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ARTICLE TYPE

Synthesis, Structure and Reactivity of [*o*-(2,6-diisopropylphenyliminomethinyl) phenyl]selenenyl selenocyanate (RSeSeCN) and Related Derivatives

Prakul Rakesh,[a] Harkesh B. Singh,*[a] Jerry P. Jasinski[b] and James A. Golen[b]

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Synthesis and the first X-ray structural characterization of a selenenyl selenocyanate, [*o*-(2,6-diisopropylphenyliminomethinyl)phenyl]selenenyl selenocyanate (**DiPhSeSeCN**), with a stable Se-Se bond is described. The isolation of stable **DiPhSeSeCN**, both in the solid state and in solution, is facilitated by strong intramolecular Se···N interaction. Compound **DiPhSeSeCN**, an example of unsymmetrical diselenide, did not exhibit any glutathione peroxidase-like activity. The reaction of **DiPhSeSeCN** with thiophenol afforded (3H-benzo[c][1,2]diselenol-3-yl)(phenyl)sulfane.

Introduction

Glutathione peroxidase (GPx), a selenoenzyme, reduces harmful hydrogen peroxide and organic peroxides at the expense of co-factor glutathione (GSH).[1,2]The active site of the enzyme contains a selenocysteine residue, which undergoes a redox cycle. Selenol (ESeH), the active form of selenoenzyme, reduces peroxides and gets oxidized to selenenic acid (ESeOH). Then the selenenic acid (ESeOH) reacts with reduced glutathione (GSH) to form the selenenyl sulfide adduct (ESeSG). The active form of the enzyme is regenerated by the attack of second glutathione on ESeSG to form oxidized glutathione (GSSG) (Figure 1).

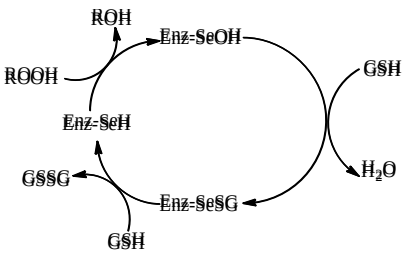


Figure 1. Proposed catalytic mechanism of glutathione peroxidase

Diorganodiselenides act as synthetic mimics of GPx enzyme.[1-5] The GPx-like activity of diorganodiselenides depends on the activation of Se-Se bond towards the oxidative cleavage and generation of selenols and selenosulfides as the key intermediates. The Se-Se bond can be activated by an intramolecular secondary bonding interaction of the type Se···N/O. However, Sarma and Mugesh have reported that the Se···N/O intramolecular interaction also increases the electrophilicity of Se centre and hence increases the possibility of attack of the RS^- ion on selenium centre of the selenosulfide adduct rather than the sulfur centre (Figure 2).[6] This is detrimental to GPx-like acivities of the enzyme mimics.

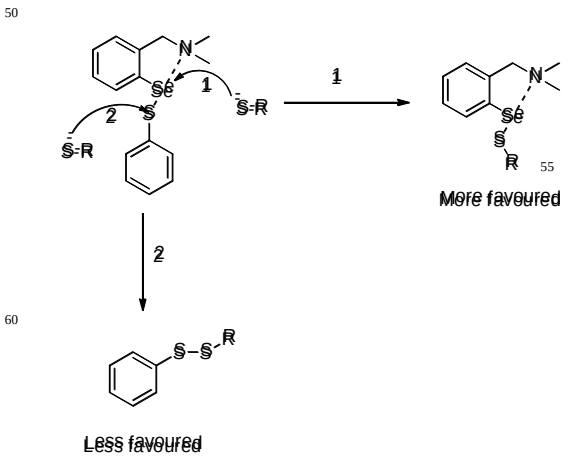


Figure 2. Nucleophilic attack of thiol at selenium or sulfur centre

Alternatively, the Se-Se bond in diselenides can also be activated by using unsymmetrical diselenides ($RSe^{\delta+}$-$^{\delta-}SeR'$) with different organic substituents bonded to the selenium atoms. This would lead to a polar Se-Se bond. However, reports on the synthesis of unsymmetrical diorgano diselenides are rare. Rheinboldt and Giesbrecht reported the synthesis of unsymmetrical diselenides (RSeSeR' where R = *o*-$O_2NC_6H_4$, 4,2-$Cl(O_2N)C_6H_3$, *o*-$O_2NC_6H_4$ R'= Ph).[7] The synthesis of the unsymmetrical diselenides was achieved by the reaction of corresponding RSe^+ (R = *o*-$O_2NC_6H_4SeCl$) with $PhSe^-$ (R = Ph). However, these unsymmetrical diselenides were poorly characterized. The problem of this synthetic route is the formation of two more symmetrical side products along with the desired product. The purification of the desired product proved very difficult since the polarities of the product and the side products were almost the

same. The first well characterized unsymmetrical diselenide, i.e. $CF_3SeSeCF_2Cl$, was synthesized by electrophilic addition of CF_3SeCl to $Se{=}CF_2$.[8] Unsymmetrical diselenide, $CF_3SeSeCH_3$, has also been synthesised by mixing of an equimolar mixture of $CH_3SeSeCH_3$ and $CF_3SeSeCF_3$.[8]

Rheinboldt and Giesbrecht have reported the synthesis of arylselenenyl selenocynates (**1**-**4**) containing a polar Se-Se bond by the reaction of arylselenenyl bromides and potassium selenocyanate.[9] The first account on the well characterized arylselenenyl selenocynates (**5**-**7**) was described by Renson and Piette.[10] The chemical structures of **1**-**7** suggest that the intramolecular interaction may be responsible for the stability of these compounds. However, the compounds have not been characterized by single crystal X-ray diffraction studies. Further, the GPx-like activity of any ArSeSeCN has not been reported in the literature.

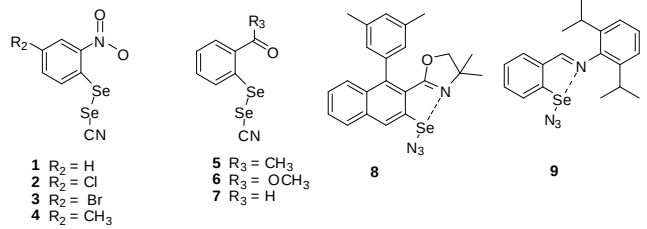
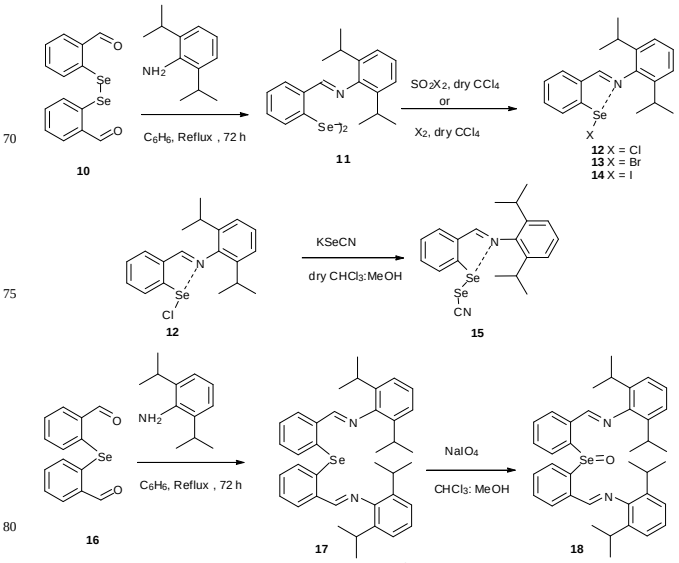


Figure 3. Aromatic selenenyl selenocynates and azides

Intramolecular secondary bonding interaction has been extensively used for the isolation of unstable organoselenium compounds.[1,11,12] Recently, Singh and coworkers have successfully isolated a series of organoselenenyl azides (**8** and **9**) by using the intramolecular interaction approach.[13] The selenenyl azide, [*o*-(2,6-diisopropylphenyliminomethinyl)phenyl]selenenyl azide (**9**) was the most stable azide among the reported oraganoselenium azides due to the shortest Se···N bond distance.[13]Selenenyl azide **9** has the highest secondary bonding interaction energy as well. This clearly indicated that the increasing bulkiness around nitrogen could also result in significant gain in the stabilization energy. In view of the isolation of the most stable azide (**9**), it was envisaged that [*o*-(2,6-diisopropylphenyliminomethinyl)phenyl]selenenyl substrates could prove to be suitable synthons for the isolation of stable ArSeSeCN. Moreover, in view of the shortest Se···N bond distance calculated in **9**, we were also interested in structural aspects of other related low-valent selenium derivatives containing *o*-(2,6-diisopropylphenyliminomethinyl)phenyl moiety.

Results and discussion

[*o*-(2,6-Diisopropylphenyliminomethinyl)phenyl]selenenyl selenocyanate (**15**) was obtained by the metathesis reaction of [*o*-(2,6-diisopropylphenylimino-methinyl)phenyl]selenium(II) chloride (**12**) with potassium selenocynate in dry methanol at 0 ^oC (Scheme 1). Precursor **12** was prepared by chlorination of bis[*o*-(2,6-diisopropylphenyliminomethinyl)phenyl]diselenide **(11)**[13, 14] and the Schiff base diselenide **(11)** was obtained by the reaction of bis(*o*-formylphenyl)diselenide (**10**) with 2,6-diisopropylbenzenamine in the presence of catalytic amount of acetic acid. Diselenide **11** was further derivatized into [*o*-(2,6-diisopropylphenyliminomethinyl)phenyl]selenenyl(II) bromide (**13**) and [*o*-(2,6-diisopropylphenyliminomethinyl)phenyl]selenenyl(II) iodide (**14**) by reactions of Br_2 and I_2 respectively at 0 ^oC. In order to synthesize a Se(IV) derivative, the precursor selenide (**17**), was prepared by the reaction of bis(*o*-formylphenyl)selenide (**16**)[14] with 2,6-diisopropylbenzenamine. Selenide **17** was oxidized by $NaIO_4$ in the presence of catalytic amount of phase transfer catalyst, tertiarybutylammonium bromide (TBAB), to get bis[*o*-(2,6-diisopropylphenyliminomethinyl)phenyl]selenoxide (**18**).



Scheme 1. Synthesis of [*o*-(2,6-diisopropylphenyliminomethinyl)phenyl]selenenyl derivatives

The title compound **15** is stable for 15 days at room temperature and -20 ^oC for a period of six months. All the other compounds (**12, 13** and **14**) are stable at room temperature for indefinite period of time. In the ^1H NMR spectrum of **15**, the azomethine proton is observed at 8.71 ppm, which is upfield shifted as compared to that observed for **12** (8.94 ppm) and **13** (8.84 ppm). However, it is downfield shifted compared to that observed for **14** (8.50 ppm). The -CH_3 peak of **15** indicated chemical non-equivalency of both the –CH_3 group in solution. The chemical non-equivalency of both the –CH_3 groups in solution was further indicated by ^{13}C NMR spectra of **15**, **13** and **14** as they showed two peaks for both the –CH_3 groups. The chemical shift of ^{77}Se NMR of **13** (1021 ppm) is downfield as compared to bis[*o*-(R)-(methylbenzyliminomethinyl)-phenyl]selenenyl bromide (1006 ppm) and {2-[1-(3,5-dimethylphenyl)-2-naphthyl]-4,5-dihydro-4,4-dimethyl-1,3-oxazol-2-yl}selenenyl bromide (837 ppm).[14] However, it is slightly upfield as compared to the chemical shift of ^{77}Se NMR of (2-phenylazophenyl-C,*N*')selenenyl bromide (1093 ppm).[13] The observation of two signals in ^{77}Se NMR spectrum of **15** at 892 and 110 ppm indicated the presence of two types of Se atoms. The peak at 892 ppm is close to the chemical shift observed in [*o*-(2,6-diisopropylphenyliminomethinyl)phenyl]selenenyl azide (1026 ppm)[13] and the peak at 110 ppm is close to the chemical shift observed for metal selnolates, in which selenium centre is anionic in nature.[15] In order to get a better insight of the charge on both selenium centre in **15**, the geometry of [*o*-(2,6-diisopropylphenyliminomethinyl)phenyl]selenenyl selenocyanate (**15**) was optimized at the B3LYP level of theory with the use of

the 6-31+G(d,p) basis sets.[16] The natural bond orbital (NBO) charges showed that both selenium atoms were positively charged i.e. Se1 (+0.443) and Se2 (+0.043) (Figure S41 of ESI). However, Se2 atom was less positive than the Se1 atom. The calculated ^{77}Se NMR chemical shifts (905, 69 ppm) of **15** are close to the observed values. The $\nu_{C=N}$ stretching frequency of **15** (1599 cm^{-1}) was similar to that observed for the other halo derivatives [**12** (1595 cm^{-1}), **13** (1591 cm^{-1}) and **14** (1589 cm^{-1})]. However, the peak at 2110 cm^{-1} corresponding to –C≡N, is significantly shifted as compared with KSeCN (2070 cm^{-1}).[17]

In ^{1}H NMR spectrum of **18**, the peaks due to –CH_3 and –CH show downfield shift as compared to precursor **17**. The peak observed at 1329 ppm in the ^{77}Se NMR spectrum of **18** compares well with other selenoxides,[18] however, it is significantly downfield shifted as compared to selenide **17** (396 ppm). Selenoxide **18** shows peaks at 1597 cm^{-1} and 749 cm^{-1} in FT-IR spectrum. These correspond to $\nu_{C=N}$ and $\nu_{Se=O}$.[18] The lower $\nu_{C=N}$ stretching frequency (1597 cm^{-1}) of selenoxide **18** compared to selenide **17** (1637), indicates stronger coordination of N to Se.

The molecular structure of **15** is shown in Figure 4a. The coordination geometry around Se1 atom can be considered as T-shaped in which C1 atom and the two lone pairs are in the equatorial position and N1, Se2 atoms are in the axial positions. The bond angle of N1-Se1-Se2 (172.93(6)) is close to 180^{o}. The intramolecular N1···Se1 distance (2.116(2) Å) of **15** is longer than the intramolecular N(sp^2)···Se selenenyl halides **13** (1.982(2) Å) and **14** (1.993(17) Å). This indicates a weaker intramolecular interaction in **15** as compared to **13** and **14**. The N1(sp^2)···Se1 distance of **15** is close to the intramolecular N(sp^2)···Se interaction (2.145(16) Å) of [2-[1-(3,5-dimethylphenyl)-2-naphthyl]-4,5-dihydro-4,4-dimethyloxazole] selenenyl(II) azide.[13] The geometry around the other Se2 atom is V- shaped and the bond angle of C20-Se2-Se1 is 101.93(9)^{o}.The coordination geometries around the Se1 atoms in compounds **13** (Figure 4b) and **14** (Figure S1) are quite similar to that observed for **15**. Interestingly, the intramolecular N1···Se1 distance of **13** (1.982(2) Å) is shorter than the corresponding N···Se distances of {2-[1-(3,5-dimethylphenyl)-2-naphthyl]-4,5-dihydro-4,4-dimethyl-1,3-oxazol-2-yl}selenenyl bromide (2.052(2) Å) and (2-phenylazophenyl-C,*N*')selenenyl bromide (2.025(2) Å).[13] However, it is slightly longer than that observed distance (1.899(2) Å) in selenenium cation, (2-nitro-6-((phenylimino)methyl)phenyl)selenenyl(II) tribromide[12] and bis[o-(R)-(methylbenzyliminomethinyl)-phenyl]selenenyl bromide (1.943(3) Å).[14]

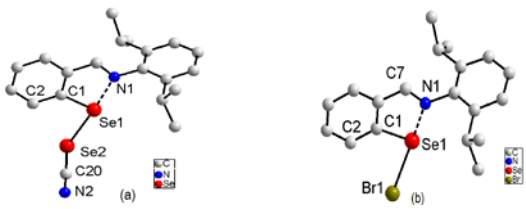


Figure 4. (a) Molecular structure of **15** and selected bond lengths (Å) and angles (°). Hydrogen atoms are omitted for clarity. Se1-C1 1.917(2), Se1-Se2 2.6069(4), Se1···N1 2.116(2); N1-Se1-Se2 172.93(6), C1-Se1-Se2 97.60(8), C20-Se2-Se1 101.93(9). **(b)** Molecular structure of **13** and selected bond lengths (Å) and angles (°). Se1-C1 1.890(3), Se1-Br1 2.7012(4), Se1···N1 1.982(2); N1-Se1-Br1 176.23(7), C1-Se1-Br1 94.96(8)

The Se1-Se2 bond length (2.6069(4) Å) in **15** is longer than Se-Se bond length in related symmetrical diselenides i.e. bis[3-(4,5-dihydro-4,4-dimethyl-1,3-oxazol-2-yl)-4-(3,5-dimethylphenyl)-2-naphthyl] diselenide[19] (2.3216(15) Å) and [2-(2-oxazolinyl)phenyl]diselenide[20] (2.343(13) Å). The Se1-Se2 bond length (2.6069(4) Å) is even longer than the longest Se-Se bond distance reported for diselenides i.e. [N-(6'-n-propyl-4'-pyrimidone) (6-n-propyl-2-selenouracil)$_2$(Se—Se)] (2.4427(6) Å).[21]

The molecular structure of **17** is shown in Figure 5. The coordination geometry around the Se atom can be considered as T-shaped in which ClB atom and the two lone pairs are in the equatorial positions and N1B and C1A atoms are in the axial positions. The intramolecular N1B···Se distance is 2.803(13) Å and the N1B···Se–C1A angle of about 164.36(5)°. The distance is shorter than that reported for bis[(N,N-dimethylamino)benzyl]selenide[22] (3.190 Å), however, it is longer than the Se···N bond distances of bis-(2-phenylazophenyl-C,N')selenide[23] (2.621 Å). In **17** only one of the N atoms, i.e. N1B coordinates with Se and the other N1A is twisted away from Se. This behaviour is similar to bis-(2-phenylazophenyl-C,N')selenide. However, in bis[(N,N-dimethylamino)benzyl]selenide, both nitrogens weakly coordinate to Se.

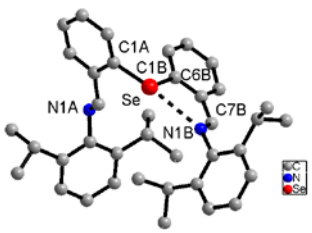


Figure 5. Molecular structure of **17** and selected bond lengths (Å) and angles (°). Hydrogen atoms are omitted for clarity. Se-C1A 1.928(17), Se-C1B 1.929(15) N1B-Se 2.803(13); N1B-Se1-C1A 164.36(5), C1A-Se-C1B 96.34(7)

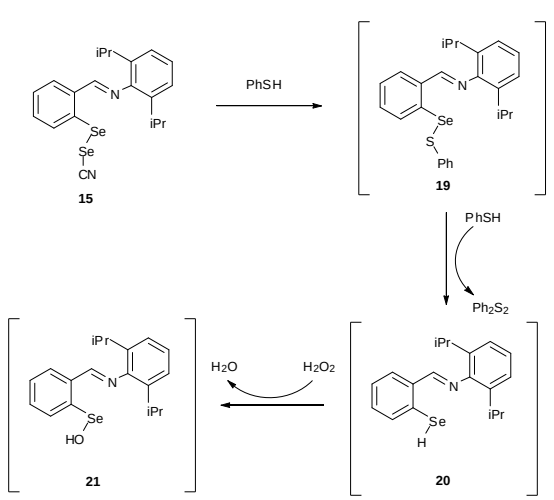
The GPx-like activity of **15** was measured using ebselen as the reference.[3b] The catalytic reaction was monitored by measuring the rate of the formation of Ph_2S_2 spectrophotometrically at 305 nm (ε_{max} = 1.24 x 10^3 M^{-1}cm^{-1}). The initial rates for all the compounds was measured at least three times and calculated from the first 5–10% of the reaction. Compound **15** was found to be almost inactive (Table 1).

Table 1. GPx-like activities of organoselenium compounds (Initial reduction rates (V_0) of H_2O_2 (2 mM) with PhSH (1 mM) in methanol (solvent) in the presence of selenium catalyst (0.01 mM)).

Entry	Catalyst	V_o(μM/min)
1	None	2.25 ± 0.04
2	Ebselen	2.98 ± 0.01
3	**15**	3.43 ± 0.04

In order to rationalize the poor GPx-like activity, the reactions of **15** with the substrate i.e. PhSH and H_2O_2 were followed by ^{77}Se NMR spectroscopy experiments (Scheme 2). When **15** was treated with PhSH (2 equiv.) in $CDCl_3$, three new peaks (629, 529 and 365 δ) were observed (Figure 6). The peaks at 529 and 365 δ were assigned to compound **22** (*vide infra*) and the peak at 629 δ was due to the corresponding selenenyl sulfide **19**. [3,4,24] The

titration experiments suggest that **15** when treated with thiophenol, converts into **22** and corresponding selenenyl sulfide **19**. On treatment of **15** with H_2O_2 (2 equiv.), a new signal at 424 ppm was observed. This peak is in the region of ^{77}Se NMR chemical shifts of selenides or diselenides.[3] Further addition of H_2O_2 (12 equiv.) did not lead to any change in the ^{77}Se NMR spectrum. There is no evidence for the formation of seleninic acid **21** in this experiment. This could be the reason for the inactivity of catalyst **15** towards GPx-like activities.



Scheme 2. Expected reactions of PhSH and H_2O_2 with **15**

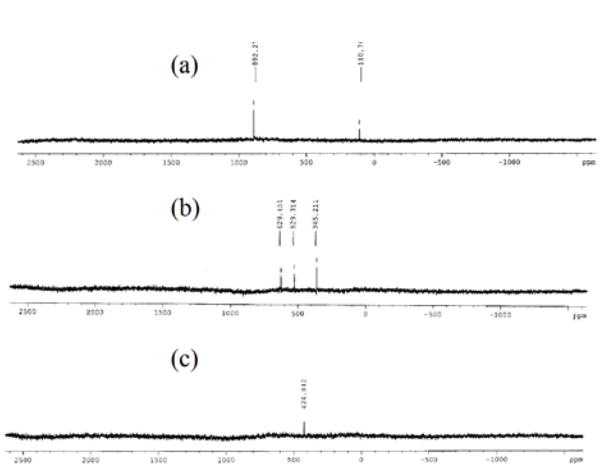
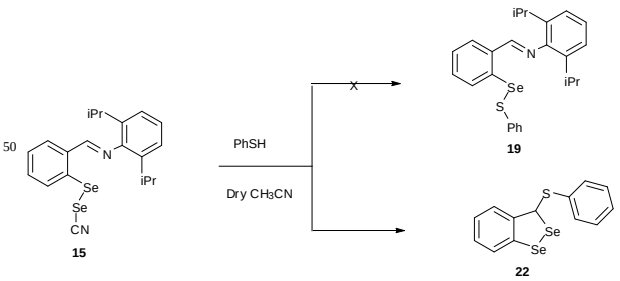
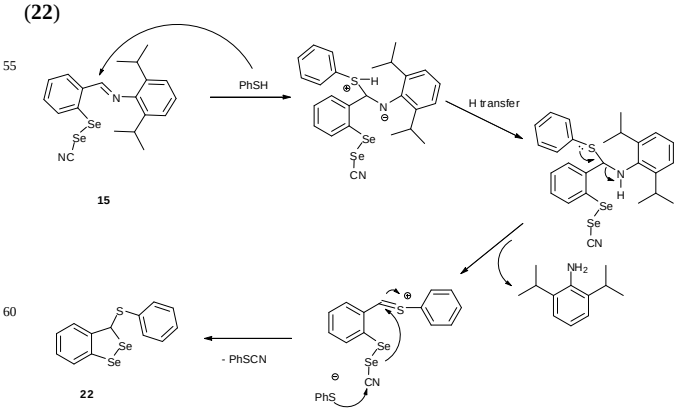


Figure 6. The ^{77}Se NMR spectrum of (a) catalyst **15** (b) catalyst **15** and 2 equiv. of PhSH (c) catalyst **15**, 2 equiv. of PhSH and 2 equiv. of H_2O_2

In an order to isolate **19**, when compound **15** was compound reacted with thiophenol, an unexpected (3H-benzo[c][1,2]diselenol-3-yl)(phenyl)sulfane (**22**) was obtained (Scheme 3). In the ^{1}H NMR spectrum of **22**, the expected peaks of -CH=N, -CH and $-CH_3$ were absent. The peak at 6.11 ppm in **22** indicates the presence of a highly downfield shifted aliphatic proton. The azomethine peak was absent in the ^{13}C NMR spectrum and one aliphatic carbon peak (61.7 ppm) was present in **22**. Compound **22** also shows two signals (364, 528 ppm) in ^{77}Se NMR spectrum, however, both signals are in the range for the diorgano diselenides. Singh and coworkers have earlier isolated a similar compound i.e. 7-nitro-3H-benzo[c][1,2]diselenol-3-yl)(phenyl)sulfane by the reaction of selenenium cation with thiophenol.[12] The formation of **22** can be explained in two steps (i) addition elimination reaction i.e. nucleophilic addition reaction of thiophenol on –C=N bond followed by the intramolecular elimination reaction of amine and (ii) nucleophilic addition reaction of Se on –C=S bond (Scheme 4). All attempts of isolate the compound having a chemical shift of 424 ppm in ^{77}Se NMR were unsuccessful.



Scheme 3. Synthesis of 3H-benzo[c][1,2]diselenol-3-yl)(phenyl)sulfane (**22**)



Scheme 4. Plausible mechanism for the synthesis of **22**

Conclusions

Compound **15** is the first example of a structurally characterized RSeSeCN. The elongation in the bond length of Se-Se (2.6069(4) Å) and a large difference in the ^{77}Se NMR chemical shifts (892, 110 ppm) of the two different Se atoms suggest that the Se-Se bond is partially ionic in **15**. Compound **15** was inactive catalyst in thiophenol assay for GPx-like activities. The reaction of **15** with thiophenol gives unusual product **22** in the place of the expected selenenyl sulphide. DFT calculations on **15** show that both Se atoms were positively charged, however, the charge on Se1 atom was more positive than the charge on Se2 atom.

Experimental section

General procedures

All reactions were carried out under N_2 atmosphere. Solvents were purified and dried by standard techniques.[25] Melting points were recorded in capillary tubes and are uncorrected. ^{1}H and ^{13}C spectra were obtained at 399.88 and 100.56 MHz respectively in $CDCl_3$ on a Bruker AV 400 spectrometer. ^{77}Se NMR spectra were recorded at 94.75 MHz in $CDCl_3$ on a Bruker AV 400 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 analysis was performed on a Carlo-Erba model 1106 CHNS elemental analyzer. Infrared spectra were recorded in the range 4000 – 400 cm^{-1} on a Nicolet Impact 400 FT-IR spectrophotometer. ES-MS spectra were recorded at room temperature on a Q-Tof (YA-105) micromass spectrometer. The catalytic activities were recorded in 1 ml cuvet on a Cary 100 bio UV-Vis spectrophotometer at room temperature.

Bis[*o*-(2,6-diisopropylphenyliminomethinyl)phenyl]diselenide (11)

Bis(o-formylphenyl)diselenide (**10**)[14] (1 g, 2.7 mmol), 2,6-diisopropylphenylamine (0.63 g, 5.4 mmol) and two drops of acetic acid were refluxed azeotropically in benzene (200 mL) with using a Dean-Stark trap till the completion of the reaction (by IR). The reaction was complete in 72 hours. The resulting reaction mixture was evaporated and washed with cold ethanol to remove the unreacted amine. The solid thus obtained was crystallized from chloroform/hexane (1:4) to give pale yellow crystals of **11**. Yield: 0.84 g, 45 %; mp 159-161 ^{o}C. Anal. Calcd for $C_{38}H_{44}N_2Se_2$: C, 66.46; N, 4.08; H, 6.46. Found C, 66.79; N, 4.42; H, 6.35. ^{1}H NMR ($CDCl_3$): δ1.19 (d, 24H), 3.05–3.11 (m, 4H), 7.14–7.20 (m, 6H), 7.31-7.33 (m, 4H), 7.66 (m, 2H), 8.01 (d, 2H), 8.49 (s, 2H). ^{13}C NMR ($CDCl_3$): δ23.9, 28.2, 123.2, 124.8, 126.0, 131.3, 131.8, 132.7, 134.6, 134.8, 138.1, 147.5, 162.5. ^{77}Se NMR ($CDCl_3$): δ467. ES-MS: (m/z) 344 ($C_{19}H_{22}NSe^+$ (100 %)). HRMS (EI): m/z [$C_{38}H_{22}N_2Se_2^+$ (M^+) calcd: 689.1913, Found: 689.1929. IR (KBr, cm^{-1}): 1634 ($\nu_{C=N}$).

[*o*-(2,6-Diisopropylphenyliminomethinyl)phenyl]selenenyl(II) bromide (13)

To a solution of bis[*o*-(2,6-diisopropylphenyliminomethinyl)phenyl]diselenide (**11**) (0.15 g, 0.21 mmol) in dry CCl_4 (10 mL) was added drop-wise a solution of Br_2 (0.03 g, 0.21 mmol) in dry CCl_4 (10 mL) at 0 ^{o}C. The reaction was further stirred for 2 hour at room temperature. The solvent was removed under vacuum and the sticky solid so obtained was treated with hexane to obtain an off-white solid. The solid thus obtained was crystallized from dichloromethane/hexane to give pale yellow crystals (**13**). Yield: 0.13 g, 72 %; mp 184-186 ^{o}C. Anal. Calcd for $C_{19}H_{22}NSeBr$: C, 53.92; N, 3.31; H, 5.24. Found C, 53.51; N, 4.10; H, 5.19. ^{1}H NMR ($CDCl_3$): δ1.12 (d, 6H), 1.24 (d, 6H), 2.58 (m, 2H), 7.26 (d, 2H), 7.43 (t, 1H), 7.64 (t, 1H), 7.80 (t, 1H), 8.11 (d, 1H), 8.84 (s, 1H), 9.11 (d, 1H). ^{13}C NMR ($CDCl_3$): δ24.2, 25.2, 28.6, 124.2, 127.1, 130.2, 130.4, 131.7, 131.8, 133.0, 136.5, 143.5, 152.4, 159.0. ^{77}Se NMR ($CDCl_3$): δ1021. ES-MS: (m/z) 344 ($C_{19}H_{22}NSe^+$ (100 %)). IR (KBr, cm^{-1}): 1591 ($\nu_{C=N}$).

[*o*-(2,6-Diisopropylphenyliminomethinyl)phenyl]selenenyl(II) iodide (14)

To a stirred solution of **11** (0.1 g, 0.14 mmol) in dry CCl_4 (40 mL) was added a solution of I_2 (0.035 g, 0.014 mmol) and the reaction followed in a similar manner to that described above for the synthesis of **13** to obtain a brown precipitate. The compound was recrystallized from $CHCl_3$/ hexane (1:4) mixture to give brown crystals of **15**. Yield: 0.095 g, 73 %; mp 127-129 ^{o}C. Anal. Calcd for $C_{19}H_{22}NSeI$: C, 48.53; N, 2.98; H, 4.72. Found C, 48.22; N, 3.45; H, 4.68. ^{1}H NMR ($CDCl_3$): δ1.12 (d, 6H), 1.24 (d, 6H), 2.65 (m, 2H), 7.27 (d, 2H), 7.43 (t, 1H), 7.66 (t, 1H), 7.73 (t, 1H), 7.99 (d, 1H), 8.50 (s, 1H), 8.94 (d, 1H). ^{13}C NMR ($CDCl_3$): δ23.9, 25.0, 28.5, 124.1, 127.1, 129.6, 130.8, 132.2, 132.8, 135.0, 137.1, 142.9, 147.4, 158.3. ^{77}Se NMR ($CDCl_3$): δ970. ES-MS: (m/z) 344 ($C_{19}H_{22}NSe^+$ (100 %)). IR (KBr, cm^{-1}): 158 ($\nu_{C=N}$).

[*o*-(2,6-Diisopropylphenyliminomethinyl)phenyl]selenenyl selenocyanate (15)

To a solution of [*o*-(2,6-diisopropylphenylimino-methinyl)phenyl]selenium(II) chloride[13] (**12**) (0.1 g, 0.26 mmol) in a mixture of dry $CHCl_3$ (2 mL) and dry methanol (5 ml) was added dropwise a solution of KSeCN (0.03 g, 0.26 mmol) in dry methanol (5 mL) at 0 ^{o}C. After the addition was completed, the reaction mixture was allowed to stir at room temperature for 2 hours. The reaction mixture was filtered and the solvent was removed under vacuum to get a pale yellow solid. The solid thus obtained was crystallized from $CHCl_3$/hexane to give pale yellow crystal (**15**). Yield: 0.09 g, 76 %; mp 129-131 ^{o}C. Anal. Calcd for $C_{20}H_{22}N_2Se_2$: C, 53.58; N, 6.25; H, 4.95. Found C, 53.51; N, 6.10; H, 5.19. ^{1}H NMR ($CDCl_3$): δ1.19- 1.25 (d, 12H), 2.73 (m, 2H), 7.25 (d, 2H), 7.33 (m, 1H), 7.56 (t, 1H), 7.70 (t, 1H), 7.92 (d, 1H), 8.46 (d, 1H), 8.71 (s, 1H). ^{13}C NMR ($CDCl_3$): δ24.2, 24.7, 28.5, 104.6, 123.9, 126.9, 128.4, 131.5, 131.8, 132.85, 132.9, 139.5, 141.4, 143.5, 161.3. ^{77}Se NMR ($CDCl_3$): δ892, 110. ES-MS: (m/z) 344 ($C_{19}H_{22}NSe^+$ (100 %)). HRMS (EI): m/z [$C_{20}H_{22}N_2Se_2K^+$ (M^+) calcd: 488.9750, Found: 488.9773. IR (KBr, cm^{-1}): 1599.4 ($\nu_{C=N}$), 2110 ($\nu_{C\equiv N}$).

Bis[*o*-(2,6-diisopropylphenyliminomethinyl)phenyl]selenide (17)

Bis(o-formylphenyl)selenide (**16**)[14] (0.5 g, 1.7 mmol) was refluxed azeotropically in benzene (100 mL), with 2,6-diisopropylphenylamine (0.39 g, 3.4 mmol) and two drops of acetic acid. The reaction was continued in a similar manner to that described above for the synthesis of **11**. The resulting reaction mixture was evaporated and washed with cold ethanol to remove the unreacted amine. The yellow compound was recrystallized from $CHCl_3$/ hexane (1:4) mixture to give pale yellow crystals of **17**. Yield: 0.54 g, 50 %; mp 159-161 ^{o}C. Anal. Calcd for $C_{38}H_{44}N_2Se$: C, 75.10; N, 4.61; H, 7.30. Found C, 74.82; N, 4.42; H, 7.05. ^{1}H NMR ($CDCl_3$): δ1.06 (d, 24H), 2.87–2.95 (m, 4H), 7.05–7.13 (m, 6H), 7.31-7.36 (m, 4H), 7.41 (m, 2H), 8.00 (d, 2H), 8.54 (s, 2H). ^{13}C NMR ($CDCl_3$): δ23.7, 28.0, 123.1, 124.4, 127.7, 130.9, 131.7, 134.3, 135.3, 136.6, 137.8, 148.6, 162.9. ^{77}Se NMR ($CDCl_3$): δ396. ES-MS: (m/z) 344 ($C_{19}H_{22}NSe^+$ (100 %)). IR (KBr, cm^{-1}): 1637 ($\nu_{C=N}$).

Bis[*o*-(2,6-diisopropylphenyliminomethinyl)phenyl]selenoxide (18)

To a stirred solution of bis[*o*-(2,6-diisopropylphenylimino-methinyl)phenyl]selenide (**17**) (0.15 g, 0.24 mmol) in a mixture of $CHCl_3$ (2 ml) and ethanol (10 mL), with tetrabutylammonium bromide in a catalytic amount, was added dropwise a solution of $NaIO_4$ (0.05 g, 0.24 mmol) in distilled water (5 mL) at room temperature. The reaction mixture was allowed to stir at room temperature for 24 hours. The solvent was filtered and removed under vacuum and the sticky solid so obtained was treated with hexane to obtain a white solid. The solid thus obtained was crystallized from dichloromethane/hexane to give white crystal

(**18**). Yield: 0.04 g, 28 %; mp 115-117 ^{o}C. Anal. Calcd for $C_{38}H_{44}N_2SeO$: C, 73.17; N, 4.49; H, 7.11; O, 2.57. Found C, 73.82; N, 4.62; H, 7.05; O, 2.29. ^{1}H NMR ($CDCl_3$): δ1.21 (d, 24H), 3.35 (m, 4H), 7.23 (m, 6H), 7.42 (t, 4H), 7.67 (m, 4H), 8.14 (d, 2H). ^{77}Se NMR ($CDCl_3$): δ1329. ES-MS: (m/z) 361 ($C_{19}H_{22}NOSe^+$ (100 %)). IR (KBr, cm^{-1}): 1597 ($\nu_{C=N}$), 749 ($\nu_{Se=O}$).

(3H-Benzo[c][1,2]diselenol-3-yl)(phenyl)sulfane (22)

To a solution of [*o*-(2,6-diisopropylphenyliminomethinyl)phenyl]selenenyl selenocyanate (**15**) (0.1 g, 0.20 mmol) in a mixture of dry dichloromethane (2 mL) and dry acetonitrile (10 ml) was added thiophenol (0.04 g, 0.4 mmol) at room temperature. The colour of the solution was changed from yellow to red. The reaction mixture was allowed to stir at room temperature for 2 hours. This organic layer was washed twice with water, dried and evaporated to obtain a reddish liquid. It was recrystallized from hexane to get red crystals (**22**). Yield: 0.025 g, 31 %; mp 128-130 ^{o}C. Anal. Calcd for $C_{13}H_{10}SSe_2$: C, 43.83; S, 9.00; H, 2.83. Found C, 43.51; S, 9.10; H, 3.19. ^{1}H NMR ($CDCl_3$): δ6.11 (s, 1H), 7.04 (m, 2H), 7.18-7.20 (m, 1H), 7.30 (m, 4H), 7.47 (m, 2H). ^{13}C NMR ($CDCl_3$): δ61.7, 125.8, 127.1, 127.6, 128.4, 128.8, 129.2, 134.0, 134.4, 137.8, 142.8. ^{77}Se NMR ($CDCl_3$): δ364, 528. ES-MS: (m/z) 248 ($C_7H_5Se_2^+$ (100 %)).

X-ray Crystallographic Studies

The diffraction measurements for compounds **13**, **14**, **15** and **17** were performed at 200 K on a Oxford Diffraction Gemini diffractometer using graphite-monochromated Mo Kα radiation (λ = 0.7107 Å).. The structures were solved by routine heavy-atom using SHELXS 97[26] 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 Å^2 using the SHELXL 97 program.[27] The hydrogens were partially located from difference electron-density maps, and the rest were fixed at calculated positions. Scattering factors were from common sources.[28] Some details of data collection and refinement are given in Table 2.

Computational studies

All the theoretical calculations were executed by the Gaussian 03 suite of quantum chemical programs. The geometry optimizations were carried out at the B3LYP level of DFT by using the 6-31+G(d) basis sets. The ^{77}Se NMR calculations were performed at B3LYP/6-311+G (d,p) level on B3LYP/6-31+G(d)-level optimized geometries by using the gauge-including atomic orbital (GIAO) method (referenced with respect to the peak of Me_2Se).[29] The quantifications of orbital interaction were done by natural bond orbital (NBO) analysis at B3LYP/6-311+G(d,p) level.[30]

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Notes and references

[a] *Department of Chemistry, Indian Institute of Technology Bombay, Powai, Mumbai 400 076, India. Fax: 9122 2576 7152; Tel: 9122 2576 7190; E-mail: chhbsia@chem.iitb.ac.in*
[b] *Department of Chemistry, Keene State College, 229 Main Street, Keene, NH 03435-2001, USA*

†Electronic Supplementary Information (ESI) available: The spectroscopic data (^{1}H, ^{13}C, ^{77}Se NMR spectra, CHN analysis, ESI-Mass spectra and FT-IR spectra) for all the compounds (**11**, **13**, **14**, **15**, **17**, **18** and **22**. CCDC reference numbers (959142-959145).

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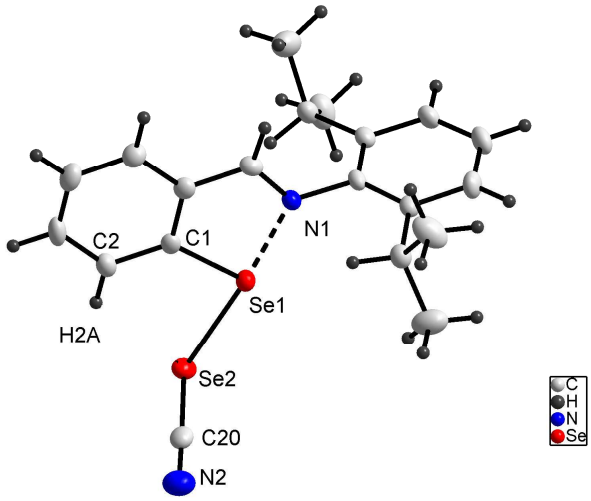
Table of content

The synthesis, structure and reactivity of a stable selenenyl selenocynates having a strong Se-Se bond, is reported.



Molecular structure of [*o*-(2,6-diisopropylphenyliminomethinyl)phenyl]selenenyl selenocyanate