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Molecular Complex Formation of Diphenyl Selenides with Bromine. Electronic and Steric Requirements

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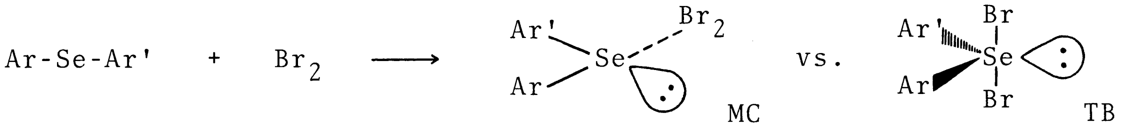
The structure of *o*-, *m*-, and *p*-substituted diphenyl selenide dibromides ($ArSeBr_2Ar'$) is described. The adducts were MC's for Ar = Ar' = $2\text{-}ClC_6H_4$, 3- and $4\text{-}NCC_6H_4$, 3- and $4\text{-}O_2NC_6H_4$, $3,5\text{-}Cl_2C_6H_3$, and $2,4,6\text{-}Me_3C_6H_2$, while they were TB's for Ar = Ar' = $2\text{-}MeC_6H_4$ and $4\text{-}EtOCOC_6H_4$ and (Ar, Ar') = ($3,5\text{-}(O_2N)_2C_6H_3$, Ph). The electronic and steric requirements were discussed based on the CV data of the parent selenides.

The formation and the stability of hypervalent bonds, contained in trigonal bipyramidal adducts (TB's), have been the subject of interest.[1,2) It seemed necessary, however, to study the hypervalent bonds from different viewpoints for the better description. We have directly investigated the destabilizing factors of TB's with the bonds, taking diphenyl selenide dibromide (**1** (Y = H)$\cdot Br_2$) as a model compound, resulting in the formation of molecular complexes (MC's), contrary to the general rule.[2a,3a)



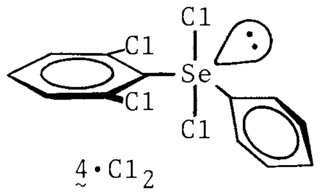
1: Ar=Y-C_6H_4; Ar'=Ph, **2**: Ar=Ar'=Y-C_6H_4, **3**: Ar=$3,5\text{-}(O_2N)_2C_6H_3$; Ar'=Ph,
4: Ar=$2,6\text{-}Cl_2C_6H_3$; Ar'=Ph, **5**: Ar=Ar'=$3,5\text{-}Cl_2C_6H_3$, **6**: Ar=Ar'=$2,4,6\text{-}Me_3C_6H_2$.

Although the TB structure of diphenyl selenide dibromide has been well established,[2) TB's will be destabilized if the effective electronegativity of the selenium atom in a given compound or the bulkiness around the atom is increased. Our recent findings suggested the possibility to obtain MC's of diphenyl selenides with bromine.[3b) The investigation was, therefore, focused to look for MC's of substituted diphenyl selenides with bromine and to elucidate the electronic and steric requirements for the MC formation.

Table 1. ^{1}H and ^{13}C NMR Chemical Shifts of Some o-, m-, and p-Substituted Diphenyl Selenides and the Halogen Adducts$^{a)}$

Compound	H(2,6)	C(1)	C(2)	C(3)	C(4)	C(5)	C(6)	TB/MC
2 (Y = 4-COOEt)	7.49	136.6	132.4	130.3	129.6			
	0.00	0.0	0.0	0.0	0.0			
2 (4-COOEt)·Cl_2	0.61	10.1	-1.2	0.3	3.9			TB
2 (4-COOEt)·Br_2	0.62	6.1	-0.1	0.5	3.6			TB
2 (4-COOEt)·I_2	0.02	-0.5	-0.1	0.1	0.5			MC
2 (Y = 4-CN)	7.56	136.5	133.1	132.8	111.6			
	0.00	0.0	0.0	0.0	0.0			
2 (4-CN)·Cl_2	0.61	10.6	-1.1	0.4	4.5			TB
2 (4-CN)·Br_2	0.00	-0.1	0.0	0.0	0.2			MC
2 (4-CN)·I_2	0.01	-0.1	0.0	0.0	0.1			MC
2 (Y = 3-NO_2)	8.34	131.6	127.6	148.6	123.0	130.3	138.8	
	0.00	0.0	0.0	0.0	0.0	0.0	0.0	
2 (3-NO_2)·Cl_2	0.57	12.5	-1.2	-0.2	3.9	0.6	-2.4	TB
2 (3-NO_2)·Br_2	0.00	0.0	0.1	0.1	0.1	0.1	-0.1	MC
2 (3-NO_2)·I_2	0.00	-0.1	0.0	0.0	0.1	0.1	-0.1	MC
3$^{b)}$	8.36	138.8	135.9	148.5	116.1			
	0.00	0.0	0.0	0.0	0.0			
3·$Cl_2$$^{b)}$	0.82	8.3	-4.8	0.2	5.3			TB
3·$Br_2$$^{b,c)}$	0.88	5.0	-3.7	-0.5	5.3			TB
3·$I_2$$^{b)}$	0.00	0.0	-0.1	0.1	0.1			MC
2 (Y = 2-Me)	7.3	131.2	139.7	130.1	127.4	126.6	133.0	
	0.0	0.0	0.0	0.0	0.0	0.0	0.0	
2 (2-Me)·Cl_2	0.6	11.1	-1.8	1.0	5.0	0.6	-1.5	TB
2 (2-Me)·$Br_2$$^{c)}$	0.6	3.5	-1.6	1.7	4.9	1.1	-1.2	TB
2 (2-Me)·I_2	0.0	-1.0	-0.2	0.4	0.8	0.4	0.0	MC
2 (Y = 2-Cl)	7.4	130.3	136.3	129.7	129.0	127.5	134.1	
	0.0	0.0	0.0	0.0	0.0	0.0	0.0	
2 (2-Cl)·Cl_2	0.6	11.8	-2.8	1.8	3.7	0.5	-2.3	TB
2 (2-Cl)·Br_2	0.0	-0.9	-0.1	0.4	1.1	0.4	-0.2	MC
2 (2-Cl)·I_2	0.0	-0.3	0.0	0.1	0.2	0.0	0.0	MC
4$^{b)}$	7.4$^{d)}$	130.4	141.7	128.3	130.5			
	0.0	0.0	0.0	0.0	0.0			
4·$Cl_2$$^{b,e)}$	1.2$^{d)}$	9.1	-6.5	1.8	1.8			TB
			-6.6	3.3				
4·$Br_2$$^{b,c)}$	0.0$^{d)}$	-0.6	-1.4	0.6	1.2			MC
4·$I_2$$^{b)}$	0.0$^{d)}$	0.0	0.0	0.0	0.0			MC
6	2.24$^{f)}$	129.3	141.2	128.8	136.8			
	0.00	0.0	0.0	0.0	0.0			
6·Cl_2	0.45$^{f)}$	10.3	-0.1	2.4	4.9			TB
6·$Br_2$$^{c,g)}$	0.01$^{f)}$	-0.5	-0.1	0.1	0.4			
		0.7	-0.2	0.2	0.7			MC
6·I_2	0.00$^{f)}$	0.0	0.1	0.1	0.2			MC

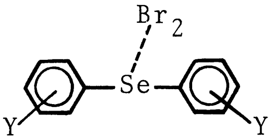
a) Chemical shifts (ppm) are given from TMS for selenides and from the parent selenides for the halogen adducts. b) Chemical shifts of the phenyl group are not given. c) At -30 °C. d) The value of o-protons of the phenyl group. e) Suggesting the TB structure with the dichlorophenyl plane locked perpendicular to the hypervalent Cl-Se-Cl bond. f) The value of o-methyl protons. g) The two mesityl groups may not be magnetically equivalent at low temperature.



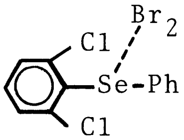
4·Cl_2

Table 1 shows ^{1}H and ^{13}C NMR chemical shifts of some diphenyl selenides bearing various substituents at o-, m-, and p-positions and the halogen adducts. Table 2 summarizes the structure of the adducts and the cyclic voltammetric (CV) data of the parent selenides (1 - 6).[4)]

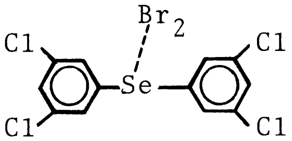
The chlorine and iodine adducts in Table 1 were concluded to be TB's and MC's, respectively, based on the criteria for distinguishing MC's from TB's in solutions based on NMR.[3a)] The structure of the bromine adducts of 2 (Y = 4-COOEt), 2 (Y = 2-Me), and 3 was also concluded to be TB based on the criteria. On the other hand, the chemical shifts of the bromine adducts of 2 (Y = 4-CN), 2 (Y = 3-NO_2), 2 (Y = 2-Cl), and 4 were quite different from those of the chlorine adducts but they were very close to



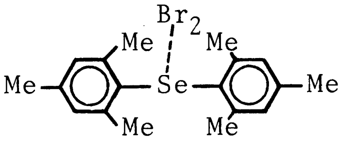
2•Br_2: Y=3-CN; 4-CN; 3-NO_2; 4-NO_2; 2-Cl.



4•Br_2



5•Br_2



6•Br_2

Table 2. Structure of Halogen Adducts and CV Data of o-, m-, and p-Substituted Diphenyl Selenides and $\Sigma\sigma^{+}$ Values for the Substituents

Selenide	Structure of adduct X = Cl	Br	I	$\Sigma\sigma^{+}$ a)	E_{ox} b)
2 (Y = 4-OMe)	TB	TB	MC	-1.556	1.65
2 (Y = 4-Me)	TB	TB	MC	-0.622	1.81
2 (Y = H)	TB	TB	MC	0.000	1.86
2 (Y = 4-Cl)	TB	TB	MC	0.228	2.00
2 (Y = 3-Cl)	TB	TB	MC	0.798	----
2 (Y = 4-COOEt)	TB	TB	MC	0.964	2.00 c)
1 (Y = 4-NO_2)	TB	TB	MC	0.790	2.08
3	TB	TB	MC	1.348 - α d)	2.18
2 (Y = 3-CN)	TB	MC	MC	1.124	2.19
2 (Y = 4-CN)	TB	MC	MC	1.318	2.22
2 (Y = 3-NO_2)	TB	MC	MC	1.348	2.23
2 (Y = 4-NO_2)	TB	MC	MC	1.580	2.27
5	TB	MC	MC	1.596 - α d)	----
2 (Y = 2-Me)	TB	TB	MC	-0.622	1.89
6	TB	MC	MC	-1.866 - α d)	1.92
4	TB	MC	MC	0.228 - α d)	2.09
2 (Y = 2-Cl)	TB	MC	MC	0.228	2.13

a) The total σ^{+} value of the substituent(s): σp^{+} values are used for o-substituents. See Ref. 9. b) Oxidation potentials are given vs. an Ag/AgI reference electrode with the ferrocene redox pair as a standard, measured in MeCN containing 0.1 M Et_4NClO_4 as a supporting electrolyte with a Pt electrode. c) Y = 4-COOMe for the E_{ox}. d) The interaction between substituents in a benzene ring is shown by α.

those of the iodine adducts. These results can be well explained by assuming that the latter bromine adducts were MC's.5) The structure of 6•Br_2 was also suggested to be MC, judging from the shift values.

As shown in Table 2, a strong electron-withdrawing substituent, such as the cyano or nitro group, was necessary to attach at the 3- or 4-position of each benzene ring of diphenyl selenide to give MC's with bromine if the electronic effect is examined: the bromine adducts were TB's when the substituents in 2 were less electronegative than the ethoxycarbonyl group. Four chloro groups in 5 worked effectively, whereas one nitro group in 1 (Y = 4-NO_2) and two nitro groups in 3 did not. The steric hindrance of two chloro groups in 2 (Y = 2-Cl) and 4 and four methyl groups in 6 was strong enough, whereas that of two methyl groups in 2 (Y = 2-Me) was not. Since the bulkiness of methyl and chloro groups is expected to be similar,6) the electronic effect of the o-substituents must play an additional role for the MC formation. The CV data7) will throw light on the importance of the steric effect, as well as the electronic effect, for the MC formation.

Since the pure $n(p_z)$-orbital of the selenium atom in diphenyl selenide plays an important role in TB formation1,8) and its HOMO has π- and $n(p_z)$-characters, the oxidation potentials corresponding to HOMO's of substituted diphenyl selenides are expected to serve as a good measure to predict the structure of the bromine adducts: the adducts were MC's if the values were larger than ca. 2.2 V (Table 2). However, the E_{ox}'s of the o-substituted diphenyl selenides that gave MC's with bromine were smaller than 2.2 V, which exhibited the importance of the steric effect in these selenides.

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4) Elementary analyses (C and H) were satisfactory for the new selenides.
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