

Intramolecular Se...N Nonbonding Interactions in Low-Valent Organoselenium Derivatives: A Detailed Study by ^1H and ^{77}Se NMR Spectroscopy and X-Ray Crystallography

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Abstract: A series of novel low-valent organoselenium compounds stabilized by Se...N intramolecular interactions has been synthesized. The existence of Se...N nonbonding interactions was determined by ^1H and ^{77}Se NMR spectroscopy and X-ray crystallography. These interactions result in an apparent downfield shift of the ^{77}Se NMR signals; the shift values roughly correspond with the strength of the Se...N interaction. Single-crystal X-ray studies show that the strength of the Se...N interactions depends on the relative electronegativity of the group attached to the selenium and the nature of the heteroatom. These interactions lengthen the Se–X (X = Se, Cl, Br, I, CH_2) bond *trans* to the N...Se bond and increase the possibility of nucleophilic attack on the selenium. In

addition to the Se...N intramolecular interaction, Se...X (X = Cl, Br, I) intermolecular interactions were observed in [2-(4,4-dimethyl-2-oxazoliny)phenyl]selenenyl chloride (**4**), bromide (**5**), and iodide (**6**), indicative of the hypervalent (pseudo-high-valent) nature of the selenium. The strength of the Se...N intramolecular interaction decreases in the order RSeCl, RSeBr, RSeI, whereas the Se...X intermolecular interaction increases in the same order. The aryl benzylic compounds [2-(4,4-dimethyl-2-oxazoliny)phenyl]benzyl selenide (**7**), α,α' -di[2-(4,4-dimethyl-2-oxazoliny)-

phenylselenenyl]-*m*-xylene (**8**), α,α' -di[2-(4,4-dimethyl-2-oxazoliny)phenylselenenyl]-*o*-xylene (**9**), and 1,3,5-tri[2-(4,4-dimethyl-2-oxazoliny)phenylselenenyl]-2,4,6-trimethylbenzene (**10**) are unusually stable and also show weak Se...N interactions in the solid state. The strong Se...N interactions in all the compounds suggest that the sp^2 nitrogen may coordinate with the selenium more strongly than the sp^3 nitrogen and the resonance contributions from the five-membered heterocyclic rings further increase the extent of Se...N interactions between selenium and tertiary nitrogen. A correlation between the Se...N intramolecular distance and the ^{77}Se chemical shift was attempted.

Keywords: halides • hypervalent compounds • intramolecular coordination • selenides • selenium

Introduction

The chemistry of organoselenium derivatives stabilized by intramolecular nonbonded Se...X (X = H, N, O, S, Se, F, Cl) interactions has attracted considerable current interest. These derivatives are remarkably versatile as they afford: a) novel, hypervalent, stable organoselenium compounds where the divalent selenium further interacts with a nearby heteroatom (O, N, Se, etc.) to form a pseudo-high-valent selenium species,^[1] b) chiral reagents for asymmetric synthesis,^[2] c) ligands for achiral and chiral catalysis,^[3] d) ligands for the isolation of monomeric MOCVD (metal–organics chemical

vapor deposition) precursors,^[4] and e) synthetic models for the glutathione peroxidase family of enzymes.^[5] Interestingly, all these low-valent selenium compounds have a heteroatom in close proximity to the selenium atom, and the nonbonding secondary interactions arise as a result of the intramolecular coordination between the heteroatom and selenium. The nature of these interactions has been analyzed by Ramasubbu et al.,^[6] Goldstein et al.,^[7] and Barton et al.,^[8] and the electronic structure around the selenium atom has been interpreted in terms of a $3c-4e$ X...Se–R bond (hypervalent bond).

Organoselenium compounds, in particular those having Se...N intramolecular interactions, are of current interest and are challenging targets for organic and organometallic chemists because of their role in chiral induction and antioxidant activity. Uemura et al.^[2i-r] have extensively used optically active ferrocenyl diselenides with in-built donor sp^3 nitrogen for very high chiral induction, whereas Tomoda et al.^[2s-u, 3a, b] have demonstrated in a series of papers that organoselenium derivatives with a coordinating amino group

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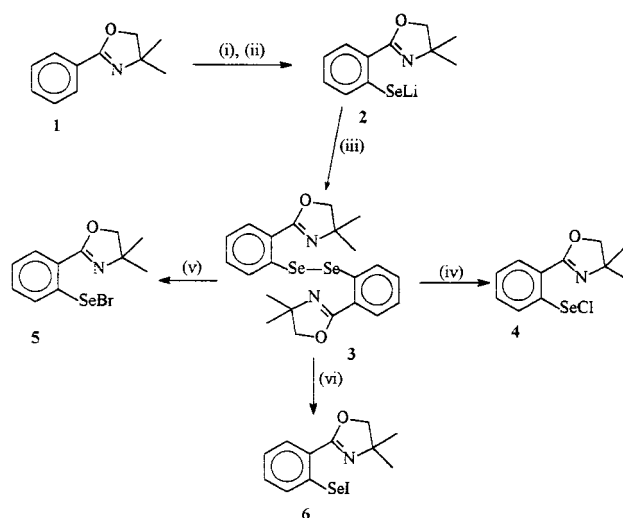
can be used not only for the catalytic conversion of olefins to allylic ethers but also for asymmetric inter- and intraoxy-selenenylation reactions. The $\text{Se} \cdots \text{N}$ interactions are also of great interest from a biological point of view as these interactions stabilize the selenenic acid, the key intermediate in the glutathione peroxidase catalytic cycle, and synthetic model compounds.^[5] Also the hypervalent interactions between the tertiary amino nitrogen and the selenium atoms activate the $\text{Se}-\text{Se}$ bond for oxidative cleavage.

However, the effects of substituents attached to the selenium on the $\text{Se} \cdots \text{N}$ nonbonding interactions have not been studied systematically with X-ray structure analysis. This would give more information about the existence of $\text{Se} \cdots \text{N}$ interactions in the solid state. In addition, although the $\text{Se} \cdots \text{N}$ interaction between divalent selenium and tertiary amine possessing a sp^3 nitrogen has been studied to some extent,^[9] there is no detailed study concerning the nature of the $\text{Se} \cdots \text{N}$ interactions between the selenium and a sp^2 nitrogen. In continuation of our work on intramolecular-coordinated organochalcogens,^[10] we describe in this paper the synthesis, crystallographic study, and spectroscopic analysis of a range of organoselenium compounds derived from (4,4-dimethyl-2-phenyl)oxazoline. These include the first authentic example of a structurally characterized areneseelenenyl chloride **4**, the third example of a structurally characterized areneseelenenyl bromide **5**, and the second example of a selenenyl iodide **6**. In addition, we report here the syntheses and the first structural characterization of some stable aryl benzyl selenides **7–14** stabilized by intramolecular $\text{Se} \cdots \text{N}$ interactions.

Results and Discussion

Synthesis: The synthesis of the key intermediate, diselenide **3**,^[11] was approached by the organolithium route. The lithium areneseelenolate, OxSe^-Li^+ (**2**), was easily prepared by the direct metallation of 4,4'-dimethyl-2-phenyloxazoline (**1**) with *n*BuLi in hexane followed by the addition of selenium powder in ether.^[11] Oxidation of the lithium selenolate **2** then afforded the desired diselenide (Scheme 1). The stable chloro compound **4** was obtained as a crystalline solid in good yield by reacting the diselenide **3** with a stoichiometric amount of sulfonyl chloride. The bromo compound **5** was synthesized by a similar method, with a stoichiometric amount of bromine. Attempts to synthesize the Se^{IV} bromide, RSeBr_3 , by the reaction of excess bromine with the diselenide **3** were unsuccessful. Although there was some indication for the formation of the Se^{IV} compound in the reaction mixture, the compound was found to be unstable in solution and decomposed within a few hours to give the monobromide **5**. This observation is consistent with the recent studies^[12] which have shown that the oxidative addition of Br_2 to Se^{II} compounds is a reversible process.

It is known that the diorgano diselenides (R_2Se_2) react with iodine to give only charge-transfer adducts ($\text{R}_2\text{Se}_2 \cdot \text{I}_2$) instead of selenenyl iodides (RSeI).^[13] The isolation of stable binary compounds of iodine and selenium has been difficult owing to their similar electronegativities.^[14] Du Mont et al. used a more hindered bis(2,4,6-tri-*tert*-butylphenyl) diselenide to synthe-



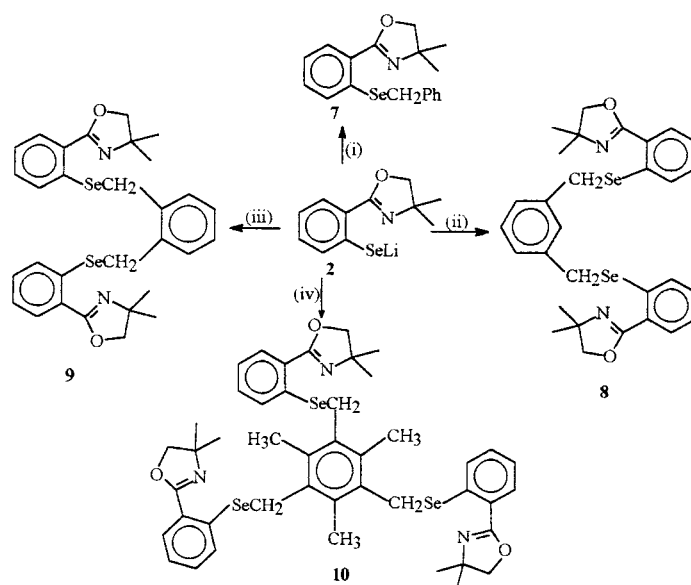
Scheme 1. Synthetic route to the [2-(4,4-dimethyl-2-oxazoliny)phenyl]selenenyl halides **4**, **5**, and **6**. Reagents and conditions: i) *n*BuLi, hexane, room temperature, 1 h; ii) Se powder, ether, 0 °C, 3 h; iii) O₂, NaHCO₃(aq); iv) SO₂Cl₂, CCl₄, 0 °C, 1 h; v) Br₂, CCl₄, 0 °C, 1 h; vi) I₂, CCl₄, 0 °C, 1 h.

size a stable selenenyl iodide, which they characterized by X-ray crystallography.^[15] However, it was later reported by the same authors that a slight reduction in the steric bulk (from *tert*-butylphenyl to *iso*-propylphenyl) again leads to the formation of a charge-transfer complex.^[16] When the reaction of **3** was carried out with a stoichiometric amount of iodine the novel monoiodide **6** was obtained. In compound **6** intramolecular stabilization leading to the formation of 10- $\text{Se}-3$ selenane (10 valence electrons, 3 bound ligands) seems to be responsible for the formation of a covalent bond rather than a charge-transfer adduct.^[17]

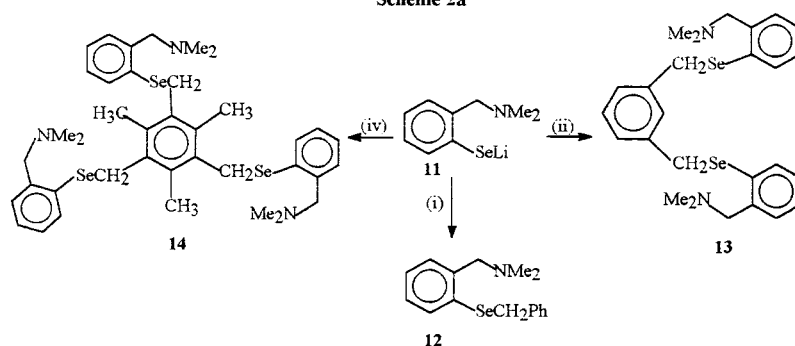
In general, aryl benzyl and aryl allyl selenides are unstable and decompose readily to give coupled hydrocarbon products and free selenium.^[18] Although the unsymmetrical selenides are useful synthetic reagents in heterocyclic chemistry,^[19–21] there is no structural evidence for stable aryl benzyl selenides. Reaction of OxSe^-Li^+ (**2**) with an equimolar amount of benzyl chloride gave **7** in moderate yield. Compounds **8**, **9**, and **10** were synthesized from the appropriate bromo compounds (Scheme 2a). For comparison, we have also prepared some novel benzylic compounds, **12**, **13**, and **14**, derived from *N,N*-dimethylbenzylamine which has a sp^3 nitrogen atom (Scheme 2b). Although these compounds are slightly unstable, they are stable enough for satisfactory analysis and NMR spectrometry.

Spectroscopic behavior:

¹H NMR spectra: The ¹H NMR chemical shifts for **1** and **3–14** are listed in Table 1. At ambient temperature there was no evidence for significant $\text{Se} \cdots \text{N}$ interactions as no anisochronous resonances were observed for the $-\text{C}(\text{CH}_3)_2$ group and an AB quartet was observed for the $-\text{CH}_2\text{O}-$ protons. However, the trend in the chemical shifts gave some information about the $\text{Se} \cdots \text{N}$ interaction. Compounds **3**, **4**, **5**, **6**, and **7–10** can be categorized into three groups. Compounds **4**, **5**, and **6** fall into the first category, in which



Scheme 2a



Scheme 2b

Scheme 2. Synthetic routes to the aromatic selenenyl derivatives a) **4–10** and b) **12–14**. Reagents and conditions: i) PhCH₂Cl, 0 °C, 2 h; ii) *α,α*-dibromo-*m*-xylene, 0 °C, 2 h; iii) *α,α*-dibromo-*o*-xylene, 0 °C, 2 h; iv) 1,3,5-bromomethyl mesitylene, 0 °C, 2 h.

Table 1. ¹H NMR chemical shifts for methylene and methyl protons, and ⁷⁷Se data.^[a]

Compound	–C(CH ₃) ₂	–CH ₂ O (or N)	⁷⁷ Se ^[b]
1	1.38(s)	4.10(s)	–
3	1.46(s)	4.14(s)	454.8
4	1.86(s)	4.71(s)	855.9
5	1.64(s)	4.68(s)	849.5
6	1.58(s)	4.50(s)	762.2
7	1.37(s)	4.05(s)	420.5
8	1.38(s)	4.06(s)	361.9
9	1.37(s)	4.05(s)	349.4
10	1.38(s)	4.06(s)	304.9
12	2.18(s)	3.41(s)	321.1
13	2.17(s)	3.41(s)	320.8
14	2.20(s)	3.47(s)	256.8

[a] Chemical shifts measured in CDCl₃ at RT. [b] Chemical shifts δ relative to Me₂Se.

the Se...N interaction is very strong. For these compounds the –CH₃ signals spanned a range from δ = 1.58 to 1.86 and the –CH₂– signals from 4.50 to 4.71, considerable downfield shifts compared with the free amine (δ = 1.38 for –CH₃ and 4.10 for –CH₂–). The chemical shifts for the methyl and methylene protons mainly depend upon the electronegativity of the atom

attached to the selenium. The trend RSeCl > RSeBr > RSeI suggests a much stronger Se...N interaction in compound **4**, where the selenium is bonded to a highly electronegative atom chlorine. Du Mont et al. have reported a partial redistribution of RSeI compounds when they are dissolved in benzene or in aliphatic hydrocarbons. The solutions give rise to peaks for the diselenide.^[15] Interestingly, for compound **6** no such observation was made; this fact indicates its higher stability as a result of the formation of a five-membered chelate which arises from Se...N interactions. Compound **3** belongs to group two, in having an intermediate Se...N interaction. However, this interaction is considerably stronger than that reported for some diselenides with similar basic amino groups. The downfield shift (0.08 ppm) observed for **3** is considerably larger than that observed for the diselenide derived from *N,N*-dimethylbenzylamine (0.02 ppm)^[3d] indicating a stronger interaction in **3**. The third group, which contains selenides **7–10**, shows only a weak Se...N interaction. The

signals due to the –CH₂– protons were shifted slightly downfield for these compounds suggesting that the introduction of benzylic groups reduces the Se...N interaction. The same trend was observed for compounds **12–14**, which also fall into the third category.

Interestingly, for all the compounds based on the oxazoline substrate, the signals due to the methylene protons are more affected by the substituent on the selenium than by the methyl protons, although both the protons are three bonds away from the nitrogen. It is seen from the table that the signals due to methylene protons are shifted downfield for compounds **4, 5**, and **6** whereas the shift is upfield for compounds **7–10**. This may well be due to the involvement of oxygen in a resonance contribution to the oxazoline ring when the nitrogen atom interacts with the selenium (Figure 1). Therefore the methylene protons are more affected by the substituents than the



Figure 1. Postulated contribution of the oxygen atom to resonance stabilization of the oxazoline ring in compounds **3–8**.

methyl protons. This conclusion is further supported by the X-ray crystallography data (vide infra). For compounds **7–10** the signals for the $-\text{SeCH}_2-$ protons appear in the range of $\delta = 4.07\text{--}4.24$, in close agreement with the literature values for related compounds.^[22, 23] However, the Se–H coupling constants ($^2J_{\text{Se-H}}$) observed in all the benzylic compounds except **8** and **9** are much lower than the values obtained for related compounds.^[24] Since the peaks due to the $-\text{CH}_2-$ protons of the oxazoline ring merge with the $-\text{SeCH}_2-$ peaks, the coupling constants for compounds **8** and **9** could not be calculated. For compounds **12–14**, upfield shifts for the methyl protons were observed but the signals due to methylene protons were not shifted much.

⁷⁷Se NMR spectra: The ⁷⁷Se NMR chemical shifts (Table 1) proved quite informative about the Se \cdots N nonbonding interactions. The suggestion that the intramolecular Se \cdots N nonbonding interaction results in a downfield shift of the ⁷⁷Se NMR peaks is now widely accepted, although the values for the shift do not correspond exactly with the strength of the Se \cdots N interaction.^[9] In the monohalides **4–6** a large deshielding is observed with respect to the diselenide **3** (454 ppm) and the trend is RSeCl **4** (855 ppm) > RSeBr **5** (849 ppm) > RSeI **6** (762 ppm). This result is consistent with the report of McFarlane and Wood^[25] that selenium resonances become increasingly deshielded as the electronegativity of the attached substituent increases. It is worth noting that the halo derivatives are quite stable in solution for a long time and particularly in the case of **6** no peaks were detected for the diselenide **3** indicating much greater stability as a result of the intramolecular Se \cdots N coordination. This contrasts with a previous report where the authors had observed an equilibrium between the diselenide and its iodo derivative.^[15] The ⁷⁷Se chemical shifts for compounds **4** and **5** are lower than for the chloro and bromo derivatives reported by Tomoda et al.: {(N-cyclohexyl-N-methylaminomethyl)phenyl}selenium bromide 1010 ppm;^[24] {(N-cyclohexyl-N-methylaminomethyl)phenyl}selenium chloride, 1050.3 ppm;^[26] {2-(dimethylaminomethyl)phenyl}selenium bromide, 987 ppm; simple phenylselenenyl halides: PhSeCl, 1042 ppm; PhSeBr, 869 ppm; and a cationic selenium species, 1203 ppm.^[27] The ⁷⁷Se chemical shifts for the benzylic compounds **7–14** are shifted relatively upfield (240.9–349.4 ppm) owing to the presence of benzylic groups, which are covalently bonded to the Se atom and cannot accept further electron density from selenium. The ⁷⁷Se chemical shifts for these compounds are comparable with the chemical shift values for the benzylic selenides derived from *N-tert*-butylbenzanilide (367 ppm)^[19] and *N*-cyclohexylbenzanilide (369 ppm).^[19]

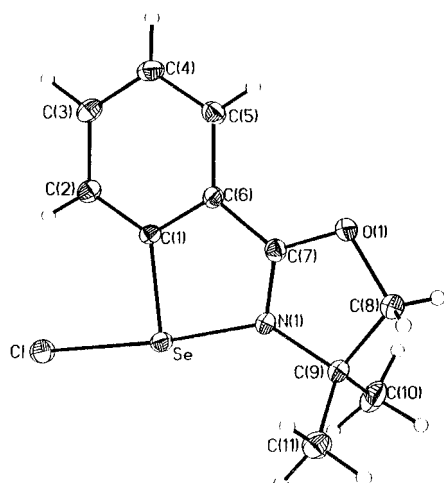
Mass spectra: Molecular-ion peaks were observed in low intensities for compounds **4** and **5**, but there is no indication for the formation of the diselenides. The mass spectrum of compound **6**, however, exhibited a peak at $m/z = 506$ for the formation of diselenide **3**. In fact, the intensity of the diselenide peak is much greater than that of the molecular-ion peak. A peak at $m/z = 254$ along with the base peak can be certainly assigned to molecular iodine. This suggests that a charge-transfer adduct $\text{R}_2\text{Se}_2 \cdot \text{I}_2$, which is the normal product

in the reaction between diselenide and iodine,^[13, 14] may be formed under the mass spectroscopic conditions. Compound **7** displayed a straightforward mass spectrum. However, the clear sets of peaks for several fragments confirm the higher stability of this compound. In all cases the base peaks observed at $m/z = 252\text{--}254$ can be assigned to the RSe^+ fragment. This strongly suggests a weakening of the Se–X (X = Se, Cl, Br, I or $-\text{CH}_2-$) bond *trans* to the Se \cdots N fragment. In contrast with the X-ray structures, compounds **4**, **5**, and **6** did not show any peaks corresponding with the dimer (vide infra).

X-ray crystallographic studies:

Crystal structure of 3: The details of the structure of compound **3** will be reported elsewhere.^[11] Here we present only the salient features of the structure for comparison. The coordination geometry around the selenium atoms is nearly T-shaped with each selenium atom bonded to a selenium, a carbon, and a nitrogen atom. The Se–Se distance of 2.354(8) Å relates well to the corresponding distances reported for other diselenides, which range from 2.29 to 2.39 Å. This value is also close to others reported for related compounds, bis[2-(dimethylaminomethyl)phenyl] diselenide^[3d] [2.357(1) Å] and 2,2'-diselenobis(*N*-cyclohexylmethylbenzylamine) [2.36 Å].^[24] Of particular interest in the structure is the intramolecular interaction of the tertiary nitrogen with the selenium. The atomic distances of Se(1) \cdots N(1) and Se(2) \cdots N(2) are 2.819(5) and 2.705(5) Å respectively, both of which are larger than the sum of their covalent radii (1.80 Å; Se, 1.17 Å; N(sp²), 0.63 Å) but significantly shorter than the sum of the corresponding van der Waals radii (3.5 Å). One of the five-membered rings lies in the plane, whereas for the other ring, there is a twist about the C(26)–C(27) bond such that the nitrogen atom present in this ring is directed slightly away from the selenium atom. The torsion angle C(11)–Se(1)–Se(2)–C(21) is 87.50°. The unequal Se \cdots N bond lengths [Se(1) \cdots N(1), 2.819(5) Å; Se(2) \cdots N(2), 2.705(5) Å] indicate that steric effects may play an important role.

Crystal structure of 4: An ORTEP^[28] view of compound **4** is shown in Figure 2, and the corresponding bond lengths and angles are listed in Table 2. The geometry around Se is T-shaped. The strongest, nonbonded Se \cdots N interaction [Se \cdots N, 2.052(2) Å] was observed for this compound compared with all other compounds in this study and related compounds reported in the literature. This bond length is 0.139 Å shorter than the Se \cdots N distance in ArSeCl [2.191 Å] reported by Tomoda et al.^[26] where the Se–Cl bond is stereoelectronically stabilized by strong intramolecular N \cdots Se–Cl interactions. This is also shorter than the Se \cdots N bond length reported for [2-(dimethylaminomethyl)phenyl]selenium chloride from ab initio molecular orbital (MO) calculations [2.331 Å(3-21*G method)] and 2.359 Å (LANL1DZ method).^[26] Although the interaction between selenium and a heteroatom (O, N, S, etc.) is expected to be strong in all the hypervalent compounds with highly electronegative substituents, the Se \cdots N interaction in compound **4** is quite unusual

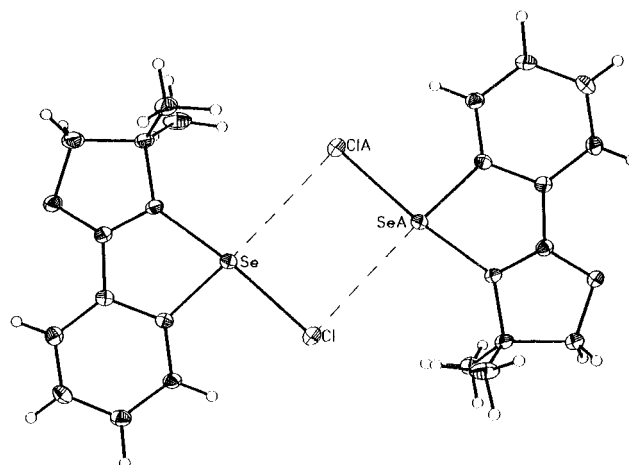
Figure 2. Crystal structure of compound **4**.Table 2. Significant bond lengths [Å] and angles [°] for **4**.

Se–C(1)	1.922(3)	Se···N(1)	2.052(2)
Se–Cl	2.482(8)	N(1)–C(7)	1.283(4)
Se···Cl(A)	3.476(8)	C(1)–Se–N(1)	81.38(10)
C(1)–Se–Cl	93.68(8)	N(1)···Se–Cl	175.06(7)
C(1)–Se···Cl(A)	173.7(2)	N(1)···Se–Cl(A)	94.6(2)
Cl–Se···Cl(A)	90.3(2)		

since the Se···N bond length approaches the Se–N single-bond length (1.80 Å). It is surprising that the Se···N distance of 2.052 Å is even lower than the corresponding value reported for a cationic species, chloro-substituted σ -ammoselenane, in which the observed Se···N length is 2.191 Å.^[29] The Se–Cl bond is quite long [2.482(8) Å] when compared with the sum of the atomic covalent radii (2.16 Å). This value is also longer than the Se–Cl distances reported for the cationic species chloro-substituted σ -ammoselenane (Se–Cl 2.296 Å).^[29] The approximately linear alignment of the Se–Cl covalent bond and the corresponding nitrogen [\angle N(1)···Se–Cl 175.06(7)°] may allow an effective orbital interaction between the nitrogen lone pair and the σ^* orbital of the Se–Cl bond and it may lead to the elongation of the Se–Cl bond and it may lead to the elongation of the Se–Cl bond. The observed Se–Cl bond length of compound **4** is longer by 0.182 Å than that of the inorganic selenenyl chloride reported by Barton et al.^[8]

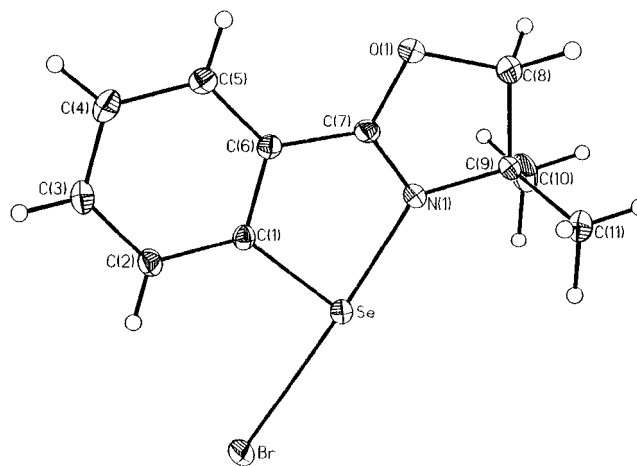
Although the molecule is a monomer, it may dimerize through weak intermolecular Se···Cl contacts (Figure 3). The intermolecular distance of 3.476(8) Å for Se···Cl(A) is about 0.324 Å shorter than the van der Waals contact distance (3.80 Å). This Se···Cl contact length between discrete units is very close to the values reported for Me₂SeCl₂ (Se···Cl 3.406–3.614 Å).^[30] The angle N···Se–Cl, 175.06(7)°, shows that the N···Se–Cl deviates a little from linearity. This may be due to the intermolecular interaction between Cl and Se. If we assume the intramolecular Se···N interaction leads to a linear arrangement for the N···Se–Cl bond, it appears that subsequent intermolecular interaction with consequent deviation from linearity leads to a weakening of the Se···N interaction.

Crystal structure of 5: The molecular structure of compound **5** is shown in Figure 4. Table 3 gives the significant bond lengths

Figure 3. Crystal structure of compound **4** showing the intermolecular Se···Cl interactions.Table 3. Significant bond lengths [Å] and angles [°] for **5**.

Se–C(1)	1.926(4)	Se···N(1)	2.063(3)
Se–Br	2.6318(7)	Se···Br(A)	3.556(9)
C(1)–Se···N(1)	80.9(2)	C(1)–Se–Br	95.24(12)
N(1)···Se–Br	176.14(10)	Br–Se···Br(A)	88.0(2)
N(1)–Se–Br(A)	95.9(10)	C(1)–Se–Br(A)	172.9(12)

and angles. The geometry around Se is T-shaped with selenium bonded to carbon, nitrogen, and bromine. The N···Se separation of 2.063(3) Å is well within the sum of the van der Waals radii as reported by Pauling^[31] [N, 1.5; Se, 2.0 Å]. This distance is shorter than that reported for [2-(dimethylaminomethyl)phenyl]selenium bromide [2.143(6) Å].^[34] and is also shorter than the average Se···N distance in the diselenide **3**, but marginally longer than in the chloro compound **4**. As in the case of **4**, the Se–Br distance of

Figure 4. Crystal structure of compound **5**.

2.631(9) Å is longer than the sum of the single-bond covalent radii for Se and Br (2.31 Å). A similar observation has been made for the molecular structure of 2-formylbenzeneselenenyl bromide^[32] where the deviation of the Se–Br bond from the phenyl plane is significantly reduced by Se···O interactions accompanied by an increase in the Se–Br bond length.

However, the Se–Br bond length is very close to that reported for [2-(dimethylaminomethyl)phenyl]selenium bromide.^[3d] The intermolecular distance between Se and Br(A) [3.556(9) Å] is longer than the sum of the single-bond covalent radii (2.310 Å) but considerably shorter than the sum of the van der Waals radii (3.95 Å). These intermolecular contact distances are shorter than those reported for Me₂SeBr₂ (3.604–3.630 Å).^[30]

Crystal structure of 6: The molecular structure of **6** is shown in Figure 5. Table 4 gives significant selected bond lengths and angles. **6** is isostructural with **4** and **5**. There is only one RSeI

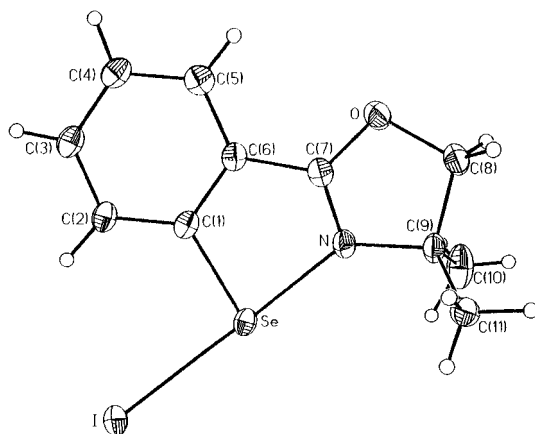


Figure 5. Crystal structure of compound **6**.

Table 4. Significant bond lengths [Å] and angles [°] for **6**.

Se–C(1)	1.945(5)	Se···N	2.133(4)
I–Se	2.7773(7)	Se···I(0A)	3.725(2)
C(1)–Se–N	80.9(2)	C(1)–Se–I	97.39(14)
N–Se–I	177.69(12)	N–Se···I(0A)	96.0(12)
I–Se···I(0A)	85.9(3)	C(1)–Se···I(0A)	171.7(3)

compound reported in the literature which has been characterized by X-ray crystallography and in this case the Se–I bond was stabilized by the sterically bulky 2,4,6-tri-*tert*-butylphenyl group.^[15] Compound **6** is the first example of a structurally characterized R–Se–I compound where the Se–I bond is strongly stabilized by Se···N nonbonding interactions. The Se···N distance, 2.133(4) Å, is slightly longer than the corresponding distances observed for **4** and **5** but much shorter than the sum of the van der Waals radii (3.5 Å). The Se–I distance 2.7773(7) Å is long compared with the sum of the single-bond covalent radii (2.50 Å). However, the elongation of the Se–I bond is relatively small compared with the chloro and bromo derivatives. It is worth mentioning that this distance is considerably greater than that observed for 2,4,6-tri-*tert*-butylphenyl (iodo)selenide, [Se–I = 2.529(1) Å]^[15] and is also longer than the Se–I bond in Passmore's cationic species containing uniconordinate iodine.^[33, 34] The C(1)–Se–I bond angle, 97.39(14)°, is comparable with the ∠C–Se–I unit reported for 2,4,6-tri-*tert*-butylphenyl (iodo)selenide [97.5(1)°]. The N···Se–I unit is nearly linear [177.69(12)°] owing to the Se···N interaction. As in **4** and **5**, weak

intermolecular interactions between I and Se of the neighboring molecule were observed. The interatomic distance between Se and I(0A) is 3.725(1) Å, which is more than the sum of the covalent radii (2.50 Å) but about 0.425 Å shorter than the van der Waals contact distance (4.15 Å). In contrast with the Se–X intramolecular bond lengths, which decrease from Cl to I, the intermolecular interaction in this compound is much stronger than for **4** and **5**. The Se–C(1) bond length 1.945(5) Å is slightly longer than that of the chloro and bromo compounds but very close to the diselenide **3**.

Crystal structure of 7: An ORTEP view of **7** is shown in Figure 6, and selected bond lengths and angles are listed in Table 5. The selenium atom is bonded to two carbon atoms [Se–C(1) 1.916(3) Å and Se–C(12) 1.966(3) Å] derived from

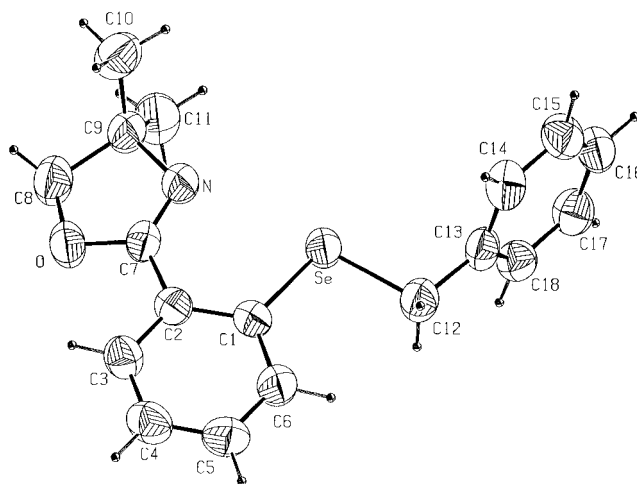


Figure 6. Crystal structure of compound **7**.

Table 5. Significant bond lengths [Å] and angles [°] for **7**.

Se···N	2.798(3)	Se–C(1)	1.916(3)
C(1)–Se–C(12)	100.19(12)	Se–C(12)	1.966(3)
C(2)–C(1)–Se	120.6(2)	C(6)–C(1)–Se	121.3(2)
C(13)–C(12)–Se	107.0(2)	C(12)–Se···N	175.4(3)

different organic substituents. The Se–C bond lengths found in **7** are similar to the Se–C(Ph) bond lengths reported for the related systems. Of particular interest in the structure is the nature of the Se···N interaction and the arrangement of Se–C(12) *trans* to the Se···N bond. The Se···N separation [2.798(3) Å] is greater than the sum of the covalent radii (1.80 Å), but significantly shorter than the sum of the van der Waals radii (3.5 Å) for these two atoms. This distance is also shorter than that reported for the related *p*-ethoxyphenyl-2-(2-pyridyl) selenide.^[35] The N···Se–C(12) bond angle 175.4° indicates that the arrangement of the N···Se–C atoms is almost linear. As can be seen from Figure 6, the Se and N atoms lie in the same plane in contrast with the observation made for the *p*-ethoxyphenyl-2-(2-pyridyl) selenide, where there is a twist about the C–C bond such that the nitrogen atom is directed away from the selenium. This planar arrangement of the atoms may be due to the formation of a

rigid, five-membered ring arising from the Se...N interactions. Although the crystal structure shows the existence of nonbonding Se...N interactions, the Se...N bond is considerably weaker compared with the halo derivatives. However, this Se...N interaction has lengthened the *trans* Se–C(12) bond. This elongation is also clear from a comparison of Se–C(1) and Se–C(12) bond lengths. The Se–C(12)(benzyl) bond is considerably longer (1.966(3) Å) than the Se–C(1)(phenyl) bond (1.916(3) Å).

The remaining interatomic contacts show no abnormal features. There is no significant intermolecular contact between Se...Se as the closest distance between the atoms is 4.882 Å, which is much greater than the sum of the van der Waals radii for these two atoms.

Crystal structure of 8: The molecular structure of **8** is shown in Figure 7, and selected bond lengths and angles are listed in Table 6. The two selenium atoms attached to the *m*-xylyl

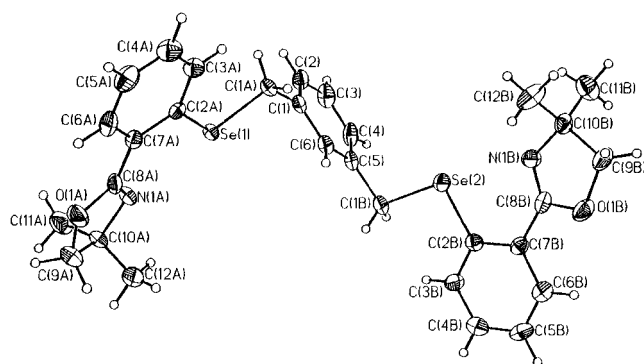


Figure 7. Crystal structure of compound **8**.

Table 6. Significant bond lengths [Å] and angles [°] for **8**.

Se(1)–C(2A)	1.920(5)	Se(1)–C(1A)	1.977(5)
Se(2)–C(2B)	1.916(6)	Se(2)–C(1B)	1.990(6)
Se(1)...N(1A)	2.793(3)	Se(2)...N(1B)	2.772(3)
C(1A)–Se(1)...N(1A)	174.5(6)	C(2A)–Se(1)...N(1A)	75.2(6)
C(1)–C(1A)–Se(1)	106.3(4)	C(3A)–C(2A)–Se(1)	121.0(4)
C(5)–C(1B)–Se(2)	103.7(4)	C(2B)–Se(2)...N(1B)	74.9(6)
C(7B)–C(2B)–Se(2)	120.7(5)	C(1B)–Se(2)...N(1B)	174.1(6)

group interact directly with the nitrogens. One of the Se...N bond lengths, 2.793(5) Å, is identical to the corresponding length in **7** while the other, 2.772(6) Å, is slightly shorter than that observed for **7**. Almost linear arrangements observed for Se(1)...N(1A)–C(1A) (174.5°) and Se(2)...N(1B)–C(1B) (174.1°) indicate the *trans* influence of the benzylic group as shown by Barton et al. for the phenyl group.^[8] The bond lengths Se(1)–C(1A)(benzyl) (1.977(5) Å) and Se(2)–C(1B)(benzyl) (1.990(6) Å) are slightly longer than for Se(1)–C(2A)(phenyl) (1.920(5) Å) and Se(2)–C(2B)(phenyl) (1.916(6) Å), like the lengthening of bonds observed for **7** and other compounds. Although aryl benzyl selenides are rare, some Re, Pd, and Pt complexes of dibenzyl diselenide are known in which the selenium acts as a normal two-electron donor.^[36] The reported Se–CH₂ bond lengths 2.018(21) and 1.987(21) Å

for the Pt^{II} complex compare well with the Se(1)–C(1A) [1.977(5) Å] and Se(2)–C(1B) [1.990(6) Å] values found in compound **8**.

Common features: The observed Se...N interatomic distance increases in the order **4** < **5** < **6** < **8** < **3** < **7**, which is completely in accordance with the experimental results obtained from ¹H NMR chemical shift values of these compounds. In all the compounds the nitrogen atom present in the five-membered heterocyclic ring interacts directly with the selenium atom to form another five-membered ring. Although the heterocycle has one oxygen donor atom, there is no indication of any intramolecular or intermolecular interaction of oxygen with the selenium. The strong Se...N interactions and the unusual stability of the compounds may arise from the fact that the lone pair of electrons present on the oxygen atom may be involved in a resonance contribution with the π systems, as shown in Figure 1.

The bond lengths for the oxazoline ring reflect certain similarities with other five-membered heterocycles containing O and N atoms such as *iso*-oxazoline^[37] and oxazolo^[38] compounds. The C(7)–O lengths for compounds **3–8** (1.313–1.366 Å) are significantly shorter than the C(8)–O bond lengths (1.438–1.474 Å), while the same is true for the C(7)–N lengths (1.259–1.303 Å) with respect to the C(9)–N bond lengths (1.465–1.492 Å). This indicates similar double-bond character in both C(7)–O and C(7)–N, as reflected in the resonance structures in Figure 1. Owing to the charged nature of the second resonance structure B, one may expect N to be a strong electron donor and O to be a poor donor. This diminishes the possibility of any intramolecular or intermolecular interaction of the oxygen atom with the selenium. The Se...N interactions in all the compounds may also be correlated with the C(7)–O distances. For compounds **4**, **5**, and **6** where the Se...N interaction is very strong, the C(7)–O bond lengths (1.313–1.332 Å) lie between C–O (1.43 Å) and C=O (1.25 Å). The same is true for the diselenide **3** and the benzylic compounds **7** and **8**. Similar correlations can be made for the C(7)–N bond lengths with the Se...N distances. The C(7)–N bond lengths are longer for the halo derivatives [1.275–1.303 Å] (shorter Se...N distances) whereas the corresponding bond lengths are shorter for the diselenides and benzylic compounds [1.239–1.265 Å] (longer Se...N distances). On the other hand, the Se–C bond lengths [1.946(5) and 1.937(5) (**3**), 1.922(3) (**4**), 1.926(4) (**5**), 1.933(97) (**6**), 1.916(3) (**7**), 1.916(6) and 1.990(6) Å (**8**)] do not show any clear correlation with the Se...N distances. However, for compounds **3**, **4**, **5**, **6**, and **7** the Se–C bond lengths are shorter than the normal Se–C single bond (1.94 Å). From these observations, it is clear that the involvement of the oxazoline ring in a resonance contribution would certainly shorten the Se...N and C(7)–O distances simultaneously.

Structural comparisons among the halides **4–6** give some additional information about the Se...N interaction (Table 7). It is observed that the deviation of the Se–X (X = Cl, Br, I) bond from the phenyl plane is significantly reduced by the Se...N interaction, accompanied by an increase in the Se–X bond length.^[35,39] The deviations of the Se–X bond

Table 7. Structural comparison of the halides **4–6**.

Compound	Se...N [Å]	Se–X [Å]	Se...X(A) [Å]	N...Se–X [°]	C–Se...X(A) [°]	C–Se...N [°]	C–Se–X [°]
4	2.052	2.482	3.476	175.1	173.7	81.38	93.68
5	2.063	2.631	3.556	176.1	172.9	80.9	95.24
6	2.133	2.777	3.725	177.7	171.7	80.9	97.39

lengths from the corresponding covalent radii sum for **4**, **5**, and **6** (0.322, 0.321, and 0.277 Å) suggest that the elongation of the Se–X bond decreases in the order Se–Cl \approx Se–Br > Se–I. The C–Se–X bond angles increase in the order **4** < **5** < **6** whereas the C–Se...N bond angles are almost equal for all three compounds. It is known that a strong Se...N interaction causes shortening of the Se...N interatomic distance and an increase in the linearity of the N...Se–X alignment.^[26] Interestingly, the X-ray study of compounds **4–6** shows that the bond angles of N...Se–X deviate from 180° as the Se...N interaction increases (N...Se–Cl, 175.06°; N...Se–Br, 176.14°; N...Se–I, 177.69°). This is probably due to the presence of intermolecular interactions between Se and X which is greatest in the case of **6**. The dimer formation observed for **4–6** is not very common in organoselenium compounds and for the first time we have observed such intermolecular interactions in divalent selenium compounds. This structural similarity with Se^{IV} compounds reasonably confirms the hypervalent nature of the N...Se–X interaction. The intermolecular interaction increases when the electronegativity of the halogen atom decreases. Very strong Se...X intermolecular interactions were found in compound **6** compared with **4** and **5**. The deviations of the Se...X interatomic distances from the corresponding covalent radii sum for **4**, **5**, and **6** (1.316, 1.246, and 1.225 Å) suggest that the strength of the intermolecular interaction decreases in the order Se...I > Se...Br > Se...Cl. These significant secondary Se...X interactions in the solid state link the discrete RSeX molecules into centrosymmetric dimers, the selenium atoms adopting distorted octahedral geometry.

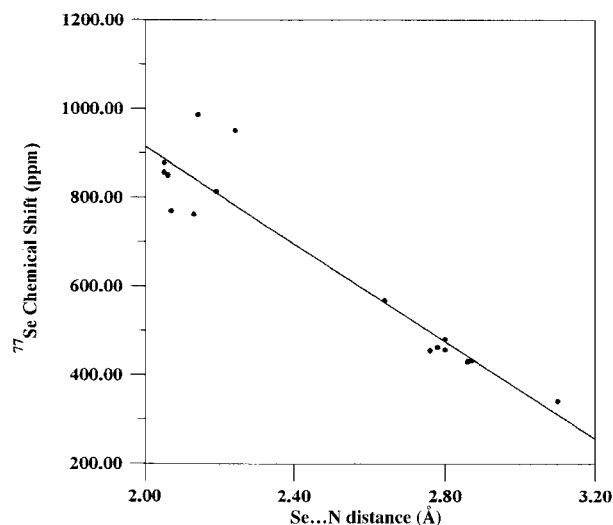
A correlation between the Se...N interaction and ⁷⁷Se NMR chemical shifts:

It has been reported that the intramolecular Se...N nonbonding interaction results in an apparent downfield shift of the ⁷⁷Se NMR^[9] signals, but no correlation was made between the strength of the Se...N or Se...O interactions and the values of the chemical shifts. However, we find that the ⁷⁷Se NMR chemical shifts generally change with the strength of the Se...N interaction, with some exceptions (Table 8 and Figure 8). Also it is not possible to correlate the results in detail as the deviations for the distances are very high. The Se...N bond lengths for the remaining compounds for which structures are not available (**9**, **10**, and **12–14**) may be roughly estimated by substituting the ⁷⁷Se chemical shift values in the linear equation derived from Figure 8. The Se...N bond lengths obtained by this method for these compounds (**9**, 3.03 Å; **10**, 3.12 Å; **12**, 3.09 Å; **13**, 3.09 Å; **14**, 3.22 Å) are consistent with the values obtained for **7**, **8**, and other related compounds.

Table 8. ⁷⁷Se NMR chemical shifts and Se... distances of compounds **3–8** and **15–24**.

Compound	Se...N distance [Å]	⁷⁷ Se (δ)	Ref.
3	2.76	454.8	this work
4	2.05	855.9	this work
5	2.06	849.5	this work
6	2.13	762.2	this work
7	2.80	420.5	this work
8	2.78	461.9	this work
15 ^[a]	2.86	430.0	[3d]
16 ^[b]	2.14	987.0	[3d]
17 ^[c]	2.87	431.9	[25]
18 ^[d]	2.19	813.4	[29]
19 ^[e]	3.10	340.8	[39a]
20 ^[f]	2.64	566.9	[11]
21 ^[g]	2.24	951.1	[39a]
22 ^[h]	2.80	456.6	[11]
23 ^[i]	2.05	877.7	[39b]
24 ^[j]	2.07	769.3	[39b]

[a] Bis[2-(dimethylaminomethyl)phenyl] diselenide. [b] [2-(dimethylaminomethyl)phenyl]selenium bromide. [c] 2,2'-Diselenobis(*N*-cyclohexylmethylbenzylamine). [d] Chloro σ -ammonioselenane. [e] Bis-(*N,N*-dimethylaminobenzylamine) selenide. [f] Bis[8-(dimethylamino)-1-naphthyl] diselenide. [g] 8-(dimethylamino)-1-naphthylselenium iodide. [h] Bis[2-(4-ethyl-2-oxazolonyl)phenyl] diselenide. [i] [2-(4-Ethyl-2-oxazolonyl)phenyl]selenenyl bromide. [j] [2-(4-Ethyl-2-oxazolonyl)phenyl]selenenyl iodide.

Figure 8. Plot of Se...N bond lengths against ⁷⁷Se NMR chemical shifts.

Conclusions

From the current results and their comparison with those of other intramolecular-stabilized, organoselenium compounds, it is apparent that the strength of the Se...N interaction depends on the nature of the nitrogen atom used as an *ortho* chelating group. The use of more rigid, planar, five-membered

heterocyclic rings with sp²-hybridized nitrogen increases the Se...N nonbonding interaction considerably and lengthens the Se...X bond (X = Se, Cl, Br, I, or CH₂–). This elongation of the Se–X bond increases the possibility of nucleophilic attack on the selenium atom. The strong Se...N interactions and the unusual stability of the compounds may arise from the resonance contribution of the lone pair of electrons present on the oxygen to the π systems. The Se...N distances also depend on the nature of the group attached to the selenium. A large downfield shift in the ¹H and ⁷⁷Se NMR spectra in compounds **4**, **5**, and **6** confirms the existence of strong Se...N nonbonding interactions even in solution. As well as the Se...N distances, the nature of X also affects the Se...X intermolecular interaction. It appears that the Se...X intermolecular interaction reduces the strength of the Se...N bond. The correlation between ⁷⁷Se chemical shifts and Se...N distances may be useful in determining the approximate strength of Se...N interactions for compounds for which structures are not available.

Experimental Section

General procedure: All reactions were carried out under nitrogen or argon with standard vacuum-line techniques. Solvents were purified by standard procedures^[40] and were freshly distilled before use. Melting points were recorded in capillary tubes and are uncorrected. ¹H, ¹³C, and ⁷⁷Se NMR spectra were obtained at 300, 75.42, and 57.22 MHz in CDCl₃ on a Varian VXR 300S spectrometer. Chemical shifts are cited with respect to SiMe₄ as internal (¹H and ¹³C) and Me₂Se (⁷⁷Se) as external standards. Elemental analyses were determined with a Carlo–Erba model 1106 elemental analyzer. Mass spectra were recorded at room temperature on a JEOL D-300 (EI/CI) mass spectrometer. Fast atom bombardment (FAB) mass spectra were recorded at room temperature on a JEOL SX 102/DA-6000 mass spectrometer/data system with xenon (6 kV, 10 mV) as the bombarding gas. The accelerating voltage was 10 kV. *m*-Nitrobenzyl alcohol was used as the matrix with cation detection. For isotopes the value given is for the most intense peak.

Synthesis of [2-(4,4-dimethyl-2-oxazoliny)phenyl]selenenyl chloride (4): To a solution of **3**^[11] (0.51 g, 1 mmol) in CCl₄ (25 mL) at room temperature was added a solution of SO₂Cl₂ (0.134 g, 1 mmol) in CCl₄. The reaction mixture was stirred for 1 h at room temperature. The resulting solution was concentrated to give a yellow, crystalline product. This was recrystallized from a methanol/hexane mixture to give pale yellow crystals of **4**. Yield: 0.25 g (85%). M.p. 186–188 °C; C₁₁H₁₂NOSeCl: calcd C 45.76, H 4.16, N 4.85; found C 45.63, H 4.12, N 4.74; ¹H NMR (CDCl₃): δ = 1.86 (s), 4.71 (s), 7.45–7.48 (t), 7.65–7.70 (t), 7.83–7.86 (d), 8.80–8.83 (d); ¹³C NMR (CDCl₃): δ = 28.50, 66.71, 85.19, 119.12, 126.46, 126.76, 129.79, 132.95, 150.73, 166.27; *m/z*: 289 [*M*⁺], 254 (100%), 200, 182, 156, 130, 103, 70, 55.

Synthesis of [2-(4,4-dimethyl-2-oxazoliny)phenyl]selenenyl bromide (5): To a cold solution of diselenide **3** (0.51 g, 1 mmol) in CCl₄ (25 mL) was added a solution of bromine (0.162 g, 1 mmol) in CCl₄. The addition was carried out dropwise over a period of 0.5 h and the mixture was allowed to come to room temperature. The solution obtained was concentrated to give a yellow, crystalline product. This was recrystallized from a chloroform/hexane mixture to give yellow crystals of **5**. Yield: 0.55 g (82.7%). M.p. 188–190 °C; C₁₁H₁₂NOSeBr: calcd C 39.65, H 3.60, N 4.21; found C 39.41, H 3.59, N 4.18; ¹H NMR (CDCl₃): δ = 1.64 (s), 4.68 (s), 7.43–7.49 (t), 7.60–7.66 (t), 7.79–7.82 (d), 8.81–8.85 (d); ¹³C NMR (CDCl₃): δ = 28.59, 66.81, 85.11, 119.35, 131.15, 131.25, 133.12, 134.50, 148.37, 165.89; *m/z*: 333 [*M*⁺], 252 (100%), 199, 181, 155, 116, 54.

Synthesis of [2-(4,4-dimethyl-2-oxazoliny)phenyl]selenenyl iodide (6): To a cold solution of diselenide **3** (0.51 g, 1 mmol) in CCl₄ (25 mL) was added a solution of iodine (0.254 g, 1 mmol) in CCl₄. The addition was carried out dropwise over a period of 1 h and the mixture was allowed to come to room temperature. The stirring was continued for an additional 2 h. The solution

obtained was concentrated to give a red, crystalline product. This was recrystallized from a chloroform/hexane mixture to give brick-red crystals of **6**. Yield: 0.64 g (84.2%). M.p. 122–124 °C; C₁₁H₁₂NOSeI: calcd C 34.76, H 3.16, N 3.69; found C 34.77, H 3.19, N 3.84; ¹H NMR (CDCl₃): δ = 1.58 (s), 4.50 (s), 7.41–7.54 (m), 7.71–7.74 (d), 8.55–8.58 (d); ¹³C NMR (CDCl₃): δ = 28.68, 67.09, 83.57, 121.22, 126.80, 127.31, 132.94, 134.62, 140.84, 164.38; *m/z*: 507 (R₂Se₂), 380 [*M*⁺], 254 (I₂), 253 (100%), 200, 184, 154, 136, 105, 55.

Synthesis of [2-(4,4-dimethyl-2-oxazoliny)phenyl]benzyl selenide (7): To a solution of **1** (0.85 mL, 5 mmol) in dry THF (75 mL) was added a 1.6 M solution of *n*-butyllithium in hexane (3.4 mL, 5.5 mmol) by means of a syringe under N₂ at 0 °C. The mixture was stirred for 2 h at this temperature to give the lithiated compound. Se powder (0.4 g, 5 mmol) was added under a brisk flow of N₂ gas. After 1 h stirring at 0 °C, 0.6 mL (5 mmol) of benzyl chloride was added with the syringe. The reaction mixture was allowed to come to room temperature and the stirring was continued for an additional 2 h. The resulting solution was evaporated to dryness then dissolved in ether, washed with water, dried over Na₂SO₄, filtered, and concentrated to give a white solid. X-ray quality crystals were obtained by recrystallization from a chloroform/hexane mixture. Yield: 0.86 g (50%). M.p. 158–160 °C; C₁₈H₁₉NOSe: calcd C 62.80, H 5.52, N 4.07; found C 62.84, H 5.69, N 3.98; ¹H NMR (CDCl₃): δ = 1.37 (s), 4.05 (s), 4.09 (s), 7.17–7.35 (m), 7.38–7.47 (m), 7.77–7.80 (d); ¹³C NMR (CDCl₃): δ = 28.83, 31.17, 68.78, 78.93, 125.02, 127.11, 127.29, 128.47, 129.60, 130.23, 131.08, 137.06, 137.49, 128.80, 161.61; *m/z*: 254 (100%), 200, 182, 156, 130, 103, 84, 70, 55.

Synthesis of α,α' -di[2-(4,4-dimethyl-2-oxazoliny)phenylselenenyl]-*m*-xylylene (8): To a solution of **1** (1.75 mL, 1.79 g, 10 mmol) in dry hexane (75 mL) was added a 1.6 M solution of *n*BuLi in hexane (6.8 mL, 11 mmol) by means of a syringe under N₂ at room temperature. This was stirred for 1 h at room temperature and allowed to settle. The solvent was removed by syringe and the white, lithiated compound was dissolved in dry ether (75 mL). The solution was cooled to 0 °C then 0.8 g (10 mmol) of selenium powder was added under a brisk flow of N₂ gas. After 2 h stirring at this temperature 1.3 g (5 mmol) of α,α' -dibromo-*m*-xylene in ether (10 mL) was added dropwise and stirring was continued for an additional 1 h at 0 °C followed by 1 h at room temperature. The resulting mixture was washed with water, dried, and evaporated to give a yellow, crystalline solid. Pure white crystals were obtained by recrystallization of the crude product from a chloroform/hexane mixture. Yield: 0.66 g (43%). M.p. 160–162 °C; C₃₀H₃₂N₂O₂Se₂: calcd C 58.97, H 5.24, N 4.59; found C 58.82, H 5.13, N 4.72; ¹H NMR (CDCl₃): δ = 1.38 (s), 4.06 (s), 4.07 (s), 7.17–7.35 (m), 7.44–7.46 (d), 7.78–7.81 (d); ¹³C NMR (CDCl₃): δ = 28.56, 30.74, 68.49, 78.64, 124.74, 127.01, 127.88, 128.23, 128.74, 129.92, 130.24, 130.82, 136.70, 137.54, 161.32.

Synthesis of α,α' -di[2-(4,4-dimethyl-2-oxazoliny)phenylselenenyl]-*o*-xylylene (9): Compound **9** was synthesized by a similar method described for the synthesis of compound **8**, with a solution of α,α' -dibromo-*o*-xylene (1.30 g, 5 mmol). Compound **9** was obtained as a white solid. Yield: 0.61 g (40%). M.p. 168–170 °C; C₃₀H₃₂N₂O₂Se₂: calcd C 58.97, H 5.24, N 4.59; found C 58.80, H 5.12, N 4.45; ¹H NMR (CDCl₃): δ = 1.37 (s), 4.05 (s), 4.24 (s), 7.16–7.46 (m), 7.77–7.80 (d); ¹³C NMR (CDCl₃): δ = 28.34, 28.94, 68.40, 77.23, 124.10, 125.37, 126.90, 127.95, 129.23, 130.37, 131.61, 135.53, 136.69, 161.44.

Synthesis of 1,3,5-tri[2-(4,4-dimethyl-2-oxazoliny)phenylselenenyl]-2,4,6-trimethylbenzene (10): 1,3,5-Bromomethyl mesitylene^[41] (1.32 g, 3.3 mmol) was added to lithium selenolate (10 mmol) in ether (30 mL) at 0 °C. The stirring was continued for 2 h at 0 °C and 3 h at room temperature. The resulting solution was washed with water. The organic layer was separated and dried over Na₂SO₄. Evaporation of the ether did not give any product. The aqueous layer was again washed twice with chloroform. The organic layer was washed twice with brine and then separated. The combined organic layers were dried over Na₂CO₃ and the solvent was evaporated to give a yellow oil. The oil was dissolved in CH₂Cl₂ and filtered through Celite. After the volume of the solution had been reduced, pentane was added. The white precipitate obtained was filtered, washed with pentane, and dried. Yield: 3.8 g (42%). M.p. 150–152 °C; C₄₅H₅₁N₃O₃Se₃: calcd C 58.82, H 5.56, N 4.58; found C 58.62, H 5.33, N 4.24; ¹H NMR (CDCl₃): δ = 1.38 (s), 2.53 (s), 4.06 (s), 4.13 (s), 7.21–7.26 (m), 7.36–7.52 (m), 7.79–7.83 (m); ¹³C NMR (CDCl₃): δ = 16.35, 27.67, 28.63, 68.59, 78.79, 124.63, 127.39, 128.31, 130.16, 130.94, 131.58, 136.26, 137.97, 161.48.

Synthesis of [2-(*N,N*-dimethylaminomethyl)phenyl]benzyl selenide (12): A stirred solution of *N,N*-dimethylbenzylamine (1.5 mL, 10 mmol) in dry

ether (75 mL) was treated dropwise by means of a syringe with a 1.6 M solution of *n*BuLi in hexane (6.8 mL, 11 mmol) under N₂ at room temperature. On stirring for 24 h at this temperature, a white slurry of the lithiated product was obtained. Selenium powder (0.78 g, 10 mmol) was added to this mixture under a brisk flow of N₂ gas, and stirring was continued for an additional 2 h at room temperature. The selenium was found to be converted after this period to the corresponding lithium areneseelenolate.^[34] A solution of 0.5 mL (5 mmol) of benzyl chloride in 10 mL of dry ether was added dropwise to the lithium selenolate at 0 °C. Stirring was continued for 2 h at 0 °C and then the reaction mixture was allowed to attain room temperature. The resulting mixture was washed with water and the aqueous layer was extracted thrice with ether. The combined organic layers were dried over Na₂SO₄, filtered, and evaporated to give a yellow oil. White crystals of the desired product were obtained by the addition of hexane and storage of the solution at 0 °C for two days. Yield: 0.15 g, (55 %). M.p. 158–160 °C; C₁₄H₁₉NSe: calcd C 54.45, H 5.39, N 3.97; found C 54.58, H 5.58, N 3.67; ¹H NMR (CDCl₃): δ = 2.18 (s), 3.41 (s), 4.03 (s), 7.12–7.26 (m), 7.45–7.48 (m).

Synthesis of α,α' -di[2-(*N,N*-dimethylaminomethyl)phenylselenenyl]-*m*-xylylene (13): Compound **13** was synthesized by a method similar to that described for the synthesis of compound **12**, with a solution of α,α' -dibromo-*m*-xylene (1.3 g, 5 mmol). Compound **13** was obtained as a yellow solid. Yield: 1.06 g (20 %). M.p. 162–164 °C; C₂₆H₃₂N₂Se₂: calcd C 58.87, H 6.04, N 5.28; found C 58.65, H 5.94, N 5.14; ¹H NMR (CDCl₃): δ = 2.17 (s), 3.41 (s), 4.09 (s), 7.16–7.31 (m), 7.48–7.51 (m).

Synthesis of 1,3,5-tri[2-(*N,N*-dimethylaminomethyl)phenylselenenyl]-2,4,6-trimethyl benzene (14): Compound **14** was synthesized by a method similar to that described for the preparation of compound **13**, with a solution of 1,3,5-bromomethyl mesitylene (1.317 g, 3.3 mmol). Compound **14** was obtained as a yellow solid. Yield: 3.2 g (40 %). M.p. 178–180 °C; C₃₀H₃₅N₃Se₃: calcd C 58.65, H 6.39, N 5.26; found C 58.43, H 6.25, N 5.16; ¹H NMR (CDCl₃): δ = 2.20 (s), 2.44 (s), 3.47 (s), 4.14 (s), 7.18–7.33 (m), 7.53–7.56 (m); ¹³C NMR (CDCl₃): δ = 16.19, 28.08, 44.97, 45.33, 64.47, 125.97, 127.83, 129.18, 129.76, 139.39, 132.53, 132.53, 135.13, 135.33, 140.24.

X-ray crystallography: The diffraction measurements for compounds **3**, **4**, **5**, **6**, **7**, and **8** were performed at room temperature (293 K) on a Siemens R3m/V diffractometer with graphite-monochromated MoK α radiation (λ = 0.7170 Å). The structures were determined by routine heavy-atom (with SHELXS-86^[42]) and Fourier methods and refined by full-matrix least squares with the non-hydrogen atoms anisotropic and hydrogens with fixed isotropic thermal parameters of 0.07 Å² by means of the SHELXL-93 program.^[43] The hydrogens were partially located from difference electron-density maps and the rest were fixed at predetermined positions. Scattering factors were from common sources.^[44] Some details of the data collection and refinement are given in Tables 9 and 10.

Crystallographic data (excluding structure factors) for the structures reported in this paper have been deposited with the Cambridge Crystallographic Data Centre as supplementary publications nos. CCDC-102795 (**4**), 102796 (**5**), 102797 (**6**), 102798 (**7**), and 102799 (**8**). Copies of the data can be obtained free of charge on application to CCDC, 12 Union Road, Cambridge CB21EZ, UK (fax: (+44) 1223-336-033; e-mail: deposit@ccdc.cam.ac.uk).

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Table 9. Crystal data and structure refinement for **4**, **5**, and **6**.

	4	5	6
empirical formula	C ₁₁ H ₁₂ ClNOSe	C ₁₁ H ₁₂ BrNOSe	C ₁₁ H ₁₂ INOSe
<i>M_r</i>	288.63	333.09	380.08
crystal system	monoclinic	monoclinic	monoclinic
space group	<i>P</i> 2 ₁ / <i>n</i>	<i>P</i> 2 ₁ / <i>n</i>	<i>P</i> 2 ₁ / <i>n</i>
<i>a</i> [Å]	11.195(2)	11.412(2)	11.7210(10)
<i>b</i> [Å]	9.3192(13)	9.436(2)	9.6820(10)
<i>c</i> [Å]	12.278(2)	12.312(2)	12.5000(10)
α [°]	90	90	90
β [°]	114.158(8)	114.771(9)	115.160
γ [°]	90	90	90
<i>V</i> [Å ³]	1168.7(3)	1203.8(3)	1283.9(2)
<i>Z</i>	4	4	4
ρ_{calcd} [Mg m ⁻³]	1.640	1.838	1.966
<i>T</i> [K]	293(2)	293(2)	293(2)
λ [Å]	0.71073	0.71073	0.71073
abs coeff [mm ⁻¹]	3.414	6.412	5.304
obsd refls [<i>I</i> > 2 σ]	2648	2606	2544
final <i>R</i> (<i>F</i>) [<i>I</i> > 2 σ] ^[a]	0.0312	0.0392	0.0347
<i>wR</i> (<i>F</i> ²) indices [<i>I</i> > 2 σ]	0.0697	0.0834	0.0908
data/restraints/parameters	2647/0/185	2604/0/185	2543/0/185
goodness of fit on <i>F</i> ²	1.055	1.027	1.059

[a] Definitions: $R(F_o) = \sum ||F_o| - |F_c|| / \sum |F_o|$ and $wR(F_o^2) = \{\sum [w(F_o^2 - F_c^2)^2] / \sum [w(F_o^2)]^{1/2}\}$. Additional crystallographic details are available from CCDC.

Table 10. Crystal data and structure refinement for **7** and **8**.

	7	8
empirical formula	C ₁₈ H ₁₉ NOSe	C ₃₀ H ₃₂ N ₂ O ₂ Se ₂
<i>M_r</i>	344.30	610.50
crystal system	triclinic	monoclinic
space group	<i>P</i> 1	<i>P</i> 2 ₁ / <i>n</i>
<i>a</i> [Å]	8.0699(8)	15.190(2)
<i>b</i> [Å]	9.1119(9)	11.397(2)
<i>c</i> [Å]	12.2642(12)	16.614(2)
α [°]	79.942(5)	90
β [°]	71.005(5)	95.08(2)
γ [°]	68.530(6)	90
<i>V</i> [Å ³]	791.96(14)	2864.9(7)
<i>Z</i>	2	4
ρ_{calcd} [Mg m ⁻³]	1.444	1.415
<i>T</i> [K]	293(2)	293(2)
λ [Å]	0.71073	0.71073
abs coeff [mm ⁻¹]	2.369	2.609
obsd refls [<i>I</i> > 2 σ]	3319	5565
final <i>R</i> (<i>F</i>) [<i>I</i> > 2 σ] ^[a]	0.0355	0.0557
<i>wR</i> (<i>F</i> ²) indices [<i>I</i> > 2 σ]	0.0639	0.0946
data/restraints/parameters	3319/0/267	5562/0/361
goodness of fit on <i>F</i> ²	1.174	1.020

[a] Definitions: $R(F_o) = \sum ||F_o| - |F_c|| / \sum |F_o|$ and $wR(F_o^2) = \{\sum [w(F_o^2 - F_c^2)^2] / \sum [w(F_o^2)]^{1/2}\}$. Additional crystallographic details are available from CCDC.

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