New synthesis of hypervalent T-shaped coordination compounds of selenium by the reaction of bis(2-bromoethyl)selenium dibromide with pyridine and its derivatives

Masatsugu Miura, Yoshinori Takanohashi, Yoichi Habata and Sadatoshi Akabori*
Department of Chemistry, Faculty of Science, Toho University, Funabashi, Chiba 274, Japan

The reaction of bis(2-bromoethyl)selenium dibromide 1 with pyridine 2a and its derivatives as nucleophile gave T-shaped coordination compounds of selenium 3a–3e with two halogen atoms in the *trans* positions in moderate to good yields. However, the reaction of bis(2-bromoethyl)selenide 4 with 2a gave 1,1′-(selanediyldiethylene) dipyridin-1-ium dibromide 5 as a normal substituted product in 42% yield. In addition, 1-(2-selanylethyl) pyridin-1-ium bromide 11 was obtained by the reaction of (2-bromoethyl)phenylselenium dibromide 10 with 2a in 29% yield. The crystal structures of 3a, 3b, 3d, 3e, 5 and 11 have been determined by X-ray analyses. The X-ray analysis of 11 revealed that two conformers about the CH$_2$–CH$_2$ bond exist in one crystal unit at room temperature; however, the ^{1}H NMR spectra of the compound at room temperature showed relatively free rotation about the CH$_2$–CH$_2$ bond in solution.

Linear three-centred systems of selenium atoms are already known in the complexes of triselenocyanate[1] or tris(selenourea) ions.[2] In these ions, a linear selenium–selenium–selenium chain exists and the central selenium atoms assumes a T-shaped coordination. Organic compounds having selenium in a T-shaped coordination have been reported in which there is an almost linear halogen–selenium–halogen sequence[3,4] instead of the Se–Se–Se chain. In previous papers, we have investigated the reactivity of dialkylselenium dihalides for example in the selective reduction of tertiary amides to the corresponding amines using bis(2-bromoethyl)selenium dibromide 1–sodium borohydride,[5-7] a one-pot preparation of 2,5-bis(alkoxymethyl)tetrahydroselenophenes[8] by cycloaddition of 1 to hexa-1,5-diene, and alkoxyselenation of cyclohexene.[9] In connection with the above investigations we report here the reactions of 1 and its homologues with pyridine and its derivatives as the nucleophilic reagents.[10] Furthermore, the detailed structures of the reaction products have been investigated by X-ray analyses.

Results and discussion

Reaction of bis(2-bromoethyl)selenium dibromide 1 with pyridine 2a and its derivatives 2b–2e

When 1 was allowed to react with 2a as a nucleophile, we first thought that the resulting product 3a was the normal

1   2   3
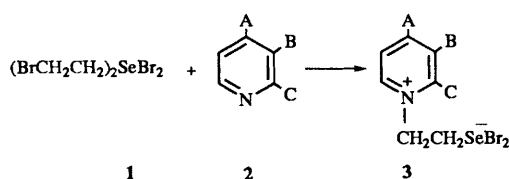
2a,3a A,B,C = H

2b,3b A,C = H, B = Br

2c,3c A,C = H, B = CN
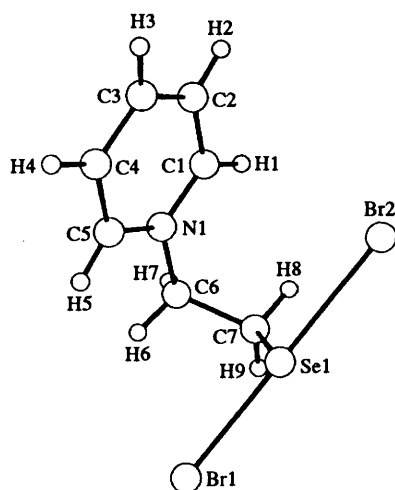
2d,3d A = CN, B,C = H

2e,3e A = H, B,C = -CH=CH-CH=CH-

Scheme 1

disubstituted compound, 1,1′-(selanediyldiethylene)dipyridin-1-ium dibromide 5. It is known that the reaction of a 2-substituted selenide with some anionic nucleophiles gave rise to substituted products; in the ^{1}H NMR spectra of 3a the ratio between the integration of the two triplet peaks due to the methylene protons appearing at δ 5.09 and 3.93 as the A$_2$B$_2$ pattern and the ratio of the multiplet peaks of the pyridine moiety at δ 8.80–7.97 was 4:4:10. As described below, the X-ray analysis of 3a, however, revealed dibromo[2-(pyridin-1-ium-1-yl)ethyl]selanuide 3a as an unexpected product, in which the selenium atom assumes T-shaped coordination. As shown in Scheme 1, a similar reaction of 1 with 3-bromopyridine 2b, 3-cyanopyridine 2c, 4-cyanopyridine 2d and quinoline 2e afforded the corresponding selanuide products 3b–3e in moderate to good yields. The structures of 3b, 3d and 3e were also shown by X-ray analyses to have T-shapes.† Selected bond lengths, and bond and torsion angles of 3a, 3b, 3d and 3e are listed in Table 1. The perspective views with the atomic numbering schemes for 3a, 3b, 3d and 3e are illustrated in Figs. 1–4. The selenium atoms in these compounds are three-coordinate with a carbon atom and two bromine atoms in a T-shaped structure. The Br–Se–Br angles are in the range of 176.8(1) to 178.8(1)°, which is close to 180°. The Br–Se–C bond angles are in the range of 88.8(8) to 92.6(6)°, which is close to 90°. Therefore, the Br–Se–Br sequence is nearly linear and the Se–C bond is nearly perpendicular to the Br–Se–Br chain. The Se–C bond seems to be a commonplace two-centre, two-electron (2c–2e) bond consisting of an overlapping σ-orbital of the selenium atom with an sp^3-hybrid orbital of the carbon atom in the alkyl group. There is no significant difference between the length of the Se–C bond which is in the range of 1.95(1) to 199(2) Å and that of the covalent bond 1.94 Å which is the sum of the covalent radius of Se (1.17 Å)[11] and of sp^3 hybridized carbon (0.767 Å).[12] In addition, the shortest Se–Br bond length [2.463(3) Å of 3b] among the compounds (3a, 3b,

---

† Compound 3c failed to produce a crystal acceptable for X-ray analysis so that its detailed structure was not accurately deduced. However, compound 3c seems to have coordination on the Se atom similar to the other compounds as evidenced by the similarity of the ^{1}H NMR chemical shifts for the methylene chain of the series 3a–e.
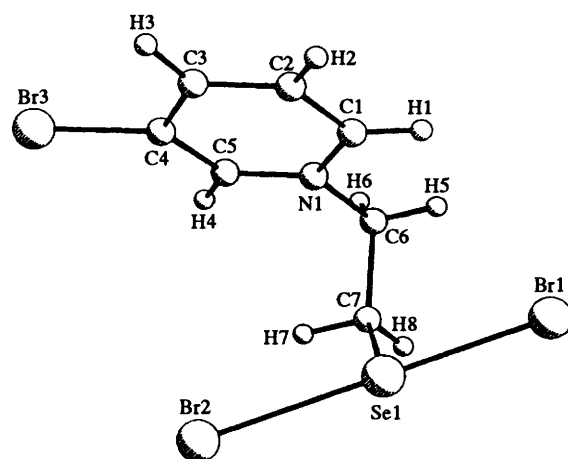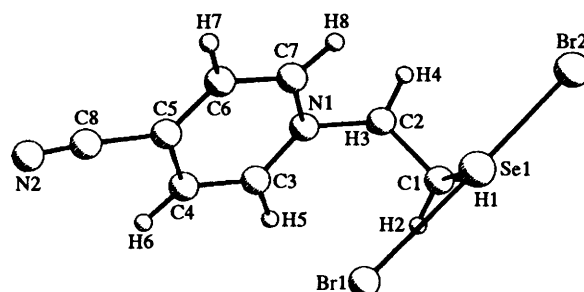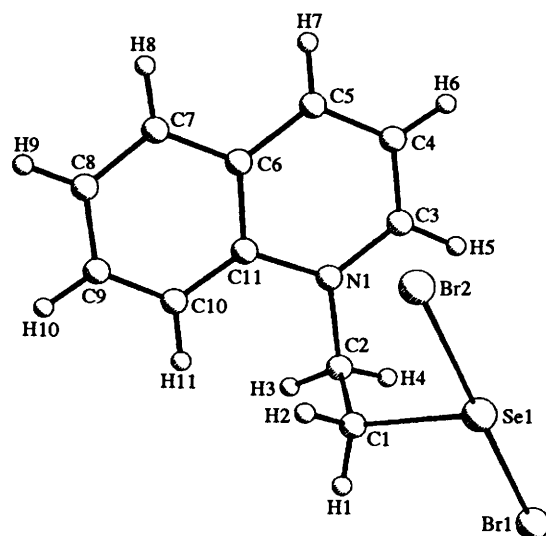
Table 1 Selected bond lengths (Å) and bond angles (°) for **3a**, **3b**, **3d** and **3e**

1	2	3	4	1–2	1–2–3	1–2–3–4
For 3a						
Br(1)	Se(1)	Br(2)		2.499(3)	176.8(1)	
Br(1)	Se(1)	C(7)	C(6)		90.7(6)	74(1)
Br(2)	Se(1)	C(7)	C(6)	2.687(3)	92.1(6)	−105(1)
Se(1)	C(7)	C(6)	N(1)	1.95(2)	114(1)	56(2)
N(1)	C(6)	C(7)		1.48(2)	114(1)	
C(6)	C(7)			1.51(2)		
For 3b						
Br(1)	Se(1)	Br(2)		2.463(3)	177.3(1)	
Br(1)	Se(1)	C(7)	C(6)		92.6(6)	−62(1)
Br(2)	Se(1)	C(7)	C(6)	2.767(3)	89.6(6)	116(1)
Se(1)	C(7)	C(6)	N(1)	1.95(1)	116(1)	−48(2)
N(1)	C(6)	C(7)		1.52(2)	110(1)	
C(6)	C(7)			1.52(2)		
Br(3)	C(4)			1.88(2)		
For 3d						
Br(1)	Se(1)	Br(2)		2.718(5)	178.5(2)	
Br(1)	Se(1)	C(1)	C(2)		88.8(8)	97(2)
Br(2)	Se(1)	C(1)	C(2)	2.480(5)	90.5(8)	−82(2)
Se(1)	C(1)	C(2)	N(1)	1.95(3)	114(2)	−63(3)
N(1)	C(2)	C(1)		1.46(3)	112(2)	
C(1)	C(2)			1.55(4)		
N(2)	C(8)	C(5)		1.11(3)	180(4)	
C(5)	C(8)			1.41(4)		
For 3e						
Br(1)	Se(1)	Br(2)		2.541(3)	178.8(1)	
Br(1)	Se(1)	C(1)	C(2)		89.5(5)	−85(1)
Br(2)	Se(1)	C(1)	C(2)	2.641(3)	90.0(5)	94(1)
Se(1)	C(1)	C(2)	N(1)	1.99(2)	115(1)	−74(1)
N(1)	C(2)	C(1)		1.52(2)	111(1)	
C(1)	C(2)			1.48(2)		

Fig. 2 A perspective view of compound **3b** with the atomic numbering scheme

Fig. 3 A perspective view of compound **3d** with the atomic numbering scheme

Fig. 1 A perspective view of compound **3a** with the atomic numbering scheme

Fig. 4 A perspective view of compound **3e** with the atomic numbering scheme

3d and **3e**) is evidently longer than the single covalent bond (2.31 Å) formed by the covalent radius of Br (1.14 Å)[3] and Se (1.17 Å). These values appear to be in agreement with the linkage of the Br–Se–Br sequence being a straight three-centre, four-electron (3c–4e) bond. Further evidence supporting this bonding is that the average lengths of the two Se–Br bonds, which are in the range of 2.591 to 2.615 Å, are close to 2.60 Å. This value is in agreement with the total of the covalent radius of Br (1.14 Å) and the 'half p-bond' radius of divalent selenium (1.46 Å).[13]

It is known that the total bond length of the three-centred

sequence (Se–Se–Se) in the triselenocyanate ions increases with increasing asymmetry, so that there is a relationship between the total bond length and the asymmetry of the sequence.[2] The same observation is found in the Br–Se–Br sequences in the compounds **3**. The differences between the two Se–Br bond lengths are 0.100 Å in **3e**, 0.188 Å in **3a**, 0.238 Å in **3d** and 0.304 Å in **3b**, and the corresponding total bond lengths of the Br–Se–Br chain are 5.182, 5.186, 5.198 and 5.230 Å, respectively.

The ammonium salts of similar T-shaped coordination compounds of selenium with linear halogen–selenium–halogen sequences have been reported.[3,4,14,15] These salts have been
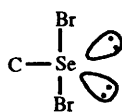
Fig. 5

shown to consist of discrete ammonium cations and selenium anions. In contrast, the crystal structures of **3a**, **3b**, **3d** and **3e** showed the coexistence of a cation and an anion in the molecule. That is, the nitrogen atom of the pyridinium moiety probably serves as a cation and the Br–Se–Br sequence may act as an anion in the molecule. Therefore, 3 forms a zwitterionic molecule.

The structures of the alkylammonium dihalogenoselenocyanates have already been elucidated by X-ray analyses.[3,4] The relationship between the Se–halogen bond length and the corresponding halogen–Se–C angle, that is, the lone pair repulsion of the selenium atom, should have the most influence on the longest Se–halogen bond with the smallest bond angle. As shown in Figs. 1–4, the lengths of the Se–Br bonds which have the Br atom closer to the pyridinium moiety were much longer than those of the other Se–Br bond in the present products 3. Therefore, it is suggested that the effect of the pyridinium moiety is more influential than the lone pair repulsion. Hence, it was surmised that the longer Se–Br bond was slightly weaker than the other Se–Br bond; the negative charge of the entire bromine–selenium–bromine sequence, which balances the positive charge on the nitrogen atom of the pyridine moiety, was biased to the closer Br, and this Br atom acted as a slightly independent anion. There was also no intermolecular contact.

Some T-shaped compounds have been reported other than the above salts,[15–17] and were synthesized from phenylselenenyl halide,[3,15] ammonium selenocyanate,[3,4,14] alkyl or arylselenium trihalide[15,16] and carbon diselenide[17] as the corresponding starting materials. Hence, to our knowledge this is the first preparation of selenium compounds in which the Se atom has a T-shaped configuration with two *trans* halogen atoms from dialkylselenium dihalide as a starting material. Petragnani *et al.* assumed that the T-shaped configuration of selenium and tellurium atoms resulted from the disposition of three bonding and two non-bonding electron pairs.[18,19] Similarly, it is also expected that the configuration about the Se atom in compounds **3a–e**, as shown in Fig. 5, consists of two lone pairs of electrons occupying each of two equatorial sites, a bond to carbon on another equatorial site and two Br–Se bonds on axial sites. Consequently, the products should be hypervalent compounds of selenium.

The reaction of bis(2-bromoethyl)selenide **4**, which has no additional bromine, with pyridine **2a** was studied for comparison with the reaction of 1 with **2a** (Scheme 2).

4   2a   5
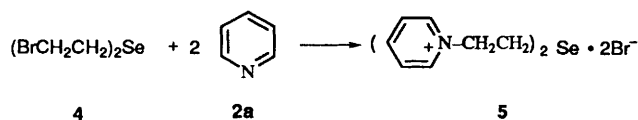
Scheme 2

1,1′-(Selanediyldiethylene)dipyridin-1-ium dibomide **5** was obtained from this reaction as the normal substituted product and the structure was confirmed by X-ray analysis in agreement with the reported substituted products from the reaction of 2-halogeno substituted selenide with some nucleophiles.

A perspective view with the atomic numbering scheme for 5 is illustrated in Fig. 6, and selected bond lengths, bond and torsion angles are listed in Table 2. The two Se–C bond lengths are 1.95(2) and 1.92(2) Å. The torsion angles of Se(1)–C(1)–C(2)–
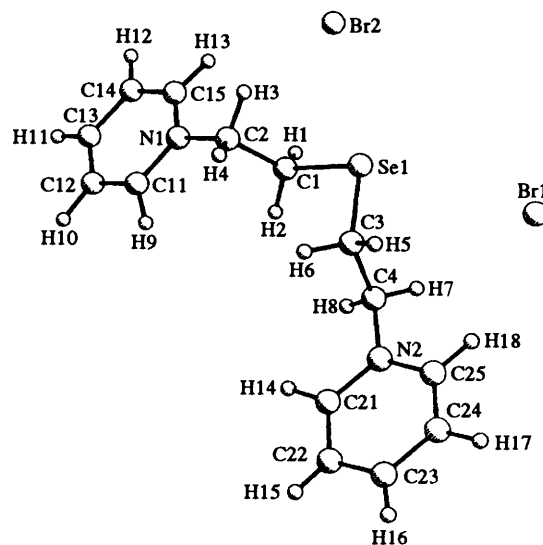

Fig. 6 A perspective view of compound 5 with the atomic numbering scheme

Table 2 Selected bond lengths (Å), and bond and torsion angles (°) for 5

1	2	3	4	1–2	2–3	1–2–3	1–2–3–4
C(1)	Se(1)	C(3)	C(4)	1.95(2)		100.9(6)	80(1)
C(3)	Se(1)	C(1)	C(2)	1.92(2)			89(1)
Se(1)	C(1)	C(2)	N(1)		1.52(2)	111(1)	174(1)
Se(1)	C(3)	C(4)	N(2)		1.53(2)	111(1)	168(1)
N(1)	C(2)	C(1)	Se(1)	1.47(2)		109(1)	
N(2)	C(4)	C(3)	Se(1)	1.50(2)		108(1)	

N(1) and Se(1)–C(3)–C(4)–N(2) are 174(1) and 168(1)°, respectively. Each nitrogen atom of the two pyridinium rings forms a coordination bond with the C(2) or C(4) carbon atom of the ethylene group, and these bond lengths are 1.47(2) and 1.50(2) Å, respectively. Both of the pyridiniumylethyl groups on the selenium atom are roughly symmetrical with the centred selenium atom. The two individual bromine atoms exist as counter anions for the resulting two positively charged nitrogen atoms of each pyridine moiety, and the distances between Br(1) and N(2) and between Br(2) and N(1) are over 4.0 Å. Although oxygen appeared in the molecule, the source of the oxygen was not determined, however, it may be due to water of crystallisation.

## Plausible formation mechanism for T-shaped coordination compounds of selenium 3

It has been proposed that a three-membered episelenonium ion is the common intermediate formed in the reaction of 2-halogeno substituted selenide **4** with nucleophilic reagents.[20] The normal substituted product is provided by nucleophilic attack on the carbon of the cyclic intermediate. The nucleophile attacks the positively charged selenium atom to form a 4-episelane as an intermediate which is readily converted into a selenenyl compound. In a similar manner, the formation of the disubstituted product 5 probably occurred through the nucleophilic attack of the pyridine nitrogen atom on the carbon of the episelenonium ion. In addition, an equilibrium between 1 and 4 is known[21] as shown in Scheme 3. The disubstituted product 5 would be produced from 1 even if the reaction proceeds through 4 by debromination of 1. Formation of **3a** from 1 suggests that the reaction should proceed without debromination and through a different pathway. This seems to be a novel method of synthesizing T-shaped compounds as described below (Scheme 4). It is expected that a bromine
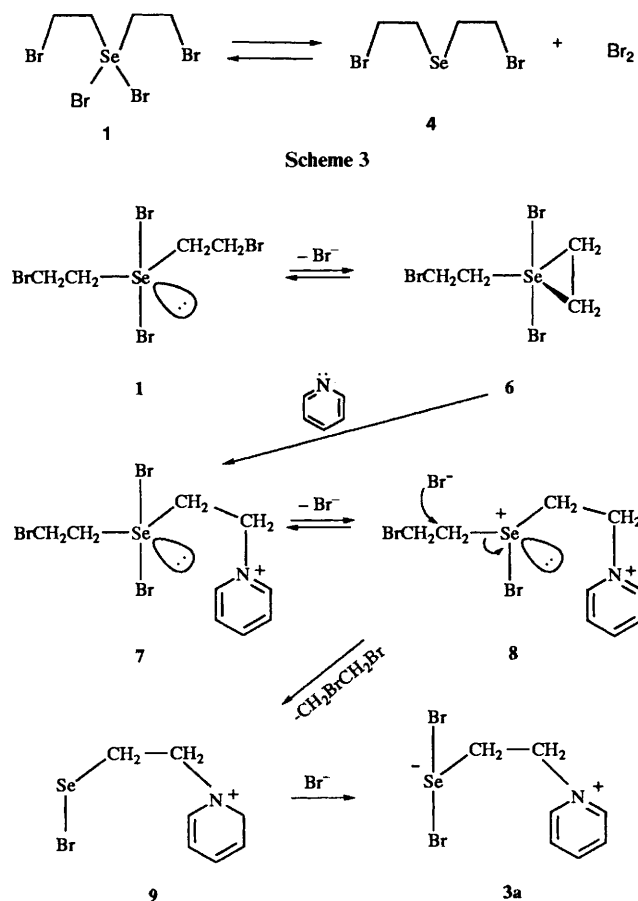
Scheme 3

Scheme 4 Possible formation mechanism for T-shaped coordination compound of selenium **3a**

adduct of the episelenonium ion **6** was formed, and then the three-membered intermediate was attacked by pyridine to give the mono-substituted product **7**. The latter underwent reversible conversion into **8** which was further attacked by a bromine anion to produce **9**. Finally, **3a** was formed by the addition of a bromine anion to **9**.

Reaction of (2-bromoethyl)phenylselenium dibromide 10 with 2a

Compound **10** was allowed to react with **2a** (Scheme 5).

Scheme 5
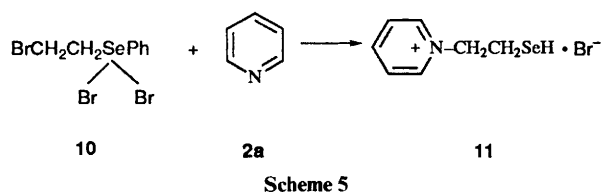
1-(2-Selanylethyl)pyridin-1-ium bromide **11** was obtained in 29% yield from the reaction together with diphenyl diselenide (57%). 1,2-Dibromoethane was also formed in 59% yield. The structure of **11** was determined by X-ray analysis. In addition to substitution of pyridine **2a** for the bromine of the bromoethyl group, elimination of the phenyl group occurred in the reaction. Furthermore, two crystal forms existed in the crystal lattice. Perspective views with the atomic numbering scheme are illustrated in Fig.. 7, and some bond lengths and bond and torsion angles are summarized in Table 3. The Se–C bond lengths of the two forms are 1.96(2) and 1.93(2) Å, and the Se–H bond lengths are 0.948 and 0.954 Å. The Se–C–C bond angles are 109(2) and 113(2)° and the C–Se–H bond angles are 108.98
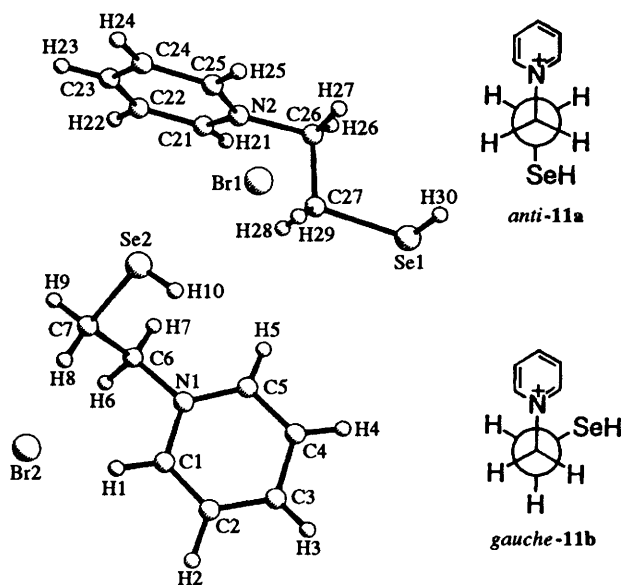

Fig. 7 A perspective view of compound 11 with the atomic numbering scheme

Table 3 Selected bond lengths (Å), and bond and torsion angles (°) for 11

1	2	3	4	1–2	1–2–3	1–2–3–4
For *anti*-11						
Se(1)	C(27)	C(26)		1.96(2)	109(2)	
H(30)	Se(1)	C(27)		0.948	108.98	
N(2)	C(26)	C(27)	Se(1)	1.51(3)	106(2)	172(2)
For *gauche*-11						
Se(2)	C(7)	C(6)		1.93(3)	113(2)	
H(10)	Se(2)	C(7)		0.954	109.03	
N(1)	C(6)	C(7)	Se(2)	1.49(3)	111(2)	64(2)

and 109.03°. A comparison of the two crystal forms shows that the bond lengths and angles are similar. The fundamental difference between the two molecules is the dihedral angle of N–C–C–Se. As shown in Fig. 7, one is the *anti* type with a dihedral angle of 172(2)° and the other is the *gauche* type with a dihedral angle of 65(3)°. The ^{1}H NMR spectra for the two methylene moieties of **11** in CD_3OD showed two triplets at δ 4.05 (J 5.8) and 5.10 (J 5.8) at room temperature; thus the CH_2–CH_2 bond seems to be able to undergo comparatively free rotation at room temperature in solution. Our interest in the rotation around the CH_2–CH_2 bond in **11** led us to study the low-temperature ^{1}H NMR spectra (*ca.* 300, 273, 223 and 193 K). No significant changes in any of the spectral patterns or chemical shifts were observed, although the chemical shift of the *ortho* protons of the pyridinium moiety were slightly shifted downfield (0.10 ppm). It was of special note that the triplet peak due to the two adjacent methylene protons at δ 4.05 and 5.10 at room temperature remained unchanged even at 193 K, indicating that the CH_2–CH_2 bond in **11** rotates freely at low temperature (193 K) in solution, although the *anti* and *gauche* conformers (**11a** and **11b**) exist in the crystal at room temperature.

Experimental

Melting points were recorded with a MELT-TEMP II apparatus and are uncorrected. ^{1}H NMR spectra were obtained using Bruker AC 250 instruments with tetramethylsilane as the internal standard. *J* Values are given in Hz. Infrared

spectra were recorded with a JASCO IR-810 infrared spectro-photometer.

Materials

Bis(2-bromoethyl)selenium dibromide 1, bis(2-bromoethyl) selenide 4 and (2-bromoethyl)phenylselenium dibromide 10 were prepared according to the methods described in the literature.[22-24] Pyridine was purified by distillation in the usual manner. The other pyridine derivatives, quinoline and all solvents purchased from commercial sources were used without further purification.

Dibromo[2-(pyridin-1-ium-1-yl)ethyl]selanuide 3a

To a solution of dibromide 1 (5.0 g, 11 mmol) in dichloro-methane (70 cm^3) was added pyridine 2a (3.5 g, 44 mmol) and the mixture was stirred at room temperature for 4 h. The resulting precipitate was collected by filtration, washed with small amounts of dichloromethane, dried, and then recrystallized from methanol to give the title compound 3a as yellow–orange crystals (2.4 g, 63%), mp 108–110 °C (Found: C, 24.3; H, 2.6; N, 4.0. Calc. for C$_7$H$_9$Br$_2$NSe: C, 24.30; H, 2.62; N, 4.05%); δ_H(250 MHz; CD$_3$CN) 8.80–7.97 (m, 5 H, pyridine ring), 5.09 (t, 2 H, J 5.8, CH$_2$) and 3.93 (t, 2 H, J 5.8, CH$_2$).

Dibromo[2-(3-bromopyridin-1-ium-1-yl)ethyl]selanuide 3b

To a solution of dibromide 1 (1.00 g, 2.2 mmol) in acetonitrile (50 cm^3) was added 3-bromopyridine 2b (0.705 g, 4.46 mmol) and the mixture was stirred at room temperature for 5 h. The reaction mixture was concentrated under reduced pressure. The resulting crystals from the concentrated solution were collected by filtration and recrystallized from methanol to give the title compounds 3b as orange crystals (0.55 g, 59%), mp 131–133 °C (Found: C, 19.9; H, 1.5; N, 3.15. Calc. for C$_7$H$_8$Br$_3$NSe: C, 19.79; H, 1.90; N, 3.30%); δ_H(250 MHz; CD$_3$CN) 9.03–7.87 (m, 4 H, pyridine ring), 5.06 (t, 2 H, J 5.8, CH$_2$) and 3.93 (t, 2 H, J 5.8, CH$_2$).

Dibromo[2-(3-cyanopyridin-1-ium-1-yl)ethyl]selanuide 3c

To a solution of dibromide 1 (1.5 g, 3.3 mmol) in tetra-hydrofuran (50 cm^3) was added 3-cyanopyridine 2c (1.4 g, 13 mmol) and the mixture was stirred at room temperature for 4 h. The solution was concentrated under reduced pressure, and then methanol was added until a yellow powder was precipitated. The precipitate was isolated, washed with a small quantity of methanol and dried to give the title compound 3c as a yellow powder (0.75 g, 61%). The powder was recrystallized from methanol as yellow–orange crystals, mp 129–130 °C (Found: C, 26.3; H, 1.9; N, 7.6. Calc. for C$_8$H$_8$Br$_2$N$_2$Se: C, 25.90; H, 2.17; N, 7.55%); δ_H(250 MHz; CD$_3$CN) 9.27–8.12 (m, 4 H, pyridine ring), 5.48 (t, 2 H, J 6.1, CH$_2$) and 4.01 (t, 2 H, J 6.1, CH$_2$); ν_{max}(KBr)/cm^{-1} 2245m (CN).

Dibromo[2-(4-cyanopyridine-1-ium-1-yl)ethyl]selanuide 3d

To a solution of dibromide 1 (1.5 g, 3.3 mmol) in acetonitrile (50 cm^3) was added 4-cyanopyridine 2d (1.37 g, 13.2 mmol) and the mixture was agitated at room temperature for 4 h. The solution was concentrated under reduced pressure. The resulting crude crystals were isolated and recrystallized from methanol to give the title compound 3d as orange crystals (0.57 g, 46%), mp 150–151 °C (Found: C, 26.3; H, 2.25; N, 7.3. Calc. for C$_8$H$_8$Br$_2$N$_2$Se: C, 25.90; H, 2.17; N, 7.55%); δ_H(250 MHz; CD$_3$CN) 8.99 (d, 2 H, J 6.6, pyridine ring), 8.33 (d, 2 H, J 6.6, pyridine ring), 5.15 (t, 2 H, J 5.4, CH$_2$) and 3.94 (t, 2 H, J 5.4, CH$_2$); ν_{max}(KBr)/cm^{-1} 2240w (CN).

Dibromo[2-(quinolin-1-ium-1-yl)ethyl]selanuide 3e

To a solution of dibromide 1 (2.1 g, 4.6 mmol) in dichloromethane (50 cm^3) was added quinoline 2e (0.6 g, 4.65

mmol) and the mixture was stirred at reflux for 4 h. After cooling, the resulting precipitate was collected by filtration, washed with a small amount of dichloromethane and dried to give a powder. The powder was recrystallized from methanol to give the title compound 3d as yellow–orange crystals (0.98 g, 53%), mp 175–176 °C (Found: C, 33.3; H, 2.7; N, 3.45. Calc. for C$_{11}$H$_{11}$Br$_2$Se: C, 33.36; H, 2.80; N, 3.54%); δ_H(250 MHz; CD$_3$CN) 9.18–7.92 (m, 7 H, quinoline ring), 5.48 (t, 2 H, J 6.1, CH$_2$) and 4.01 (t, 2 H, J 6.1, CH$_2$).

1,1′-(Selanediyldiethylene)dipyridin-1-ium dibromide 5

To a solution of bis(2-bromoethyl) selenide 4 (0.431 g, 1.43 mmol) in dichloromethane (50 cm^3) was added pyridine 2a (0.451 g, 5.70 mmol) and the mixture was stirred at room temperature for 13 h. The reaction mixture was concentrated under reduced pressure, and the residue was recrystallized from acetonitrile. Colourless crystals of the title compound 5 were obtained by filtration and dried (0.274 g, 42%), mp 140–141 °C (Found: C, 34.6; H, 4.0; N, 5.7. Calc. for C$_{14}$H$_{18}$Br$_2$N$_2$Se: C, 35.69; H, 4.28; N, 5.95%); δ_H(250 MHz; CD$_3$CN) 9.81–8.51 (m, 10 H, pyridine ring), 5.53 (t, 4 H, J 7.7, CH$_2$) and 3.87 (t, 4 H, J 7.7, CH$_2$).

1-(2-Selanylethyl)pyridin-1-ium bromide 11

To a solution of dibromide 10 (2.50 g, 5.90 mmol) in chloroform (50 cm^3) was added pyridine 2a (1.87 g, 23.6 mmol) and the mixture was stirred at room temperature for 12 h. The reaction mixture was concentrated under reduced pressure. The residue was chromatographed on silica gel using chloroform–ethanol (3 : 1, v/v) as eluent to give crude diphenyl diselenide (0.52 g, 57%) and the title compound 11 (0.46 g, 29%). Recrystallization of the crude 11 from acetonitrile–benzene gave pure 11 as colourless crystals, mp 119–121 °C (Found: C, 31.6; H, 3.6; N, 4.3. Calc. for C$_7$H$_{10}$BrNSe: C, 31.48; H, 3.77; N, 5.25%); δ_H(250 MHz; CD$_3$OD) 9.20–8.07 (m, 5 H, pyridine ring), 5.10 (t, 2 H, J 5.8, CH$_2$) and 4.05 (t, 2 H, J 5.8, CH$_2$).

X-Ray crystallography of compounds 3a, 3b, 3d, 3e, 5 and 11

Compound 3a. C$_7$H$_9$Br$_2$NSe, M 345.92, crystal dimensions 0.450 × 0.100 × 0.100 mm, orthorhombic, space group $P2_12_12_1$, $a = 9.695(3)$, $b = 14.441(5)$, $c = 7.478(6)$ Å, $V = 1047(2)$ Å^3, $Z = 4$, $D_c = 2.195$ g cm^{-3}, μ(Mo-Kα) = 110.56 cm^{-1}; $R = 0.050$, $R_w = 0.034$, $2\theta < 55.0°$ [$\omega = 4F_o^2/\sigma^2(F_o^2)$ for 485 independent reflections with $I = 3\sigma(I)$].

Compound 3b. C$_7$H$_8$Br$_3$NSe, M 424.82, crystal dimensions 0.300 × 0.300 × 0.250 mm, monoclinic, space group $P2_1/c$, $a = 9.386(2)$, $b = 9.700(2)$, $c = 13.211(2)$ Å, $\beta = 102.50(1)°$, $V = 1174.3(4)$ Å^3, $Z = 4$, $D_c = 2.403$ g cm^{-3}, μ(Mo-Kα) = 132.32 cm^{-1}; $R = 0.048$, $R_w = 0.035$, $2\theta < 50.0°$ [$\omega = 4F_o^2/\sigma^2(F_o^2)$ for 816 independent reflections with $I > 3\sigma(I)$].

Compound 3d. C$_8$H$_8$Br$_2$N$_2$Se, M 370.93, crystal dimensions 0.300 × 0.300 × 0.100 mm, orthorhombic, space group $Pna2_1$, $a = 9.978(5)$, $b = 15.34(2)$, $c = 7.245(4)$ Å, $V = 110.9(1)$ Å^3, $Z = 4$, $D_c = 2.221$ g cm^{-3}, μ(Mo-Kα) = 104.45 cm^{-1}; $R = 0.046$, $R_w = 0.051$, $2\theta < 50.1°$ [$\omega = 4F_o^2/\sigma^2(F_o^2)$ for 602 independent reflections with $I > 3\sigma(I)$].

Compound 3e. C$_{11}$H$_{11}$Br$_2$NSe, M 395.98, crystal dimensions 0.100 × 0.250 × 0.250 mm, monoclinic, space group $P2_1/n$, $a = 8.819(4)$, $b = 7.214(3)$, $c = 19.71(1)$ Å, $\beta = 92.86(5)°$, $V = 1253(1)$ Å^3, $Z = 4$, $D_c = 2.100$ g cm^{-3}, μ(Mo-Kα) = 92.55 cm^{-1}; $R = 0.047$, $R_w = 0.054$, $2\theta < 50.1°$ [$\omega = 4F_o^2/\sigma^2(F_o^2)$ for 957 independent reflections with $I > 3\sigma(I)$].

Compound 5. C$_{14}$H$_{18}$Br$_2$N$_2$SeO, M 469.08, crystal dimensions 0.400 × 0.400 × 0.100 mm, monoclinic, space group $P2_1/a$, $a = 7.840(6)$, $b = 14.781(6)$, $c = 15.555(5)$ Å, $\beta = 103.08(4)°$, $V = 1756(2)$ Å^3, $Z = 4$, $D_c = 1.774$ g cm^{-3}, μ(Mo-Kα) = 66.22 cm^{-1}; $R = 0.047$, $R_w = 0.039$, $2\theta < 50.1°$ [$\omega = 4F_o^2/\sigma^2(F_o^2)$ for 985 independent reflections with $I > 3\sigma(I)$].

Compound 11. $C_7H_{10}BrNSe$, M 267.03, crystal dimensions $0.250 \times 0.250 \times 0.370$ mm, monoclinic, space group $P2_1/c$, $a = 11.182(7)$, $b = 12.330(4)$, $c = 13.633(2)$ Å, $\beta = 96.07(3)°$, $V = 1869(2)$ Å^3, $Z = 8$, $D_c = 1.898$ g cm^{-3}, μ(Mo-Kα) = 81.45 cm^{-1}; $R = 0.056$, $R_w = 0.045$, $2\theta < 50.0°$ [$\omega = 4F_o^2/ \sigma^2(F_o^2)$ for 833 independent reflections with $I > 3\sigma(I)$].

All measurements were carried out with a Rigaku AFC5S four-circle automated diffractometer with graphite mono-chromated Mo-Kα radiation and a 12 kW rotating anode generator. Cell contacts and an orientation matrix for data collection were obtained from a least-squares refinement. The data were collected at 23 ± 1 °C using the ω–2θ scan technique to an above maximum 2θ value of $55.0°$. All intensities were corrected for Lorentz and polarization effects. The structures were solved by direct methods. The non-hydrogen atoms were refined anisotropically. All calculations were performed using the TEXSAN crystallographic software package from Molecular Structure Corporation.[25] Tables of fractional atomic coordinates, bond lengths and angles, torsion angles and thermal parameters have been deposited at the Cambridge Crystallographic Data Centre.‡

---

‡ For details of the deposition scheme, see 'Instructions for Authors', *J. Chem. Soc., Perkin Trans. 1*, 1995, Issue 1.

References

1 S. Hauge, *Acta Chem. Scand.*, 1971, **25**, 1134; S. Hauge and J. Sletten, *Acta Chem. Scand.*, 1971, **25**, 3094; S. Hauge, *Acta Chem. Scand., Ser. A*, 1975, **29**, 163.

2 S. Hauge, D. Opedal and J. Arskog, *Acta Chem. Scand., Ser. A*, 1975, **29**, 225.

3 S. Bjornevag, P. U. Gahre, S. Hauge and O. Vikane, *Acta Chem. Scand., Ser. A*, 1984, **38**, 175.

4 S. Hauge and K. Maroy, *Acta Chem. Scand.*, 1992, **46**, 1166.

5 S. Akabori and Y. Takanohashi, *Chem. Lett.*, 1990, 251.

6 S. Akabori and Y. Takanohashi, *J. Chem. Soc., Perkin Trans. 1*, 1991, 479.

7 S. Akabori, Y. Takanohashi, S. Aoki and S. Sato, *J. Chem. Soc., Perkin Trans. 1*, 1991, 3121.

8 Y. Takanohashi, N. Tabata, T. Tanase and S. Akabori, *J. Organomet. Chem.*, 1993, **450**, 103.

9 Y. Takanohashi, N. Tabata, T. Tanase and S. Akabori, *J. Chem. Soc., Perkin Trans. 1*, 1993, 813.

10 Preliminary report, M. Miura, Y. Takanohashi, Y. Habata and S. Akabori, *Tetrahedron Lett.*, 1994, **35**, 8213.

11 L. Pauling, *The Chemical Bond*, Cornell University Press, Ithaca, NY, 1967.

12 O. Bastiansen and M. Tretteberg, *Tetrahedron*, 1962, **17**, 147.

13 O. Foss, *Acta Chem. Scand.*, 1962, **16**, 779.

14 K. J. Wynne and J. Golen, *Inorg. Chem.*, 1974, **13**, 185.

15 K. J. Wynne and P. S. Pearson, *Inorg. Chem.*, 1972, **11**, 1196.

16 K. J. Wynne, P. S. Pearson, M. G. Newton and J. Golen, *Inorg. Chem.*, 1972, **11**, 1192.

17 S. Larsen and L. Henriksen, *Acta Chem. Scand., Ser. A*, 1984, **38**, 289.

18 N. Petragnani, L. Torres, K. J. Wynne and W. Maxwell, *J. Organomet. Chem.*, 1973, **55**, 295.

19 N. Petragnani and L. Torres, *J. Organomet. Chem.*, 1974, **76**, 241.

20 B. Lindgren, *Acta Chem. Scand., Ser. B*, 1976, **30**, 941.

21 K. A. Jensen and A. Kjaer, *The chemistry of organic selenium and tellurium compounds*, eds. S. Patai and Z. Rappoport, Wiley, Chichester, 1986, vol. 1, p. 15.

22 H. C. Bell and C. S. Gibson, *J. Chem. Soc.*, 1925, 1877.

23 H. Funk and W. Papenroth, *J. Prakt. Chem.*, 1959, **8**, 256.

24 B. Lindgren, *Acta Chem. Scand., Ser. B*, 1977, **31**, 1.

25 Texan-Texray Structure Analysis Package, Molecular Structure Corporation, 1985.