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**Experimental and Theoretical Investigations of Structural Trends for Selenium(IV)
Imides and Oxides: X-ray Structure of Se₃(NAd)₂**

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Abstract

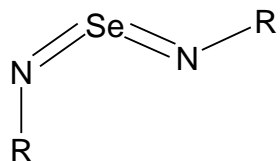
The thermal decomposition of $\text{Se}(\text{NAd})_2$ (Ad = 1-adamantyl) in THF was monitored by ^{77}Se NMR and shown to give the novel cyclic selenium imide $\text{Se}_3(\text{NAd})_2$ as one of the products. An X-ray structural determination showed that $\text{Se}_3(\text{NAd})_2$ is a puckered five-membered ring with $d(\text{Se-Se}) = 2.404(1) \text{ \AA}$ and $|d(\text{Se-N})| = 1.873(4) \text{ \AA}$. On the basis of ^{77}Se NMR data other decomposition products include the six-membered ring $\text{Se}_3(\text{NAd})_3$, and the four-membered rings $\text{AdNSe}(\mu\text{-NAd})_2\text{SeO}$ and $\text{OSe}(\mu\text{-NAd})_2\text{SeO}$. The energies for the cyclodimerization of $\text{E}(\text{NR})_2$ and RNEO (E = S, Se; R = H, Me, ^tBu , SiMe_3), and the cycloaddition reactions of RNSeO with $\text{E}(\text{NR})_2$, RNSO_2 with $\text{Se}(\text{NR})_2$, and $\text{S}(\text{NR})_2$ with $\text{Se}(\text{NR})_2$ have been calculated at MP2, CCSD and CCSD(T) levels of theory using the cc-pVDZ basis sets and B3PW91/6-31G* optimized geometries. Sulfur(IV) and selenium(IV) diimide monomers are predicted to be stable, the sole exception being $\text{Se}(\text{NSiMe}_3)_2$ that shows a tendency towards cyclodimerization. The cyclodimerization energy for the RNSeO and the cycloaddition reaction energies of RNSeO with $\text{Se}(\text{NR})_2$ as well as that of RNSO_2 with $\text{Se}(\text{NR})_2$ are negative, consistent with the observed formation of $\text{OSe}(\mu\text{-N}^t\text{Bu})_2\text{SeO}$, $\text{OSe}(\mu\text{-N}^t\text{Bu})_2\text{SeN}^t\text{Bu}$ and $\text{O}_2\text{S}(\mu\text{-N}^t\text{Bu})_2\text{SeN}^t\text{Bu}$, respectively. Cycloaddition is unlikely when one of the reactants is a sulfur(IV) diimide.

Introduction

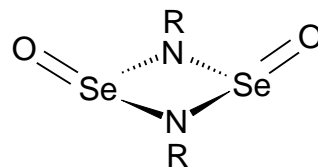
The chemistry of imido derivatives of selenium in various oxidation states has developed slowly compared to the extensively studied acyclic¹ and cyclic^{2,3} sulfur-imide systems. The first selenium(IV) diimide $\text{Se}(\text{N}^t\text{Bu})_2$ (**1a**) was reported by Sharpless *et al.* more than 25 years ago.⁴ These reactive species are efficient *in situ* reagents for allylic amination of olefins and 1,2-diamination of 1,3-dienes.^{4,5} The selenium(IV) diimide **1a** forms an *N,N'*-chelated adduct with SnCl_4 .⁶ It has also been used to generate the pyramidal dianion $[\text{Se}(\text{N}^t\text{Bu})_3]^{2-}$, isoelectronic with SeO_3^{2-} , by reaction with 2 equivalents of LiNH^tBu .⁷ Multinuclear NMR studies of **1a** by Wrackmeyer *et al.* indicated a monomeric structure with a *syn,anti* configuration in solution.⁸ Monomeric structures are also found exclusively for sulfur(IV) diimides.¹ By contrast, the corresponding tellurium(IV) imide, ${}^t\text{BuNTe}(\mu\text{-N}^t\text{Bu})_2\text{TeN}^t\text{Bu}$, is dimeric in solution and in the solid state.⁹ Consistently, density functional calculations on the model systems $\text{E}(\text{NMe})_2$ ($\text{E} = \text{S}, \text{Se}, \text{Te}$) predict that the dimerization is highly exothermic for $\text{E} = \text{Te}$ and endothermic for $\text{E} = \text{S}$, in agreement with experimental observations, but approximately thermoneutral for $\text{E} = \text{Se}$.¹⁰

In a preliminary communication we showed by X-ray crystallography that $\text{Se}(\text{NAd})_2$ (**1b**, Ad = 1-adamantyl) is a *syn,anti*-monomer in the solid state,¹¹ in agreement with the conclusions of solution NMR studies of **1a**.⁸ Interestingly, the hybrid imido-oxo system (seleninyl amine) $\text{OSe}(\mu\text{-N}^t\text{Bu})_2\text{SeO}$ (**2a**) first reported by Herberhold in 1986,¹² forms a dimer with the oxo ligands in a *cis* configuration in the solid state.¹¹ The third member of this isoelectronic series, $(\text{SeO}_2)_\infty$ (**3**), has a polymeric chain structure.¹³ The

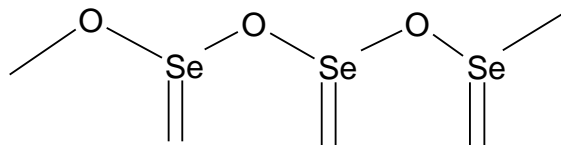
unsymmetrical imido-oxo species ${}^t\text{BuNSe}(\mu\text{-N}{}^t\text{Bu})_2\text{SeO}$ (**4a**) has a cyclic structure similar to that of **2a**.¹⁴



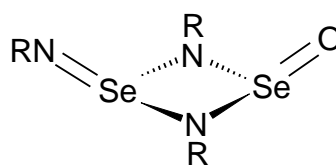
1a, R = ${}^t\text{Bu}$
1b, R = Ad



2a, R = ${}^t\text{Bu}$
2b, R = Ad

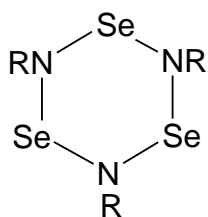


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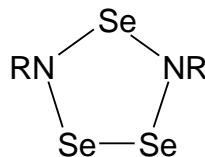


4a, R = ${}^t\text{Bu}$
4b, R = Ad

The limited information available on cyclic selenium imides indicates the existence of a more varied series of macrocycles compared to their sulfur analogues, which are primarily limited to eight-membered rings $\text{S}_{8-x}(\text{NH})_x$ ($x = 1-4$) that are structurally related to cyclooctasulfur.^{2,3} Early work by Roesky *et al.* led to the structural characterization of the eight-membered ring $\text{Se}_6(\text{N}{}^t\text{Bu})_2$ and the fifteen-membered ring $\text{Se}_9(\text{N}{}^t\text{Bu})_6$.¹⁵ More recently, we have shown that the six-membered ring $\text{Se}_3(\text{N}{}^t\text{Bu})_3$ (**5a**) is formed, in addition to the acyclic imidoselenium(II) dihalides $\text{ClSe}[\text{N}{}^t\text{BuSe}]_n\text{Cl}$ ($n = 1,2$), from the reaction of SeCl_2 with *tert*-butylamine in THF.¹⁶ The tellurium analogue $\text{Te}_3(\text{N}{}^t\text{Bu})_3$ is also known.⁹ Subsequently, it was shown that **5a** and $\text{Se}_9(\text{N}{}^t\text{Bu})_6$ are the major products of the thermal decomposition of **1a**.¹⁴ A third product of this decomposition was identified, on the basis of analytical and spectroscopic data, as a member of the homologous series $[\text{Se}_3(\text{N}{}^t\text{Bu})_2]_n$ ($n = 1$ or 2).¹⁴



5a, R = ^tBu
5b, R = Ad



6a, R = ^tBu
6b, R = Ad

We have now investigated by ^{77}Se NMR the thermal decomposition of **1b** which leads to the novel five-membered ring **6b**, in addition to the six-membered ring **5b** and the partial hydrolysis products **2b** and **4b**. In order to rationalize the structures of the imidoselenium(V) systems **1**, **2** and **4**, we have also carried out high level quantum chemical calculations of the energetics for the cyclodimerization of $\text{E}(\text{NR})_2$ and RNEO ($\text{E} = \text{S}, \text{Se}$; $\text{R} = \text{H}, \text{Me}, {}^t\text{Bu}, \text{SiMe}_3$), and some related cycloaddition reactions.

Experimental Section

General Considerations. All manipulations involving air-sensitive materials were conducted under an argon atmosphere by using Schlenk techniques or in a drybox. Solvents were dried and distilled under an argon atmosphere prior to use: tetrahydrofuran and diethylether (LiAlH_4) and *n*-hexane (Na/benzophenone). ${}^t\text{BuNH}_2$ (Aldrich) was distilled over KOH and stored over molecular sieves. Selenium powder, SeCl_4 , and SO_2Cl_2 and 1-adamantylamine (AdNH_2) (Aldrich) were used without further purification. $\text{Se}(\text{NAd})_2$ was prepared by the reaction of AdNH_2 with SeCl_4 in THF as previously

described.¹¹ ^tBuNSeO was obtained from OSeCl₂ with ^tBuNH₂ by the literature procedure.¹²

Instrumentation. ¹H NMR spectra were recorded on a Bruker AC-200 or a Bruker AM-400 spectrometer. The ¹³C, ¹⁴N, and ⁷⁷Se NMR spectra were recorded on a Bruker AM-400 or a Bruker DPX-400 spectrometer operating at 100.614, 28.915, and 76.312 MHz, respectively. The spectral widths were 23.81, 29.41, and 100.00 kHz, yielding the respective resolutions of 1.45, 3.59, and 6.10 Hz/data point. The ¹³C pulse width was 3.50 μs, for ¹⁴N 20.0 μs, and for ⁷⁷Se 9.00 μs. The ¹³C, ¹⁴N, and ⁷⁷Se accumulations contained 1000-20000, 20000-200000, and 15000-30000 transients, respectively. Relaxation delays used were ¹³C 3.0 s, ¹⁴N 1 ms, and ⁷⁷Se 2 s. The ¹⁴N NMR spectra are reported relative to neat CH₃NO₂. All ⁷⁷Se NMR spectra were referenced externally to a saturated solution of SeO₂ in D₂O at room temperature. The chemical shifts are reported relative to neat Me₂Se at room temperature [$\delta(\text{Me}_2\text{Se}) = \delta(\text{SeO}_2) + 1302.6$].

Preparation of Se₃(NAd)₂ (6b). A white slurry of 1-adamantylamine (2.055 g, 13.59 mmol) in diethyl ether (10 mL) was added to a pale yellow slurry of SeCl₄ (0.500 g, 2.265 mmol) in diethyl ether (15 mL) at -38°C. The reaction mixture was allowed to reach *ca.* 23°C and, after 4 h, a pale yellow precipitate was removed by filtration through a sintered glass filter disk (8 μm) and PTFE syringe filter (0.45 μm). The precipitate was shown to be primarily [AdNH₃]Cl (2.243 g) by ¹H NMR. Removal of solvent from the yellow filtrate under vacuum gave a yellow solid (0.153 g, 0.286 mmol, 38% based on Se), which contained no [AdNH₃]Cl (¹H and ¹³C NMR, IR). Yellow-orange needles of

Se₃(NAd)₂ were obtained from a C₇D₈ solution of this product in an NMR tube. Anal. Calcd. For C₂₀H₃₀N₂Se₃: C, 44.87; H, 5.65; N, 5.23. Found: C, 45.81; H, 5.78; N, 5.33. NMR: δ ⁷⁷Se (C₇D₈, 25°C) 1380 and 1083 (relative intensities 1:2).

X-ray Analysis. Diffraction data for **6b** were collected on a Nonius KappaCCD 4-Circle Kappa FR540C diffractometer using graphite monochromated MoK α radiation (λ = 0.71073 Å). Crystallographic data are given in Table 1. The intensity data were corrected for Lorentz and polarization effects, and for absorption (SADABS).¹⁷

A yellow needlelike crystal of **6b** (0.15 x 0.08 x 0.03 mm) was coated with Paratone oil and mounted in a nylon CryoLoop. The structure was solved by using direct methods with SHELXS-97¹⁸ and refined by full-matrix least-squares methods on F^2 with SHELXL97-2.¹⁹ The non-hydrogen atoms were refined anisotropically. Hydrogen atoms were included at geometrically idealized positions (C-H = 0.95 Å) and were not refined.

Computational Details

All calculations were carried out with Gaussian 98²⁰ and Molpro²¹ sets of programs. Geometries of all molecules were fully optimized at the B3PW91^{22,23} level of theory using standard Pople-type 6-31G* basis set as implemented in Gaussian 98.²⁴ All possible conformers were considered in the calculations (see Scheme 1). The fundamental frequencies were also calculated in order to assess the nature of the stationary points and to estimate the zero-point correction to the energy (ZPE).

Three different higher-level theoretical methods were employed in the computation of more accurate energetics. Single point calculations at all optimized geometries were carried out with the MP2,²⁶ CCSD and CCSD(T) methods.²⁷ However, coupled cluster calculations required excessive computational resources for ^tBu or SiMe₃ derivatives and were not carried out. Therefore, single point MP2 calculations utilizing B3PW91/6-31G* optimized geometries provide the most accurate energies that could be computed for all molecular systems reported in this work. Dunning's correlation consistent basis sets of double-zeta and triple-zeta quality, namely cc-pVDZ and cc-PVTZ, were used in all single point calculations.²⁸

Results and Discussion

⁷⁷Se NMR Study of the Decomposition of Se(NAd)₂ (1b**).** We have previously monitored the decomposition of **1a** over a period of 8 days by ⁷⁷Se NMR.¹⁶ The major products are the six-membered ring **5a**, the heterocycle [Se₃(N^tBu)₂]_n (n = 1 or 2), which was not structurally characterized, and the fifteen-membered ring Se₉(N^tBu)₆. In order to obtain further insights into the formation of cyclic selenium imides from acyclic selenium(IV) diimides, we have now investigated the thermal decomposition of the new derivative **1b**⁹ by ⁷⁷Se NMR.

The ⁷⁷Se NMR spectrum of the THF solution of **1b** that is recorded immediately after the preparation exhibits only one major resonance at 1662.4 ppm. Within one day, several minor resonances have appeared and their relative intensities with respect to that

of **1b** continue to grow with time. The ^{77}Se NMR spectrum of the solution after three days is shown in Figure 1 together with the assignments of the resonances, based on the identification of the decomposition products of $\text{Se}(\text{N}^t\text{Bu})_2$.

The major resonance at 1361 ppm is attributed to the six-membered ring $\text{Se}_3(\text{NAd})_3$ (**5b**). The *tert*-butyl derivative **5a** exhibits a ^{77}Se resonance at 1396 ppm.¹⁶ The two resonances at 1380 and 1083 ppm (approximate intensity ratio 1:2) are assigned to the five-membered ring $\text{Se}_3(\text{NAd})_2$ (**6b**), *cf.* 705 and 522 ppm for the related ring system $\text{Se}_3(\text{AsPh})_2$.²⁹ The substantial downfield shift of these resonances in **6b** may be attributed to the higher electronegativity of nitrogen compared to that of arsenic. Compound **6b** was isolated in 38% yield after two weeks at room temperature. It was also obtained in *ca.* 40% yield from the reaction of SeCl_4 with 1-adamantylamine in a 1:6 molar ratio in diethyl ether. The crystal structure of **6b** is described below.

The resonance at 1213 ppm is assigned to $\text{OSe}(\mu\text{-NAd})_2\text{SeO}$ (**2b**). The corresponding *tert*-butyl derivative $\text{OSe}(\mu\text{-N}^t\text{Bu})_2\text{SeO}$ (**2a**) shows a resonance at 1242 ppm. The two signals of equal intensity at 1146 and 900 ppm are similarly assigned to the inequivalent selenium environments in $\text{OSe}(\mu\text{-N}^t\text{Bu})_2\text{SeNAd}$ (**4b**) [*cf.* $\delta(^{77}\text{Se}) = 1157$ and 882 for **4a** in hexane].

The hybrid imido-oxo selenium(IV) ring systems **2b** and **4b** are presumably formed by partial hydrolysis of the extremely moisture-sensitive selenium diimide **1b**. We have not been able to identify the compound(s) responsible for the resonances at 1102 and 811 ppm. We note, however, that the former falls in the range for an NSeSe selenium environment.¹⁴

X-ray Structure of $\text{Se}_3(\text{NAd})_2$ (6b**).** An X-ray structural determination of **6b** revealed a five-membered $\overline{\text{SeSeNSeN}}$ ring (Figure 2). Although five-membered rings are known for selenium-nitride systems, e.g. $\text{Se}_3\text{N}_2\text{Cl}^+$,³⁰⁻³³ the heterocycle **6b** represents a previously unknown ring size for chalcogen imides. It is the first member of the homologous series $[\text{Se}_3(\text{NR})_2]_n$ ($n = 1, 2, 3$) for which only the fifteen-membered ring $\text{Se}_9(\text{N}^t\text{Bu})_6$ has been structurally characterized.¹⁵ Herberhold and Jellen claimed the formation of “ $\text{Se}_3(\text{N}^t\text{Bu})_2$ ” from the decomposition of **1a**,¹² but subsequent studies showed that this product is $\text{Se}_9(\text{N}^t\text{Bu})_6$.¹⁴ This new finding suggests that the smaller oligomer $[\text{Se}_3(\text{N}^t\text{Bu})_2]_n$ ($n = 1$ or 2), which was isolated from the reaction of SeCl_2 with *tert*-butylamine in THF,¹⁴ is also a five-membered ring ($n = 1$). The structure of a related five-membered ring $\text{Se}_3(\text{AsPh})_2$ has been reported.²⁹

The metrical parameters for **6b** are summarized in Table 2 and compared with those for other cyclic selenium imides in Table 3. The two Se-N bonds in the N(1)-Se(1)-N(2) fragment [1.892(4) and 1.881(4) Å] are significantly longer than those in the N(1)-Se(2)-Se(3)-N(2) fragment [1.846(4) and 1.860(5) Å]. The latter pair may be compared to the value of 1.834 Å for the Se-N-Se units in **4a**.¹⁴ The Se-Se bond distance of 2.404(1) Å in **6b** is also markedly longer than the mean Se-Se bond lengths in $\text{Se}_9(\text{N}^t\text{Bu})_6$ (2.336 Å)¹⁵ and $\text{Se}_3(\text{AsPh})_2$ (2.334 Å).²⁹ The elongated bonds are likely the result of ring strain in the five-membered ring, which is highly puckered with torsion angles ranging from 16.1(3) to 46.7(2)° (see Table 2). The high value about the Se(2)-Se(3) bond presumably reflects the avoidance of lone pair-lone pair interactions on adjacent selenium atoms. The endocyclic bond angles at Se(2) and Se(3) are *ca.* 12° smaller than that at Se(1). The geometry at the nitrogen atoms is distinctly pyramidal ($\Sigma \angle\text{N}(1) = 343.0^\circ$, $\Sigma \angle\text{N}(2) =$

344.2°) in marked contrast to the almost planar configuration at the nitrogen atoms in the chair-shaped six-membered ring **5a**.¹⁴

Structural Comparison of the Isoelectronic Series (SeO₂)_∞, (RNSeO)₂ and Se(NR)₂. The structures of Se(NAd)₂ (**1b**) and *cis*-OSe(μ -N^tBu)₂SeO (**2a**) were reported in a preliminary communication.¹¹ It is informative to consider the structural trends within the isoelectronic series, **1b**, **2a** and **3** in the context of the isovalent analogues formed by the other chalcogens (see Scheme 2). The sulfur(IV) analogues of **1**, **2** and **3** are, without exception, monomers.¹ By contrast, a trend from monomers through dimers to polymer is observed for the series of selenium(IV) imides and oxides.³⁴ The tendency to form singly bonded in preference to doubly bonded molecules is even more pronounced for tellurium. Tellurium(IV) diimides are dimeric^{9,35} whereas tellurium dioxide is a three-dimensional polymer consisting of only Te-O single bonds.³⁶ Hybrid imido-oxo tellurium(IV) species (RNTeO)_n are unknown, but a polymeric structure seems likely in view of the above trends and the propensity of telluroxides to dimerize e.g. [^tBuNTe(μ -N^tBu)₂(μ -O)]₂³⁷ and [OC(μ -N^tBu)₂Te(μ -O)]₂.³⁸ We have recently isolated the tetramer OTe(μ -N^tBu)₂Te(μ -O)₂Te(μ -N^tBu)₂TeO by complexation of the terminal Te=O groups with B(C₆F₅)₃.³⁹

A comparison of the structural parameters for selenium(IV) imides and oxides is given in Table 4.⁴⁰ For this series of compounds terminal Se=O bond lengths fall within the narrow range 1.62-1.63 Å (*cf.* 1.617(4) Å in OSe(NPPh₃)₂⁴³ and 1.612(5) Å in OSeCl₂).⁴⁴ The terminal Se=N(R) bond lengths are somewhat longer with a range of

1.68-1.73 Å. For both SeO and SeN bonds the difference between single and double bonds is *ca.* 0.19 Å.

Cyclodimerization of Chalcogen Diimides and Related Cycloaddition

Reactions. In order to provide further insights into the structural trends observed for multiply bonded chalcogen(IV) systems we have calculated the gas phase cyclodimerization energies for E(NR)₂ and RNEO (E = S, Se; R = H, Me, ^tBu, SiMe₃) and cycloaddition energies for reactions in Eq. 1-3 at different levels of theory.



The optimized structures of all molecules are given in Supporting Information. For all reaction products, the structural parameters are very similar in different conformations and are therefore reported only for the all-*cis*-conformation (conformation **a** in Scheme 1) since it was found to be generally the most favorable in energy (see below).

In the case of sulfinyl and seleninyl amines the optimized geometries can be compared with experimental values determined for various RNSO structures. The optimized parameters agree reasonably well with the experimental values determined by electron diffraction⁴⁵ or microwave spectroscopy.⁴⁶⁻⁴⁸ As found for sulfur and selenium diimides,²⁵ *syn*-E=N bonds are shorter than *anti*-E=N bonds, *syn*-ENA (A = H, C, or Si) bond angles are wider than *anti*-ENA bond angles, and ENA bond angles in selenium

compounds are narrower than those in the corresponding sulfur compounds. The structural trends in sulfinyl and seleninyl amines seem to depend mainly on steric factors with electronic factors playing only a minor role.

The optimized bond parameters of the dimerization and cycloaddition products (Eq. 1-3) can be compared with the experimental values^{11,14} and with the molecular parameters that have been observed for monomeric sulfur⁴⁹ and selenium diimides.¹¹ The calculated parameters are found to be close to the experimental values, where available: the RMS deviation between the calculated and observed bond lengths is only 0.023 Å and that of the bond angles is 3°.

In sulfur and selenium dimers, the exocyclic chalcogen-nitrogen bond lengths (EN) are in a good agreement with experimental values for the EN double bonds in monomeric chalcogen(IV) diimides. The endocyclic chalcogen-nitrogen bonds are predicted to be *ca.* 0.2 Å longer than the exocyclic chalcogen-nitrogen bonds for both sulfur and selenium diimide dimers, indicating that the bonds in the ENEN ring are single bonds. This is consistent with the experimental observations. The endocyclic EN bonds are systematically shorter in $O_xE(\mu-NR)_2SeNR$ ($E = S, Se; x = 1, 2$) than in the corresponding diimide dimers. The bond parameters in the ENEN rings in different dimerization products are rather similar, as exemplified by the endocyclic bond angles $\angle SNS = 98.6-102.0^\circ$ and $\angle SeNSe = 96.8-102.1^\circ$. The endocyclic bond angles $\angle NEN$ span a range of $77.2-80.7^\circ$ and $76.8-82.6^\circ$ in sulfur and selenium compounds, respectively. By contrast, the torsion angle τ_{ENEN} expectedly depends on the size of the exocyclic substituent. Similar trends in structural parameters are also observed for all calculated cycloaddition structures.

Total energies for all molecules calculated at MP2/cc-pVDZ//B3PW91/6-31G*, CCSD/cc-pVDZ//B3PW91/6-31G* and CCSD(T)/cc-pVDZ//B3PW91/6-31G* levels of theory are presented in Supporting Information. The *syn*-conformation for the monomeric sulfinyl and seleninyl amines appears to be more stable than the *anti*-conformation. This is in agreement both with the experimental observations⁴⁵⁻⁴⁸ and previous theoretical calculations.⁵⁰ At the CCSD(T)/cc-pVDZ//B3PW91/6-31G* level of theory the *syn*-conformation is 25 kJ mol⁻¹ and 30 kJ mol⁻¹ more stable for sulfur and selenium compounds, respectively. This conformational preference has been rationalized in terms of the interactions between the nitrogen lone pair and chalcogen p and d orbitals.^{10,50}

For most cyclodimerization and cycloaddition products, the conformation with the lowest energy was found to be all-*cis*-conformation (configuration **a** in Scheme 1). The experimental information is restricted to ^tBu derivatives which all adopt the conformation in which the exocyclic and endocyclic R groups are mutually *cis*, but on opposite sides of the ENEN ring (conformation **b** in Scheme 1). The difference in the experimental and calculated conformational preference can, however, be explained by noting that the theoretical calculations do not take packing effects into account and that the energies of different conformations are in general very close to each other.⁵¹ In the case of tellurium diimide dimers, both *cis* and *trans* conformers have been observed and structurally characterized,^{9,35} but the *trans* conformer is known to convert into the *cis* conformer in solution at room temperature.⁵²

The [2+2] cyclodimerization energies of sulfur and selenium diimides and sulfinyl and seleninyl amines are presented in Table 5, and the corresponding energies of various cycloaddition reactions (Eq. 1-3) in Table 6.⁵³ It can be seen from Tables 5 and 6 that the

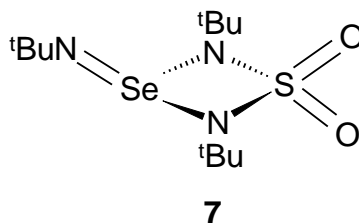
theoretically most reliable CCSD(T) reaction energies fall between the MP2 and CCSD values, and are 10-20 kJ mol⁻¹ smaller than the MP2 values. While it was not possible to carry out CCSD and CCSD(T) calculations for all molecular systems, the trends can be utilized to produce energy estimates for these levels of theory, as shown in Figure 3.⁵⁵

For sulfur diimides, the reaction energies are found to be positive at all levels of theory, thereby indicating an endothermic process. For selenium diimides the process is predicted to be energetically neutral, the signs of the energy values being somewhat dependent on the level of theory.⁵⁶ This is consistent with the experimental observations that **1a** and **1b** are monomeric species.^{8,11} It has recently been shown that the difference in reaction energies for sulfur and selenium diimides can be ascribed to the lower π -bond energies of Se=N bonds which makes the coupling of the two fragments energetically more preferable.¹⁰

Figure 3 shows that the cyclodimerization and cycloaddition energies are rather independent of the identity of the R group (H, Me and ^tBu derivatives). However, according to the present calculations the reaction energies of SiMe₃ derivatives behave anomalously. For example, the cyclodimerization energy of Se(NSiMe)₃ is negative at all levels of theory. This derivative has been reported as a dark red oil,⁵⁷ but the solid-state structure is unknown. It is a useful synthon for different Se-N heterocycles.⁵⁸ The origin of the anomalous behavior of SiMe₃ amines has been a topic of much discussion thereby preventing any definite statements to be made.⁵⁹ It has mostly been attributed to the bonding interactions involving N p orbitals and either Si d orbitals or Si-C σ^* orbitals (negative hyperconjugation).

As indicated in Tables 5 and Figure 3(a), the cyclodimerization energies for RNSeO are negative at all levels of theory, in agreement with the observed stability of **2a**.¹¹ By contrast, the cyclodimerization energies for RNSO are clearly positive, which is consistent with the observed monomeric structures of sulfinyl amines. It can also be seen from Table 5 that the reaction energies are lower for the chalcogen imido-oxo systems than for the corresponding diimides. The observed trend most likely originates from the high electronegativity of oxygen which results in further destabilization of the chalcogen nitrogen double bond. This conclusion is supported by the energy decomposition analysis which indicates 40 kJ mol⁻¹ smaller preparation energies for imido-oxo systems than for diimides.

The cycloaddition energies for the reaction (1) (E = Se) are also slightly negative [see Table 6 and Figure 3(b)] consistent with the observed structure of **4a**.¹⁴ Negative reaction energies are also predicted for the cycloaddition reactions (2), consistent with the formation of the selenium(IV)-sulfur(VI) species **7**.¹⁴ Finally, we note that the cycloaddition energies are found to be positive for all reactions where one of the reagents is a sulfur(IV) diimide, e.g. Eq. (3).



Conclusions

The thermal decomposition of $\text{Se}(\text{NAd})_2$ ($\text{Ad} = 1\text{-adamantyl}$) in THF leads to the formation of the novel cyclic selenium imide $\text{Se}_3(\text{NAd})_2$ together with the six-membered $\text{Se}_3(\text{NAd})_3$, and the partial hydrolysis products $\text{AdNSe}(\mu\text{-NAd})_2\text{SeO}$ and $\text{OSe}(\mu\text{-NAd})_2\text{SeO}$. The recently reported X-ray structures of $(\text{AdN})_2\text{Se}$, ${}^t\text{BuNSe}(\mu\text{-N}{}^t\text{Bu})_2\text{SeO}$, $\text{OSe}(\mu\text{-N}{}^t\text{Bu})_2\text{SeO}$, and $(\text{SeO}_2)_\infty$ allow a comparison of structural trends within the isoelectronic series spanning from selenium(IV) diimides to selenium(IV) dioxide. Selenium diimides are monomeric, while the hybrid imido-oxo species are dimeric and selenium dioxide is a two-dimensional polymer with SeO single and double bonds. The sulfur(IV) analogues of **1**, **2** and **3** are, without exception, monomers. However, the tendency to form singly bonded in preference to doubly bonded molecules is even more pronounced for tellurium than for selenium. Tellurium(IV) diimides are dimeric and tellurium dioxide is a three-dimensional polymer consisting of only Te-O single bonds.

Theoretical calculations for the energetics of the [2+2] cyclodimerization and cycloaddition reactions predict both sulfur(IV) and selenium(IV) diimides to be monomeric with the sole exception of $\text{Se}(\text{NSiMe}_3)_2$ that may show a tendency to dimerize. The cyclodimerization of RNSeO and the cycloaddition of RNSeO with $\text{Se}(\text{NR})_2$ as well as that of RNSO_2 with $\text{Se}(\text{NR})_2$ are energetically favored processes consistent with the observed structures of $\text{OSe}(\mu\text{-N}{}^t\text{Bu})_2\text{SeO}$, $\text{OSe}(\mu\text{-N}{}^t\text{Bu})_2\text{SeN}{}^t\text{Bu}$ and $\text{O}_2\text{S}(\mu\text{-N}{}^t\text{Bu})_2\text{SeN}{}^t\text{Bu}$, respectively. However, the calculations indicate that cycloaddition is unlikely when one of the reactants is sulfur(IV) diimide.

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Supporting Information Available Two X-ray crystallographic files in CIF format and twelve tables of optimized geometries and energies are available on the Internet only. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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the semi-quantitative consideration of trends in reaction energies. For discussion of BSSE in tightly bound systems, see for example references 54b and 54c

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- (55) The trends in the reaction energetics at different correlated levels of theory seem to depend mainly on the identity of the chalcogen atoms in the molecule. By considering energy values of the molecules that could be calculated at all three correlated levels, the semi-quantitative contributions of one sulfur and selenium atom (C_E , $E = S$, or Se) to the correction of the reaction energies could be established, as follows: $MP2 \rightarrow CCSD$: $C_S = -9(1) \text{ kJ mol}^{-1}$, $C_{Se} = -15(2) \text{ kJ mol}^{-1}$; $MP2 \rightarrow CCSD(T)$: $C_S = -4(1) \text{ kJ mol}^{-1}$, $C_{Se} = -7(2) \text{ kJ mol}^{-1}$. It can be seen from Figure 3 that these contributions establish reasonable estimates for the $CCSD/cc\text{-pVDZ//B3PW91/6-31G}^*$ and $CCSD(T)/cc\text{-pVDZ//B3PW91/6-31G}^*$ reaction energies, when the corresponding $MP2/cc\text{-pVDZ//B3PW91/6-31G}^*$ energy values are known.
- (56) Reaction energies have only been calculated at highly correlated levels of theory, since the inclusion of electron correlation was found to be critical in order to obtain a proper description of the energetics of the studied systems. The lower level methods $HF/6\text{-31G}^*$, $MP2/6\text{-31G}^*$ and $B3PW91/6\text{-31G}^*$ predict significantly less positive energies for cyclodimerization. Whereas in the case of sulfur diimides these calculations correctly imply endothermic processes, the uncorrelated methods of theory indicate that the cyclodimerization of selenium diimides is exothermic.

When electron correlation is properly taken into account, the reaction energies of selenium diimides become approximately zero or slightly negative, indicating an energetically neutral process.

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Table 1. Crystallographic Data for Se₃(NAd)₂ (**6b**)

| | |
|---|--|
| formula | C ₂₀ H ₃₀ N ₂ Se ₃ |
| fw | 535.34 |
| crystal system | Monoclinic |
| space group | C2/c (No. 15) |
| <i>a</i> , Å | 27.2590(2) |
| <i>b</i> , Å | 6.5850(4) |
| <i>c</i> , Å | 21.6340(9) |
| <i>α</i> , deg | 90 |
| <i>β</i> , deg | 100.152(1) |
| <i>γ</i> , deg | 90 |
| <i>V</i> | 3822.5(3) |
| <i>Z</i> | 8 |
| <i>T</i> , K | 173 |
| ρ calcd, g cm ⁻³ | 1.860 |
| μ (MoK α), cm ⁻¹ | 75.80 |
| <i>R</i> ₁ ^a | 0.0543 |
| <i>wR</i> ₂ ^b | 0.0784 |

^a $R_1 = [\sum||F_o| - |F_c||] / [\sum|F_o|] [I \geq 2\sigma(I)]$.

^b $wR_2 = \{[\sum w(F_o^2 - F_c^2)^2] / [\sum w(F_o^2)^2]\}^{1/2}$ [all data].

Table 2. Selected Bond Lengths (Å), Bond Angles (°) and Torsion Angles (°) for Se₃(NAd)₂ (**6b**)

| Bond Lengths | | Bond Angles | |
|------------------------|-----------|--------------------|------------|
| Se(1)-N(2) | 1.881(4) | N(2)-Se(1)-N(1) | 105.76(17) |
| Se(1)-N(1) | 1.892(4) | N(1)-Se(2)-Se(3) | 93.95(14) |
| Se(2)-N(1) | 1.846(4) | N(2)-Se(3)-Se(2) | 92.92(14) |
| Se(2)-Se(3) | 2.4044(8) | C(10)-N(1)-Se(2) | 118.9(3) |
| Se(3)-N(2) | 1.860(5) | C(10)-N(1)-Se(1) | 112.8(3) |
| N(1)-C(10) | 1.516(7) | Se(2)-N(1)-Se(1) | 111.30(19) |
| N(2)-C(20) | 1.508(7) | C(20)-N(2)-Se(3) | 120.0(3) |
| Torsion Angles | | C(20)-N(2)-Se(1) | 113.7(4) |
| N(1)-Se(2)-Se(3)-N(2) | 46.7(2) | Se(3)-N(2)-Se(1) | 110.46(19) |
| Se(3)-Se(2)-N(1)-Se(1) | -37.6(3) | | |
| N(2)-Se(1)-N(1)-Se(2) | 16.1(3) | | |
| Se(2)-Se(3)-N(2)-Se(1) | -41.7(2) | | |
| N(1)-Se(1)-N(2)-Se(3) | 23.4(3) | | |

Table 3. Bond Lengths (Å) and Bond Angles (°) for Cyclic Selenium Imides

| Ring System | $r(\text{Se-N})$ | $r(\text{Se-Se})$ | $\angle\text{NSeN}$ | $\angle\text{NSeSe}$ | $\angle\text{SeNSe}$ | $\Sigma \angle\text{N}^a$ |
|--|--|-------------------|---------------------|----------------------|----------------------|---------------------------|
| $\text{Se}_3(\text{NAd})_2$ | 1.853(4) ^b 1.886(4) ^b | 2.4044(8) | 105.8(2) | 93.5(1) | 110.9(2) | 343.6 |
| $\text{Se}_9(\text{N}^t\text{Bu})_6^c$ | | 2.336(3) | 101.0(7) | 111.5(4) | 114(1) | 351 |
| $\text{Se}_3(\text{N}^t\text{Bu})_3^d$ | 1.831(8) ^b | | 106.6(2) | | 113.3(2) | 358.9 |
| $\text{Se}_6(\text{N}^t\text{Bu})_2^c$ | 1.830(4) | 2.333(1) | | 110.0(1) | 114.8(2) | 358.6 |

^a Sum of angles at nitrogen atoms. ^b Mean value. ^c Ref. 15. ^d Ref. 14.

Table 4. Bond Lengths (Å) for Selenium(IV) Imides and Oxides

| Compound | <i>r</i>(Se-O) | <i>r</i>(Se=O) | <i>r</i>(Se-N) | <i>r</i>(Se=N) | Ref. |
|---|-----------------------|-----------------------|-----------------------|-----------------------|------------------------|
| (SeO ₂) _∞ | 1.8171(3) | 1.631(3) | | | This work ^b |
| (SeO ₂) _∞ | 1.7951(1) | 1.624(2) | | | 13b ^c |
| OSe(μ-N ^t Bu) ₂ SeO | | 1.621(2) | 1.885(3) ^a | | 11 |
| OSe(μ-N ^t Bu) ₂ SeN ^t Bu | | 1.628(4) | 1.864(2) ^a | 1.687(4) | 14 |
| | | | 1.937(6) ^a | | |
| Se(NAd) ₂ | | | | 1.679(8) | 11 |
| | | | | 1.732(7) | |

^a Mean value. ^b 173K. ^c 139K.

Table 5. Cyclodimerization Energies of E(NR)₂ and RNEO (E = S, Se; R = H, Me, ^tBu, SiMe₃) (kJ mol⁻¹)^a

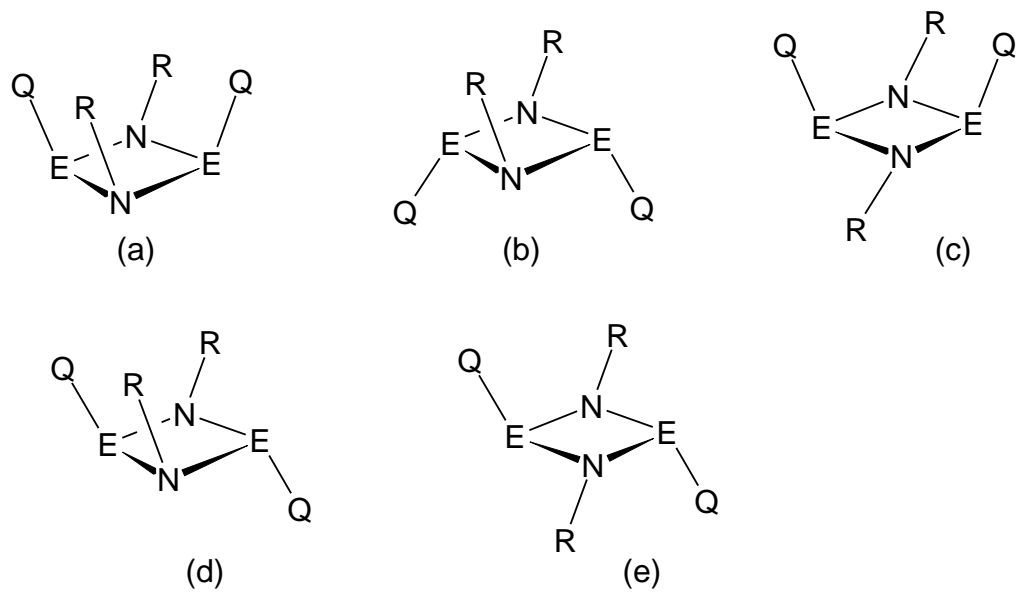
| | H | Me | ^t Bu | SiMe ₃ |
|---|-----|-----|-----------------|-------------------|
| 2RNSNR → RNS(μ-NR)₂SNR^b | | | | |
| MP2/cc-pVDZ | 120 | 98 | 105 | 67 |
| CCSD/cc-pVDZ | 102 | 83 | | |
| CCSD(T) /cc-pVDZ | 114 | 91 | | |
| 2RNSeNR → RNSe(μ-NR)₂SeNR^b | | | | |
| MP2/cc-pVDZ | 40 | 24 | 25 | -28 |
| CCSD/cc-pVDZ | 4 | -8 | | |
| CCSD(T) /cc-pVDZ | 23 | 7 | | |
| 2RNSO → OS(μ-NR)₂SO | | | | |
| MP2/cc-pVDZ | 83 | 66 | 60 | 46 |
| CCSD/cc-pVDZ | 65 | 50 | 42 | 26 |
| CCSD(T) /cc-pVDZ | 77 | 60 | 52 | 34 |
| 2RNSeO → OSe(μ-NR)₂SeO | | | | |
| MP2/cc-pVDZ | -6 | -19 | -26 | -48 |
| CCSD/cc-pVDZ | -38 | -42 | -56 | -83 |
| CCSD(T) /cc-pVDZ | -18 | -25 | -38 | -66 |

^a Values include unscaled zero point energy corrections. ^b Density functional calculations gave values of 34.9 and -2.8 kJ mol⁻¹ for E = S and E = Se, respectively.¹⁰

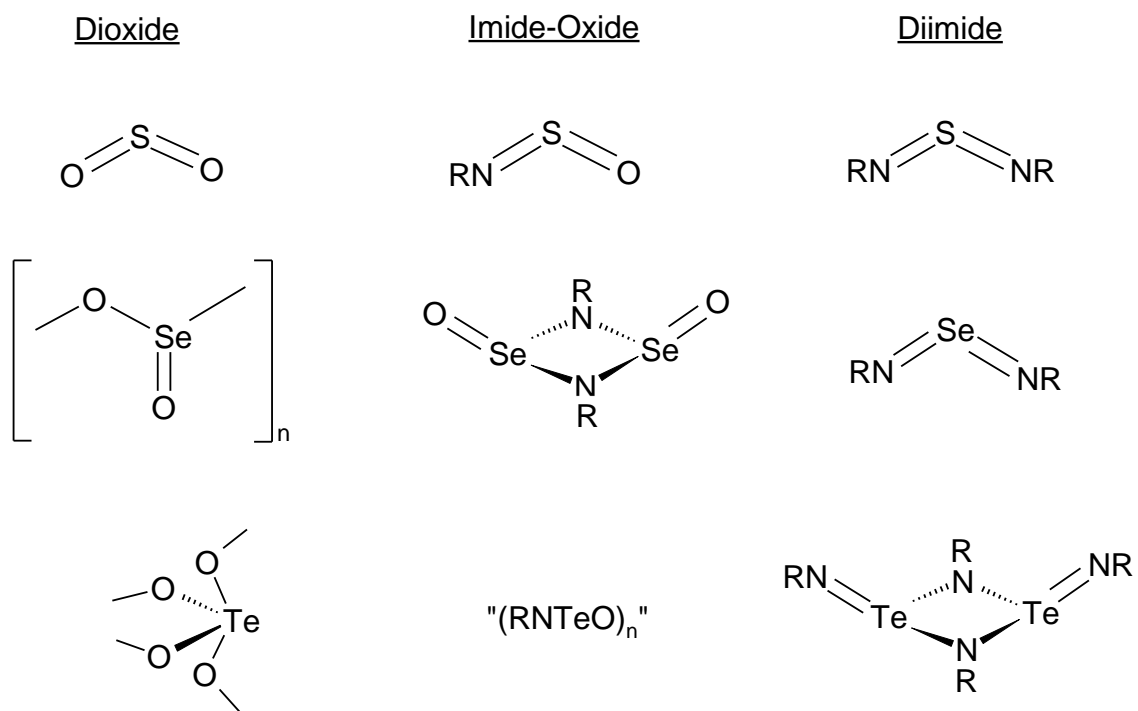
Table 6. Energies of Various Asymmetric [2+2] Cycloaddition Reactions (kJ mol⁻¹)^a

| | H | Me^b | ^tBu | SiMe₃ |
|--|----------|-----------------------|-----------------------|-------------------------|
| RNSeO + RNSNR → OSe(μ-NR)₂SNR | | | | |
| MP2/cc-pVDZ | 56 | 39 | 40 | 8 |
| CCSD/cc-pVDZ | 31 | 20 | | |
| CCSD(T) /cc-pVDZ | 46 | 32 | | |
| RNSeO + RNSeNR → OSe(μ-NR)₂SeNR | | | | |
| MP2/cc-pVDZ | 18 | 1 | -1 | -40 |
| CCSD/cc-pVDZ | -16 | -26 | | |
| CCSD(T) /cc-pVDZ | 3 | -10 | | |
| RNSO₂ + RNSeNR → O₂S(μ-NR)₂SeNR | | | | |
| MP2/cc-pVDZ | -20 | -53 | -53 | -73 |
| CCSD/cc-pVDZ | -46 | -76 | | |
| CCSD(T) /cc-pVDZ | -30 | -64 | | |
| RNSNR + RNSeNR → RNS(μ-NR)₂SeNR | | | | |
| MP2/cc-pVDZ | 80 | 62 | 67 | 19 |
| CCSD/cc-pVDZ | 53 | 38 | | |
| CCSD(T) /cc-pVDZ | 69 | 50 | | |

^a Values include unscaled zero point energy corrections.



Scheme 1. Conformations of studied cycloaddition and dimerization structures [E = S, Se; Q = NR, O_x (x = 1, 2); R = H, Me, ^tBu, SiMe₃].



Scheme 2. Multiple bonding in chalcogen(IV) imides and oxides.

Figure Captions

Figure 1. The ^{77}Se NMR spectrum of the decomposition mixture of $\text{AdN}=\text{Se}=\text{NAd}$ (**1b**) in THF at 25°C after three days.

Figure 2. Molecular structure of $\text{Se}_3(\text{NAd})_2$ (**6b**) showing the atomic numbering scheme.

Figure 3. The trends in the energies of (a) cyclodimerization reactions and (b) cycloaddition reactions at different correlated levels of theory.

- Reaction energies calculated at MP2/cc-pVDZ//B3PW91/6-31G* level of theory
- Reaction energies calculated at CCSD/cc-pVDZ//B3PW91/6-31G* level of theory
- ▲ Reaction energies calculated at CCSD(T)/cc-pVDZ//B3PW91/6-31G* level of theory
- , ▲ Estimates based on the trends calculated by the above-mentioned MP2, CCSD, and CCSD(T) calculations.⁵⁸

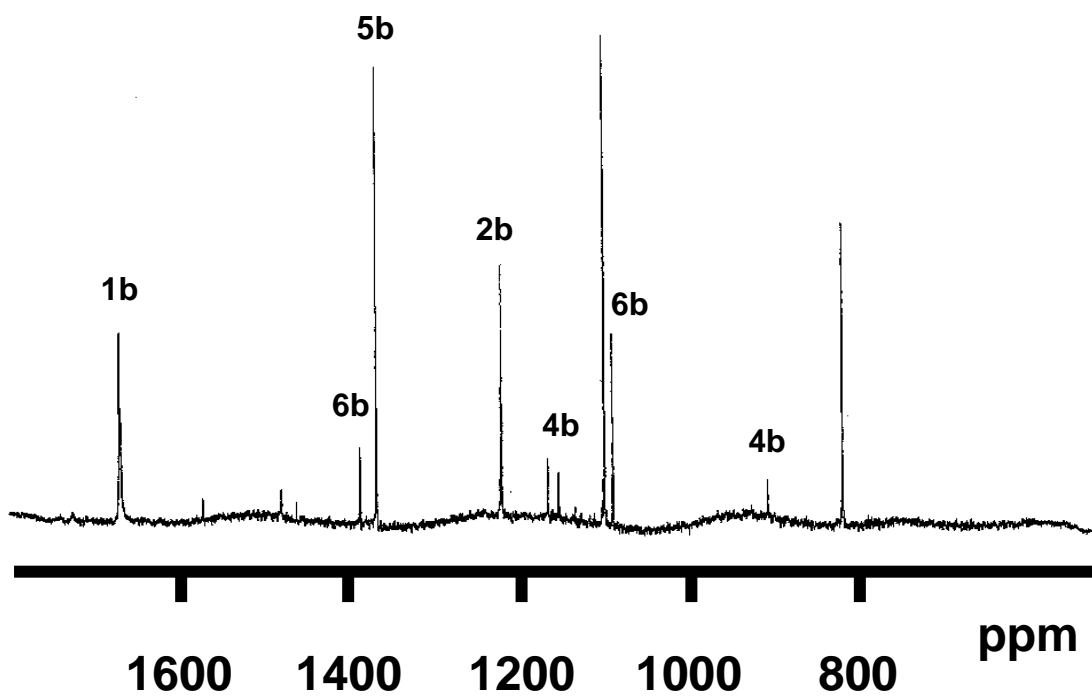


Figure 1

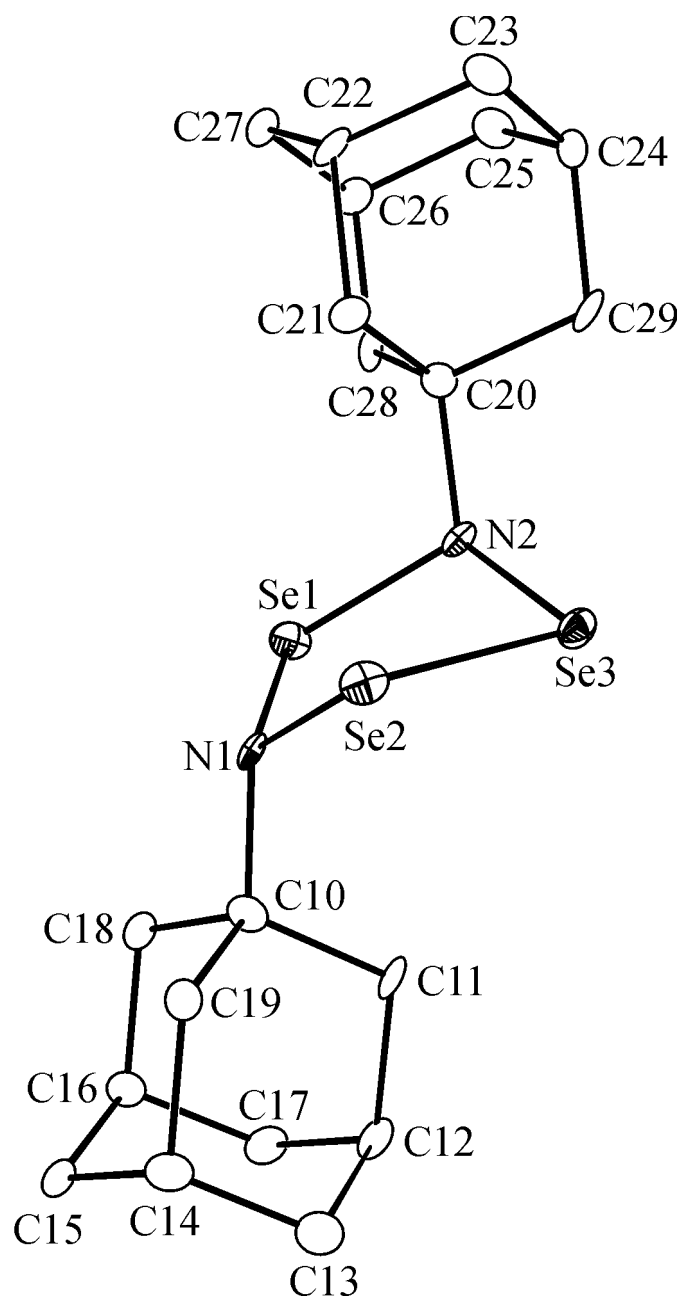
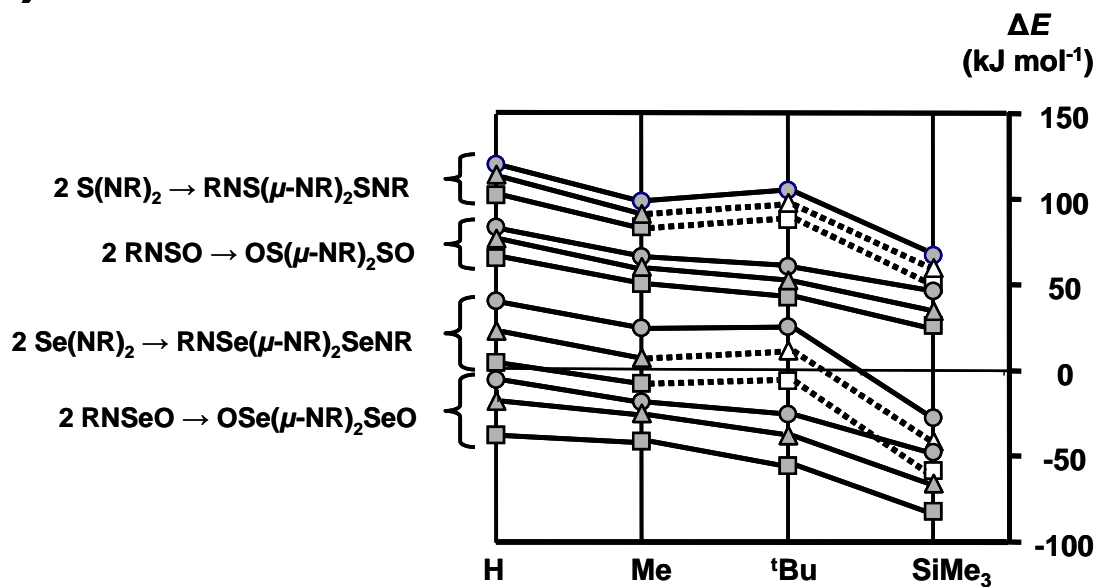


Figure 2

(a)



(b)

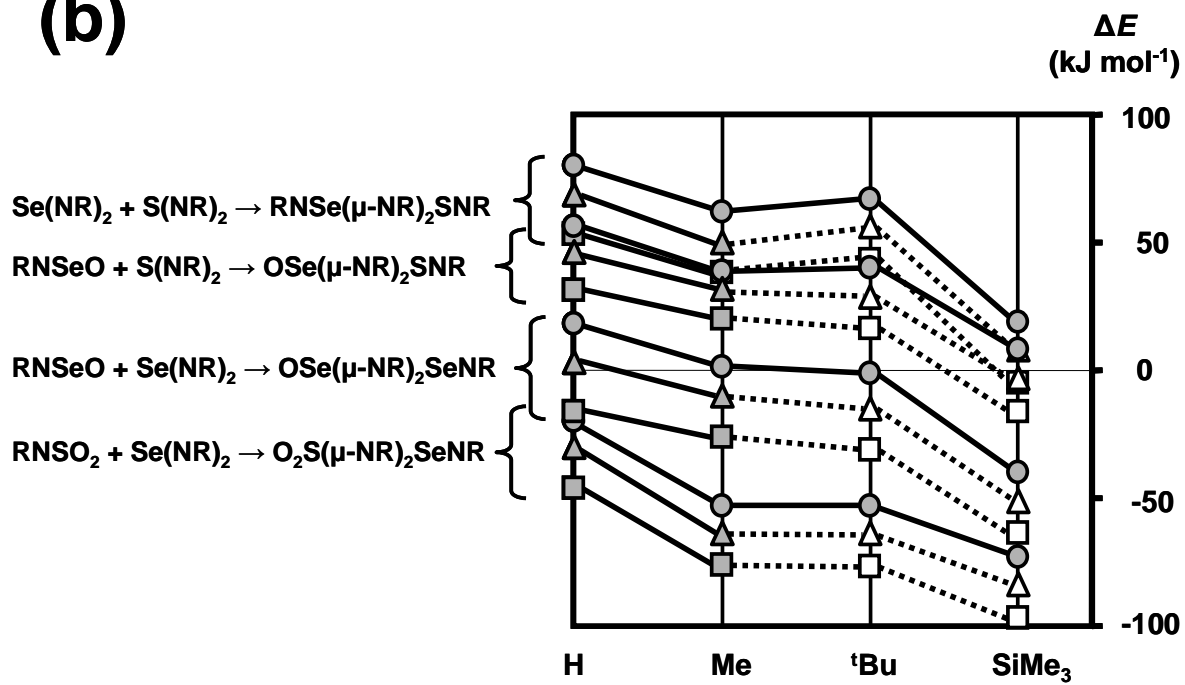


Figure 3