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Attractive Interaction Caused by the Linear F$\cdots$Se−C Alignment in Naphthalene Peri Positions

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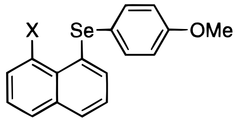
Abstract: The X-ray crystallographic analysis of 8-fluoro-1-(*p*-anisylselanyl)naphthalene (**1**) revealed that the F and Se atoms and the *ipso*-carbon of the *p*-anisyl group (C(An)) aligned linearly. The F atom and the Se−C(An) bond lay on the naphthyl plane: the nonbonded distance between F and Se atoms was 2.753(3) Å and the FSeC(An) angle was 175.0(1)°. Ab initio MO calculations with the 6-311++G(3df,2pd) basis sets performed on the model compound of **1**, HF$\cdots$SeH$_2$, where the aryl groups of **1** were replaced by hydrogens. The calculations exhibited that the energy minimum was achieved when the F, Se, and C(An) atoms aligned linearly. Charge transfer in the formation of HF$\cdots$SeH$_2$ was suggested to occur from F to SeH$_2$ on the basis of natural population analysis, which supported the np_x(F)−σ^*(Se−C(An)) interaction.

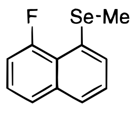
Introduction

Nonbonded interactions between heteroatoms containing group 16 elements in naphthalene 1,8-positions are of current interest.[1] We have also been interested in the nonbonded interaction between a fluorine atom with a small size of the valence orbitals and other heteroatoms in proximity in space, such as a selenium atom. Lone pair−lone pair interactions have been elucidated to play an important role in the nonbonded spin−spin couplings between fluorine−fluorine,[2] fluorine−nitrogen,[3] and selenium−selenium[1d,g,4] atoms. Electrostatic[5a] and charge-transfer[5b] mechanisms were proposed to explain the attractive interactions between oxygen and selenium atoms in close proximity, together with the downfield shifts of the ^{77}Se NMR chemical shifts by the neighboring oxygen, but they are controversial.

In the course of our investigation on the intramolecular interactions between naphthalene peri positions containing the selenium atom(s) were prepared 8-fluoro-1-(*p*-anisylselanyl)-naphthalene (**1**) and 8-fluoro-1-(methylselanyl)naphthalene (**2**).



1 (X = F)
3 (X = H)



2 (X = F)
4 (X = H)

The ^{77}Se NMR chemical shifts of **1** and **2** were observed at much downfield (ca. 90 ppm) relative to those of 1-(*p*-anisylselanyl)naphthalene (**3**) and 1-(methylselanyl)naphthalene (**4**), respectively.[6] It is puzzling how the fluorine atom at the 8-position in **1** and **2** causes such large downfield shifts. The selenium atom in **1** is expected to be electron-rich due to the *p*-methoxyl group, which would be disadvantageous for the electrostatic mechanism, since the mechanism requires the positive charge development at the Se atom.[5a] It is very interesting if the fluorine atom interacts attractively with the selenium atom or the Se−C(An) bond (the bond between the selenium atom and the *ipso*-carbon atom of the *p*-anisyl group) in **1** by the through-space mechanism irrespective of its small size of the valence orbitals. In this paper, we report the structure of **1** studied by the X-ray crystallographic analysis and by the ab initio molecular orbital calculations, exhibiting the linear

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(6) The ^{77}Se chemical shifts of **1**, **2**, **3**, and **4** were δ 440.9, 250.4, 354.2, and 159.0, respectively.

S0002-7863(97)04070-5 CCC: $15.00

Table 1. Selected Crystal Data and Structure Refinement for **1**

formula	$C_{17}H_{13}FOSe$
fw, g mol^{-1}	331.25
cryst syst	triclinic
space group	$P\bar{1}$ (No. 2)
color	colorless
a, Å	13.649(7)
b, Å	14.068(8)
c, Å	8.184(5)
α, deg	93.06(5)
β, deg	100.20(5)
γ, deg	68.21(4)
V, Å^3	1436(1)
D_{calcd}, g cm^{-3}	1.532
Z	4
θ range for data collected, deg	2.0−27.5
data	4292
parameter	362
R	0.045
Rw	0.044
GOF	1.4291

alignment of the F···Se−C(An) atoms with the analysis of the charge-transfer[5b] mechanism for the interaction.

Results and Discussion

Single crystals of **1** were obtained via slow evaporation of a hexane solution and one of suitable crystals was subjected to X-ray crystallographic analysis. The crystallographic data are collected in Table 1. There are two types of structures of **1** in the crystal (structure **A** and structure **B**). The selected interatomic distances, angles, and torsional angles of structure **A** and structure **B** are shown in Table 2. One of the structures of **1** (structure **A**) is shown in Figure 1.[7] For structure **A**, the planarity of the naphthyl and anisyl planes was very good. The anisyl plane was perpendicular to the naphthyl plane (the torsional angle C(1)−Se−C(11)−C(16) being 89.0(4)°). The fluorine atom and the Se−C(An) bond lay on the naphthyl plane: the torsional angles of F−C(9)−C(10)−C(1), Se−C(1)−C(10)−C(9), and C(11)−Se−C(1)−C(10) were 1.2(6)°, −0.1(5)°, and −179.2(3)°, respectively. The F−Se−C(An) angle in the naphthyl plane ($\angle$FSeC(An)) was 175.0(1)°. The nonbonded distance between F and Se atoms (r(F,Se)) was 2.753(3) Å, which was shorter than the sum of the van der Waals radii[8] of F and Se atoms (3.35 Å) by 0.60 Å.

Why do the fluorine, selenium, and carbon atoms align linearly? Since the π-orbitals in naphthalene ring, together with p-type lone pairs of F and Se atoms, are perpendicular to those of the anisyl ring, the interaction between the two π-systems would be negligible. Two types of interactions are possible: one is the interaction of the π-framework of naphthalene ring cooperated by the p-type orbitals of fluorine and selenium atoms and the other is the n(F)−σ*(Se−C(An)) type interaction, which is strongly suggested by the linear alignment of the F···Se−C(An) atoms in **1**.[9,10]

The n(F)−σ*(Se−C(An)) type interaction is examined first. Ab initio molecular orbital calculations were performed on the model compound of **1**, $HF\cdots SeH_aH_b$, to elucidate the nature of the nonbonded interaction between the atoms: the aryl groups in **1** are replaced by hydrogens in the model compound and H_a and H_b denote the hydrogens near HF and far from HF, respectively (Scheme 1). The 6-311++G(3df,2pd) basis sets of the Gaussian 94[11] program at HF and MP2 levels were employed for the calculations. Calculations were carried out for the two structures. For structure **a**, all atoms are placed on the xz plane and the Se atom is placed at the origin. The angle θ_1 is defined as the sum of the angles between F−Se bond and the y axis and between y axis and Se−H_b bond (namely, θ_1 is equal to the torsional angle HH_aSeH_b), which is therefore fixed at 180.0°. The $\angle$HFSe, $\angle$FSeH_b (θ_2; θ_2 is defined as 360.0 − ($\angle$FSeH_a + $\angle H_a$SeH_b)° when θ_1 is not 180.0°), and $\angle H_a$SeH_b in $HF\cdots SeH_aH_b$ are fixed at 100.0°, 185.0°, and 100.8°, respectively. The r(F,Se) value is fixed at 2.753 Å and r(F,H), r(Se,H_a), and r(Se,H_b) are optimized (Scheme 1a). For structure **b**, all atoms are placed on the xz plane except for H_b and the Se atom is placed at the origin. The $\angle$HFSe, $\angle$FSeH_a, and the torsional angle H−F−Se−H_a in $HF\cdots SeH_aH_b$ are fixed at 90.0°, 90.0°, and 0.0°, respectively, while θ_1 and θ_2 (and therefore $\angle H_a$SeH_b) are optimized. The r(F,Se) value is fixed at 2.753 Å, and r(F,H), r(Se,H_a), and r(Se,H_b) are optimized (Scheme 1b). Calculations on HF and SeH_2 were also performed similarly for convenience of comparison.

The results of the MO calculations on structure **a** at the HF and MP2 levels with the 6-311++G(3df,2pd) basis sets are shown in Table 3. The MO calculations were performed with variously fixed θ_1 for structure **b** at the MP2/6-311++G(3df,2pd) level, and two energy minima existed. The one corresponds to structure **b** with θ_1 = 180.0°,[12,13] and the other to structure **b** with θ_1 = 65.4°. The energy of the adduct was plotted against θ_1, and the results are shown in Figure 2. Structure **b** with θ_1 = 180.0° was shown to be more stable than structure **b** with θ_1 = 65.4° by 0.0073 au (19 kJ mol^{-1}). The results, together with those at the HF level, are also shown in Table 3. Structure **b** with θ_1 = 65.4° brought out the importance of the linear F···Se−H_b interaction in structure **b** with θ_1 = 180.0°. The bond distances, especially r(Se,H_b), of structure **b** with θ_1 = 180.0° became longer and the bond angle of the adduct became smaller relative to the corresponding values of the free components whereas those of structure **b** with θ_1 = 65.4° were close to those of the components. Both of the r(Se,H_a) and r(Se,H_b) values of structure **b** with θ_1 = 180.0° increased, whereas only r(Se,H_b) was increased in structure **a** in the formation of the adduct. The results of MO calculations support that the linear alignment of F···Se−C(An) atoms is not due to the crystal packing effect but the results of the energy lowering effect caused by the linear alignment of the F atom and the Se−C(An) bond.

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(7) Although the discussion is focused on structure **A**, it is also valid on structure **B**.

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(12) In the actual calculations on structure **b**, the angles θ_1 and θ_2 were optimized to be 180.11 and 179.16°, respectively, at the HF level and 180.03 and 181.12°, respectively, at the MP2 level. However, precisely the same results, such as bond lengths and angles, and energies were obtained at both levels when the calculations were performed with θ_1 of structure **b** fixed at 180.00°. The potential surface must be almost flat near θ_1 = 180°.

(13) The energy of the adduct was evaluated to be larger than the sum of those for HF and H_2Se. The results exhibit that the adduct is destabilized relative to the free components. The fluoro and selanyl groups cannot exist this close if the two groups are not joined by the naphthalene 1,8-positions.

Table 2. Selected Interatomic Distances (Å), Angles (deg), and Torsional Angles (deg) of **1**

structure **A**		structure **B**	
Interatomic Distances			
SeA−C1A	1.928(4)	SeB−C1B	1.932(4)
SeA−C11A	1.918(4)	SeB−C11B	1.906(4)
FA−C9A	1.352(5)	FB−C9B	1.346(6)
SeA−FA	2.753(3)	SeB−FB	2.744(3)
C1A−C10A	1.422(5)	C1B−C10B	1.427(5)
C9A−C10A	1.412(5)	C9B−C10B	1.409(6)
Angles			
C1A−SeA−C11A	100.8(2)	C1B−SeB−C11B	99.6(2)
SeA−C1A−C10A	120.5(3)	SeB−C1B−C10B	120.7(3)
FA−C9A−C10A	119.1(3)	FB−C9B−C10B	118.7(4)
C1A−C10A−C9A	125.9(3)	C1B−C10B−C9B	125.6(4)
FA−SeA−C11A	175.0(1)	FB−SeB−C11B	164.3(1)
Torsional Angles			
C11A−SeA−C1A−C10A	−179.2(3)	C11B−SeB−C1B−C10B	−162.8(3)
C1A−SeA−C11A−C16A	89.0(4)	C1B−SeB−C11B−C16B	−110.5(4)
SeA−C1A−C10A−C9A	−0.1(5)	SeB−C1B−C10B−C9B	−0.9(6)
FA−C9A−C10A−C1A	1.2(6)	FB−C9B−C10B−C1B	−3.7(6)

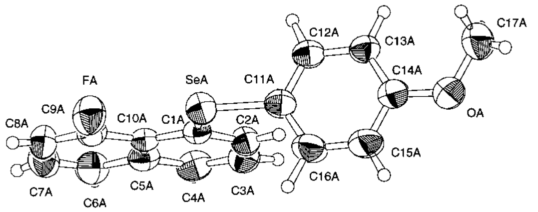
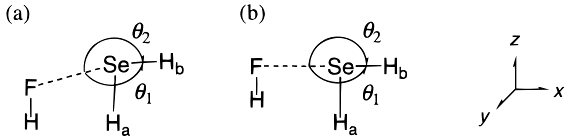


Figure 1. ORTEP drawing of **1** (structure **A**).

Scheme 1



Molecular orbitals were drawn using the MacSpartan Plus program[14] with the 3-21G$^{(*)}$ basis sets for structure **a** and the corresponding structures of HF and SeH_2: the single point calculations were performed on the structures that were partially optimized at the MP2/6-311++G(3df,2pd) level, as shown in Table 3. Figure 3 shows the diagram in the formation of HF···SeH_2, exemplified by structure **a**, together with the np_x(F) orbital of HF and the $4B_2$, $9A_1$, $10A_1$, and $5B_2$ orbitals of SeH_2. The $4B_1$ orbital of SeH_2, which is HOMO consisted of the $4p_z$ orbital of the Se atom, is not shown in Figure 3, since the orbital does not interact with the np_x(F) due to its symmetry.[15]

Although the molecular orbitals of SeH_2 do not interact with each other due to the orthogonality, if the molecule is far from others, they begin to interact with each other, as well as with the np_x(F) orbital when HF comes close to SeH_2.[16] While the energy levels of $4B_2$ and $9A_1$ orbitals of SeH_2 must be considerably higher than that of the np_x(F) of HF, the three orbitals become to interact to make new molecular orbitals in the formation of HF···SeH_2. The np_x(F) orbital also interacts with the unoccupied orbitals such as $10A_1$ and $5B_2$ of SeH_2 by the same reason. The interaction with the unoccupied orbitals must be important since it stabilizes the bond of the adduct and modifies the new orbitals of the adduct to some extent. Such orbital interaction in HF···SeH_2 results in the contribution of the np_x(F)−σ^*(Se−H_b) interaction[16] as well as the charge transfer from HF to SeH_2.

Natural charges (Qn) were computed by natural population analysis[17] for structure **a** and structure **b** and the corresponding structures of SeH_2 and HF with the 6-311++G(3df,2pd) basis sets of both the HF and MP2 levels. The results are collected in Table 3. The fluorine atom became substantially more positive when the adducts of structure **a** and structure **b** with $\theta_1 = 180.0°$ were formed, which showed that the fluorine atom acted as an electron donor in this interaction. The change transfer shown in the Qn can be explained by assuming the two processes: (i) the charge transfer from F to SeH_2 and (ii) the charge transfer from np_x(F) to σ^*(Se−H_b) resulting from the linear F···Se−H_b interaction. If the linear F···Se−H_b interaction can be recognized as the unsymmetrical three center−four electron (3c−4e) F···Se−H_b interaction, the F, Se, and H_b atoms are expected to be more negative, positive, and negative, respectively.[18] The positive and negative charges developed on the Se and H_b atoms in the formation of the adduct are well explained by the 3c−4e model. The positive and negative charge development at the F and H_a atoms must show the contribution of the charge transfer from F to SeH_2 (see also Figure 3). On the other hand, the electrons at the F and Se atoms of structure **b** with $\theta_1 = 65.4°$ moved to hydrogens. The lone pair−lone pair repulsive interaction of the F and Se atoms must expel electrons to hydrogens, mainly to H_a. The Se−H_b bond no longer play an important role, and the HF molecule does not act as an electron donor in the adduct.

Parthasarathy et al. have suggested that there are two types of directional preferences of nonbonded atomic contacts with divalent sulfur, Y−S−Z.[9] Type I contacts with electrophiles which have S···X directions in YZS···X where *n*-electrons of sulfides are located and type II contacts with nucleophiles tending to lie along the extension of one of sulfur's bond. Electrophiles should interact preferentially with HOMO of the sulfur lone pair and nucleophiles with LUMO of the σ^*(S−Y) or σ^*(S−Z) orbital. Similar directional preferences of non-

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[14] MacSpartan Plus Ver. 1.0, Hehre, H. J. Wavefunction, Inc.

[15] The results for structure **b** with $\theta_1 = 180.0°$ and the corresponding molecules were essentially the same as those exhibited in Figure 3.

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Table 3. Structures, Energies, and Natural Charges (Qn) in HF···SeH_2, HF, and SeH_2 Calculated with the 6-311++G(3df,2pd) Basis Sets[a]

	level	E (au)	r(F,H) (Å)	r(Se,H_a) (Å)	r(Se,H_b) (Å)	θ_1 (deg)	$\angle H_aSeH_b$ (deg)	Qn(F)	Qn(H)	Qn(Se)	Qn(H_a)	Qn(H_b)
						Structure **a**						
HF···SeH_2[b,c]	HF	−2501.0175	0.8979	1.4509	1.4559	180.0[d]	100.8[d]	−0.5517	0.5581	−0.0772	0.0346	0.0361
HF	HF	−100.0577	0.8973					−0.5581	0.5581			
SeH_2	HF	−2400.9668		1.4515	1.4515		100.8[d]			−0.1144	0.0572	0.0572
Δ		0.0070	0.0006	−0.0006	0.0044		0.0	0.0064	0.0000	0.0372	−0.0226	−0.0211
HF···SeH_2[b,c]	MP2	−2501.4645	0.9184	1.4562	1.4617	180.0[d]	100.8[d]	−0.5556	0.5620	−0.0781	0.0350	0.0367
HF	MP2	−100.3321	0.9172					−0.5617	0.5617			
SeH_2	MP2	−2401.1363		1.4568	1.4568		100.8[d]			−0.1161	0.0580	0.0580
Δ		0.0039	0.0012	−0.0006	0.0049		0.0	0.0061	0.0003	0.0380	−0.0230	−0.0213
						Structure **b**						
HF···SeH_2[e]	HF	−2501.0177	0.8979	1.4563	1.4577	180.0[f]	90.8[g,h]	−0.5507	0.5573	−0.0784	0.0364	0.0355
HF	HF	−100.0577	0.8973					−0.5581	0.5581			
SeH_2	HF	−2400.9684		1.4530	1.4530		93.2[g]			−0.1064	0.0532	0.0532
Δ		0.0084	0.0006	0.0033	0.0047		−2.4	0.0074	−0.0008	0.0280	−0.0168	−0.0177
HF···SeH_2[e]	MP2	−2501.4658	0.9184	1.4622	1.4643	180.0[f]	88.9[g,i]	−0.5547	0.5614	−0.0787	0.0366	0.0354
HF	MP2	−100.3321	0.9172					−0.5617	0.5617			
SeH_2	MP2	−2401.1385		1.4591	1.4591		91.3[g]			−0.1072	0.0536	0.0536
Δ		0.0048	0.0012	0.0031	0.0052		−2.4	0.0070	−0.0003	0.0285	−0.0170	−0.0182
HF···SeH_2[e]	MP2	−2501.4585	0.9176	1.4604	1.4559	65.4[g]	91.7[g]	−0.5610	0.5606	−0.0843	0.0354	0.0493
Δ		0.0121	0.0004	0.0013	0.0008		0.4	0.0007	−0.0011	0.0229	−0.0182	−0.0043

[a] r(F,Se) fixed at 2.753 Å. [b] θ_2 fixed at 185.0°. [c] ∠HFSe fixed at 100.0°. [d] Fixed value. [e] ∠HFSe fixed at 90.0°. [f] See ref 12. [g] Optimized value. [h] θ_2 optimized to be 179.2°. [i] θ_2 optimized to be 181.1°.

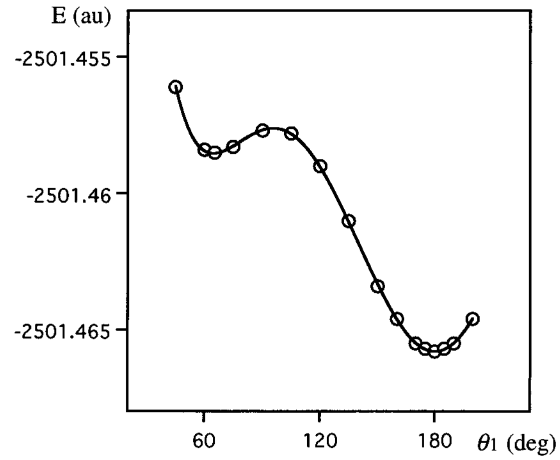
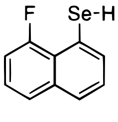


Figure 2. Plot of energy against θ_1 in structure **b**.

bonded atomic contacts have also shown with divalent selenium.[10] The linear alignment of F, Se, and C(An) atoms in **1** apparently belongs to type II with the central atom of Se. The F atom as the type II in F···Se−C(An) linear alignment should be recognized as a nucleophile and must act as an electron donor accompanied by the σ*(Se−C(An)) orbital as an acceptor in the close proximity. The MO calculations, containing the natural population analysis, support the n(F)−σ*(Se−C(An)) interaction in **1**.

Contributions of π-orbitals were also examined. 8-Fluoro-1-naphthaleneselenole (**5**), together with 1-naphthaleneselenole (**6**) and 1-fluoronaphthalene (**7**), was calculated with the 6-311+G(d,p) basis sets at the HF level. The fluorine atom



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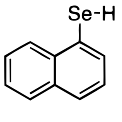

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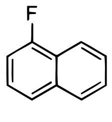


7

and the Se−H bond were optimized to be placed on the plane of the naphthalene ring. The ∠CSeH, ∠FSeH, and r(F,Se) values in **5** were estimated to be 93.7°, 166.4°, and 2.779 Å, respectively. Natural charges (Qn) were also computed, and the results are shown in Table 4. The Qn values of F, Se, and H(Se) became more positive, positive, and negative, respectively, relative to those of the corresponding atoms in **6** and **7**, which was the same trend calculated on the models shown in Table 3. The structure of **5** was also optimized using the MacSpartan Plus program with the 3-21G(*) basis sets. The

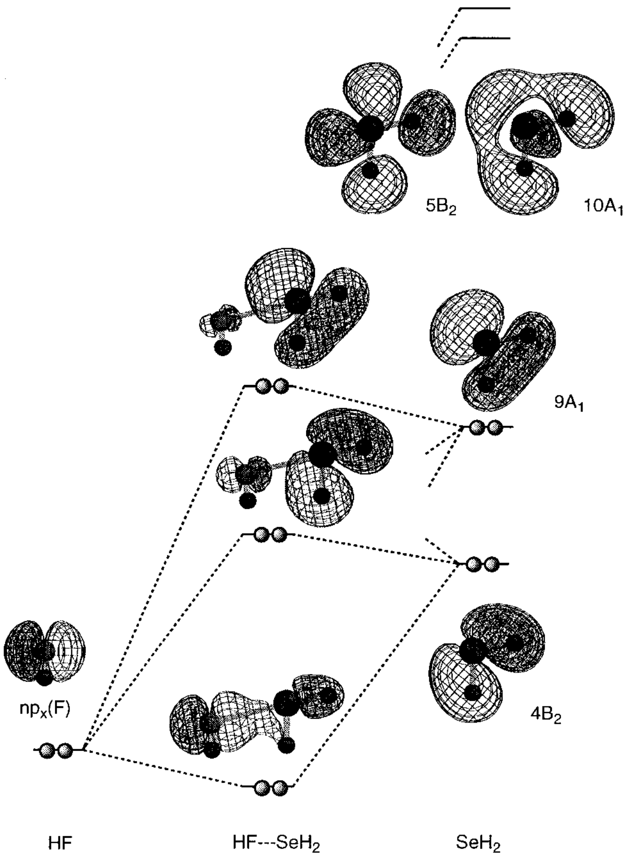


Figure 3. Diagram in the formation of HF···SeH_2 from HF and SeH_2 (see text).

Table 4. Natural Charges (Qn) in **5** − **7** Calculated with 6-311+G(d,p) Basis Sets at the HF Level

compd	Qn(F)	Qn(Se)	Qn(H)
5	−0.3922	0.2086	0.0252
6		0.1560	0.0489
7	−0.3950		
ΔQn	0.0028	0.0526	−0.0237

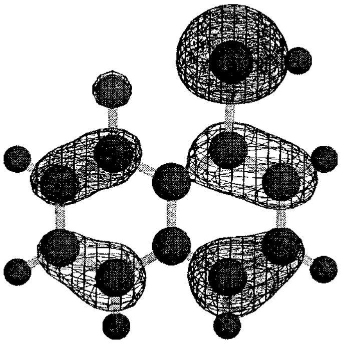
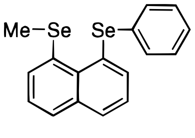


Figure 4. HOMO of 8-fluoro-1-naphthaleneselenole (**5**).

HOMO of **5** is shown in Figure 4. The p-orbitals of F and Se atoms contribute to the π-type HOMO. The $n\mathrm{p}_x(\mathrm{F})-\sigma^*(\mathrm{Se}-\mathrm{H_b})$ type interaction was shown to contribute to the lower energy orbitals.

The nonbonded r(F,Se) of 2.753(3) Å was shorter than the sum of the van der Waals radii[8] of F and Se atoms by 0.60 Å (Δr_v(F,Se) = 0.60 Å). The nonbonded Se···Se distances in 1-(methylselanyl)-8-(phenylselanyl)naphthalene (**8**)[19] and bis[8-(phenylselanyl)naphthyl] diselenide (**9**)[1f] are 3.070(1) and 3.053(1) Å, respectively, on average. Since the sum of the van der Waals radii of the two Se atoms is 4.00 Å, the nonbonded Se···Se distances in **8** and **9** are shorter than the value by 0.93−0.95 Å (Δr_v(Se,Se) = 0.93−0.95 Å). Indeed the r(F,Se) must be mostly determined by the peri positions where the two atoms are joined, but the fluorine atom in **1** might contribute to decrease the distance to some extent since the Δr_v(F,Se) in **1** is larger than a half of the Δr_v(Se,Se) in **8** and **9**. The observed r(F,Se) value would be consistent with the attractive interaction caused by the linear $n(\mathrm{F})-\sigma^*(\mathrm{Se}-\mathrm{C(An)})$ alignment in **1**, although the energy of structure **b** with $\theta_1 = 180.0°$ is evaluated to be higher than the free components by 0.0048 au (13 kJ mol^{-1}) at the MP2/6-311++G(3df,2pd) level.[13]



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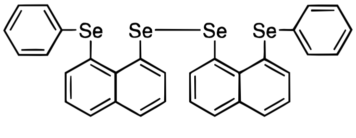

9

Four bond couplings between F and Se atoms (^4J(F,Se)) of **1** and **2** were observed to be 285.0 and 276.7 Hz, respectively, while ^4J(F,F) in 1,8-difluoronaphthalene[2b] and ^4J(Se,Se) in 1-(methylselanyl)-8-(phenylselanyl)naphthalene[1g] were reported to be 58.8 and 322.4 Hz, respectively. The ^5J(F,C) values in the F···Se−C bonds of **1** and **2** were detected to be 18.2 and 14.9 Hz, respectively. The role of the linear F···Se−C alignment on the downfield shifts of the ^{77}Se NMR chemical shifts and the large J values containing the Se nucleus in **1** and **2**, together with some novel reactions[20] correlated with the formation of the compounds, is in progress.

Experimental Section

Chemicals were used without further purification unless otherwise noted. Solvents were purified by standard methods. Melting points were recorded on a YANAKO Model MP and uncorrected. ^{1}H, ^{13}C, and ^{77}Se NMR spectra were recorded on a JEOL Lambda 400 spectrometer operating at 399.7, 100.4, and 76.2 MHz, respectively. Coupling constants (J) are given in hertz. 1-(Methylselanyl)naphthalene (**4**) was prepared according to the method in the literature.[1c]

8-Fluoro-1-(*p*-anisylselanyl)naphthalene (1). To an ethereal solution of 8-(fluoronaphthyl)magnesium bromide, resulting from 8-bromo-1-fluoronaphthalene[21,22] and magnesium, was added an ethereal solution of di(*p*-anisyl) diselenide under argon atmosphere. After usual workup, was obtained **1**. Recrystallization from hexane gave colorless prisms: yield 67%; mp 83−84.5 °C; ^{1}H NMR (399.65 MHz, CDCl$_3$) δ 3.86 (s, 3H), 6.89 (dd, J = 1.0, 7.8, 1H), 6.96 (d, J = 9.4, 2H), 7.15 (t, J = 7.8, 1H), 7.17 (ddd, J = 1.0, 7.8, 13.2, 1H), 7.37 (dt, J = 5.4, 8.1, 1H), 7.56 (dd, J = 1.0, 7.8, 1H), 7.58 (dd, J = 1.0, 7.8, 1H), 7.64 (d, J = 9.4, 2H). Anal. Calcd for $C_{17}H_{13}FOSe$: C, 62.00; H, 3.96. Found: C, 62.21; H, 4.05.

8-Fluoro-1-(methylselanyl)naphthalene (2). Sodium 8-fluoro-1-naphthaleneselenate was allowed to react with methyl iodide in a THF−water mixed solvent under argon atmosphere to give **2**. After chromatography on silica gel with hexane as an eluent, recrystallization from hexane gave colorless prisms: yield 93%; mp 59−60 °C; ^{1}H NMR (399.65 MHz, CDCl$_3$) δ 2.38 (s, 3H), 7.14 (ddd, J = 1.2, 7.8, 13.2, 1H), 7.30 (br d, J = 7.3, 1H), 7.36 (t, J = 7.8, 1H), 7.36 (dt, J = 4.8, 7.8, 1H), 7.59 (dd, J = 0.9, 8.3, 1H), 7.62 (dd, J = 1.0, 8.3, 1H). Anal. Calcd for $C_{11}H_9FSe$: C, 55.25; H, 3.79. Found: C, 55.48; H, 3.99.

Sodium 8-fluoro-1-naphthaleneselenate was prepared from bis(8-fluoronaphthyl)-1,1′-diselenide.[23] The diselenide was obtained in the reaction of 8-bromo-1-fluoronaphthalene,[21,22] magnesium, and selenium powder in diethyl ether under argon atmosphere followed by oxidation with air and recrystallized from hexane.

1-(*p*-Anisylselanyl)naphthalene (3). To an ethereal solution of naphthylmagnesium bromide, resulting from 1-bromonaphthalene and magnesium, was added an ethereal solution of di(*p*-anisyl) diselenide under argon atmosphere. After usual workup, was obtained **3**. Recrystallization from hexane gave colorless prisms: yield 62%; mp 100.0−101.0 °C; ^{1}H NMR (399.65 MHz, CDCl$_3$) δ 3.78 (s, 3H), 6.82 (d, J = 8.9, 2H), 7.30 (dd, J = 7.3, 8.2, 1H), 7.45 (d, J = 8.9, 2H), 7.46−7.55 (m, 3H), 7.75 (d, J = 8.2, 1H), 7.83 (dd, J = 2.2, 7.2, 1H), 8.28 (ddd, J = 0.9, 2.0, 7.6, 1H). Anal. Calcd for $C_{17}H_{14}OSe$: C, 65.18; H, 4.50. Found: C, 65.23; H, 4.46.

X-ray Structural Determination of 1. The colorless single crystals of **1** were grown by slow evaporation of a hexane solution at room temperature. A crystal of dimensions 0.60 × 0.30 × 0.30 mm^3 was measured on a Rigaku AFC7R diffractometer with graphite-monochromated Mo Kα radiation (λ = 0.710 69 Å). The structure was solved by direct methods using *SHELXS-86*[24] and was refined by block diagonal least-squares using *UNICS III*.[25] The function minimized was $\Sigma w(|F_\mathrm{o}| - |F_\mathrm{c}|)^2$, where $w = 1/[\sigma^2(|F_\mathrm{o}|) + 0.001|F_\mathrm{o}|^2]$. The non-hydrogen atoms were refined anisotropically. All hydrogen atoms were

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[19] Nakanishi, W.; Hayashi, S.; Toyota, S. Unpublished results.

[20] We have encountered a facile reductive C−F bond cleavage in the reaction of sodium 8-fluoro-1-naphthaleneselenate with *p*-(methoxybenzene)diazonium chloride, which yields not **1** but **3**. The C−F bond cleavage must be, we believe, the reflection of the nonbonded interaction between F and Se atoms.

[21] Adcock, W.; Matthews, D. G.; Rizvi, S. Q. A. *Aust. J. Chem.* **1971**, *24*, 1829.

[22] The compound was prepared according to the literature and obtained the same results for elemental analyses.[21] The observed value for carbon was ca. 1% larger than that of the calculated one while that for hydrogen was satisfactory.

[23] It was also difficult to purify the compound similarly to the case of ref 22. Further investigation containing the C−F bond cleavage[20] is in progress, and the results will be reported elsewhere.

[24] Sheldrick, G. M. *Acta Crystallogr. Sect. A* **1990**, *A46*, 467.

[25] Sakurai, T.; Kobayashi, K. *Rep. Inst. Phys. Chem. Res.* **1979**, *55*, 69.

located on a Fourier difference map and not refined. The final cycle of block diagonal least-squares refinement was based on 4292 observed reflections ($I > 3.00\sigma(F)$) and 362 variable parameters and converged with unweighted and weighed agreement factors to give $R = 0.045$ and $Rw = 0.044$ for independent observed reflections.

MO Calculations. Ab initio molecular orbital calculations were performed on a Power Challenge L computer using the Gaussian 94 program with the 6-311++G(3df,2pd) and 6-311+G(d,p) basis sets at the HF and/or MP2 levels. The molecular orbitals in Figures 3 and 4 were drawn by a Power Macintosh 8500/180 personal computer using MacSpartan Plus program (Ver. 1.0) with 3-21G$^{(*)}$ basis sets.

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Supporting Information Available: Tables of crystal data and structure refinement, atomic coordinates for non-hydrogen atoms, together with the bond lengths, bond angles, and tosional angles for **1** and geometries and energies for structure **b** with variously fixed angles θ_1, together with the optimized ones for θ_1, calculated with 6-311++G(3df,2pd) basis sets at the MP2 level (11 pages, print/PDF). See any current masthead page for ordering information and Web access instructions.

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