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Synthesis, Structure and Reactivity of \([\sigma-(2,6\text{-}diisopropylphenyliminomethinyl)}\text{phenyl}\text{]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, \([\sigma-(2,6\text{-}diisopropylphenyliminomethinyl)}\text{phenyl}\text{]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 \((3\text{H-benzo[c][1,2]diselenol-3-yl)}\text{(phenyl)sulfane.}

Introduction

Glutathione peroxidase (GPx), a selenoenzyme, reduces harmful hydrogen peroxide and organic peroxides at the expense of co-factor glutathione (GSH). 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](image1)

Diorganodiselenides act as synthetic mimics of GPx enzyme. The GPx-like activity of diorganodiselenides depends on the activation of Se-Se bond towards the oxidative cleavage and generation of selenols and selenol sulfides 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 Muges 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 selenol sulfide adduct rather than the sulfur centre (Figure 2). This is detrimental to GPx-like activities of the enzyme mimics.

![Figure 2. Nucleophilic attack of thiol at selenium or sulfur centre](image2)

Alternatively, the Se-Se bond in diselenides can also be activated by using unsymmetrical diselenides (RSe\(^{\delta+}\), R'Se\(^{-}\)) 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 diorganodiselenides are rare. Rheinboldt and Giesbrecht reported the synthesis of unsymmetrical diselenides (RSeSeR' where \(R = \sigma-O\text{CN}_{6}\text{H}_{4}, 4,2\text{-Cl(O2N)C}_{6}\text{H}_{3}, \sigma-O\text{NC}_{3}\text{H}_{4}\text{, } \text{R' = Ph})\). The synthesis of the unsymmetrical diselenides was achieved by the reaction of corresponding RSe\(^{-}\) (\(R = \sigma\text{-O}_2\text{NC}_{3}\text{H}_{4}\text{SeCl})\) with PhSe\(^{-}\) (\(R = \text{Ph})\). 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. CF3SeSeCF2Cl, was synthesized by electrophilic addition of CF3SeCl to Se=CF2.8 Unsymmetrical diselenide, CF3SeSeCH3, has also been synthesized by mixing of an equimolar mixture of CH3SeSeCH3 and CF3SeSeCF3.8 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 selenocynate.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.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, [α-(2,6-disoproplyphenylimonomethyl)phenyl]selenenyl azide (9) was the most stable azide among the reported organoselenium 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 [α-(2,6-disoproplyphenylimonomethyl)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 α-(2,6-disoproplyphenylimonomethyl)phenyl moiety.

Results and discussion

[α-(2,6-disoproplyphenylimonomethyl)phenyl]selenenyl selenocyanate (15) was obtained by the metathesis reaction of [α-(2,6-disoproplyphenylimino-methyl)phenyl]selenium(II) chloride (12) with potassium selenocyanate in dry methanol at 0°C (Scheme 1). Precursor 12 was prepared by chlorination of bis[α-(2,6-disoproplyphenylimonomethyl)phenyl]diselenide (11)14,15 and the Schiff base diselenide (11) was obtained by the reaction of bis[α-formylphenyl]diselenide (10) with 2,6-disopropylbenzeneamine in the presence of catalytic amount of acetic acid. Diselenide 11 was further derivatized into [α-(2,6-disoproplyphenylimonomethyl)phenyl]selenenyl(II) bromide (13) and [α-(2,6-disoproplyphenylimonomethyl)phenyl]selenenyl(II) iodide (14) by reactions of Br2 and I2 respectively at 0°C. In order to synthesize a Se(IV) derivative, the precursor selenide (17), was prepared by the reaction of bis[α-formylphenyl]selenide (16)14 with 2,6-disopropylbenzeneamine. Selenide 17 was oxidized by NaIO4 in the presence of catalytic amount of phase transfer catalyst, tertiarybutylammonium bromide (TBAB), to get bis[α-(2,6-disoproplyphenylimonomethyl)phenyl]selenoxide (18).

Scheme 1. Synthesis of [α-(2,6-disoproplyphenylimonomethyl)phenyl]selenenyl derivatives

The title compound 15 is stable for 15 days at room temperature and -20°C 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 -CH3 peak of 15 indicated chemical nonequivalency of both the –CH3 group in solution. The chemical nonequivalency of both the –CH3 groups in solution was further indicated by 13C NMR spectra of 15, 13 and 14 as they showed two peaks for both the –CH3 groups. The chemical shift of 77Se NMR of 13 (1021 ppm) is downfield as compared to bis[α(R)-(2-methylbenzylidimethyl(phenyl)phenyl)selenenyl]bromide (1066 ppm) and [2-(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 77Se NMR of (2-phenylazophenyl-C,N)selenenyl bromide (1093 ppm).13 The observation of two signals in 77Se NMR spectrum of 15 at 892 and 900 ppm indicated the presence of two types of Se atoms. The peak at 892 ppm is close to the chemical shift observed in [α-(2,6-disoproplyphenylimonomethyl)phenyl]selenenyl azide (1026 ppm)13 and the peak at 1100 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 [α-(2,6-disoproplyphenylimonomethyl)phenyl]selenenyl selenocyanate (15) was optimized at the B3LYP level of theory with the use of
the 6-31+G(d,p) basis sets. The natural bond orbital (NBO) charges showed that both selenium atoms were positively charged i.e. Se1 (+0.443) and Se2 (+0.043) (Figure S4 of ESI). However, Se2 atom was less positive than the Se1 atom. The calculated 77Se NMR chemical shifts (905, 69 ppm) of 15 are close to the observed values. The νC=S 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 νC=Se and νSe=O.\(^{18}\) The lower νC=Se stretching frequency (1591 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°. The intramolecular N1-Se1-Se2 distance (2.116(2) Å) of 15 is longer than the intramolecular N(sp\(^3\))-Se1 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\(^3\))-Se1 distance of 15 is close to the intramolecular N(sp\(^3\))-Se interaction (2.145(16) Å) of [2-[1-(3,5-dimethylphenyl)-2-naphthyl]-4,5-dihydro-4,4-dimethyloxazole] selenenyli(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)°. 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-bromide (1.943(3) Å).\(^{14}\) 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-oxazolyl)phenyl]diselenide\(^{20}\) (2.343(13) Å). The Se1-Se2 bond distance (2.6069(4) Å) is even longer than the longest Se-Se bond distance reported for diselenides i.e. [N-(6’-n-propyl-4’-pyrimidime) (6-n-propyl-2-selenouracil)](Se–Se) \(^{21,22}\) (2.4427(6) Å).

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 CIB atom and the two lone pairs are in the equatorial positions and NIB and C1A atoms are in the axial positions. The intramolecular NIB-Se distance is 2.803(13) Å and the NIB-Se-C1A angle of about 164.36(5)°. The distance is shorter than that reported for bis(N,N-dimethylamino)benzylselenide\(^{22}\) (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]benzylselenide, both nitrogens weakly coordinate to Se.

![Figure 4. (a) Molecular structure of 15 and selected bond lengths (Å) and angles (°). Hydrogen atoms are omitted for clarity. Sel-C1 1.917(2), Sel-Se1 2.0696(4), Sel–N1 2.116(2); N1-Sel-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 (°). Sel-C1 1.890(3), Sel-Br1 2.7012(4), Sel–N1 1.982(2); N1-Sel-Br1 176.23(7), C1-Se1-Br1 94.96(8)](Image 63x134 to 144x208)

The GPx-like activity of 15 was measured using ebselein as the reference.\(^{19}\) The catalytic reaction was monitored by measuring the rate of the formation of PhS\(_2\) spectrophotometrically at 305 nm (\(\epsilon_{max}=1.24 \times 10^3\ \text{M}^{-1}\text{cm}^{-1}\)). 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>
<thead>
<tr>
<th>Entry</th>
<th>Catalyst</th>
<th>(V_0) (µM/min)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>None</td>
<td>2.25 ± 0.04</td>
</tr>
<tr>
<td>2</td>
<td>Ebselein</td>
<td>2.98 ± 0.01</td>
</tr>
<tr>
<td>3</td>
<td><strong>15</strong></td>
<td>3.43 ± 0.04</td>
</tr>
</tbody>
</table>

In order to rationalize the poor GPx-like activity, the reactions of 15 with the substrate i.e. PhSH and H\(_2\)O\(_2\) 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$_2$O$_2$ (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. Further addition of H$_2$O$_2$ (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.

In 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-

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. 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$_2$Se ($^{77}$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) (1 g, 2.7 mmol), 2,6-diisopropylphenyamine (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 ºC. Anal. Calcd for C20H22N2Se2: C, 53.58; N, 6.25; H, 4.95. Found C, 53.51; N, 6.10; H, 5.19. ¹H NMR (CDCl₃): δ1.19 (d, 2H), 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). ¹³C NMR (CDCl₃): δ23.9, 28.2, 123.2, 124.8, 126.0, 131.3, 131.8, 132.7, 134.6, 138.1, 147.5, 162.5. ⁷⁷Se NMR (CDCl₃): δ467. ES-MS: (m/z) 344 (C₁₉H₂₂N₂Se⁺ (100 %)). HRMS (EI): m/z [C₃₈H₄₄N₂Se₂⁺] calcd: 689.1913, Found: 689.1929. IR (KBr, cm⁻¹): 1637 (C≡N). ¹⁰⁰ Se NMR (CDCl₃): δ396. ES-MS: (m/z) 344 (C₁₉H₂₂N₂Se⁺ (100 %)). HRMS (EI): m/z [C₃₈H₄₄N₂Se₂⁺K⁺] calcd: 488.9750, Found: 488.9773. IR (KBr, cm⁻¹): 1599.4 (v(C≡N)), 2110 (v(C≡N)).

**[o-(2,6-Diisopropylphenyliminomethyl)phenyl]selenenyldiselenocyanate (15)**

To a solution of [o-(2,6-diisopropylphenyliminomethyl)phenyl]selenenyldiselenocyanate (11) (0.15 g, 0.24 mmol) in dry CHCl₃ (10 mL) was added drop-wise a solution of KSeCN (0.03 g, 0.26 mmol) in dry CHCl₃ (10 mL) at 0 ºC. 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 CHCl₃/hexane to give pale yellow crystals (15). Yield: 0.095 g, 73%; mp 127-129 ºC. Anal. Calcd for C₃₈H₄₄N₂Se₂: C, 75.10; N, 4.61; H, 7.30. Found C, 75.05; N, 4.61; H, 7.29. ¹H NMR (CDCl₃): δ1.21-1.25 (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). ¹³C NMR (CDCl₃): δ24.2, 24.7, 28.5, 104.6, 123.9, 126.9, 128.4, 131.5, 131.8, 132.8, 132.9, 139.5, 141.4, 143.5, 161.3. ⁷⁷Se NMR (CDCl₃): δ892, 110. ES-MS: (m/z) 344 (C₃₈H₄₄N₂Se⁺ (100 %)). HRMS (EI): m/z [C₃₈H₄₄N₂Se₂⁺K⁺] calcd: 488.9750, Found: 488.9773. IR (KBr, cm⁻¹): 1599.4 (v(C≡N)), 2110 (v(C≡N)).

**Bis(o-(2,6-diisopropylphenyliminomethyl)phenyl)diselenide (17)**

Bis(o-formylphenyl)diselenide (16) (0.5 g, 1.7 mmol) was refluxed azeotropically in benzene (100 mL), with 2,6-diisopropylphenyamine (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 CHCl₃/hexane (1:4) mixture to give pale yellow crystals of 17. Yield: 0.50 g, 50%; mp 159-161 ºC. Anal. Calcd for C₃₈H₄₄N₂Se₂: C, 75.70; N, 4.61; H, 7.30. Found C, 74.82; N, 4.42; H, 7.05. ¹H NMR (CDCl₃): δ1.06 (d, 2H), 2.87-2.95 (m, 4H), 7.05-7.13 (m, 6H), 7.31-7.36 (m, 4H), 7.41 (m, 2H), 6.00 (d, 2H), 8.54 (s, 2H). ¹³C NMR (CDCl₃): 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. ⁷⁷Se NMR (CDCl₃): δ396. ES-MS: (m/z) 344 (C₃₈H₄₄N₂Se⁺ (100 %)). IR (KBr, cm⁻¹): 1637 (v(C≡N)).
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atom using SHELXS 97 and Fourier methods and refined by 30 stirs at room temperature for 2 hours. This organic layer was 15 changed from yellow to red. The reaction mixture was allowed to λ = \[\text{GIAO}\text{ method (referenced with respect to the peak of Me}_2\text{Se).29}\]

45 δ 1329. ES-MS: (m/z) 361 (C\text{19H}_{22}\text{NOSe}^+) (100 %)). IR (KBr, cm\text{-1}): 73.82; N, 4.62; H, 7.05; O, 2.29. 1H NMR (CDCl\text{3}): C38H44N2SeO: C, 73.17; N, 4.49; H, 7.11; O, 2.57. Found C, 73.19; H, 7.11; O, 2.56.

9.10; H, 3.19. 1H NMR (CDCl\text{3}): δ 6.11 (s, 1H), 7.04 (m, 2H), 7.18-7.20 (m, 1H), 7.30 (m, 4H), 7.47 (m, 2H). 13C NMR (CDCl\text{3}): δ 61.7, 125.8, 127.1, 127.6, 128.4, 128.8, 129.2, 134.0, 134.4, 137.8, 142.8. 77Se NMR (CDCl\text{3}): δ 364, 528. ES-MS: (m/z) 248 (C\text{19H}_{22}\text{NOSe}^+) (100 %)).

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

To a solution of \([\alpha,\beta,\gamma,\delta\text{disopropylphenyliminomethinyl}](+\text{phenyl})\text{selenenyl selenocyanate}\) (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 °C. Anal. Calcd for C38H44N2SeO: C, 73.17; N, 4.49; H, 7.11; O, 2.57.

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 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\textsuperscript{2} using the SHELXL 97 program.\textsuperscript{25} The hydrogens were partially located from difference electron-density maps, and the rest were fixed at calculated positions. Scattering factors were from common sources.\textsuperscript{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 77Se NMR calculations were performed at B3LYP/6-311+G (d,p) level on B3LYP/6-31+G(d)-level optimized geometries using the gauge-including atomic orbital (GIAO) method (referenced with respect to the peak of Me\text{2Se}).\textsuperscript{29}

The quantifications of orbital interaction were done by natural bond orbital (NBO) analysis at B3LYP/6-311+G(d,p) level.\textsuperscript{30}

Acknowledgements

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Notes and references


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