Synthesis, Structural Characterization and Fluorescence Properties of Organoselenium Compounds Bearing a Ligand Containing Both Bulky and Nonbonding Groups − The First Observation of Both Intramolecular Se···N and Se···O Interactions in a Diselenide Structure

Karuppasamy Kandasamy,[a] Sangit Kumar,[a] Harkesh B. Singh,*[a] Ray J. Butcher,[b] and K. Travis Holman[c]

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The synthesis of bis[3-(4,5-dihydro-4,4-dimethyl-1,3-oxazol-2-yl)-4-(3,5-dimethylphenyl)-2-naphthyl] diselenide, R_2Se_2 (**4**), was achieved by a facile ortholithiation route. Further reaction of the diselenide with a stoichiometric amount of SO_2Cl_2 or Br_2 afforded the corresponding selenenyl halides RSeX [X = Cl (**5**), X = Br (**6**)]. The novel selenenyl iodide RSeI (**7**), in which the selenium and iodine are covalently bonded to each other, was obtained by treatment of the diselenide with an equimolar amount of iodine. The stable aryl benzyl selenide **8** was prepared by the reaction of benzyl chloride with lithium areneselenolate (**3**) at low temperature. Surprisingly, the reaction of the diselenide with 1,2-dibromo-*o*-xylene gave the selenenyl bromide (**6**) instead of the arylselenium derivative **9**. Elemental analysis, multinuclear (^{1}H, ^{13}C, ^{77}Se) NMR spectroscopic and mass spectrometric techniques were used for the identification of products. Compounds **4**, **6**, **7**, and **8** were also characterized by single-crystal X-ray diffraction studies.

Introduction

In recent years organoselenium chemistry has been receiving much attention from the whole chemical community because of its potential applications in various fields. Selenium reagents have been extensively used in a variety of organic reactions.[1] Other major applications are: i) ligand chemistry,[2] ii) precursors for the preparation of thin films in metal-organic chemical vapor deposition (MOCVD),[3] and iii) biochemistry.[4] Nevertheless, organoselenium compounds are known to be very unstable, highly reactive and very difficult to synthesize. Recent studies show that the use of sterically more hindered groups and intramolecularly coordinating groups has been successful in synthesizing some stable organoselenium compounds. Arnold et al.[5] and Bochmann et al.[6] have used sterically more hindered groups to stabilize unstable organoselenium compounds. Intramolecular Se···X (X = H,[7] S,[8] O,[9] F,[10] N,[4i,11] Cl and Br[10b,12]) interactions have also been successfully used for the same purpose. Ramasubbu et al.,[13] Goldstein et al.,[14] and Barton et al.[15] have analyzed the nature of the intramolecular interactions, and the electronic structure around the selenium atom has been interpreted in terms of a three center, four electron X···Se−R bond (hypervalent bond). These interactions are also expected to be responsible for the specific redox reactivity of organoselenium compounds[16] as well as stabilization of selenenic acid, the key intermediate in the glutathione peroxidase catalytic cycle.[4]

Although intramolecular coordination and steric effects have been employed individually for the synthesis of stable organoselenium compounds, to the best of our knowledge there are no reports of their combined use for the stabilisation of organoselenium compounds. The use of (4,4-dimethyl-2-phenyl)oxazoline for the preparation of some novel organoselenium compounds has been reported recently by our group.[11d] Metal thiolates[17] and selenolates[2k] incorporating the same substrate have also been synthesized and characterized. In zinc thiolate and selenolate complexes, chirality was observed as a result of the diastereotopic methylene protons of the oxazoline ring, which arises from the strong "hard-hard" interactions between the zinc and the imine nitrogen atoms. However, attempts to

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[a] Department of Chemistry, Indian Institute of Technology, Bombay,
Powai, Mumbai 400 076, India
Fax: (internat.) + 91-22/2572-3480
E-mail: chhbsia@chem.iitb.ac.in
[b] Department of Chemistry, Howard University,
Washington, DC 20059, USA
Fax: (internat.) + 1-202-806-5442
E-mail: rbutcher@fac.howard.edu
[c] Department of Chemistry, Georgetown University,
Washington, DC 20057, USA
Fax: (internat.) + 1-202-687-6209
E-mail: kth7@georgetown.edu

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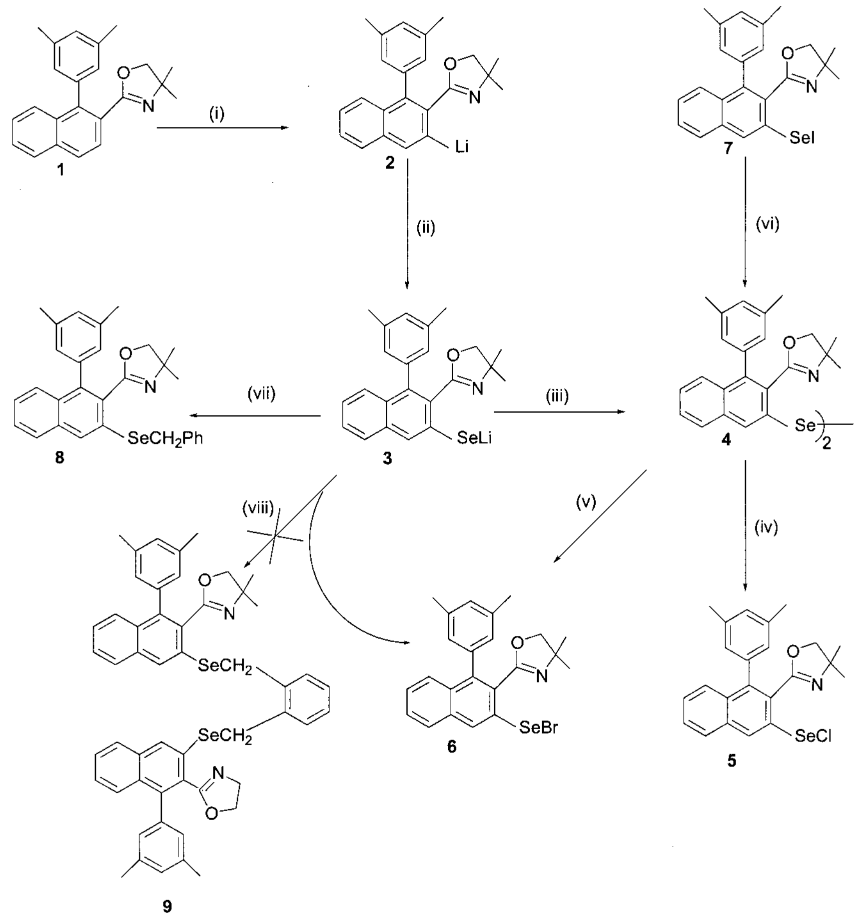
obtain crystals of group 12 tellurolates[18] were unsuccessful due to the facile decomposition of the complexes in common solvents. In this context, we thought it worthwhile to use a ligand that can induce both steric and intramolecular coordination effects together as it could provide greater stability than ligands having either an *o*-chelating group or a sterically more demanding group. This would also provide an opportunity to study Se···N interactions in the presence of sterically more demanding group.

We report here the synthesis and characterization of some novel organoselenium complexes of 2-[1-(3,5-dimethylphenyl)-2-naphthyl]-4,5-dihydro-4,4-dimethyl-1,3-oxazole. This substrate has been synthesized as one of the intermediates in the preparation of mevanolactones, which are used as inhibitors in cholesterol biosynthesis.[19] A comparison of structural and spectroscopic properties with similar compounds derived from the sterically less hindered 4,4-dimethyl-2-phenyloxazoline and other ligands is also described.

Results and Discussion

Synthesis

The synthesis of the synthetically important diselenide **4** was achieved by an ortholithiation route. The lithium areneselenolate **3** was prepared by the direct metalation of 2-[1-(3,5-dimethylphenyl)-2-naphthyl]-4,5-dihydro-4,4-dimethyl-1,3-oxazole (**1**) with a 1.6 M solution of *n*BuLi in hexane followed by the addition of finely ground selenium powder. Oxidative work up gave the desired diselenide. Treatment of the diselenide with sulfuryl chloride gave the stable selenenyl chloride **5**. The stable bromo derivative **6** was obtained as a yellow crystalline solid by the reaction of diselenide with a stoichiometric amount of bromine. Isolation of the stable binary compounds containing selenium and iodine was difficult because of their similar electronegativity and their tendency to form charge-transfer adducts.[20] Although isolation has been possible using more hindered groups, like the 2,4,6-tri-*tert*-butylphenyl group,[21] a slight



i). n-BuLi, Et$_2$O, 0^{o}C, ii) Se^o, Et$_2$O, 0^{o}C iii). [O]/H$_2$O, iv) SO$_2$Cl$_2$, CCl$_4$, 0^{o}C, v). Br$_2$, CCl$_4$, 0^{o}C, (vi) I$_2$, CCl$_4$, 0^{o}C, vii) PhCH$_2$Cl, (viii)1, 2 - dibromo-o-xylene, 0^{o}C

Scheme 1. Synthetic route for the synthesis of organoselenium derivatives reduction of their steric bulkiness again led to the formation of the charge-transfer adduct.[22] However, our group has succeeded in isolating stable binary compounds containing selenium and iodine using ligands such as 4,4-dimethyl-2-phenyl-1,3-oxazoline,[11d] *N*,*N*-dimethylbenzylamine,[11e] and *N*,*N*-dimethylnaphthylamine.[11c] Here also, the reaction of the diselenide with stoichiometric amounts of iodine led to the formation of the novel mono-iodide **7**. This consistent isolation of stable Se−I bonded compounds regardless of bulkiness proves that the intramolecular approach is a more effective method for the isolation of unstable compounds than the steric approach. In general, aryl benzyl and allyl aryl selenides are unstable and decompose readily to give coupled hydrocarbon products and free selenium.[23] Treatment of the lithium areneselenolate **3** with equimolar amounts of benzyl chloride gave the stable benzylselenium derivative **8**. All these reactions are shown in Scheme 1.

The treatment of α,α-dibromo-*o*-xylene with the lithium areneselenolate **3** gave, unexpectedly, the selenenyl bromide **6** instead of the expected compound **9**. The reaction of Se(dtc)$_2$ with the lithiated product **2** was expected to give a stable symmetrical selenide. The yellow-colored product formed in this reaction decomposed immediately to give the starting material. It is worth mentioning that the reaction of 4,4-dimethyl-2-phenyl-1,3-oxazoline with Se(dtc)$_2$ afforded the expected bis(4,4-dimethyl-2-phenyl-1,3-oxazolin-2-yl) selenide.[24] Hence, the decomposition may be due to the steric crowding around the selenium atom. All attempts to synthesize a stable bis{2-[1-(3,5-dimethylphenyl)-2-naphthyl]-4,5-dihydro-4,4-dimethyl-1,3-oxazol-2-yl} selenide, lithium selenolate and selenol were unsuccessful.

Spectroscopic Studies

The ^{1}H NMR spectra of the diselenide **4** and aryl benzyl selenide **8** are not particularly informative as the peaks are only shifted slightly downfield (ca. 0.09 ppm) from those in the free ligand **1**, thus indicating the presence of a weak Se···N interaction. However, much larger downfield shifts (ca. 0.7 ppm for the methylene proton and ca. 0.4 ppm for the methyl protons) were observed for the selenenyl halides **5**, **6**, and **8**. This indicates a strong Se···N interaction. These ^{1}H NMR chemical shifts are in good agreement with those in other intramolecularly stabilized organoselenium compounds.[11c−11e]

The ^{77}Se NMR chemical shifts are quite informative about the Se···N nonbonding interactions. The ^{77}Se NMR spectrum of **4** exhibits a single peak at $\delta = 450$ ppm, which is more downfield shifted than systems having sp^3 nitrogen atoms.[11c,11e] However, it is close to the diselenide of 4,4-dimethyl-2-phenyl-1,3-oxazoline.[11d] Interestingly, the crystal structure of the diselenide reveals that only one of the nitrogen atoms interacts with the Se atom, with the other being much further away (vide infra). The ^{77}Se NMR chemical shift of compound **8** lies upfield ($\delta = 351$ ppm) from that of the corresponding diselenide (**4**; $\delta = 450$ ppm). This may be due to the presence of the benzyl group, which cannot accept electron density from the selenium; the Se···N interaction may also be very weak. The crystal structure of **8** confirmed this very weak Se···N interaction (vide infra). The ^{77}Se NMR chemical shifts of compounds **5**, **6**, and **7** are very close to each other and downfield of the diselenide. This shows that their Se···N interactions are almost equal and stronger than Se···N interaction of **4**. This is also confirmed by the crystal structures of **6** and **7** (vide infra).

In the IR spectra, the $\nu_{C=N}$ vibrations for compounds **4**−**8** are found in the range 1670−1760 cm^{-1} and are shifted by 20−100 cm^{-1} to higher frequency relative to the free ligand, indicating that the nitrogen of the oxazoline ring is coordinated to the selenium atom. These shifts to higher frequencies may be due to the presence of negative hyperconjugation between the selenium and the nitrogen atom. The $\nu_{C=N}$ frequencies of compounds **5** and **6** are observed at higher frequencies than compounds **4** and **8**, indicating the stronger coordination of nitrogen in the selenenyl halides than in the diselenide or benzyl selenide.

Compounds **4**, **6**, **7**, and **8** exhibit similar absorption spectra, with a strong peak in the 280−310 nm region and an absorption maximum at 295 nm due to the ligand core. Fluorescence emission spectra for compounds **4**, **5**, **6**, **8**, and free ligand **1** were recorded to probe their fluorescence emission properties in methanol at an excitation wavelength of 285 nm. The quantum yield of fluorescence emission was determined with naphthalene ($\Phi_f = 0.23$) as a standard.[25] From the quantum yield of the fluorescence emission of selenium derivatives **4** ($\Phi_f = 0.038$), **5** ($\Phi_f = 0.018$), **6** ($\Phi_f = 0.021$), and **8** ($\Phi_f = 0.043$) compared to the fluorescence emission of free ligand **1** ($\Phi_f = 0.067$) it is clear that the fluorescence emissions are quenched in the selenium compounds compared to the ligand **1** due to the substitution of heavy metal atoms.[26]

Mass spectra were recorded for compounds **4**−**6**, and **8** to identify the constitution of the product under mass spectrometric conditions. The presence of seven isotopes of selenium leads to a highly characteristic group of selenium fragments. Molecular ion peaks were observed in low intensities for all compounds. In all cases except **5**, the base peaks observed at $m/z = 402-412$ with high intensity can be assigned to RSe$^+$ fragments. This strongly suggests a weakening of the Se−X (X = SeR, Br, CH$_2$Ph) bond *trans* to the Se···N fragment.

X-ray Crystallographic Studies

The significant bond lengths and bond angles of compounds **4**, **6**, **7**, and **8** are listed in Table 1.

Molecular Structure of 4

The X-ray crystal structure of **4** is shown in Figure 1. The coordination geometry around the selenium atom is distorted T-shaped with each selenium atom bonded to selenium, carbon and a nitrogen/oxygen atom. The most interesting feature of the structure is the existence of both Se···N and Se···O interactions between selenium and nitrogen/oxygen in the same molecule. This is the first structure, to the best of our knowledge, to be reported where both intramolecular Se···N and Se···O interactions exist in the same mol-

Table 1. Important bond lengths (Å) and bond angles (°) for **4**, **6**, **7**, and **8**

Compound **4**			
Se(1A)···N(1A)	2.976(8)	Se(1B) ···O(1B)	2.9815(5)
Se(1A)−Se(1B)	2.3216(15)	N(1A)···Se(1A)−Se(1B)	173.88(17)
O(1B) ···Se(1B)−Se(1A)	152.28(2)	C(24C)−Se(1C)−N(1C)	164.3(2)
N(1B) ···Se(1B)−Se(1A)	118.28(12)	C(1A)−Se(1A)−Se(1B)	101.9(3)
C(1B)−Se(1B)−Se(1A)	101.5(3)		
Compound **6**		Compound **7**	
Se···N	2.052(3)	Se···N	2.059(5)
Se−Br	2.6485(7)	Se−I	2.8297(8)
O−C(11)	1.353(5)	O−C(11)	1.337(7)
N−C(11)	1.288(5)	N−C(11)	1.289(7)
N···Se−Br	175.15(10)	N···Se−I	175.26(14)
C(1)−Se−Br	95.91(12)	C(1)−Se−I	97.51(15)
C(1)−Se···N	81.03(15)	C(1)−Se···N	80.8(2)
Compound **8**			
Se(1A)−C(1A)	1.916(5)	Se(1A)−C(24A)	1.979(7)
Se(1B)−C(1B)	1.903(6)	Se(1B)−C(24B)	1.952(7)
Se(1C)−C(24C)	1.911(7)	Se(1C)−C(1C)	1.918(5)
Se(1D)−C(1D)	1.935(5)	Se(1D)−C(24D)	1.944(7)
C(1A)−Se(1A)−C(24A)	98.0(2)	C(1B)−Se(1B)−C(24B)	98.4(3)
C(24C)−Se(1C)−C(1C)	98.1(3)	C(1D)−Se(1D)−C(24D)	98.0(2)
C(1A)−C(10A)−C(11A)−N(1A)	−72.6(7)	C(1A)−C(10A)−C(11A)−O(1A)	106.7(6)
C(1B)−C(10B)−C(11B)−N(1B)	73.1(8)	C(1B)−C(10B)−C(11B)−O(1B)	104.9(6)
C(1C)−C(10C)−C(11C)−N(1C)	−77.8(7)	C(1C)−C(10C)−C(11C)−O(1C)	102.6(6)
C(1D)−C(10D)−C(11D)−N(1D)	75.2(7)	C(1D)−C(10D)−C(11D)−O(1D)	104.9(6)

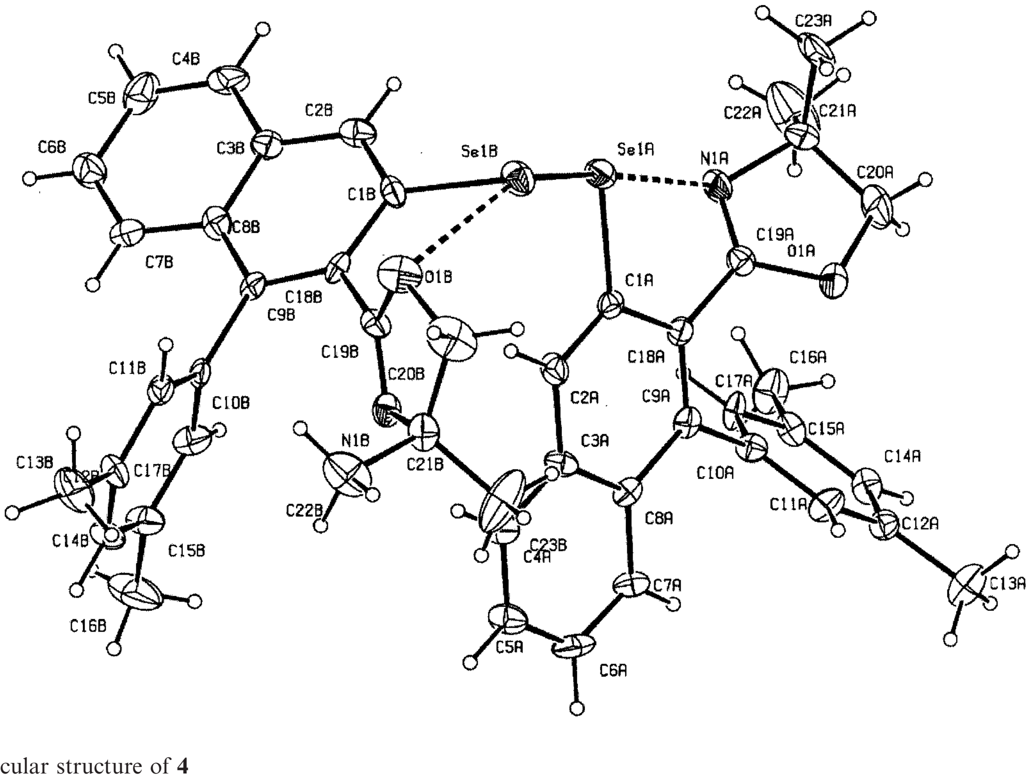


Figure 1. Molecular structure of **4**

ecule. Several structures of selenium compounds incorporating 4,4-dimethyl-2-phenyloxazoline,[2k,4i,17,18,24,27] have been reported by our group. In all cases only Se···N interactions were observed. Thus, the unusual observation of an intramolecular Se···O interaction in the structure of **4** may be explained by the orientation of the oxazoline rings.

These rings are twisted about the C(18)−C(19) axis in opposite orientations such that in one oxazoline ring the nitrogen atom is directed towards the selenium [C(1A)−C(18A)−C(19A)−N(1A) = −48.27(14)° vs. C(1A)−C(18A)−C(19A)−O(1A) = 131.72(8)°], whereas in the other ring the oxygen atom is directed towards the selenium [C(1A)−C(18A)−C(19A)−O(1A) = 53.69(12)° vs. C(1A)−C(18A)−C(19A)−N(1A) = −127.58(10)°]. The orientation of the oxazoline rings may be due to the influence of steric crowding imposed by the sterically bulkier substituents present in the system. The Se(1A)···N(1A) [2.976(8) Å] and Se(1B)···O(1B) [2.9815 Å)] distances are similar to the respective distances in other related diselenides.[4i,28] The observed Se−Se distance [2.3216(16) Å] is also shorter than in bis(4,4-dimethyl-2-phenyl-1,3-oxazolin-2-yl) diselenide [2.354(8) Å],[11d] bis{2-[(dimethylamino)methyl]-phenyl} diselenide [2.357(1) Å][11e] and bis[2-(dimethylamino)naphthyl] diselenide[11c] [2.383(2) Å]. Another interesting feature in this structure is the "*cisoid*" conformation of the diselenide. Sandman et al.[29] have reported the crystal structures of two conformational polymorphs of bis(2-naphthyl) ditelluride. The "*cisoid*" conformations have a C−Se−Se−C torsion angle of less than 90° and the "*transoid*" conformations have a C−Se−Se−C torsion angle greater than 90°. In the case of **4** the C(1A)−Se(1A)−Se(1B)−C(1B) torsion angle is 81.42° and thus has a "*cisoid*" conformation. From the unusual intramolecular Se···N and Se···O interactions, the shorter Se−Se distance, and the "*cisoid*" conformation it may be concluded that the Se−Se and Se···N bond lengths are lengthened to minimize the steric crowding imposed by the sterically more demanding group present in this system. There are no significant intermolecular Se···Se contacts. The shortest intermolecular Se···Se distance [8.618 Å] is much longer than the sum of the van der Waals radii (3.8 Å). However, intermolecular Se···H [Se1A···H13AA: 3.1096 Å; Se1A···H2BA: 3.2678 Å; Se1B···H2AA: 2.7981 Å; Se1B···H13BB: 2.8697 Å] contacts exist that are much shorter than the sum of the van der Waals radii (3.35 Å). These short Se···H contacts may be a result of optimized dense packing of the molecules.

Molecular Structure of ***6***

An ORTEP view of **6** is shown in Figure 2. The geometry around Se is T-shaped and the methyl groups attached to the oxazoline are disordered. The strong nonbonded Se···N interaction [2.052(3) Å] is very close to the corresponding distance in [2-(4,4-dimethyl-1,3-oxazolin-2-yl)phenyl]selenium bromide [2.063(3) Å][11d] and shorter than in {2-[(dimethylamino)methyl]phenyl}selenium bromide [2.143(6) Å].[11e] The Se−Br bond length [2.6485(7) Å] is longer than the sum of the single-bond covalent radii of Se and Br (2.31 Å). The lengthening of the Se−Br bond length can be attri-

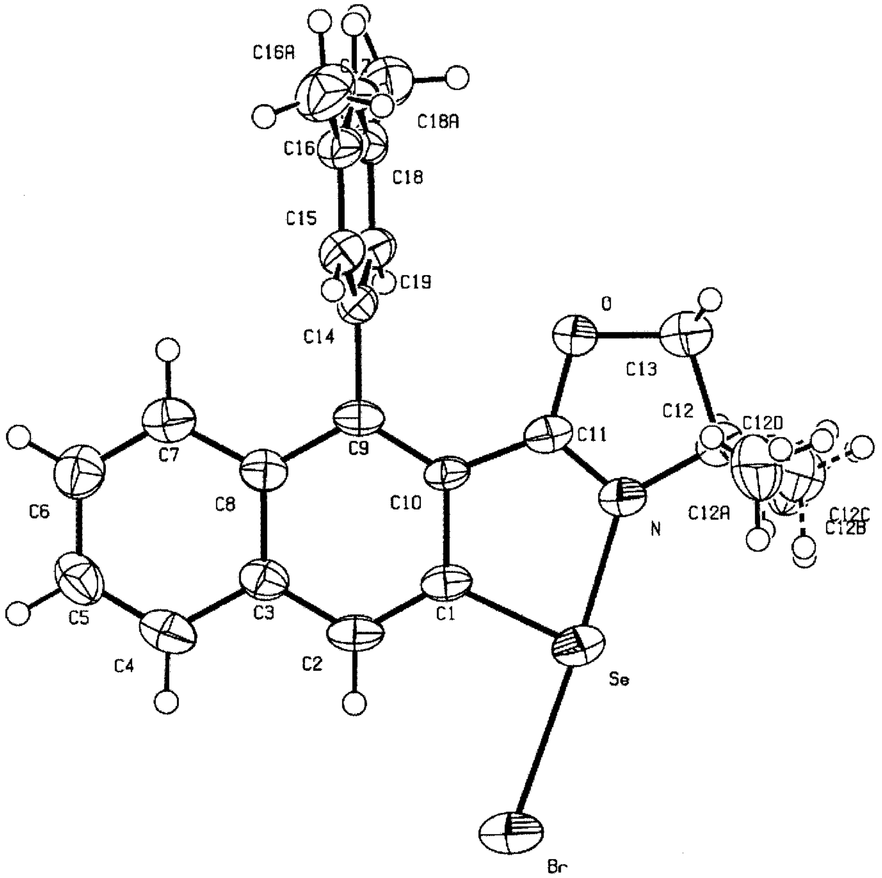


Figure 2. Molecular structure of **6**

buted to the strong *trans* influence of the Se···N interaction. A similar observation has been made for the molecular structure of 2-formylbenzeneselenenyl bromide.[30] The Se−Br bond length in **6** [2.6485(7) Å] is also similar to the reported values for [2-(4,4-dimethyl-1,3-oxazolin-2-yl)phenyl]selenium bromide [2.631(9) Å] and {2-[(dimethylamino)methyl]phenyl}selenium bromide [2.634(1) Å]. The Se···N−Br angle [175.16 (10)°] is close to linear. From the C(1)−Se−Br [95.91(12)°] and C(1)−Se···N [81.03(15)°] bond angles the coordination around selenium can be regarded as trigonal bipyramidal if the lone pairs are taken into account. However, the packing pattern of this structure is significantly different from the other intramolecularly stabilized organoselenium bromides, including [2-(4,4-dimethyl-2-phenyloxazolinyl)phenyl]selenium bromide. In all the organoselenium bromides the formation of weak dimers by intermolecular interactions between selenium and bromine were observed.[11c−11e,31] However, in the case of **6** such intermolecular Se···Br interactions are absent. The shortest intermolecular Se···Br contact [4.8914 Å] is greater than the sum of the van der Waals radii (3.9 Å). The absence of intermolecular Se···Br interactions clearly suggests that the sterically more demanding group present in this system prevents the formation of weak dimers and thus confirms the formation of a truly monomeric selenium bromide. Intermolecular Br···H (Br···H2A: 2.7190 Å; Br···H19Aa: 3.1953 Å; Br···H4Ab: 3.1463 Å; Br···H5Ab: 3.0838 Å) and Se···H12C (3.1405 Å) contacts are observed in the packing diagram. The Br···H and Se···H distances are shorter than the sum of their van der Waals radii, at 3.45 Å and 3.35 Å, respectively. The short Se···H contacts may be a result of optimized dense packing of molecules as for the above structure.

Molecular Structure of 7

The molecular structure of **7** is given in Figure 3. This is isostructural with **6**. In this structure the methyl groups attached to the oxazoline rings are disordered. The observed intramolecular Se···N distance [2.059(5) Å] is considerably shorter than the corresponding distances in [2-(4,4-dimethyl-2-oxazoline)phenyl]selenium iodide [2.133(4) Å],[11d] and [8-(dimethylamino)-1-naphthyl]selenium iodide [2.242(5) Å],[11c] whereas the Se−I distance [2.8297(8) Å] is considerably longer than the corresponding distance in [2-(4,4-dimethyl-1,3-oxazolin-2-yl)phenyl]selenium iodide [2.7773(7) Å] and [8-(dimethylamino)-1-naphthyl]selenium iodide [2.742(9) Å]. The Se−I distance is also longer than in 2,4,6-tri-*tert*-butylphenyl iodo selenide [2.529(1) Å].[21] The elongation of the Se−I bond length may be attributed to the presence of a shorter (strong) Se···N interaction *trans* to the Se−I fragment. The N···Se−I bond angle

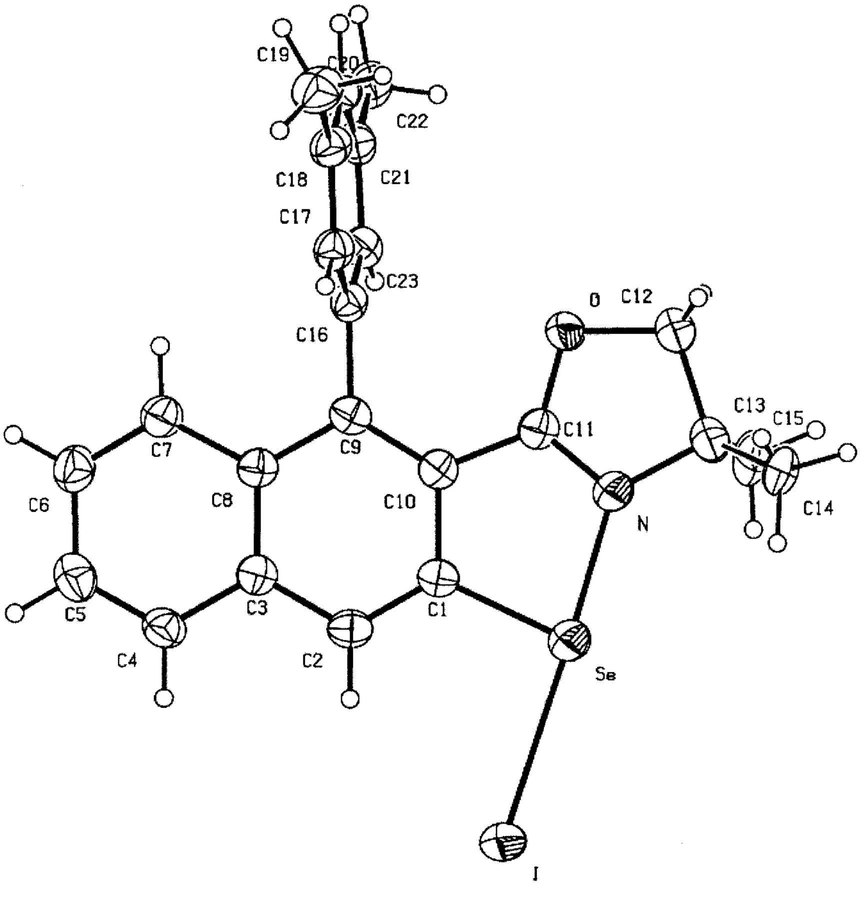


Figure 3. Molecular structure of **7**

[175.26(14)°] is close to linear. In the packing diagram of **7** the shortest intermolecular contact between the selenium and iodine is 4.811 Å, about 0.8 Å greater than the sum of the van der Waals radii (4.02 Å). Intermolecular Se···H and Se···H contacts are also observed here that are shorter than the sum of the van der Waals radii, which may be due to the optimized dense packing of the molecules.

Molecular Structure of 8

The molecular structure of **8** is shown in Figure 4 as an ORTEP view. This compound crystallizes in the monoclinic system with four symmetry-independent molecules in the asymmetric unit cell. The geometry around the selenium atom is V-shaped. The selenium atom is bonded to two carbon atoms derived from two different organic substituents. It is worth noting that the C(1)−Se(1) [C(1A)−Se(1A): 1.916(5) Å; C(1B)−Se(1B): 1.903(6) Å; C(1C)−Se(1C): 1.918(5) Å; C(1D)−Se(1D): 1.935(5) Å] and C(24)−Se(1) [C(24A)−Se(1A): 1.979(7) Å; C(24B)−Se(1B): 1.952(7) Å; C(24C)−Se(1C): 1.911(7) Å; C(1D)−Se(1D): 1.944(7) Å] bond lengths, and the C(1)−Se(1)−C(24) [C(1A)−Se(1A)−C(24A): 98.0(2)°; C(1B)−Se(1B)−C(24B): 98.4(3)°; C(1C)−Se(1C)−C(24C): 98.1(3)°; C(1D)−Se(1D)−C(24D): 98.0(2)°] bond angle are significantly different for all four independent molecules. The Se−C(Ph) and Se−CH_2Ph bond lengths are in good agreement with the corresponding distances reported for the related systems.[11d,32] One of the interesting features is the longer Se−CH_2Ph [Se(1A)−C(24A): 1.979(7) Å] distance compared to that in the sterically less hindered benzyl 2-(4,4-dimethyl-1,3-oxazolin-2-yl)phenyl selenide [1.966(3) Å], even though the intramolecular Se···N interaction (3.3842 Å) was found to be much weaker than in the latter case [2.798(3) Å]. The lengthening of the Se−CH_2Ph distance even in the presence of a weak Se···N interaction suggests that the sterically more demanding group present in the system plays an important role. The very weak Se···N interaction may be a result of the perpendicular orientation of the oxazoline ring, which is twisted about the C(10)−C(11) bond axis such that the nitrogen atom is slightly away from the selenium. Figure 4 shows that Se and N atoms lie in a different plane, in contrast to the benzyl (4,4-dimethyl-1,3-oxazolin-2-yl)phenyl selenide where both the selenium and nitrogen are in same plane.

Conclusion

Novel organoselenium compounds, including a diselenide, with both intramolecular Se···N and Se···O interactions, incorporating a ligand with steric and intramolecularly coordinating groups, have been prepared and characterized. From the current results and their comparison with intramolecularly stabilized organoselenium compounds derived from sterically less-hindered ligands, it is apparent that the strength of the Se···N interaction also depends on the nature of the substituents (steric groups) present in the system, in addition to the nature of the nitrogen atom used as an *ortho* chelating group and the electronegativity of the group attached to the selenium atom. The Se···N nonbonding interactions are considerably stronger than in organoselenium

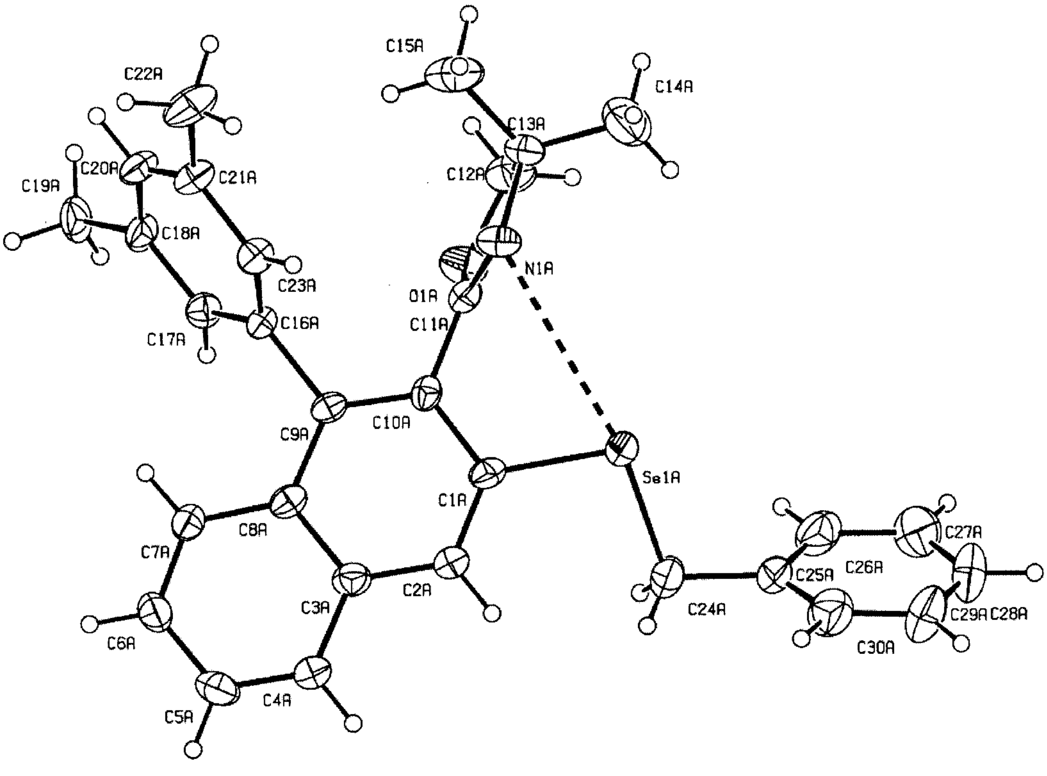


Figure 4. Molecular structure of **8**

compounds derived from the sterically less-hindered ligands. The Se···N nonbonding interactions lengthen the Se···X bond (X = −Se, Br, I, or CH_2) and enhance the possibility of nucleophilic attack at the selenium atom. The intermolecular Se···X (X = Cl, Br, I) interactions generally observed in the other reported organoselenium halides are absent, possibly due to the presence of the sterically more-demanding group. Thus, selenium halides derived from this substrate can be considered as true monomers in the solid state. Although the intermolecular Se···X interactions of the organoselenium halides described here are not within the sum of the van der Waals radii, the intermolecular Se···X contacts decrease (strong interaction) as the size of the halogen atom increases. This may be attributed to the decrease of ligand-ligand repulsions (steric repulsions) as the size of the atom increases.

Experimental Section

General: All reactions were carried out in an inert atmosphere using nitrogen or argon with standard vacuum-line techniques. All solvents were purified by following the literature method and freshly distilled prior to use.[33] 2-[1-(3,5-Dimethylphenyl)-2-naphthyl]-4,5-dihydro-4,4-dimethyloxazole (Aldrich) and *n*-butyllithium (E. Merck) were reagent grade and used as received. $Se(dtc)_2$ was prepared by a reported procedure.[34] Melting points were recorded in capillary tubes and are uncorrected. ^{1}H, ^{13}C and ^{77}Se NMR were obtained at 300, 75.42 and 57.22 MHz, respectively, in $CDCl_3$ on a Varian VXR 300S spectrometer. Chemical shifts are cited with respect to $SiMe_4$ as internal (^{1}H and ^{13}C) and Me_2Se (^{77}Se) as external standard. Elemental analyses were determined with a Carlo−Erba model EA 1112 CHNS analyzer. Infrared spectra were recorded in the range of 4000−400 cm^{-1} on a Nicolet Impact 400 FT-IR spectrometer. UV/Vis spectra were recorded on a Shimadzu UV-160A spectrophotometer and fluorescence spectra on a Perkin−Elmer LS-55 Luminescence spectrometer. Fast atomic 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 Diselenide 4: Addition of 1.6 M solution of *n*BuLi in hexane (3.45 mL, 5.5 mmol) to a diethyl ether (50 mL) solution of 2-[1-(3,5-dimethylphenyl)-2-naphthyl]-4,5-dihydro-4,4-dimethyloxazole (1.647 g, 5 mmol) under N_2 at 0 °C resulted in a dark brown solution of the lithiated compound. After 2 hours, finely ground selenium powder (0.4 g, 5 mmol) was added at 0 °C and the temperature maintained for 2 hours to give the lithium areneselenolate. The reaction mixture was then poured into a beaker containing cold aqueous $NaHCO_3$ and O_2 was passed at a moderate rate for 30 min and the mixture extracted with diethyl ether (50 mL). The organic phase was washed with water, and dried over Na_2SO_4. The filtrate was concentrated to give a yellow oil, which solidified upon addition of hexane. The compound was recrystallized from a hexane/dichloromethane (4:1) mixture to give yellow crystals of **4**. Yield: 0.97 g, 25%. M.p. 196−198 °C. $C_{46}H_{44}N_2O_2Se_2$ (816.2): calcd. C 67.83, H 5.44, N 3.44; found C 67.52, H 5.41, N 3.22. UV/Vis (dichloromethane): λ_{max} (ε) = 303.5 nm (18000 dm^3 mol^{-1} cm^{-1}), 350 (8000). ^{1}H NMR (300 MHz, $CDCl_3$, 298 K): δ = 1.29 (s), 2.37 (s), 3.78 (s), 1.29 (s), 2.37 (s), 3.78 (s), 7.05 (s), 7.35 (t), 7.65 (t), 7.75 (t), 8.3 (s) ppm. ^{13}C NMR (300 MHz, $CDCl_3$, 298 K): δ = 21.2, 28.0, 68.1, 79.4, 126.1, 127.0, 127.6, 127.8, 128.0, 129.0, 129.4, 131.2, 134.6, 137.1, 137.6, 140.9, 160.1 ppm. ^{77}Se NMR (300 MHz, $CDCl_3$, 298 K): δ = 450 ppm. IR (KBr): $\tilde{\nu}$ = 1670 cm^{-1} ν(C=N). FAB-MS: *m*/*z* = 816 [M^+].

Synthesis of Selenenyl Chloride 5: Treatment of a solution of the diselenide (0.16 g, 0.2 mmol) in carbon tetrachloride (25 mL) with a carbon tetrachloride solution of SO_2Cl_2 (0.6 mL of 2.1 g, 50 mL, 0.2 mmol) at room temperature gave a yellow precipitate after 1 hour. The mixture was evaporated to dryness under vacuum in order to give the desired compound. The yellow crystalline product was obtained after recrystallization from methanol/chloroform (2:1). Yield: 0.083 g, 93%. M.p. (decomp.) > 200 °C. $C_{23}H_{22}ClNOSe$ (443.05): calcd. C 62.39, H 5.01, N 3.16; found C 62.33, H 5.33, N 3.23. ^{1}H NMR (300 MHz, $CDCl_3$, 298 K): δ = 1.63 (s), 2.39 (s), 4.45 (s), 6.92 (s), 7.13 (s), 7.45 (t), 7.59 (d), 7.7 (t), 8.05 (d), 9.36 (s) ppm. ^{13}C NMR (300 MHz, $CDCl_3$, 298 K): δ = 21.3, 27.9, 65.3, 84.9, 115.8, 126.4, 127.4, 127.6, 128.2, 129.0, 129.9, 131.0, 134.9, 135.8, 137.2, 141.9, 143.8, 167.1 ppm. ^{77}Se NMR (300 MHz, $CDCl_3$, 298 K): δ = 839 ppm. IR (KBr): $\tilde{\nu}$ = 1755 cm^{-1} ν(C=N). FAB-MS: *m*/*z* = 443 [M^+].

Synthesis of Selenenyl Bromide 6: The procedure followed was the same as that used for the preparation of compound **5**, except the addition of Br_2/CCl_4 was carried out for 4 hour at 0 °C. The compound was recrystallized from a dichloromethane/hexane mixture to give yellow crystals. Yield: 0.06 g, 68%. M.p. (decomp.) > 216 °C. $C_{23}H_{22}BrNOSe$ (487.0): calcd. C 56.70, H 4.55, N 2.87; found C 56.51, H 4.39, N 2.70. UV/Vis (dichloromethane): λ_{max} (ε) = 399.5 nm (9540 dm^3 mol^{-1} cm^{-1}), 303.5 (11950). ^{1}H NMR (300 MHz, $CDCl_3$, 298 K): δ = 1.64 (s), 2.39 (s), 4.47 (s), 6.9 (s), 7.13 (s), 7.43 (t), 7.53 (d), 7.63 (t), 8.01 (d), 9.4 (s) ppm. ^{13}C NMR (300 MHz, $CDCl_3$, 298 K): δ = 21.3, 27.9, 65.2, 84.7, 115.9, 126.4, 127.6, 128.2, 129.1, 129.5, 129.8, 131.2, 134.9, 135.9, 137.2, 139.7, 143.8, 166.7 ppm. ^{77}Se NMR (300 MHz, $CDCl_3$, 298 K): δ = 836 ppm. IR (KBr): $\tilde{\nu}$ = 1660 cm^{-1} ν(C=N). FAB-MS: *m*/*z* = 488 [M + 1]$^+$, 487 [M^+].

Synthesis of Selenenyl Iodide 7: Here the procedure used for the preparation of compound **6** was also followed, with the addition of I_2 instead of SO_2Cl_2. The solution obtained was concentrated to give a yellow crystalline product. The compound was recystallized from a dichloromethane/hexane mixture (1:2). Yield: 0.42 g, 79%. M.p. (decomp.) > 240 °C. $C_{23}H_{22}INOSe$ (535.0): calcd. C 51.71, H 4.15, N 2.62; found C 51.68, H 4.12, N 2.46. UV/Vis (dichloromethane): λ_{max} (ε) = 400 nm (7890 dm^3 mol^{-1} cm^{-1}), 303 (17760). ^{1}H NMR (300 MHz, $CDCl_3$, 298 K): δ = 1.59 (s), 2.4 (s), 3.8 (s), 4.3 (s), 6.9 (s), 7.4 (m), 7.6 (m), 7.72 (d), 8.0 (d), 9.31 (s) ppm. ^{13}C NMR (300 MHz, $CDCl_3$, 298 K): δ = 21.6, 28.4, 65.4, 84.2, 117.0, 126.4, 127.5, 127.7, 127.9, 128.8, 129.7, 131.6, 132.3, 134.9, 136.2, 137.1, 143.5 ppm. ^{77}Se NMR (300 MHz, $CDCl_3$, 298 K): δ = 782 ppm.

Synthesis of Aryl Benzyl Selenide 8: The benzyl chloride (0.635 mL, 5 mmol) was added to the lithium selenolate at 0 °C and stirring continued for 2 hours. The usual work up followed by evaporation under reduced pressure gave the desired yellow compound, which was recrystallized from an acetonitrile/dichloromethane mixture (2:1). Yield: 0.7 g, 28%, M.p. 158−160 °C. $C_{30}H_{29}NOSe$ (500.2): calcd. C 72.29, H 5.86, N 2.81; found C 72.59, H 5.95, N 2.66. UV/Vis (dichloromethane): λ_{max} (ε) = 350 nm (3000 dm^3 mol^{-1} cm^{-1}), 303.5 (18420). ^{1}H NMR (300 MHz, $CDCl_3$, 298 K): δ = 1.12 (s), 2.35 (s), 3.83 (s), 4.22 (s), 7.02 (s), 7.39 (t), 7.6−7.49 (t),

Table 2. Crystal data and structure refinement for **4**, **6**, **7** and **8**

Compound	**4**	**6**	**7**	**8**
Empirical formula	$C_{46}H_{44}N_2O_2Se_2$	$C_{23}H_{22}BrNOSe$	$C_{23}H_{22}INOSe$	$C_{30}H_{29}NOSe$
Molecular mass	814.75	487.29	534.28	498.50
Crystal system	Monoclinic	Monoclinic	Monoclinic	Monoclinic
Space group	$P2_1/c$	$P2_1/c$	$P2_1/c$	Cc
a (Å)	24.394(5)	11.3367(15)	11.4446(14)	14.6082(12)
b (Å)	8.1678(16)	9.8765(13)	9.8991(12)	14.6368(11)
c (Å)	21.307(5)	18.873(2)	18.675(2)	47.449(4)
β (deg)	106.944(17)	93.826(2)	91.865(7)	92.7850(10)
V (Å^3)	4061.0(15)	2108.5(5)	2114.6(4)	10133.5(14)
Z	4	4	4	16
D(calcd.) (Mg/m^3)	1.333	1.535	1.678	1.307
Abs coeff (mm^{-1})	1.860	3.688	3.248	1.504
Obsd. refls. [$I > 2\sigma(I)$]	5310	5066	2885	22326
Final $R(F)$ [$I > 2\sigma(I)$][a]	0.0732	0.0556	0.0515	0.0539
$wR(F^2)$ [$I > 2\sigma(I)$]	0.1073	0.1222	0.1510	0.1193
Data/restraints/parameters	5310/0/ 521	5066/6/270	2885/4/ 270	22326/2/1206
Goodness of fit on F^2	1.002	0.874	1.173	1.024

[a] $R(F_o) = ||F_o| - |F_c||/|F_o|$ and $wR(F_o^2) = \{[w(F_o^2 - F_c^2)^2]/[w(F_c^2)^2\}^{1/2}$.

7.72 (d), 7.87 (s) ppm. ^{13}C NMR (300 MHz, $CDCl_3$, 298 K): δ = 21.2, 27.7, 67.9, 126.4, 126.7, 127.4, 128.2, 129.0, 130.4, 131.4, 133.3, 134.0, 137.0, 137.5, 138.3, 141.1, 161.7 ppm. ^{77}Se NMR (300 MHz, $CDCl_3$, 298 K): δ = 351 ppm. IR (KBr): $\tilde{\nu} = 1670$ cm^{-1} ν(C=N). FAB-MS: *m*/*z* = 500 [M$^+$].

Attempted Synthesis of 9: A solution of α,α-dibromo-*o*-xylene (2.5 mmol) in 5 mL of diethyl ether was added dropwise at 0 °C to a diethyl ether solution of arenelithium selenolate (5 mmol). The mixture was stirred at 0 °C for 2 hours. The resulting mixture was washed with water, dried and the solvents evaporated to give a yellow solid which was characterized as the selenenyl bromide **6**.

X-ray Crystallography: The diffraction measurements for compounds **4**, **6**, and **7** were performed on a Siemens R3m/V diffractometer and compound **8** on a Bruker SMART diffractometer with graphite-monochromated Mo-K_α radiation (λ = 0.7170 Å). The structures were determined by routine heavy-atom and Fourier methods using SHELXS-86[35] and refined by full-matrix least-squares with the non-hydrogen atoms anisotropic and hydrogens with fixed isotropic thermal parameters of 0.07 Å^2 by means of the SHELXL-97 program.[36] Hydrogens were partially located from difference electron-density maps and the rest were fixed at predetermined positions. Scattering factors were from common sources. Some details of the structural refinement are given in Table 2.
CCDC-217082 to -217085 (**4**, **6**, **7**, and **8**, respectively) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge at www.ccdc.cam.ac.uk/conts/retrieving.html [or from the Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; Fax: (internat.) + 44-1223-336-033; E-mail: deposit@ccdc.cam.ac.uk].

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