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

Hisashi Fujihara,^{*,†} Hisatomo Mima,[†] Tomoki Erata,[‡] and Naomichi Furukawa^{*,†}

Department of Chemistry and Institute of Applied Physics University of Tsukuba Tsukuba, Ibaraki 305, Japan

Received June 10, 1993

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)-5H,7Hdibenzo[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 ¹⁵N-labeling technique and a derivative (5).



We employed N-bromosuccinimide [NBS, $Br \cdot N(CO \cdot CH_2)_2$] 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.

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 CDCl₃ at 25 °C

(1) For a review: Hayes, R. A.; Martin, J. C. Sulfurane Chemistry. In

Scheme I



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 CD₃CN 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 ⁷⁷Se NMR spectrum of 4 in CD₃CN 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 CDCl₃.⁹ The ⁷⁷Se 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 ¹H 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 ¹⁵N (40.56 MHz) and ⁷⁷Se (76.31 MHz) NMR spectra of the ¹⁵N-labeled selenurane, $4^{-15}N$ (20% and 40% ¹⁵N isotope enrichment).¹⁰ The ¹⁵N NMR spectrum of $1^{-15}N$ in CDCl₃ shows a single peak at δ 33.9.^{11,12} The proton-decoupled ¹⁵N NMR spectrum of the selenurane $4^{-15}N$ in CD₃CN exhibits two

(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-H₂O (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, CHCl₃-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 PF₆ salt upon treatment with NH₄PF₆. (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.

into 4 (Z = Br) by a stepwise transannular substitution by each amino group. (6) NMR data. 1 (CDCl₃): ¹H δ 3.27 (s, 4 H, exocyclic-CH₂), 4.02, 5.47 (AB q, J = 14.4 Hz, 8 H, endocyclic-CH₂), 6.74-6.82 (m, 4 H, ArH), 6.91– 7.00 (m, 2H, ArH), 7.22-7.40 (m, 10 H, ArH); ¹³C δ 52.6, 61.3, 126.7, 126.9, 128.3, 129.9, 139.6, 139.9, 143.9. 2 (CDCl₃): ¹H δ 1.45 (br s, 1 H, NH), 3.25 (s, 2 H, CH₂), 4.02, 5.45 (AB q, J = 14.6 Hz, 4 H, CH₂), 4.09, 5.17 (AB q, J = 14.3 Hz, 4 H, CH₂), 6.74-6.82 (m, 2 H, ArH), 6.99-7.05 (m, 4 H, ArH), 7.22-7.40 (m, 5 H, ArH); ¹³C 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 (CDCl₃): ¹H δ 1.08 (br s, 2 H, NH), 4.10, 5.15 (AB q, J = 14.2 Hz, 8 H, CH₂), 6.97-7.05 (m, 4 H, ArH), 7.06-7.14 (m, 2 H, ArH); ¹³C δ 58.5, 128.4, 129.7, 138.0, 147.4; ⁷⁷Se δ 208.5 (s). 4 (CD₂CN): ¹H δ 3.85, 4.57 (AB q, J = 16.6 Hz, 4 H, CH₂), 4.37, 4.92 (AB q, J = 15.9 Hz, 4 H, CH₂), 4.34 (s, 2 H, CH₂), 7.24-7.69 (m, 11 H, ArH); ¹³C 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; ³¹P δ -145.0 (sept, J_{PF} = 707 Hz; relative to H₃-PO₄), in the region of ionic FF₆- 5 (CD₃CN): ¹H δ 4.35, 5.05 (AB q, J = 16.2 Hz, 8 H, CH₂), 4.83 (s, 4 H, CH₂), 7.48-7.57 (m, 10 H, ArH), 7.67-7.76 (m, 6 H, ArH); ¹³C δ 60.7, 63.2, 120.8, 128.8, 130.4, 131.0, 131.5, 132.8, 136.5, 137.9; ⁷⁷Se δ 939.9 (s) as a characteristic of selenurane; ³¹P δ -145.0 (sept, J_{PF} = 707 Hz). 5 exists solely as a boat form from -50 to +130 °C

136.5, 137.9; "Se 0 939.9 (s) as a characteristic of scienturane; "F o -143.0 (sept, $J_{PF} = 707$ Hz). 5 exists solely as a boat form from -50 to +130 °C as evidenced by its ¹H NMR spectrum. (7) 4 (PF₆⁻): mp 240 °C dec. Anal. Calcd for C₂₃H₂₁N₂SePF₆: C, 50.29; H, 3.85; N, 5.10. Found: C, 50.12; H, 3.83; N, 5.04. 5 (PF₆⁻): mp 269 °C dec. Anal. Calcd for C₃₀H₂₈N₂SeP₂F₁₂: 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

(11) ¹⁵N chemical shifts (¹⁵N, spin ¹/₂) were measured by using acetonitrile as an internal or external reference (δ 239.5) and were evaluated from a ¹⁵NH₃ external standard.¹²

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

© 1993 American Chemical Society

[†] Department of Chemistry.

[‡] Institute of Applied Physics.

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.

^{(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) ⁷⁷Se chemical shifts (⁷⁷Se, spin ¹/₂, natural abundance 7.6%) are relative to Me₂Se.

^{(10) &}lt;sup>15</sup>N-Labeled selenurane, 4-¹⁵N, was obtained from ¹⁵N-labeled selenide, 1-¹⁵N (¹⁵N, 20%, 40%).



Figure 1. Proton-decoupled ⁷⁷Se NMR spectra (76.31 MHz) of (A) 40% ¹⁵N-enriched selenurane 4-¹⁵N, (B) 20% ¹⁵N-enriched selenurane 4-¹⁵N, and (C) unlabeled selenurane ¹⁴N-4 in CD₃CN. 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 ⁷⁷Se satellite peaks due to the ¹⁵N-⁷⁷Se coupling about the resonances at δ 58.8 (J_{N-Se} = 17.0 Hz) and 73.6 (J_{N-Se} = 45.9 Hz). These ¹⁵N-⁷⁷Se coupling constants determined from the ¹⁵N NMR spectrum are in full agreement with those from the ⁷⁷Se NMR spectrum (*vide infra*). Furthermore, both ¹⁵N resonances display the doublet peak due to the ¹⁵N-¹⁵N coupling (² J_{N-N} = 4.5 Hz) about each central peak.

Figure 1 reveals the proton-decoupled ⁷⁷Se NMR spectra for the 40% ¹⁵N-enriched selenurane 4-¹⁵N (spectrum A), the 20% ¹⁵N-enriched selenurane 4-¹⁵N (spectrum B), and the unlabeled selenurane 4 (spectrum C). The isotopomers of 4-¹⁵N are as follows (¹⁴N is denoted as N): N-Se-N⁺-Bnz (4a), ¹⁵N-Se-N⁺-Bnz (4b), N-Se-¹⁵N⁺-Bnz (4c), and ¹⁵N-Se-¹⁵N⁺-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 ⁷⁷Se–¹⁵N of the quaternary ammonium ion ($J_{Se-N} = 17.0 \text{ Hz}$) in isotopomer **4c**. An upfield isotope shift of 0.112 ppm resulting from substitution of ¹⁵N for ¹⁴N on the ⁷⁷Se NMR chemical shift of isotopomer **4b** was observed, i.e., the doublet peak *b* is due to the coupling of ⁷⁷Se–¹⁵N of the tertiary amine ($J_{Se-N} = 45.9 \text{ Hz}$) in isotopomer **4b**.^{15,16} Peak *d* is attributable to the ⁷⁷Se–¹⁵N 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 ⁷⁷Se and ¹⁵N 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, SmI₂,¹⁷ 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 SmI₂ 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 (RSeNR₂).² Further work is currently in progress in this and related areas.

Acknowledgment. This work was supported by the Grant-in-Aid for Scientific Research on Priority Area of Organic Unusual Valency No. 04217101 from the Ministry of Education, Science and Culture, Japan. One of us (H.F.) thanks a Scientific Research Grant (No. 03640435) from the Ministry of Education, Science and Culture, Japan, and CIBA-GEIGY Foundation (Japan) for the Promotion of Science.

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

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

⁽¹⁴⁾ The proton-nondecoupled ¹⁵N NMR spectrum of 4-¹⁵N in CD₃CN shows that the ¹⁵N peak at δ 73.6 appears as a triplet (²J_{N·H} = 6.6 Hz) which can be assigned to the tertiary amine. The value of ²J(¹⁵N, H_A, or H_B) is likely related to the N-C-H dihedral angle.¹²

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

⁽¹⁶⁾ The isotope shift on the ⁷⁷Se chemical shift of ⁷⁷Se⁻¹⁵N (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.