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Isolable, Stable Diselenocarboxylate and Selenothiocarboxylate Salts: Syntheses, Structures, and Reactivities of 2-(1,3-Dimethylimidazolidinio)diselenocarboxylate and 2-(1,3-Dimethylimidazolidinio)selenothiocarboxylate

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Abstract: 2-(1,3-Dimethylimidazolidinio)diselenocarboxylate (**16**) was obtained in 48% yield as thermally stable, dark green crystals by reaction of 2-methylene-1,3-dimethylimidazolidine (**7**) with Se_2Cl_2 in the presence of Et_3N. The reaction of **16** with elemental sulfur gave 2-(1,3-dimethylimidazolidinio)dithiocarboxylate (**20**) in 95% yield by exhaustive selenium−sulfur exchange, whereas the use of a limited amount of sulfur allowed the preparation of 2-(1,3-dimethylimidazolidinio)selenothiocarboxylate (**19**) as dark red crystals. X-ray crystallographic analyses revealed that the planes of the carbenium ion and CX_2^- ($X = S$, Se) parts of **16** and **20** are nearly perpendicular to each other. The observed geometries (including bond angles and lengths) of **16** and **20** were reproduced satisfactorily by ab initio calculations (B3LYP/6-31G* level). Discussion is also made on the structures of **16**, **19**, and **20** on the basis of spectroscopic data (NMR, IR, and UV/vis). Methylation of **16** with MeI furnished the carbenium iodide (**26a**), which possesses a diselenoester moiety, as thermally labile, green crystals. The reaction of **16** with two molar amounts of DMAD provided the 1:2 adduct (**30a**) in 67% yield. The reaction of **16** with *N*-[(*p*-tolylsulfonyl)imino]phenyliodinane gave the inner salt (**35**) in 68% yield with loss of selenium atom from the initial adduct (**33**).

Introduction

We report here the syntheses, isolation, structures, and reactions of the hitherto unknown diselenocarboxylate and selenothiocarboxylate salts given in the title.[1−3] For several years, we have been investigating the synthesis, structure, and reactivities of 2,2-bis(diethylamino)-2-ethylium-1-dithiocarboxylate (**1**) and related compounds.[4−7] The inner salt **1** is unique, and its structure and reactivities are of particular interest. The plane of the carbenium ion part and that of the dithiocarboxylate part of **1** are nearly perpendicular to each other.[5b] Its sulfur atom reacts not only with MeI to give the carbenium iodide (**2**)[5a,b] but also with RLi (RMgX) to provide the thiolates (**3**)[5g,h] in high yields, thus revealing a unique ability to serve both as a nucleophile and as an electrophile. In this connection, we had become interested in the preparation and properties of the selenium analogue (**4**). The inner salt **1** is obtainable in a high yield by treatment of the chloroenediamine (**5**) with elemental sulfur at room temperature.[5a,b] The attempted synthesis of **4** by reaction of **5** with elemental selenium in boiling benzene or chlorobenzene, unexpectedly, produced the hexaselenacyclooctane derivative (**6**) in good yield.[5l] Interestingly, however, compound **6** behaved as the equivalent of **4** in spectroscopic properties in polar solvents and also in reactivities. We therefore thought that replacement of the diethylamino groups of **4** by more carbenium ion-stabilizing groups makes this type of diselenocarboxylate salts stable enough to be isolated. This hypothesis led us to the successful synthesis of the title compound.

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[2] The reaction of CSe_2 with Et_2Zn to form zinc salts of diselenoic acid is the only example of the synthesis of diselenoic acid. Attempts to hydrolyze this salt have been reported to give the dimer of the acid.[1]

[3] For preparation of $(R_2NCSe_2^-)_2M^{2+}$ ($M = Zn$, Ni, Pd, Pt) and related compounds, see: (a) Barnard, D.; Woodbridge, D. T. *J. Chem. Soc.* **1961**, 2922. (b) Jensen, K. A.; Krishnan, V. *Acta Chem. Scand.* **1967**, *21*, 2904. (c) Pan, W.-H.; Fackler, J. P., Jr. *J. Am. Chem. Soc.* **1978**, *100*, 5783.

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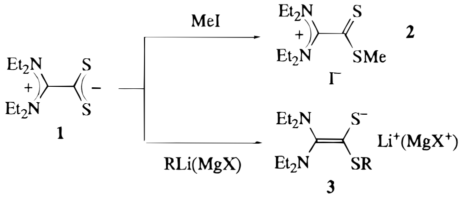

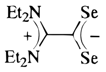
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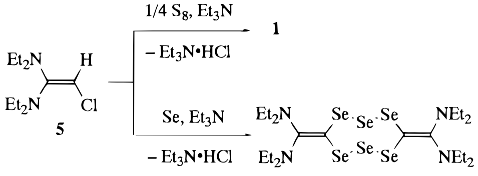

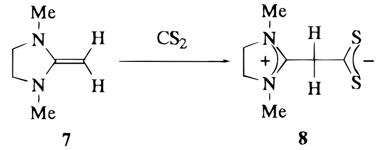

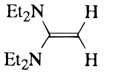
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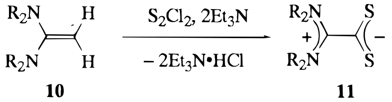

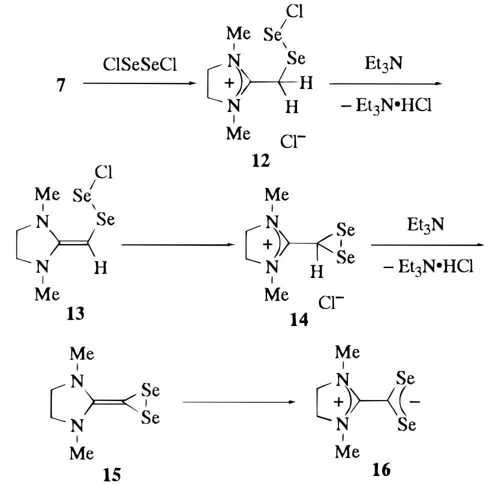

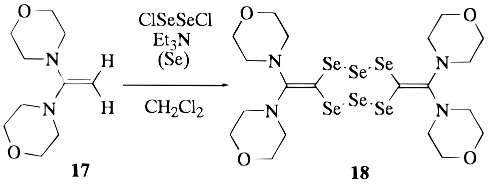

Results and Discussion

Syntheses. Recently, we reported that the addition of carbon disulfide to a cyclic enediamine (**7**) provided the stable inner salt (**8**) where the carbenium ion and the dithiocarboxylate parts are insulated by an sp^3 carbon atom,[5i,k] whereas the adducts of an acyclic enediamine (**9**) and related compounds with carbon disulfide are unstable and are not isolated in pure form.[5d,e,7] These findings indicate that the carbenium ion is more stabilized by adjacent nitrogen atoms when it was placed in a cyclic system than in an acyclic system. We have also developed an improved synthesis of inner salts (**11**) by reactions of enediamines (**10**) with disulfur dichloride.[5c] Taking these all into account, the reaction of **7** with diselenium dichloride was the method of our choice for obtaining a diselenocarboxylate salt which is stable enough to be isolated. Addition of 1 equiv of diselenium dichloride to a solution of **7** in CH_2Cl_2 at −78 °C resulted in the separation of a red solid to which the structure (**12**) was assigned tentatively. Et_3N was then added, and the mixture was warmed slowly to room temperature, during which the mixture turned dark green with dissolution of the red solid. The mixture was evaporated, after the elemental selenium had been removed by filtration, to give the expected inner salt (**16**) as a dark green crystalline solid in 48% yield. The structure of **16** was determined by spectroscopies and X-ray crystallographic analysis as discussed later. The mechanism depicted below, involving the initial formation of the adduct **12** and the final formation of the diselenirane (**15**), may best explain the formation of **16**. Although diselenoic acid esters RC(=Se)SeR′ were first synthesized in 1993,[8] neither diselenoic acids RC(=Se)SeH nor diselenocarboxylates RC(=Se)Se$^-$ have been synthesized.[1−3] The salt **16** thus provides the first example of a diselenocarboxylate that was satisfactorily synthesized and isolated.

Application of the reaction to the enediamine (**17**) failed to give the corresponding diselenocarboxylate inner salt, but gave a complex, dark red solid mixture. Although the mixture might contain the hexaselenacyclooctane (**18**), cf. **6**, it could not be isolated in pure form. The addition of elemental selenium to the reaction mixture to compensate for the shortage of selenium atoms also gave a complex mixture.

Our previous paper showed that the selenacyclooctane **6** served as the equivalent of the selenium inner salt **4**, whose selenium atoms were replaced by sulfur atoms by treatment with elemental sulfur to produce the sulfur inner salt **1** in high yield.[5l,9] Treatment of the diselenocarboxylate salt **16** with elemental sulfur (excess) in refluxing $CHCl_3$ for 4 h thus provided the dithiocarboxylate salt **20** in 95% yield. The mechanism, initiated by nucleophilic attack of **16** on S_8 and involving the intermediary formation of the selenothiocarboxylate (**19**), is proposed for the reaction. Indeed, when **16** was treated with one equivalent of sulfur in $CDCl_3$ at room temperature, a mixture of **16**, **19**, and **20** in the ratio 2:2:1 was formed; the methyl signals of these three compounds appeared at δ 3.13, 3.12, and 3.11, respectively, in the ^1H NMR spectra (Table 1). The reaction, carried out in CH_2Cl_2 at room temperature, allowed the isolation of **19** by silica gel column chromatography in 14% yield as dark red crystals. In this way, diselenocarboxylate, selenothiocarboxylate, and dithiocarboxylate salts, **16**, **19**, and **20**, were provided, thus enabling a comparison study of these unique inner salts. However, heating **16** with CS_2 did not produce **20**.

Structures. ^1H-, ^{13}C-, and ^{77}Se NMR spectral data of **16**, **19**, and **20** are summarized in Table 1. Methyl and methylene hydrogen signals of these compounds appeared in very narrow

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(8) (a) Murai, T.; Mizutani, T.; Kanda, T.; Kato, S. *J. Am. Chem. Soc.* **1993**, *115*, 5823. (b) Murai, T.; Mizutani, T.; Kanda, T.; Kato, S. *Heteroat. Chem.* **1995**, *6*, 241. For a review, see: (c) Murai, T.; Kato, S. *Sulfur Rep.* **1998**, *20*, 397.

(9) ArC(=Se)OMe are converted to ArC(=S)OMe by heating with elemental sulfur without solvent. (a) Klages, C.-P.; Voss, J. *Angew. Chem.* **1977**, *89*, 743. (b) Klages, C.-P.; Malmberg, W.-D.; Voss, J. *J. Chem. Res. (S)* **1979**, 160.

Table 1. ^{1}H-, ^{13}C-, and ^{77}Se NMR Data for Salts **16**, **19**, and **20**[a]

	^{1}H NMR[b]		^{13}C NMR				
compd	CH_3	CH_2	carboxylate C	carbocation C	CH_3	CH_2	^{77}Se NMR
16	3.13	3.84	221.1	177.2	33.7	49.4[d]	946.4
19	3.12	3.84[c]	225.1	171.6	33.7	49.4[d]	
20	3.11	3.86	225.3	167.2	33.6	49.4	

[a] ^{1}H- and ^{13}C NMR (400 MHz and 100.6 MHz, respectively), TMS as internal standard; ^{77}Se NMR (76.3 MHz), D_2SeO_3 as external standard; chemical shift values in δ; $CDCl_3$ as solvent. [b] At 27 °C. [c] Chemical shift value of the center of an AA′BB′ multiplet (see Figure 1). [d] At 0 °C.

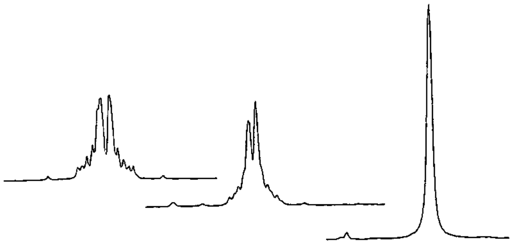
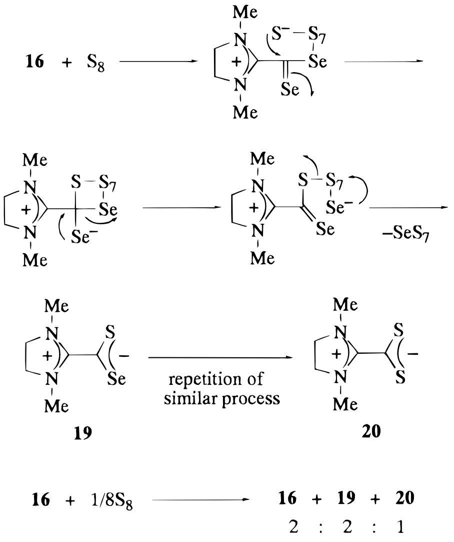


Figure 1. ^{1}H NMR spectra of the methylene signal of the selenothiocarboxylate **19** at 0 °C (left, $CDCl_3$ as solvent), 25 °C (middle, $CDCl_3$ as solvent), and 70 °C (right, coalescence temperature, $CDCl_2CDCl_2$ as solvent).



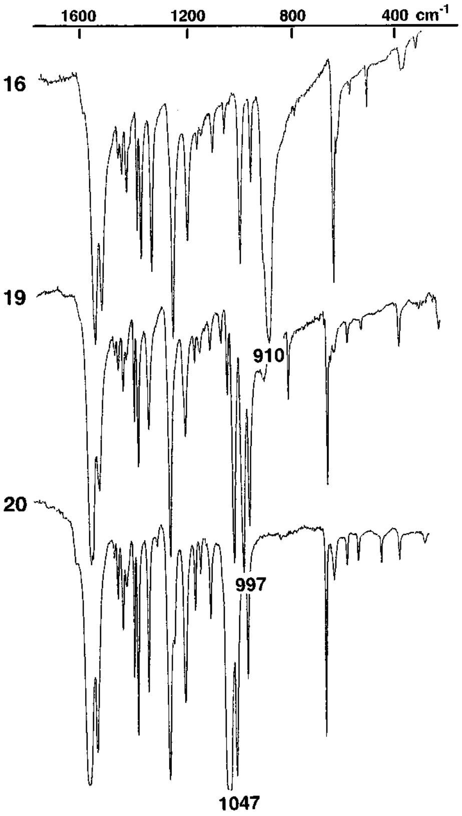
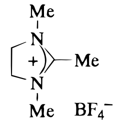


Figure 2. IR spectra (400−1600 cm^{-1} region, KBr disk) of **16** (top), **19** (middle), and **20** (bottom).

ranges of δ 3.11−3.13 for the methyl and 3.84−3.86 for the methylene. Most noteworthy are the observations that the methylene hydrogen signal of **19** appeared as an AA′BB′ multiplet at 0 °C (Figure 1), whereas those of **16**, **20**, and **21** (precursor of **7**)[10] appeared as sharp singlets. This suggests that the preferred conformation of **19** is the one where the carbenium ion and the selenothiocarboxylate units are perpendicular to each other, thus making the hydrogens H_a and H_b nonequivalent by restricted rotation about the $C^+{-}CSSe^-$ bond (see structure **19′**). The multiplet turned to a sharp singlet at elevated temperatures with a coalescence temperature of 70 °C in $C_2D_2Cl_4$ (Figure 1).[11] No marked differences of chemical shift values between **16**, **19**, and **20** were observed in the ^{13}C NMR spectra. The carbenium carbon peaks moved to a higher field in the order **16**, **19**, and **20**, while the carboxylate carbon peaks showed a slight low-field shift in this order. The ^{77}Se NMR spectrum of **16** showed a single resonance at δ 946.4.



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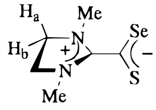

19′

IR spectra of **16**, **19**, and **20** are shown in Figure 2. Since differences in these three spectra originate in the absorptions by the CSe_2^-, $CSeS^-$, and the CS_2^- groups, comparison of the spectra enables us to assign the asymmetric stretching vibrations of these groups, which have never been reported.[12] Thus, the very intense bands at 910 for **16**, 997 for **19**, and 1047 cm^{-1} for **20** were assigned to the asymmetric stretching vibrations of the CSe_2^-, $CSeS^-$, and CS_2^- groups, respectively.[13] Ab initio MO calculations (B3LYP/6-31G* level)[14] predicted that the asymmetric stretching vibrations of the CSe_2^-, $CSeS^-$, and CS_2^- groups of these compounds appear at 904, 979, and 1041 cm^{-1}, respectively. Meanwhile, the very weak bands, which appeared at 805 for **16**, 830 for **19**, and 860 cm^{-1} for **20**, are probably assigned to the symmetric stretching vibrations. The calculations predicted that the symmetric stretching vibrations of **16**, **19**, and **20** are very weak and are observed at 788, 795, and 830 cm^{-1}, respectively. The sharp absorptions at 661 for **16**, 675 for **19**, and 686 cm^{-1} for **20** were calculated to be assigned to

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[10] Gruseck, U.; Heuschmann, M. *Chem. Ber.* **1987**, *120*, 2053.

[11] Because of the ill-defined structure of the multiplet even at low temperatures, we could not determine the coupling constant values that lead to determination of activation parameters of the rotation.

[12] No assignment of $\nu_{as}(CS_2)$ and $\nu_s(CS_2)$ in $(R_2N)_2C^+CS_2^-$ has been reported.

[13] For $\nu_{as}(CS_2)$ and $\nu_s(CS_2)$ of HCS_2^-, $MeCS_2^-$, $EtCS_2^-$, *iso*-$PrCS_2^-$, and $PhCS_2^-$, see: Voss, J. In *The Chemistry of Acid Derivatives, Part 2*, Supplement B; Patai, S., Ed.; John Wiley: New York, 1979; Chapter 18.

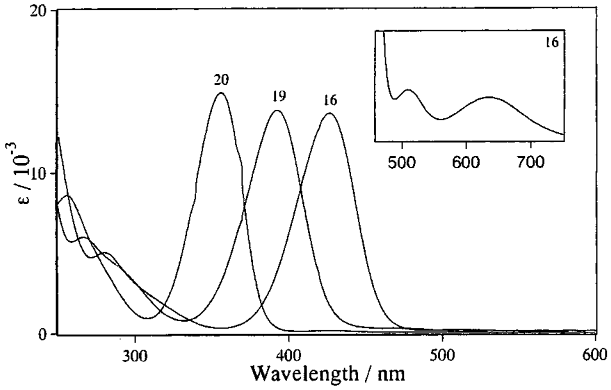
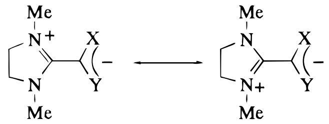


Figure 3. UV/vis spectra of **16**, **19**, and **20** and the 500−700 nm region spectrum of **16** (CH_2Cl_2 as solvent.)

the vibrational modes of the five-membered ring, but not the symmetric stretching vibrations of the CX_2^- groups. The calculations also predicted that the more intense bands of greater frequencies in the region 1550−1600 cm^{-1} are assigned to the asymmetric stretching vibrations of the $N-C^+-N$ group, while the less intense bands of smaller frequencies are attributed to the symmetric stretching vibrations. Appearance of these bands in the above region is indicative of the double bond character of the C−N bonds by contribution of the canonical structures **22a** and **22b**.[5b,6f]



22a **22b**

X = Y = Se
X = Se, Y = S
X = Y = S

UV/vis spectra of **16**, **19**, and **20** show that the replacement of sulfur by selenium atom results in a regular bathochromic effect (Figure 3). Thus, the most intense bands of **16**, **19**, and **20**, which are ascribable to the $\pi \rightarrow \pi^*$ transitions of the CX_2^- groups, appear at 426 (14260), 393 (13840), and 356 nm (ϵ 14920), respectively. The diselenocarboxylate **16** shows two, weak and broad, $n \rightarrow \pi^*$ bands at 508 (ϵ 155) and 635 nm (134), the latter of which is the origin of the dark green color of the compound.

Figures 4 and 5 show the molecular and crystal structures of **16** and **20** which were determined by X-ray crystallographic analyses; those of **19** could not be determined because of the disordered arrangement of the $CSSe^-$ group in the crystal. Both molecular and crystal structures of **16** and **20** closely resemble each other. The planes of the carbenium ion part and that of the chalcogenocarboxylate part are nearly perpendicular; 86.3° for **16** and 88.1° for **20**. The perpendicular conformations of **16** and **20** must be retained in solution by analogy with the ^1H NMR analysis of **19**. The dihedral angles predicted by the ab initio calculations are 88.5° for **16**, 89.4° for **19**, and 89.5° for **20**.[14] The Coulombic interactions between the carbenium ion carbon and the lone pair electrons of the negatively charged chalcogen atoms would best explain the observed conformation (Figure 6). The attractive interactions are reflected in the reduction of the bond angles C^+-C-X (X = S, Se) to 114° both for **16** and **20** (calculated angle, 113° both for **16** and **20**), which also results in the shortening of the nonbonded distances between the carbenium carbon and the chalcogen atoms, 2.75 for **16** and 2.65 Å for **20** (calculated distances, 2.73 for **16** and 2.64 Å for **20**;[14] sum of the van der Waals radii, 3.60 for **16** and 3.50 Å for **20**[15]). The shortened bond lengths of the $C^+-CX_2^-$ bond, 1.46 for **16** and 1.48 Å for **20**, would be also ascribed to Coulombic interactions; calculated bond lengths are

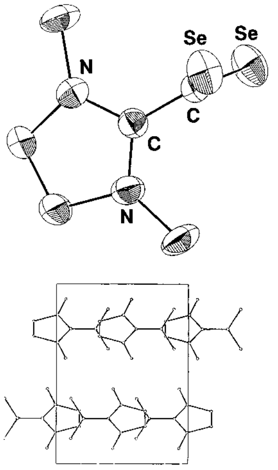


Figure 4. Molecular and crystal structures of **16**.

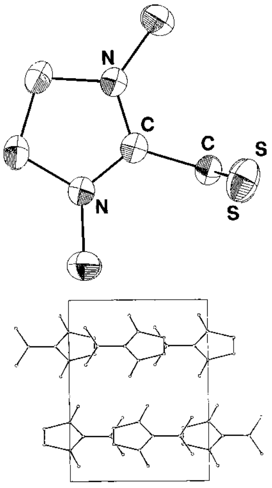


Figure 5. Molecular and crystal structures of **20**.

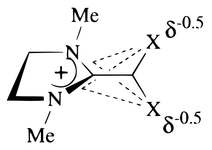


Figure 6.

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[14] The calculations have been performed by using the *Gaussian 98* (revision A.7) program on home-assembled workstations running RedHat Linux 6.0. All of the geometry optimization and vibrational frequency calculations have been carried out at the B3LYP/6-31G* level. All of the calculated frequncies are multiplied by 0.9613. Frisch, M. J.; Trucks, G. W.; Schlegel, H. B.; Scuseria, G. E.; Robb, M. A.; Cheeseman, J. R.; Zakrzewski, V. G.; Montgomery, J. A., Jr.; Stratmann, R. E.; Burant, J. C.; Dapprich, S.; Millam, J. M.; Daniels, A. D.; Kudin, K. N.; Strain, M. C.; Farkas, O.; Tomasi, J.; Barone, V.; Cossi, M.; Cammi, R.; Mennucci, B.; Pomelli, C.; Adamo, C.; Clifford, S.; Ochterski, J.; Petersson, G. A.; Ayala, P. Y.; Cui, Q.; Morokuma, K.; Malick, D. K.; Rabuck, A. D.; Raghavachari, K.; Foresman, J. B.; Cioslowski, J.; Ortiz, J. V.; Baboul, A. G.; Stefanov, B. B.; Liu, G.; Liashenko, A.; Piskorz, P.; Komaromi, I.; Gomperts, R.; Martin, R. L.; Fox, D. J.; Keith, T.; Al-Laham, M. A.; Peng, C. Y.; Nanayakkara, A.; Gonzalez, C., Challacombe, M.; Gill, P. M. W.; Johnson, B.; Chen, W.; Wong, M. W.; Andres, J. L.; Gonzalez, C.; Head-Gordon, M.; Replogle, E. S.; Pople, J. A. Gaussian, Inc.: Pittsburgh, PA, 1998.

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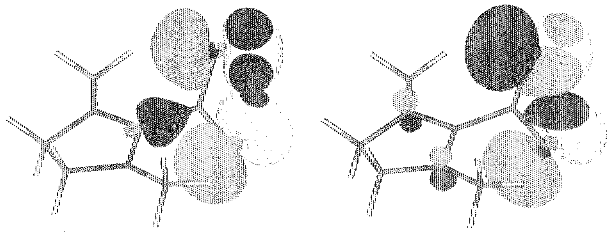
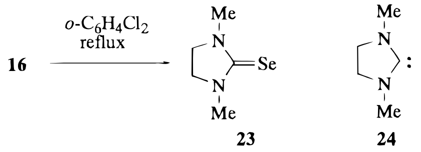


Figure 7. HOMO-1 (left) and HOMO (right) of **16** by ab initio calculations (B3LYP/6-31G*).

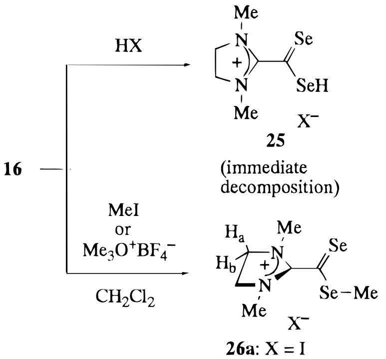
1.47 for **16**, 1.48 for **19**, and 1.49 Å for **20**.[14] The bond lengths of the two C−X (X = S, Se) bonds are equal and 1.80 for **16** and 1.66 Å for **20** (calculated bond lengths; 1.81 for **16** and 1.68 Å for **20**). These values are much closer to the bond distances of the common C−Se (1.76) and C−S (1.67 Å) double bonds than those of the C−Se (1.94) and C−S (1.75 Å) single bonds.[16] The $C^+{-}N$ bonds are 1.33 for **16** and 1.32 Å for **20** (calculated bond lengths, 1.34 Å both for **16** and **20**), which are shorter than the common C(sp^2)-N(sp^3) bond lengths, 1.36 Å, indicating the contribution of the canonical structures **22**.

Some explanation of the geometry of the compounds described above is provided by consideration of molecular orbitals.[14] Figure 7 shows the HOMO-1 and HOMO of **16.**[17] The HOMO-1, in which the σ-like orbital extends from the five-membered ring carbon to the dithiocarboxylate carbon, may partly contribute to the shortening of the $C^+{-}CS_2^-$ bond, while the HOMO, in which the p-orbitals on the sulfur atoms extend to the upper and lower sides of the five-membered ring carbon, may correspond to the interaction given in Figure 7. The HOMO-1 and HOMO, which closely resemble those of **16**, were also obtained for **20**.[14]

Reactivities. Although pure **16** is thermally stable (mp, dec > 192 °C), the crude compound tends to decompose with liberation of selenium even at room temperature both in solution and at solid state; it also decomposes during purification by silica gel column chromatography. Heating pure **16** in refluxing *o*-dichlorobenzene produced a complex mixture containing 2-selenoxo-1,3-dimethylimidazolidine (**23**) in 11% yield. The formation of **23** may be explained as the result of the reaction of the carbene (**24**) and selenium, which were formed from **16**; the decomposition of **16** in the presence of elemental selenium increased the yield of **23** to 21%.[18]

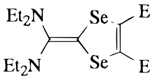


All attempts to obtain free acids (**25**) by dissolving **16** in neat acids or solutions containing these acids, such as CH_3CO_2H, CF_3CO_2H, CF_3SO_3H, HBF_4, and H_2SO_4, brought about the immediate decomposition of the resulting **25** even at low temperatures with formation of red selenium. The diselenoic acid esters (**26a**) and (**26b**)[8] could be obtained easily as dark green crystals in high yields by treatment with MeI and $Me_3O^+BF_4^-$, respectively. In the ^{1}H NMR spectrum at −10 °C, the methylene hydrogen signals of **26a** appeared as an AA′BB′ multiplet because of the restricted rotation about the $C^+{-}CSe_2$ bond, which makes H_a and H_b nonequivalent. The same is true of **26b**. Both **26a** and **26b** are thermally labile and decompose with liberation of elemental selenium at room temperature to give complex mixtures both in solution and at solid state.



26a: X = I
26b: X = BF_4

The reaction of **6** with dimethyl acetylenedicarboxylate (DMAD) produces the 1,3-diselenole (**27**), the 1,3-dipolar cycloadduct of **4** and DMAD, in excellent yield.[5l] In contrast, the reaction of **16** with DMAD in a 1:1 molar ratio failed to give the corresponding adduct (**28**) (E = CO_2Me) but gave a complex mixture containing a small amount of the 1:2 adduct (**30a**). The reaction of **16** with DMAD in a 1:2 molar ratio gave **30a** in 67% yield. The 1,3-diselenole **27** did not react with DMAD. The reaction of **16** with diethyl acetylenedicarboxylate (DEAD) (1:2 molar ratio) also gave the 1:2 adduct **30b** in 60% yield. The electron-rich system **28**, which is highly polarized by contribution of the canonical structure **31**, should be reactive toward DMAD and DEAD and undergoes a stepwise [2 + 2] cycloaddition with these acetylenes to afford (**29**) with release from the unfavorable 8π-structure of the 1,3-diselenole ring. The opening of the four-membered ring of **29** leads to the final product **30**. The same reaction was also reported with the sulfur analogue **20**.[6f]



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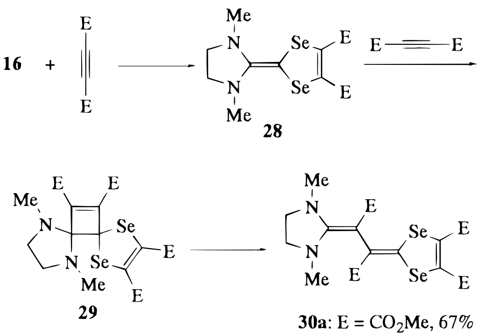
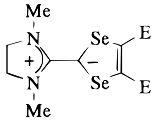


30a: E = CO_2Me, 67%
30b: E = CO_2Et, 60%



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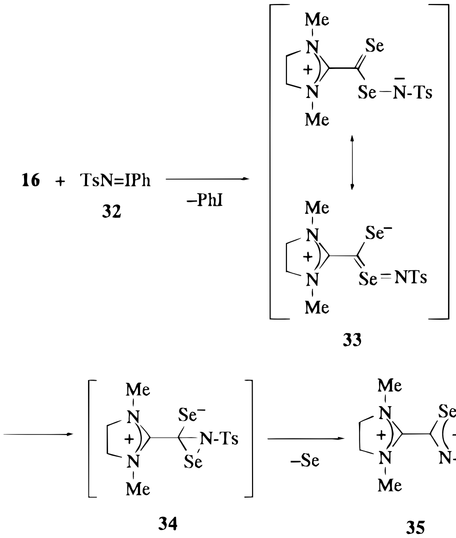
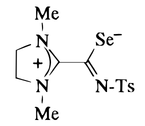
(16) Allen, F. H.; Kennard, O.; Watson, D. G.; Brammer, L.; Orpen, A. G.; Taylor, R. *J. Chem. Soc., Perkin Trans. 2* **1987**, S1.

(17) Molecular orbitals were visualized by using the Molden program; Schaftenaar, G.; Noordik, J. H. *J. Comput.-Aided Mol. Design* **2000**, *14*, 123.

(18) The *N*-phenyl analogue of **20** was reported to give 2-selenoxo-1,3-diphenylimidazolidine when heated with elemental selenium at 220 °C in 53% yield.[6g]

Addition of *N*-[(*p*-tolylsulfonyl)imino]phenyliodinane (**32**) to a solution of **16** in CH_2Cl_2 at −10 °C gave a red mixture with immediate disappearance of the original green color. Purification of the mixture by silica gel column chromatography gave another interesting inner salt (**35**) as thermally stable, orange crystals in 31% yield. The expected initial adduct (**33**), a selone-*Se*-imide, was not isolated in pure form despite much effort. When the mixture was heated at reflux for 6 h after the addition of **32** to **16**, the yield of **35** was improved to 68%. The formation of **35** is explained as the result of deselenation of **33** through the three-membered ring intermediate (**34**). This type of desulfurization has been often observed with thione-*S*-imides.[19] The carbon atom peak of the CSeNTs group of **35** appeared at δ 183, which is lower by 38 ppm than that of **16**, suggesting that the canonical structure **35′** is the major contributor of the compound.





35′

Attempted conversion to the corresponding selenoketene, by elimination of one selenium atom from **16** with Ph_3P, did not take place.

Experimental Section

Solvents were purified and dried in the usual manner. All of the reactions were carried out under argon. Silica gel column chromatography was performed on silica gel 7734 (Merck, 70−230 mesh). Melting points were determined on a Mel-Temp capillary tube apparatus and are uncorrected. ^1H- and ^{13}C NMR spectra were recorded on a Bruker ARX400, a Bruker AM400, a Bruker AM300, or a Bruker AC200 spectrometer using $CDCl_3$ as the solvent with TMS as the internal standard. IR and UV/vis spectra were recorded on a Hitachi 270-50 and a JASCO V-560 spectrophotometer, respectively. Elemental analyses were performed by the Chemical Analysis Center of Saitama University.

Preparation of the Diselenocarboxylate 16. Slow addition of a solution of 0.92 g (8.2 mmol) of 2-methylene-1,3-dimethylimidazolidine (**7**)[10] in ether (10 mL) to a solution of 1.88 g (8.2 mmol) of Se_2Cl_2 in CH_2Cl_2 (40 mL) at −78 °C resulted in the separation of a dark red solid. Et_3N (2.0 mL, 16.5 mmol) was then added at −78 °C and the mixture warmed slowly to room temperature over a period of 12 h. The mixture begins to turn green at about −30 °C with dissolution of the dark red solid. The resulting dark green mixture was filtered to remove the red selenium, which separated during the reaction. The filtrate was washed with water, dried over $MgSO_4$, and evaporated to leave 1.06 g (48%) of dark green crystalline solid of **16**: mp dec > 192 °C; dark green needles (CH_2Cl_2/hexane); ^1H NMR (400 MHz) δ 3.13 (s, 6H, CH_3), 3.84 (s, 4H, CH_2); ^{13}C NMR ($CDCl_3$, 100.6 MHz) δ 33.7, 49.4, 177.2, 221.1; IR (KBr) 1576, 1549, 1398, 1358, 1278, 1219, 1019, 910, 661 cm^{-1}; UV/vis(CH_2Cl_2) λ_{max} (ϵ) 635 (134), 508 (135), 426 (14260), 279 nm (5330). Anal. Calcd for $C_6H_{10}N_2Se_2$: C, 26.88; H, 3.76; N, 10.45. Found: C, 27.01; H, 3.67; N, 10.20.

Conversion of 16 to the Selenothiocarboxylate 19 and Dithiocarboxylate 20. A mixture of 104 mg (0.4 mmol) of **16** and elemental sulfur (103 mg, 0.4 mmol as S_8) in 5 mL of $CHCl_3$ was heated under reflux for 4 h. The selenium, separated during the reaction, was removed by filtration and the filtrate was evaporated. The residue was purified by silica gel column chromatography using AcOEt as the eluent to give 66 mg (95%) of **20**; mp dec > 257 °C (lit.,[5c] mp dec > 263 °C); UV/vis (CH_2Cl_2) λ_{max} (ϵ) 496 (58), 428 (164), 356 (14920), 256 nm (8610); for IR and NMR, see Table 1 and Figure 2.

A mixture of 134 mg (0.5 mmol) of **16** and elemental sulfur (24 mg, 0.1 mmol as S_8) in 5 mL of CH_2Cl_2 was stirred for 48 h at room temperature. The selenium, separated during the reaction, was removed by filtration, and the filtrate was evaporated. The residue was chromatographed on a column of silica gel with AcOEt as the eluent to give 15 mg (14%) of **19** and 38 mg (44%) of **20** in this order. The unreacted diselenocarboxylate **16** decomposed during purification by the column chromatography. **19**: mp dec 216−220 °C; dark red plates (CH_2Cl_2/hexane); ^1H NMR (400 MHz) δ 3.12 (s, 6H, CH_3), 3.84 (s, 4H, CH_2); ^{13}C NMR (100.6 MHz) δ 33.7, 49.4, 171.6, 225.1; IR (KBr) 1581, 1575, 1548, 1398, 1280, 1032, 997, 972, 675 cm^{-1}; UV/vis (CH_2Cl_2) λ_{max} (ϵ) 564 (109), 455 (290, sh), 393 (13840), 230 nm (18350). Anal. Calcd for $C_6H_{10}N_2SSe$: C, 32.58; H, 4.56; N, 12.67. Found: C, 32.67; 4.55; N, 12.58.

Thermolysis of 16. A solution of 134 mg (0.5 mmol) of **16** in 5 mL of *o*-dichlorobenzene was heated at 170−175 °C for 4 days. The resulting dark red mixture was purified by silica gel column chromatography with AcOEt as the eluent to give 10 mg (11%) of 2-selenoxo-1,3-dimethylimidazolidine (**23**), mp 142−145 °C, whose IR data agreed with those reported.[20] The thermolysis of 134 mg (0.5 mmol) of **16** in the presence of 40 mg (0.5 mmol) of selenium gave 19 mg (21%) of **23**.

Conversion of 16 to the Carbenium Iodide 26a and Tetrafluoroborate 26b. To a solution of 268 mg (1.0 mmol) of **16** in 5 mL of CH_2Cl_2 was added 70 μL (1.1 mmol) of MeI at room temperature. After stirring for 5 min, the selenium, separated in a trace amount, was removed by filtration and the filtrate was evaporated at 0 °C. The oily residue solidified, when kept in a refrigerator overnight by adding 10 mL of hexane, to give 375 mg (91%) of **26a**; mp dec 91−92 °C; dark green needles (CH_2Cl_2/hexane); ^1H NMR (400 MHz, −10 °C) δ 2.78 (s, 3H, $SeCH_3$), 3.14 (s, 6H, NCH_3), 3.97−4.01 (m, 2H, CH_2), 4.53−4.58 (m, 2H, CH_2); ^{13}C NMR (100.6 MHz, −40 °C) δ 19.8, 34.1, 50.6, 172.6, 207.3; UV/vis(CH_2Cl_2) λ_{max} (ϵ) 386 (10170), 236 (23370). Anal. Calcd for $C_7H_{13}N_2Se_2I$; C, 20.51; H, 3.20; N, 6.83. Found: C, 20.32; H, 3.07; N, 6.60.

The reaction of 134 mg (0.5 mmol) of **16** and 74 mg (0.5 mmol) of $Me_3O^+BF_4^-$ gave 159 mg (86%) of the tetrafluoroborate salt **26b**: mp dec > 88 °C; dark green crystals; ^1H NMR (400 MHz, −20 °C) δ 2.80 (s, 3H), 3.11 (s, 6H), 4.05−4.10 (m, 2H), 4.30−4.35 (m, 2H); ^{13}C NMR (100.6 MHz, −20 °C) δ 19.2, 33.7, 50.2, 171.8, 207.5.

Reactions of 16 with DMAD and DEAD. Addition of a solution of 142 mg (1.0 mmol) of dimethyl acetylenedicarboxylate in 1 mL of CH_2Cl_2 to a solution of 134 mg (0.5 mmol) of **16** in 5 mL of CH_2Cl_2 resulted in the immediate disappearance of the green color due to **16** to afford a red mixture. After stirring for 0.5 h, the mixture was filtered

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(19) (a)Tamagaki, S.; Sakaki, K.; Oae, S. *Heterocycles* **1974**, *2*, 1974. (b) Tangerman, A.; Zwanenburg, B. *Recl. Trav. Chim. Pays-Bas* **1979**, *98*, 127. (c) Motoki, S.; Toba, Y.; Karakasa, T.; Saito, T. *Chem. Lett.* **1988**, 319. (d) Nakayama, J.; Masui, N.; Sugihara, Y.; Ishii, A. *Bull. Chem. Soc. Jpn.* **1998**, *71*, 1181.

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to remove the resulting small amount of selenium and evaporated. The residue was purified by silica gel column chromatography using AcOEt as the eluent to give 186 mg (67%) of **30a**: mp dec 207−209 °C; yellow plates (CH_2Cl_2/hexane); ^{1}H NMR (400 MHz) δ 2.63 (broad s, 3H, NCH_3), 3.01 (broad s, 3H, NCH_3), 3.45 (broad s, 2H, CH_2), 3.57 (s, 3H, CO_2CH_3), 3.74 (s, 3H, CO_2CH_3), 3.78 (broad s, 2H, CH_2), 3.82 (s, 3H, CO_2CH_3), 3.85 (s, 3H, CO_2CH_3); ^{13}C NMR (100.6 MHz) δ 36.3, 38.7, 50.3, 50.4, 50.5, 52.3, 53.08, 53.14, 72.2, 118.8, 133.6, 141.8, 149.2, 162.6, 163.0, 164.7, 166.6, 168.6; IR (KBr) 1727, 1710, 1663, 1575, 1538, 1435, 1412, 1313, 1235, 1179, 1157, 1064 cm^{-1}. Anal. Calcd for $C_{18}H_{22}N_2O_8Se_2$: C, 39.14; H, 4.02; N, 5.07. Found: C, 39.39; 4.02; N, 4.81.

The reaction of **16** (0.3 mmol) with diethyl acetylenedicarboxylate (0.6 mmol) in CH_2Cl_2 gave 110 mg (60%) of **30b**: mp dec 154−156 °C; yellow plates (CH_2Cl_2/hexane); ^{1}H NMR (300 MHz) δ 1.15 (t, $J = 7.1$ Hz, 3H), 1.24 (t, $J = 7.0$ Hz, 3H), 1.31 (t, $J = 7.1$ Hz, 3H), 1.32 (t, $J = 7.0$ Hz, 3H), 2.63 (broad s, 3H, NCH_3), 2.97 (broad s, 3H, NCH_3), 3.22−3.62 (m, ring CH_2), 3.68−3.89 (m, ring CH_2), 4.17−4.33 (m, 8H); ^{13}C NMR (100.6 MHz) δ 13.9, 14.0, 14.4, 14.8, 36.3, 38.9, 50.2, 50.9, 58.7, 60.9, 62.3, 62.7, 72.7, 118.9, 134.0, 141.5, 149.2, 162.4, 162.5, 164.9, 166.4, 168.3; IR (KBr) 1727, 1716, 1661, 1538, 1234, 1058 cm^{-1}. Anal. Calcd for $C_{22}H_{30}N_2O_8Se_2$: C, 43.43; H, 4.97; N, 4.60. Found: C, 43.49; H, 4.92; N, 4.55.

Conversion of 16 to the Inner Salt 35. Addition of 113 mg (0.3 mmol) of **32**[21] to a solution of 54 mg (0.2 mmol) of **16** in 3 mL of CH_2Cl_2 resulted in the immediate disappearance of the green color due to **16** to give a red mixture. After stirring for 12 h, the resulting insoluble materials were removed by filtration, and the filtrate was evaporated. The residue was chromatographed on a column of silica gel using AcOEt as the eluent to give 22 mg (31%) of the inner salt (**35**). When 56 mg (0.21 mmol) of **16** and 102 mg (0.27 mmol) of **32** had been allowed to react in $CHCl_3$ at room temperature and the resulting mixture heated under reflux for 6 h, 51 mg (68%) of **35** was obtained. The probable intermediate **33** could not be isolated, although the reaction and the workup of the reaction mixture were carried out at low temperatures. **35**: mp 188−191 °C; orange plates (CH_2Cl_2/hexane); ^{1}H NMR (200 MHz) δ 2.40 (s, 3H, CH_3), 3.00 (s, 6H, NCH_3), 3.82 (s, 4H, CH_2), 7.24 (m, 2H), 7.96 (m, 2H); ^{13}C NMR (50 MHz) δ 21.5, 33.6, 49.7, 128.3, 128.7, 137.1, 143.0, 164.5, 182.9; IR (KBr) 1602, 1430, 1412, 1304, 1287, 1145, 1084, 769, 682, 554, 544 cm^{-1}. Anal. Calcd for $C_{13}H_{17}N_3O_2SSe$: C, 43.58; H, 4.78; N, 11.73. Found: C, 43.52; H, 4.69; N, 11.48.

X-ray Crystallographic Analysis of 16 and 20. Single crystals of **16** and **20** were mounted on a MAC Science DIP3000 diffractometer with a graphite-monochromator at 23 °C. Oscillation and nonscreen Weissenberg photographs were collected on the imaging plates of the diffractometer by using Mo Kα radiation ($\lambda = 0.71073$ Å), and the data collection was made by the MAC DENZO for all observed reflections. The structure were solved by direct methods using SIR[22] in the CRYSTAN-GM program system. The atomic coordinates and the anisotropic thermal parameters of the non-H atoms were refined by full matrix least squares.[23] Crystal data of **16**: chemical formula, $C_6H_{10}N_2Se_2$; formula weight, 268.08; crystal size, $0.58 \times 0.11 \times 0.08$ mm; unit-cell dimensions, $a = 7.730(1)$ Å, $b = 10.585(2)$ Å, $c = 10.918(2)$ Å; volume of unit cell, 893.3(2) Å^3; crystal system, orthorhombic; space group, P_{bna}; Z, 4; D_x, 1.993 Mg m^{-3}; number of total reflections measured, 1417; number of observed reflections 966 [$I > 1.00\ \sigma(I)$]; number of parameters varied, 54; R, 0.060; R_w, 0.052; S, 2.016. Crystal data of **20**: chemical formula, $C_6H_{10}N_2S_2$; formula weight, 174.29; crystal size, $0.18 \times 0.16 \times 0.16$ mm; unit-cell dimensions, $a = 7.651(1)$ Å, $b = 10.259(1)$ Å, $c = 10.769(2)$ Å; volume of unit cell, 845.3(1) Å^3; crystal system, orthorhombic; space group, P_{bna}; Z, 4; D_x, 1.369 Mg m^{-3}; number of total reflections measured, 1432; number of observed reflections 1032 [$I > 2.00\ \sigma(I)$]; number of parameters varied, 67; R, 0.046; R_w, 0.062; S, 1.459.

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Supporting Information Available: Complete crystallographic data for **16** and **20** (PDF). This material is available free of charge via the Internet at http://pubs.acs.org.

JA001213R

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