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Structural Study of Aryl Selenides in Solution Based on ^{77}Se NMR Chemical Shifts: Application of the GIAO Magnetic Shielding Tensor of the ^{77}Se Nucleus

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The ^{77}Se NMR chemical shifts (δ_{obsd}(Se)) of *p*-YC_6H_4SeMe (**1**: Y = H (**a**), OMe (**b**), Me (**c**), Cl (**d**), Br (**e**), COOR (**f**), and NO_2 (**g**)) and *p*-YC_6H_4SePh (**2**) were determined or redetermined in chloroform-*d*. The δ_{obsd}(Se) values of **2**, *p*-YC_6H_4SeR (R = CN (**3**), Bz (**4**), H (**5**), Br (**6**), Et (**7**), C_6H_4Y-*p* (**8**), $CH{=}CH_2$ (**9**), $CH{=}CHCl$-*t* (**10**), and $CHCH_2CCl_2$-*cyclo* (**11**)), 1,1′-[8-(*p*-YC_6H_4Se)$C_{10}H_6Se$]$_2$ (**12**), and 1-(MeSe)-8-(*p*-YC_6H_4-Se)$C_{10}H_6$ (**13**) were plotted against those of **1**. The plots were analyzed as two correlations. For example, the points corresponding to **a**−**c** make a group (g(**m**)), and those of **d**−**g** belong to another one (g(**n**)). This must be a reflection of the differences in the dihedral angles between the aryl rings and the Se−R bonds, which should result in the different contributions of the inductive and mesomeric effects of the substituents Y on the δ_{obsd}(Se) values. After reexamination of the applicability of the GIAO magnetic shielding tensor for the selenium nucleus (σ(Se)) in selenium compounds of various structures, σ(Se) was calculated for the model compounds, **5**, with the B3LYP/6-311+G(d,p) method, to explain the δ_{obsd}(Se) values of **1**−**13** uniformly: δ_{calcd}(Se) was defined as $-(\sigma(\mathrm{Se}) - \sigma(\mathrm{Se})_{MeSeMe})$. Each selenol was optimized to be the planar structure (**14**) or the perpendicular one (**15**). New parameters were devised such as $\delta_{calcd}(\mathrm{Se}{:}\theta_B) = (1 - \sin\theta_B)\delta_{calcd}(\mathrm{Se})_{\mathbf{14}} + \sin(\theta_B)\delta_{calcd}(\mathrm{Se})_{\mathbf{15}}$. The δ_{obsd}(Se) values of **1**−**13** correlated well with the new parameters, $\delta_{calcd}(\mathrm{Se}{:}\theta_B)$, which gave the best-fitted θ_B values. The structures of **1**−**13** in solutions were explained uniformly by the evaluated θ_B values. The observed ratios of the slopes for g(**m**) versus those of g(**n**) were also correlated with the θ_B values.

Introduction

Organic selenium compounds are well-known to show versatile reactivities, and they afford many structurally interesting compounds.[1] ^{77}Se NMR spectroscopy, as well as ^{1}H and ^{13}C NMR spectroscopies, plays an important role in studying organic selenium chemistry.[2] The observed ^{77}Se NMR chemical shifts (δ_{obsd}(Se)) of organic selenium compounds have been interpreted based on the Karplus−Pople equation (eq 1).[3]

$$\sigma_i^{para} = -\frac{\mu_o \mu_B^{\ 2}}{2\pi\Delta E}\langle r^{-3}\rangle[Q_i + \sum_{j\neq i} Q_j] \qquad (1)$$

The ΔE factor, the average excitation energy, could be estimated by the energy difference between the HOMO and the LUMO of the compound if the 4p atomic orbitals of the selenium atom substantially contribute to both of the orbitals. The $\langle r^{-3}\rangle$ factor of the 4p orbitals is expected to be proportional to the atomic charge on the Se atom being observed. The quantities Q_i and Q_j represent the elements of the charge density and bond order matrices in the molecular orbital theory of the unperturbed molecule. The ΔE factor, for example, is expected to play an important role in the δ_{obsd}(Se) of diselenides, while the $\langle r^{-3}\rangle$ factor would be operating in hypervalent compounds or oxides relative to the corresponding selenides.[2] However, the δ_{obsd}(Se) values are not proportional to the ΔE and/or $\langle r^{-3}\rangle$ factors in some cases, since the values are governed by the complex conjugation of the two factors, together with other factors.

The δ(Se) values are reflected much by the structural change of the selenium compounds. Therefore, it must be very useful not only in the structural study of the selenium compounds, but also in the preparation of new compounds, that the calculated ^{77}Se NMR chemical shifts (δ_{calcd}(Se)) explain the δ_{obsd}(Se) values well. Recently, the magnetic shielding tensor is shown to be reliable for some nuclei containing carbon, oxygen, and hydrogen, calculated with the gauge-including atomic orbitals (GIAO) theory.[4] Efforts have also been made to calculate the magnetic shielding tensor for the ^{77}Se nucleus on the theoretical background, and the reliability has been essentially established so far.[5,6]

This encouraged us to interpret uniformly the δ_{obsd}(Se) values of para-substituted phenyl selenides, *p*-YC_6H_4SeR (ArSeR: **1**−**13**), in relation to their structures in solutions, based on the δ_{calcd}(Se) values. Before discussion of the δ(Se) values of *p*-YC_6H_4SeR, the GIAO magnetic shielding tensor for the ^{77}Se nucleus (σ(Se)) in selenium compounds[7] of versatile structures was calculated and/or recalculated using the Gaussian 94 program[8] with some basis sets. The calculations showed us which method (basis sets and the level) is practically suitable for our purpose to calculate the δ_{calcd}(Se) values of *p*-YC_6H_4-SeR.

The calculations could be performed variously. To learn how the calculations should be carried out for a better interpretation of the δ_{obsd}(Se) values uniformly, the characters of δ_{obsd}(Se) for **1**−**13** were reexamined briefly by plotting the δ_{obsd}(Se) values of **2**−**13** against those of **1**. The results confirmed our calculations of the δ_{calcd}(Se) values for para-substituted benzeneselenols (**5**). Two structures are optimized for each selenol

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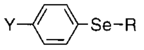
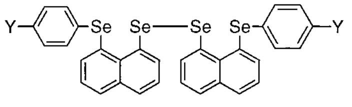


1 (R = Me) **5** (R = H) **9** (R = CH=CH$_2$)
2 (R = Ph) **6** (R = Br) **10** (R = CH=CHCl-*trans*)
3 (R = CN) **7** (R = Et) **11** (R = CHCH$_2$CCl$_2$-*cyclo*)
4 (R = Bz) **8** (R = C$_6$H$_4$Y-*p*)



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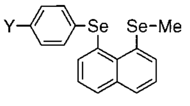
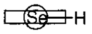


13

		a	b	c	d	e	f	g	h	i	j	k	l
Y	=	H	OR	Me	Cl	Br	CO$_2$R	NO$_2$	NH$_2$	F	CF$_3$	CHO	CN

if the calculations are performed assuming C_s symmetry: one is the planar structure of which the Se−H bond is in the aryl plane (**14**), and the other is the perpendicular one where the Se−H bond is perpendicular to the aryl plane (**15**). The σ(Se) values were calculated for **14** and **15** based on the GIAO theory. The electronic effect of Y and R and the steric effect of R in *p*-YC$_6$H$_4$SeR affect the structure of ArSeR, especially around the Se atom, namely, θ_R in **16**. New parameters (δ_{calcd}(Se:θ)) are devised, of which the θ values are expected to correlate roughly to the angle θ_R. The δ_{obsd}(Se) values are well-explained by the devised parameters, which consequently enables us to understand the electronic and/or steric effects of R on the δ_{obsd}(Se) values.



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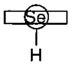

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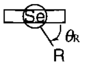


16

Here we present the results of the calculations for the δ_{calcd}(Se) values based on the GIAO theory, emphasizing how they are useful in explaining the δ_{obsd}(Se) values and understanding the organic selenium chemistry based on ^{77}Se NMR spectroscopy.

Results and Discussion

GIAO Magnetic Shielding Tensor for the ^{77}Se Nucleus of Various Selenium Compounds. To know which method of calculations is suitable for explaining the δ_{obsd}(Se) values of *p*-YC$_6$H$_4$SeR (**1**−**13**), the GIAO magnetic shielding tensor for the ^{77}Se nucleus (σ(Se)) of selenium compounds with various structures is calculated and/or recalculated using the Gaussian 94 program.[8] The employed selenium compounds for the calculations and the optimized symmetry of the compounds are shown in Table 1. The 6-311++G(3df,2pd), 6-311+G(d,p), and 3-21G basis sets were applied at the DFT (B3LYP) level.[9] The HF level was also applied with the 6-311+G(d,p) basis set. Table 1 exhibits the calculated chemical shifts (δ_{calcd}(Se)) relative to dimethyl selenide (δ_{calcd}(Se) = −(σ(Se) − σ(Se)$_{MeSeMe}$)), together with the parent σ(Se) values of dimethyl selenide. Natural charges (Qn) calculated by natural population analysis[10,11] and the energy differences ($\Delta\epsilon$) between the HOMO and the LUMO of the selenium compounds are also given in Table 1, calculated with the 6-311++G(3df,2pd) basis sets at the B3LYP level. Table 1 also contains the δ_{obsd}(Se) values of the selenium compounds.[2]

To begin with, the δ_{obsd}(Se) values are plotted against Qn(Se) and $\Delta\epsilon$ calculated with the B3LYP/6-311++G(3df,2pd) method. The results are shown in Figures 1 and 2, respectively, which show that those values cannot explain the wide range of δ_{obsd}(Se) values. However, they may be useful for the discussion when applied to a small range of shift values and/or to the selected structures. One must confirm that the p orbitals of the Se atom contribute to both the HOMO and the LUMO of the selenium compound in question when $\Delta\epsilon$ is applied to the discussion.[3,7]

Figure 3 exhibits the plot of δ_{obsd}(Se) against δ_{calcd}(Se) obtained with the B3LYP/6-311++G(3df,2pd) method. Table 2 collects the correlations of δ_{obsd}(Se) against δ_{calcd}(Se) obtained with the various methods shown in Table 1. The method with the 6-311++G(3df,2pd) basis set at the B3LYP level is excellent among the results shown in Table 2 (r = 0.998).[12] The 6-311+G(d,p) basis set is also recommended for the calculations of the σ(Se) values since the correlation coefficients are also good when the 6-311+G(d,p) basis set is employed at both the B3LYP and the HF levels (Table 2). Those obtained with the B3LYP/3-21G method could not explain the observed values (r = 0.971) well. Table 2 also contains the constants and the coefficients for the correlations where the point corresponding to MeSeSeMe is omitted from the correlations. The r values were much improved for the B3LYP/3-21G method. The poor accuracy for the optimized structure of MeSeSeMe is mainly responsible for the discrepancy of the calculated values with the 3-21G basis set at the B3LYP level.[13]

Correlations in the δ_{obsd}(Se) Values of Aryl Selenides. Before we discuss the δ_{obsd}(Se) values of aryl selenides based on the calculated values, the correlations between the observed values were examined first. The δ_{obsd}(Se) values of *p*-YC$_6$H$_4$SeMe (**1**: **1a**−**g**) and *p*-YC$_6$H$_4$SePh (**2**) were determined or redetermined in CDCl$_3$ using an FT NMR spectrometer. The values are given in Table 3. Table 3 also collects the δ_{obsd}(Se) values of various para-substituted phenyl selenides,[2,14−18] containing those reported for **1** determined in neat liquid by the INDOR ^{1}H−{^{77}Se} technique (shown by **1′**).[14] The δ_{obsd}(Se) values of **1′** (δ_{obsd}(Se)$_{\mathbf{1'}}$) were plotted against those of **1**. Equation 2 shows the results. The correlation was good

$$\delta_{obsd}(\mathrm{Se})_{\mathbf{1'}} = 0.939\delta_{obsd}(\mathrm{Se})_{\mathbf{1}} + 6.0 \qquad r = 0.995 \qquad (2)$$

irrespective of the different conditions of the measurements. The proportionality constant of 0.939 and the correlation coefficient (r) of 0.995 show that the solvent effect may not work as much in the correlation of the two.

The δ_{obsd}(Se) values of **2**−**13** were plotted against that of δ_{obsd}(Se)$_{\mathbf{1}}$. Figure 4 shows the plot for **3**, for example. The plot should be analyzed as two correlations. One of the groups contains the points corresponding to Y = OMe, Me, and H (group **m** (g(**m**)) and another group consists of those of Y = Cl, Br, COOR, and NO$_2$ (group **n** (g(**n**)). Since the points corresponding to Y = H, Cl, and Br exist at the crossing area of the two groups, there must be other classifications. Another possibility of the classification is as follows. The points corresponding to Y = OMe, Me, Cl, and Br make a group (g(**m′**)), and those with Y = H, COOR, and NO$_2$ make another (g(**n′**)). The g(**m**) and g(**n**) classifications explain the δ_{obsd}(Se) values better than the g(**m′**) and g(**n′**) groupings. The g(**m′**) and g(**n′**) groupings may be rationalized based on the theoretical background. The Cl and Br atoms donate electrons by the mesomeric mechanism, but H is not an electron donor.[19] The planar structure **14** is calculated to be less stable than the perpendicular structure **15** for g(**m′**), whereas the former is

TABLE 1: δ_{calcd}(Se) and δ_{obsd}(Se) Values of Selenium Compounds of Various Structures, Together with the Qn(Se) and $\Delta\epsilon$ Values[a]

compd (no)	structure[b]	Qn(Se)[c]	$\Delta\epsilon$[c,d]	δ_{calcd}(Se) *c*	*e*	*f*	*g*	δ_{obsd}(Se)	solvent
MeSeMe (i)	C_{2v}	0.2719	0.203	1656.4	1624.4	1942.5	1895.9		
				0.0	0.0	0.0	0.0	0.0	$CDCl_3$
H_2Se (ii)	C_{2v}	−0.1695	0.232	−412.6	−412.1	−233.1	−207.1	−344.75[h]	gas phase[i]
MeSeH (iii)	C_s	0.0543	0.208	−187.7	−189.9	−107.2	−93.3	−154.67[j]	gas phase[i]
Me_3Se^+ (iv)	C_3	1.0229	0.309	220.9	190.0	186.5	140.1	253	H_2O
MeSeSeMe (v)	C_2	0.1269	0.179	341.2	375.5	217.8	558.5	281	$CDCl_3$
$MeSeCl_2Me$ (vi)	C_{2v}	1.0477	0.193	401.9	377.0	398.0	322.4	448	CH_2Cl_2
SeF_6 (vii)	O_h	2.9570	0.295	632.7	718.9	555.7	533.9	610.3	neat
Me_2SeO (viii)	C_s	1.3485	0.221	768.0	757.9	679.9	608.9	812	H_2O
F_2SeO_2 (ix)	C_{2v}	2.7655	0.247	914.6	961.7	1032.1	917.5	948	neat
SeF_4 (x)	C_{2v}	2.1805	0.257	1115.0	1244.4	925.1	1029.4	1083	CH_3F
F_2SeO (xi)	C_s	1.9940	0.252	1353.0	1438.6	1336.0	1270.8	1378.2	neat

[a] The calculated σ(Se) values are shown for MeSeMe, and those relative to MeSeMe are given for other compounds (see text). [b] Optimized symmetry. [c] B3LYP/6-311++G(3df,2pd). [d] In au. [e] B3LYP/6-311+G(d,p). [f] HF/6-311+G(d,p). [g] B3LYP/3-21G. [h] Value is −288 in D_2O. [i] Reference 5g. [j] Value is −130 in $CDCl_3$.

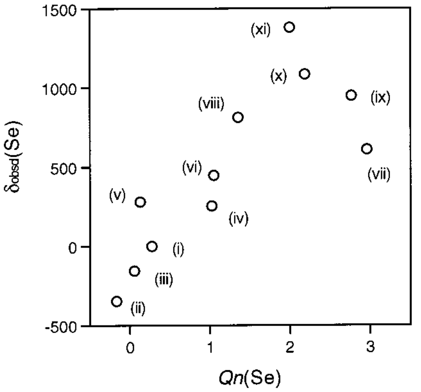


Figure 1. Plot of δ_{obsd}(Se) versus Qn(Se) calculated with the B3LYP/6-311++G(3df,2pd) method. The numbers shown in the figure correspond to those in Table 1.

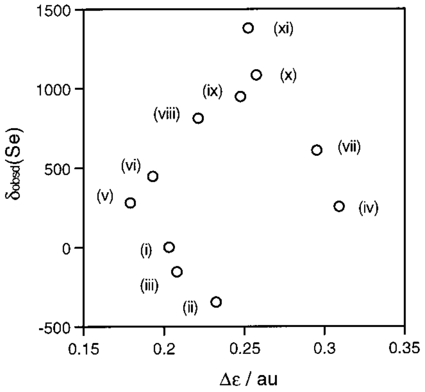


Figure 2. Plot of δ_{obsd}(Se) versus $\Delta\epsilon$ calculated with the B3LYP/6-311++G(3df,2pd) method. The numbers shown in the figure correspond to those in Table 1.

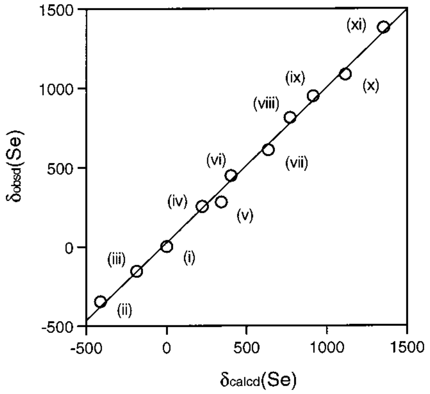


Figure 3. Plot of δ_{obsd}(Se) versus δ_{calcd}(Se) calculated with the B3LYP/6-311++G(3df,2pd) method. The numbers shown in the figure correspond to those in Table 1.

TABLE 2: Correlations of δ_{obsd}(Se) versus δ_{calcd}(Se) with Various Methods[a]

method	*a*	*b*	*r*
Versus δ_{calcd}(Se)			
B3LYP/6-311++G(3df,2pd)	0.981	24.3	0.998
B3LYP/6-311+G(d,p)	0.914	29.2	0.993
HF/6-311+G(d,p)	1.066	−0.6	0.990
B3LYP/3-21G	1.092	−21.2	0.971
Versus δ_{calcd}(Se) without the Point for MeSeSeMe			
B3LYP/6-311++G(3df,2pd)	0.977	33.8	0.999
B3LYP/6-311+G(d,p)	0.911	40.1	0.994
HF/6-311+G(d,p)	1.071	−8.0	0.990
B3LYP/3-21G	1.106	3.2	0.989

[a] $\delta_{obsd}(Se) = a\delta_{calcd}(Se) + b$, with *r* (correlation coefficient).

evaluated to be more stable than the latter for g(**n′**) with the B3LYP/6-311+G(d,p) method (see Table 6). Table 4 collects the results for the g(**m**) and g(**n**) classifications.[20] The parameters of the correlations for g(**m**) and g(**n**) are given by a_x, b_x, and r_x, where x = m or n, as shown in eq 3. Table 4 also contains correlations similarly treated for $\delta_{obsd}(Se)_{\mathbf{8}}$ versus $\delta_{obsd}(Se)_{\mathbf{2}}$.

$$\delta_{obsd}(Se)\text{ of ArSeR} = a\delta_{obsd}(Se)_{\mathbf{1}} + b \qquad r\text{: correlation coeff} \quad (3)$$

Why can the correlations be well-analyzed by the two groups, g(**m**) and g(**n**)? The phenomena can be explained by considering the following factors, which contribute to the correlations. (1) The aryl selenides **1**−**13** exist as **16** with θ_R. (2) Since the p-type lone pair of the Se atom in ArSeR is filled with electrons, the interaction between the lone-pair orbital and the orbitals of the Ar and/or R groups will stabilize the compound more effectively, if the electron-withdrawing ability of Ar and/or R becomes higher. (3) The electronic and the steric effects of R in ArSeR mainly determine θ_R, which affects the substituent effect of Y on the δ_{obsd}(Se) values. (4) The θ_R value would be larger if the electron-withdrawing ability of R becomes larger. (5) The θ_R value might depend on Y, but the change is usually not as large. (6) The proportionality constants a_m and a_n would be the reflection not only of the electronic effect of R but also of $\Delta\theta_R$ (=(θ_R of **2**−**13**) − (θ_R of **1**)), which determines the overlap

TABLE 3: δ_{obsd}(Se) Values of Some Aryl Selenides

	aryl selenide; solvent													
Y	**1**;[a] $CDCl_3$	**1′**; neat	**2**;[a] $CDCl_3$	**3**; $CDCl_3$	**4**; $CDCl_3$	**5**; neat	**6**; $CDCl_3$	**7**; CH_2Cl_2	**8**; $CDCl_3$	**9**; *b*	**10**; *b*	**11**; *b*	**12**; $CDCl_3$	**13**; $CDCl_3$
H	207.8	202.0	423.6	320.8	641.5	145	869.0	327	423.6	395.5	368.6	370.2	429.0	434.3
OMe	197.4	189.5	408.1	308.8	628.9	122	887.7	318	395.6	386.7	361.8	356.8	416.2	424.5
Me	200.6	196.1	415.0	313.0	634.4	128	876.9	323[c]	407.4	390.9	364.6	362.9	422.0	427.7
F		200.0		318.3	634.4	141		324	412.9					
Cl	210.3	203.6	421.9	321.0	637.0	142			419.9	395.4	366.3	370.5	429.1	431.6
Br	210.6		422.3	321.7	637.4				416.5	396.0	366.5	371.5	429.6	432.4
COOR	227.9[d,e]	218.1[f]	433.3[g]	329.4[g]	642.3[g]				436.7[g]				442.5[g]	442.4[g]
NO_2	241.2	233.4	446.3	338.8	645.7		823.0		447.4	404.9	377.0	396.8	456.1	453.9

[a] This work. [b] Not specified. [c] Neat. [d] R = H. [e] Reference 7. [f] R = Me. [g] R = Et.

TABLE 4: Correlations in δ_{obsd}(Se) of Aryl Selenides[a]

correlation	a_m	b_m	r_m	*n*	a_n	b_n	r_n	*n*	a_m/a_n
2 vs **1**	1.440	124.7	0.988	3	0.767	260.4	0.994	4	1.88
3 vs **1**	1.142	83.6	0.999	3	0.553	204.8	0.994	4	2.07
4 vs **1**	1.173	398.0	0.989	3	0.279	578.6	0.999	4	4.20
5 vs **1**	2.237	320.0	0.999	3					
6 vs **1**	−1.410	1162.8	0.996	4[b]					
7 vs **1**	0.813	158.5	0.960	3					
8 vs **1**	2.617	−119.7	0.992	3	0.964	215.6	0.993	4	2.71
9 vs **1**	0.811	227.2	0.982	3	0.299	332.7	0.999	3	2.71
10 vs **1**	0.637	236.3	0.993	3	0.345	293.9	1.000	3	1.85
11 vs **1**	1.242	112.5	0.986	3	0.839	194.4	1.000	3	1.48
12 vs **1**	1.187	182.7	0.987	3	0.854	249.4	0.997	4	1.39
13 vs **1**	0.938	239.4	1.000	3	0.696	285.2	0.995	4	1.35
8 vs **2**	1.810	−343.1	1.000	3	1.234	-101.7	0.979	3	1.47

[a] The constants a_x, b_x, and r_x (x = m or n) are defined by eq 3 and applied for g(**m**) and g(**n**), respectively. [b] Containing **6g**.

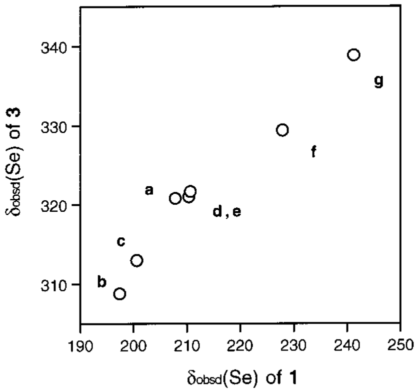


Figure 4. Plot of δ_{obsd}(Se) of **3** versus those of **1**.

TABLE 5: Energies and *δ*(Se) for 5a Calculated with the B3LYP/6-311+G(d,p) Method

θ_H,[a] deg	*E*, au	ΔE,[b] kJ mol^{-1}	δ_{calcd}(Se)[c]
0.00[d] (**14a**)	−2633.855 03	0.18	81.66
15.00[e]	−2633.855 05	0.13	74.43
30.00[e]	−2633.855 07	0.08	59.15
37.30[f]	−2633.855 10	0.00	51.68
45.00[e]	−2633.855 06	0.11	45.46
60.00[e]	−2633.855 05	0.13	38.28
75.00[e]	−2633.855 01	0.24	38.68
90.00[d] (**15a**)	−2633.854 99	0.29	39.99

[a] The torsional angle of C_oC_iSeH. [b] $E(\theta_H) - E(\theta_H = 37.30°)$. [c] The σ(Se) value for MeSeMe being 1624.36. [d] Full-optimized assuming C_s symmetry. [e] Partially optimized with θ_H fixed at a given value. [f] Fully optimized assuming C_1 symmetry, starting the partially optimized structure with θ_H fixed at 30.00°.

TABLE 6: Energies and *δ*(Se) for 14 and 15 Calculated with the B3LYP/6-311+G(d,p) Method

	E			δ_{calcd}(Se)	
Y	**14**[a]	**15**[a]	$\Delta E^{b,c}$	**14**	**15**
NH_2 (**h**)	−2689.2290	−2689.2325	9.2	58.6	11.1
OH (**b**)	−2709.1011	−2709.1027	4.2	69.9	16.9
Me (**c**)	−2673.1825	−2673.1829	1.1	73.5	25.1
F (**i**)	−2733.1224	−2733.1232	2.1	81.4	28.2
Cl (**d**)	−3093.4771	−3093.4773	0.5	84.3	32.4
Br (**e**)	−5207.3968	−5207.3969	0.3	84.5	33.3
H (**a**)	−2633.8550	−2633.8550	0.0	81.7	40.0
CF_3 (**j**)	−2971.0044	−2971.0034	−2.6	100.8	49.4
COOH (**f**)	−2822.4927	−2822.4909[d]	−4.7	104.6	47.8
CHO (**k**)	−2747.2138	−2747.2117[d]	−5.5	109.5	53.0
CN (**l**)	−2726.1216	−2726.1200	−4.2	112.3	59.3
NO_2 (**g**)	−2838.4188	−2838.4165	−6.0	119.0	55.3

[a] In au. [b] $E(\mathbf{14}) - E(\mathbf{15})$. [c] In kJ mol^{-1}. [d] The Se−H bond being assumed perpendicular to the phenyl plane.

integrals between the p-type lone pair and the π orbital of the Ar group.

The ratio a_m/a_n is expected to be the reflection of θ_R. The torsional angle or "average torsional angle" in ArSeR must change when R in ArSeR is replaced by R′. The change must be the cause for the δ_{obsd}(Se) values of ArSeR analyzed as the two correlations, although it would additionally depend on Y, since Y could affect the torsional angle to some extent. As the average torsional angle becomes larger, the ratio a_m/a_n is expected to increase, if the contributions of R on the a_m/a_n ratios are similar for the two selenides. The a_m/a_n values for **2**, **3**, and **4** are 1.88, 2.07, and 4.20, respectively, which may show that the torsional angles become larger in the order **1** < **2** ≈ **3** < **4** among the four aryl selenides in solutions.[21] And the a_m/a_n values in Table 4 are all larger than unity, which would be the reflection of the larger θ_R values of **2**−**13** relative to that of **1** in solutions.

After brief examination of the δ_{obsd}(Se) values of aryl selenides, the next extension of our investigation is to explain the δ_{obsd}(Se) values of **1**−**13** using the δ_{calcd}(Se) values based on the GIAO theory, in relation to those suggested above.

Structure and δ_{calcd}(Se) for 5a. Ab initio molecular orbital calculations were performed on **5a** as the model compound using

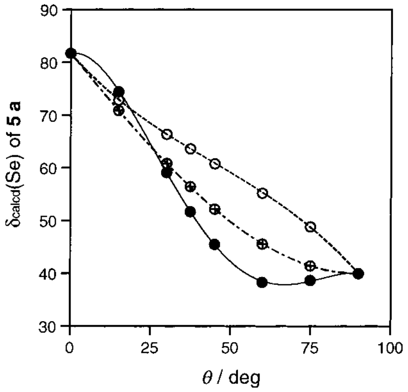


Figure 5. Plots of δ_{calcd}(Se) of **5a** versus θ: ● stands for δ_{calcd}(Se:θ) of **5a**, together with the calibration curve given in eq 4, ○ for a trial function, δ_{calcd}(Se:θ_A), defined by eq 5, and ⊗ for a trial function, δ_{calcd}(Se:θ_B), defined by eq 6.

the Gaussian 94 program[8] with the 6-311+G(d,p) basis set at the B3LYP level. The structures of **14a** and **15a** were optimized for **5a** when the calculations were performed assuming C_s symmetry, where the Se−H bond is placed in the phenyl plane and the bond is perpendicular to the phenyl plane as shown in **14** and **15**, respectively. However, one imaginary frequency was predicted for each of the optimized structures in the frequency analysis (−164.3 cm^{-1} for **14a** and −169.7 cm^{-1} for **15a**). The negative frequencies correspond to the motion of the Se−H protons around the Se−C bonds of **14a** and **15a**. The results show that **14a** and **15a** are not the energy minima but correspond to the transition states. The optimized structure with all positive frequencies is obtained at $\theta = 37.30°$.[22] The results are shown in Table 5.

Ab initio MO calculations were also performed on **5a** with the torsional angle C_oC_iSeH (θ_H) fixed at 15t° (t = 1, 2, 3, 4, and 5). The results of the calculations are collected in Table 5. The angular dependence of the energy is shown to be very small.[22] The GIAO magnetic shielding tensor for the Se nucleus (σ(Se)) was calculated with the B3LYP/6-311+G(d,p) method for the partially optimized structures of **5a** with θ_H fixed at the given values shown in Table 5, together with the optimized structures of **14a** and **15a**. The results, which are reduced to the δ_{calcd}(Se) values, are also collected in Table 5.

Before a discussion of δ_{obsd}(Se) based on δ_{calcd}(Se), the angular dependence of $\delta_{calcd}(\mathrm{Se})_{\mathbf{5a}}$ in Table 5 was examined. Figure 5 shows the plots of $\delta_{calcd}(\mathrm{Se})_{\mathbf{5a}}$ against θ. The solid curve in the figure is drawn according to eq 4: the correlation coefficient for the calibration curve is excellent (r = 1.000). The trial functions are devised for the angular dependence of δ(Se), which are defined by eqs 5[23] and 6. The θ values are

$$\delta_{calcd}(\mathrm{Se}{:}\theta) = -4.246 \times 10^{-6}\theta^4 + 8.871 \times 10^{-4}\theta^3 - 5.193 \times 10^{-2}\theta^2 + 0.1208\theta + 81.63 \tag{4}$$

$$\delta_{calcd}(\mathrm{Se}{:}\theta_A) = (\delta_{calcd}(\mathrm{Se})_{\mathbf{14}} \cos\theta + \delta_{calcd}(\mathrm{Se})_{\mathbf{15}} \sin\theta)/(\cos\theta + \sin\theta) \tag{5}$$

$$\delta_{calcd}(\mathrm{Se}{:}\theta_B) = \delta_{calcd}(\mathrm{Se})_{\mathbf{14}}(1 - \sin\theta) + \delta_{calcd}(\mathrm{Se})_{\mathbf{15}} \sin\theta \tag{6}$$

shown by θ_A and θ_B, respectively. The δ_{calcd}(Se:θ_A) and δ_{calcd}(Se:θ_B) curves given by eqs 5 and 6 are also drawn in Figure 5. The coincidence of the curves with that of eq 4 is better for δ_{calcd}(Se:θ_B) than that for δ_{calcd}(Se:θ_A). Equations 4−6 will be applied to the δ_{obsd}(Se) in ArSeR based on the δ_{calcd}(Se) of **5** in the following section.

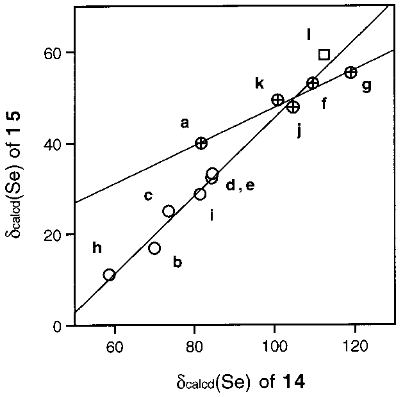


Figure 6. Plots of δ_{calcd}(Se) of **15** versus those of **14** calculated with the B3LYP/6-311+G(d,p) method: ○ stands for g(**m′**), ⊗ for g(**n′**), and □ for Y = CN.

Interpretation of δ_{obsd}(Se) in ArSeR Based on the δ_{calcd}(Se) of 5. Ab initio molecular orbital calculations were also performed on **5b**−**l** using the Gaussian 94 program[8] with the B3LYP/6-311+G(d,p) method. The structures of **14** and **15** were optimized for **5** except for **15f** and **15k**, when C_s symmetry was assumed in the calculations (or the calculations were started from a similar geometry). θ_H is fixed at 90° in the calculations for **15f** and **15k** in order to obtain the δ_{calcd}(Se) values for the structures. Structures **14** and **15** must be recognized as the standard points that give δ_{calcd}(Se) at θ_H = 0° and 90°, respectively. Table 6 collects the energies of **14** and **15** bearing various substituents at the para positions. Structure **15** is predicted to be more stable for Y = NH_2 (**h**), OH (**b**), F (**i**), Me (**c**), Cl (**d**), and Br (**e**) (g(**m′**)), which donate electrons by the mesomeric mechanism. Structure **14** is estimated to be more stable for Y = CN (**l**), COOH (**f**), CHO (**k**), NO_2 (**g**), and CF_3 (**j**) (g(**n′**)), which accept electrons through the π framework, except for Y = CF_3 (**j**), an electron-withdrawing group mainly through the σ framework. The g(**n′**) also contains Y = H (**a**), a nonelectron donor.

The σ(Se) values were calculated using the optimized structures of **14** and **15** (partially optimized ones for **15f** and **15k**) with the B3LYP/6-311+G(d,p) method. Table 6 collects the δ_{calcd}(Se) values for **14** and **15**. Figure 6 shows the plot of $\delta_{calcd}(\mathrm{Se})_{\mathbf{15}}$ against $\delta_{calcd}(\mathrm{Se})_{\mathbf{14}}$. The plot should be analyzed as the two correlations with g(**m′**) and g(**n′**), as mentioned above. The correlations are shown in eqs 7 and 8, respectively. The

$$\delta_{calcd}(\mathrm{Se})_{\mathbf{15}} = 0.860\delta_{calcd}(\mathrm{Se})_{\mathbf{14}} - 40.2 \quad \text{for g}(\mathbf{m'}) \qquad r = 0.980 \tag{7}$$

$$\delta_{calcd}(\mathrm{Se})_{\mathbf{15}} = 0.416\delta_{calcd}(\mathrm{Se})_{\mathbf{14}} + 6.2 \quad \text{for g}(\mathbf{n'}) \qquad r = 0.974 \tag{8}$$

point corresponding to Y = CN is omitted in the correlation in eq 8 since the point deviates from the correlation. The point behaves as if it were contained in g(**m′**). The cyano group might interact with the p-type lone pair at the Se atom of **15**. The omission of the cyano group in the correlation will not affect the following discussion.

The proportionality constants are less than unity in eqs 7 and 8, which shows that the interaction between the lone-pair orbital(s) at the Se atom and the orbital(s) at the substituent Y is stronger in **14** than that in **15**. The proportionality constant for g(**m′**) in eq 7 is 2.1 times larger than that for g(**n′**) in eq 8. The results show that the susceptibility of Y on the δ(Se) values is larger in **14** than in **15**, especially for g(**n′**). It must be the reflection of the more effective electron extension of the (p-

TABLE 7: Correlations of δ_{obsd}(Se) versus δ_{calcd}(Se:θ_A) and δ_{calcd}(Se:θ_B), Together with $\theta_{(A)}$ and $\theta_{(B)}$

compd	a_A	b_A	r_A	θ_A	$\theta_{(A)}$	a_B	b_B	r_B	θ_B	$\theta_{(B)}$	n
1	0.899	134.9	1.000	−1	0[a]	0.884	134.9	1.000	−1	0[a]	7
1′	0.755	136.2	0.996	10	14	0.876	134.6	0.996	9	14	7
2	0.578	373.4	0.994	44	28	0.825	374.5	0.994	32	29	7
3	0.458	281.3	0.991	43	28	0.644	281.1	0.991	28	27	8
4	0.633	629.6	0.996	104	90[b]	0.422	623.0	0.984	90	90[b]	8
5	1.144	40.5	0.989	23	20	1.512	38.1	0.988	16	20	5
6	−1.120	966.4	0.997	12	15	−1.321	967.1	0.997	9	14	4
7	0.337	305.8	0.972	71	38	0.444	303.9	0.972	43	36	4
8	1.088	366.0	0.996	80	44	1.256	366.2	0.995	58	44	8
9	0.329	374.5	0.985	69	38	0.426	374.6	0.985	47	37	6
10	0.263	348.8	0.994	62	34	0.358	348.8	0.994	40	34	6
11	0.649	311.9	0.999	24	21	0.857	311.9	0.999	18	21	6
12	0.640	371.2	0.996	20	19	0.818	371.0	0.996	15	19	7
13	0.465	391.0	0.990	25	21	0.617	390.9	0.990	18	21	7

[a] Assumed to be 0°. [b] Assumed to be 90°.

type) lone pair of the Se atom over Y of the electron-withdrawing g(**n′**) than those over electron-donating g(**m′**). The mesomeric mechanism must mainly contribute to the interaction in **14**, especially for g(**n′**).

The new parameters, δ_{calcd}(Se:θ_A) and δ_{calcd}(Se:θ_B) defined by eqs 5 and 6, are applied in the plots of the δ_{obsd}(Se) values of **1**−**13** in Table 3. The predicted θ values must serve as a measure for θ_R in **16**. The results are shown in Table 7:[24] the coefficients of the correlations and the predicted angles are represented by a_X, b_X, r_X, and θ_X where X = A and B (cf. eq 3). The r_B values are very close to those of r_A except for the case of **4**. The r values are larger than 0.99 except r_A for **5**, **7**, and **9** and r_B for **4**, **5**, **7**, and **9**. The insufficient accuracy of the reported chemical shifts would be responsible for the poor correlations for **5** and **7**.[2a] The Se−H group cannot be a good model for the SeCH=CH$_2$ group in **9**: the π-type interaction must be important in the SeCH=CH$_2$ group.

The predicted θ_B values are smaller than θ_A, which must be due to the difference in the function of eqs 5 and 6. The θ values, which satisfy eq 4, are also calculated from the θ_A and θ_B values: the values are determined so that the δ_{calcd}(Se:θ) values defined by eq 4 (δ_{calcd}(Se:$\theta_{(A)}$) and δ_{calcd}(Se:$\theta_{(B)}$)) give the same values as δ_{calcd}(Se:θ_A) and δ_{calcd}(Se:θ_B) for **5a**, respectively. The $\theta_{(B)}$ values are substantially the same as the $\theta_{(A)}$ values, which are also collected in Table 7. The $\theta_{(A)}$ (and $\theta_{(B)}$) values are almost linearly correlated with θ_A and θ_B.

While the θ_A values were calculated in the desired range of $-1° \leq \theta_A \leq 90°$, except 104° for **4**, the range for θ_B examined was $-1° \leq \theta_B \leq 90°$. The ($\theta_A$, θ_B) values for **5** are estimated to be (23°, 16°), which are smaller than the calculated θ_H value of 37.30°. The insufficient accuracy of the reported chemical shifts in **5**,[2a] together with the very shallow energy minimum,[22] must be responsible for the difference. The θ_B values of −1° for **1** and 90° for **4** strongly suggest that the structures in the solution are nearly planar and perpendicular, respectively, although the perturbation in the substituent effect on δ_{calcd}(Se) by R is not considered. The θ_R value of **1a** is reported to be 40°.[25a] The observed value for **1a** is much larger than the calculated θ_B value, but ab initio MO calculations on **1a** itself predicted the planar structure with the B3LYP/6-311+G(2d,p) method, even if the calculations are started assuming C_1 symmetry, although not shown. The θ_R value of 1,4-bis(selenocyanato)benzene is reported to be ca. 48°:[25b] the predicted (θ_A, θ_B) for **3** are (43°, 28°). The observed value in the crystal is close to θ_A. The crystal packing effect containing the intermolecular interaction and the electronic effect of the cyano group at the other para position in 1,4-bis(selenocyanato)benzene must play an important role in determining the structure of the bis(selenocyanato)benzene in crystals. The (θ_A, θ_B) for **2** and **8** were predicted to be (44°, 32°) and (80°, 58°), respectively. The θ_R value of di-*p*-tolyl selenide (**8c**)[26a] is reported to be 55°, which is very close to the θ_B value for **8**. The θ_R value of **6a**[26b] is reported to be 68°, which is much larger than the θ_A and θ_B values predicted for **6**. The real angular dependence of δ_{obsd}(Se) must determine the θ_R values of ArSeR. Therefore, the predicted θ values will be close to the observed ones when the calibration curve reproduces the real one for ArSeR in solutions. The above results may show that the real curves for ArSeR in solutions are sometimes different from those calculated for **5a** by eqs 5 and 6, although the θ_R values are not measured in solutions.

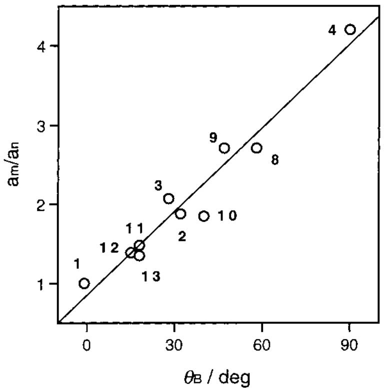


Figure 7. Plot of a_m/a_n versus θ_B.

The θ_A values correlated well with the θ_B values. Equation 9 shows the correlation. Therefore, we employ θ_B for the following discussion, although three types of θ values are tabulated. The θ_B values explain the a_m/a_n values estimated based on δ_{obsd}(Se) of **1**−**13** in solutions, which are expected to correlate with the θ_R values, although they are not directly measured. The ratios of a_m/a_n for **1**−**4** and **8**−**13** are plotted against θ_B. Figure 7 shows the plot, and the correlation is given in eq 10. It is demonstrated that the a_m/a_n ratio is correlated with θ_B, which suggests that θ_B can be a measure of θ_R in solutions.

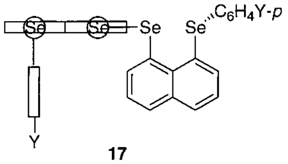
$$\theta_A = 1.25\theta_B + 4.72 \qquad r = 0.978 \tag{9}$$

$$a_m/a_n = 0.0353\theta_B + 0.85 \qquad r = 0.975 \tag{10}$$

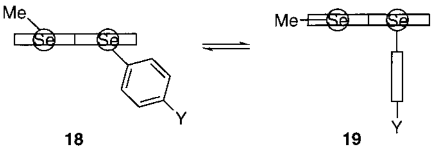
There are mainly three cases in the Y dependence of θ: (a) The θ value is substantially equal for all Y examined. (b) The value changes from Y to Y′, but the substantial change is limited only for strong electron-withdrawing Y, such as COOR and/or NO_2 groups. (c) The value explicitly changes from Y to Y′. In case a, the *r* values in Table 7 must be very good. The coefficients are not as good, but they will be much improved if the points corresponding to the COOR and/or NO_2 groups are omitted in the plots in case b. In case c, the coefficients will not be improved without the points corresponding to the COOR and NO_2 groups in the plots.

The correlations were reexamined for **3**, **9**, and **13**, of which the *r* values were less than 0.992. The points corresponding to Y = OMe, Me, H, Cl, and Br were plotted against $\delta_{calcd}(\mathrm{Se}:\theta_B)$ with a single θ_B value. The (θ_B, r_B) values for **3**, **9**, and **13** become (13°, 0.999), (18°, 0.991), and (48°, 0.999), respectively.[27] The θ_B values for the two omitted points are evaluated based on the correlations. The (Y, θ_B) values are (COOR, 23°) and (NO_2, 24°) for **3**, (NO_2, ca. 32°) for **9**, and (COOR, 41°) and (NO_2, 26°) for **13**. The correlations are much improved for **3** and **13**, which shows that **3** and **13** belong to case b. **9** must be case c, since it did not improve. The plot of $\delta_{obsd}(\mathrm{Se})_\mathbf{9}$ against $\delta_{calcd}(\mathrm{Se}:\theta_B = 47°)$ gives an inversely proportional curve. The point for the methoxyl group actually deviates from the line even when the COOR and NO_2 groups are omitted in the plot.

We would like to discuss the structures of **12** and **13** in more detail. Structures **17**,[28a,b] **18**,[28b] and **19**[28c] are demonstrated in crystals for Y = H. The structure of **12** can be described as **17** with some twisting around the Se−C(C_6H_4Y) bonds[29] judging from the (θ_B, r_B) value of (15°, 0.996). How can the structure of **13** in the solution be explained by the treatment? Its correlation is much improved. Our explanation is as follows: **13** is in equilibrium with two conformers, **18** and **19**, in the solution. The molar ratio in **13** is not substantially changed for Y = OMe, Me, H, Cl, and Br, while the ratio of **19** would increase for Y = COOR and NO_2. The contribution of **19** must decrease the θ_B value, which is in accordance with the increased θ_B value when the two points are omitted.



17



18 **19**

These results exhibit that the GIAO method can be a powerful tool to investigate the selenium chemistry containing the structural dependence of the δ(Se) values if one employs the method supporting ^{77}Se NMR spectroscopy. A study containing nonbonded interactions with the method is in progress.

Experimental Section

Chemicals were used without further purification unless otherwise noted. Solvents were purified by standard methods. Melting points were uncorrected. ^{1}H, ^{13}C, and ^{77}Se NMR spectra were measured at 400, 100, and 76 MHz, respectively. The ^{1}H, ^{13}C, and ^{77}Se chemical shifts are given in ppm relative to those of internal $CHCl_3$ slightly contaminated in the solution, $CDCl_3$ as the solvent, and external MeSeMe, respectively. Column chromatography was performed on silica gel (Fujidebison BW-300), acidic alumina, and basic alumina (E. Merck).

p,*p*′-Disubstituted diphenyl diselenides,[30] which were prepared according to the method in the literature or the improved method, were reduced by $NaBH_4$ in aqueous THF and then allowed to react with methyl iodide, which gave para-substituted selenoanisoles (**1a**−**g**).[2a,16] The NMR spectra of these materials were in good agreement with the literature data.[16] Using a similar method for **1a**, compound **1f** gave 84% yield as a colorless oil. ^{13}C NMR ($CDCl_3$, 100 MHz) δ 6.43 (^1J(C,Se) = 64.3 Hz), 126.47, 128.61, 130.47, 141.08, 171.85. ^{77}Se NMR ($CDCl_3$, 76 MHz) δ 227.9. Anal. Calcd for $C_8H_8O_2Se_1$: C, 44.67; H, 3.75. Found: C, 44.64; H, 3.77.

The diselenides[30] were reduced by $NaBH_4$ in aqueous THF and the corresponding para-substituted benzene diazonium chlorides were added at a low temperature. After the usual workup, the crude products were chromatographed on silica gel containing acidic and basic alumina. Then the para-substituted diphenyl selenides (**2a**−**g**)[31] were obtained. Using a similar method for **2a**, compound **2f** gave 74% yield as a colorless oil. ^{77}Se NMR ($CDCl_3$, 76 MHz) δ 433.3. Anal. Calcd for $C_{15}H_{14}O_2Se_1$: C, 59.03; H, 4.62. Found: C, 59.07; H, 4.65. Compound **2g** gave 81% yield as yellow crystals, mp 58.0−58.5 °C. ^{13}C NMR ($CDCl_3$, 100 MHz) δ 123.85, 127.12, 129.29, 129.60, 129.94, 135.77, 143.86, 146.11. ^{77}Se NMR ($CDCl_3$, 76 MHz) δ 446.3. Anal. Calcd for $C_{12}H_9N_1O_2Se_1$: C, 51.82; H, 3.26; N, 5.04. Found: C, 51.79; H, 3.29; N, 5.07.

The details for the preparation and the properties of *p*,*p*′-disubstituted bis[8-(phenylselanyl)naphthyl]1,1′-diselenide (**12a**−**g**) and *p*-substituted 1-(methylselanyl)-8-(phenylselanyl)naphthalenes (**13a**−**g**) will be reported elsewhere.

MO Calculations. Ab initio molecular orbital calculations were performed on Origin and/or Power Challenge L computers using the Gaussian 94 program[8,9] with 6-311++G(3df,2pd), 6-311+G(d,p), 3-21G, and the LANL2DZ basis sets at the DFT (B3LYP level). The calculations at the HF level were also carried out with the 6-311+G(d,p) basis set. The calculations of the σ(Se) values based on the GIAO theory were performed by the NMR keyword of the Gaussian 94 program. The natural populations were calculated by the natural population analysis[10] of the program.

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(13) Although the correlation coefficient was not improved in the calculations with the B3LYP/6-311+G(d,p) method on the structures obtained with the B3LYP/3-21G method ($r = 0.976$), the results of the calculations on the σ(Se) values with the 3-21G basis set at the B3LYP level on the structures obtained with the B3LYP/6-311+G(d,p) method gave a better r value of 0.980.

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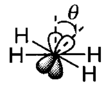
(20) The substituent effect of **6** on the δ_{obsd}(Se) values was inversely correlated with those of **1**. Therefore, we must be careful to discuss in detail those for **6**.

(21) The a_{m}, a_{n}, and $a_{\mathrm{m}}/a_{\mathrm{n}}$ values were 1.81, 1.23, and 1.47, respectively, for the plot of $\delta_{\mathrm{obsd}}(\mathrm{Se})_{\mathbf{8}}$ against $\delta_{\mathrm{obsd}}(\mathrm{Se})_{\mathbf{2}}$. Since **8** bears two substituents at both para positions, whereas **2** has only one, the substituent effect on $\delta_{\mathrm{obsd}}(\mathrm{Se})_{\mathbf{8}}$ is expected to be twice that of $\delta_{\mathrm{obsd}}(\mathrm{Se})_{\mathbf{2}}$. Indeed the a_{m} value of 1.81 is close to that expected, but the a_{n} value of 1.23 would be too small from the expectation, which may be explained by the saturating effect of the second substituents on δ_{obsd}(Se) operating especially for g(**n′**).

(22) Indeed, structure **16** with $\theta_{\mathrm{H}} = 37.30°$ is optimized for **5a** with the B3LYP/6-311+G(d,p) method when the calculations are started at the partially optimized structure, with θ_{H} being fixed at 30.00°, but the calculations are stopped at $\theta_{\mathrm{H}} = 18.48°$ when they are started at the partially optimized structure, with θ_{H} being fixed at 15.00°.

(23) The parameters are devised on the basis that the atomic overlap integral S between carbon 2p π_{a} and 2p π_{b} orbitals of the ethylene-type π orbital, where the two atomic orbitals are crossing with θ, is proportional to cos θ, $S = \langle\chi_{\mathrm{a}}|\chi_{\mathrm{b}}\rangle = \langle 2\mathrm{p}\pi_{\mathrm{a}}|\cos(\theta)2\mathrm{p}\pi_{\mathrm{b}} + \sin(\theta)2\mathrm{p}\pi_{\mathrm{b}}'\rangle = \cos(\theta)\langle 2\mathrm{p}\pi_{\mathrm{a}}|2\mathrm{p}\pi_{\mathrm{b}}\rangle = \cos(\theta)S_{\mathrm{o}}$ ($2\mathrm{p}\pi_{\mathrm{b}}'$ being orthogonal to $2\mathrm{p}\pi_{\mathrm{b}}$).



(24) The best-fitted correlations were obtained by the following steps. The $\delta_{\mathrm{calcd}}(\mathrm{Se}{:}\theta')$ values were calculated for every 5−10°. A θ' value was looked for that gives the largest r value among the $\delta_{\mathrm{calcd}}(\mathrm{Se}{:}\theta')$ values. Then the best-fitted θ value was determined, as it gave the largest r values among the $\delta_{\mathrm{calcd}}(\mathrm{Se}{:}\theta)$ calculated every 1° near the θ' value.

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(27) The (a_{B}, b_{B}, r_{B}, θ_{B}, n) values for **3**, **9**, and **13** are (0.835, 260.5, 0.999, 13, 6), (0.563, 357.1, 0.991, 18, 5), and (0.488, 409.5, 0.999, 48, 5), respectively.

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(29) The correlations were similarly reexamined for **3**, **9**, and **13** with θ_{A}. The evaluated (a_{A}, b_{A}, r_{A}, θ_{A}, n) values for **3**, **9**, and **13** are (0.666, 261.0, 0.999, 17, 6), (0.426, 357.1, 0.991, 24, 5), and (0.384, 409.5, 0.999, 71, 5), respectively. The (Y, θ_{A}) values for the omitted points were estimated to be (COOR, 51°) and (NO_2, 52°) for **3**, (NO_2, ca. 57°) for **9**, and (COOR, 66°) and (NO_2, 54°) for **13**.

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