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SHORT COMMUNICATION

STRUCTURAL STUDIES OF BROMINE ADDUCTS OF 1,2- AND 1,4-BIS(PHENYLSELENO)BENZENES. EVIDENCE FOR THE (TB, MC) STRUCTURE OF 1,2-$(PhSeBr_2)_2C_6H_4$

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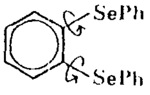
1,2-Bis(phenylseleno)benzene reacted with equimolar amount of bromine to yield a trigonal bipyramidal (TB) adduct, in contrast to the molecular complex (MC) structure of selenanthrene with bromine. Whereas the structure of 1,4-$(PhSeBr_2)_2C_6H_4$ was (TB, TB) at the two selenium atoms, that of the 1,2-derivative was demonstrated to be (TB, MC), *the first example of an MC structure of* $PhSeC_6H_4Y$ *with* Br_2 [Y = 2-$PhBr_2Se$(TB)]. Both electronic and steric effects of the group must play an important role in MC formation. Rapid structural exchange in this tetrabromide, (TB, MC) ⇌ (MC, TB), was also observed.

We have been interested in the intramolecular interactions between selenium atoms, in close proximity in space, which affect their reactivities with each other, and have recently reported the formation of a molecular complex (MC) in the reaction of selenanthrene with bromine,[1a] contrary to the general rule:[2] whereas the iodine adducts of selenides are MCs, they react with bromine, chlorine or fluorine to give trigonal bipyramidal (TB) adducts. The structure of these adducts, together with those of ethers, sulphides and tellurides, has been well established by x-ray crystallography.[2] The structure of the adducts in solutions has also been investigated by means of NMR: MC or TB formation exhibits characteristic changes in ^{1}H, ^{13}C and ^{77}Se chemical shifts, which have been reported as criteria for distinguishing MCs from TBs.[1b] TB formation causes large downfield shifts for *ortho* protons (*ca* 0·6 ppm) and *ipso* and *para* carbons (6–11 ppm depending on halogens and *ca* 4 ppm independent of halogens, respectively), whereas the shift values are small ($\leqslant$1 ppm) and the upfield shifts in *ipso* carbons (*ca* − 1 ppm) are characteristic for MC formation when diphenyl selenides are examined.[1b]

The reason for the MC structure cannot be electronic as the first ionization potential of selenanthrene is very similar to that of diphenyl selenide,[3] which would be favourable for TB formation.[4] If the C—Se bonds in selenanthrene could rotate, we wondered whether different results might be obtained, that is, the rigid roof structure of the compound would prevent the formation of a TB. This idea led us to examine the structure of halogen adducts of 1,2-bis(phenylseleno)benzene (**1**), together with those of 1,4-bis(phenylseleno)benzene (**2**) and 1,4-bis(*p-tert*-butylphenylseleno)benzene (**3**) and the results of the study are presented in this paper.

The physical properties of **1**, **1**·$2Cl_2$ and **2** agreed well with those in the literature.[5] Elemental analyses were satisfactory (the deviations being less than 0·3% for C and H) for **1**·Cl_2 [m.p. 119–121 °C (decomp)], **1**·Br_2 [m.p. *ca* 107 °C (decomp)], **1**·$2Br_2$ [m.p. *ca* 77 °C (decomp)] and **3**. The ^{1}H and ^{13}C NMR spectra of **3**



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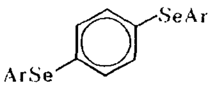
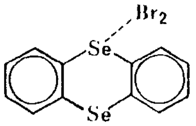


2 : Ar = Ph
3 : Ar = p-t-BuC_6H_4



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[m.p. 104–106 °C] the halogen adducts were those expected for the compounds. The ArAr′SeX_2 structure of the adducts was confirmed by the reported method.[6]

Table 1 gives the ^{13}C NMR chemical shifts of **1** and its halogen adducts. Table 2 gives the ^{1}H and ^{13}C NMR chemical shifts of **3** and the halogen adducts; ^{13}C NMR spectra of the chlorine and bromine adducts of **2** could not be recorded effectively, owing to the low solubility. The H-2 proton chemical shifts of **2**, **2**·$2Cl_2$, **2**·$2Br_2$, **2**·$4Br_2$ (**2**·$2Br_2$ + $2Br_2$) and **2**·$2I_2$ were δ 7·30, 8·58, 8·58 (−30 °C), 8·58 (−30 °C) and 7·32, respectively. Tables 1 and 2 also show the structures of the adducts determined according to the criteria for distinguishing MCs from TBs in solutions based on NMR.[1b]

As shown in Tables 1 and 2, the structure of the chlorine adducts of **1** and **3** was concluded to be TB (**1**·Cl_2) or (TB, TB) (**1**·$2Cl_2$ and **3**·$2Cl_2$) at the selenium atoms, based on the criteria, whereas that of the iodine adducts was MC (**1**·I_2) or (MC, MC) (**1**·$2I_2$ and **3**·$2I_2$). Although the iodine migration in the adducts was fast relative to the NMR time scale (at 60 MHz and at an ambient NMR probe temperature of *ca* 27 °C), the chlorine migration in **1**·Cl_2 was slow; two sets of ^{13}C signals were observed for the dichloride, but only one for the iodides. Since the ^{1}H and ^{13}C NMR chemical shifts of the bromine adduct **3**·$2Br_2$ were very close to those of the chlorine adduct **3**·$2Cl_2$, the structure of **3**·$2Br_2$ must be (TB, TB). The structure of the halogen adducts of **2** was also concluded to be the same as that in **3**·$2X_2$, based on ^{1}H NMR chemical shifts (see above). The electronic effect of the PhX_2Se group in **2**·X_2 and the *p*-*t*-$BuC_6H_4X_2Se$ group in **3**·X_2 (X = Cl or Br) would not change the reactivity of another ArSe group (Ar = Ph in **2** or *p*-*t*-BuC_6H_4 in **3**) dramatically to give MCs with chlorine or bromine, although their effect is expected to be very large.[1] The electronic and steric effects of the $PhCl_2Se$ group in **1**·$2Cl_2$ did not make the structure of the adduct (TB, MC) either. As an extension of the study, the structure of bromine adducts of **1** was examined.

The ^{13}C NMR spectrum of the bromine adduct **1**·Br_2 consisted of several relatively sharp and broad signals at the NMR probe temperature in chloroform-*d*. The rate of the bromine migration between the two selenium

Table 1. ^{13}C NMR chemical shifts of 1,2-bis(phenylseleno)benzene (**1**) and its halogen adducts[a,b]

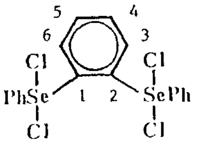
Compound[c]	C-1 C-2	C-3 C-6	C-4 C-5	C-*ipso* C-*ipso*′	C-*o* C-*o*′	C-*m* C-*m*′	C-*p* C-*p*′	Structure
1	135·8	132·9	127·8	130·6	133·9	129·4	127·7	Selenide
	0·0	0·0	0·0	0·0	0·0	0·0	0·0	
1·Cl_2[d]	15·7	4·7	4·0	8·2	−0·4	0·2	4·3	TB
	−1·9	−3·4	0·3	1·9	−0·4	0·2	0·2	
1·$2Cl_2$	11·0	2·0	4·0	12·7	−1·5	0·1	4·2	(TB, TB)
1·Br_2[e]	—[f]	0·7	2·0	3·3	0·3	0·2	2·9	TB
1·$2Br_2$[g]	4·4	0·5	2·2	3·0	0·2	0·3	3·3	(TB, MC)
1·$3Br_2$	4·2	0·6	2·3	2·9	0·1	0·3	3·5	(TB, MC)
1·I_2	−0·5	0·3	0·5	−0·6	−0·3	0·2	0·9	MC
1·$2I_2$	−0·8	0·5	0·8	−1·0	−0·4	0·3	1·4	(MC, MC)

[a] Chemical shifts (ppm) are given from TMS for **1** and from **1** for the adducts.
[b] In $CDCl_3$.
[c] Carbons adjacent to the selenium atom which has no halogens are numbered as C-2 and C-*ipso*′ for **1**·Cl_2.
[d] Assignments are partly tentative even after SEL mode measurements.
[e] Although the signal separation was not complete, two sets of broad signals were observed at −60 °C in CD_2Cl_2 (e.g. 133·1, 134·1 and *ca* 129·3 ppm for C-*o*, C-*o*′ and C-*m*,*m*′, respectively).
[f] Not observed owing to broadening.
[g] The signals were broad ($\nu_{1/2}$ = 1–4 Hz) at −60 °C in CD_2Cl_2.

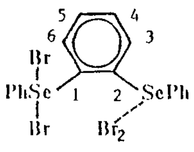
Table 2. ^{1}H and ^{13}C NMR chemical shifts of 1,4-bis(*p*-*tert*-butylphenylseleno)benzene (**3**) and its halogen adducts[a,b]

Compound	H-2	H-*o*	C-1	C-2	C-*ipso*	C-*o*	C-*m*	C-*p*	Structure
3	7·27	7·38	130·6	133·4	126·4	132·7	126·9	150·8	Selenide
	0·00	0·00	0·0	0·0	0·0	0·0	0·0	0·0	
3·$2Cl_2$	0·88	0·60	16·0	−1·3	11·6	−1·6	0·7	5·3	(TB, TB)
3·$2Br_2$	0·83	0·62	12·0	−0·2	7·3	−0·3	1·0	5·1	(TB, TB)
3·$2I_2$	0·03	0·04	0·4	−1·1	−1·1	−0·3	0·4	1·2	(MC, MC)

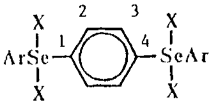
[a] Chemical shifts (ppm) are given from TMS for **3** and from **3** for the adducts.
[b] In $CDCl_3$.



1·2Cl_2



1·2Br_2



2,**3**·2X_2 : X=Cl, Br

atoms in **1**·Br_2 should be comparable to the NMR time scale. Although the separation was not complete, two sets of broad signals were observed at −60 °C in CD_2Cl_2, indicating the formation of a TB. However, the chemical shifts obtained at *ca* 27 °C were employed for the discussion of the structure, since the signals of some carbons could not be recorded effectively owing to broadening and to the low solubility under the conditions used; the chemical shifts of C-*p* and C-4 in **1**·Br_2 are very close to the average values of those of C-*p* and C-*p*′ and those of C-4 and C-5 in the chlorine adduct **1**·Cl_2, respectively (cf. the criteria for *para* carbons; see above).

TB formation often requires C—Se bond rotation to make two new apical bonds with ligands. This requirement can be satisfied in **1** to give TBs with chlorine and bromine, whereas it could not be accomplished in selenanthrene owing to its rigid roof structure, yielding an MC with bromine or a chlorine adduct of unknown structure.[1a]

The ^{13}C signals of **1**·Br_2 became sharp when bromine was added to the solution. Although the signals of C-*p* and C-4 appeared at 0·4 and 0·2 ppm downfield relative to those of **1**·Br_2, that of C-*ipso* shifted upfield by 0·3 ppm when an equimolar amount of bromine was added to the solution. The signals of **1**·2Br_2 became broadened ($\nu_{1/2} = 1$–4 Hz) at −60 °C in CD_2Cl_2. These results can be well explained by assuming that the second bromine molecule attacks the divalent selenium atom in **1**·Br_2 to give an MC at the selenium atom and the rapid exchange of the structures began to take place in **1**·2Br_2, (TB, MC) ⇌ (MC, TB) [equation (1)].[7] The chemical shifts of **1**·3Br_2 (**1**·2Br_2 + Br_2), relative to those of **1**·2Br_2, supported the conclusion that an MC is in equilibrium with the components.[1b]

$$o\text{-}PhSeBr_2(TB)-C_6H_4-SeBr_2(MC)Ph$$
$$\rightleftharpoons o\text{-}PhSeBr_2(MC)-C_6H_4-SeBr_2(TB)Ph \quad (1)$$

The intramolecular interaction between the $PhBr_2Se$ and PhSe groups in **1**·Br_2 changed the reactivity of the latter, resulting in the formation of an MC with bromine. Both electronic and steric effects of the $PhBr_2Se$(TB) group may play an important role in (TB, MC) formation in **1**·2Br_2, since the structure of **2**·2Br_2 and **3**·2Br_2 was demonstrated to be (TB, TB) and the electronic effect is expected to be similar in *ortho* and *para* positions.

The present study demonstrates that (i) the structure of **1**·Br_2 is TB, in contrast to the MC structure of selenanthrene dibromide, showing the prevention of TB formation for this adduct owing to its rigid roof structure, (ii) **1**·Br_2 reacts with bromine to yield a (TB, MC), which is the first example of an MC structure of a substituted diphenyl selenide with bromine, and (iii) rapid exchange in **1**·2Br_2, (TB, MC) ⇌ (MC, TB), takes place even at low temperature.

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