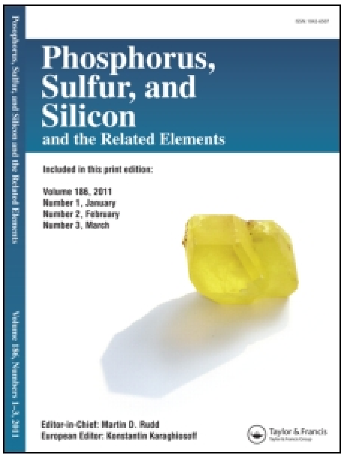

Phosphorus, Sulfur, and Silicon and the Related Elements
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713618290

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To cite this Article Nakanishi, War , Sakamoto, Kazuyo , Isaka, Kazumi and Hayashi, Satoko(1992) 'Molecular Complex Formation of Diphenyl Selenides with Bromine: Electronic and Steric Effects', Phosphorus, Sulfur, and Silicon and the Related Elements, 67: 1, 79 — 82

To link to this Article: DOI: 10.1080/10426509208045822

URL: http://dx.doi.org/10.1080/10426509208045822

Phosphorus, Sulfur, and Silicon, 1992, Vol. 67, pp. 79–82
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MOLECULAR COMPLEX FORMATION OF DIPHENYL SELENIDES WITH BROMINE: ELECTRONIC AND STERIC EFFECTS

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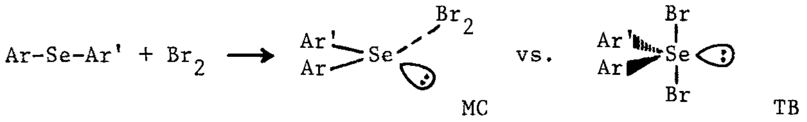
Abstract The structure of bromine adducts of diphenyl selenides, bearing various substituents at the 2-, 3-, and 4-positions, ($ArAr'SeBr_2$) are described. The MC structure of the adducts was demonstrated for Ar = Ar' = $4\text{-}NCC_6H_4$, $4\text{-}O_2NC_6H_4$, $3,5\text{-}Cl_2C_6H_3$, and $2\text{-}ClC_6H_4$ and (Ar, Ar') = ($2,6\text{-}Cl_2C_6H_3$, Ph), contrary to the expectation, whereas the adducts were TB's for Ar = Ar' = $3\text{-}ClC_6H_4$, $4\text{-}ClC_6H_4$, and $4\text{-}EtO_2CC_6H_4$ and (Ar, Ar') = ($4\text{-}O_2NC_6H_4$, Ph).

INTRODUCTION

The σ^*-orbital of iodine has been well established to accept the n-electrons of selenides to yield molecular complexes (MC's).[1] Since such electron-transfer to bromine, as well as chlorine and flourine, becomes much larger, depending on the electronegativity, the halogen can no longer exist as a halogen molecule resulting in the formation of trigonal bipyramidal adducts (TB's):[1,2] TB's contain highly polar hypervalent $X^{\delta-}\text{-}Se^{\delta+}\text{-}X^{\delta-}$ bonds. During the course of our study on the stability of the hypervalent bonds, we wondered, there should exsist such selenides that yield MC's with bromine, if the effective electronegativity of selenium in a given compound is chemically increased.[3a] The steric hindrance around the selenium atom would also be favorable for the MC formation. This idea led us to look for MC's of selenides with bromine.



The investigation was focused to explore the structure of variously substituted diphenyl selenides with bromine, based on our recent findings; the MC formation of selenoxanthone and selenanthrene with bromine[3a] and the (TB, MC) structure of 1,2-bis(phenyldibromoseleno)-benzene.[4] Here we would like to present the results.

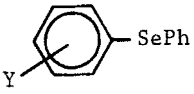
TABLE I ^1H and ^{13}C NMR chemical shifts of some substituted diphenyl selenides and the halogen adducts.a,b)

Compound	H(2)	C(1)	C(2)	C(3)	C(4)	C(5)	C(6)	TB/MC
1 (Y = 4-NO_2)c)	7.4	143.8	129.6	123.8	146.1			
	0.0	0.0	0.0	0.0	0.0			
1 (4-NO_2)·Cl_2c)	0.8	5.7	1.7	0.6	3.0			TB
1 (4-NO_2)·Br_2c)	0.8	1.9	3.2	0.8	2.5			TB
1 (4-NO_2)·I_2c)	0.0	-0.8	0.2	0.1	0.2			MC
2 (Y = 4-Cl)	7.34	128.9	134.2	129.5	133.8			
	0.00	0.0	0.0	0.0	0.0			
2 (4-Cl)·Cl_2	0.60	11.5	-1.6	0.4	4.7			TB
2 (4-Cl)·Br_2	0.61	7.8	-0.7	0.7	4.5			TB
2 (4-Cl)·I_2	0.02	-0.6	-0.2	0.2	0.6			MC
2 (Y = 3-Cl)	7.4	131.9	132.6	135.0	127.9	130.4	131.0	
	0.0	0.0	0.0	0.0	0.0	0.0	0.0	
2 (3-Cl)·Cl_2	0.6	11.3	-1.6	0.4	4.3	0.2	-1.7	TB
2 (3-Cl)·Br_2	0.5	6.8	-0.5	0.7	3.8	0.4	-0.5	TB
2 (3-Cl)·I_2	0.0	-0.5	-0.1	0.1	0.4	0.1	-0.1	MC
2 (Y = 4-NO_2)	7.61	138.8	133.2	124.5	147.6			
	0.00	0.0	0.0	0.0	0.0			
2 (4-NO_2)·Cl_2d)	0.68	9.8	-0.6	0.4	2.0			TB
2 (4-NO_2)·Br_2	0.00	-0.1	0.0	0.0	0.0			MC
2 (4-NO_2)·I_2	0.00	-0.1	-0.1	0.0	0.0			MC
4 (Y = Cl)	7.32	132.2	130.9	135.7	128.3			
	0.00	0.0	0.0	0.0	0.0			
4 (Cl)·Cl_2	0.59	11.6	-1.7	0.5	4.2			TB
4 (Cl)·Br_2	0.06	-0.2	-0.1	0.1	0.7			MC
4 (Cl)·I_2	0.01	-0.1	0.0	0.0	0.1			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

a) Elementary analyses were satisfactory for new selenides. b) Chemical shifts (ppm) are given from TMS for selenides and from the selenides for the adducts in $CDCl_3$. c) Chemical shifts of the phenyl group were not given: the *ipso*-carbon chemical shift of the selenide was δ 127.1 and the shift values of *ipso*-carbons of the chlorine, bromine, and iodine adducts were 14.6, 9.5, and -0.2 ppm from the selenide, respectively. d) Shift values in CD_2Cl_2 from the selenide recorded in CD_2Cl_2.

THE STRUCTURE OF BROMINE ADDUCTS OF DIPHENYL SELENIDES

Table I shows ^{1}H and ^{13}C NMR chemical shifts of several 2-, 3-, and 4-substituted diphenyl selenides, together with the structure of the adducts determined according to the criteria for distinguishing MC's from TB's in solutions based on NMR.[3b] Table II summarizes the structure of the adducts studied in this work. The $\Sigma\sigma^+$ values for the substituents of the selenides were also contained.



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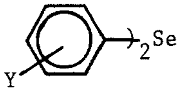

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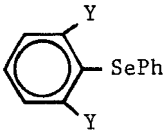

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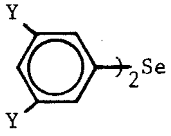

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Electronic and Steric Effects on the MC Formation of ArAr'Se with Br_2

The TB structure of bromine adduct of diphenyl selenide (1 (Y = H)) itself has been well established.[1] Its chlorine and iodine adducts are a TB and an MC, respectively. The structure of the chlorine and iodine adducts listed in Table I was identified to be TB's and MC's, respectively, based on the criteria: large downfield shifts were observed for chlorine adducts and upfield shifts of C(1)-carbons for iodine adducts.

While the chemical shifts of bromine adducts of 1 (Y = 4-NO_2), 2 (Y = 4-Cl), and 2 (Y = 3-Cl) were very similar to those of the chlorine adducts, the values of 2 (Y = 4-NO_2), 4 (Y = Cl), and 2 (Y = 2-Cl) were quite different from those of the chlorine adducts, but very close to those of the iodine adducts: the upfield shifts were observed for the C(1)-carbons of the latter adducts. These results are well explained by assuming that the bromine adducts of the latter group are MC's whereas TB's for the former.

As shown in Table II, the electronic effect of two cyano or two nitro groups at *para*-positions and of four chloro groups at every *meta*-position was demonstrated to be strong enough for the MC formation of diphenyl selenides with bromine, whereas that of a nitro or a phenyldibromoseleno group at a *para*-position and of two chloro or two ethoxycarbonyl groups at *para*- and/or *meta*-positions was not strong enough. The $\Sigma\sigma^+$ values for the substituents of the selenides should be a good measure to predict the structure of bromine adducts.

On the other hand, two chloro groups at *ortho*-positions as well as

TABLE II Structure of halogen adducts of ArAr'Se and the $\Sigma\sigma^{+}$ values.

Selenide	Structure of the adduct			$\Sigma\sigma^{+}$ a)
	X = Cl	Br	I	
1 (Y = H)	TB	TB	MC	0.000
2 (Y = 4-Cl)b)	TB	TB	MC	0.228
1 (Y = 4-$SeBr_2Ph$)c)	TB	TB	MC	
1 (Y = 4-NO_2)	TB	TB	MC	0.790
2 (Y = 3-Cl)b)	TB	TB	MC	0.798
2 (Y = 4-COOEt)	TB	TB	MC	0.964
2 (Y = 4-CN)	TB	MC	MC	1.318
2 (Y = 4-NO_2)	TB	MC	MC	1.580
4 (Y = Cl)	TB	MC	MC	1.596
1 (Y = 2-SePh)c)	TB	TB	MC	
1 (Y = 2-$SeBr_2Ph$)c)	TB	MC	MC	
2 (Y = 2-Cl)	TB	MC	MC	(0.228)d)
3 (Y = Cl)	TB	MC	MC	(0.228)d)

a) The interaction between the substituents was neglected in the calculation of the values. b) The same results were obtained for methoxyl and methyl groups at the 3- or 4-positions. c) Ref. 4. d) The value of the *para*-derivative was used.

a phenyldibromoseleno group at the *ortho*-position did work in the MC formation, while a phenylseleno group at an *ortho*-position did not.

These results exhibit that the MC's of diphenyl selenide dibromides do exist and the electronic and steric effects of substituents play a very important role in the structure of the adducts. The additional electronic effect must also be working for some *ortho*-substituents.

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