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Preparation and Structure of New Diazaselenuranes. Transannular Hypervalent Bond between Seleno and Diamino Groups

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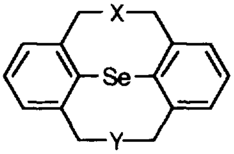
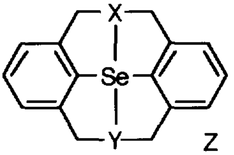
Abstract: The transannular reaction of *N*-benzyl derivatives of 1,11-(methanoaminomethano)-5*H*,7*H*-dibenzo[*b*,*g*][1,5]selenazocine (**1** and **2**) with *N*-bromosuccinimide (NBS) gave an aminoammonio-selenurane **4** which is the first example of an isolable diazaselenurane with two unsymmetrical apical nitrogen ligands of tertiary amino- and quaternary ammonio-groups. X-ray analysis of the aminoammonioselenurane Br^- salt (**4a**) showed the twin-boat form; the distances of Se···N are 1.918 Å and 2.419 Å respectively. The structure of selenurane **4** in solution was confirmed by ^{77}Se and ^{15}N NMR spectroscopy using the ^{15}N-enriched aminoammonio-selenurane **4**-^{15}*N*. The apical tertiary amine of selenurane **4** behaves as a nucleophile toward benzylbromide to give the bisammonio-selenurane **5**. The aminoammonio and bisammonio-selenuranes **4** and **5** were converted into the neutral amines upon treatment with 2 equiv. of SmI_2.

There is considerable interest on the structure and reactivity of σ-sulfuranes which consist of a five-membered ring by linking two symmetrical electronegative groups such as oxygen atoms or halogen atoms at the apical positions, and sulfuranes with apical nitrogen ligands are little known.[1,2] Further, much less is known about the chemistry of hypervalent selenuranes. We recently reported that the transannular interaction between two heteroatoms (Se-N) of selenium heterocycles produced the hypervalent σ-ammonioselenurane with apical ammonio ligand.[3]

More recently, we have reported that the transannular multiheteroatoms interaction in quadruply *ortho*-bridged biphenyl ring system induced the hypervalent selenuranes containing transannular three-center bond, i.e., the three-center transannular interaction between selenium and two nitrogen atoms of *N*-benzyl derivatives of 1,11-(methanoaminomethano)-5*H*,7*H*-dibenzo[*b*,*g*][1,5]selenazocine (**1** and **2**) produced the stable aminoammonio-selenurane (**4**) which is a new type of an isolable cyclic diazaselenurane with two unsymmetrical apical nitrogen ligands of tertiary alkyl amino- and quaternary alkyl ammonio-groups.[4] This paper presents the preparation, X-ray crystal structure, and the chemical property of a new cyclic σ-selenurane having two unsymmetrical apical amino and ammonio ligands or two symmetrical ammonio groups.



1 : X, Y = N-$\mathrm{CH_2Ph}$
1-^{15}*N* : X, Y = ^{15}N-$\mathrm{CH_2Ph}$
2 : X = NH, Y = N-$\mathrm{CH_2Ph}$
3 : X, Y = NH
6 : X, Y = N-$\mathrm{CH_3}$
7 : X, Y = $\mathrm{N^+}$-$\mathrm{(CH_3)_2}$
anion = $\mathrm{2CF_3SO_3^-}$



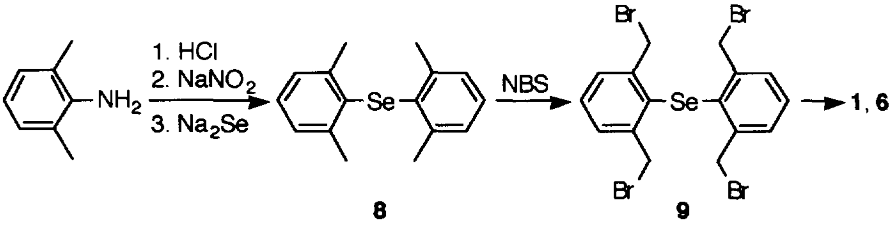
4 : X = N, Y = $\mathrm{N^+}$-$\mathrm{CH_2Ph}$, Z = $\mathrm{PF_6^-}$
4-^{15}*N* : X = ^{15}N, Y = $^{15}\mathrm{N^+}$-$\mathrm{CH_2Ph}$
Z = $\mathrm{PF_6^-}$
5 : X, Y = $\mathrm{N^+}$-$\mathrm{CH_2Ph}$, Z = $\mathrm{2PF_6^-}$

Results and Discussion

Synthesis of Cyclic Selenides

Compounds (**1** and **6**) were prepared as follows (Scheme 1). Treatment of the diazonium salt of 2,6-dimethylaniline with $\mathrm{Na_2Se}$ gave bis(2,6-dimethylphenyl)selenide (**8**) which was irradiated using a high-pressure mercury lamp after addition of *N*-bromosuccinimide (NBS) to afford the tetra-bromide **9**. The compound **9** was treated with benzylamine or methylamine using a high dilution technique at room temperature to give the compound **1** or **6**. ^{15}N-Labeled amine, **1**-^{15}*N* (^{15}N isotope enrichment, 20% and 40%, respectively), was prepared in the reaction of tetra-bromide **9** with ^{15}N-enriched benzylamine (^{15}N: 20% and 40%).

Scheme 1



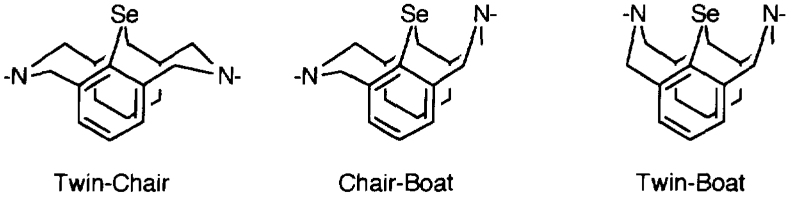
Conformation of Cyclic Diaminoselenide

The conformational behaviors in cyclic selenides (**1**-**3** and **6**) concerning eight-membered ring are of interest, because in general, three different conformers, *i.e.*, twin-chair, boat-chair, and twin-boat forms can exist as shown in Chart 1.

The conformers can be assigned by the ^1H NMR spectral data for the benzylic protons of the eight-membered ring.[5] The ^1H NMR spectra of **1** and of **2** in $CDCl_3$ at 25 °C show the benzylic methylene protons as an AB quartet peak at δ 4.02, 5.47 (J = 14.4 Hz) for **1** and at δ 4.02, 5.45 (J = 14.6 Hz) and 4.09, 5.17 (J = 14.3 Hz) for **2**, which are assigned to the twin-chair form. Similarly, the conformation of **3** or **6** is twin-chair form by ^1H NMR analysis. These conformational analyses are consistent with that of the sulfur analogous compound of **1** and **6** which was characterized by X-ray diffraction method and the ^1H NMR spectroscopy.[6]

In such compound, if one could generate a cationic species on the one group, the other functional group could interact to stabilize the cationic species, resulting in the generation of a transannular bond.

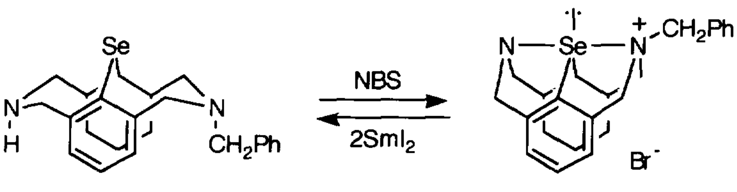
Chart 1



Diazaselenuranes

N-Bromosuccinimide [NBS, Br·N(CO·CH_2)$_2$] was used to prepare the selenide **2** and the selenurane **4**, bearing unsymmetrical apical nitrogen ligands, from **1**. NBS has been employed for the conversion of selenides into bromoselenonium cations and of tertiary amines into secondary amines.[2,7] A new structural type of aminoammonio-selenurane (**4**) was isolated from the reaction of the selenide **1** or **2** with NBS (Scheme 2). Thus, the stepwise substitution of the amino functions in **1** or **2** leads to **4**.

Scheme 2



2 **4a**

The crystal structure of the aminoammonioselenurane Br^- salt (**4a**: Z = Br^-) was determined by X-ray diffraction analysis. The X-ray data reveal no interaction between the counter anion and cation at all (Figure

1). The conformation of the selenurane **4a** is a twin-boat form. The Se-N distances are 1.918(4) Å and 2.419(4) Å which are remarkably shorter than the sum of the van der Waals radii (3.5 Å) of the two elements, indicating the transannular bond formation between Se and N. Normally, the bond length of the covalent bond of Se-N is 1.87 Å. The angle of N···Se···N is 157.5(2)° which is strongly distorted from a linear arrangement. The X-ray data suggest that the hypervalent species is considered to be stabilized by the neighboring group participation of the two nitrogen atoms.

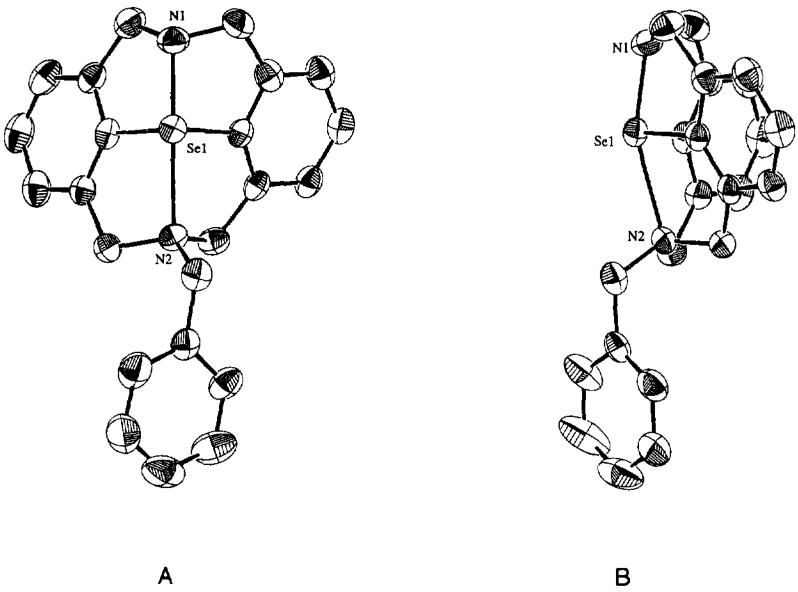


Figure 1. The crystal structure of aminoammonioselenurane **4a**. $\mathrm{Br^-}$ anion and H_2O are removed for clarity. (A) View from top. (B) Side-on view. Selected bond lengths (Å) and angles (deg): Se(1)-N(1) 1.918(4), Se(1)-N(2) 2.419(4), Se(1)-$\mathrm{C_{eq}}$ 1.885(5) and 1.906(5); N(1)-Se(1)-N(2) 157.5(2), $\mathrm{C_{eq}}$-Se(1)-$\mathrm{C_{eq}}$ 99.9(2).

The aminoammonioselenurane $\mathrm{PF_6^-}$ salt **4** was characterized by multinuclear NMR (^{1}H, ^{13}C, ^{77}Se, and ^{31}P) spectroscopy. The conformation of **4** was assigned by the ^{1}H NMR spectral data for the benzylic protons of the eight-membered ring. The ^{1}H NMR spectrum of **4** in CD_3CN at 25 °C shows the benzylic methylene protons as an AB quartet peaks at δ 3.85, 4.57 (ABq, J = 16.6 Hz) and 4.37, 4.92 (ABq, J = 15.9 Hz) which are assigned to the twin-boat form. The ^{77}Se NMR spectrum of **4** in CD_3CN shows a remarkable downfield shift to δ 846 (singlet) from δ 189 (s) for **1** and δ 198 (s) for **2** in $CDCl_3$. The ^{77}Se chemical shift of **4** is in the range characteristic for a selenurane. The selenurane **4** exists solely as a single conformer from

-40 to +170 °C as evidenced from the variable temperature ^{1}H NMR spectra. The conformation of **4** is fixed as a twin-boat form by three-center transannular bond between the selenio and two amino groups.

In order to confirm the existence of a N-Se-N$^+$ bond in the aminoammonioselenurane **4**, we prepared the ^{15}N-labeled selenurane, **4**-^{15}*N* (20% and 40% ^{15}N isotope enrichment), which was analyzed by the ^{15}N (40.56 MHz) and ^{77}Se (76.31 MHz) NMR spectroscopy. The ^{15}N NMR spectrum of **1**-^{15}*N* in CDCl$_3$ shows a single peak at δ 33.9.[8] The proton-decoupled ^{15}N NMR spectrum of the selenurane **4**-^{15}*N* in CD$_3$CN exhibits two resonances at δ 58.8 and at δ 73.6; the former resonance is assigned to the quarternary ammonium ion and the latter peak to the tertiary amine.[10,11] Particularly, each peak exhibits ^{77}Se satellite peaks due to the ^{15}N-^{77}Se coupling about the resonance at δ 58.8 ($J_{\text{N-Se}}$ = 17.0 Hz) and at δ 73.6 ($J_{\text{N-Se}}$ = 45.9 Hz). These ^{15}N-^{77}Se coupling constants determined from the ^{15}N NMR spectrum are in full agreement with those from the ^{77}Se NMR spectrum (*vide infra*). Furthermore, both ^{15}N resonances display the doublet peak due to the ^{15}N-^{15}N coupling ($^2J_{\text{N-N}}$ = 4.5 Hz) about each central peak.

Figure 2 shows the proton-decoupled ^{77}Se NMR spectra for the 40% ^{15}N-enriched selenurane **4**-^{15}*N* (spectrum A), the 20% ^{15}N-enriched selenurane **4**-^{15}*N* (spectrum B), and the unlabeled selenurane **4** (spectrum C). The isotopomers of **4**-^{15}*N* are as follows (^{14}N is denoted as N): N-Se-N$^+$-Bnz (*4a*), ^{15}*N*-Se-N$^+$-Bnz (*4b*), N-Se-^{15}*N*$^+$-Bnz (*4c*), and ^{15}*N*-Se-^{15}*N*$^+$-Bnz (*4d*). Each peak of *a-d* in Figure 2A is assigned as follows. The single peak *a* corresponds to the Se-N bond of isotopomer *4a*, and the satellite peaks *c* is due to the coupling of ^{77}Se-^{15}N of the quarternary ammonium ion ($J_{\text{Se-N}}$ = 17.0 Hz) in isotopomer *4c*. An upfield isotope shift of 0.112 ppm resulting from substitution of ^{15}N for ^{14}N on the ^{77}Se NMR chemical shift of isotopomer *4b* was observed; i.e., the doublet peak *b* is due to the coupling of ^{77}Se-^{15}N of the tertiary amine ($J_{\text{Se-N}}$ = 45.9 Hz) in isotopomer *4b*.[12,13] Peak *d* is attributable to the ^{77}Se-^{15}N coupling of an isotopomer *4d*. The intensities of peaks, *b-d*, in Figure 2A are ca. 24% for peaks *b* and *c*, and ca. 16% for peak *d*, respectively, these values being consistent with the population of the isotopomers. The ^{77}Se and ^{15}N spectral data clearly indicates the existence of a transannular N-Se-N bond.

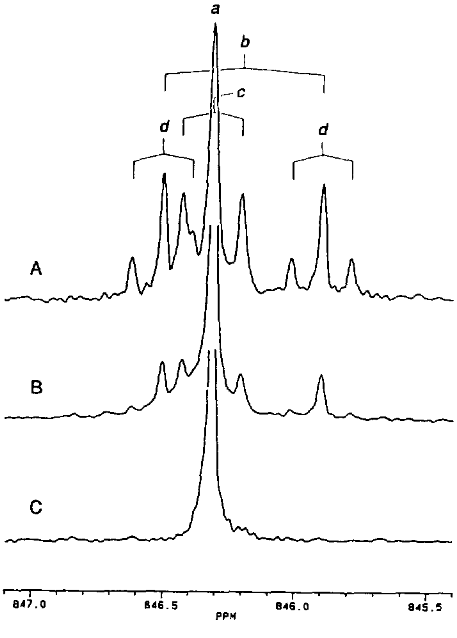


Figure 2. Proton-decoupled ^{77}Se NMR spectra (76.31 MHz) of (A) 40% ^{15}N-enriched selenurane **4**-^{15}*N*, (B) 20% ^{15}N-enriched selenurane **4**-^{15}*N*, and (C) unlabeled selenurane ^{14}N-**4** in CD$_3$CN. Coupling constant for each peak: (*b*) $J_{\text{Se-N}}$ = 45.9 Hz and (*c*), (*d*) $J_{\text{Se-N}}$ = 17.0 Hz.

Interestingly, **4** was reacted with benzylbromide (1 equiv) to give the first bisammonio-selenurane having two symmetrical apical ammonium cations (**5**), where the selenium-bonded tricoordinated nitrogen atom of **4** is basic in character. The conformation of **5** in CD_3CN is a twin-boat form, *i.e.*, the benzylic methylene protons appear at δ 4.35 and 5.05 (ABq, J = 16.2 Hz). The tetracoordinated selenium species should be formed as evidenced by the ^{77}Se NMR spectrum (δ 940) of **5**. The bisammonioselenurane **5** was stable and **5** exists solely as a single conformer, twin-boat form, from -50 to +130 °C as evidenced from the variable-temperature ^{1}H NMR spectra. Treatment of **4** or **5** with 2 equiv of samarium (II) iodide, SmI_2,[14] at room temperature resulted in formation of the neutral **1** or **2** in a good yield.

Bisammonio-selenide

From the above results, the transannulation of the selenide **1** was proceeded by addition of the electrophile such as NBS. Therefore, the selenide **1** was treated with methyl triflate ($CF_3SO_3CH_3$, TfOMe) to study the conformational change of **1**; however, the corresponding methylated product gave the complex NMR spectra which could not analyzed the conformational properties. On the other hand, the reaction of **6** with 2 equiv of TfOMe led to the methylated product ($\mathbf{7}\cdot 2CF_3SO_3^-$) which can be characterized by multinuclear NMR spectroscopy. The ^{77}Se NMR spectrum of the product **7** in CD_3CN shows the singlet peak at δ 241 in the region of diaryl selenides, i.e., **7** is a bisammonio-selenide. The ^{1}H NMR spectrum of **7** in CD_3CN shows the methylene protons at δ 4.50, 5.92 (ABq, J = 13.5 Hz) which indicates the twin-chair form. Thus, the conformational change of **6** did not occur by the methylation.

Summary

The transannulation process that accompanies conformational change of the selenide **1** can produce the aminoammonio-selenurane **4** which is remarkably stabilized by three-center bond formation between selenium and two nitrogen atoms from its unique quadruply *ortho*-bridged biphenyl ring system. The apical tertiary amine of **4** behaves as a nucleophile toward benzylbromide to form the bisammonio-selenurane **5**. Reduction of **4** and **5** with SmI_2 led to the neutral amines **1** and **2**. Thus, two-electron reduction of **4** and **5** is accompanied by conformational changes. These hypervalent diazaselenuranes **4** and **5** containing N-Se-N bond are new functional groups.

Experimental Section

All NMR spectra were measured on a JEOL LMN-EX-270, or a BRUKER MSL-400 spectrometer. IR spectra were obtained on a JASCO A-3 spectrometer. Mass spectra were taken with a Shimazu QP-2000 and a JEOL JMX SX102 mass spectrometer. Elemental analyses were carried out by the Chemical Analysis Center at this university.

All reagents were obtained from Wako Pure Chemical Industries Ltd., Tokyo Kasei Co. Ltd., or Aldrich Chemical Co. The reagents used as reaction solvents were further purified by general methods.

Synthesis of Cyclic Diazaselenides (1 and 6). To 2,6-dimethylaniline (77 g, 0.6 mol) was added 6 N hydrochloric acid (160 ml). After cooling the resulting hydrochloride at 0 °C, to the stirred mixture was added an aqueous $NaNO_2$ (46 g, 0.64 mol) solution. Then, to a stirred solution of K_2Se (0.6 mol) was added the solution of the diazonium salt of 2,6-dimethylaniline at 40 °C and then the mixture was heated at 65 °C for 2 h. The organic layer was extracted with n-hexane. The mixture was purified by column chromatography (silica gel, eluent; hexane) and recrystallized from n-hexane to afford bis(2,6-dimethylphenyl)selenide (**8**) as white crystals in 11% yield. **8**: mp 84-85 °C; ^{1}H-NMR ($CDCl_3$) δ 2.27 (s, 12H, Me), 6.97-7.10 (m, 6H, ArH); ^{13}C-NMR ($CDCl_3$) δ 23.6. 127.3, 128.0, 133.0, 141.5; ^{77}Se-NMR ($CDCl_3$) δ 255 (s); MS, *m/z* 290 (M^+). Anal. Calcd for $C_{16}H_{18}Se$: C, 66.43; H, 6.27. Found: C, 66.41; H, 6.28.

The mixture of selenide **8** (6.4 g, 22.1 mmol) and *N*-bromosuccinimide (16.6 g, 92.8 mmol) in dry CCl_4 (350 ml) was irradiated using a high-pressure mercury lamp under an Ar atmosphere for 24 h. The resulting white precipitates were filtered and the mixture was purified by column chromatography (silica gel, eluent; n-hexane-$CHCl_3$) to afford tetra-bromide (**9**) as white crystals in 21% yield. **9**: mp 160-168 °C; ^{1}H-NMR ($CDCl_3$) δ 4.63 (s, 8H, Me), 7.28-7.36 (m, 2H, ArH), 7.40-7.46 (m, 4H, ArH); ^{13}C-NMR ($CDCl_3$) δ 34.2, 129.5, 132.0, 132.3, 141.9. Anal. Calcd for $C_{16}H_{14}SeBr_4$: C, 31.77; H, 2.33. Found: C, 31.59; H, 2.22.

Solutions of tetra-bromide **9** (2 g, 3.31 mmol) in CH_2Cl_2 (100 ml) and benzylamine (2.85 ml, 26.1 mmol) in CH_2Cl_2 (100 ml) were added separately and simultaneously over 70 min to a vigorously stirred solution of CH_2Cl_2 (600 ml). The whole mixture was stirred for 12 h at room temperature. After the usual work-up, the crude product was purified by silica-gel column chromatography (eluent, *n*-hexane/$CHCl_3$ = 1/1) to give **1** (66%). **1**: mp 142-144 °C (decomp); ^{1}H-NMR ($CDCl_3$) δ 3.27 (s, 4H, CH_2), 4.02, 5.47 (ABq, *J* = 14.4 Hz, 8H, CH_2), 6.74-6.82 (m, 4H, ArH), 6.91-7.00 (m, 2H, ArH), 7.22-7.40 (m, 10H, ArH); ^{13}C-NMR ($CDCl_3$) δ 52.6, 61.3, 126.7, 125.9, 128.3, 129.9, 139.6, 139.9, 143.9; ^{77}Se-NMR ($CDCl_3$) δ 189 (s); MS, *m/z* 496 (M^+). Anal. Calcd for $C_{30}H_{28}N_2Se$: C, 72.72; H, 5.70; N, 5.65. Found: C, 72.51; H, 5.72; N, 5.53.

The *N*-methyl derivative **6** was prepared by the same procedures as **1**. **6**: mp 226-227 °C (decomp); ^{1}H-NMR ($CDCl_3$) δ 1.92 (s, 6H, CH_3), 3.89, 5.47 (ABq, *J* = 14.0 Hz, 8H, CH_2), 6.96-7.06 (m, 6H, ArH); ^{13}C-NMR ($CDCl_3$) δ 37.2, 63.3, 127.0, 130.1, 140.1, 143.1; ^{77}Se-NMR ($CDCl_3$) δ 193 (s); MS, *m/z* 344 (M^+). Anal. Calcd for $C_{18}H_{20}N_2Se$: C, 62.97; H, 5.87; N, 8.16. Found: C, 63.11; H, 5.82; N, 8.17.

Preparation of Diazaselenide (2 and 3) and Aminoselenurane (4). (a) To a solution of **1** (500 mg, 1.01 mmol) in dioxane (30 ml) was added a solution of *N*-bromosuccinimide (NBS) (180 mg, 1.01 mmol) in dioxane-H_2O (10 ml, 9 : 1) at room temperature; the solution was stirred for overnight, followed by addition of 0.25 *N* NaOH solution. After the usual work-up, the residues were purified by silica-gel column chromatography (eluent, $CHCl_3$-MeOH) to give **2** (66% yield), **3** (8%), and **4a** (Z = Br) (11%). (b) Similar treatment of **1** with 2 equiv of NBS gave **3** (22%), **4** (Z = Br) (45%), and none of **2**. (c) **4** (Z = Br) was also produced in 47% yield from the reaction of **2** with 1 equiv of NBS. (d) The Br^- salt of **4** was converted to its PF_6 salt upon treatment with NH_4PF_6. (e) Probably, **4a** (Z = Br) was formed from the reaction of **2** produced after *N*-debenzylation of **1**; *i.e.*, the reaction likely proceeds through the initial formation of the bromoselenonium ion of **2**, which subsequently is converted into **4** (Z = Br) by a stepwise transannular substitution by each amino-group. **2**: ^{1}H-NMR ($CDCl_3$) δ 1.45 (br s, 1H, NH), 3.25 (s, 2H, CH_2), 4.02, 5.45 (ABq, *J* = 14.6 Hz, 4H, CH_2), 4.09, 5.17 (ABq, *J* = 14.3 Hz, 4H, CH_2), 6.74-6.82 (m, 2H, ArH), 6.99-7.05 (m, 4H, ArH), 7.22-7.40 (m, 5H, ArH); ^{13}C-NMR ($CDCl_3$) δ 52.6, 58.5, 61.2, 126.7, 128.18, 128.23, 128.3, 128.4, 129.8, 139.0, 139.5, 143.9, 147.4; ^{77}Se-NMR ($CDCl_3$) δ 198 (s); MS, *m/z* 406 (M^+). **3**: ^{1}H-NMR ($CDCl_3$) δ 1.08 (br s, 2 H, NH), 4.09, 5.17 (ABq, *J* = 14.3 Hz, 8 H, CH_2), 6.97-7.05 (m, 4 H, ArH), 7.06-7.14 (m, 2 H, ArH); ^{13}C-NMR ($CDCl_3$) δ 58.5, 128.4, 129.7, 138.0, 147.4; ^{77}Se-NMR ($CDCl_3$) δ 209 (s). **4a** (Z = Br): mp 212-213 °C (decomp); ^{1}H-NMR (CD_3CN) δ 3.83, 4.64 (ABq, *J* = 16.5 Hz, 4 H, CH_2), 4.36, 4.94 (ABq, *J* = 16.2 Hz, 4 H, CH_2), 4.43 (s, 2 H, CH_2), 7.22-7.68 (m, 11 H, ArH); ^{13}C-NMR (CD_3CN) δ 57.1, 60.7, 65.0, 125.5, 127.1, 129.0, 129.5, 129.7, 131.7, 133.9, 135.2, 137.9, 143.0; ^{77}Se NMR (CD_3CN) δ 847 (s). **4** (Z = PF_6^-): mp 237-240 °C (decomp); ^{1}H-NMR (CD_3CN) δ 3.85, 4.57 (ABq, *J* = 16.6 Hz, 4 H, CH_2), 4.37, 4.92 (ABq, *J* = 15.9 Hz, 4 H, CH_2), 4.34 (s, 2 H, CH_2), 7.24-7.69 (m, 11 H, ArH); ^{13}C-NMR (CD_3CN) δ 57.0, 60.9, 64.9, 125.7, 127.3, 127.8, 129.7, 129.8, 131.7, 134.3, 134.9, 137.8, 143.0; ^{77}Se-NMR (CD_3CN) δ 846 (s); ^{31}P-NMR (CD_3CN) δ -145 (sept, J_{PF} = 707 Hz; relative to H_3PO_4), in the region of ionic PF_6^-. Anal. Calcd for $C_{23}H_{21}N_2SePF_6$: C, 50.29; H, 3.85; N, 5.10. Found: C, 50.12; H, 3.83; N, 5.04.

X-Ray Analysis of Aminoammonioselenurane Br⁻ Salt (4a). A colorless cubic crystal of $C_{23}H_{23}BrSeN_2O$ having approximate dimensions of 0.30 X 0.50 X 0.60 mm was mounted on a glass fiber. All measurements were made on an Enraf-Nonius CAD4 diffractometer with graphite monochromated Mo-KALPHA radiation. Crystal data for **4a**: $C_{23}H_{23}BrSeN_2O$, monoclinic, space group P21/n, *a* = 11.075(2) Å, *b* = 14.090(2) Å, *c* = 14.147(2) Å, β = 111.11(1)°, V = 2059.5 Å^3, Z = 4, Dc = 1.62 g/cm^3, Mo-Kα radiation (λ = 0.71073 Å), F(000) = 1008, a CAD4 diffractometer, 3982 reflections (2°<θ<60°), 3239 observed with $I > 3\sigma(I)$. The structure was solved by direct methods and refined anisotropically by full-matrix least-squares using the SDP program package. The final *R* value was 0.034. The crystal data have been deposited at the Cambridge Crystallographic Data Centre.

Bisammonioselenurane (5). To a solution of aminoammonioselenurane Br⁻ salt **4a** (84 mg, 0.174 mmol) in MeOH (5 ml) was added benzylbromide (22ml, 0.181 mmol) and the mixture was stirred overnight. After the usual work-up, the solid was recrystallized from ether-CH_2Cl_2-MeOH gave the bisammonioselenurane Br⁻ salt (**5a**) in 61% yield. The Br⁻ salt **5a** was converted to the PF_6^- salt (**5**) on treatment with NH_4PF_6. **5a** (Z = Br): mp 224-227 °C (decomp); ^{1}H-NMR (CD_3OD) δ 4.48, 5.32 (ABq, *J* = 16.2 Hz, 8 H, CH_2), 5.10 (s, 4 H, CH_2), 7.51-7.60 (m, 10 H, ArH), 7.68-7.77 (m, 2 H, ArH), 7.80-7.90 (m, 4 H, ArH); ^{13}C-NMR (CD_3OD) δ 62.2, 64.5, 129.5, 131.5, 132.5, 132.7, 133.8, 137.2, 139.2; ^{77}Se-NMR (CD_3OD) δ 976 (s). **5** (PF_6^-): mp 269 °C (decomp); ^{1}H-NMR (CD_3CN) δ 4.35, 5.05 (ABq, *J* = 16.2 Hz, 8 H, CH_2), 4.83 (s, 4 H, CH_2), 7.48-7.57 (m, 10 H, ArH), 7.67-7.76 (m, 6 H, ArH); ^{13}C-NMR (CD_3CN) δ 60.7, 63.2, 120.8, 128.8, 130.4, 131.0, 131.5, 132.8, 136.5, 137.9; ^{77}Se-NMR (CD_3CN) δ 940 (s); ^{31}P-NMR (CD_3CN) δ -145 (sept, J_{PF} = 707 Hz); **5** exists solely as a boat form from -50 to +130 °C as evidenced by its ^{1}H NMR spectrum. Anal. Calcd for $C_{30}H_{28}N_2SeP_2F_{12}$: C, 45.88; H, 3.59; N, 3.57. Found: C, 45.98; H, 3.52; N, 3.58.

Reduction of Diazaselenuranes 4 and 5 with SmI_2. To a solution of aminoammonioselenurane **4** (50 mg, 0.103 mmol) in anhydrous THF (5 ml) was added a solution of SmI_2 (2.2 ml, 0.22 mmol) at 0 °C for 1.5 h and then water was added. After reaction, the organic layer was extracted with ether and then the solvents were evaporated to give the amine **2** in 89% yield. The yield of the amine **1** from the reduction of bisammonioselenurane **5** was 72%.

Bisammonio-selenide. To a solution of selenide **6** (100 mg, 0.292 mmol) in anhydrous CH_2Cl_2 (10 ml) was added $CF_3SO_3CH_3$ (69.5 μl, 0.614 mmol) at -20 °C under an Ar atmosphere. The mixture was stirred at -20 °C for 1 h and then stirred at room temperature for 7 h. The resulting precipitates were recrystallized from ether-CH_2Cl_2-MeOH to give white solid **7** (45% yield). **7**: mp 350-355 °C (decomp); ^{1}H-NMR (CD_3CN) δ 2.59 (s, 6H, Me), 3.54 (s, 6H, Me), 4.50, 5,92 (ABq, J = 13.5 Hz, 8 H, CH_2), 7.37-7.45 (m, 2 H, ArH), 7.55-7.62 (m, 4 H, ArH); ^{13}C-NMR (CD_3CN) δ 47.6, 59.7, 72.7, 130.8, 134.5, 137.9, 146.4; ^{77}Se-NMR (CD_3CN) δ 241 (s). Anal. Calcd for $C_{22}H_{26}N_2SeF_6S_2O_6$: C, 39.35; H, 3.90; N, 4.17. Found: C, 39.40; H, 3.90; N, 4.12.

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11. The proton-non-decoupled ^{15}N NMR spectrum of **4**-^{15}N in CD_3CN shows that the ^{15}N peak at δ 73.6 appears as a triplet ($^2J_{N\text{-}H}$ = 6.6 Hz) which can be assigned to the tertiary amine. The value of $^2J(^{15}N, H_A$ or $H_B)$ is likely related to the N-C-H dihedral angle.[10]

12. (a) Isotope-induced shifts on ^{77}Se NMR spectra are described: Chapter 6 of Ref. 2a. (b) The ^{77}Se chemical shift in the ^{77}Se-^{15}N (tertiary amine) bond of **4**-^{15}N was shifted upfield by 0.112 ppm relative to that of the ^{77}Se-^{14}N bond of **4**.
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