A New Tetracoordinated Cyclic Diazaselenurane with Amino and Ammonio Groups as Two Unsymmetrical Apical Ligands and Its Bisammonioselenurane

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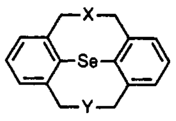
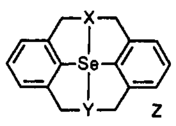
The chemistry of hypervalent selenuranes is much less developed than that of sulfuranes, and sulfuranes with apical nitrogen ligands are little known.[1,2] Although we recently reported that the transannular interaction between two heteroatoms of selenium heterocycles produced a hypervalent species, such behavior by fourth-row elements and multiheteroatoms has received less attention.[3] We have now found that the three-center transannular interaction between selenium and two nitrogen atoms of new *N*-benzyl derivatives of 1,11-(methanoaminomethano)-5*H*,7*H*-dibenzo[*b*,*g*][1,5]selenazocine (**1** and **2**) provides the stable aminoammonioselenurane **4** which is a new type of an isolable cyclic diazaselenurane with two unsymmetrical apical nitrogen ligands of tertiary alkylamino and quaternary alkylammonio groups. Generally, selenuranes have two symmetrical electronegative groups such as oxygen or halogen atoms at the apical positions.[2] This paper reports the characterization of **4** using the ^{15}N-labeling technique and a derivative (**5**).



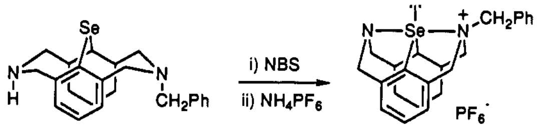


1 : X, Y = N-CH$_2$Ph
2 : X = NH, Y = N-CH$_2$Ph
3 : X, Y = NH
1-^{15}*N* : X, Y = ^{15}N-CH$_2$Ph

4 : X = N, Y = N$^+$-CH$_2$Ph, Z = PF$_6^-$
5 : X, Y = N$^+$-CH$_2$Ph, Z = 2PF$_6^-$
4-^{15}*N* : X = ^{15}N, Y = ^{15}N$^+$-CH$_2$Ph
Z = PF$_6^-$

We employed *N*-bromosuccinimide [NBS, Br·N(CO·CH$_2$)$_2$] to prepare the selenide **2** and the selenurane **4**, bearing unsymmetrical apical nitrogen ligands, from **1**. NBS has been used for the conversion of selenides into bromoselenonium cations and of tertiary amines into secondary amines.[2,4] A new structural type of aminoammonioselenurane (**4**) was isolated from the reaction of the selenide **1** or **2** with NBS (Scheme I).[5–7] Thus, the stepwise substitution of the amino functions in **1** or **2** leads to **4**.

Scheme I



2 **4**

The structure of **4** in solution was characterized by multinuclear NMR (^{1}H, ^{13}C, ^{77}Se, and ^{31}P) spectroscopy.[6] With regard to the conformational properties of selenides **1** and **2**, the chair and the boat forms can exist.[8] The conformers can be assigned by the ^{1}H NMR spectral data for benzylic protons of the eight-membered ring.[8] The ^{1}H NMR spectra of **1** and of **2** in CDCl$_3$ at 25 °C show the endocyclic benzylic methylene protons as AB quartet peaks 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 (Scheme I). In contrast, the conformation of **4** in CD$_3$CN is a twin-boat form, i.e., the benzylic methylene protons appear at δ 3.85, 4.57 (AB q, J = 16.6 Hz), and 4.37, 4.92 (AB q, J = 15.9 Hz). The ^{77}Se NMR spectrum of **4** in CD$_3$CN shows a remarkable downfield shift to δ 846.3 (singlet) from δ 188.9 (s) for **1** and δ 198.1 (s) for **2** in CDCl$_3$.[9] The ^{77}Se chemical shift of **4** is in the range characteristic for a selenurane.[2] 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 a three-center transannular bond between the selenio and two amino groups.

Evidence for the existence of a N–Se–N$^+$ bond is derived from the ^{15}N (40.56 MHz) and ^{77}Se (76.31 MHz) NMR spectra of the ^{15}N-labeled selenurane, **4**-^{15}*N* (20% and 40% ^{15}N isotope enrichment).[10] The ^{15}N NMR spectrum of **1**-^{15}*N* in CDCl$_3$ shows a single peak at δ 33.9.[11,12] The proton-decoupled ^{15}N NMR spectrum of the selenurane **4**-^{15}*N* in CD$_3$CN exhibits two

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(1) For a review: Hayes, R. A.; Martin, J. C. Sulfurane Chemistry. In *Organic Sulfur Chemistry, Theoretical and Experimental Advances*; Bernardi, F., Csizmadia, I. G., Mangini, A., Eds.; Elsevier: Amsterdam, 1985; Chapter 8.

(2) (a) *The Chemistry of Organic Selenium and Tellurium Compounds*; Patai, S., Rappoport, Z., Eds.; Wiley: New York, 1986; Vol. 1, Chapters 3, 6, and 14; 1987; Vol. 2. The term selenurane (selenane) has been used for tetracoordinate selenium(IV) compounds. (b) *Selenium Reagents and Intermediates in Organic Synthesis*; Paulmier, C., Eds.; Pergamon Press: New York, 1986.

(3) Fujihara, H.; Mima, H.; Ikemori, M.; Furukawa, N. *J. Am. Chem. Soc.* **1991**, *113*, 6337–6338.

(4) Dunstan, S.; Henbest, H. B. *J. Chem. Soc.* **1957**, 4905–4908.

(5) (a) To a solution of **1** (500 mg, 1.01 mmol) in dioxane (30 mL) was added a solution of NBS (180 mg, 1.01 mmol) in dioxane–H$_2$O (10 mL, 9:1) at room temperature; the solution was stirred overnight, followed by addition of 0.25 N NaOH solution. After the usual workup, the residues were purified by silica gel column chromatography (eluent, CHCl$_3$–MeOH) to give **2** (66% yield), **3** (8%), and **4** (Z = Br) (11%). (b) Similar treatment of **1** with 2 equiv of NBS gave **3** (22%), **4** (Z = Br) (45%), and no **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** or **5** was converted to its PF$_6$ salt upon treatment with NH$_4$PF$_6$. (e) Probably, **4** (Z = Br) is 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.

(6) NMR data. **1** (CDCl$_3$): ^{1}H δ 3.27 (s, 4 H, exocyclic-CH$_2$), 4.02, 5.47 (AB q, J = 14.4 Hz, 8 H, endocyclic-CH$_2$), 6.74–6.82 (m, 4 H, ArH), 6.91–7.00 (m, 2H, ArH), 7.22–7.40 (m, 10 H, ArH); ^{13}C δ 52.6, 61.3, 126.7, 126.9, 128.3, 129.9, 139.6, 139.9, 143.9. **2** (CDCl$_3$): ^{1}H δ 1.45 (br s, 1 H, NH), 3.25 (s, 2 H, CH$_2$), 4.02, 5.45 (AB q, J = 14.6 Hz, 4 H, CH$_2$), 4.09, 5.17 (AB q, J = 14.3 Hz, 4 H, CH$_2$), 6.74–6.82 (m, 2 H, ArH), 6.99–7.05 (m, 4 H, ArH), 7.22–7.40 (m, 5 H, ArH); ^{13}C 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. **3** (CDCl$_3$): ^{1}H δ 1.08 (br s, 2 H, NH), 4.10, 5.15 (AB q, J = 14.2 Hz, 8 H, CH$_2$), 6.97–7.05 (m, 4 H, ArH), 7.06–7.14 (m, 2 H, ArH); ^{13}C δ 58.5, 128.4, 129.7, 138.0, 147.4; ^{77}Se δ 208.5 (s). **4** (CD$_3$CN): ^{1}H δ 3.85, 4.57 (AB q, J = 16.6 Hz, 4 H, CH$_2$), 4.37, 4.92 (AB q, 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 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; ^{31}P δ −145.0 (sept, J_{PF} = 707 Hz; relative to H$_3$PO$_4$), in the region of ionic PF$_6^-$. **5** (CD$_3$CN): ^{1}H δ 4.35, 5.05 (AB q, 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 δ 60.7, 63.2, 120.8, 128.8, 130.4, 131.0, 131.5, 132.8, 136.5, 137.9; ^{77}Se δ 939.9 (s) as a characteristic of selenurane; ^{31}P δ −145.0 (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.

(7) **4** (PF$_6^-$): mp 240 °C dec. Anal. Calcd for C$_{23}$H$_{21}$N$_2$SePF$_6$: C, 50.29; H, 3.85; N, 5.10. Found: C, 50.12; H, 3.83; N, 5.04. **5** (PF$_6^-$): mp 269 °C dec. Anal. Calcd for C$_{30}$H$_{28}$N$_2$SeP$_2$F$_{12}$: C, 45.88; H, 3.59; N, 3.57. Found: C, 45.98; H, 3.52; N, 3.58. All attempts at growing X-ray quality crystals of **4** and **5** have, so far, been unsuccessful.[18]

(8) (a) Gellatly, R. P.; Ollis, W. D.; Sutherland, I. O. *J. Chem. Soc., Perkin Trans. 1*, **1976**, 913–925. (b) Brieaddy, L. E.; Hurlbert, B. S.; Mehta, N. B. *J. Org. Chem.* **1981**, *46*, 1630–1634 and references cited therein.

(9) ^{77}Se chemical shifts (^{77}Se, spin $^1/_2$, natural abundance 7.6%) are relative to Me$_2$Se.

(10) ^{15}N-Labeled selenurane, **4**-^{15}*N*, was obtained from ^{15}N-labeled selenide, **1**-^{15}*N* (^{15}N, 20%, 40%).

(11) ^{15}N chemical shifts (^{15}N, spin $^1/_2$) were measured by using acetonitrile as an internal or external reference (δ 239.5) and were evaluated from a ^{15}NH$_3$ external standard.[12]

(12) Levy, G. C.; Lichter, R. L. *Nitrogen-15 Nuclear Magnetic Resonance Spectroscopy*; John Wiley & Sons: New York, 1979.

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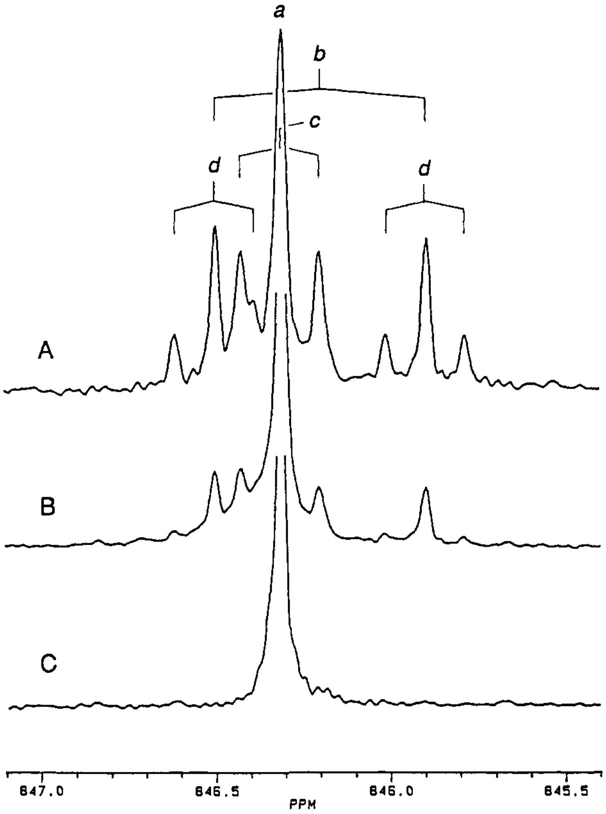

Figure 1. Proton-decoupled ^{77}Se NMR spectra (76.31 MHz) of (A) 40% ^{15}N-enriched selenurane 4-^{15}N, (B) 20% ^{15}N-enriched selenurane 4-^{15}N, and (C) unlabeled selenurane ^{14}N-4 in CD$_3$CN. Coupling constant for each peak: (*b*) $J_{\text{Se-N}}$ = 45.9 Hz and (*c*), (*d*) $J_{\text{Se-N}}$ = 17.0 Hz.

resonances at δ 58.8 and 73.6; the former resonance is assigned to the quaternary ammonium ion and the latter peak to the tertiary amine.[13,14] Particularly, each peak exhibits ^{77}Se satellite peaks due to the ^{15}N–^{77}Se coupling about the resonances at δ 58.8 ($J_{\text{N-Se}}$ = 17.0 Hz) and 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 1 reveals 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 1A is assigned as follows. The single peak *a* corresponds to the Se–N bond of isotopomer **4a**, and the satellite peaks *c* are due to the coupling of ^{77}Se–^{15}N of the quaternary 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**.[15,16] Peak *d* is attributable to the ^{77}Se–^{15}N coupling of an isotopomer **4d**. The intensities of peaks *b*–*d* in Figure 1A 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 indicate the existence of a transannular N–Se–N bond.

The chemical properties of the selenurane **4** were examined, since little information on the reactivity of selenuranes was available.[2] It is of particular interest that **4** was reacted with benzyl bromide (1 equiv) to give the first bisammonioselenurane having two symmetrical apical ammonium cations (**5**, 61% yield), where the selenium-bonded tricoordinated nitrogen atom of **4** is basic in character.[5d–7] Treatment of **4** or **5** with 2 equiv of samarium(II) iodide, SmI$_2$,[17] at room temperature resulted in formation of the neutral **1** or **2** in a good yield. This represents an unprecedented mode of two-electron reduction with SmI$_2$ to hypervalent molecules.

In summary, the transannulation process that accompanies conformational change of the selenide **2** can produce the aminoammonioselenurane **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 benzyl bromide to form the bisammonioselenurane **5**. These hypervalent diazaselenuranes **4** and **5**, containing N–Se–N bonding, are new functional groups, although there are a few examples of selenides with a Se–N bond, e.g., selenenamides (RSeNR$_2$).[2] Further work is currently in progress in this and related areas.

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Supplementary Material Available: ^{15}N NMR spectrum of ^{15}N-enriched aminoammonioselenurane 4-^{15}N, and details of preparation and/or spectral data of compounds **1**–**5** (4 pages). Ordering information is given on any current masthead page.

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[13] The proton-nondecoupled ^{15}N NMR spectrum of 4-^{15}N shows two positive peaks at δ 58.8 and 73.6. While the signal of δ 58.8 is negative in the proton-decoupled ^{15}N NMR spectrum of 4-^{15}N, namely, the ^{15}N peak at δ 58.8 shows the nuclear Overhauser effect (NOE, –160%) which can be attributed to the benzyl-substituted quaternary ammonium cation of 4-^{15}N.[12] The ^{15}N NMR spectrum of 4-^{15}N is described in the supplementary material.

[14] The proton-nondecoupled ^{15}N NMR spectrum of 4-^{15}N in CD$_3$CN shows that the ^{15}N peak at δ 73.6 appears as a triplet ($^2J_{\text{N-H}}$ = 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.[12]

[15] (a) Isotope-induced shifts on ^{77}Se NMR spectra are described: ref 2, Chapter 6. (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.

[16] The isotope shift on the ^{77}Se chemical shift of ^{77}Se–^{15}N (quaternary ammonium ion) bond of 4-^{15}N was negligible in this case.

[17] Soderquist, J. A. *Aldrichim. Acta* **1991**, *24*, 15–23 and references cited therein.

[18] X-ray data of selenium compounds containing nitrogen atom were reported in the following references: Chapter 3 of ref 2a and ref 3.