Ishida, M.; Nakajima, T.; Honda, Y.; Kitao, O.; Nakai, H.; Klene, M.; Li, X.; Knox, J. E.; Hratchian, H. P.; Cross, J. B.; Bakken, V.; Adamo, C.; Jaramillo, J.; Gomperts, R.; Stratmann, R. E.; Yazyev, O.; Austin, A. J.; Cammi, R.; Pomelli, C.; Ochterski, J. W.; Ayala, P. Y.; Morokuma, K.; Voth, G. A.; Salvador, P.; Dannenberg, J. J.; Zakrzewski, V. G.; Dapprich, S.; Daniels, A. D.; Strain, M. C.; Farkas, O.; Malick, D. K.; Rabuck, A. D.; Raghavachari, K.; Foresman, J. B.; Ortiz, J. V.; Cui, Q.; Baboul, A. G.; Clifford, S.; Cioslowski, J.; Stefanov, B. B.; Liu, G.; Liashenko, A.; Piskorz, P.; Komaromi, I.; Martin, R. L.; Fox, D. J.; Keith, T.; Al-Laham, M. A.; Peng, C. Y.; Nanayakkara, A.; Challacombe, M.; Gill, P. M. W.; Johnson, B.; Chen, W.; Wong, M. W.; Gonzalez, C.; Pople, J. A.; *Gaussian 03*, revision B.05; Gaussian, Inc.: Pittsburgh, PA, 2004.

(8) Curtiss, L. A.; Raghavachari, K.; Pople, J. A. *J. Chem. Phys.* **1993**, *98*, 1293−1298.

(9) (a) Raty, J. Y.; Saul, A.; Gaspard, J. P.; Bichara, C. *Phys. Rev. B: Condens. Matter Mater. Phys.* **1999**, *60*, 2441−2448. (b) Suzuki, S.; Maruyama, K.; Misawa, M. *J. Phys. Soc. Jpn.* **2000**, *69*, 3576−3580. (c) Cutler, M. *Phys. Rev. B: Condens. Matter Mater. Phys.* **1979**, *20*, 2981−2990.

repeatedly been proposed[9] and also disputed[10] but have never been detected experimentally.

Supporting Information Available: Selected bond and torsion angles as well as atomic coordinates of the molecules shown in Figure 1. This material is available free of charge via the Internet at http://pubs.acs.org.

IC048220R

---

(10) Edeling, M.; Freyland, W. *Ber. Bunsen-Ges. Phys. Chem*. **1981**, *85*, 1049−1054.