Heteroatom Chemistry
Volume 12, Number 5, 2001

On the Equilibrium between Molecular Complexes and Trigonal Bipyramidal Adducts of Diaryl Selenide Dibromides in Solution

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Received 5 January 2001; revised 16 February 2001

ABSTRACT: *A method to visualize the equilibrium between molecular complexes (MCs) and trigonal bipyramidal (TB) adducts for* $ArSeBr_2Ar'$ *has been devised. The TB formation causes large downfield shifts for the ipso carbons* $\delta(C_i)$*, whereas the upfield shifts are characteristic for* $\delta(C_i)$ *in the MC formation. Therefore, the equilibrium is clearly proved if such an ArSeAr' is prepared that shows an upfield shift at one of ipso carbons, whereas the other goes downfield, when bromine is added to the ArSeAr' solution. The halogen-induced chemical shifts (Δδ) are measured for 4-*YC_6H_4SePh *(***1a–1g***), 2-*YC_6H_4SePh *(***2d, 2e, 2h***), 2-*$YC_6H_4SeC_6H_4Br$*-p (***3d, 3e, 3h***), 2-*$O_2NC_6H_4SeC_6H_4Y$*-p (***4a, 4e, 4i***), and 2,4-*$(O_2N)_2C_6H_3SeC_6H_4Y$*-p (***5a, 5e, 5i***), where Y = H (***a***), OMe (***b***), Me (***c***), Cl (***d***), Br (***e***), COOEt (***f***),* NO_2 *(***g***), I (***h***), and t-Bu (***i***). Positive values (downfield shifts) are observed for both* $\delta(C_i)$ *in* **2** *and* **3***, positive and negative values are recorded for each* $\delta(C_i)$ *in* **4***, and negative values are detected for both* $\delta(C_i)$ *in* **5***. The equilibrium between MC's and TB adducts is clearly shown in* **4***. The equilibrium constants K (K = [MC]/[TB]) are also calculated: they are ca. 0.20 for* **2** *and* **3** *and 0.16, 0.33, and 0.73 for* **4i**, **4a***, and* **4e***, respectively. The contribution of MC is negligible in* **1a***, and the contribution of the TB adduct is negligible in* **5***. The results show that TB adducts become unstable relative to MCs, when the effective electronegativity of the selenium atom and/or the bulkiness around the atom in a selenide are increased.* © 2001 John Wiley & Sons, Inc. Heteroatom Chem 12:369–379, 2001

INTRODUCTION

Organic chalcogen compounds are well known to show versatile reactivities, and they afford many structurally interesting compounds [1]. Among such compounds and reactivities, we have been interested in those arising from the lone-pair orbitals, which must act as electron donors [2]. On the other hand, the σ^*-orbitals of halogens have been well established to accept n-electrons of chalcogenides [3–5]. Charge transfer (CT) occurs from the lone-pair orbitals to the σ^*-orbitals when the chalcogenides come close to the halogens. Molecular compounds or molecular complexes (MCs) [3] will be formed, when CT from chalcogenides to halogens is small. However, the halogens can no longer exist as halogen molecules if CT becomes larger, resulting in the formation of trigonal bipyramidal (TB) adducts with the highly polar 3c–4e hypervalent bonds, $X^{\delta-}$–$Z^{\delta+}$–$X^{\delta-}$ [6]. The Z–X–X bonds in MCs are shown to be analyzed with the 3c–4e model [7]. The magnitude of CT can be estimated by the electronegativity of the elements [8]: TB adducts are formed if the electronegativity of halogens (χ_x) is larger than that of chalcogens (χ_z), while MCs are formed when χ_x is less than χ_z (general rule) [1c,d,9,10].

Dedicated to Prof. Naoki Inamoto on the occasion of his 72nd birthday.

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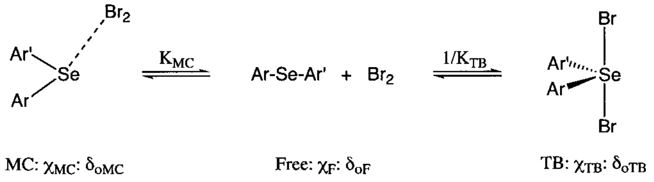


(1)

The MC structure has become popular in the literature in addition to the TB structure and/or ionic ones, since X-ray crystallographic studies have increased the number of examples with the MC structure in the solid state [11]. The structure of the iodine monochloride adduct of 1-selena-4-oxane is demonstrated to be $O(CH_2CH_2)_2Se–I–Cl$ (MC) in the solid [12]. However, we have encountered the formation of a mixture of $O(CH_2CH_2)_2Se–I–I$ (MC) and $O(CH_2CH_2)_2SeCl_2$ (TB), when $O(CH_2CH_2)_2Se–I–Cl$ (MC) is dissolved in $CDCl_3$ [7]. A similar trend is observed for the interhalogen adducts of some selenides [7]. These findings suggest that the stability of MCs and TB structures is comparable in some cases, which means that the stability of the Z–X–X bond in the MC must be comparable to that of the X–Z–X bond in the TB in such cases [7]. While the structure of selenide dibromides is expected to be TB based on the general rule, it can be MC in some cases since the difference of the electronegativity between Br and Se is small. TB structures of selenide dibromides [13a–c], as well as MC structures with iodine [10,13b–d], have been established to equilibrate with the components in solutions. Although TB structures must also equilibrate with MCs in some cases, as shown in Equation 1, the equilibrium has scarcely been mentioned. We looked for such diaryl selenides (ArSeAr′) that give MC with bromine by modulating the electronic and steric environment around the Se atom of the ArSeAr′ in question.

The criteria to distinguish MCs from TB structures for halogen adducts of aryl chalcogenides based on the NMR chemical shifts (δ) have been established as the experimental rule [9,10,14]. The criteria are also confirmed by molecular orbital (MO) calculations containing the magnetic shielding tensor based on the gauge-including atomic orbitals (GIAO) theory [15], which has recently been developed and applied to some nuclei that contain carbon, hydrogen, and selenium [16]. By applying the criteria, typical examples of the MC formation are found for some bromine adducts of ArSeAr′ ($ArSeBr_2Ar'$) in solutions [17,18].

We devised a method to visualize the equilibrium between MCs and TB structures for $ArSeBr_2Ar'$ based on typical MC formation in some $ArSeBr_2Ar'$ compounds in solutions [19]. In this article, we report the results of the investigations concerning the equilibrium between MCs and TB structures in $ArSeBr_2Ar'$, together with the evaluation of the equilibrium constants.

STRATEGY TO VISUALIZE THE EQUILIBRIUM

The chemical shifts of the ipso carbons of ArSeAr′ ($\delta(C_i)$) are employed to visualize the equilibrium between MC and TB formations, since they change dramatically with the structures of the adducts. The TB formation causes large downfield shifts for $\delta(C_i)$, whereas the upfield shifts are characteristic for $\delta(C_1)$ in the MC formation [10,14]. Therefore, the equilibrium can be clearly proved if such an ArSeAr′ is prepared that shows an upfield shift at one of the ipso carbons, whereas the other goes downfield when bromine is added to the ArSeAr′ solution. The $\delta(C_p)$ values will also be employed to estimate the equilibrium constants.

The equilibrium among MCs, TB structures, and the components is shown in Equation 1, exemplified by bromine. The equilibrium constant $K = [MC]/[TB]$ is given by K_{TB}/K_{MC} (Equation 2), where K_{TB} and K_{MC} are dissociation constants for TB and MC, respectively. The intrinsic chemical shifts of $ArSeX_2Ar'$ (MC), $ArSeX_2Ar'$ (TB), and free ArSeAr′ are shown by δ_{oMC}, δ_{oTB}, and δ_{oF}, respectively, and their intrinsic halogen-induced chemical shifts, $\Delta\delta_{oMC}$, $\Delta\delta_{oTB}$, and $\Delta\delta_{oF}$, are given by $\Delta\delta_{oA} = \delta_{oA} - \delta_{oF}$ where A = MC, TB, and F, respectively (Equation 3). Their molar fractions are shown by χ_{MC}, χ_{TB}, and χ_F, respectively. The observed chemical shifts (δ_{obsd}) for the equilibrium mixture is given by Equation 4. The observed halogen-induced chemical shifts ($\Delta\delta_{obsd}$) of the mixture is given by Equation 5, since $\Delta\delta_{oF} = 0$. The halogen-induced ipso carbon chemical shifts in the MC and TB formations are negative and positive, respectively ($\Delta\delta_{MC}(C_i) < 0$ and $\Delta\delta_{TB}(C_i) > 0$). Therefore, $\Delta\delta_{obsd}(C_i)$ is positive if (χ_{MC}/χ_{TB}) is less than $-(\Delta\delta_{TB}(C_i)/\Delta\delta_{MC}(C_i))$, and it is negative if (χ_{MC}/χ_{TB}) is larger than $-(\Delta\delta_{TB}(C_i)/\Delta\delta_{MC}(C_i))$, (Equations 6 and 7, respectively). The minus signs are given for $\Delta\delta_{MC}(C_i) < 0$.

$$K = [MC]/[TB] = ([MC]/[ArSeAr']\cdot[Br_2])/([TB]/[ArSeAr']\cdot[Br_2]) = \chi_{MC}/\chi_{TB} = K_{TB}/K_{MC} \quad (2)$$

$$\Delta\delta_{oA} = \delta_{oA} - \delta_{oF} \ (A = MC, TB, \text{and } F) \quad (3)$$

$$\delta_{obsd} = \delta_{oMC}\chi_{MC} + \delta_{oTB}\chi_{TB} + \delta_{oF}\chi_{F} \quad (4)$$

$$\Delta\delta_{obsd} = \Delta\delta_{oMC}\chi_{MC} + \Delta\delta_{oTB}\chi_{TB} \quad (5)$$

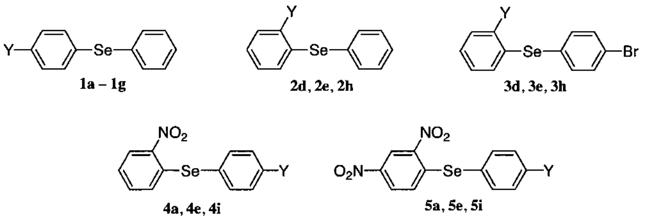
$$\Delta\delta_{obsd}(C_i) > 0, \text{ if } (\chi_{MC}/\chi_{TB}) < -(\Delta\delta_{oTB}(C_i)/\Delta\delta_{oMC}(C_i)) \quad (6)$$

$$\Delta\delta_{\mathrm{obsd}}(\mathrm{C}_i) < 0, \text{ if } (\chi_{\mathrm{MC}}/\chi_{\mathrm{TB}}) > -(\Delta\delta_{\mathrm{oTB}}(\mathrm{C}_i)/\Delta\delta_{\mathrm{oMC}}(\mathrm{C}_i)) \qquad (7)$$

An ArSeAr′ contains two ipso carbons, C_1 and C_i. Therefore, it is possible that $\delta(C_1)$ and $\delta(C_i)$ shifts upfield and downfield, respectively, with a common χ_{MC}/χ_{TB} for the two carbons, when bromine is added to the ArSeAr′ solution. In order to observe such phenomena, it is necessary to design the ArSeAr′, of which the bromine adduct has suitable $\Delta\delta_{oMC}(C_1)$, $\Delta\delta_{oMC}(C_i)$, $\Delta\delta_{oTB}(C_1)$, $\Delta\delta_{oTB}(C_i)$, and K values in solution. The existence of the equilibrium among MC, TB, and the components in the $ArSeBr_2Ar'$ will be clearly exhibited if signals of C_1 and C_i of the ArSeAr′ shift upfield and downfield, respectively, when it react with bromine.

RESULTS AND DISCUSSION

The Δδ values are examined for 4-YC_6H_4SePh (**1a–1g**), 2-YC_6H_4SePh (**2d, 2e, 2h**), 2-$YC_6H_4SeC_6H_4Br$-*p* (**3d, 3e, 3h**), 2-$O_2NC_6H_4SeC_6H_4Y$-*p* (**4a, 4e, 4i**), and 2,4-$(O_2N)_2C_6H_3SeC_6H_4Y$-*p* (**5a, 5e, 5i**), where Y = H (**a**), OMe (**b**), Me (**c**), Cl (**d**), Br (**e**), COOEt (**f**), NO_2 (**g**), I (**h**), and *t*-Bu (**i**). Aromatic carbons in **1–5** are numbered 1, 2, —, 6 for 2-YC_6H_4, 4-YC_6H_4, 2-$O_2NC_6H_4$, and 2,4-$(O_2N)_2C_6H_3$ groups and named *i, o, m, p* for Ph and *p*-YC_6H_4 groups. The equilibrium constants are calculated by a trial-and-error method by applying Equations 2–5.



		a	b	c	d	e	f	g	h	i
Y	=	H	OMe	Me	Cl	Br	COOEt	NO_2	I	t-Bu

Behavior of ipso and para Carbon Chemical Shifts in 4-YC_6H_4SePh

Table 1 shows chlorine- and iodine-induced Δδ(C) of 4-YC_6H_4SePh (**1a–1g**). Table 1 also contains Δδ(C) for $PhSeBr_2R$ (TB) and $\Delta\delta_o(C)$ for $PhSeI_2R$ (MC) [R = Me and Ph (**1a**)] [10]. The observed $\Delta\delta_{TB}(C_1)$ and $\Delta\delta_{TB}(C_i)$ values for $\mathbf{1}\cdot Cl_2$ can be $\Delta\delta_{oTB}(C_1)$ and $\Delta\delta_{oTB}(C_i)$, respectively, since the dissociation of $ArSeCl_2Ar'$ is negligible [13b,c]. The former decreases and the latter increases as Y becomes more electron withdrawing. However, $\Delta\delta_{oMC}(C_1)$ and $\Delta\delta_{oMC}(C_i)$ can not be directly determined from the observed values since $ArSeI_2Ar'$ is in equilibrium with the components [10,13b–d]. In the case of $\mathbf{1b}\cdot Cl_2$, $\Delta\delta_{oTB}(C_1)$ is larger than $\Delta\delta_{oTB}(C_i)$, whereas the former is much smaller than the latter for $\mathbf{1g}\cdot Cl_2$. On the contrary, $-\Delta\delta_{MC}(C_1)$ is smaller than $-\Delta\delta_{MC}(C_i)$ in $\mathbf{1b} + I_2$, while the former is much larger than the latter for $\mathbf{1g} + I_2$.

TABLE 1 Halogen-Induced ^{13}C NMR Chemical Shifts for 4-YC_6H_4SePh (**1**) and PhSeMe[a,b]

Compound	C_1	C_4	C_i	C_p	$\Delta\delta(C_1)/\Delta\delta(C_i)$	$\Delta\delta(C_4)/\Delta\delta(C_p)$
$\mathbf{1b}\cdot Cl_2$	11.69	2.39	9.85	5.23	1.19	0.46
$\mathbf{1c}\cdot Cl_2$	11.98	5.07	10.61	4.82	1.13	1.05
$\mathbf{1a}\cdot Cl_2$	11.37	4.47	11.37	4.47	1.00	1.00
$\mathbf{1d}\cdot Cl_2$	10.93	4.89	11.82	4.27	0.92	1.15
$\mathbf{1e}\cdot Cl_2$	10.89	5.34	12.02	4.21	0.91	1.27
$\mathbf{1f}\cdot Cl_2$	7.94	4.75	13.24	3.52	0.60	1.35
$\mathbf{1g}\cdot Cl_2$	5.71	2.99	14.57	2.94	0.39	1.02
$\mathbf{1b} + I_2$	−0.85	0.64	−1.36	1.36	0.63	0.47
$\mathbf{1c} + I_2$	−0.98	1.30	−1.26	1.28	0.78	1.02
$\mathbf{1a} + I_2$	−1.05	1.15	−1.05	1.15	1.00	1.00
$\mathbf{1d} + I_2$	−0.95	1.02	−0.87	0.91	1.09	1.12
$\mathbf{1e} + I_2$	−0.95	1.01	−0.78	0.81	1.22	1.25
$\mathbf{1f} + I_2$	−1.00	0.57	−0.40	0.41	2.50	1.39
$\mathbf{1g} + I_2$	−0.78	0.22	−0.19	0.20	4.11	1.10
$\mathbf{1a}\cdot Br_2$	7.92	4.33	7.92	4.33	1.00	1.00
$\mathbf{1a}\cdot I_2$[c]	−1.93	2.11	−1.93	2.11	1.00	1.00
$PhSeBr_2Me$	6.4	6.4	5.7	5.7	1.00	1.00
$PhSeI_2Me$[c]	−3.6	−3.6	3.4	3.4	1.00	1.00

[a] Halogen-induced chemical shifts (Δδ) are given from their parent selenides.
[b] [ArSeAr′] = 0.10 mol L^{-1} in $CDCl_3$.
[c] The intrinsic values ($\Delta\delta_o(C)$).

The ratios of $\Delta\delta_{oTB}(C_1)/\Delta\delta_{oTB}(C_i)$ and $\Delta\delta_{MC}(C_1)/\Delta\delta_{MC}(C_i)$ are examined in order to avoid the influence of the dissociation of $\mathbf{1}\cdot I_2$. The former decreases and the latter increases as Y becomes more electron withdrawing [20]: they show inverse trends depending on Y. The ratios $\Delta\delta_{oTB}(C_4)/\Delta\delta_{oTB}(C_p)$ and $\Delta\delta_{MC}(C_4)/\Delta\delta_{MC}(C_p)$ are similarly calculated. Both ratios are substantially the same for a common Y, although they change depending on Y.

The behavior in $\Delta\delta(C_1)$ and $\Delta\delta(C_i)$ is useful to set up suitable systems to visualize the equilibrium. And the results of $\Delta\delta(C_4)$ and $\Delta\delta(C_p)$ are also applied to set up the primitive rules which are necessary to evaluate the equilibrium constants for $ArSeBr_2Ar'$.

Halogen-Induced Chemical Shifts for ArSeAr′

Table 2 shows Δδ(C) of **2d, 2e**, and **2h**, together with $\delta_o(C)$ of the parent selenides. Table 2 also contains $\delta_o(C)$ and Δδ(C) for 2,6-dichlorophenyl phenyl selenide (**6**). Table 3 exhibits Δδ(C) for **3d, 3e**, and **3h**,

TABLE 2 Halogen-Induced ^{13}C NMR Chemical Shifts for 2-YC_6H_4SePh (**2**) and 2,6-$Cl_2C_6H_3SePh$ (**6**), and the Chemical Shifts of the Parent Selenides[a,b]

Compound	C_1	C_2	C_3	C_4	C_5	C_6	C_i	C_o	C_m	C_p
2d	133.4	133.7	129.3	128.7	127.2	130.6	127.8	135.9	129.6	127.2
	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0
2d·Cl_2	10.9	−1.1	1.8	4.0	1.0	−2.2	8.7	−2.5	0.1	5.0
2d + 1.1Br_2	4.5	−0.4	1.5	2.6	1.0	−0.8	3.7	−1.0	0.3	4.0
2d + 1.6Br_2	4.9	−0.4	1.7	3.3	1.2	−0.9	4.2	−1.1	0.4	4.4
2d + I_2	−0.6	−0.1	0.2	0.5	0.2	0.0	−0.6	−0.3	0.2	0.7
2e	136.3	123.4	132.6	128.8	127.7	130.4	128.4	136.1	129.7	127.2
	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0
2e·Cl_2	10.4	−1.6	1.9	3.9	1.3	−2.1	8.5	−2.5	0.1	5.0
2e + 1.2Br_2	3.6	−0.5	1.6	2.5	1.1	−0.5	3.6	−1.1	0.3	4.1
2e + 2.2Br_2	4.4	−0.5	1.8	3.1	1.3	−0.6	4.0	−1.2	0.3	4.4
2e + I_2	−0.7	−0.1	0.2	0.4	0.0	0.1	−0.5	−0.3	0.2	0.7
2e + 2I_2	−1.0	−0.1	0.2	0.5	0.3	0.1	−0.5	−0.4	0.2	0.8
2e + 3I_2	−1.1	−0.2	0.3	0.6	0.3	0.1	−0.7	−0.5	0.3	1.0
2h	140.5	99.0	139.3	128.6	128.7	130.1	129.8	135.7	129.8	127.3
	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0
2h·Cl_2	10.2	−3.7	1.8	3.7	1.1	−2.1	8.0	−2.1	0.0	4.8
2h + 1.2Br_2	3.5	−1.8	1.7	2.7	1.0	−0.5	3.6	−0.7	0.2	4.0
2h + 2.2Br_2	4.4	−2.0	1.8	3.0	1.1	−0.6	3.9	−0.8	0.2	4.5
2h + I_2	−0.6	0.1	0.3	0.3	0.5	0.4	−0.6	−0.2	0.2	0.7
2h + 2I_2	−1.4	0.0	0.3	0.3	0.7	0.3	−0.6	−0.5	0.2	1.0
6	130.4	141.7	128.3	130.5	128.3	141.7	131.2	130.8	129.1	126.8
	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0
6·Cl_2	11.2	−6.5	1.8	1.8	3.3	−6.6	8.3	2.3	−0.2	5.1
6 + Br_2	*c*	−0.5	0.2	0.4	0.2	−0.5	*c*	−0.1	0.2	0.7
6 + 8Br_2[d]	−1.3	−2.1	0.9	1.7	2.6	−2.1	−1.6	−1.0	0.8	2.4
6 + I_2	0.0	0.0	0.1	0.1	0.1	0.0	−0.1	−0.1	0.1	0.0

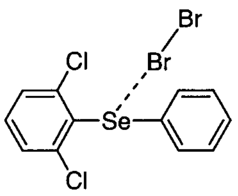
[a] Chemical shifts of selenides (δ) are given from TMS and the halogen-induced chemical shifts ($\Delta\delta$) are from their parent selenides.

[b] [ArSeAr′] = 0.10 mol L^{-1} in $CDCl_3$.

[c] Not observed due to broadening.

[d] At −30°C.

together with δ_o(C) of the parent selenides. Table 4 collects δ_o(C) of **4a, 4e**, and **4i** and their $\Delta\delta$(C) values and Table 5 shows δ_o(C) of **5a, 5e**, and **5i** and their $\Delta\delta$(C) values. The $\Delta\delta_{obsd}$(C) values for **6** + 8Br_2 measured at −30°C are regarded as $\Delta\delta_o$(C) for **6**·Br_2 (MC) [21]. The $\Delta\delta$(C) of chlorine and iodine adducts of **2–5** exhibit the characteristics of the TB and MC formation, respectively.



6•Br₂

The bromine-induced $\Delta\delta_o(C_1)$ and $\Delta\delta_o(C_i)$ values are both negative for **6** (Table 2), which must be the reflection of the exclusive contribution of MC in **6**·Br_2. Then the structures of related bromine adducts, **2** and **3**, are examined. The bromine-induced $\Delta\delta_{obsd}(C_1)$ and $\Delta\delta_{obsd}(C_i)$ are both positive for **2** and **3** (see Tables 2 and 3). Although the behavior in $\Delta\delta_{obsd}(C_1)$ and $\Delta\delta_{obsd}(C_i)$ for **2**·Br_2 and **3**·Br_2 would suggest that they are in equilibration among MC, TB, and the components, at first glance the values do not show the existence of the equilibrium so clearly.

The structures of bromine adducts of 2-nitrophenyl selenides **4** are examined next. The C_1 and C_i signals shift downfield and upfield, respectively, when bromine is added to the $CDCl_3$ solution of **4**. The magnitude of the shift values monotonically becomes larger as the amount of bromine is increased (Table 4). The behavior of the two ipso carbons must be the clear evidence for **4**·Br_2 to be in equilibrium among MC, TB, and the components. The $\Delta\delta(C_1)$ and $\Delta\delta(C_i)$ values are also measured for 2,4-di(nitro)phenyl selenides **5**. The values are both negative (Table 5). The successive change in $\Delta\delta(C_1)$ and $\Delta\delta(C_i)$ observed in **2–5** must suggest the reflection of the equilibrium.

TABLE 3 Halogen-Induced ^{13}C NMR Chemical Shifts for 2-$YC_6H_4SeC_6H_4Br$-*p* (**3**) and the Chemical Shifts of the Parent Selenides[a,b]

Compound	C_1	C_2	C_3	C_4	C_5	C_6	C_i	C_o	C_m	C_p
3d	133.3	133.9	129.5	127.3	127.7	131.0	127.0	137.1	132.8	123.3
	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0
3d · Cl_2	11.3	−1.4	1.7	5.5	0.8	−3.0	8.2	−2.1	0.0	4.2
3d + Br_2	2.9	−0.3	0.8	3.0	0.3	−0.7	2.7	−0.6	0.2	2.0
3d + $2Br_2$	3.8	−0.4	1.3	4.1	0.6	−1.1	2.9	−0.8	0.3	2.9
3d + $3Br_2$	4.3	−0.5	1.5	4.6	0.8	−1.2	3.1	−1.0	0.3	3.3
3d + I_2	−0.6	0.0	0.0	0.1	0.3	0.0	−0.4	−0.2	0.1	0.2
3e	135.5	123.8	132.8	127.7	127.9	130.8	127.8	137.3	132.9	123.4
	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0
3e · Cl_2	11.1	−2.1	1.7	5.2	1.2	−2.8	7.7	−2.2	0.0	4.1
3e + Br_2	2.9	−0.6	1.0	2.9	0.8	−0.7	1.8	−0.7	0.2	2.2
3e + $2Br_2$	3.9	−0.8	1.4	3.9	1.1	−0.9	2.5	−1.0	0.2	3.0
3e + $3Br_2$	4.2	−0.8	1.6	4.3	1.2	−1.0	2.9	−1.0	0.3	3.3
3e + I_2	−0.5	0.0	0.1	0.3	0.1	0.0	−0.5	−0.2	0.1	0.2
3h	139.7	99.9	139.5	127.7	128.7	130.5	129.2	136.9	132.9	123.3
	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0
3h · Cl_2	10.9	−4.4	1.8	4.8	1.2	−2.8	7.3	−1.8	0.0	4.1
3h + Br_2	2.8	−1.7	1.0	2.5	0.7	−0.6	1.6	−0.4	0.1	2.0
3h + $2Br_2$	3.7	−2.0	1.4	3.5	1.0	−0.8	2.4	−0.6	0.2	2.8
3h + $3Br_2$	4.0	−2.2	1.6	3.8	1.1	−0.9	2.7	−0.6	0.2	3.1
3h + I_2	−0.7	−0.1	0.2	0.5	0.2	0.1	−0.6	−0.2	0.1	0.4

[a] Chemical shifts of selenides (δ) are given from TMS, and the halogen-induced chemical shifts ($\Delta\delta$) are from their parent selenides.
[b] [ArSeAr′] = 0.10 mol L^{-1} in $CDCl_3$.

TABLE 4 Halogen-Induced ^{13}C NMR Chemical Shifts for 2-$O_2NC_6H_4SeC_6H_4Y$-*p* (**4**) and the Chemical Shifts of the Parent Selenides[a,b]

Compound	C_1	C_2	C_3	C_4	C_5	C_6	C_i	C_o	C_m	C_p
4a	135.8	145.4	125.4	125.6	133.5	130.1	128.0	137.3	130.0	129.8
	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0
4a · Cl_2	4.9	−0.7	0.2	6.6	1.6	0.1	9.5	−3.8	−0.3	2.5
4a + $0.5Br_2$	−0.3	−0.1	0.2	1.6	0.5	0.2	1.0	−0.7	0.7	0.5
4a + $1.1Br_2$	−0.4	−0.1	0.3	2.3	0.7	0.3	1.5	−0.9	0.0	0.9
4a + $2Br_2$	−0.5	−0.4	0.4	3.6	1.0	0.4	2.3	−1.4	0.1	1.4
4a + I_2	−0.7	0.1	0.1	0.4	0.1	−0.2	−0.2	−0.2	0.0	0.3
4e	135.1	145.6	126.1	126.0	133.8	130.0	126.9	138.9	133.3	124.8
	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0
4e · Cl_2	5.6	−1.3	0.1	6.3	1.4	−0.2	9.3	−3.9	−0.5	2.9
4e + Br_2	−0.3	−0.2	0.1	1.3	0.3	0.1	0.7	−0.7	0.0	0.6
4e + $2Br_2$	−0.5	−0.3	0.2	2.0	0.5	0.2	1.1	−0.9	0.0	0.9
4e + $3Br_2$	−0.6	−0.4	0.3	2.5	0.7	0.2	1.4	−1.1	0.0	1.2
4e + I_2	−0.2	0.0	0.0	0.1	0.0	0.0	−0.1	−0.1	0.0	0.0
4i	136.2	145.4	125.9	125.5	133.5	130.2	124.5	137.0	127.1	153.2
	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0
4i · Cl_2	4.5	−1.0	0.1	6.6	1.5	−0.1	9.1	−3.8	−0.2	3.1
4i + $0.5Br_2$	0.0	−0.2	0.2	1.6	0.5	0.1	1.2	−0.7	0.0	0.8
4i + Br_2	−0.1	−0.3	0.3	3.1	0.8	0.2	2.1	−1.1	0.1	1.4
4i + $2Br_2$	−0.2	−0.5	0.5	4.6	1.3	0.4	3.1	−1.6	0.1	2.2
4i + $3Br_2$	−0.3	−0.6	0.6	5.3	1.5	0.5	3.5	−1.9	0.1	2.6
4i · Br_2[c]	−0.5	−0.7	0.7	6.1	1.7	0.6	4.0	−2.2	0.1	2.9
4i + I_2	−0.8	0.0	0.0	0.4	0.1	0.0	−0.3	−0.2	0.1	0.2

[a] Chemical shifts of selenides (δ) are given from TMS, and the halogen-induced chemical shifts ($\Delta\delta$) are from their parent selenides.
[b] [ArSeAr′] = 0.10 mol L^{-1} in $CDCl_3$.
[c] Extrapolated value.

TABLE 5 Halogen-Induced ^{13}C NMR Chemical Shifts for 2,4-$(O_2N)_2C_6H_3SeC_6H_4Y$-*p* (**5**) and the Chemical Shifts of the Parent Selenides[a,b,c]

Compd	C_1	C_2	C_3	C_4	C_5	C_6	C_i	C_o	C_m	C_p
5a	145.5	145.3	121.3	144.9	126.6	131.2	126.9	137.1	130.5	130.7
	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0
5a · Cl_2	0.7	−1.0	0.0	4.0	2.5	−0.1	9.6	−3.7	−0.4	2.3
5a + Br_2	−0.4	0.1	0.0	0.0	0.1	0.0	−0.1	−0.1	0.1	0.0
5a + $2Br_2$	−0.7	0.2	0.0	0.0	0.2	0.0	−0.2	−0.1	0.1	0.1
5a + $3Br_2$	−1.0	0.3	0.0	0.0	0.2	0.0	−0.2	−0.2	0.1	0.2
5a + I_2	0.0	0.0	0.0	0.0	0.0	0.0	−0.1	0.0	0.0	0.0
5a + $2I_2$	−0.1	0.0	0.0	0.0	0.0	0.0	−0.1	0.0	0.1	0.0
5e	144.6	145.5	121.3	144.9	126.8	131.0	125.7	138.6	133.8	125.8
	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0
5e · Cl_2	1.2	−1.0	0.2	4.2	2.5	−0.3	9.3	−3.7	−0.5	2.7
5e + Br_2	−0.1	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0
5e + $2Br_2$	−0.2	0.1	0.0	0.0	0.0	0.0	−0.1	0.0	0.0	0.1
5e + $3Br_2$	−0.3	0.1	0.0	0.0	0.1	0.0	−0.1	0.0	0.1	0.1
5e + I_2	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0
5e + $2I_2$	−0.1	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0
5i	145.9	145.3	121.3	144.9	126.6	131.3	123.4	136.8	127.6	154.3
	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0
5i · Cl_2	0.5	−0.8	0.0	4.0	2.6	−0.2	9.1	−3.6	−0.3	2.8
5i + Br_2	−0.3	0.0	0.0	0.0	0.0	0.0	−0.1	−0.1	0.1	0.1
5i + $2Br_2$	−0.6	0.2	0.0	0.0	0.1	0.0	−0.1	−0.1	0.1	0.1
5i + $3Br_2$	−0.9	0.3	0.0	0.0	0.2	0.0	−0.2	−0.2	0.1	0.2
5i + I_2	−0.1	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0
5i + $2I_2$	−0.2	0.0	0.0	0.0	0.0	0.0	−0.1	0.0	0.1	0.0

[a] Chemical shifts of selenides (δ) are given from TMS, and the halogen-induced chemical shifts ($\Delta\delta$) are from their parent selenides.
[b] [ArSeAr′] = 0.10 mol L^{-1} in $CDCl_3$ if not specified.
[c] [**5** · Cl_2] are less than 0.1 mol L^{-1} in $CDCl_3$.

After establishment of the equilibrium among MC, TB, and the components for $ArSeBr_2Ar'$, the next extension of our investigation is to evaluate the equilibrium constants.

Evaluation of Equilibrium Constants

The equilibrium constants among MC, TB, and the components for $ArSeBr_2Ar'$ are evaluated. The $\Delta\delta_o(C)$ values for ipso and para carbons for $ArSeBr_2Ar'$ (MC), $ArSeBr_2Ar'$ (TB), and ArSeAr′ are roughly estimated based on the primitive rules. Then the molar fractions for $ArSeBr_2Ar'$ (MC), $ArSeBr_2Ar'$ (TB), and ArSeAr′, and the equilibrium constants *K* are calculated using the roughly estimated $\Delta\delta_o(C)$ values. The values are improved with a trial-and-error method until differences between predicted and observed chemical shifts are less than 0.1 ppm. Details of the calculations, together with the primitive rules, are shown in the Appendix.

TABLE 6 Calculated Bromine-Induced $\Delta\delta$ of ipso and para Carbons, Molar Fractions χ_{MC}, χ_{TB}, and χ_F and the Equilibrium Constants for **4a, 4e**, and **4i** under Given Conditions and the Intrinsic $\Delta\delta$ for **4i** · Br_2 (MC) and **4i** · Br_2 (TB)[a]

Compd	C_1	C_i	C_4	C_p	χ_{MC}	χ_{TB}	χ_F	*K ([MC]/[TB])*
4i + Br_2	−0.2	1.9	3.1	1.4	0.07	0.42	0.51	0.17
4i + $2Br_2$	−0.3	3.0	4.6	2.2	0.10	0.64	0.26	0.16
4i + $3Br_2$	−0.4	3.5	5.4	2.6	0.12	0.75	0.13	0.16
4i · Br_2[b]	−0.6	3.9	6.2	2.9	0.14	0.86	0.00	0.16
4a + $2Br_2$	−0.6	2.2	3.6	1.4	0.15	0.46	0.39	0.33
4e + $2Br_2$	−0.4	1.0	2.0	0.9	0.16	0.22	0.62	0.73
4i · Br_2 (MC)[c]	−8.0	−2.9	4.0	1.9	1.00	0.00	0.00	
4i · Br_2 (TB)[c]	0.8	5.1	6.6	3.1	0.00	1.00	0.00	

[a] [ArSeAr′] = 0.10 mol L^{-1} in $CDCl_3$.
[b] Calculated for the extrapolated shift values.
[c] Estimated chemical shifts for the intrinsic structures starting from the rules, see Appendix.

Calculated bromine-induced $\Delta\delta_{obsd}(C)$ of ipso and para carbons, molar fractions, χ_{MC}, χ_{TB}, and χ_F, and the equilibrium constants *K* for **4a, 4e**, and **4i** under various conditions are shown in Table 6. The $\Delta\delta_o(C)$ values for **4i** · Br_2 (MC) and **4i** · Br_2 (TB), which give the best-fitted results, are also shown in Table 6, for example. The calculated bromine-induced $\Delta\delta_{obsd}(C)$ are the same as those observed values within less than 0.1 ppm (see also Table 4). The *K* values for **4i** are actually constant against the different concentrations of bromine under the conditions, although the molar fractions are monotonically changed. The results show that the method is reliable. Table 7 collects the molar fractions and the equilibrium constants for **1–5** under the conditions of [ArSeAr′] = 0.10 mol/L^{-1} and [Br_2] = 0.20 mol/L^{-1} in $CDCl_3$.

The *K* value of **1a** is much less than 0.01 since χ_{MC} and χ_{F} are negligible: **1a**·Br_2 itself exists as TB in solution [22]. The *K* values for **2** and **3** are all about 0.20. Relatively large χ_{TB} in **2** and **3** may contribute to the *K* values. This consideration would be in accord with the positive $\Delta\delta_{\mathrm{obsd}}(\mathrm{C})$ values for both C_1 and C_i in **2** and **3**. The halogen atoms in an ortho position and/or a para position in **2** and **3** do not disturb so strongly the formation of TB. On the other hand, it is worthwhile to comment on the behavior of 2-nitrophenyl selenides **4**. Although χ_{MC} for **4a** is the same as the χ_{MC} values for **2e** and **2h** (0.15 for the three), the χ_{TB} for **4a** is much smaller than the χ_{TB} values for **2e** and **2h** (0.46 vs. 0.73–0.75). The electronic and steric effects of the nitro group are close to those of bromine or iodine in the formation of MC. However, their effects are very different for the TB formation. The electronic effect of *p*-Y in **4** is also of interest. The χ_{TB} and χ_{F} values increase and decrease, respectively, as the *p*-Y goes from *t*-Bu to H then Br. The χ_{MC} value is almost constant. (Although it may slightly increase as the *p*-Y goes from *t*-Bu to H then Br, it must be the reflection of much increase in χ_{F}.) As the result, *K* becomes larger if the electron-withdrawing ability of Y increases. In the case of 2,4-di(nitro)phenyl selenides **5**, χ_{TB} are negligible, which means that the structure of **5**·Br_2 is MC.

Indeed, **1a**·Br_2 itself exists as TB in solution, but the substitution at the ortho position with a halogen or a nitro group accelerates the dissociation to the components, which equilibrate with MC. The existence of the equilibrium among MC and TB, and the components, is clearly demonstrated for some $ArSeBr_2Ar'$ compounds. The equilibrium constants are also calculated. Both MCs and TB adducts become unstable when the effective electronegativity of the selenium atom and/or the bulkiness around the atom in a selenide are increased. The magnitude of the effects should be more severe for TB adducts than for MCs. TB adducts are negligible in 2,4-di(nitro)-phenyl derivatives.

TABLE 7 Evaluated Molar Fractions for MC, TB, and the Components for **1–5** under Given Conditions[a]

Compound	χ_{MC}	χ_{TB}	χ_F	*K*
1a	0.00	1.00	0.00	[b]
2e	0.15	0.75	0.10	0.20
2h	0.15	0.73	0.12	0.21
3d	0.13	0.64	0.23	0.20
3e	0.13	0.65	0.22	0.20
3h	0.13	0.63	0.24	0.21
4i	0.10	0.64	0.26	0.16
4a	0.15	0.46	0.39	0.33
4e	0.16	0.22	0.62	0.73
5i	0.10	0.00	0.90	[c]
5a	0.10	0.00	0.90	[c]
5e	0.04	0.00	0.96	[c]

[a] [ArSeAr′] = 0.10 mol L^{-1} and [Br_2] = 0.20 mol L^{-1} in $CDCl_3$.
[b] Very small.
[c] Very large.

EXPERIMENTAL

General

^{1}H (90 MHz) and ^{13}C (22.4 MHz) NMR spectra were recorded on a JEOL EX-90 spectrometer, and/or ^{1}H (300 MHz) and ^{13}C (75 MHz) NMR spectra were recorded on a JEOL JNM-AL 300 spectrometer. The ^{1}H and ^{13}C chemical shifts are given in ppm relative to those of internal $CHCl_3$ slightly contaminated in the $CDCl_3$ solution and $CDCl_3$ as the solvent, respectively. ^{13}C NMR spectra in the Tables were measured under the conditions at [ArSeAr′] = 0.10 mol/L^{-1} with or without bromine or iodine in the given ratios. Those for [$ArSeCl_2Ar'$] were also at 0.10 mol/L^{-1} except for some chlorine adducts such as **5**·Cl_2, of which spectra were measured at the saturated concentrations. Chemicals were used without further purification unless otherwise noted. Solvents were purified by standard methods. Melting points were measured with a Yanako-MP apparatus and were uncorrected. Column chromatography was performed on silica gel (Fuji Silysia BW-300), acidic alumina and basic alumina (E. Merk).

Synthesis

Diphenyl diselenide [23] and bis(*p*-bromophenyl) diselenide [23] were prepared according to the method in the literature or the improved method.

Bis[*p*-(*t*-butyl)phenyl] diselenide was prepared similarly to diphenyl diselenide. m.p. 79–81°C. ^{13}C NMR($CDCl_3$)δ 31.24, 34.52, 126.14, 127.62, 131.49, 150.92. Anal. Calc. for $C_{20}H_{26}Se_2$: C, 56.61; H, 6.18. Found: C, 56.72; H, 6.23%.

The diselenides were reduced by $NaBH_4$ in aqueous THF, and the resulting selenate anions were allowed to react with benzene diazonium chloride or the 2-halo, 4-nitro, or 2,4-di(nitro) derivatives at low temperature. After usual work-up, the crude products were chromatographed on silica gel containing acidic and basic alumina. Then **2–5** were obtained [24]. Selenide dichlorides were prepared by the reaction of the selenides with chlorine or sulfuryl chloride in an inert solvent, such as carbon tetrachloride, hexane, or ether. NMR spectra of bromine and iodine adducts were measured for the mixtures of the selenides with the halogens of the given ratios.

The physical properties, ^{1}H NMR data, and the results of elementary analyses of **2–5** and their chlorine adducts are as follows. Their ^{13}C NMR data are shown in Tables 2–5.

2d: m.p. 35.5–36.5°C. ^{1}H NMR (CDCl$_3$) δ 6.91 (dd, J = 1.7 and 7.8 Hz, 1H), 7.02 (dt, J = 1.5 and 7.5 Hz, 1H), 7.11 (dt, J = 1.7 and 7.6 Hz, 1H), 7.34 (dd, J = 1.5 and 7.7 Hz, 1H), 7.35–7.43 (m, 3H), 7.59–7.65 (m, 2H). Anal. Calc. for $C_{12}H_9ClSe$: C, 53.86; H, 3.39. Found: C, 54.07; H, 3.39%.

2d$\cdot$Cl$_2$: m.p. 109–110°C. ^{1}H NMR (CDCl$_3$) δ 7.39 (dt, J = 1.5 and 7.6 Hz, 1H), 7.51 (dt, J = 1.5 and 7.6 Hz, 1H), 7.56 (dd, J = 1.5 and 8.1 Hz, 1H), 7.60 (dd, J = 1.5 and 8.1 Hz, 1H), 7.63–7.68 (m, 3H), 8.36–10.44 (m, 2H). Anal. Calc. for $C_{12}H_9Cl_3Se$: C, 42.58; H, 2.68. Found: C, 42.88; H, 2.53%.

2e: m.p. 48–49°C. ^{1}H NMR (CDCl$_3$) δ 7.11 (t, J = 7.8 Hz, 1H), 7.23 (dd, J = 1.3 and 7.6 Hz, 1H), 7.26 (t, J = 7.8 Hz, 1H), 7.36–7.44 (m, 3H), 7.60–7.67 (m, 2H), 7.77 (dd, J = 0.9 and 8.1 Hz, 1H). Anal. Calc. for $C_{12}H_9BrSe$: C, 46.19; H, 2.91. Found: C, 46.22; H, 2.88%.

2e$\cdot$Cl$_2$: m.p. 129–130°C. ^{1}H NMR (CDCl$_3$) δ 7.45–7.54 (m, 2H), 7.54–7.66 (m, 3H), 7.97 (t, J = 8.2 Hz, 1H), 8.05 (d, J = 7.7 Hz, 1H), 8.25–8.33 (m, 2H). Anal. Calc. for $C_{12}H_9BrCl_2Se$: C, 37.64; H, 2.37. Found: C, 37.32; H, 2.34%.

2h: m.p. 73–74°C. ^{1}H NMR (CDCl$_3$) δ 6.82–6.87 (m, 2H), 7.12 (dt, J = 1.4 and 7.5 Hz, 1H), 7.28–7.43 (m, 3H), 7.61–7.64 (m, 2H), 7.76 (dd, J = 1.4 and 8.1 Hz, 1H). Anal. Calc. for $C_{12}H_9ISe$: C, 40.14; H, 2.53. Found: C, 40.24; H, 2.63%.

2h$\cdot$Cl$_2$: m.p. 155–157 °C. ^{1}H NMR (CDCl$_3$) δ 7.23 (t, J = 7.9 Hz, 1H), 7.47 (t, J = 7.7 Hz, 1H), 7.55 (d, J = 8.1 Hz, 1H), 7.62–7.70 (m, 3H), 7.99 (d, J = 7.9 Hz, 1H), 8.40–8.48 (m, 2H). Anal. Calc. for $C_{12}H_9Cl_2ISe$: C, 33.52; H, 2.11. Found: C, 33.63; H, 2.22%.

3d: m.p. 39–40°C. ^{1}H NMR (CDCl$_3$) δ 6.89 (dd, J = 1.7 and 7.9 Hz, 1H), 6.99 (dt, J = 1.5 and 7.5 Hz, 1H), 7.08 (dt, J = 1.5 and 7.5 Hz, 1H), 7.29 (dd, J = 1.3 and 7.9 Hz, 1H), 7.40 (d, J = 8.5 Hz, 2H), 7.41 (d, J = 8.4 Hz, 2H). Anal. Calc. for $C_{12}H_8BrClSe$: C, 41.60; H, 2.33. Found: C, 41.64; H, 2.49%.

3d$\cdot$Cl$_2$: m.p. 102–104°C. ^{1}H NMR (CDCl$_3$) δ 7.39 (t, J = 7.6 Hz, 1H), 7.46–7.56 (m, 2H), 7.61 (d, J = 7.9 Hz, 1H), 7.77 (d, J = 8.8 Hz, 2H), 8.28 (d, J = 8.8 Hz, 2H). Anal. Calc. for $C_{12}H_8BrCl_3Se$: C, 34.53; H, 1.93. Found: C, 34.44; H, 1.85%.

3e: m.p. 62°C. ^{1}H NMR (CDCl$_3$) δ 6.90 (dd, J = 2.1 and 7.3 Hz, 1H), 7.05 (dt, J = 1.8 and 7.4 Hz, 1H), 7.10 (dt, J = 1.8 and 7.4 Hz, 1H), 7.49 (d, J = 8.9 Hz, 2H), 7.50 (d, J = 8.9 Hz, 2H), 7.52 (dd, J = 2.1 and 7.3 Hz, 1H). Anal. Calc. for $C_{12}H_8Br_2Se$: C, 36.87; H, 2.06. Found: C, 37.11; H, 2.13%.

3e$\cdot$Cl$_2$: m.p. 158–160°C. ^{1}H NMR (CDCl$_3$) δ 7.41–7.51 (m, 3H), 7.75–7.82 (m, 3H), 8.31 (d, J = 9.0 Hz, 2H). Anal. Calc. for $C_{12}H_8Br_2Cl_2Se$: C, 31.21; H, 1.75. Found: C, 31.27; H, 1.81%.

3h: m.p. 101–102°C. ^{1}H NMR (CDCl$_3$) δ 6.89 (dt, J = 1.3 and 7.5 Hz, 1H), 6.92 (dd, J = 1.5 and 7.9 Hz, 1H), 7.15 (dt, J = 1.2 and 7.6 Hz, 1H), 7.47 (d, J = 8.5 Hz, 2H), 7.49 (d, J = 8.5 Hz, 2H), 7.78 (dd, J = 1.4 and 7.8 Hz, 1H). Anal. Calc. for $C_{12}H_8BrISe$: C, 32.91; H, 1.84. Found: C, 32.90; H, 1.70%.

3h$\cdot$Cl$_2$: m.p. 142–143°C. ^{1}H NMR (CDCl$_3$) δ 7.26 (t, J = 8.3 Hz, 1H), 7.47 (t, J = 8.3 Hz, 1H), 7.48 (d, J = 7.5 Hz, 1H), 7.77 (d, J = 8.8 Hz, 2H), 7.99 (d, J = 7.5 Hz, 1H), 8.33 (d, J = 8.8 Hz, 2H). Anal. Calc. for $C_{12}H_8BrCl_2ISe$: C, 28.32; H, 1.59. Found: C, 28.55; H, 1.48%.

4a: m.p. 88.5–89.0°C. ^{1}H NMR (CDCl$_3$) δ 6.99 (dd, J = 2.0 and 7.4 Hz, 1H), 7.26 (dt, J = 2.0 and 7.0 Hz, 1H), 7.30 (dt, J = 2.0 and 7.0 Hz, 1H), 7.43–7.54 (m, 3H), 7.68–7.73 (m, 2H), 8.31 (dd, J = 1.8 and 7.2 Hz, 1H). Anal. Calc. for $C_{12}H_9NO_2Se$: C, 51.82; H, 3.26; N, 5.04. Found: C, 51.68; H, 3.29; N, 5.07%.

4a$\cdot$Cl$_2$: m.p. 156–157°C. ^{1}H NMR (CDCl$_3$) δ 7.60–7.68 (m, 3H), 7.73–7.79 (m, 3H), 8.28–8.38 (m, 3H). Anal. Calc. for $C_{12}H_9Cl_2NO_2Se$: C, 41.29; H, 2.60; N, 4.01. Found: C, 41.32; H, 2.58; N, 4.12%.

4e: m.p. 105–106°C. ^{1}H NMR (CDCl$_3$) δ 6.97 (dd, J = 1.8 and 7.5 Hz, 1H), 7.29 (dt, J = 1.7 and 7.3 Hz, 1H), 7.34 (dt, J = 1.7 and 7.3 Hz, 1H), 7.57 (d, J = 8.8 Hz, 2H), 7.58 (d, J = 8.8 Hz, 2H), 8.33 (dd, J = 1.8 and 7.9 Hz, 1H). Anal. Calc. for $C_{12}H_8BrNO_2Se$: C, 40.37; H, 2.26; N, 3.92. Found: C, 40.57; H, 2.34; N, 3.96%.

4e$\cdot$Cl$_2$: m.p. 161–162°C. ^{1}H NMR (CDCl$_3$) δ 7.54 (br.s, 4H), 8.17 (br.s, 1H), 8.40 (br.s, 1H), 8.54 (br.s, 1H), 8.64 (br.s, 1H). Anal. Calc. for $C_{12}H_8BrCl_2NO_2Se$: C, 33.68; H, 1.88; N, 3.27. Found: C, 33.61; H, 1.79; N, 3.17%.

4i: m.p. 75–76°C. ^{1}H NMR (CDCl$_3$) δ 1.37 (s, 9H), 7.03 (dd, J = 1.7 and 7.8 Hz, 1H), 7.26 (dt, J = 1.5 and 7.8 Hz, 1H), 7.32 (dt, J = 1.7 and 7.2 Hz, 1H), 7.47 (d, J = 8.1 Hz, 2H), 7.61 (d, J = 8.1 Hz, 2H), 8.31 (dd, J = 1.7 and 7.9 Hz, 1H). Anal. Calc. for $C_{16}H_{17}NO_2Se$: C, 57.49; H, 5.13; N, 4.19. Found: C, 57.57; H, 5.20; N, 4.15%.

4i$\cdot$Cl$_2$: m.p. 136–137°C. ^{1}H NMR (CDCl$_3$) δ 1.40 (s, 9H), 7.63 (d, J = 8.6 Hz, 2H), 7.76–7.84 (m, 3H), 8.21 (d, J = 8.8 Hz, 2H), 8.34–8.38 (m, 1H). Anal.

Calc. for $C_{16}H_{17}Cl_2NO_2Se$: C, 47.43; H, 4.23; N, 3.46. Found: C, 47.22; H, 4.18; N, 3.44%.

5a: m.p. 130–131°C. ^1H NMR ($CDCl_3$) δ 7.17 (d, J = 8.8 Hz, 1H), 7.50–7.65 (m, 3H), 7.65–7.75 (m, 2H), 8.09 (dd, J = 2.6 and 8.8 Hz, 1H), 9.15 (d, J = 2.6 Hz, 1H). Anal. Calc. for $C_{12}H_8N_2O_4Se$: C, 44.60; H, 2.50; N, 8.67. Found: C, 44.88; H, 2.63; N, 8.77%.

5a$\cdot Cl_2$: m.p. 114–115°C (dec.). ^1H NMR ($CDCl_3$) δ 7.65–7.73 (m, 3H), 8.00 (d, J = 8.6 Hz, 1H), 8.32 (dd, J = 1.7 and 7.3 Hz, 2H), 8.53 (dd, J = 2.2 and 8.6 Hz, 1H), 9.12 (d, J = 2.0, 1H). Anal. Calc. for $C_{12}H_8Cl_2N_2O_4Se \cdot 0.5H_2O$: C, 35.73; H, 2.23; N, 6.95. Found: C, 35.74; H, 2.06; N, 6.82%.

5e: m.p. 143–144°C. ^1H NMR ($CDCl_3$) δ 7.17 (d, J = 9.0 Hz, 1H), 7.57 (d, J = 8.3 Hz, 2H), 7.66 (d, J = 8.1 Hz, 2H), 8.13 (dd, J = 2.6 and 9.0 Hz, 1H), 9.16 (d, J = 2.6 Hz, 1H). Anal. Calc. for $C_{12}H_7BrN_2O_4Se$: C, 35.85; H, 1.76; N, 6.97. Found: C, 35.90; H, 1.82; N, 7.03%.

5e$\cdot Cl_2$: m.p. 123–124°C (dec.). ^1H NMR ($CDCl_3$) δ 7.81 (d, J = 8.8 Hz, 2H), 7.90 (d, J = 8.6 Hz, 1H), 8.22 (d, J = 8.8 Hz, 2H), 8.54 (dd, J = 2.1 and 8.9 Hz, 1H), 9.13 (d, J = 2.2 Hz, 1H). Anal. Calc. for $C_{12}H_7BrCl_2N_2O_4Se$: C, 30.47; H, 1.49; N, 5.92. Found: C, 30.41; H, 1.36; N, 5.88%.

5i: m.p. 147–148°C. ^1H NMR ($CDCl_3$) δ 1.39 (s, 9H), 7.22 (d, J = 9.0 Hz, 1H), 7.53 (d, J = 8.2 Hz, 2H), 7.61 (d, J = 8.2 Hz, 2H), 8.11 (dd, J = 2.4 and 9.0 Hz, 1H), 9.15 (d, J = 2.4 Hz, 1H). Anal. Calc. for $C_{16}H_{16}N_2O_4Se$: C, 50.67; H, 4.25; N, 7.39. Found: C, 50.98; H, 4.28; N, 7.34%.

5i$\cdot Cl_2$: m.p. 136–137°C (dec.). ^1H NMR ($CDCl_3$) δ 1.42 (s, 9H), 7.68 (d, J = 8.6 Hz, 2H), 7.99 (d, J = 8.6 Hz, 1H), 8.22 (d, J = 8.6 Hz, 2H), 8.55 (dd, J = 2.2 and 8.6 Hz, 1H), 9.13 (d, J = 2.1 Hz, 1H). Anal. Calc. for $C_{16}H_{16}Cl_2N_2O_4Se$: C, 42.69; H, 3.58; N, 6.22. Found: C, 42.58; H, 3.51; N, 6.17%.

APPENDIX

Characters in $\Delta\delta_{obsd}(C)$ of $ArSeX_2Ar'$

The calculations of the equilibrium constants require $\Delta\delta_o(C)$ for $ArSeBr_2Ar'$ (MC) and $ArSeBr_2Ar'$ (TB). The values are estimated based on the extrapolated values for **1a**$\cdot I_2$ (MC) [10], $PhSeI_2Me$ (MC) [10], and **6**$\cdot Br_2$ (MC) [21], which are shown in Tables 1 and 2. Examination of those values, together with other characters in $ArSeX_2Ar'$ (X = Cl, Br, and I), leads to primitive rules to evaluate $\Delta\delta_o(C)$ for $ArSeBr_2Ar'$ (MC) and $ArSeBr_2Ar'$ (TB).

The characters in $\delta_{obsd}(C)$ for $ArSeX_2Ar'$ (X = null, Cl, Br, and I) are as follows [The C_i and C_p stand for (C_1 and C_i) and (C_4 and C_p), respectively.]. (1) The $\delta(C_i)$ value of **1a**$\cdot Br_2$ is observed at 3.45 ppm upfield from that of **1a**$\cdot Cl_2$: The differences between $ArSeBr_2Ar'$ and $ArSeCl_2Ar'$ are usually ca. 4 ppm, if the dissociation of $ArSeBr_2Ar'$ to the components is negligible. (2) The $-\Delta\delta(C_i)$ values for **1**$\cdot I_2$ become larger as $\Delta\delta(C_i)$ for **1**$\cdot Cl_2$ become smaller. (3) The $\delta(C_i)$ values of $2,6\text{-}Cl_2C_6H_3$ and phenyl groups in **6**$\cdot Br_2$ (MC) are 12.5 and 9.9 ppm upfield of those of **6**$\cdot Cl_2$ (TB), respectively. (4) The $\delta(C_p)$ value of **1a**$\cdot Br_2$ is very close to that of **1a**$\cdot Cl_2$: The values of $ArSeBr_2Ar'$ (TB) are also very close to those of $ArSeCl_2Ar'$ (TB). (5) The $\Delta\delta(C_p)$ values for **1a**$\cdot I_2$ (MC) are proportional to those for **1a**$\cdot Cl_2$ (TB). (6) The $\Delta\delta_o(C_p)$ of **6**$\cdot Br_2$ (MC) are 0.59 times larger than those of **6**$\cdot Cl_2$ (TB) in the average.

Primitive Rules

Primitive rules to estimate the chemical shifts for $ArSeBr_2Ar'$ (MC) and $ArSeBr_2Ar'$ (TB) are proposed based on the previous results. (1) Dissociation of $ArSeCl_2Ar'$ (TB) to the components is negligible. (2) The $\Delta\delta_o(C_i)$ value for $ArSeBr_2Ar'$ (TB) is smaller than that of the corresponding $ArSeCl_2Ar'$ (TB) by 4.0 ppm if $\Delta\delta_o(C_i)$ for $ArSeCl_2Ar'$ (TB) is larger than 5 ppm. Equation A1 is applied, if $\Delta\delta_o(C_i)$ for $ArSeCl_2Ar'$ (TB) is less than 5 ppm. (3) The $\Delta\delta_o(C_i)$ value for $ArSeBr_2Ar'$ (MC) is smaller than that of $ArSeBr_2Ar'$ (TB) by 8.0 ppm. (4) The $\Delta\delta_o(C_p)$ value for $ArSeBr_2Ar'$ (TB) is the same as those of $ArSeCl_2Ar'$ (TB). (5) The $\Delta\delta_o(C_p)$ value for $ArSeBr_2Ar'$ (MC) is 0.60 times that for $ArSeBr_2Ar'$ (TB). The primitive rules are summarized in Scheme A1.

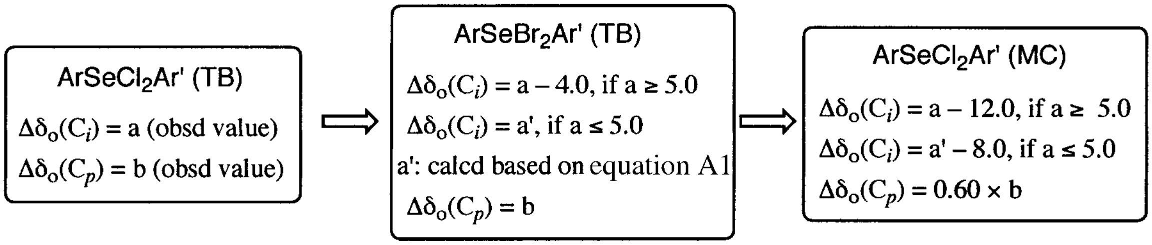
$$\Delta\delta_o(C_i) \text{ for } ArSeBr_2Ar' \text{ (TB)} = 0.04 \times (\Delta\delta_o(C_i) \text{ for } ArSeCl_2Ar')^2 \quad \text{(A1)}$$

Calculation of Equilibrium Constants

(1) The starting $^1\Delta\delta_o(C_i)$ and $^1\Delta\delta_o(C_p)$ for $ArSeBr_2Ar'$ (MC) and $ArSeBr_2Ar'$ (TB) are obtained by applying the primitive rules. (2) ^1K, the first obtained K values shown in Equation 2, are calculated based on Equations A2 and A3. (3) The first obtained molar fractions, $^1\chi_{MC}$, $^1\chi_{TB}$, and $^1\chi_F$, together with the expected chemical shifts, are calculated using the $^1\Delta\delta_o(C)$ and ^1K values. (4) The $^1\Delta\delta_o(C_i)$ and $^1\Delta\delta_o(C_p)$ values are improved with a trial-and-error method until differences between predicted and observed chemical shifts are less than 0.1 ppm for several different concentrations of bromine.

$$(^1\Delta\delta_{oMC}(C_1) + {}^1\Delta\delta_{oTB}(C_1)/{}^1K)/(^1\Delta\delta_{oMC}(C_4) + {}^1\Delta\delta_{oTB}(C_4)/{}^1K) = \Delta\delta_{obsd}(C_1)/\Delta\delta_{obsd}(C_4) \quad \text{(A2)}$$

$$(^1\Delta\delta_{oMC}(C_i) + {}^1\Delta\delta_{oTB}(C_i)/{}^1K)/(^1\Delta\delta_{oMC}(C_p) + {}^1\Delta\delta_{oTB}(C_p)/{}^1K) = \Delta\delta_{obsd}(C_i)/\Delta\delta_{obsd}(C_p) \quad \text{(A3)}$$



SCHEME A1

The final $\Delta\delta_o$(C) values for **4i**$\cdot Br_2$ (MC) and **4i**$\cdot Br_2$ (TB) are shown in Table 6. Their $^1\Delta\delta_o(C_1)$ values (−7.2 and 0.8 ppm, respectively) are improved to be −8.0 and 0.7 ppm, respectively, for example.

The · in **n**$\cdot X_2$ is used for the adducts (1) of which dissociation to the components is negligible (e.g., X = Cl), (2) of which NMR data are extrapolated ($PhSeI_2R$ being the same meaning), and (3) where the dissociation is substantially negligible with very high concentration of X_2 (in the case of **6** + $8Br_2$). The + in **n** + mX_2 shows that a selenide **n** is dissolved in a solution which contains *m* times mol of X_2.

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TB formation, whereas the values are small in the formation of MC. (4) A large downfield shift of the ortho protons in the TB formation are also useful.

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[21] As shown in Table 2, two sets of carbon signals, ($\delta(C_2)$ and $\delta(C_3)$) and ($\delta(C_6)$ and $\delta(C_5)$), are observed for the 2,6-$Cl_2C_6H_3$ group in **6**·Cl_2 (TB), which shows that the steric conditions around the Se atom in **6**·Cl_2 (TB) are very severe for the Se–C_{Ar} bond rotation. The chemical shifts of **6** are little affected by the addition of iodine, exhibiting the difficult approach of iodine to the Se atom of **6**. Therefore, it must be difficult for bromine to construct the TB with the selenium atom of **6**. The TB could be negligible in **6**·Br_2.

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