Characterization of an Intramolecular Nonbonded Interaction between Selenium and Fluorine in Solution

Michio Iwaoka, Hiroto Komatsu, and Shuji Tomoda*
Department of Life Science, Graduate School of Arts and Sciences, The University of Tokyo, Komaba, Meguro, Tokyo 153-8902

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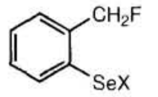
NMR measurements of $J_{\mathrm{Se}\cdots\mathrm{F}}$ coupling constants (22.7–84.2 Hz) of *o*-selenobenzyl fluoride derivatives in solution provided strong evidence for weak intramolecular selenium-fluorine nonbonded interaction, in which fluorine donates electrons to selenium.

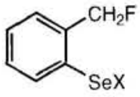
The specific character of a divalent organic selenium as an electron-pair acceptor[1] has recently been successfully applied to asymmetric reactions[2] as well as enzyme-mimetic catalytic reactions.[3] However, nature of the interaction originated from this character has remained unclear, especially in solution. We have recently reported for the first time a quantitative analysis of such an interaction, *i.e.*, an intramolecular Se···N nonbonded interaction, in solution.[4] On the other hand, several examples of a similar nonbonded interaction between Se and F have also been reported in the solid state[5] and recently in a linear F···Se–C alignment in naphthalene peri positions.[6] In this paper, we present the first NMR spectroscopic evidence for the presence of a weak intramolecular Se···F interaction in solution using compounds **1a-f** (X=CN, Cl, Br, SPh, SeAr, Me) that are free from steric constraints.

Model compounds **1a-f**[7] were obtained in spectrally pure form except for **1b** and **1d**: **1b** contained small amounts of **1e** and an unknown by-product, and **1d** slowly disproportionated into **1e** and PhSSPh at room temperature. In addition, **2-5**[8] were synthesized as reference compounds. These compounds were selected because **2** has a negative charge on Se, which would prevent close contact between Se and F, while **3-5** should have such contact by structural reasons.[9]

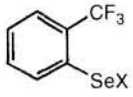


(=ArSeX)

1a, X=CN **1d**, X=SPh
1b, X=Cl **1e**, X=SeAr
1c, X=Br **1f**, X=Me



2, X=B(OMe)$_3$ Na



3, X=CN
4, X=Me
5, X=B(OMe)$_3$ Na

Observed ^{77}Se and ^{19}F NMR chemical shifts (δ) and $J_{\mathrm{Se}\cdots\mathrm{F}}$ coupling constants are collected in Table 1. For **1a-f**, a pair of doublet signals were observed in ^{77}Se NMR due to the nuclear spin coupling with ^{19}F ($J_{\mathrm{Se}\cdots\mathrm{F}}$ = 22.7–84.2 Hz), whereas a singlet signal was observed for **2** ($J_{\mathrm{Se}\cdots\mathrm{F}}$ = 0 Hz). The coupling constants observed for **1a** and **1b** are unusually large compared with those reported for 2,4,6-tris(trifluoromethyl)phenylseleno derivatives ($^4J_{\mathrm{SeF}}$ = 10–28 Hz).[10] On the other hand, a set of quartet signals was observed in the ^{77}Se NMR spectra of **3-5** due to the coupling with magnetically equivalent three F atoms, indicating the presence of rapid rotation of the trifluoromethyl group. This rotation could not be frozen spectrally even at –90 °C at 500 MHz for **3** and **4**.

Table 1. ^{77}Se and ^{19}F NMR chemical shifts (δ) and $J_{\mathrm{Se}\cdots\mathrm{F}}$ coupling constants observed for **1a-f** and **2-5** at 298 K[a]

Comp	X	^{77}Se NMR[b] δ_{Se} /ppm	^{19}F NMR[c] δ_{F} /ppm	Coupling Constant[d] $J_{\mathrm{Se}\cdots\mathrm{F}}$ /Hz
1a	CN	288.6 (d)	–204.3	84.2
1b	Cl	978.5 (d)	–205.2	80.1
1c	Br	801.0 (d)	–208.0	43.1
1d	SPh	499.7 (d)	–206.3	38.7
1e	SeAr	437.3 (d)	–208.1	23.6
1f	Me	161.1 (d)	–208.1	22.7
2	B(OMe)$_3$Na	–24.1 (s)[e]	–217.6[e]	0[e]
3	CN	341.7 (q)	–60.6	63.2
4	Me	217.7 (q)	–61.7	48.4
5	B(OMe)$_3$Na	69.5 (s)[e]	–63.6[e]	15.6[e]

[a] All NMR spectra were measured in CDCl$_3$ except for **2** and **5**. [b] Chemical shifts from Me$_2$Se. The letter in parentheses represents singlet(s), doublet(d), and quartet(q). [c] Chemical shifts from CFCl$_3$. [d] Measured from expanded ^{77}Se NMR spectra. [e] Measured in CD$_3$OD.

Conformational search indicates two stable rotational isomers for **1** (Figure 1); one is conformer A which has a close intramolecular contact between Se and F, and the other is conformer B which does not have such a contact. These two conformers must attain a rapid equilibrium in solution as suggested by rapid rotation of the trifluoromethyl group of **3-5**. Hence the observed values of δ_{Se}, δ_{F}, and $J_{\mathrm{Se}\cdots\mathrm{F}}$ represent the weighted average between these conformers. Since the coupling was not observed for **2**, for which conformer A should not be populated by electrostatic repulsion between Se and F, the value of $J_{\mathrm{Se}\cdots\mathrm{F}}$ would be uniformly zero for conformer B of **1a-f**. Contrary, assuming that the weak coupling observed for **5** (15.6 Hz) could be assigned to the through-bond coupling ($^4J_{\mathrm{SeF}}$), it is strongly suggested that the $J_{\mathrm{Se}\cdots\mathrm{F}}$ coupling observed for **1a-f**, **3**, and **4** is mostly due to Se···F nonbonded interaction. It should be noted that the observed Se···F interaction is significantly weak compared with the corresponding Se···N interaction[4] based on rapid rotation of the fluoromethyl group.

Relatively similar values of $J_{\mathrm{Se}\cdots\mathrm{F}}$ observed for **3** (63.2 Hz) and **4** (48.4 Hz), in contrast to those for **1a** (84.2 Hz) and **1f** (22.7 Hz), suggest that the change in the magnitude of $J_{\mathrm{Se}\cdots\mathrm{F}}$ should not be large for conformer A of **1a-f**. Therefore, it can be assumed that relative populations of conformers A and B, which are considered as a measure of strength of the Se···F interaction, are roughly reflected by the apparent values of $J_{\mathrm{Se}\cdots\mathrm{F}}$ observed for **1a-f**. The coupling constant between weakly interacting atoms can be a reasonable measure of covalent character of the

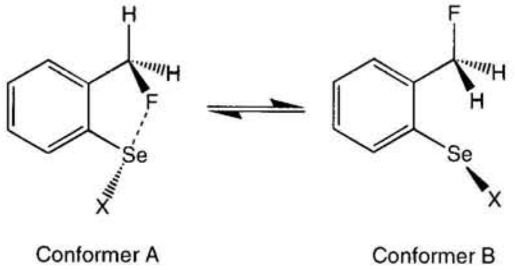


Figure 1. A rapid equilibrium between two stable conformers A and B of **1** due to the rotation of the fluoromethyl group.

interaction (*i.e.*, the extent of the electron delocalization between the two atoms).[11] It follows, therefore, that the observed Se···F interaction is most likely to possess such a character. Moreover, the correlation between the magnitude of $J_{Se\cdots F}$ and the downfield shift of ^{19}F NMR observed for **1a-f**, except for **1c** (X=Br),[12] suggests that F donates electrons to Se in the Se···F interaction.

Fluorine is the most electronegative element in the periodic table except for rare gas elements;[13] hence it is usually considered to have a very low ability to coordinate. However, previous investigations have pointed out importance of lone pair electron delocalization in alkyl fluoride.[6,14] In the Se···F nonbonded interaction observed in this work, such a character also appears to be an important element that stabilizes the interaction in solution. This fact conversely suggests that a divalent organic selenium functions as a good electron-pair acceptor toward a variety of hetero-functional groups, similarly to hydrogen bond donors. Other attractive forces, such as electrostatic attraction between the positively charged selenium and the negatively charged fluorine, may also contribute to stabilize the Se···F interaction. Relative importance of these elements will be discussed in a full account in due course.

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7 **1e** was synthesized by fluorination of bis[2-(chloromethyl)-phenyl] diselenide[15] using the activated mixture of KF and CaF_2[16] in refluxing butyronitrile for 85 h. Diselenide **1e** was then converted into **1a-d** and **1f** by application of the methods that were employed for the synthesis of a series of model compounds having a Se···N interaction.[4] Detailed synthetic procedures and full structural characterization of **1a-f** will be described elsewhere.

8 **2** and **5** were generated *in situ* by treating the corresponding diselenides with sodium borohydride in CD_3OD.[17] **2** was present as a monomer at the beginning, but it gradually dimerized to *6H,12H*-dibenzo-[*b,f*][1,5]diselenocin[18] during the prolonged measurement of NMR spectra. **3**: *o*-(Trifluoromethyl)aniline was allowed to react with $NaNO_2$, and then with KSeCN by application of the literature method.[15] **4**: **3** was treated with sodium borohydride in methanol in the presence of methyl iodide. Detailed synthetic procedures and full structural characterization of **2-5** will be described elsewhere.

9 Molecular modeling using Spartan 4.1.1 (Wavefunction Inc., Irvine, CA) estimated that the Se···F distance is approximately 3.0 Å for **3-5**, which is shorter than the sum of van der Waals radii of Se (1.9 Å) and F (1.47 Å).

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