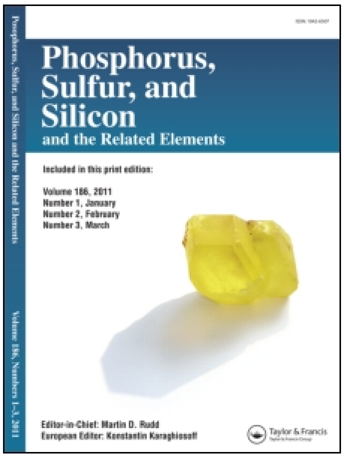

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Recent Progress in Imidoselenium Chemistry

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Recent Progress in Imidoselenium Chemistry

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Recent progress in imidoselenium chemistry is reviewed. Selenium diimides are thermally unstable and decompose forming a number of cyclic selenium imide derivatives $Se_3(NR)_2$, $Se_3(NR)_3$, $Se_6(NR)_2$, $Se_9(NR)_6$, $OSe(\mu\text{-}NR)_2SeO$, $RNSe(\mu\text{-}NR)_2SeO$, *and* $RNSe(\mu\text{-}NR)_2SO_2$ ($R = {}^tBu$ *or adamantyl). All species have been structurally characterized. The experimental and theoretical evidence for the possibility of [2 + 2] cyclodimerization of selenium diimides is discussed.*

Keywords NMR spectroscopy; selenium imides; X-ray crystallography

INTRODUCTION

Cyclic sulfur imides form a well-characterized class of compounds the most common examples being the eight-membered ring molecules $S_{8-n}(NH)_n$.[1] While the corresponding selenium imides are unknown, their organic derivatives $Se_6(N^tBu)_2$, $Se_9(N^tBu)_6$,[2] and $Se_3(N^tBu)_3$[3] have been structurally characterized. Herberhold and Jellen[4] also have suggested that cyclic $Se_3(N^tBu)_2$ can be formed from $SeCl_4$ and ${}^tBuNH_2$. The identification, however, was based only on NMR spectroscopic information.

Sulfur diimides $S(NR)_2$ have attracted considerable interest because of their utility as synthons in inorganic or organic syntheses.[5–7] While related selenium diimides $Se(NR)_2$ are thermally unstable, they are efficient *in situ* reagents for amination of olefins.[8,9]

The present contribution is concerned with the recent developments in imidoselenium chemistry. The emphasis is on the preparation and structural properties of new molecular species.

PREPARATION OF SELENIUM IMIDE DERIVATIVES

The first cyclic selenium imide derivatives $Se_6(N^tBu)_2$ and $Se_9(N^tBu)_6$ were prepared by the reaction of $LiN({}^tBu)(SiMe_3)$ with Se_2Cl_2 or $SeOCl_2$

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and characterized by NMR spectroscopy and X-ray crystallography.[2] These species can more conveniently be synthesized by treating the equimolar mixture of elemental selenium and $SeCl_4$ with $^tBuNH_2$.[3]

Pure $SeCl_2$[10] reacts with $^tBuNH_2$ to afford a mixture of novel acyclic imidoselenium dichlorides $ClSe(N^tBuSe)_nSeCl$ ($n = 1, 2$) as well as cyclic $Se_6(N^tBu)_2$, $Se_9(N^tBu)_6$, $Se_3(N^tBu)_3$, and several other species.[3] The product distribution is dependent on the molar ratio of the reactants. The reaction of RNH_2 (R = ^{t}Bu,[8] adamantyl,[11] supermesityl[12]) and $SeCl_4$ yields mainly selenium diimides.

$^tBuNSe(\pi\text{-}N^tBu)_2SO_2$ and $^tBuNSe(\pi\text{-}N^tBu)_2SeO$ can be generated either by treatment of $^tBuNH_2$ and $SeCl_4$ with SO_2Cl_2 and $SeOCl_2$, respectively, or by the [2 + 2] cycloaddition reaction of $Se(N^tBu)_2$ and ^tBuNSeO.[3]

MOLECULAR STRUCTURES

The X-ray structures of the known cyclic selenium imide derivatives are shown in Figure 1. $Se_3(N^tBu)_3$,[3] $Se_6(N^tBu)_2$, and $Se_9(N^tBu)_6$[2] show quite normal parameters single bonds. The Se—Se bond in $Se_3(NAd)_2$ (Ad = adamantyl) is somewhat longer.[13] It is a consequence of small τ_{SeSe} torsional angle in the molecule.

Three conformations are possible for sulfur and selenium diimides: (1) *s,s;* (2) *s,a;* and *a,a*. Most sulfur diimides and adamantyl selenium diimide show a *syn,anti*-conformation (see Ref. 14, and references therein). Our recent *ab initio* and DFT calculations have shown that with few exceptions, the *syn*, *anti* conformation is indeed the most stable conformation.[14]

The X-ray structures have been determined for two selenium diimides and are shown in Figure 2. Whereas adamantyl selenium diimide is a *syn,anti*-conformer,[11] supermesityl selenium diimide is an *anti,anti*-conformer.[12]

Both B3LYP/TZVPP calculated[15] and experimental ^{77}Se chemical shifts of some different imidoselenium and related species have been presented in Table 1. It can be seen that there is a qualitative agreement between the calculated and observed values.

REACTIONS OF SELENIUM DIIMIDES

Selenium diimides are thermally unstable.[6] The decomposition of $Se(NR)_2$ (R = ^{t}Bu,[3] adamantyl[13]) affords $Se_3(NR)_3$, $Se_3(NR)_2$, $RNSe(\mu\text{-}NR)_2SeO$, and $OSe(\mu\text{-}NR)_2SeO$, and in the case of $Se(N^tBu)_2$, also $Se_6(N^tBu)_2$ and $Se_9(N^tBu)_6$.[3]

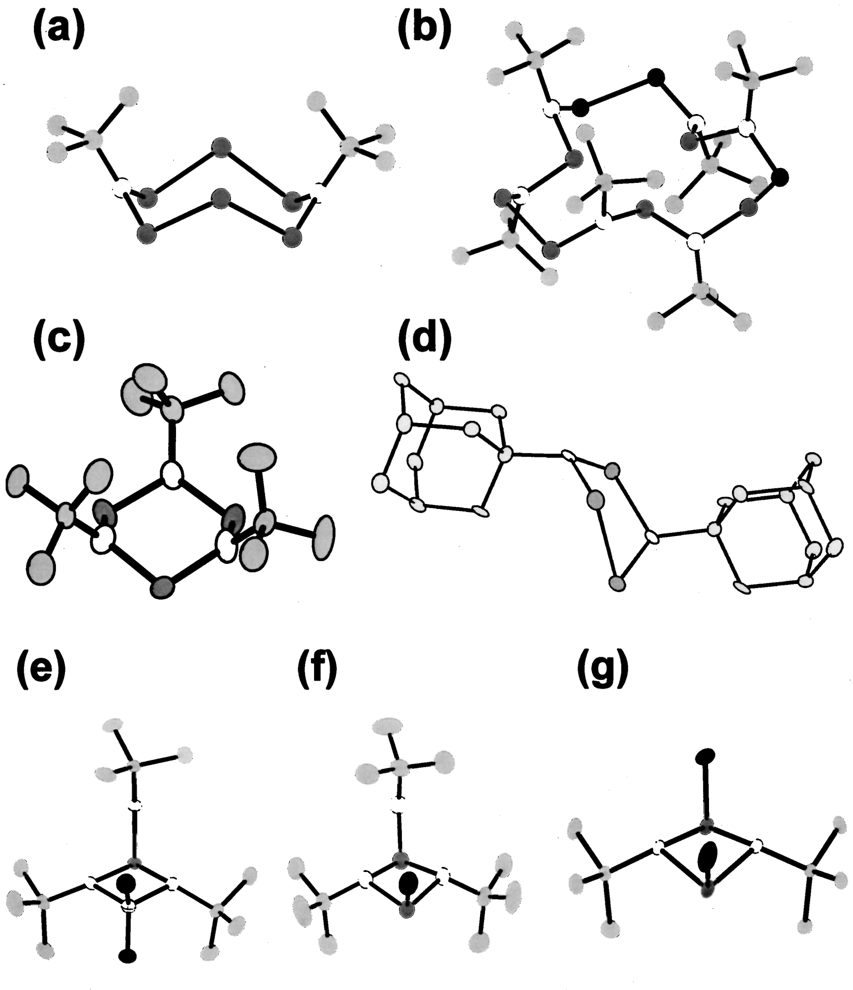

FIGURE 1 The molecular structures of (a) $Se_6(N^tBu)_2$ (redrawn from data in[2]), (b) $Se_9(N^tBu)_6$ (redrawn from data in[2]), (c) $Se_3(N^tBu)_3$ (redrawn from data in,[3] (d) $Se_3(NAd)_2$ (Ad = adamantyl; redrawn from data in[13]), (e) $^tBuNSe(\mu\text{-}N^tBu)_2SO_2$ (redrawn from data in[3]), (f) form $^tBuNSe(\mu\text{-}N^tBu)_2SeO$ (redrawn from data in[3]), (g) $(^tBuNSeO)_2$ (redrawn from data in[3]). The dark grey atoms denote oxygen, medium grey atoms selenium, light grey atoms carbon, and white atoms nitrogen. The sulfur atom in figure (e) is denoted by a white atom with a cross.

Sulfur diimides $S(NR)_2$ exist as monomeric species in solution[7] and the corresponding tellurium diimides $Te(NR)_2$ undergo a facile [2 + 2] cyclodimerization reaction to form dimeric $RNTe(\mu\text{-}NR)_2TeNR$.[16–18] The NMR spectroscopic[19] and the X-ray crystallographic[11] studies

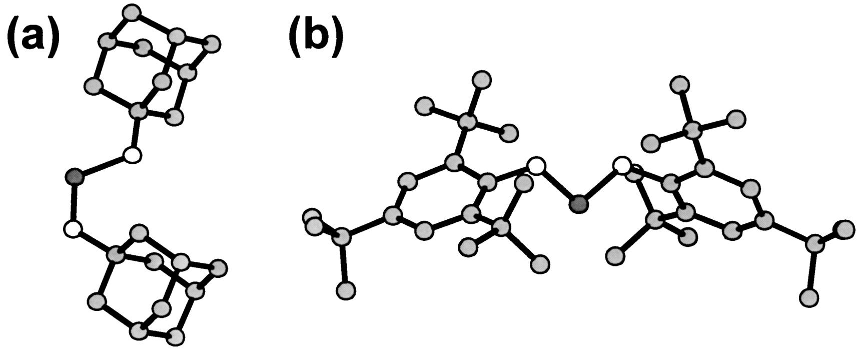

FIGURE 2 The molecular structures of $Se(NAd)_2$ (Ad = adamantyl; redrawn from data in[11]), (b) $Se(N^smes)_2$ (^{s}mes = supermesityl; redrawn from tentative data in[12]). The medium grey atoms denote selenium, light grey atoms carbon, and white atoms nitrogen.

indicate that $Se(NR)_2$ is monomeric. By contrast, ^tBuNSeO is dimeric.[11] $Se(N^tBu)_2$ and ^tBuNSeO also undergo a facile [2 + 2] cycloaddition to form $^tBuNSe(\mu\text{-}N^tBu)_2SeO$.[3]

Recent *ab initio* and DFT studies[13,15,20,21] expectedly have shown that the cyclodimerization of sulfur diimides is endothermic and that of tellurium diimides is exothermic. The cyclodimerization of selenium diimides seem approximately to be thermoneutral or slightly endothermic. These trends are summarized in Figure 3. The numerical values are strongly dependent on the level of theory.[13] The cyclodimerization

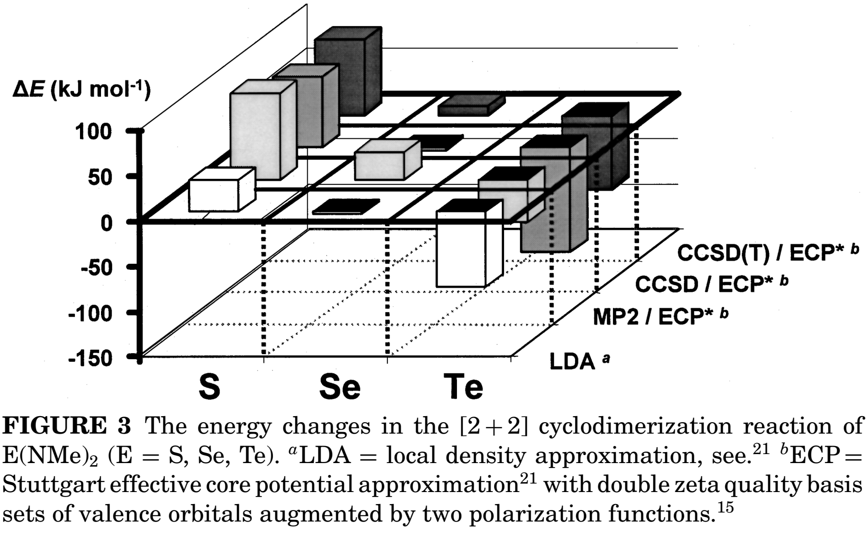

FIGURE 3 The energy changes in the [2 + 2] cyclodimerization reaction of $E(NMe)_2$ (E = S, Se, Te). [a]LDA = local density approximation, see.[21] [b]ECP = Stuttgart effective core potential approximation[21] with double zeta quality basis sets of valence orbitals augmented by two polarization functions.[15]

TABLE I Experimental and B3LYP/TZVPP-Calculated ^{77}Se Chemical Shifts of Various Imidoselenium Species

Compound	$\delta(^{77}\text{Se})_{\text{obs}}$	$\delta\ (^{77}\text{Se})_{\text{calc}}$[a]	Assignment[b]	Ref.[c]
$\text{Se(N}^t\text{Bu)}_2$				
anti,anti		1914	N=**Se**=N	
syn,anti	1653	1695	N=**Se**=N	3
syn,syn		1156	N=**Se**=N	
Se(NAd)_2				
anti,anti		2170	N=**Se**=N	
syn,anti	1651	1608	N=**Se**=N	13
anti,anti		1127	N=**Se**=N	
$\text{Se(N}^s\text{Mes)}_2$				
anti,anti	1844	2038	N=**Se**=N	12
syn,anti		1765	N=**Se**=N	
syn,syn		1349	N=**Se**=N	
$\text{OSe(}\mu\text{-N}^t\text{Bu)}_2\text{SeO}$	1242	1104	N–**Se**–N	3
$\text{OSe(}\mu\text{-NAd)}_2\text{SeO}$	1213	1101	N–**Se**=O	13
$^t\text{BuNSe(}\mu\text{-N}^t\text{Bu)}_2\text{SeO}$	1157	1089	N–**Se**=N	3
	882	802	N–**Se**=O	
$^t\text{BuNSe(}\mu\text{-N}^t\text{Bu)}_2\text{SO}_2$	824	707	N–**Se**=N	3
$\text{Se}_3\text{(N}^t\text{Bu)}_2$	1626	1684	N–**Se**–N	3
	1183	1317	N–**Se**–Se	
$\text{Se}_3\text{(N}^t\text{Bu)}_3$	1396	1346	N–**Se**–N	3
$\text{Se}_3\text{(NAd)}_3$	1361	1347	N–**Se**–N	13
$\text{Se}_6\text{(N}^t\text{Bu)}_2$	1109	1183	N–**Se**–Se	3
	518	739	Se–**Se**–Se	
$\text{Se}_9\text{(N}^t\text{Bu)}_6$	1425	1512	N–**Se**–N	3
	1203	1393	N–**Se**–Se	
$\text{Se\{N(SiMe}_3\text{)}_2\text{\}}_2$	1130	1180	N–**Se**–N	20
$\text{Se\{NH(Mes)\}}_2$	1118, 1117	1077,1076	HN–**Se**NH	12

[a] [12].

[b] The active nucleus is denoted in bold.

[c] The citations refer to the experimental chemical shifts.

of RNSeO and the cycloaddition of RNSeO with Se(NR)_2 are exothermic at all levels of theory in agreement with experimental observations.[13] By contrast, analogous cycloaddition energies are endothermic for all reactions involving sulfur diimides.

CONCLUSIONS

The progress in imidoselenium chemistry has seen considerable progress in recent years. Several new compounds have been prepared and their molecular and electronic structures as well as chemical properties have been elucidated. These compounds may serve as useful synthons in the syntheses of new selenium-nitrogen species.

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