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PAPER

Intramolecularly coordinated azobenzene selenium derivatives: Effect of strength of the Se \cdots N intramolecular interaction on luminescence[†]

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A series of selenium derivatives (6–12) of 2-phenylazophenyl have been synthesized using *o*-lithiation route. The effect of the strength of the intramolecular Se… N interaction on the absorption spectra as well as emission spectra has been studied. The studies suggest that the secondary bonding Se… N interaction give rise to fluorescence, however, the strength of Se… N interaction cannot be directly correlated with the intensity of the fluorescence. TD-DFT calculations show that the main transition involved in the absorption spectra of the compound is the ligand based π – π * type.

Introduction

Azobenzene and its derivatives are of current interest due to their promising applications as sensors in biochemical activity,¹ molecular switches,² nanodevices³ and as π -conjugate spacers.⁴ Azobenzene is a widely used chromophore⁵ and many of its derivatives are used in the dye industries as colour enhancers. It undergoes thermal or photochemical interconversion between its cis- and trans-forms due to the flexibility of the azo-group,6 and hence does not show appreciable luminescence. However, the interaction of nitrogen atoms of the azo-group, with in-built acceptor atoms capable of forming five-membered chelate ring, imparts rigidity to the structure and thereby hinders their tendency to undergo photoisomerization. There are a few reports on the study of the fluorescent properties of such azobenzene derivatives where the enhancement in emission has been achieved by the intramolecular coordination of the azobenzene nitrogen atom with palladium (1-3) (Chart 1).⁷ The interaction of the nitrogen atom lone pair of the azo group with Lewis acids not only eliminates the possibility of its further interaction with the other nitrogen atom but also imparts the required rigidity to the system giving a nearly planar configuration. Kawashima and coworkers⁸ have utilized this concept and reported the most intensely fluorescent boron substituted azobenzene system (4) (Chart 1).

It has been shown by our group⁹ and others¹⁰ that organoselenium/tellurium compounds having suitably positioned heteroatoms (N, O or S) act as good acceptors. Although McWhin-



Chart 1 *ortho*-Coordinated azobenzene derivatives exhibiting fluorescence.

nie and coworkers have synthesized a series of azobenzene derivatives of tellurium,¹¹ there are no reports for the synthesis of the selenium derivatives of azobenzene. The selenium derivatives of methyl substituted azobenzene such as 1,2-di-*p*-tolyldiazeneselenenyl chloride, bis(1,2-di-*p*-tolyldiazene)selenide, bis(1,2-di-*p*-tolyldiazene)diselenide, (1,2-di-*p*-tolyldiazene)phenyl selenide and palladium complex of (1,2-di-*p*-tolyldiazene)phenyl selenide have been reported by Jones and Ramírez de Arellano.¹² In this paper we report the synthesis, structure and the effect of the strength of the Se ··· N interaction on the fluorescence property of the selenium derivatives of 2-phenylazophenyl.

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[†] Electronic supplementary information (ESI) available: Important spectroscopic data for all the compounds, optimized geometry along with coordinates, computational details. CCDC reference numbers 777091– 777095. For ESI and crystallographic data in CIF or other electronic format see DOI: 10.1039/c0dt01319f

Results and discussion

Synthesis of the compounds

Lithiation of 2-iodoazobenzene (5) at -114 °C in ether followed by the treatment of resulting (2-phenylazophenyl-C,N')lithium with SeCl₂ yielded the desired product bis(2phenylazophenyl-C, N')selenide (6) in 19% yield along with (2-phenylazophenyl-C, N') selenenyl(II) chloride (7) and (2phenylazophenyl-C, N')selenenyl(II) iodide (8) in 14% and 8%yield respectively (Scheme 1). The formation of 7 is probably due to the partial substitution of the chloro group in SeCl₂. The exchange reaction between 7 and in situ generated LiI may result in the formation of the iodide derivative 8. Compounds 6-8 were separated by column chromatography and were crystallized from chloroform-hexane (6), ethylacetate/hexane (7) and acetone/hexane (8). All the three isolated compounds were found to be stable in the solid state as well as in solution. (2-Phenylazophenyl-C, N')selenenyl(II) chloride (7) was also prepared by reaction of SeCl₄ with bis(2-phenylazophenyl-C,N')mercuric(II) in tetrahydrofuran.^{12b}



Scheme 1 Synthesis of 6, 7, 8 and 9.

The treatment of (2-phenylazophenyl-C,N')lithium with SeBr₄ gave a dark brown solid and a red liquid (Scheme 1). The solid when dissolved in acetone/hexane mixture resulted in the isolation of red crystals of (2-phenylazophenyl-C,N')selenenyl(II) bromide (9). Decomposition of the deep red liquid during column chromatography made its purification difficult. The oxidation of bis(2-phenylazophenyl-C,N')selenide (6) by *m*-CPBA at -78 °C gave bis(2-phenylazophenyl-C,N')selenoxide (10), whereas, its reduction with LiAlH₄ under refluxing condition gave partly reduced bis(2-phenylhydrazophenyl-C,N')selenide (11) (Scheme 2). The reduced derivative 11 was found to be unstable at room temperature if kept for a few hours. Inspite of its unstable nature, we were successful in characterization of 11 by all spectroscopic techniques. Suitable crystals of 11 for structure determination could not be obtained. Treatment of the ethanolic solution of

EtOH, N2H4.H2O

rt, 3 l

(12

Scheme 2 Synthesis of 10, 11 and 12.

| Entry | ⁷⁷ Se(expt) (ppm) | ⁷⁷ Se(cal) ^{<i>a</i>} (ppm) | | |
|-------|------------------------------|---|--|--|
| 6 | 384 | 391 | | |
| 7 | 1142 | 1063 | | |
| 8 | 1074 | 1150 | | |
| 9 | 1093 | 995 | | |
| 10 | 873 | 840 | | |
| 11 | 215 | 202 | | |
| 12 | 475 | 450 | | |

7 with an excess of hydrazine hydrate at room temperature gave the desired bis(2-phenylazophenyl-C, N')diselenide (12) as a yellow precipitate (Scheme 2).

Compounds 6-12 were characterized by FT-IR, ¹H, ¹³C, ⁷⁷Se NMR spectroscopy, ES-MS and elemental analysis. ES-MS spectra of compounds 7, 8, 9, 11 and 12 did not show the molecular ion peak, however, the highest peak at m/z 261 corresponding to $[C_{12}H_9N_2Se]^+$ was observed. For compound 6 and 10 molecular ion peaks were observed at 443 $[M + 1H]^+$ and 459 $[M + 1H]^+$ respectively. The ⁷⁷Se NMR chemical shift of the synthesized derivatives is given in Table 1. The ⁷⁷Se NMR signal for **6** appeared at 384 ppm. The signal for the chloro derivative 7 appeared at 1142 ppm, whereas for the bromo derivative 9 and iodo derivative 8, the signals appeared at 1093 and 1074 ppm respectively. The upfield shift in ⁷⁷Se NMR chemical shift for compound 9 or 8 as compared to 7 can be related to their differences in electronegativity as well as to the strength of Se \cdots N interaction (vide infra). The ⁷⁷Se NMR signal for 10 appeared at 873 ppm. The upfield shifting of ⁷⁷Se NMR signal for the reduced derivative 11 compared to 6 could be due to weak Se... N interaction in the former. The ⁷⁷Se NMR spectrum for 12 showed the presence of a signal at 475 ppm.

Description of the structures

Molecular geometry of 6 is shown in Fig. 1. Selected bond lengths and bond angles are given in Table 2. The geometry around selenium atom in 6 is T-shaped. The azobenzene rings are twisted with respect to each other at an angle of 66.58°. The intramolecular $N2B \cdots$ Se distance is 2.621(5) Å with the $N2B \cdots$ Se–C1A angle of about 168.06(17)° and indicates a good overlap between the donor (N2B) and the acceptor (Se-C1A). The distance is fairly shorter than the sum of the van der Waals radii of selenium (1.90 Å) and nitrogen (1.55 Å).¹³ The C1A–Se–C1B angle is about 99.2(2)°. Due to the presence of the intramolecular Se ··· N interaction, the trans Se-C1A bond length (1.953(5) Å) is slightly longer than Se-C1B (1.918(5) Å), yet these are in close agreement to the value of 1.93 Å for Se-C bond as suggested by Pauling.¹⁴ Although, the distance between Se and N1A (3.070(4) Å) is also less than sum of the van der Waals radii of selenium and nitrogen, DFT calculations did not show any interaction between them (vide infra).

An ORTEP view of 7 is shown in the Fig. 2, and selected bond lengths and bond angles are listed in Table 2. Compound 7 crystallizes with two molecules in the asymmetric unit. The geometry around selenium is T-shaped and is close to the previously reported 1,2-di-*p*-tolyldiazeneselenenyl chloride and other derivatives.^{9e,12a,15} The intramolecular N2A...Se1 (1.965(5) Å)

n-CPBA, -78 °C CH₂CI₂, 25 min

THF, LIAIHA, 0 °C

rt, 3,5 h

| -10 |
|-----|
| |

| Entry | 6 | 7 X = Cl1 | 8 X = I | 9 X = Br | 10 X = O |
|---------------------|-------------------|------------|----------------|-----------------|---------------------|
| Se–C | 1.918(5)/1.953(5) | 1.874(6) | 1.874(5) | 1.854(2) | 1.953(16)/1.953(15) |
| $Se \cdots N$ | 2.621(5) | 1.965(5) | 2.053(5) | 2.025(2) | 2.735(9) |
| Se-X | _ `` | 2.493(16) | 2.829(7) | 2.665(4) | 1.664(12) |
| C-Se-C/X | 99.2(2) | 93.3(2) | 96.95(18) | 96.06(7) | 97.25(7) |
| $N \cdots Se{-}C/X$ | 168.06(17) | 174.13(15) | 176.39(13) | 174.73(6) | 169.26(6) |



Fig. 1 Molecular structure of 6 with 50% probability of thermal ellipsoids.



Fig. 2 Molecular structure of 7 with 50% probability of thermal ellipsoids.

and N2B···Se2 (2.002(5) Å) distances in both the asymmetric units of 7 are shorter than the related derivatives 1,2di-*p*-tolyldiazeneselenenyl chloride (2.025(3) Å)^{12a} and [2-(4,4dimethyl-2-oxazolinyl)phenyl]selenenyl chloride (2.052(2) Å).^{15b} Nonetheless, it is comparable to [2-(2-phenyl-5,6-dihydro-4*H*-1,3-oxazinyl)]selenenyl chloride (1.964(3) Å).^{9e} Another notable feature of the structure is the presence of weak intermolecular interaction between hydrogen and chlorine H3BA ··· Cl1 2.784(2) Å (C3B–H3BA ··· Cl1; 131.01(36)°).

The strength of intramolecular $Se \cdots N$ interaction depends on several factors and one of them is a proper overlap of donor and acceptor orbitals which in turn depends on the angle formed between these orbitals. It can be seen from Table 2 that the strength of intramolecular $Se \cdots N$ interaction is higher in selenenyl chloride 7, selenenyl bromide 9 (Fig. 4) and selenenyl iodide 8 (Fig. 3). This is also supported by the concomitant increase in $N \cdots Se-X$ bond angles which are closer to linearity than those in other derivatives.



Fig. 3 Molecular structure of 8 with 50% probability of thermal ellipsoids.



Fig. 4 Molecular structure of 9 with 50% probability of thermal ellipsoids.

Fig. 5 shows the molecular structure of the selenoxide 10 stabilized by intramolecular coordination. Selected bond lengths and bond angles are listed in Table 2. The geometry around selenium atom is distorted tetrahedral with N2B \cdots Se=O bond angle being 169.26(6)°. The secondary bonding Se...N2B distance 2.735(9) Å, is longer than that observed in preceding structures. The longer Se ··· N distance or weaker interaction in 10 could be probably due to the higher energy difference between the overlapping orbitals. The Se=O distance 1.664(12) Å is considerably shorter than the sum of covalent radii for oxygen and selenium (O, 0.68 Å; Se, 1.22 Å) indicating a double bond character and the value is in close agreement with that of reported structures such as bis(p-methoxyphenyl)selenoxide (1.665(2) Å), 4-[(-)menthyloxycarbonyl]phenyl 2,4,6-tri-isopropylphenyl selenoxide (1.662(7) Å), 2,3-dihydro-2-isopropyl-7-(N-isopropylcarbamoyl)-1,2-benzisoselenazole-1,1,3-oxide (1.664(3) Å), 1,1'-dinaphthyl selenoxide (1.653(3) Å), bis(2,4,6-trimethylphenyl)selenoxide (1.674(4) Å), bis(N,N-dimethylbenzylaminephenyl)selenoxide (1.701(3) Å) and many more.¹⁶ Interestingly, the structure shows



Fig. 5 Molecular structure of 10 with 50% probability of thermal ellipsoids.

the presence of a relatively strong C–H···O secondary interaction in one dimension (along *a* axis) with H···O distance being 2.324(4) Å and C–H···O angle being 164.18(11)°. In contrast to all previously reported structure of selenoxides,¹⁶ except bis(*N*,*N*dimethylbenzylaminephenyl)selenoxide^{16e} which have either polymeric or dimeric structure due to secondary Se···O interaction, in the case of **10** such interaction was absent and **10** exists as a monomer.

Absorption and emission spectroscopy

The UV-visible spectra for azobenzene, (2-phenylazophenyl-C,N')iodide (5) and compounds 6–10 and 12 (Fig. 6) were recorded at 10^{-5} M concentration at room temperature in chloroform. Also see Figure S1, S2 and S3 in Supplementary Information.† The spectra show mainly two types of transitions for all the compounds. The band lying in the range of 300–350 nm is associated with symmetry allowed ligand based π – π * transition. The relatively lower intensity bands lying in the region of 400– 470 nm originates due to n- π * transition.



Fig. 6 Graphical representation of UV-vis spectra for 5-10 and 12 in CHCl₃ at 10^{-5} M concentration.

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A considerable shift was observed in the λ_{max} for all the selenium derivatives (6–10 and 12) as compared to azobenzene and 5, suggesting a change in their electronic environment. This change may arise due to the presence of different substituents on selenium as well as difference in the secondary bonding Se… N intramolecular interaction energy (*vide infra*). In the case of 8, a relatively weak absorption at λ_{max} 297 nm due to π - π * transition is also observed. The transitions with their respective absorption coefficients are given in Table 3.

From Table 3 it can be seen that the halo derivatives 7, 8 and 9 possessing stronger secondary bonding Se… N interaction (63–75 kcal mol⁻¹) show bathochromic shift in comparison to other derivatives (6, 10 and 12), which have relatively weaker intramolecular Se… N interaction (5–18 kcal mol⁻¹). This implies that strong intramolecular Se… N interactions may play some role in reducing the energy gap between the orbitals involved in transition and thereby leading to bathochromic shift in absortion spectra.

The fluorescence studies for all compounds (azobenzene, 5-10 and 12) were carried out at 273 K in chloroform at 2×10^{-7} M concentration. When irradiated at their respective absorption wavelengths (320-355 nm), nearly all the selenium derivatives of 2-phenylazophenyl 6-10 and 12 showed emission in the region of 350-400 nm (Fig. 7). See Figure S4 and S5 in Supplementary Information.[†] Similar to the absorption spectra, a bathochromic shift was observed in the fluorescence spectra (Fig. 7). However, as expected, no remarkable enhancement of intensity in the fluorescence spectra was observed for the compounds except 6. The quantum yield for the synthesized compounds (6-10 and 12) (Table 3) was found to be lower than that reported for the intramolecularly B-N coordinated azobenzene derivative.8 However, some of the azobenzene selenium derivatives were found to exhibit higher value of quantum yield in comparison to the palladium derivative[‡] (0.012).^{7b}



Fig. 7 Emission spectra of compound 6–10 and 12 at 2×10^{-7} M.

[‡] Palladium derivative **2** in the reference 7b was synthesized and its quantum yield was measured.

Table 3 Spectroscopic data for azobenzene, 5-10 and 12 recorded in CHCl₃

| Entry | λ_{max} (Abs) (nm) | | $\epsilon \left(M^{-1} \ cm^{-1} ight)$ | | | |
|------------|----------------------------|---------------|---|---------------|----------------------------|----------------|
| | π-π* | n– π * | π–π* | n– π * | λ_{max} (Ems) (nm) | $arPsi_{ m F}$ |
| Azobenzene | 322 | 440 | 42000 | 1120 | _ | |
| 5 | 323 | 442 | 23000 | 580 | _ | |
| 6 | 322 | 404 | 58000 | 15000 | 358 | 0.040# |
| 7 | 349 | 432 | 58000 | 11700 | 387 | 0.0091# |
| 8 | 351, 297 | 472 | 40000, 40000 | 8400 | 372 | 0.0058# |
| 9 | 355 | 439 | 38000 | 12200 | 395 | 0.079# |
| 10 | 330 | 450 | 79000 | 2600 | 358 | 0.042# |
| 12 | 339 | 445 | 41000 | 1900 | 380 | 0.0072# |

 λ_{max} (Abs) = Wavelength of absorption, λ_{max} (Ems) = Wavelength of emission, # = quantum yield for all the compounds have been calculated by using "anthracene" as a standard at 0⁻⁶ M in CHCl₃. For "anthracene" the quantum yield in CHCl₃ is 0.11.¹⁷

Table 4 Comparison of the experimentally obtained structural parameters (Å and deg) with that computed at B3LYP/6-31+G(d) and NBO interaction energy at 6-311+G(d,p) level

| Entry | $r_{\text{Se} \cdots \text{N}} (\text{\AA})^a$ | $\theta_{\mathrm{N}\cdots\mathrm{Se-O/C/Se}}$ (°) ^{<i>a</i>} | $q_{\rm Se}$ | $q_{\rm N}$ | $E_{\text{Se}\cdots \text{N}}$ (kcal mol ⁻¹) |
|-------|--|---|--------------|-------------|--|
| 6 | 2.623 | 170.69 | 0.531 | -0.232 | 10.77 |
| | (2.621) | (168.06) | | | |
| 7 | 2.110 | 173.79 | 0.690 | -0.279 | 75.44 |
| | (1.965) | (174.15) | | | |
| 8 | 2.217 | 176.39 | 0.498 | -0.234 | 62.76 |
| | (2.053) | (176.39) | | | |
| 9 | 2.139 | 175.24 | 0.607 | -0.262 | 73.80 |
| | (2.025) | (174.73) | | | |
| 10 | 2.818 | 168.15 | 1.437 | -0.220 | 4.91 |
| | (2.735) | (169.26) | | | |
| 11 | 2.898 | 167.01 | 0.393 | -0.454 | 3.99 |
| | | | | | |
| 12 | 2.520 | 174.07 | 0.314 | -0.225 | 18.17 |
| | | | | | |

" Experimental values are given in parenthesis q_{se} charge on selenium, q_N charge on nitrogen

Computational studies

Quantification of Se…N interaction in the synthesized compounds. Density functional theory (DFT) calculations were performed on all the synthesized compounds (6–12) using Gaussian03 package.¹⁸ These electronic structure calculations have been used as a tool in explaining the existing secondary bonding intramolecular interactions. Beside other parameters, the Se…N distances obtained from these calculations were found to be in good agreement with that observed for the crystal geometry for compound 6–10. The second order perturbation energies were obtained from NBO analyses¹⁹ for Se…N interaction in all the compounds. These values were found to be of the order of 3.99 kcal mol⁻¹ for **11** to the maximum upto 75.44 kcal mol⁻¹ for **7**. The values are summarized in the Table 4.

Effect of the strength of Se \cdots N interaction on electronic properties. Time-dependent DFT calculations performed at the B3LYP/6-31+G(d) level of theory also support that the absorption bands in the region of λ_{max} 300–360 nm arise mainly due to π – π * transition (Table 5). The orbitals involved in the UV-vis transitions for all the compounds are mainly ligand based and transitions take place from occupied orbitals (HOMO-2, HOMO-3 and HOMO-4) to LUMO or LUMO + 1 (see Supplementary Information 

Table S1^{\dagger}). A pictorial representation of the orbitals involved in transition for **6** is shown in Table 5.

The peak at λ_{max} 297 in **8** arises due to the transition between ligand based HOMO-4 and substituent (Se–I) based LUMO orbital (see Supplementary Information Table S1).† These assignments are made by comparing the observed and the computed transitions on the basis of respective absorptivity and oscillator strength values. The details of transitions along with the molecular orbitals involved are given in Table 6. For n- π^* transitions see Table S2 in Supplementary Information.†

Experimental section

All the reactions were carried out under strict exclusion of oxygen and moisture. Starting material (2-phenylazophenyl-C,N')mercury(II) chloride,²⁰ 2-iodoazobenzene²¹ was prepared from reported literature procedure. *n*-BuLi, Selenium powder, LiAlH₄ were purchased from Sigma-Aldrich and SeBr₄ from Alfa Aesar. Solvents used were dried according to standard method and were freshly distilled under N₂ atmosphere prior to use.

Physical techniques

¹H, and ¹³C NMR spectra were recorded on Varian VXR 400S spectrometer, chemical shifts were referred by taking tetramethylsilane (Me₄Si) as internal standard. ⁷⁷Se NMR spectra were recorded on Varian VXR 300S spectrometer with dimethylselenide (Me₂Se) as external standard. FT-IR spectra were recorded as KBr pellets on a Nicolet Impact 400 FTIR spectrometer. The Electro-spray mass spectra (ES-MS) were performed in a Q-Tof micro (YA-105) mass spectrometer. Melting points was recorded on Veego VMP-I instrument. Elemental analyses were performed

| Entry | | | Excitation Wavele | | |
|-------|--------------|----------|-----------------------|-----------------------|----------------------------|
| | МО | LUMO | λ_{max} (exp) | λ_{max} (cal) | Oscillatory Strength (f) |
| 6 | HOMO-2 (37%) | LUMO + 1 | 322 | 336 & | 0.2767 |
| | HOMO-3 (64%) | | | 333 | 0.4822 |
| 7 | HOMO-2 (47%) | LUMO | 349 | 331 & | 0.1810 |
| | HOMO-3 (68%) | | | 342 | 0.1824 |
| 8 | HOMO-4 (73%) | LUMO | 351 | 349 | 0.4044 |
| 9 | HOMO-4 (57%) | LUMO | 355 | 352 & | 0.2669 |
| | HOMO-2 (54%) | | | 365 | 0.1968 |
| 10 | HOMO-2 (53%) | LUMO | 330 | 364 | 0.0804 |
| 12 | HOMO-4 (46%) | LUMO | 339 | 343 | 0.6344 |

Table 6Comparison of the experimental and computed absorption wavelength along with their respective oscillatory strength and percentagecontribution of molecular orbital at B3LYP/6-31+G(d)

on a Carlo-Erba model 1106 elemental analyzer. The UV-vis spectral analysis was recorded on a Jasco-570 spectrophotometer. Fluorescence studies were carried out using a Perkin-Elmer LS55 luminescence spectrometer.

Synthesis

bis(2-phenylazophenyl-C, N')selenide (6). To a solution of 2iodoazobenzene (3.00 g, 9.74 mmol) in dry ether (40-50 mL) was added a solution of n-BuLi (6.70 mL, 10.70 mmol) dropwise at -114 °C. The reaction mixture was stirred for 0.5 h at this temperature. To the reaction mixture was then added a solution of SeCl²² (Se; 0.39 g, 4.94 mmol, SO₂Cl₂; 0.40 mL, 4.96 mmol) in tetrahydrofuran (10 mL) (prepared in a separate Schlenk flask) dropwise. The temperature was maintained at -114 °C during the transfer. After addition, the reaction was allowed to attain the room temperature slowly. After stirring for 7 h at this temperature (monitored via TLC), the reaction mixture was filtered through celite pad and the solvent volume reduced. The crude reaction mixture was loaded on silica gel column for purification. The elution of column with petroleum ether gave unreacted azobenzene and 6, further treatment with petroleum ether/ethyl acetate (99:1; 98:2) gave 7 and 8 as yellow and black solid respectively.

6 Yield: 0.40 g, 19%. M.p 102–104 °C. ¹H NMR (400 MHz, CDCl₃): δ = 8.00–7.82 (m, 6 H), 7.53–7.41 (m, 8 H), 7.37 (td, ³*J* = 7.6 Hz, ⁴*J* = 1.2 Hz, 2H), 7.27 (td, ³*J* = 7.9 Hz, ⁴*J* = 1.5 Hz, 2H). ¹³C NMR (400 MHz, CDCl₃): δ = 152.5, 152.1, 134.3, 133.0, 131.3, 131.3, 129.2, 128.0, 123.3, 121.1. ⁷⁷Se NMR (300 MHz, CDCl₃): δ = 384. ES-MS: *m/z* 443 [M + 1H]⁺, 260 [M–1H–C₁₂H₉N₂]⁺. FT-IR: (v_{N=N}) 1583, (v_{C-H}) 772 cm⁻¹. Anal. Calc. for C₂₄H₁₈N₄Se: C, 65.31; H, 4.11; N, 12.69. Found: C, 65.20; H, 3.78; N, 12.06.

7 Yield: 0.40 g, 14%. M.p 135–137 °C. ¹H NMR (400 MHz, CDCl₃): δ = 8.98 (d, ³*J* = 8.2 Hz, 1H), 8.57 (d, ³*J* = 7.9 Hz, 1H), 8.07 (d, ³*J* = 7.0 Hz, 2H), 7.82–7.73 (m, 2H), 7.62 (d, ³*J* = 6.4 Hz, 3H). ¹³C NMR (400 MHz, CDCl₃): δ = 151.9, 147.2, 145.0, 132.9, 132.6, 130.5, 129.8, 129.7, 128.9, 122.6. ⁷⁷Se NMR (300 MHz, CDCl₃): δ = 1142. ES-MS: *m/z* 231 [M–Cl–N₂]⁺. FT-IR: (v_{N=N}) 1617, (v_{C-H}) 766 cm⁻¹. Anal. Calc. for C₁₂H₉N₂ClSe: C, 48.75; H, 3.07; N, 9.48. Found: C, 48.22; H, 2.60; N, 8.31.

8 Yield: 0.20 g, 8%. M.p 90–92 °C. ¹H NMR (400 MHz, CDCl₃): δ = 8.75 (dd, ³*J* = 6.1 Hz, ⁴*J* = 3.6 Hz, 1H), 8.44 (dd, ³*J* = 6.1 Hz, ⁴*J* = 3.6 Hz, 1H), 8.06 (d, ³*J* = 7.4 Hz, 2H), 7.75 (dd, ³*J* = 6.1 Hz, ⁴*J* = 3.6 Hz, 2H), 7.69–7.57 (m, 3H). ¹³C NMR (400 MHz, CDCl₃): δ = 151.8, 144.6, 140.7, 135.2, 132.7, 132.6, 130.5, 130.4, 128.8, 123.1. ⁷⁷Se NMR (300 MHz, CDCl₃): δ = 1074. ES-MS: *m/z* 261 [M–I]⁺. FT-IR: (v_{N=N}) 1617, (v_{C-H}) 766 cm⁻¹. Anal. Calc. for C₁₂H₉N₂ISe: C, 37.24; H, 2.34; N, 7.24. Found: C, 37.64; H, 1.65; N, 6.90.

(2-phenylazophenyl-C, N') selenenyl bromide (9). To the solution of 2-iodoazobenzene (1.20 g, 3.9 mmol) in dry ether (40 mL) was added a solution of n-BuLi (2.7 mL, 4.3 mmol) dropwise at -114 °C. The reaction mixture was stirred for 0.5 h at this temperature. To this was then added SeBr₄ (1.55 g, 3.9 mmol) and the reaction mixture was allowed to attain room temperature. Dark brown solid started precipitating after 1 h. The stirring was continued for further 2 h and reaction mixture was filtered off and volume was reduced. The brown solid obtained from filtration was dissolved in ethylacetate/acetone and kept for crystallization to afford dark black-red crystals of 9. Yield: 0.30 g, 24%. M.p 154-156 °C. ¹H NMR (400 MHz, CDCl₃): δ = 8.97 (dd, ³J = 7.6 Hz, ${}^{4}J = 1.5$ Hz, 1H), 8.54 (dd, ${}^{3}J = 7.3$ Hz, ${}^{4}J = 1.5$ Hz, 1H), 8.08 (td, ${}^{3}J = 6.7$ Hz, ${}^{4}J = 1.5$ Hz, 2H), 7.84–7.74 (m, 2H), 7.67–7.58 (m, 3H). ¹³C NMR (400 MHz, CDCl₃): δ = 151.8, 145.2, 144.8, 132.9, 132.7, 131.5, 130.5, 130.0, 129.0, 122.8. ⁷⁷Se NMR (300 MHz, CDCl₃): $\delta = 1093$. ES-MS: $m/z \ 260 \ [M-Br]^+$. FT-IR: $(v_{N=N}) \ 1617$, (v_{C-H}) 768 cm⁻¹. Anal. Calc. for C₁₂H₉N₂BrSe: C, 42.38; H, 2.67; N, 8.24. Found: C, 42.38.; H, 2.29; N, 7.74.

bis(2-phenylazophenyl-C, N')selenoxide (10). The solution of m-chloroperbenzoic acid (0.03 g, 0.17 mmol) in dry dichloromethane (15 mL) was cooled to -78 °C. To it was added 6 (0.08 g, 0.18 mmol) and the mixture was allowed to stir at this temperature for 20 to 25 min. Then it was poured into a solution containing saturated NaHCO₃ and dichloromethane, the organic layer was separated, washed thrice with water, dried over MgSO₄ and filtered. The filtrate was concentrated to give an orange solid of the desired compound. Light orange crystals of 10 were obtained from acetonitrile-hexane. Yield: 0.07 g, 87%. M.p 192-194 °C. ¹H NMR (400 MHz, CDCl₃): δ = 8.02 (dd, ³J = 7.6 Hz, ⁴J = 2.1 Hz, 2H), 7.93 (dd, ${}^{3}J = 7.0$ Hz, ${}^{4}J = 2.1$ Hz, 2H), 7.85 (dd, ${}^{3}J = 7.3$ Hz, ${}^{4}J = 1.2$ Hz, 4H), 7.64–7.57 (m, 4H), 7.44–7.40 (m, 2H), 7.31 (t, ${}^{3}J$ = 7.9 Hz, 4H). 13 C NMR (400 MHz, CDCl₃): δ = 151.8, 149.8, 141.7, 132.7, 132.2, 131.9, 129.3, 128.2, 123.5, 122.3. ⁷⁷Se NMR (300 MHz, CDCl₃): δ = 873. ES-MS: *m*/*z* 459 [M + $1H^{+}$. FT-IR: $(v_{N=N})$ 1617, (v_{Se-O}) 815, (v_{C-H}) 773 cm⁻¹. Anal. Calc. for C₂₄H₁₈N₄OSe: C, 63.02; H, 3.97; N, 12.25. Found: C, 63.42; H, 3.72; N, 11.53.

| Compound reference | 6 | 7 | 8 | 9 | 10 |
|--|---------------------|--|---|--|----------------------|
| Chemical formula | $C_{24}H_{18}N_4Se$ | C ₁₂ H ₉ ClN ₂ Se | C ₁₂ H ₉ IN ₂ Se | C ₁₂ H ₉ BrN ₂ Se | $C_{24}H_{18}N_4OSe$ |
| Formula Mass | 441.38 | 295.62 | 387.07 | 340.08 | 457.38 |
| Crystal system | Monoclinic | Orthorhombic | Monoclinic | Monoclinic | Triclinic |
| a/Å | 6.6012(2) | 21.7803(5) | 4.7893(2) | 5.0040(3) | 7.6202(3) |
| b/Å | 14.1846(5) | 7.4278(2) | 18.4538(10) | 15.4165(8) | 10.8698(7) |
| c/Å | 21.3931(6) | 28.0087(8) | 13.7159(9) | 15.0856(5) | 14.2205(11) |
| α (°) | 90.00 | 90.00 | 90.00 | 90.00 | 109.327(7) |
| β (°) | 91.785(3) | 90.00 | 91.237(6) | 90.843(3) | 91.414(5) |
| γ (°) | 90.00 | 90.00 | 90.00 | 90.00 | 109.014(5) |
| Unit cell volume/Å ³ | 2002.18(11) | 4531.2(2) | 1211.94(11) | 1163.64(10) | 1039.21(11) |
| T/K | 200(2) | 200(2) | 200(2) | 200(2) | 200(2) |
| Space group | $P12_{1}/n_{1}$ | Pbca | $P12_{1}/n_{1}$ | $P12_{1}/n_{1}$ | $P\overline{1}$ |
| No. of formula units per unit cell, Z | 4 | 16 | 4 | 4 | 2 |
| Radiation type | Μο-Κα | Μο-Κα | Μο-Κα | Μο-Κα | Μο-Κα |
| Absorption coefficient, μ/mm^{-1} | 1.893 | 3.521 | 5.618 | 6.632 | 1.830 |
| No. of reflections measured | 20121 | 127615 | 10827 | 9770 | 15375 |
| No. of independent reflections | 6503 | 7919 | 3995 | 3831 | 6806 |
| R _{int} | 0.0583 | 0.1338 | 0.0498 | 0.0433 | 0.0335 |
| Final R_1 values $(I > 2\sigma(I))$ | 0.0817 | 0.0639 | 0.0509 | 0.0327 | 0.0315 |
| Final $wR(F^2)$ values $(I > 2\sigma(I))$ | 0.1888 | 0.1548 | 0.1101 | 0.0526 | 0.0592 |
| Final R_1 values (all data) | 0.1317 | 0.1585 | 0.1091 | 0.0820 | 0.0568 |
| Final $wR(F^2)$ values (all data) | 0.2109 | 0.2254 | 0.1210 | 0.0571 | 0.0648 |
| Goodness of fit on F^2 | 1.112 | 1.094 | 0.868 | 0.840 | 0.936 |

 Table 7
 Crystal data and structural refinement parameter for 6, 7, 8, 9, and 10

bis(2-phenylhydrazophenyl-C,N')**selenide (11).** To the solution of 6 (0.46 g, 1.04 mmol) in tetrahydrofuran (15 mL) at 0 °C was added LiAlH₄ (0.04 g, 1.04 mmol) portion wise. The mixture was allowed to come to the room temperature slowly. The colour of reaction mixture changed from deep red to light orange and finally to light yellow. Reaction was stopped after 3.5 h (monitored via TLC), usual work up procedure was followed. The crude product so obtained was treated with hexane to get 11 as off-white solid. Yield: 0.12 g, 26%. M.p. ~50 °C. ¹H NMR (400 MHz, CDCl₃): δ = 7.50 (dd, ${}^{3}J = 7.6$ Hz, ${}^{4}J = 1.5$ Hz, 1H), 7.19 (t, ${}^{3}J = 7.0$ Hz, 1H), 7.10 (t, ${}^{3}J = 7.6$ Hz, 2H), 7.01 (dd, ${}^{3}J = 8.1$ Hz, ${}^{4}J = 1.2$ Hz, 1H), 6.81-6.73 (m, 2H), 6.63 (d, ${}^{3}J = 7.6$ Hz, 2H), 6.43 (s, 2H), 5.60 (s, 2H). ¹H NMR (400 MHz, CDCl₃, D₂O exchange): $\delta = 7.50$ (dd, ${}^{3}J = 7.6$ Hz, ${}^{4}J = 1.5$ Hz, 1H), 7.19 (t, ${}^{3}J = 7.0$ Hz, 1H), 7.10 (t, ${}^{3}J = 7.6$ Hz, 2H), 7.01 (dd, ${}^{3}J = 8.1$ Hz, ${}^{4}J = 1.2$ Hz, 1H), 6.81–6.73 (m, 2H), 6.63 (d, ${}^{3}J = 7.6$ Hz, 2H). ${}^{13}C$ NMR (400 MHz, CDCl₃): $\delta = 148.8, 148.4, 136.0, 130.4, 129.5, 120.4, 120.3, 112.7, 112.5.$ ⁷⁷Se NMR (300 MHz, CDCl₃): δ = 215. ES-MS: m/z 261 [M–2H– $C_{12}H_{11}N_2$]⁺. FT-IR: (v_{N-H}) 3328, (v_{C-H}) 747 cm⁻¹. Anal. Calc. for C₂₄H₂₂N₄Se: C, 64.72; H, 4.98; N, 12.58. Found: C, 65.18; H, 4.94; N, 11.78.

bis(2-phenylazophenyl-C,*N'*)**diselenide (12).** To the suspension of **6** (0.10 g, 0.34 mmol) in absolute ethanol (20 mL), was added dropwise an ethanolic solution (3 mL) of hydrazine hydrate (0.13 mL, 2.47 mmol) at room temperature. As the addition proceeded, the color of the reaction mixture changed from yellow to red. After the addition was complete, the reaction mixture was allowed to stir for 3 h at room temperature and a suspension formed. The reaction mixture was then cooled to 0 °C and filtered. The precipitate so obtained was dried under vacuum. Yield: 0.04 g, 44%. M.p. 90–92 °C. ¹H NMR (400 MHz, CDCl₃): δ = 8.06–8.03 (m, 6H), 7.90 (dd, ³*J* = 7.9 Hz, ⁴*J* = 1.2 Hz, 2H), 7.57–7.51 (m, 6H), 7.39 (td, ³*J* = 7.2 Hz, ⁴*J* = 1.2 Hz, 2H), 7.29–7.25 (m, 2H). ¹³C NMR (400 MHz, CDCl₃): δ = 151.4, 151.3, 131.8, 131.6, 131.3,

129.5, 129.1, 127.3, 126.9, 123.1. ⁷⁷Se NMR (300 MHz, CDCl₃): δ = 475. ES-MS: *m*/*z* 261 [M–C₁₂H₉N₂Se]⁺. FT-IR: (v_{N=N}) 1617, (v_{C-H}) 774 cm⁻¹. Anal. Calc. For C₂₄H₁₈N₄Se₂: C, 55.40; H, 3.49; N, 10.77. Found: C, 54.72; H, 3.69; N, 9.77.

Crystal structure determination

X-ray diffraction data (Table 7) were obtained on Oxford Diffraction Gemini diffractometer using Mo-K α radiation ($\lambda = 0.71073$ Å). The structure solution was achieved by using direct methods as implemented in SHELXS-97.²³ The structure was refined by full least-squares methods using SHELXL-97.²⁴

Conclusions

In conclusion, we have successfully synthesized and characterized a series of *ortho*-selenenylated azobenzene derivatives including the first partly reduced derivative bis(2-phenylhydrazophenyl-C,N')selenide (11). It was observed that the secondary bonding Se… N interaction gives rise to fluorescence, however, their strength cannot be directly correlated with the intensity of the fluorescence.

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