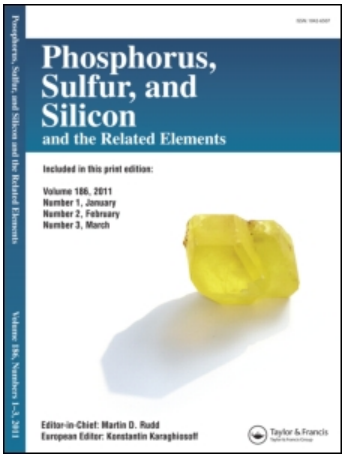

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Physical- and Bio-Organic Chemstry of Nonbonded Selenium· · ·Oxygen Interactions

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Physical- and Bio-Organic Chemstry of Nonbonded Selenium···Oxygen Interactions

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Weak nonbonded interaction between a divalent selenium and an oxygen atom (i.e., Se···O interaction) frequently plays important roles in chemical and biological functions of selenium compounds. To establish that ^{77}Se NMR is an easy experimental probe to diagnose the strength of an Se···O interaction, 3 series of 2-substituted benzeneselenenyl derivatives, which have an intramolecular Se···O interaction in solution, were employed. By comparing the ^{77}Se NMR chemical shifts (δ_{Se}) with those observed for other series of selenium compounds, which have an intramolecular Se···Y (Y = N, O, F, Cl, or Br) interaction, approximate linear correlation was found between the δ_{Se} values and the strengths of the nonbonded Se···Y interactions evaluated by natural bond orbital analysis at the B3LYP level. The correlation will be useful for estimating the strength of an Se···O interaction simply from the ^{77}Se NMR chemical shift. By extending the chemistry of nonbonded Se···O interactions to structural biology, analogous S···O interactions have been discovered in protein architecture. The directional features were, however, different from those of Se···O and S···O interactions of small organic compounds.

Keywords ^{77}Se NMR; natural bond orbital analysis; nonbonded interaction; protein; selenium compound

INTRODUCTION

Weak nonbonded interaction between a divalent selenium and an oxygen atom (i.e., Se···O interaction)[1,2] frequently plays important roles in

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chemical and biological functions of selenium compounds. For example, Goldstein et al.[3,4] reported that the molecular structure of biologically active selenazofurin is controlled by the intramolecular Se···O interaction. Wirth et al.[5–7] demonstrated that high asymmetric induction is achieved in the oxyselenenylation reaction of alkenes by use of asymmetric selenium reagents that possess a strong intramolecular Se···O interaction. Thus, nonbonded Se···O interaction is an intriguing chemical tool for controlling the structure and reactivity of organic molecules.

Structural features of Se···O interactions were clearly characterized on the basis of the solid-state molecular structures of organoselenium compounds determined by X-ray crystallography:[8,9] The O atom tends to approach the Se atom from the backside of one of the covalent bonds attached to the Se atom, and the Se atom tends to approach the O atom in the direction of the lone pair (Figure 1a). The directionality was indicative of significant contribution from the $n_O \rightarrow \sigma^*_{Se}$ orbital interaction to the stability. Although much experimental[1–9] and theoretical[10–12] information about the nature of Se···O interactions has been compiled to date, there is no easy experimental method to detect the presence nor the strength of Se···O interactions directly in solution.

In the field of structural biology, new-type nonbonded interactions, called S···Y (Y = O, N, and S) interactions, recently have been discovered in protein architecture.[13,14] Previously, structural roles of S atoms in proteins were thought to be limited in formation of disulfide (SS) linkages to stabilize the folded structure. In the other cases, the S atoms were just considered as hydrophobic groups exhibiting no significant interaction with other amino acid residues. Since selenium is a heavier analog of sulfur, it might be expected that the structural features of the S···O interactions in proteins were similar to those of Se···O interactions in small organic molecules. However, the observed directionality (Figure 1b) suggested importance of a $\pi_O \rightarrow \sigma^*_{Se}$ orbital interaction for

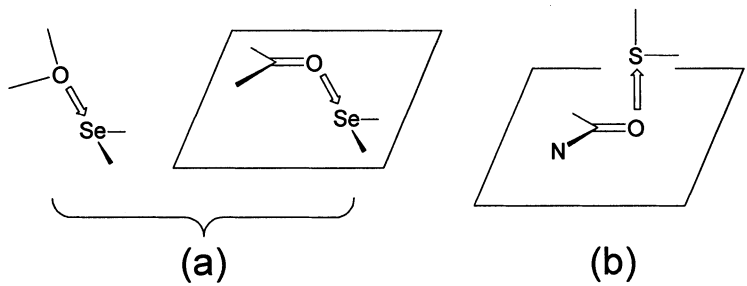

FIGURE 1 Structural features of nonbonded interactions. (a) Se···O interactions in organic molecules. (b) S···O interactions in proteins.

the stability. The discrepancy was mainly due to different types of the O atoms (i.e., an amide or not an amide) rather than the difference between Se and S atoms.[15]

We are interested in a physicochemical aspect of nonbonded interactions involving a divalent selenium in relation to their application to asymmetric synthesis, enzyme-mimetic reactions, and protein chemistry. In this paper, our recent progress in the research area of nonbonded Se···O interactions is summarized to show that the ^{77}Se NMR chemical shift (δ_{Se}) is an easy experimental probe for the strength. It also is suggested that the discovery of S···O interactions in proteins will have a significant impact in the field of protein engineering because the unique directionality is maintained in the folded structures.

METHOD

All ^{77}Se NMR data, which were collected from our previous works,[16–21] were measured at 95.35 MHz on the same NMR spectrometer (Jeol α500) under the same conditions (at 298 K in $CDCl_3$) using dimethyl selenide as an external standard.

Theoretical calculations were performed by using the Gaussian 98 program.[22] The hybrid Becke 3-Lee-Yang-Parr (B3LYP) exchange-correlation functional[23] was applied for DFT calculations. Huzinaga's 43321/4321/311 basis sets[25] were used for Se and Br, and 6-31G(d,p) basis sets were used for other atoms. The combination is denoted here as 631H basis sets. All geometries were fully optimized at the B3LYP/631H levels of theory. Simplified structures were applied for some compounds to save a computation time. The orbital interaction energies between Se and Y (Y = N, O, F, Cl, and Br) atoms ($E_{Se\cdots Y}$) were calculated at the B3LYP/631H level by using the natural bond orbital (NBO) method.[26]

Structural data of S···O interactions in small organic molecules and proteins were obtained from Cambridge Structural Database (CSD)[27] and Protein Data Bank (PDB),[28] respectively, by the same method as described previously.[15]

RESULTS AND DISCUSSION

We recently synthesized three series of 2-substituted benzeneselenenyl derivatives (**1–3**) (Figure 2), which have an intramolecular Se···O interaction in solution, and showed that the ^{17}O NMR is useful to diagnose the strength of the Se···O interactions.[1,2] However, measurement of ^{17}O NMR is not always possible unless the compounds are labeled with an ^{17}O isotope. On the other hand, the alternative ^{77}Se NMR is much easier to be measured because selenium in nature involves 7.5 % of an

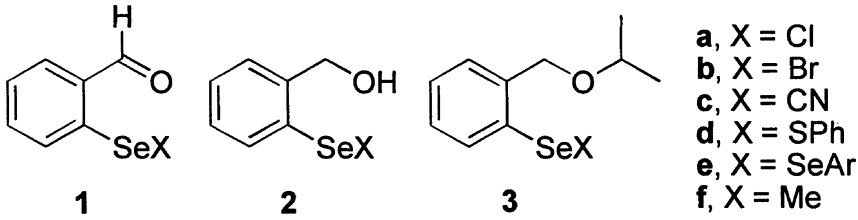

FIGURE 2 Series of model compounds having intramolecular Se···O interactions.

NMR active isotope, i.e., a ^{77}Se nucleus ($I = 1/2$). Therefore, the ^{77}Se NMR must be applied as an easier experimental probe for the strength of the Se···O interactions.

^{77}Se NMR chemical shifts (δ_{Se}) observed for model compounds **1–3** are listed in Table I along with those for other series of organoselenium compounds **4–7** (Figure 3), which have intramolecular Se···N,[8] Se···F,[9] Se···Cl,[10] and Se···Br[10] interactions, respectively. It is obvious that the δ_{Se} values for series **1** significantly is large compared with those for the corresponding compounds of other series with the same substituent X. The downfield shifts are due to the magnetic anisotropic effect from the carbonyl group present near the Se atom, giving a strong evidence of the intramolecular Se···O interactions for **1a–f**. The δ_{Se} data in Table I are used in the analyses of the Se···O interactions described below.

TABLE I ^{77}Se NMR Chemical Shifts (δ_{Se}) for Series of Compounds 1–7 Having Nonbonded Se···Y Interactions[a]

X	**1**[b] (Y = O(CHO))	**2**[b] (Y = O(OH))	**3**[b] (Y = O(O*i*Pr))	**4**[c] (Y = N)	**5**[d] (Y = F)	**6**[e] (Y = Cl)	**7**[e] (Y = Br)
a Cl	1114.1	987.1	986.5	1051.3	978.5	966.5	956.1
b Br	1029.5	839.5	857.8	1011.2	801.0	798.2	788.6
c CN	426.7	314.5	315.1	362.2	288.6	284.1	280.0
d SPh	621.7	501.8	503.8	571.5	499.7	—	—
e SeAr	458.5	433.2	412.0	431.9	437.4	442.2	437.0
f Me	259.5	157.2	166.6	181.0	161.1	165.1	165.2

[a] ^{77}Se NMR spectra were measured at 95.35 MHz in $CDCl_3$ at 298 K with Me_2Se as an external standard.
[b] The data from.[1]
[c] The data from.[8]
[d] The data from.[9]
[e] The data from.[10]

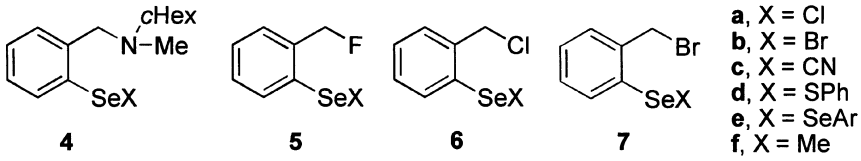

FIGURE 3 Series of model compounds having intramolecular Se···Y (Y = N, F, Cl, and Br) interactions.

To establish that ^{77}Se NMR is a useful experimental probe of Se···O interactions, it is essential to determine the strength quantitatively. For Se···N and Se···F interactions, this was possible for some stable compounds by use of the variable temperature NMR method. The strengths of the Se···N interactions for **4c** and **4d** were determined as 12.4 and 10.8 kcal/mol, respectively, by fitting the line shapes of the ^{1}H NMR spectra obtained at various temperatures.[16–18] The strengths of the Se···F interactions for **5c** and **5e** were determined as 1.23 and 0.85 kcal/mol, respectively, in CD_2Cl_2 by analyzing the magnitude of the $J_{Se\cdots F}$ coupling constant at various temperatures.[19,20] However, for the Se···O interactions of **1–3**, it was difficult experimentally to determine the strength.

Quantum chemical calculations were performed for the theoretical models of compounds **1–7** (Figure 4), some of which have simpler structures than those of the experimental models (Figures 2 and 3). It was found that the molecular structure of **1b** that was determined by X-ray

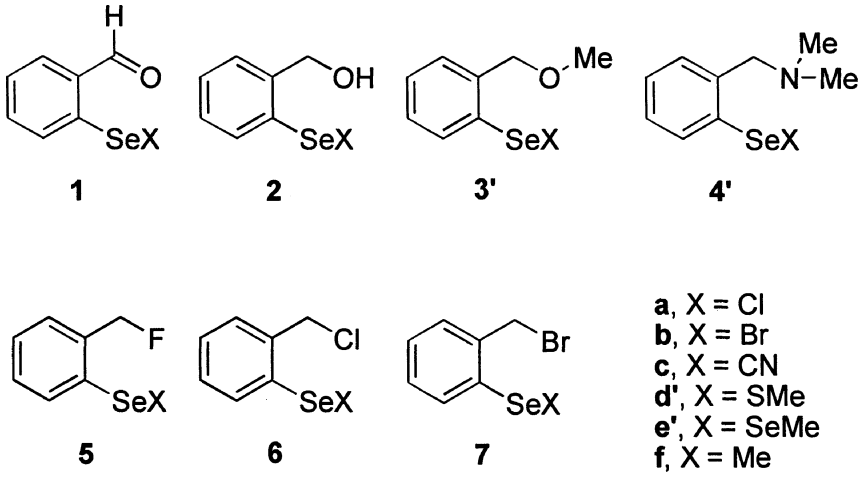

FIGURE 4 Structures of calculation models for **1–7**.

analysis[8] are well reproduced by calculation at the B3LYP/631H level (see the Method section for abbreviations): the errors were ±0.05 Å for the atomic distances and ±4° for the bond angles, and both were planar.[2] The extreme agreement between the X-ray and B3LYP structures of **1b** provided strong validity to the calculation results. The strengths of the S···O interactions for **1–3** were, therefore, estimated by theoretical calculation at the B3LYP/631H level.

Stable structures were first sought for **1–7** by systematic conformational search at the B3LYP/631H level. It was found for most of model compounds that the conformer with a short Se···Y (Y = O, N, F, etc.) atomic distance is most stable. There were some exceptions, such as **5e′**, **5f**, **6f**, and **7f**, but in those cases the difference in energy was very small (less than 0.36 kcal/mol) between the most stable structure and the one with the Se···Y interaction. Subsequently, two parameters (i.e., $r_{Se\cdots Y}$ and $E_{Se\cdots Y}$), which can be employed as indexes for the strength of Se···Y interactions, were obtained by use of the calculation results.

The first parameter (i.e., $r_{Se\cdots Y}$) is the Se···Y atomic distance for the stable conformer with an Se···Y interaction. The values of $r_{Se\cdots Y}$ obtained for **1–7** are summarized in Table II along with the relative Se···Y atomic distances to the sum of the van der Waals radii; vdw_{Se} = 1.90 Å, vdw_O = 1.52 Å, vdw_N = 1.55 Å, vdw_F = 1.47 Å, vdw_{Cl} = 1.75 Å, and vdw_{Br} = 1.85 Å.[29] The data indicated that the strength of the Se···Y interactions tends to decrease as the electrophilicity of the Se atom decreases, i.e., in the order of **a** (Cl) > **b** (Br) > **c** (CN) > **d′** (SMe) > **e′**

TABLE II Atomic Distances between Se and Y atoms ($r_{Se\cdots Y}$) Obtained for the Stable Conformers of Compounds 1–7 at the B3LYP/631H[a]

	X	**1** (Y = O(CHO))	**2** (Y = O(OH))	**3′** (Y = O(OMe))	**4′** (Y = N)	**5** (Y = F)	**6** (Y = Cl)	**7** (Y = Br)
a	Cl	2.31	2.57	2.56	2.42	2.69	3.86	4.13
		(0.67)	(0.75)	(0.75)	(0.70)	(0.80)	(1.06)	(1.10)
b	Br	2.34	2.60	2.60	2.43	2.76	3.89	4.09
		(0.68)	(0.76)	(0.76)	(0.70)	(0.82)	(1.07)	(1.09)
c	CN	2.59	2.79	2.80	2.72	2.79	3.48	3.65
		(0.76)	(0.82)	(0.82)	(0.79)	(0.83)	(0.95)	(0.97)
d′	SMe	2.64	2.87	2.88	2.76	2.91	—	—
		(0.77)	(0.84)	(0.84)	(0.80)	(0.86)	(—)	(—)
e′	SeMe	2.66	2.90	2.91	2.79	2.94	3.65	3.80
		(0.78)	(0.85)	(0.85)	(0.81)	(0.87)	(1.00)	(1.01)
f	Me	2.76	3.01	3.01	3.01	2.99	3.68	3.85
		(0.81)	(0.88)	(0.88)	(0.87)	(0.89)	(1.01)	(1.03)

[a]The values in parentheses are the relative distances to the sum of the Bondi's van der Waals radii (Ref. 17), $r_{Se\cdots Y}/(vdw_{Se} + vdw_Y)$.

(SeMe) >**f** (Me), and also that it tends to increase with enhancement of the nucleophilicity of the Y atom, i.e., in the order of **7** (Y = Br) <**6** (Y = Cl) <**5** (Y = F) <**3** (Y = O(OMe)) ≈ **2** (Y = O(OH)) <**4** (Y = N) <**1** (Y = O(CHO)). It should be noted that the order of the strength for the Se···Cl interactions of **6a–f** and that for the Se···Br interactions of **7a–f** were different from those observed for the Se···O, Se···N, and Se···F interactions. This is because the Se···Cl and Se···Br interactions are so weak that the major mechanism of the stabilization slightly may be changed.

The relative Se···Y distance is a good index for the strength of nonbonded interactions, but it does not directly correspond to a quantitative value of the strength. We, therefore, employed the second-order perturbation energy ($E_{Se\cdots Y}$) of the orbital interaction between the lone pair (n_Y) of the interacting heteroatom Y and the antibonding orbital (σ^*_{Se}) of the Se–X covalent bond as the second parameter for the strength of Se···Y interactions. The $E_{Se\cdots Y}$ energies were calculated by use of the natural bond orbital method.[26]

Table III lists the $n_Y \rightarrow \sigma^*_{Se}$ orbital interaction energies ($E_{Se\cdots Y}$) calculated for **1–7** at the B3LYP/631H level. The energies represent only the contribution from the orbital interaction, not including other elements for the stability, such as the electrostatic interaction, the dispersion force, and the steric repulsion. This implies that the value of $E_{Se\cdots Y}$ is not a perfect index for the strength of the Se···Y interactions. Nevertheless, it can be a good estimate because a dominant component of the Se···O, Se···N, and Se···F interactions reasonably has been assigned to the $n_Y \rightarrow \sigma^*_{Se}$ orbital interaction in our previous works.[1,2,16–20]

TABLE III Orbital Interaction Energies ($E_{Se\cdots Y}$) Calculated for Series of Compounds 1–7 at the B3LYP/631H[a]

	X	**1**[b] (Y = O(CHO))	**2**[b] (Y = O(OH))	**3′**[b] (Y = O(OMe))	**4′** (Y = N)	**5** (Y = F)	**6** (Y = Cl)	**7** (Y = Br)
a	Cl	36.07	14.80	14.38	30.33	7.03	0.27	0.12
b	Br	33.80	13.61	13.17	30.07	5.71	0.18	0.16
c	CN	11.33	5.95	4.86	8.56	4.33	1.96	1.82
d′	SMe	10.72	4.71	4.21	8.81	2.88	—	—
e′	SeMe	10.66	4.46	3.87	8.57	2.68	1.00	1.03
f	Me	6.19	2.57	2.26	3.26	1.89	0.62	0.67

[a]The orbital interaction energies between the Y lone pair (n_Y, Y = O, N, F, Cl, and Br) and the anti-bonding orbital (σ^*_{Se}) of the Se–X covalent bond were determined by NBO second-order perturbation analysis.

[b]The data from.[2]

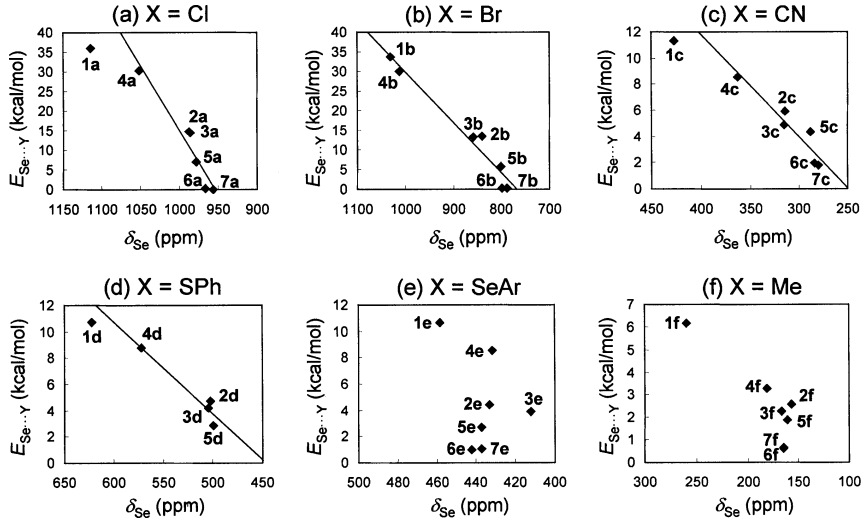

FIGURE 5 Correlation plots between the ^{77}Se NMR chemical shifts (δ_{Se}) and the $n_Y \rightarrow \sigma^*_{Se}$ orbital interaction energies ($E_{Se\cdots Y}$) for **1–7**

Correlation plots between the δ_{Se} and $E_{Se\cdots Y}$ values are shown in Figure 5 for each selenenyl derivative of **1–7**. Approximately linear correlation was obtained for **a** (X = Cl), **b** (X = Br), **c** (X = CN), and **d** (X = SPh), excluding series **1** [Y = O(CHO)] compounds; $E_{Se\cdots Y} = 0.3282\delta_{Se} - 313.0$ for **a** ($r^2 = 0.93$), $E_{Se\cdots Y} = 0.1299\delta_{Se} - 99.8$ for **b** ($r^2 = 0.93$), $E_{Se\cdots Y} = 0.0780\delta_{Se} - 19.4$ for **c** ($r^2 = 0.90$), and $E_{Se\cdots Y} = 0.0705\delta_{Se} - 31.5$ for **d** ($r^2 = 0.93$). The significant downfield shifts of ^{77}Se NMR observed for **1a–f** are due to a large magnetic anisotropic effect from the proximate formyl group as mentioned earlier. It is important to note that the stronger the nonbonded Se···Y interactions, the larger the ^{77}Se NMR shifted to downfield. The proportional correlation lines thus obtained must be useful for estimating the strength of Se···Y interactions *in situ* for other analogous compounds by measurement of the ^{77}Se NMR spectra. Sensitivity of the δ_{Se} value to the strength of Se···Y interactions depended on the substituent X on the Se atom. The magnitude of the slopes indicated that the sensitivity increases in the order, **a** (X = Cl) < **b** (X = Br) < **c** (X = CN) < **d** (X = SPh), implying that the δ_{Se} values for selenocyanates (**c**) and selenenyl sulfides (**d**) largely change even if the nonbonded Se···Y interaction is very weak. For the cases of **e** (X = SeAr) and **f** (X = Me), it was found that the δ_{Se} values do not change significantly according to the $E_{Se\cdots Y}$ values: the ^{77}Se NMR can not be applied as a probe for the Se···Y interactions in these cases.

The obtained correlation lines (Figure 5) will be useful for estimating the strength of Se···Y interactions from the δ_{Se} values. However, they should be usable only when the major element of the Se···Y interactions is the orbital interaction, because the $E_{Se\cdots Y}$ value evaluates the strength only by using the $n_Y \rightarrow \sigma^*_{Se}$ orbital interaction energy. To reconfirm the major stabilization mechanism for the Se···Y interactions of **1–7**, the correlation between the $E_{Se\cdots Y}$ values and the relative Se···Y atomic distances $[r_{Se\cdots Y}/(vdw_{Se} + vdw_Y)]$, which can be considered as an index for the total interaction energy, was investigated.

An almost linear correlation was obtained between the relative Se···Y atomic distance and the logarithm of the $n_Y \rightarrow \sigma^*_{Se}$ orbital interaction energy (Figure 6); $\log E_{Se\cdots Y} = 5.855\{1 - r_{Se\cdots Y}/(vdw_{Se} + vdw_Y)\} - 0.302$. The correlation clearly shows that all the Se···Y interactions can be treated as one class in the wide range of energy, indicating that the orbital interaction should be common as a major element for the stability. Thus, the linear correlations obtained in Figure 5 may be valid not only for the Se···O interactions but also for various types of Se···Y interactions. It is notable in Figure 6 that the Se···Cl (for **6**) and Se···Br (for **7**) interactions may fit a little different correlation line (a-dashed line in Figure 6). This may be due to a slightly different stabilization mechanism for subtle Se···Cl and Se···Br interactions (the dispersion force can be a major mechanism) or uncertainty in the definition of van der Waals radii for Cl and Br.

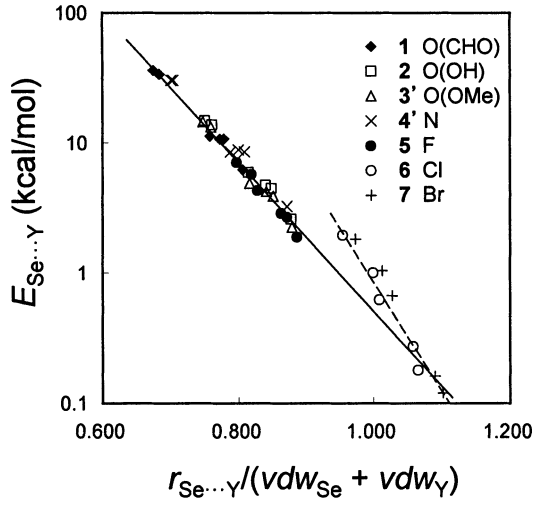

FIGURE 6 Correlation plots between the relative Se···Y atomic distances $[r_{Se\cdots Y}/(vdw_{Se} + vdw_Y)]$ and the $n_Y \rightarrow \sigma^*_{Se}$ orbital interaction energies ($E_{Se\cdots Y}$) for **1–7**.

Since S and O atoms are commonly present in proteins, similar S···O interactions as the Se···O interactions of organoselenium compounds were strongly expected in protein architecture. Indeed, we have discovered weak, but ubiquitous, S···O interactions by statistical analysis of protein structures selected from PDB.[13,14] According to MP2 calculations, the stabilization energy was estimated as 3.21 kcal/mol in the case of the interaction between the disulfide (SS) linkage and the main-chain amide O atom. The magnitude of the interaction energy was smaller than those estimated for the Se···O interactions of **1e′**, **2e′**, and **3′e′** (see the values of $E_{Se\cdots O}$ in Table III), suggesting that S···O interactions in proteins are weaker than the Se···O interactions of small organic molecules. The trend is reasonable in light of lower electrophilicity of a disulfide bond than a diselenide bond.

On the other hand, directional features of S···O interactions in proteins showed an unusual preference. Figure 7 displays the spatial distribution of S atoms with respect to the carbonyl O atom in the S···O interactions. For intramolecular 1,5-type S···O interactions of organic molecules, the S atoms tend to approach the O atom in the direction on the carbonyl plane ($\theta_2 = 90^\circ$) (Figure 7a). The directionality is identical to that of Se···O interactions of organoselenium compounds (see Figure 1a). However, the S atoms in proteins tend to approach the O atom in the direction vertical to the amide plane ($\theta_2 = 0^\circ$ or 180°) (Figure 7b), which is identical to the direction of the π orbital (π_O) (see also Figure 1b).

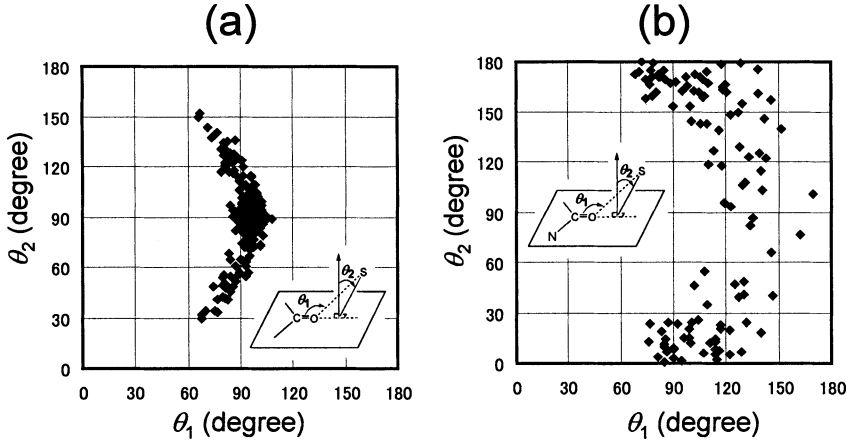

FIGURE 7 Spatial distribution of S atoms with respect to the carbonyl O atom in the S···O interactions. (a) intramolecular 1,5-type S···O interactions in small organic compounds. (b) S···O interactions in proteins. The diagrams were prepared by using the data reported in.[15]

The factors that are responsible for the observed directional discrepancy was analyzed extensively.[15] First, the 1,5-Type S···O interactions suffer from a strong conformational restriction that does not allow the vertical approach of the S atom to the carbonyl plane. In the absence of the restriction, the S atom may approach the O atom either in the direction of the lone pair or in the direction of the π orbital. Second, the S···O interactions in proteins mostly involve the amide O atom as an electron donor. According to MP2 calculations, the HOMO of amides is the π_O orbital, while that of other carbonyl compounds, such as aldehydes, ketones, and esters, is the n_O orbital. Therefore, the unique directionality observed for the S···O interactions in proteins (Figure 7b) is consistent with the natural properties of the S···O (amide) interactions. This in turn implies that the directionality of S···O (amide) interactions significantly is not affected in folded protein structures, suggesting that the S···O interactions can control protein structures to some extent.

CONCLUSIONS

We have shown that the ^{77}Se NMR chemical shift (δ_{Se}) can be used as an easy experimental probe for the strength of nonbonded Se···O interactions. The correlation lines (Figure 5) obtained between the δ_{Se} values and the $E_{Se\cdots Y}$ values, which represent the $n_Y \rightarrow \sigma^*_{Se}$ orbital interaction energies, would be applicable for a wide range of Se···Y interactions. Furthermore, the correlation shown in Figure 6 demonstrated that the major element of stabilization may be common for various Se···Y interactions. The obtained correlation line will be useful when the strength of a nonbonded Se···O interaction is estimated from the molecular structure determined by X-ray analysis. These physical organic aspects of Se···O interactions would provide valuable suggestions for design of organoselenium molecules with various functions.

On the other hand, analogous S···O interactions have been characterized in protein structures.[13–15] Although the strength was not large (~3.21 kcal/mol), it was found that the directional propensities are maintained in the folded structures. Thus, the S···O interactions can be applied as a useful chemical tool to control protein structures in the field of protein engineering. Investigation on the roles of S···O interactions in the biological functions as well as the evolution of proteins is a next stage of bio-organic aspects of Se···O interactions.

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