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STRUCTURAL STUDIES OF HALOGEN ADDUCTS OF DIORGANYL CHALCOGENIDES IN SOLUTIONS BY ^{1}H, ^{13}C, ^{77}Se AND ^{125}Te NMR*

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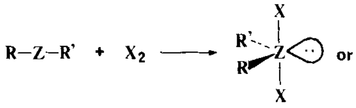
^{1}H, ^{13}C, ^{77}Se and ^{125}Te NMR spectra were measured for several sulphides, selenides, tellurides and their halogen adducts to establish the criteria for distinguishing trigonal bipyramidal (TB) adducts from molecular complexes (MCs). TB formation caused large downfield shifts for methyl protons and methyl, *ipso* and *para* carbons of methyl and phenyl selenides and tellurides. Large downfield shifts (>100 ppm) were also observed for selenium and tellurium by the formation of TB from the parent selenides or tellurides. The plots of the ^{125}Te vs ^{77}Se chemical shifts for a set of corresponding compounds gave a straight line with a slope of 1·74, showing that the linear relationship holds well for tellurides and selenides and their TB adducts examined in this work. Upfield shifts of the *ipso* carbons were characteristic of MC formation. The *para* carbon signals of MC appeared downfield relative to those of the parent selenides, although the shift values were not so large. The ^{77}Se signals for MC shifted slightly downfield ($\leqslant 10$ ppm). The dissociation constants for iodine adducts of dimethyl selenide and selenoanisole were determined. The MC structure of bromine adducts of sulphides is well demonstrated on the basis of the criteria set out. ^{1}H and ^{13}C NMR spectra of ethylbenzene and ethers were also recorded in the presence of iodine or bromine. However, their chemical shifts were the same as those in the absence of iodine or bromine, within experimental errors.

INTRODUCTION

Iodine has been well established to form charge-transfer (CT) complexes with π-, n- and possible σ-donors;[2] it can act as a σ-acceptor with its low-lying σ^*-orbital.[2–6] Bromine and chlorine also react with aromatic compounds or ethers to give CT complexes or molecular complexes (MCs).[6] Whereas iodine adducts of selenides are MCs, bromine, chlorine and fluorine react with selenides to yield trigonal bipyramidal (TB) adducts.[7,8] Halogen adducts of tellurides are all TBs.[8,9] Thus, in the reaction of diorganyl chalcogenides with electrophiles, such as halogens, TBs are formed if the electronegativity[10] of the electrophiles (χ_X) is larger than that of the Group VIB elements (χ_Z) in the compounds: the adducts will be MC when χ_X is less than χ_Z [equation (1)].[11]



(1)

$$\mathrm{TB}(\chi_X > \chi_Z)\ \ \mathrm{MC}(\chi_X < \chi_Z)$$

M (Z or X)	O	S	Se	Te	F	Cl	Br	I
χ_M	3·50	2·44	2·48	2·01	4·10	2·83	2·74	2·21

This generalization holds well in most cases. However, there are some exceptions. For example, although selenides react with bromine to give TBs in general, the structure of the bromine adduct of thiophane has been reported to be an MC,[12] contrary to expectation: the electronegativity of sulphur, and also that of selenium, is less than that of bromine. Although there are some

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* For a preliminary contribution, see Ref. 1.

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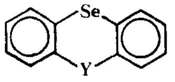
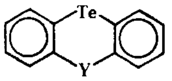
reports in the literature on the structure of the adducts studied by spectroscopic methods such as UV[6] or IR,[13] they are inadequate to establish the criteria that distinguish MCs from TBs. In this paper, we report NMR criteria for the examination of the structure of halogen adducts in solutions.

RZR': R,R' =	Me,Me	Me,Ph	Ph,Ph
Z = Se:	**1a**	**2a**	**3a**
Z = Te:	**4a**	**5a**	**6a**



7a (Y = O)
8a (Y = C = O)



9a (Y = O)
10a (Y = C = O)

$RR'ZX_2$: X =	—	F	Cl	Br	I	X_2 = O
	a	**b**	**c**	**d**	**e**	**f**

RESULTS AND DISCUSSION

The ^1H and ^{13}C NMR spectra were recorded for dimethyl selenide (**1a**), selenoanisole (**2a**), diphenyl selenide (**3a**), dimethyl telluride (**4a**), methyl phenyl telluride (**5a**), diphenyl telluride (**6a**), dimethyl sulphide, diethyl sulphide, thioanisole, diphenyl sulphide and their fluorine, chlorine, bromine and iodine adducts (e.g. **6b**, **6c**, **6d** and **6e**, respectively) in chloroform-*d* or dimethyl suphoxide-d_6. The chemical shifts are summarized in Tables 1–4 and the coupling constants are listed in Table 5. The ^1H and ^{13}C chemical shifts of iodine and bromine adducts of ethylbenzene, diethyl ether and diphenyl ether were also measured, but the data were almost the same as those of their parent compounds; the differences were within the experimental errors (less than 0·01 ppm for protons and less than 0·1 ppm for carbons).

^{77}Se and ^{125}Te NMR chemical shifts of **1a**–**6a** and of phenoxselenine (**7a**), selenoxanthone (**8a**), phenoxtellurine (**9a**) and telluroxanthone (**10a**) are given in Table 6, together with those of halogen adducts. The temperature dependence of the ^{125}Te chemical shifts of **6c** and **6d** were also measured.

When a favourable geometry is possible, π-electrons of benzenes and n-electrons of diorganyl chalcogenides or amines are easily transferred to σ^*-orbitals of halogens, since the energy levels of the σ^*-orbitals are relatively low.[2–6] The bromine– and chlorine–benzene (1 : 1) complexes[14] and halogen (iodochlorine, bromine and chlorine)–ether complexes[15] have been demonstrated to be CT complexes or molecular complexes (MCs) in the solid. The geometry of the former has D_6h symmetry[14] and that of the latter is tetrahedral.[15]

Although there is evidence in the literature for the formation of these complexes in solutions,[2c,13a] no significant differences could be detected between the ^1H and ^{13}C NMR chemical shifts of ethylbenzene, diethyl ether and diphenyl ether in the presence and absence of iodine or bromine in chloroform-*d*. These results show that the formation of such complexes under the conditions used (0·1 M in chloroform-*d*) would not be so significant based on NMR, although ethers yield stronger complexes with other hard acids.[16]

The following points should be considered when such complexes are investigated by NMR: (i) the structural change in the formation of complexes, (ii) the effect of the formation of the adducts on NMR parameters and (iii) the formation (dissociation) constants of the complexes in solution.[17]

The observed chemical shift data (δ) should be the average of those for the free compounds (δ_f) and com-

Table 1. ^1H and ^{13}C NMR chemical shifts of dimethyl selenide (**1a**), selenoanisole (**2a**), diphenyl selenide (**3a**) and their halogen adducts (TBs)[a,b]

Compound	H-Me	C-Me	C-*i*	C-*o*	C-*m*	C-*p*
MeSeMe (**1a**)	2·00	6·0				
	0·00	0·0				
$MeSeCl_2Me$ (**1c**)	1·64	38·8				
$MeSeBr_2Me$ (**1d**)	1·63	36·6				
PhSeMe (**2a**)	2·31	7·2	131·7	130·2	128·8	125·9
	0·00	0·0	0·0	0·0	0·0	0·0
$PhSeCl_2Me$ (**2c**)	1·59	38·5	9·3	−1·7	1·1	5·8
$PhSeBr_2Me$ (**2d**)	1·59	36·4	6·4	−1·1	1·4	5·7
PhSePh (**3a**)			131·1	132·9	129·2	127·2
			0·0	0·0	0·0	0·0
$PhSeCl_2Ph$ (**3c**)			11·4	−1·7	0·5	4·4
$PhSeBr_2Ph$ (**3d**)			7·9	−0·5	0·6	4·3

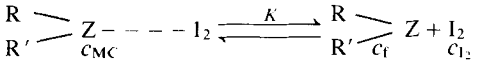
[a] In $CDCl_3$.
[b] Chemical shifts (ppm) are given from TMS for **1a**, **2a** and **3a** and from their parent compounds for the adducts.

Table 2. ^{1}H and ^{13}C NMR chemical shifts of dimethyl telluride (**4a**), methyl phenyl telluride (**5a**) and diphenyl telluride (**6a**) and their halogen adducts (TBs)[a,b]

Compound	H-Me	C-Me	C-*i*	C-*o*	C-*m*	C-*p*
MeTeMe (**4a**)[c]	1·85	−21·9				
	0·00	0·0				
$MeTeCl_2Me$ (**4c**)[d]	1·32	48·9				
$MeTeBr_2Me$ (**4d**)[d]	1·45	46·8				
PhTeMe (**5a**)	2·17	−16·6	112·8	135·2	128·9	126·5
	0·00	0·0	0·0	0·0	0·0	0·0
$PhTeCl_2Me$ (**5c**)	0·92	46·2	22·9	−2·3	0·0	4·0
$PhTeBr_2Me$ (**5d**)	1·05	43·9	19·5	−1·5	0·2	4·0
$PhTeI_2Me$ (**5e**)	1·04	40·1	e	−0·6	0·3	3·8
5a[f]	g	−17·5	113·4	136·8	129·4	127·4
	—	0·0	0·0	0·0	0·0	0·0
5e[f]	g	42·4	12·2	−1·0	0·8	4·1
PhTePh (**6a**)			114·7	137·3	129·4	127·6
			0·0	0·0	0·0	0·0
$PhTeF_2Ph$ (**6b**)			25·4	−6·2	−0·2	3·1
$PhTeCl_2Ph$ (**6c**)			23·6	−3·1	−0·4	3·0
$PhTeBr_2Ph$ (**6d**)			20·1	−1·8	−0·5	2·9
$PhTeI_2Ph$ (**6e**)			e	−0·2	−0·3	2·5
6a[f]			115·4	138·4	129·8	128·0
			0·0	0·0	0·0	0·0
6e[f]			12·9	−0·4	0·4	3·3

[a] In DMSO-d_6.
[b] Chemical shifts (ppm) are given from TMS for **4a**, **5a** and **6a** and from their parent compounds for the adducts.
[c] In C_6D_6.
[d] In $CDCl_3$.
[e] Not observed owing to broadening.
[f] In dioxane.
[g] Not measured.

plexes (δ_{MC}):

 (2)

$$\underset{c_{MC}}{RR'Z}{-}{-}{-}{-}I_2 \underset{}{\overset{K}{\rightleftharpoons}} \underset{c_f}{RR'Z} + \underset{c_{I_2}}{I_2} \tag{2}$$

$$K = \frac{[RR'Z]\,[I_2]}{[RR'Z \cdot I_2]} = \frac{c_f c_{I_2}}{c_{MC}} \tag{3}$$

$$\begin{aligned}\delta &= \frac{c_{MC}}{c_{MC} + c_f} \cdot \delta_{MC} + \frac{c_f}{c_{MC} + c_f} \cdot \delta_f \\ &= \delta_{MC} - \frac{c_f}{c_{MC} + c_f}(\delta_{MC} - \delta_f) \\ &= \delta_{MC} - \frac{K\,\Delta\delta}{K + c_{I_2}} \qquad (4)\end{aligned}$$

where $\Delta\delta = \delta_{MC} - \delta_f$

$$\delta \approx \delta_{MC} - K\,\Delta\delta\, c_{I_2}^{-1} \qquad \text{if } K \ll c_{I_2} \tag{5}$$

As the electronegativity of halogens and the donor ability of n-orbitals of diorganyl chalcogenides become higher, a larger amount of the n-electron would be transferred to the σ^*-orbitals of halogens. In such cases, more stable complexes will be formed and their dissociation constants must be smaller.[17] Moreover, as the electron transfer becomes much larger, the halogen can no longer exist as a halogen molecule. The X—X bond will cleave, since the electron transferred from the chalcogenides would reside in the antibonding orbital;[6] TB adducts would be formed when a large amount of electron is transferred.[11,18,19] Therefore, TBs should have highly polar apical bonds constructed with two negatively charged halogen atoms (X) and a positively charged central atom (Z).[18,19] Figure 1 shows the correlation diagram in the reaction of ZH_2 with X_2, starting from $ZH_2 + 2X\cdot$, which gives a TB or MC; TB will form in this case since $\Delta E_{TB} \approx \Delta E_{hp} > \Delta E_{CT} + \Delta E_\sigma \approx \Delta E_{MC}$, which is derived from $\chi_X > \chi_Z$ and $E(p_Z)$ of $X < E(p_Z)$ of Z, where the ΔEs are as given in Figure 1. The dissociation constants of TBs are expected to be very small.

^{1}H and ^{13}C chemical shifts of trigonal bipyramidal (TB) complexes

Selenides and tellurides, in general, react with fluorine, chlorine and bromine to give TBs.[7–9,11] Iodine also

Table 3. ^1H and ^{13}C NMR chemical shifts of methyl, ethyl and phenyl chalcogenides and their iodine adducts[a,b]

Compound	H-1	H-2	C-1	C-2	C-*i*	C-*o*	C-*m*	C-*p*
Me_2S	2·12		18·1					
	0·00		0·0					
$Me_2S + I_2$	0·19		2·1					
Et_2S	2·56	1·26	25·5	14·7				
	0·00	0·00	0·0	0·0				
$Et_2S + I_2$	0·16	0·07	4·2	−1·3				
PhMeS	2·48		15·9		138·3	126·6	128·7	124·9
	0·00		0·0		0·0	0·0	0·0	0·0
PhMeS + I_2	0·11		1·7		−1·9	0·6	0·3	1·3
Ph_2S					135·7	131·0	129·1	126·9
					0·0	0·0	0·0	0·0
$Ph_2S + I_2$					−0·4	−0·1	0·0	0·3
1a	2·01		5·9					
	0·00		0·0					
1a + $1/3I_2$	0·15		2·7					
1a + $2/3I_2$	0·27		4·9					
1a + I_2	0·42		7·4					
2a	2·35		7·2		131·7	130·4	128·9	126·0
	0·00		0·0		0·0	0·0	0·0	0·0
2a + $1/2I_2$	0·10		2·3		−0·9	0·1	0·3	0·9
2a + I_2	0·27		5·0		−2·0	0·2	0·6	1·9
2a + $2I_2$	0·35		7·6		−3·0	0·3	0·8	2·8
3a					131·1	132·9	129·2	127·2
					0·0	0·0	0·0	0·0
3a + $1/2I_2$					−0·6	−0·2	0·2	0·6
3a + $5/4I_2$					−1·1	−0·3	0·4	1·2
3a + $2I_2$					−1·5	−0·4	0·6	1·5

[a] In $CDCl_3$.

[b] Chemical shifts (ppm) are given from TMS for the chalcogenides and from their parent compounds for the adducts.

Table 4. ^1H and ^{13}C NMR chemical shifts of ethyl sulphide, thioanisole and diphenyl sulphide and their bromine adducts[a,b]

Compound	H-1	H-2	C-1	C-2	C-*i*	C-*o*	C-*m*	C-*p*	*T*(°C)
Et_2S	2·58	1·27	25·1	14·6					−20
	0·00	0·00	0·0	0·0					
$Et_2S + Br_2$	0·53	0·23	14·2	−3·4					−20
PhMeS	2·50		15·4		138·0	125·7	128·7	124·6	−20
	0·00		0·0		0·0	0·0	0·0	0·0	
PhMeS + $1/2Br_2$	0·20		4·0		−3·2	1·1	0·5	2·5	−20
PhMeS + Br_2	0·40		8·1		[c]	2·3	1·0	4·1	−20
Ph_2S					135·7	131·0	129·1	126·9	27
					0·0	0·0	0·0	0·0	
$Ph_2S + Br_2$ [d]					−0·8	−0·1	0·2	0·7	27
Ph_2S					135·4	130·8	129·1	126·9	−10
					0·0	0·0	0·0	0·0	
$Ph_2S + Br_2$					−2·0	−0·1	0·3	1·4	−10
$Ph_2S + 2Br_2$					−3·0	−0·1	0·5	2·1	−10

[a] In $CDCl_3$.

[b] Chemical shifts (ppm) are given from TMS for sulphides and from their parent compounds for the adducts.

[c] Not observed owing to broadening.

[d] Decomposition was observed (ca 20% after 60 min).

Table 5. Coupling constants of some selenides, tellurides and their halogen adducts[a]

Compound	^1J(Se–C)	^2J(Se–H)	^2J(Se–C)	^1J(Te–C)	^2J(Te–H)	^2J(Te–C)	^1J(C–H)	^3J(C–H)	Solvent
1a[b]	60·4	10·1					140·6	3·8	$CDCl_3$
1c	60·8	10·1					148·3	2·5	$CDCl_3$
1e	56·2	8·4					143·7	3·5	$CDCl_3$
2a[b]	63·8	11·0	11·0				141·9		$CDCl_3$
2c	61·0	10·9	13·2[b]				149·0		$CDCl_3$
2e	[c]	9·0	10·7				[d]		$CDCl_3$
3a[b]			11·0						$CDCl_3$
3c[b]			11·2						$CDCl_3$
4a				158·7	20·8		141·6	2·8	C_6D_6
4c				173·7	25·8		145·5	2·1	$CDCl_3$
4d				159·1	25·9		146·2	2·1	$CDCl_3$
6a						22·0			DMSO-d_6
6b[e]						36·8			DMSO-d_6
6c						25·8			DMSO-d_6
6d						22·0			DMSO-d_6

[a] In Hz.
[b] Ref. 31.
[c] Not observed owing to broadening.
[d] Not measured.
[e] ^1J(F–Te) = 652, ^2J(F–C) = 11·2, ^3J(F–C) = 11·7, ^4J(F–C) = 2·0 and ^5J(F–C) = 2·2 Hz.

Table 6. ^{77}Se and ^{125}Te NMR chemical shifts of some selenides, tellurides and their halogen adducts

Compound	δ(^{77}Se)[a]		Compound	δ(^{125}Te)[b]	
1a	0·0		**4a**	0·0[c]	
1c		448[f]	**4c**		749[f]
1d		389[f]	**4d**		669[f]
2a		202[f]	**5a**		330[f]
3a	419·8[c]	415[f]	**6a**	689·3	688[f]
			6b	1142·2	
3c	582·8[c]	586[f]	**6c**	995·4	981[f]
3d	545·4[c]		**6d**	978·1	980[f]
3e′[d]	424·7[c]		**6e**	928·2[e]	
7a	260·6		**9a**	432·3	424[f]
7c	381·7		**9c**	628·6	
			9d	598·4	
7e	263·4		**9e**	549·1[e]	
8a	334·7	337[f]	**10a**	471·5	468[f]

[a] In $CDCl_3$.
[b] In DMSO-d_6.
[c] In C_6D_6.
[d] The adduct **3e′** represents **3a**·$\frac{1}{2}$I$_2$; the estimated value for **3e** (1 : 1) is δ 428·0 based on ^{13}C NMR.
[e] Half-width values (non-decoupling) are as follows: 19 Hz for **3a**, 23 Hz for **3c**, 84 Hz for **3d**, 101 Hz for **3e′**, 1508 Hz (12·0 ppm) for **6c** and 275 Hz (2·2 ppm) for **9e**. The signals of **6e** and **9e** are very broad.
[f] Ref. 8 (Chap. 6) and references cited therein.

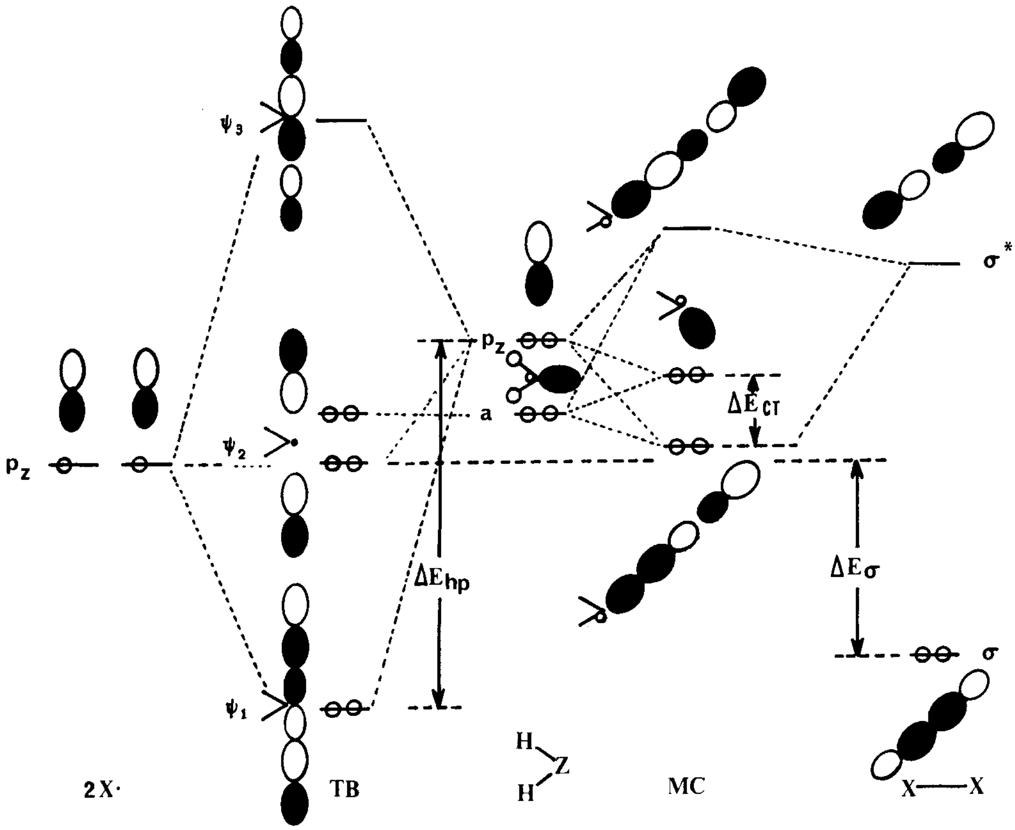


Figure 1. Correlation diagram for TBs and MCs constructed with ZH_2 fragment and p_Z-orbitals of 2X· or a σ^*-orbital of X_2 (TB will form in this case, since $\chi_X > \chi_Z$, $\Delta E_{hp} > \Delta E_{CT} + \Delta E_{\sigma^*}$). Other orbitals are omitted

yields TBs in the reaction with tellurides.[8,9,11] ^{1}H and ^{13}C chemical shifts of **1a**–**3a** and their chlorine and bromine adducts are given in Table 1. The methyl proton and carbon signals of **1c**, **1d**, **2c** and **2d** appeared ca 1·6 and 36–39 ppm downfield from those of **1a** and **2a**, respectively. Large downfield shifts were also observed for *ipso* (6·4–11·4 ppm) and *para* carbons (4·3–5·8 ppm) of the phenyl groups by the formation of TBs from **2a** and **3a**. Whereas the values for *ipso* carbons depend both on the structure of selenides and on the electronegativity of halogens, those for the *para* carbons depend only on the former.

The chemical shifts of *ipso* and *para* carbons in substituted benzenes are governed by the electronegativity and by the resonance effect of the substituents, respectively.[20] These results can be explained in the following way: (i) the amount of positive charge developed at the selenium atom is larger in chlorine adducts than in bromine adducts, (ii) the methyl group in TBs is able to neutralize the positive charge at the selenium atom more effectively than the phenyl group and (iii) the resonance effect of the selenodibromo group is not very different from that of the selenodichloro group.

Upfield shifts, although small, were observed for *ortho* carbons in TBs relative to the parent selenides, similar to the case of benzene derivatives bearing electronegative substituents. *Meta* carbons shifted downfield slightly.

As shown in Table 2, the changes in the chemical shifts in tellurane formation show a very similar trend to that in selenurane formation. Large downfield shifts were also observed for the methyl protons and the methyl, *ipso* and *para* carbons. The shifts of the *para* carbons for the tellurium compounds are smaller than those for the selenium compounds.

TB adducts contain hypervalent bonds.[19] The model of the hypervalent bond is that two ligands (X) are joined to the central atom Z through its p_Z-orbital.[19] As shown in the left-hand side of Figure 1, the bond is formed by three centres with four electrons (**3c**–**4e**). A pair of electrons are in a bonding orbital (ψ_1) and another pair in a nonbonding one (ψ_2). Since the ψ_2

orbital has the coefficients only on the ligands, the **3c—4e** bond is formed with the electron transfer from the p_Z-orbital of the central atom Z to the X ligands, resulting in the highly polar $X^{\delta-}—Z^{\delta+}—X^{\delta-}$ bond.[19]

This model is in good agreement with the observed large downfield shifts for the methyl protons and the methyl and *ipso* carbons in the TB complexes.

The larger shifts of methyl and C-1 carbons for tellurane formation relative to those for selenurane formation are due to the more polar hypervalent bonds in telluruanes compared with selenuranes. On the other hand, the downfield shifts of *para* carbons are larger in selenurane formation than those in tellurane formation. Since electrons will be transferred from the *para* carbon to the selenodihalo or tellurodihalo group through the *ipso* carbon by resonance, the resonance effect in selenuranes must be larger than that in telluruanes. Orbital interactions occur more effectively when the energy differences of the two orbitals is smaller and the overlap integral of the two becomes larger.[21] Judging from the character of p_Z-orbitals of selenium, tellurium and carbon atoms, the p_Z-orbital of selenium may interact more effectively with $p(\pi)$-orbitals of benzene rings than that of tellurium, resulting in the larger resonance effect in selenuranes.

Large downfield shifts of methyl protons and methyl, *ipso* and *para* carbons are characteristic of TB formation. The values for *ipso* carbons depend on the electronegativity of the halogens, but those for *para* carbons are independent of it.

^1H and ^{13}C chemical shifts of molecular complexes (MCs)

^1H and ^{13}C NMR chemical shifts of iodine adducts of sulphides and selenides are given in Table 3, together with those of the parent compounds. Methyl proton and carbon signals of the adduct (**1e**, 1 : 1) of dimethyl selenide (**1a**) shifted 0·42 and 7·4 ppm downfield relative to those of **1a**, respectively. These values were 0·27 and 5·0 ppm, respectively, when the NMR spectra of selenoanisole (**2a**) were measured in the presence or absence of iodine (1 : 1). Whereas a 1·9 ppm downfield shift was observed for the *para* carbon of the adduct, the *ipso* carbon signal appeared 2·0 ppm upfield relative to those of **2a**. A similar trend was also observed for diphenyl selenide (**3a**): the signals of the *ipso* and *para* carbons of the iodine adduct (**3e**) (1 : 1·25) appeared ca 1·0 ppm upfield and ca 1·0 ppm downfield, respectively relative to those of **3a**.

Similarly to the case with selenium compounds, the *ipso* and *para* carbon signals shifted upfield and downfield, respectively, although to a smaller extent (0·3–0·65 times), when NMR spectra were recorded for iodine adducts of sulphides, dimethyl sulphide, diethyl sulphide, thioanisole and diphenyl sulphide. Whereas the signals of alkyl carbons adjacent to sulphur moved downfield, those of the C-2 carbons of diethyl sulphide shifted upfield. The upfield shifts of *ipso* carbons were also observed in the phenyl groups, which are characteristic of MC formation together with relatively small shifts.

On the right-hand side of Figure 1 is presented molecular orbital correlation diagram for an MC. The extension of n-electrons of sulphides or selenides over the σ^*-orbitals of halogens stabilizes their own n-orbitals. The decrease in energy (ΔE_{CT}) in this process is the driving force for MC formation. An MC will form if χ_X is less than χ_Z, since ΔE_{CT} will be larger than $\Delta E_{hp} - \Delta E_{\sigma}$ in such cases.

Sulphides, in addition to selenides, are expected to form TBs[11] in the reaction with bromine if the electronegativity[10] of sulphur is considered ($\chi_S = 2{\cdot}44$, $\chi_{Se} = 2{\cdot}48$, $\chi_{Br} = 2{\cdot}74$). An MC structure for the bromine adduct of thiophane, however, has been proposed based on x-ray crystallography.[12]

As shown in Table 4, upfield shifts were observed for *ipso* carbons in phenyl groups and for the C-2 carbons in ethyl groups, and the signals of alkyl carbons adjacent to sulphur and of *para* carbons in phenyl groups shifted downfield when the NMR spectra of the sulphides were recorded in the presence of bromine.

The shifts are larger than those of the iodine adducts of sulphides and almost the same as those of the iodine adducts of selenides. They become larger as the measurement temperature decreases. The MC structure of bromine adducts of sulphides in solution is well established on the basis of these NMR parameters.

Coupling constants

Coupling constants between magnetic nuclei in some selenides, tellurides and their halogen adducts are given in Table 5. The formation of halogen adducts changes the structure of selenides and tellurides, which affects the couplings. ^1J(Te–C), ^2J(Te–C) and ^2J(Te–H) increase with the formation of adducts. The first two couplings depend on the electronegativity of the halogens. MC formation may decrease the ^1J(Se–C) values. The ^1J(C–H) values can be used to distinguish between the structures of adducts: the differences are ca 7 Hz on selenurane formation, compared with 3 Hz for MC formation. The difference in ^1J(C–H) values are smaller for tellurium compounds than for selenium compounds, and the values depend on the electronegativity of the halogens, but they increase when the chlorine adduct **4c** (3·9 Hz) is corrected to the bromine adduct **4d** (4·6 Hz). Coupling constants are a useful parameter for the investigation of the structure of the adducts if they are examined carefully.

Dissociation constants

As seen in Tables 3 and 4, the shifts for protons and car-

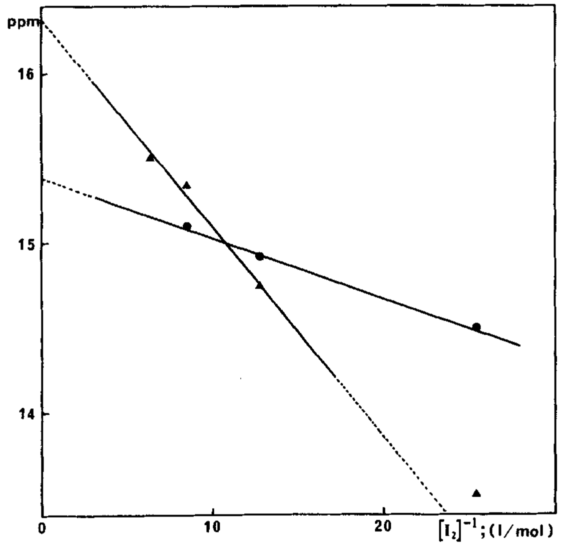


Figure 2. Estimation of the methyl carbon chemical shifts of (●) '**1e**' and (▲) '**2e**' at [**1a**] or [**2a**] = 0 and $[I_2] = \infty$

Table 7. Equilibrium constants for some iodine adducts

Compound	K (mol^{-1})	Solvent	
$Me_2S \cdot I_2$	$1{\cdot}40 \times 10^{-2}$	CCl_4	[a]
$Me_2Se \cdot I_2$	$2{\cdot}12 \times 10^{-3}$	CCl_4	[a]
	$(4{\cdot}05 \pm 0{\cdot}27) \times 10^{-3}$	$CDCl_3$	This work[b]
$PhMeSe \cdot I_2$	$(1{\cdot}67 \pm 0{\cdot}14) \times 10^{-2}$	$CDCl_3$	This work[b]
$Ph_2Se \cdot I_2$	$3{\cdot}6 \times 10^{-2}$	CCl_4	[a]

[a] Ref. 17.
[b] At 27 °C.

bons change monotonously but not linearly with the amount of iodine or bromine added. These results are easily explained by assuming that MCs are in equilibrium with the components [equations (2)–(5)].[17] To examine the structure of MCs in more detail based on NMR, the dissociation constants (K) were determined for the iodine adducts **1e** and **2e**.

The methyl carbon chemical shifts of '**1e**' and '**2e**' [δ_{MC}(**1e**) and δ_{MC}(**2e**), respectively] were estimated to be 15·38 and 16·32 ppm, respectively, as the intercepts on the ordinate (Figure 2), the abscissa being $[I_2]^{-1}$. Therefore, the values correspond to the chemical shifts under the conditions $[I_2] = \infty$ and [**1e**] or [**2e**] = 0, since the plotted values had been extrapolated to [**1e**] or [**2e**] = 0 at certain concentrations of iodine (Figure 3). The K values are calculated to be $4{\cdot}05 \times 10^{-3}$ for **1e** and $1{\cdot}67 \times 10^{-2}$ for **2e** using the estimated values (Table 7). The degree of dissociation, α, was also calculated for **1e** and **2e** under the conditions in Table 3 (0·1 M), and were 0·18 and 0·32, respectively. Thus the ratio of the concentrations of the two adducts is $(1 - 0{\cdot}18)/(1 - 0{\cdot}32) = 1{\cdot}2$. The ratio of the chemical shifts of **1e** from **1a** to **2e** from **2a** is ca 1·5. Although the conditions for the chemical shift measurements in Table 3 are not severe, the ratio of the chemical shifts (1·5) is larger than that of the concentrations (1·2), which may reflect electron transfer occurring more effectively in **1e** than in **2e** $(1{\cdot}5/1{\cdot}2 = 1{\cdot}2)$. The difference in the amount of electron transfer between **1e** and **2e** could be estimated from the chemical shifts of '**1e**' and '**2e**' from **1a** and **2a**, respectively. The value is $(15{\cdot}38 - 5{\cdot}9)/(16{\cdot}32 - 7{\cdot}2) \approx 1{\cdot}1$, which is close to

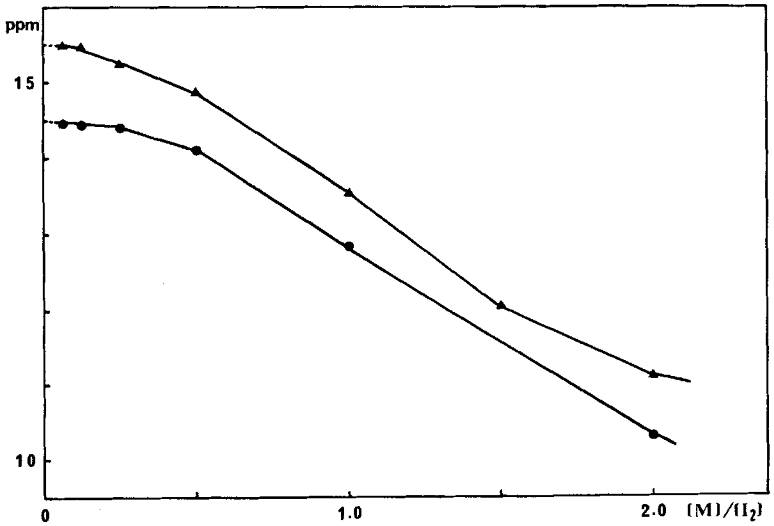


Figure 3. Estimation of the methyl carbon chemical shifts of (●) '**1e**' at $[I_2] = 4{\cdot}04 \times 10^{-2}$ M and (▲) '**2e**' at $[I_2] = 0{\cdot}157$ M

that obtained above. These results are in agreement with the donor ability of the methyl and phenyl groups, which affects the amount of electron transfer. The donor ability of a methyl group must be larger than that of a phenyl group, because the sp^2 carbon is expected to withdraw an electron more strongly than the sp^3 carbon, as represented by Taft σ_I values of $-0{\cdot}05$ and $+0{\cdot}10$ for the methyl and phenyl groups, respectively.

The ^{13}C chemical shift of **1e** from **1a** is 3·5 times larger than that of the iodine adduct of MeSMe from the parent sulphide, which could be due not only to the difference in the degree of dissociation but also to that *in the amount* of electron transfer.

The chemical shifts of 'iodine adducts (MC)' from the parent compounds are expected to be several times larger than those observed in solutions, depending on the *K* values.

^{77}Se and ^{125}Te chemical shifts

Table 6 shows ^{77}Se and ^{125}Te NMR chemical shifts of some selenides and tellurides and their halogen adducts. TB formation causes large downfield shifts (over 100 ppm). The shifts depend on the electronegativity of the halogens and on the structures of the selenides or tellurides. On the other hand, the ^{77}Se signals of the iodine adducts of selenides appear only slightly downfield (less than 10 ppm) relative to those of the corresponding selenides.

The temperature dependence of the ^{125}Te chemical shifts was also measured for **6c** and **6d**. The values were 0·17 and 0·19 ppm K^{-1} (296–319 K), respectively, which are larger than that reported for dimethyl selenide (0·025 ppm K^{-1})[22] and smaller than those for aryl diselenides (0·4 ppm K^{-1})[23] or selenocarbonyl compounds (0·34–0·48 ppm K^{-1}).[24]

Plots of the ^{125}Te chemical shifts of tellurides and their chlorine and bromine adducts *vs* the ^{77}Se chemical shifts of the corresponding selenides and the halogen adducts, which are TBs, gave straight lines with a slope of 1·74 (Figure 4). This value is very close to the reported values (1·8[25] for mainly alkyl chalcogenides with a few halogen adducts and onium ions; 1·71[26] for alkyl chalcogenides; 1·60[27] for *o*-halogenated seleno- and telluro-phenetoles). These results show that the linear relationship between ^{125}Te and ^{77}Se chemical shifts holds for a wide range of TB adducts and for tellurides and selenides.

Although larger (2·3–2·4[28]) and smaller (1·3[29]) values have also been reported for heterocyclic compounds, the plots for phenoxytellurine and phenoxyselenine and their chlorine adducts follow the straight line. The plots for their iodine adducts and **6e** and **3e′** deviate from the line (**3e′** represents $\mathbf{3a}\cdot\frac{1}{2}I_2$; the estimated value for **3e** (1 : 1) is δ 428·0 based on ^{13}C NMR). This finding is consistent with the structural differences: i.e. the iodine adducts of the tellurides are TBs but those of the selenides are MCs.

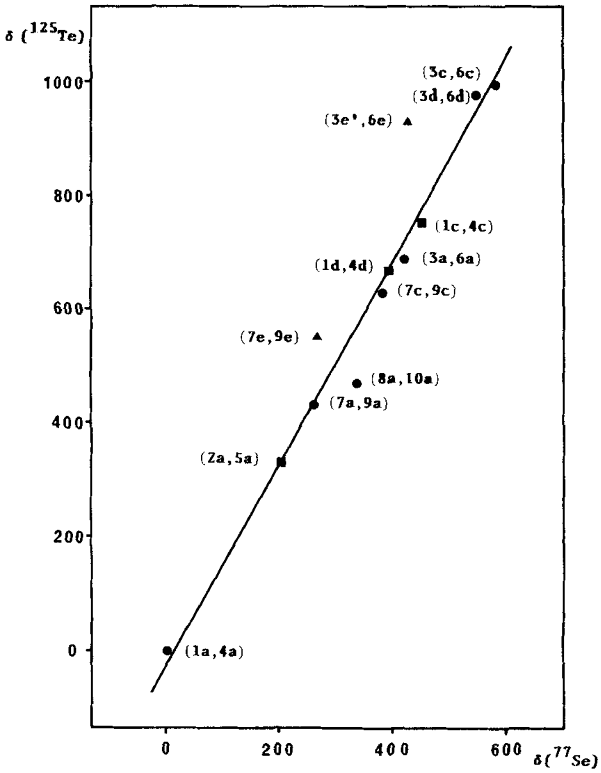


Figure 4. Plots of ^{125}Te chemical shifts vs ^{77}Se chemical shifts. (•) Data from this work; (▲) data for TB/MC; (■) literature values from Table 6

TB formation from the usual diorganyl chalcogenides causes large downfield shifts in the ^{125}Te and ^{77}Se chemical shifts, the values being very small with the formation of MCs, although upfield shifts have been reported for the formation of halogen adducts from bis(trifluoromethyl)tellurides [δ(^{125}Te) 1355 (R_2Te), 1187 (R_2TeF_2), 1118 (R_2TeCl_2), 1186 (R_2TeBr_2); $R = CF_3$][30].

The plot for telluroxanthone and selenoxanthone deviates from the straight line. This deviation, which must be a reflection of the electronic structure of the xanthones, led us to investigate the chemistry of the compounds in more detail.

EXPERIMENTAL

Spectral measurement. The ^{1}H and ^{13}C NMR spectra were obtained on a JEOL FX-60Q spectrometer operating at 60 and 15 MHz, respectively. The ^{77}Se and ^{125}Te spectra were recorded on a JNM GX-400 spectrometer (JEOL) operated at 76 and 126 MHz, respectively. Good signal-to-noise ratios were obtained by about 2000 accumulations with a 45° pulse and a pulse delay of 1·5–3·0 s, with either ^{1}H noise decoupling or the non-decoupling mode for ca 0·2 M sample solutions in a 10 mm diameter tube. The temperature of the measurement was at 22 ± 3 °C unless stated otherwise. The ^{77}Se chemical shifts were referenced to external $Se(CH_3)_2$ in $CDCl_3$ at 76 244 280 Hz in our instrument, and were precise to ± 0·1 ppm. ^{125}Te chemical shifts were referenced to external $Te(CH_3)_2$ in benzene-d_6 (ca 20%, v/v) at 126 129 960 Hz. Other conditions were almost identical with those reported earlier.[31]

Approximately 50–100 mg of sample (chalcogenides or their halogen adducts) were dissolved in 1·5 ml of chloroform-*d* or other solvents. The solutions of iodine adducts of ethers, sulphides or selenides were prepared by mixing these compounds in $CDCl_3$ (0·1 mol l^{-1} with equimolar or other molar ratio of iodine in NMR sample tubes. Bromine adducts of sulphides were prepared similarly and their spectra were recorded at low temperatures (– 10 to – 20 °C) since decomposition took place (possibly bromination).

Compounds. Dimethyl selenide (**1a**) (Tokyo Kasei), **3a**, **4a** and **6a** (Strem Chemicals) were used as received. The following compounds were prepared as described in the literature: **2a**,[7] **5a**,[8] **7a**,[32] **8a**,[33] **9a**,[34] **10a**[35] and their halogen adducts together with those[7,8,32–35] of **1a**, **3a**, **4a** and **6a**. The physical properties agreed well with those in the literature.

Method for calculating equilibrium constants. A chloroform-*d* solution of iodine ($3{\cdot}94 \times 10^{-2}$ M) was prepared using a volumetric flask. Two equivalents of a selenide, which was calculated based on the amount of iodine in 1·50 ml of the solution, were dissolved in 1·50 ml of the iodine solution. ^{1}H and ^{13}C NMR spectra were measured. Then the iodine solution (1·50 ml) was added to the selenide solution and the NMR spectra were recorded after each similar dilution. The signals of methyl protons and methyl and *para* carbons shifted downfield monotonously but not linearly when they were diluted. The values were plotted against the concentration of the selenide and the extrapolated shift values at a given concentration of iodine was obtained graphically. The estimated shift values were also obtained similarly at other iodine concentrations ($7{\cdot}87 \times 10^{-2}$, 0·118 and 0·157 M).

As shown in Equation (5), the plots of estimated values against the inverse concentration of iodine gave a straight line for **1e** and a slightly upward curvature for **2e**. These lines allow the shift value at infinite concentrations of iodine to be extrapolated as the intercepts on the ordinate. The calculated *K* values for **1e** and **2e** are $4{\cdot}03 \times 10^{-3}$ and $1{\cdot}50 \times 10^{-2}$ mol l^{-1}, respectively. Since the *K* value for **2e** is not much smaller than the I_2 concentration of $3{\cdot}94 \times 10^{-2}$ M, the *K* value was recalculated using three other points, and was $1{\cdot}67 \times 10^{-2}$ mol l^{-1}. These values were obtained by the least-squares method.

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