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Synthesis of organochalcogens stabilized by intramolecular non-bonded interactions of sterically unhindered 2-phenyl-2-oxazoline†

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The synthesis and characterization of low-valent organoselenium and -sulfur compounds incorporating sterically unhindered 2-phenyl-2-oxazoline are described. Organylselenenyl halides, RSeX (X = Cl, Br, I) were prepared from diselenide and the benzyl selenide derivative was synthesized by the reaction of *in situ* generated lithium arylselenolate, $OxSe^{-}Li^{+}$ (Ox = 2-phenyl-2-oxazoline) with benzyl chloride. These compounds in general show strong Se···N intramolecular interactions as compared with the substituted oxazoline analogues. Bis[2-(2-oxazolinylphenyl)] disulfide and [2-(2-oxazolinyl)phenyl]benzyl sulfide were synthesized by the *ortho*-lithiation method and characterized by ^{1}H and ^{13}C NMR spectroscopy. The S···N intramolecular interactions were confirmed by single crystal X-ray crystallography.

Introduction

The chemistry of intramolecularly coordinated organoselenium compounds has attracted a great deal of attention.[1] Diorgano diselenides and other selenium derivatives are used as: (a) electrophilic reagents in organic reactions such as methoxyselenylation and aminoselenylation,[2] (b) ligands for coordination chemistry[3] and chiral or achiral catalysis, (c) ligands for stabilization of MOCVD (metal-organic chemical vapor deposition) precursors[4] and (d) as synthetic models of glutathione peroxidase enzymes.[5–7]

Organoselenium compounds bearing oxazoline as the coordinating group have attracted considerable attention. Fukuzawa *et al.*[8] have used bis[(*S*,*S*)-(*iso*propyl-2-oxzolin-2-yl)ferrocenyl] diselenide for asymmetric methoxyselenenylation of alkenes. Bolm *et al.*[9] have also used chiral oxazoline ferrocenyl diselenide for the catalytic asymmetric aryl transfer to aldehyde, and recently Braga *et al.*[10] have reported bis[(*S*)-(4-*iso*propyloxazolinyl-2-phenyl)] diselenide as a ligand for copper-catalyzed conjugate addition of Grignard reagents to enones. Recently, our group has reported the glutathione peroxidase (GPx)-like activity of a series of diselenides having intramolecular coordinating groups (**1**–**5**, Chart 1).[6b,c] It was found that diselenides (**1** and **2**) having weak Se···N interactions show high GPx-like activity whereas diselenides (**3**–**5**) having a strong Se···N interaction did not show any activity.

To fine-tune the Se···N intramolecular interactions and study the consequent GPx activity, we synthesized bis[2-(2-oxazolinyl)phenyl] diselenide (**6**)[7] incorporating the sterically unhindered 2-phenyl-2-oxazoline and found that **6** showed higher GPx activity than diselenides **4** and **5**.

We report in this full paper the synthesis, solution and structural study of **6** along with a series of organoselenium compounds derived from unhindered 2-phenyl-2-oxazoline. The Se···N intramolecular interactions have been probed both in solution and in the solid state and compared with those observed in organoselenium compounds based on the α-branched 2-phenyl-2-oxazolines. Synthesis of the disulfide (**11**) and benzyl sulfide (**13**) analogues is also described and the intramolecular S···N interactions are compared with those in related organosulfides.

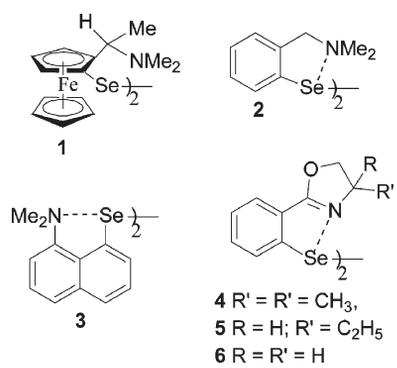

Chart 1 Diorganodiselenides having intramolecular Se···N interactions.

Results and discussion

The precursor 2-phenyl-2-oxazoline (**7**)[11] was prepared by following the literature method with minor modification. Diselenide (**6**) was obtained from 2-phenyl-2-oxazoline through the lithiation route (Scheme 1).[7] [2-(2-Oxazolinyl)phenyl]selenenyl halides (**14**–**16**) were prepared from diselenide (**6**) by using different halogenating reagents. The reaction of diselenide **6** with an equimolar amount of iodine led to the formation of the novel [2-(2-oxazolinyl)phenyl]selenenyl iodide (**16**).[12–14] Treatment of lithium arylselenolate (**9**) with an equimolar amount of benzyl chloride gave the stable selenium benzyl derivative (**12**).

In contrast to the synthesis of **6**, the synthesis of the disulfide analogue (**11**) proved to be difficult due to the higher stability of the arylthiol intermediate produced by the hydrolysis of the lithium arylthiolate and a vigorous oxidation by aqueous $K_3Fe(CN)_6$ was required to convert the thiol to disulfide.

† Electronic supplementary information (ESI) available: ^{77}Se NMR spectrum of **14**, molecular structure of **16** and packing diagram of **15**. See http://www.rsc.org/suppdata/nj/b3/b312364b/

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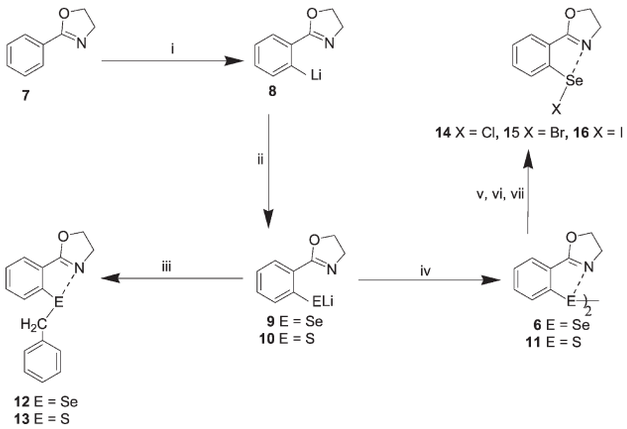

Scheme 1 Synthetic routes to organoselenium/-sulfur compounds. Reagents and conditions: (i) *n*-BuLi, Et_2O or THF, −15 °C; (ii) Se/S powder, 5 h, 0 °C; (iii) $PhCH_2Cl$, 3 h, 0 °C; (iv) aq. $NaHCO_3$ and O_2; (v) SO_2Cl_2, CCl_4, 0 °C; (vi) Br_2, CCl_4, 0 °C; (vii) I_2, CCl_4, r.t.

Reaction of OxS^-Li^+ with benzyl chloride gave benzyl sulfide (**13**) in one pot.

Spectroscopic studies

^{1}H NMR spectra. The ^{1}H chemical shifts for all selenium compounds investigated in this work exhibit a trend that is indicative of *ortho*-selenation and an Se···N interaction (Table 1). The ^{1}H chemical shifts for the organosulfur compounds (**11** and **13**) indicate a weaker (S···N) interaction compared to the selenium compounds. It is interesting to note that the signals due to the –OCH_2– protons are more affected than the corresponding methylene protons in organoselenium derivatives based on 4,4-dimethyl-2-phenyloxazoline and (*R*)-4-ethyl-4-hydro-2-phenyloxazoline.[14a,b]

^{77}Se NMR spectra. The chemical shifts for the organylselenenyl chloride **14** (1019 ppm) and bromide **15** (985 ppm) are shifted downfield more than the chemical shifts of the related [2-(4,4-dimethyl-2-oxazolinyl)phenyl]selenenyl chloride (856 ppm),[14a] bromide (850 ppm) and (*R*)-[2-(4-ethyl-4-hydrooxazolinyl)phenyl]selenenyl bromide (850 ppm).[14b] However, these values are close to those of [2-(*N*-cyclohexyl-*N*-methylaminomethyl)phenyl]selenium chloride (1050 ppm),[15] -selenium bromide (1010 ppm), [2-(*N*,*N*-dimethylaminomethyl)phenyl]-selenium bromide (987 ppm),[14d] PhSeCl (1042 ppm) and PhSeBr (869 ppm).[16] On the other hand, the ^{77}Se NMR chemical shift of selenenyl iodide (**16**; 769 ppm) is almost the same as those reported for similar organylselenenyl iodides (762 and 769 ppm).[14a,b] The ^{77}Se chemical shift for the benzylic compound **12** (376 ppm) is in close agreement with the earlier reported values of [2-(4,4-dimethyl-2-oxazolinyl)-phenyl]benzyl selenide (420 ppm)[14a] and benzylic derivatives of *N*-*tert*-butylbenzanilide (367 ppm).[17]

Table 1 ^{1}H NMR chemical shift for the methylene protons and ^{77}Se NMR data[a]

Compound	–CH_2N=	–CH_2O–	^{77}Se NMR[b]
1	4.06	4.44	–
6	4.25	4.47	465
11	4.24	4.45	–
12	4.33	4.47	376
13	4.15	4.45	–
14	4.38	4.50	1019
15	4.43	5.07	985
16	4.30	4.82	769

[a] Chemical shift (ppm) measured in $CDCl_3$ at room temperature. [b] Chemical shift relative to Me_2Se

Mass spectra. The mass spectra of compounds **14** and **15** showed no peaks higher than the expected molecular mass, indicating their monomeric nature. However, the mass spectrum of selenenyl iodide **16** shows a molecular ion peak at $m/z = 452$ due to formation of the diselenide (**6**).

X-Ray crystallographic studies

Structure of 6. An ORTEP view of **6** is shown in Fig. 1. The selected bond lengths and angles are given in Table 2. The coordination geometry around the selenium atom is nearly T-shaped with each selenium atom bonded to selenium, carbon and nitrogen atoms. The interesting feature of the structure is the existence of Se···N interactions between the selenium and nitrogen. The Se(1A)···N(1A) [2.71(6) Å] and Se(1B)···N(1B) [2.76(6) Å] distances are shorter than the sum of their van der Waals radii (3.45 Å) and almost similar to the respective distances of reported diselenides (**2**–**5**; 2.79(6)–2.86(5) Å).[6c,14d] Thus, Se···N distances in **6** indicate that the better GPx-like activity of diselenide **6** than diselenides **4** and **5** is probably due a steric effect (absence of an alkyl group in the oxazoline ring) and not due to the nature of the Se···N interaction.[7] In the case of **6**, the C(1A)–Se(1A)–Se(1B)–C(1B) torsion angle is −79.5(3)° and thus indicates a 'cisoid' conformation.

Structure of 15. A perspective view of the molecule of **15** is illustrated in Fig. 2. Selected bond distances and angles are given in Table 2. The geometry around the selenium is T-shaped. The N···Se intramolecular distance [1.98(2) Å] is significantly shorter and the Se–Br [2.6998(4) Å] distance is longer than those reported for related selenenyl bromides.[14a,b] In the crystal of **15**, the intermolecular Se···Se distance [3.86(6) Å] is comparable to the values reported for cyclic tetraselenadiynes (Se···Se = 3.58–3.90 Å).[18]

Molecular structure of 16. The molecule of **16** is isostructural with **15**. Significant bond distances and angles are given in Table 2. As was noted for **15**, the N···Se intermolecular distance [2.01(4) Å] in **16** is shorter and the Se–I distance [2.893(8) Å] is longer than those in the reported related selenenyl iodides.[14,19] In the packing of selenenyl halides **15** and **16** the molecules are self-associated. This may be attributed to optimized dense packing of molecules, which may be facilitated by the planar arrangements of these selenenyl halides (Fig. 3).

Molecular structure of 11. A PLUTON view of **11** with atom numbering is shown in Fig. 4. Selected bond distances and angle are listed in Table 2. The S(1)···N(1) [2.72(19) Å] and S(2)···N(2) [2.76(2) Å] distances are shorter than those

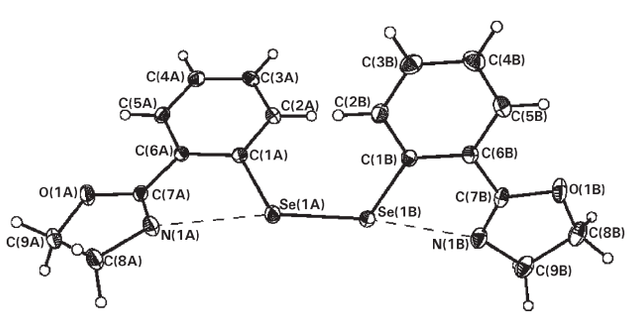

Fig. 1 Molecular structure of **6**.

Table 2 Significant bond lengths (Å) and angles (°) for organoselenium (**6**, **15** and **16**) and -sulfur (**11**, **13**) compounds

6			
Se(1A)···N(1A)	2.71(6)	Se(1B)···N(1B)	2.76(6)
Se(1A)–Se(1B)	2.343(13)	N(1B)···Se(1B)–Se(1A)	168.28(15)
N(1A)···Se(1A)–Se(1B)	177.02(16)	N(1A)···Se(1A)–C(1A)	76.10(2)
C(1A)–Se(1A)–Se(1B)–C(1B)	−79.5(3)		
15			
Se···N	1.98(2)	Se–Br	2.6998(4)
N···Se–Br	176.37(8)	C(1)–Se–Br	95.57(9)
Se···Se(_d)	3.86(6)		
16			
Se(1)···N(1)	2.01(4)	Se(2)···N(2)	2.04(4)
Se(1)–I(1)	2.8935(8)	Se(2)–I(2)	2.8513(8)
C(11)–Se(1)–I(1)	96.97(16)	N(1)···Se(1)–I(1)	178.97(16)
11			
C(1A)–S(1A)	1.792(2)	N(1B)···S(1B)	2.76(2)
S(1A)–S(1B)	2.0549(8)	C(1A)–S(1A)–S(1B)–C(1B)	80.41(11)
N(1A)···S(1A)	2.72(19)		
13			
S–C(1)	1.774(3)	N···S–C(10)	178.03(11)
S–C(10)	1.827(3)	C(1)–S–C(10)	103.04(13)
N···S	2.81(3)		

reported for bis[(4,4-dimethyl-2-phenyl)oxazoline] disulfide [S(1A)···N(1A) = 2.81(3) Å and S(1B)···N(1B) = 2.78(3) Å].[20] The S(1A)–S(1B) bond length of 2.05(8) Å is comparable to that of the reported disulfide.[20]

Molecular structure of 13. A PLUTON view of **13** is shown in Fig. 5 and selected bond distances and angles are listed in Table 2. The structure of **13** is similar to the structure of the sulfide analogue derived from 4,4-dimethyl-2-phenyloxazoline. The sulfur is in a T-shaped environment with an angle C(1)–S–C(10) = 103.04(13)°. The S···N bond separation is 2.81(3) Å. The N···S–C(10) bond angle [178.03(11)°] indicates a linear arrangement. The S···N intramolecular distance and N···S–C(10) bond angle are similar to those reported for [2-(4,4-dimethyl-2-oxazolinyl)phenyl]benzyl sulfide [S···N = 2.82(2) Å; S···N–C = 179.05°].[21]

Intramolecular interactions. The stronger intramolecular Se/S···N interactions in organoselenium (**6**, **12**, **14**–**16**) and sulfur compounds (**11**, **13**) derived from **7** when compared with related analogues derived from α-branched 4,4-dimethyl-2-phenyloxazoline, (*R*)-4-ethyl-4-hydro-2-phenyloxazoline and *N,N*-dimethylbenzylamine (*tert*-amine) suggest that the substituents on the fourth position of the oxazoline ring decrease the Se···N interactions. This observation is quite well-known for bulky alkyl amines where α-branching of alkyl substituents on nitrogen lowers its electron donor ability due to steric effects.[22] Thus, the absence of alkyl groups at the fourth position in the present case may favor the donor ability of nitrogen (B in Chart 2) and one may expect a stronger intramolecular Se···N interaction in organoselenium compounds based on 2-phenyl-2-oxazoline (**7**).

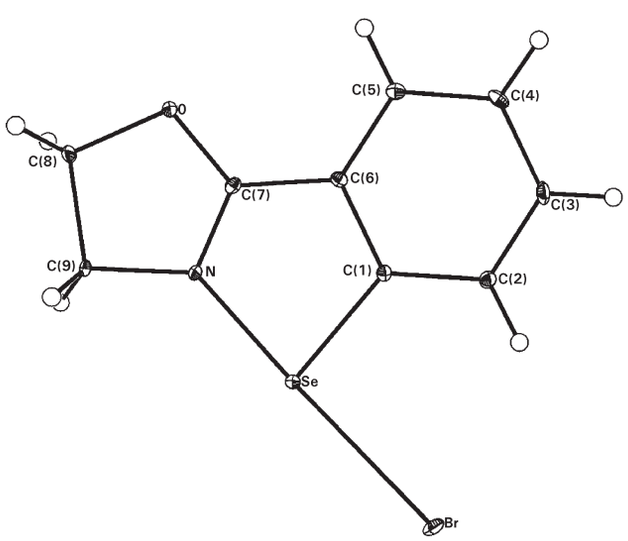

Fig. 2 Molecular structure of **15**.

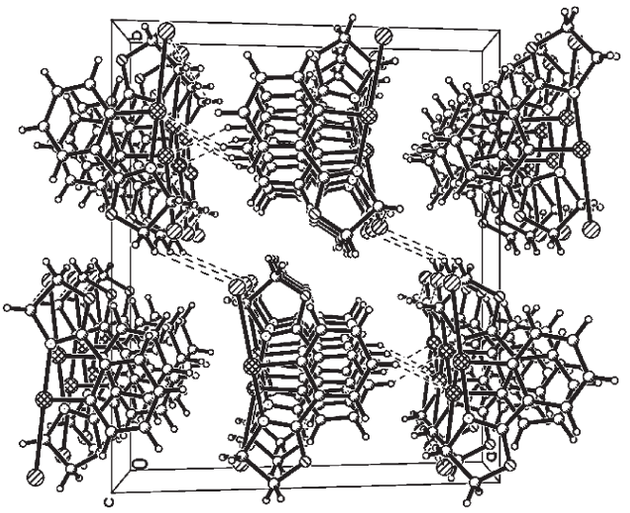

Fig. 3 Packing diagram of **16**.

Summary

From the results and their comparison with related organoselenium compounds, it is apparent that the strength of the Se···N interactions depends on the steric effect of the ligands. The strongest Se···N intramolecular interaction is observed in the selenenyl bromide (**15**) compared with other compounds in this study and related compounds reported in the literature.

Experimental section

General procedures

All reactions were carried out in inert atmosphere using nitrogen or argon with standard vacuum-line techniques. All solvents were purified by following the literature methods and freshly distilled prior to use.[23] All the chemicals used (*e.g.*, *n*-butyllithium, E-Merck) were reagent grade and used as

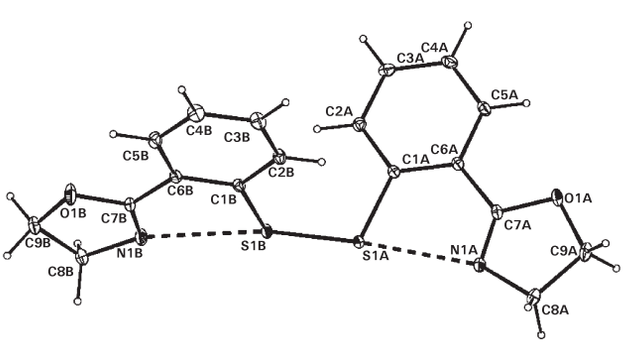

Fig. 4 Molecular structure of **11**.

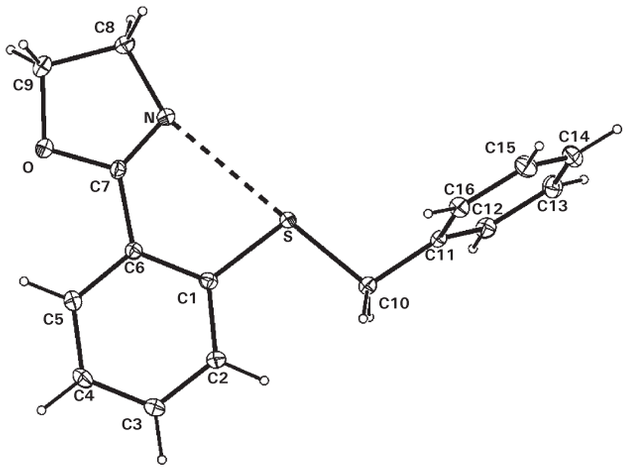

Fig. 5 Molecular structure of **13**.

received. Melting points were recorded in capillary tubes and are uncorrected. The ^{1}H, ^{13}C and ^{77}Se NMR spectra 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 $SiMe_4$ (^{1}H and ^{13}C) and Me_2Se (^{77}Se) as internal and external standards, respectively. Elemental analysis was determined with a Carlo–Erba model EA 1112 CHNS analyzer. The IR spectra were recorded on a Bio-Rod FT-IR spectrophotometer model FTS165 with KBr pellets or liquid film. 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. GC-MS analyses were obtained on a Hewlett-Packard-1800 system equipped with a capillary column using electron ionization detector.

Syntheses

2-Phenyl-2-oxazoline (7). Ligand **7** was synthesized by following the literature method with slight modifications.[11] A stirred solution of benzonitrile (51.56 g, 0.5 mol) in chlorobenzene was refluxed with ethanolamine (45.75 g, 0.75 mol) in the presence of $Cd(CH_3COO)_2{\cdot}2H_2O$ (0.66 g, 0.0025 mol) for 26 h. The reaction residue was washed with water (100 mL) twice and extracted back with CH_2Cl_2, then dried over sodium sulfate. The solvent was evaporated and the colorless liquid of **7** was purified by vacuum distillation. Yield 65.42 g (89%). ^{1}H NMR ($CDCl_3$): δ 4.06 (t, 2H) 4.44 (t, 2H), 7.36–7.52 (m, 3H), 7.92–7.98 (m, 2H). GC-MS (%): 147, M^+ (70), 105 (100), 103 (60) 77 (72), 51 (20). IR (KBr pellets): ν 3057, 2942, 2897, 2860, 1656, 1486, 1450, 1354, 1274,1137, 936, 792 cm^{-1}.

Bis[2-(2-oxazolinyl)phenyl] disulfide (11). A stirred solution of 2-phenyl-2-oxazoline (1.3 mL, 1.47 g, 10 mmol) in dry THF (50 mL) was treated dropwise with a 1.6 M solution of *n*-BuLi in hexane (6.4 mL, 10.2 mmol) under N_2at 0 °C. On stirring the reaction mixture for 0.5 h at this temperature, the lithiated product was obtained. After the addition of sulfur powder (0.32 g, 10 mmol) at 0 °C, the reaction mixture was allowed to reach room temperature and stirring was continued for an additional 1 h. The reaction mixture was then poured into a beaker containing a cold aqueous $K_3Fe(CN)_6$ (3.29 g, 10 mmol) solution. The red oily product was extracted with ether and then washed with water. The organic phase was separated, dried over Na_2SO_4 and filtered. The filtrate was concentrated to give a white solid of the disulfide **11**, which was crystallized from CH_2Cl_2–CH_3OH (2:1) as white plates. Yield: 0.96 g (69%). M.p. 209–211 °C. Anal. calcd for $C_{18}H_{16}N_2O_2S_2$ (356.46): C, 60.67, H, 4.52, N, 7.85; S, 18.00; found: C, 60.32; H, 4.22; N, 8.07; S, 17.83%. ^{1}H NMR ($CDCl_3$): δ 4.24 (t, 4H), 4.45 (t, 4H), 7.17–7.28 (m, 2H), 7.30–7.38 (m, 2H), 7.72–7.78 (m, 2H), 7.85–7.92 (m, 2H), ^{13}C NMR ($CDCl_3$): δ 55.53, 66.99, 125.26, 125.63, 125.82, 130.03, 131.18, 138.19, 163.32. IR (KBr pellets): ν 3050, 2941, 2905, 2840, 1663, 1630, 1586, 1460, 1052, 756 cm^{-1}.

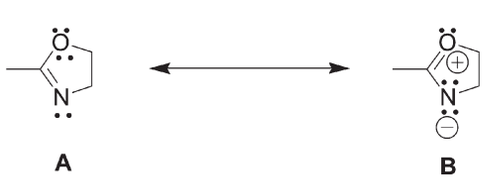

Chart 2 Postulated contribution of the oxygen atom to resonance stabilization of the oxazoline ring in compounds **6** and **11**–**16**.

[2-(2-Oxazolinyl)phenyl]benzyl selenide (12). To a solution of **7** (0.65 mL, 5 mmol) in dry THF (50 mL) was added *n*-BuLi (3.4 mL, 5.5 mmol, 1.6 M solution in hexane) under N_2 at 0 °C. The mixture was stirred for 1 h at this temperature to give the lithiated product. To this selenium powder (0.4 g, 5 mmol) was added under a brisk flow of N_2 and the reaction mixture was stirred for 2 h. Benzyl chloride (0.6 mL, 5 mmol) was added to the reaction mixture, which was allowed to come to room temperature and stirring was continued for an additional 3 h. Standard work-up gave a yellowish oil of **12**, which was crystallized from CH_2Cl_2–hexane (1:1) to give a white crystalline solid. Yield: 1.3 g (82%). M.p. 124–127 °C. Anal. calcd for $C_{16}H_{15}NOSe$ (316.16): C, 60.78, H, 4.78, N, 4.43; found: C, 60.07, H, 4.29, N, 4.42%. ^{1}H NMR ($CDCl_3$): δ 4.11 (s, 2H), 4.33 (t, 2H), 4.47 (t, 2H), 7.21–7.35 (m, 6H), 7.40–7.42 (d, 1H), 7.84–7.86 (m, 2H). ^{13}C NMR ($CDCl_3$): δ 30.78, 54.98, 66.94, 124.59, 125.62, 126.83, 127.84, 129.25, 129.67, 130.56, 130.89, 131.38, 136.93, 163.94. IR (KBr pellets): ν 3062, 2966, 2927, 2895, 1648, 1462, 1353, 1264, 1149, 1097, 765 cm^{-1}.

[2-(2-Oxazolinyl)phenyl]benzyl sulfide (13). The procedure followed was the same as that used for the preparation of compound **12**, except that sulfur was added place of selenium. The compound was recrystallized from a $CHCl_3$–CH_3OH (4:1) mixture to give white plates of **13**. Yield: 1.2 g (89%). M.p. 128–130 °C. Anal. calcd for $C_{16}H_{15}NOS$ (269.36): C, 71.36; H, 5.61; N, 5.20; S, 11.89; found: C, 71.57, H, 5.74; N, 4.91; S, 12.04%. ^{1}H NMR ($CDCl_3$): δ 4.15 (t, 2H), 4.17 (s, 2H), 4.45 (t, 2H), 7.13–7.18 (m, 2H), 7.26–7.38 (m, 5H), 7.45 (d, 1H), 7.84 (d, 1H). ^{13}C NMR ($CDCl_3$): δ 30.79, 55.59, 66.78, 124.20, 125.66, 126.09, 127.20, 127.49, 128.49, 129.04, 130.28, 130.74, 136.32, 139.64, 163.52. IR (KBr pellets): ν 3050, 2923, 2854, 1682, 1657, 1586, 1572, 1028, 931, 743 cm^{-1}.

[2-(2-Oxazolinyl)phenyl]selenenyl chloride (14). To a solution of **6** (0.45 g, 1 mmol) in CCl_4 (35 mL) at room temperature was added a solution of SO_2Cl_2 (0.134 g, 1 mmol) in CCl_4. The reaction mixture was stirred for 1.5 h at room temperature. The resulting solution was concentrated to give a yellowish-white, crystalline product. Yield: 0.43 g (83%). M.p. 210–212 °C. Anal. calcd for $C_9H_8NOSeCl$ (260.48): C, 41.50; H, 3.09; N, 5.37; found: C, 41.97; H, 3.11; N, 5.67%. ^{1}H NMR ($CDCl_3$): δ 4.38 (t, 2H), 4.50 (t, 2H), 7.23–7.28 (t, 1H), 7.29–7.36 (t, 1H), 7.52–7.58 (d, 1H), 7.88–7.94 (d, 1H). FAB-MS: m/z 263 (M^+). IR (KBr pellets): ν 3073, 2947, 2890, 1742, 1635, 1287, 1126, 720 cm^{-1}.

[2-(2-Oxazolinyl)phenyl]selenenyl bromide (15). To a cold solution of diselenide **6** (0.45 g, 1 mmol) in CCl_4 (30 mL) was added a solution of bromine (0.16 g, 1 mmol) in CCl_4

Table 3 Crystal data and structure refinement for organoselenium (**6**, **15** and **16**) and -sulfur (**11**, **13**) compounds

Compound	**6**	**15**	**16**	**11**	**13**
Empirical formula	C_9H_8NOSe	$C_9H_8BrNOSe$	$C_{18}H_{16}I_2N_2O_2Se_2$	$C_{18}H_{16}N_2O_2S_2$	$C_{16}H_{15}NOS$
Formula weight	225.12	305.03	704.05	356.45	269.35
Crystal system	Triclinic	Orthorhombic	Monoclinic	Triclinic	Orthorhombic
Space group	*P*-1	*Pbna*	*P*2(1)/*c*	*P*-1	*P*2(1)2(1)2(1)
a/Å	7.893(2)	7.3118(6)	15.416(3)	7.7728(7))	5.6512(10)
b/Å	7.901(2)	15.2642(12)	17.917(3)	7.7691(6)	7.9702(14)
c/Å	15.805(5)	17.2559(14)	7.8119(12)	15.5568(13)	30.441(5)
α/°	85.564(5)	90	90	85.376(5)	90
β/°	84.968(5)	90	102.816(4)	85.840(7)	90
γ/°	62.449(5)	90	90	63.251(7)	90
U/Å^3	869.8(5)	1925.9(3)	2103.9(6)	835.48(12)	1371.1(4)
Z	4	8	4	2	4
D_c/Mg m^{-3}	1.719	2.104	2.223	1.417	1.305
μ/mm^{-1}	4.263	8.005	6.464	2.998	0.227
Temp. (K)	293(2)	93(2)	293(2)	293(2)	293(2)
Total reflect.	8283	10791	18422	2434	1033
Obsd. reflect.	6322	2379	5193	2243	1033
Obsd reflect. [$I > 2\sigma(I)$]	1033	10 791	18 422	2434	1033
R_{int}	0.0000	0.0751	0.0757	0.0146	0.0000
$R(F)$ [$I > 2\sigma(I)$][a]	0.0708	0.0282	0.0342	0.0318	0.0306
$wR(F^2)$ [$I > 2\sigma(I)$]	0.1774	0.0515	0.0370	0.0323	0.0314

[a] Definitions: $R(F_0) = \sum||F_0| - |F_c||/\sum|F_0|$ and $wR(F_0^2) = \{\sum[w(F_0^2 - F_c^2)^2]/\sum[w(F_c^2)^2]\}^{1/2}$

(25 mL). The addition was carried out dropwise over a period of 1 h and the solution then allowed to come to room temperature. The solution obtained was concentrated to give yellow crystalline product **15**, which was recrystallized from $CHCl_3$–CH_3OH (2:1) to give reddish crystals. Yield: 0.48 g (79%). M.p. 189–191 °C. Anal. calcd for $C_9H_8NOSeBr$ (304.94): C, 35.45; H, 2.64; N, 4.59; found: C, 34.71; H, 2.46; N, 4.85%. ^{1}H NMR ($CDCl_3$): δ 4.43 (t, 2H), 5.07 (t, 2H), 7.36–7.42 (t, 1H), 7.58–7.68 (t, 1H), 8.18–8.27 (d, 1H), 8.74–8.84 (d, 1H). ^{13}C NMR ($CDCl_3$): δ 31.49, 42.31, 125.71, 126.43, 126.89, 130.63, 133.62, 141.43, 169.13. FAB-MS: *m*/*z* 305 (M^+). IR (KBr pellets): ν 3068, 2927, 2857, 1718, 1622, 1283, 1123, 720 cm^{-1}.

[2-(2-Oxazolinyl)phenyl]selenenyl iodide (*16*). To a cold solution of diselenide **6** (0.45 g, 1 mmol) in CCl_4 (25 mL) was added a solution of iodine (0.25 g, 1 mmol) in CCl_4. The addition was carried out dropwise over a period of 1 h and the solution then allowed to come to room temperature with stirring continued for an additional 2 h. The solution obtained was concentrated to give a yellowish red crystalline product, which was recrystallized from $CHCl_3$–hexane (3:1) mixture to give brick red needles of **16**. Yield: 0.62 g (88%). M.p. 169–170 °C. Anal. calcd for C_9H_8NOSeI (351.94): C, 30.72; H, 2.29; N, 3.97; found: C, 30.80; H, 2.51; N, 3.79%. ^{1}H NMR ($CDCl_3$): δ 4.30 (t, 2H), 4.82 (t, 2H), 7.38–7.46 (t, 1H), 7.48–7.56 (t, 1H), 7.68–7.74 (d, 1H), 8.42–8.52 (d, 1H). ^{13}C NMR ($CDCl_3$ + DMSO): δ 50.59, 72.22, 122.37, 125.45, 126.40, 127.18, 132.70, 134.00, 170.23. FAB-MS: *m*/*z* 353 (M^+), 453 (R_2Se_2; **6**). IR (KBr pellets): ν 3073, 2965, 2854, 1735, 1663, 1283, 1123, 728 cm^{-1}.

Crystallography

The diffraction measurements for compounds **6**, **11**, **13, 15** and **16** were performed on a Siemens R3m/V diffractometer with graphite-monochromated Mo/Kα radiation ($\lambda = 0.7170$ Å). The structures were determined by routine heavy-atom and Fourier methods by using SHELXS-86[24] and refined by full-matrix least-squares with the non-hydrogen atoms anisotropic and hydrogen with fixed isotropic thermal parameters of 0.07 Å^2 by means of the SHELXL-97 program.[25] 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 and refinement are given in Table 3.‡

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