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Synthesis, characterisation and reactions of bis[2-(dimethylaminomethyl)-phenyl] diselenide: its structure and that of [2-(dimethylaminomethyl)phenyl]-selenium bromide

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Bis[(2-dimethylaminomethyl)phenyl] diselenide $(RSe)_2$ was obtained by the organolithium route. It underwent facile reaction with stoichiometric amounts of bromine and iodine to give the corresponding arylselenium halides RSeBr and novel RSeI in which the selenium is covalently bonded to iodine. With an excess of bromine it gave the corresponding tribromide $RSeBr_3$ but a similar reaction with iodine gave only RSeI. With diazomethane it gave the selenoether $(RSe)_2CH_2$ and with HCl the known bis(hydrochloride) $(RSe)_2$·2HCl. A catalytic conversion of alkenes into allylic acetates using $(RSe)_2$ was carried out. The compounds were characterised by elemental analyses, mass, multinuclear NMR (^1H, ^{13}C, ^{77}Se), IR, Fourier-transform-Raman spectrometry and conductance measurements. The compound $RSeBr_3$ shows evidence for the existence of Se · · · N interaction in solution and was found to equilibrate between co-ordinated and non-co-ordinated forms. The structures of the diselenide $(RSe)_2$ and its bromo derivative RSeBr were determined by X-ray crystallography. The compounds are isostructural and exhibit Se · · · N intramolecular co-ordination. The Se atom has T-shaped three-co-ordination in both structures and the five-membered chelate rings formed by the Se, C and N atoms are puckered and exist in an envelope conformation. The Se · · · N interaction in RSeBr [Se–N 2.143(6) Å] is, however, considerably stronger than that in $(RSe)_2$ [Se(1)–N(1) 2.856(3), Se(2)–N(2) 2.863(4) Å].

The application of organoselenium compounds in diverse fields has led to a rapid development of organoselenium chemistry. The use of selenium-based synthetic methods is well established in organic syntheses.[1] Other applications are in areas such as ligand chemistry,[2] in various metal–organic chemical vapour deposition (MOCVD) processes as precursors for the formation of thin films,[3] as π-electron donors in organic conductors[4] and in biochemistry.[5]

Organoselenium compounds containing a Se–Se bond are of particular interest since these are (*a*) useful reagents in selective organic synthesis,[1,6] (*b*) they are used for the preparation of arylselenium halides which are themselves important electrophilic reagents,[7] (*c*) the Se–Se bond undergoes cleavage under photochemical and thermal conditions enabling a variety of transformations[8] and (*d*) they are suggested to be intermediates[9] in a biologically important process involving glutathione peroxidase, a selenium-containing compound.

Recently a number of hybrid (Se, N) diselenides have been reported. Bis[2-(dimethylaminomethyl)ferrocenyl] diselenide[10] and the chiral analogues bis[2-(1-dimethylaminoethyl)-ferrocenyl] diselenides[11] have been synthesised. The latter has been used for the rhodium(I)-catalysed asymmetric hydrosilylation of several alkyl aryl ketones.[12] Schiff-base diselenides have been synthesised and used for the preparation of tin(IV) complexes by the electrochemical cleavage of the diselenide bond.[13] Diaryl diselenides having chiral pyrrolidine rings have been developed and used for asymmetric methoxyselenenylation and asymmetric intramolecular oxyselenenylation reactions.[14]

We have earlier reported intramolecularly stabilized organyltellurenyl halides derived from *N*,*N*-dimethylbenzylamine[15] and (*S*)-(−)-*N*,*N*-dimethyl-1-phenylethylamine[16] which are otherwise unstable. It was thought worthwhile to synthesise and study the analogous selenium derivatives for comparison. We report here the synthesis and characterisation of bis[2-(dimethylaminomethyl)phenyl] diselenide and its further reaction with halogens.

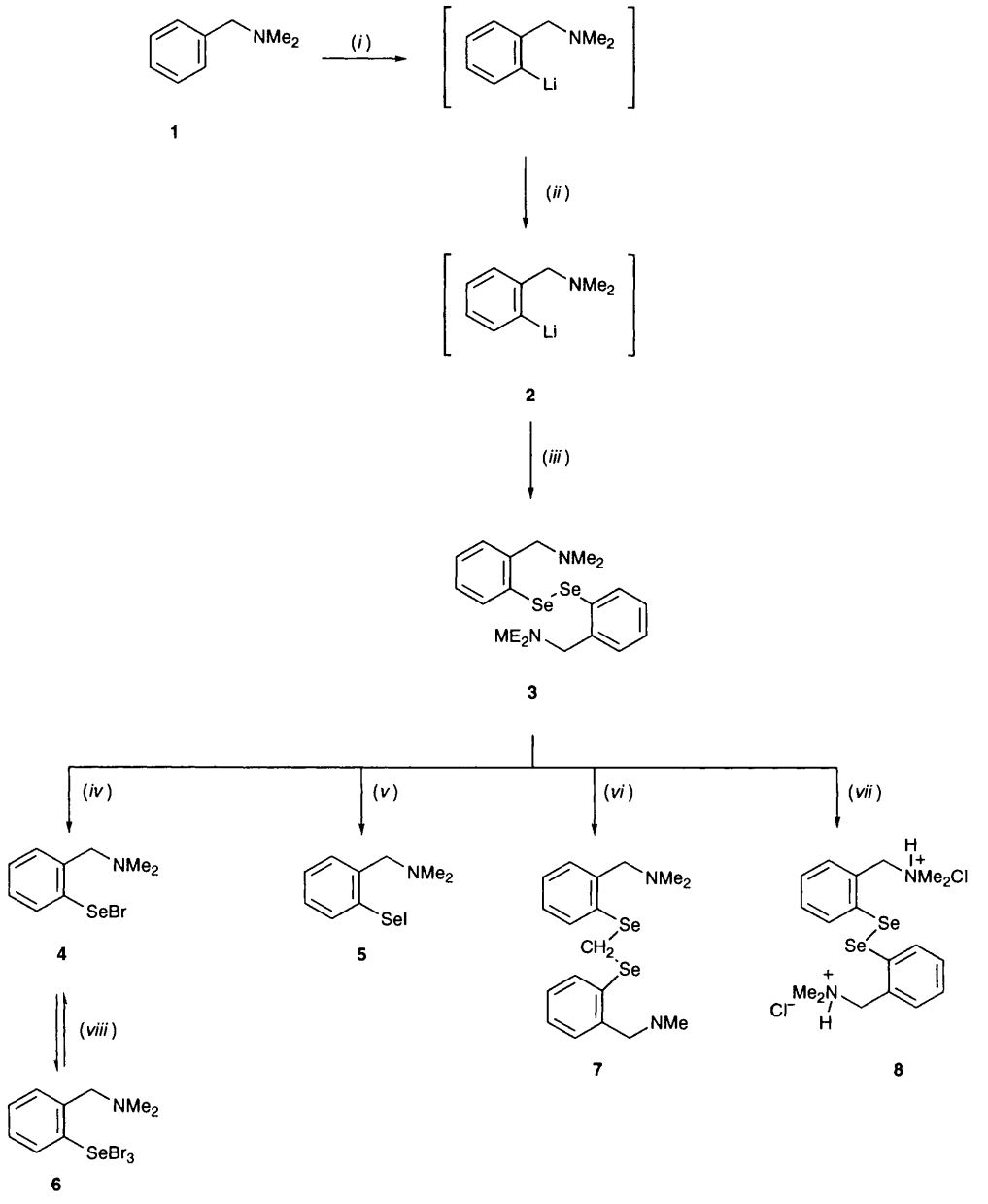
It is interesting that the hydrochloride salt of this diselenide, 2,2′-diselenobis[(*N*,*N*-dimethylaminomethyl)benzene] dihydrochloride, and some other related amino selenium compounds have recently been patented by Wilson and co-workers.[17] Those authors have tested these compounds for glutathione peroxidase (GPX) activity. However, the isolation of the compound and its characterisation remained unrealised.[18] Subsequently, the same salt was used by Engman *et al.*[19] for studying thiol peroxidase activity. Other diselenides, 2,2′-diselenobis-{*N*,*N*-di[2-(2-pyridyl)ethyl]benzylamine} and (*N*-cyclohexyl-*N*-methylbenzylamine) having internal tertiary amines, were developed by Iwaoka and Tomoda and used not only for studying the effect of the amino group on the antioxidant activity of GPX[20] but also for the catalytic conversion of alkenes into allylic ethers and esters.[21] An important factor in all cases was the stabilization of the otherwise elusive selenenic acid intermediate due to the proximate nitrogen base. In another study, it was suggested that the participation of the chalcogen atom in intramolecular interactions with heteroatoms was responsible for controlling the secondary and tertiary structures of macrocycles.[22]

Here we also describe the structures of $(2\text{-}Me_2NCH_2C_6H_4Se)_2$ and the [2-(dimethylaminomethyl)phenyl]selenium(II) bromide which will complement a better understanding of this system. The potential of the diselenide as a catalyst for the conversion of cyclic alkenes into allylic esters was also tested. The successful use of this compound for obtaining monomeric mercury selenolato complexes has been reported elsewhere.[23]

Results and Discussion

Syntheses

Bis[2-(dimethylaminomethyl)phenyl] diselenide **3** was synthesised from *o*-lithio-*N*,*N*-dimethylbenzylamine[24] and elemental



Scheme 1 (*i*) LiBu^n; (*ii*) Se; (*iii*) O_2; (*iv*) Br_2; (*v*) I_2; (*vi*) CH_2N_2; (*vii*) HCl; (*viii*) excess of Br_2

selenium (Scheme 1). Wilson *et al.*[18] attempted the synthesis and reported that the work-up gave a viscous oil which was handled as its hydrochloride salt. We have found that the unreacted amine poses a major problem in the crystallisation of the compound, but this can easily be circumvented by slight modifications of the synthetic and work-up procedures. It is desirable to use equimolar ratios of the amine, *n*-butyllithium and selenium rather than an excess of either. It is also necessary to deprotonate the areneselenolate **2** by quenching with a saturated solution of $NaHCO_3$ before it is oxidised by the passage of oxygen. A critical observation during work-up is the difficulty in extracting the diselenide from the ether layer if it is not quenched with $NaHCO_3$. It is also desirable to use peroxide-free ether for both the reaction and the work-up. Crystallisation of **3** was achieved with considerable difficulty (see Experimental section). After crystallization 79% of the solid product is obtained. There is no decomposition during the oxidation process. The yield is higher and the product appears to be more stable compared to the analogous ditelluride[15b] as there are no signs of further oxidation.

Compound **3** underwent facile bromination with a stoichiometric amount of bromine to give the corresponding monobromide **4** in nearly quantitative yield. The structure of **4**, a potential electrophile has been determined by X-ray crystallography (see below). It is known that diorgano selenides and diorgano diselenides react with iodine to give only charge-transfer adducts. Stable binary compounds between iodine and selenium are rare on account of their similar electronegativities. Du Mont *et al.*[25] have reported molecules in which bulky aryl substituents have been used to obtain stable covalent Se–I bonds. When the reaction of **3** was carried out with a stoichiometric amount of iodine a novel monoiodide **5** was obtained. A conductance measurement of the compound in dimethylformamide (dmf) showed it to be non-conducting. The UV/VIS spectrum revealed the absence of any charge-transfer bands in the region 400–700 nm and was found to be very similar to that of the analogous tellurium compound (RTeI) (R = 2-$Me_2NCH_2C_6H_4$)[15b] the crystal structure of which showed Te covalently bonded to iodine. In **5** intramolecular stabilisation leading to the formation of 10-Se-3 selane (10 valence electrons, 3 bound ligands)[26] seems to be responsible for the formation of a covalent compound rather than a charge-transfer adduct.

Treatment of compound **3** with an excess of bromine gave the

tribromide **6** which is unstable in solution and decomposes over a few days to give the monobromide. Recent studies have shown oxidative addition of bromine to selenium(II) compounds to be a reversible process.[27] A conductance measurement of the mono- and tri-bromide was carried out in dmf. While **4** was non-conducting the conductance of **6** corresponded to a 1 : 2 electrolyte, presumably due to the presence of $[\mathbf{4}]^{2+}$ and $2Br^-$. However, the tribromide is stable enough to obtain a satisfactory NMR spectrum. The corresponding reaction of **3** with an excess of iodine failed to give the triiodide and gave only **5**. Diazomethane reacted with **3** to give the selenoether **7**. However, the compound was found to be impure. Column chromatography was not effective and resulted only in increasing the impurities. Hence spectra were recorded on the oily residue obtained immediately after the reaction. Treatment of crystalline **3** with HCl gave the known salt **8**. Its spectral parameters were found to be slightly different from those reported.[18]

Spectroscopic behaviour

The ^{1}H NMR spectra of the selenium compounds are given in Table 1. At ambient temperature there was no evidence for significant Se · · · N interaction (except in the case of **6**) as no anisochronous resonances were obtained for the NMe_2 group. However, the trend in the chemical shifts of the compounds suggested some Se · · · N interaction. The NMe_2 signals spanned a range of δ 2.18–2.96 showing both up- and down-field shifts compared to the free amine (δ 2.24). An upfield shift was, however, observed only in the case of the selenoether **7** (δ 2.18) where there is a less electronegative substituent attached to Se. Downfield shifts were observed in all other cases, *i.e.* **3**–**6** where there are more electronegative atoms like Se, Br and I attached to Se compared to the free amine. The maximum downfield shift was observed in the case of **6** (δ 2.96) where selenium is bonded to the maximum number of electronegative groups. In the case of the hydrochloride salt **8** a considerable downfield shift of NMe_2 was observed due to protonation of the nitrogen atom (δ 2.77, 2.67[18]). The CH_2 signals in all cases showed downfield shifts (δ 3.42–4.54) with respect to the free amine.

For compound **6** which was partially soluble in $CDCl_3$, the ^{1}H NMR spectra were recorded in $CDCl_3$, Me_2SO and a mixture of both. In $CDCl_3$ anisochronous resonances were seen both for the NMe_2 methyl [δ 2.94 (s), 2.96 (s)] and CH_2 protons [δ 4.52 (s), 4.54 (s)]. These results indicate a strong Se · · · N co-ordination in **6** at ambient temperature. In Me_2SO the anisochronous resonances disappear and only one set of broad resonances is observed for both NMe_2 [δ 2.86 (s)] and CH_2 protons [δ 4.24 (s)]. Further, as the concentration of **6** is increased in Me_2SO low-intensity signals reappear, similar to the set obtained in $CDCl_3$. A plausible interpretation is that **6** exists in two forms having intramolecularly co-ordinated and non-co-ordinated sp^3 nitrogen. In $CDCl_3$ only the co-ordinated form exists and in Me_2SO the non-co-ordinated form exists when the solvent replaces the co-ordinated nitrogen atom. This interpretation is supported by the NMR spectrum in a mixture of $CDCl_3$ and Me_2SO where signals for both co-ordinated and non-co-ordinated forms were obtained. This type of interchanging sp^3 N–E (E = Te) interaction has also been reported by McWhinnie and co-workers.[28] For compound **7** the $SeCH_2$ occurs at δ 4.09 [^2J(Se–H) = 12 Hz] in close agreement with the literature values[29] of related compounds. After column chromatography, other species containing $SeCH_2$ were also detected by ^{1}H NMR spectroscopy.

In the ^{13}C NMR spectra (Table 2) the *ipso*-carbon resonances are found in the range δ 134.8–140.4 and the carbon resonances in the range δ 134.7–139.8. In the case of compound **5** the *ipso*-carbon resonance was not observed further suggesting a direct attachment of the heavy atom I to Se.

The ^{77}Se resonances (Table 1) of the compounds occur in the expected range.[30] In case of the monohalides **4** and **5** a large deshielding is observed with respect to the diselenide (δ 430) and the trend is RSeBr (δ 987) > RSeI (δ 818). McFarlane and Wood[31] have reported that selenium resonances are increasingly deshielded as the electronegativity of the substituent attached increases. However, no significant difference between the chemical shifts of bis(2,4,6-tri-*tert*-butylphenyl)-diselane (δ 515.8) and iodo(2,4,6-tri-*tert*-butylphenyl)selenium (δ 516.0) has been reported for the only known RSeI compound.[25a] In this particular case the authors had also observed an equilibrating phenomenon between the diselenide and its iodo derivative, however, for **5** no peaks were detected for the diselenide indicating higher stability as a result of intramolecular co-ordination. For **8** the signal obtained is slightly deshielded with respect to **3**.

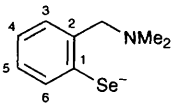
Mass spectra were recorded for representative compounds to confirm the constitution of the products. That of **8** showed the presence of the molecular ion peak along with a peak due to the loss of successive chlorine atoms. This is contrary to a report of the diselenide peak as the highest recorded molecular peak.[18] Molecular ion peaks were observed for both **3** and **4**. In the mass spectrum of **6** peaks for **3** and **4** were also observed.

Table 1 Proton and ^{77}Se NMR data in $CDCl_3$ for the hybrid (Se,N) compounds derived from *N*,*N*-dimethylbenzylamine

	δ(^{1}H)			
Compound	$N(CH_3)_2$	CH_2	Aryl protons	δ(^{77}Se)
1 Me_2NCH_2Ph	2.24 (s)	3.40 (s)	7.2 (m)	
3 (2-$Me_2NCH_2C_6H_4Se)_2$	2.26 (s)	3.55 (s)	7.09–7.13 (m) 7.77–7.81 (m)	430
4 (2-$Me_2NCH_2C_6H_4$)SeBr	2.77 (s)	3.97 (s)	7.09–7.34 (m) 8.13–8.16 (d)	987
5 (2-$Me_2NCH_2C_6H_4$)SeI	2.63 (s)	3.80 (s)	7.02–7.26 (m) 8.06–8.09 (m)	818
6 (2-$Me_2NCH_2C_6H_4$)$SeBr_3$	2.94 (s) 2.96 (s) 2.86 (s)[a]	4.52 (s) 4.54 (s) 4.24 (s)	7.36–7.50 (m) 8.22–8.25 (m) 7.26–7.33 (m) 7.96–7.98 (d)	1033
7 (2-$Me_2NCH_2C_6H_4Se)_2CH_2$[b]	2.18 (s)	3.42 (s)	7.07–7.23 (m) 7.57–7.58 (m)	294 (12)[c]
8 (2-$Me_2NCH_2C_6H_4Se)_2$·2HCl	2.77 (s)[d] 2.67 (s)[e]	4.06 (s) 3.98 (s)	7.40–7.58 (m) 7.73–7.75 (d) 7.36 (m), 7.45 (m), 7.73 (d)	477

[a] In Me_2SO. [b] δ 4.09 (s, $SeCH_2$). [c] ^2J(Se–H) in Hz. [d] In D_2O. [e] Values from ref. 18.

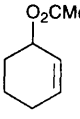
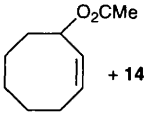
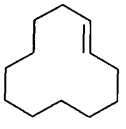
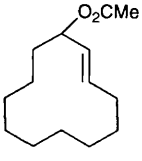
Table 2 Carbon-13 NMR data (δ) in $CDCl_3$ for the hybrid (Se,N) compounds derived from *N*,*N*-dimethylbenzylamine



Compound	$N(CH_3)_2$	CH_2	Aryl carbons (C^1–C^6)
1	44.7	63.9	128.4, 138.4, 128.4, 127.6, 126.4, 127.6
3	44.3	64.56	134.8, 139.1, 125.7, 128.0, 128.4, 131.3
4	47.1	66.18	135.9, 134.7, 125.2, 125.3, 129.2, 131.2
5	46.1	65.24	n.o., 136.1, 135.5, 126.4, 125.6, 129.2
6[a]	48.1	66.18	140.4, 136.2, 126.0, 126.8, 129.0, 130.5
7[b]	44.5	64.3	139.7, 131.2, 130.4, 129.3, 127.7, 125.7
8[c]	45.1	63.3	135.4, 135.7, 141.7, 134.9, 134.6, 133.9

n.o. = Not observed. [a] In Me_2SO. [b] δ 18.4 ($SeCH_2$). [c] In D_2O.

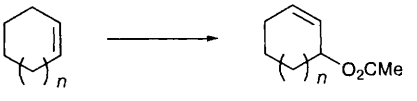
Table 3 Conversions of alkenes into allylic acetates catalysed by compound **3**

Substrate	*t*/h	Products	Isolated yield* (%)
 **9**	48	 **12**	72
 **10**	72	 **13**	57
 **11**	72	 **15**	85

* Actual yields of allylic acetates considering the amounts of alkenes recovered.

Table 4 Bond lengths (Å) and angles (°) with estimated standard deviations (e.s.d.s) in parentheses for compound **3**

Se(1)–Se(2)	2.357(1)	Se(2)–N(2)	2.863(4)
Se(1)–N(1)	2.856(3)	Se(2)–C(10)	1.933(4)
Se(1)–C(1)	1.940(4)	C(10)–C(11)	1.391(5)
C(1)–C(2)	1.379(5)	C(11)–C(12)	1.377(6)
C(2)–C(3)	1.382(6)	C(12)–C(13)	1.366(6)
C(3)–C(4)	1.362(7)	C(13)–C(14)	1.373(7)
C(4)–C(5)	1.379(6)	C(14)–C(15)	1.388(6)
C(5)–C(6)	1.382(6)	C(10)–C(15)	1.389(5)
C(1)–C(6)	1.408(5)	C(15)–C(16)	1.511(6)
C(6)–C(7)	1.499(5)	C(16)–N(2)	1.449(6)
C(7)–N(1)	1.447(5)	N(2)–C(17)	1.453(6)
N(1)–C(8)	1.451(6)	N(2)–C(18)	1.460(6)
N(1)–C(9)	1.452(7)		
Se(1)–C(1)–C(2)	122.5(2)	Se(2)–C(10)–C(11)	121.9(2)
Se(1)–C(1)–C(6)	117.8(2)	Se(2)–C(10)–C(15)	118.2(2)
C(1)–C(2)–C(3)	120.4(3)	C(10)–C(11)–C(12)	119.6(3)
C(2)–C(1)–C(6)	119.6(2)	C(11)–C(10)–C(15)	119.9(2)
C(1)–C(6)–C(5)	118.3(2)	C(10)–C(15)–C(14)	118.9(3)
C(1)–C(6)–C(7)	120.6(2)	C(10)–C(15)–C(16)	120.6(3)
C(2)–C(3)–C(4)	120.6(3)	C(11)–C(12)–C(13)	120.8(3)
C(3)–C(4)–C(5)	119.4(3)	C(12)–C(13)–C(14)	119.9(3)
C(4)–C(5)–C(6)	121.7(3)	C(13)–C(14)–C(15)	120.9(3)
C(5)–C(6)–C(7)	121.1(3)	C(14)–C(15)–C(16)	120.4(3)
C(6)–C(7)–N(1)	111.6(2)	C(15)–C(16)–N(2)	111.7(3)
C(7)–N(1)–C(8)	110.2(3)	C(16)–N(2)–C(17)	112.3(3)



Scheme 2 n = 1, 3 or 7. Conditions: compound **3** + $Cu(NO_3)_2 \cdot 3H_2O$, $Na_2S_2O_8$, molecular sieves (3 Å), $MeCO_2H$, room temperature

Catalytic reactions of compound 3

Catalytic conversions of alkenes into allylic acetates using diselenide **3** as a catalyst were carried out. The approach employed is that recently used by Iwaoka and Tomoda.[21] The reaction was performed in acetic acid solution using copper(II) nitrate as the co-oxidant and $Na_2S_2O_8$ as the oxidant. The ratio of catalyst to substrate was 1 : 10. However, for cyclohexene a ratio 1 : 20 of catalyst and substrate was used and found to be effective. The yields of the allylic acetates are listed in Table 3 and the strategy is shown in Scheme 2.

There are considerable differences in the reactivity among substrates. Cyclohexene reacted within 50 h to give good yields (72%) of the allylic acetate **12**. However, both cyclooctene and cyclododecene reacted slowly requiring nearly 72 h. The reasons for the differences can probably be attributed to the conformational factors in the intermediate η^2 complexes (or possibly η^3-allylic complexes) in 8–12-membered ring substrates.[32]

Also the reactivities of the desired allylic acetates are of importance, and low yields in the case of cyclooctene **13** (57%) can be correlated with further oxidation to diacetates **14** (28%). In this particular case the primary product is about as reactive as the starting material. No unconsumed cyclooctene was recovered at the end of the reaction. However, cyclododecene gave an essentially quantitative yield of the allylic acetate (85%, based on consumed cycloalkene). No unreacted catalyst **3** was recovered at the end of the reaction. Also, addition of molecular sieves gives better yields indicating that removal of water formed as the reaction proceeds is essential for the smooth addition of selenenic acid to the alkene.

Attempts to obtain allylic ethers (using MeOH) were unsuccessful, leading to decomposition of the catalyst **3** and extrusion of selenium.

Crystal structure of compound 3

A PLUTO[33] view of compound **3** is shown in Fig. 1. Bond distances and angles are in Table 4. The co-ordination geometry around the selenium atoms is almost identical (distorted T-shaped) with each selenium atom bonded to a selenium, a carbon and a nitrogen atom. The Se–Se distance of 2.357(1) Å relates well to the corresponding distances reported for other diselenides[34,42] (Table 5) which range from 2.29 to 2.39 Å. This distance is also close to the similar distance of 2.36 Å reported for related compounds $Se_2\{(C_5H_5)Fe[C_5H_3(CH_2NMe_2)]\}_2$[10] and

Table 5 Distances and dihedral angles in various diselenides

Compound	d(Se–Se)/Å	d(Se–C)/Å	C–Se–Se–C/°	Ref.
$Se_2\{(C_5H_5)Fe[C_5H_3(CH_2NMe_2)]\}_2$	2.36	1.90	84.8	10
Se_2Ph_2	2.29	1.93	82	34
$Se_2(C_6F_5)_2$	2.32	1.91	75	35
$Se_2(CHPh_2)_2$	2.39	1.97	82	36
$Se_2(NC_4H_8O)_2$	2.33	2.28	104.5	37
$Se_2(C_6H_4Cl\text{-}p)_2$	2.33	1.93	74.5	38
$Se_2(C_6H_4NO_2\text{-}p)_2$	2.30	1.92	87.8	39
$Se_2[C_6H_2(CF_3)_3]_2$	2.32	2.01	104.1	40
$Se_2(C_6H_2Me_3\text{-}2,4,6)_2$	2.34	1.93	128.3	41
$Se_2\{C_6H_4[CH_2NMe(C_6H_{11})_2]\}_2$	2.36	1.94	102	42

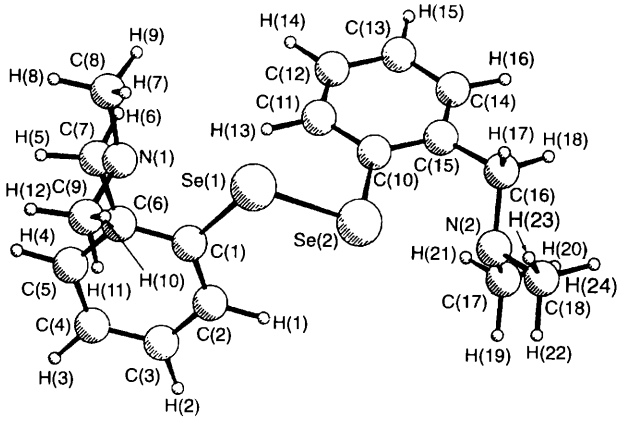


Fig. 1 Molecular structure of $(2\text{-}Me_2NCH_2C_6H_4Se)_2$ **3**

2,2′-diselenobis(*N*-cyclohexyl-*N*-methylbenzylamine).[42] The Se–C bond lengths [Se–C(1) 1.940(4), Se–C(10) 1.933(4) Å] are also in agreement with the value of 1.93 Å suggested by Pauling[43] a typical values for other diselenides.[34-42] Of particular interest in the structure is the intramolecular interaction of the amino nitrogen with selenium. The Se–N distances [Se(1)–N(1) 2.856(3), Se(2)–N(2) 2.863(4) Å] are longer than the sum of Pauling's[43] single-bond covalent radii for Se and N (1.87 Å) but significantly shorter than the sum of the van der Waals radii (3.5 Å). Also, as can be seen from Fig. 1, the nitrogen is directed towards the selenium atom. Further, the five-membered ring formed by the Se, N and C atoms is puckered. Atoms Se, C(1), C(6), C(7) are coplanar and the nitrogen is displaced by 1.03 Å from their mean plane. The torsion angle C(1)–Se(1)–Se(2)–C(10) is 93.8(2)°, in the range observed for other diselenides (74–128°). It is, however, significantly different from the value 102(1)° reported for 2,2′-diselenobis(*N*-cyclohexyl-*N*-methylbenzylamine).[42] The angles C(1)–Se(1)–Se(2) and C(10)–Se(2)–Se(1) are 101.8(1) and 101.5(1)° respectively. Further, the angles N(1)–Se(1)–Se(2) 174.0(1) and N(2)–Se(2)–Se(1) 172.7(1)° suggest an almost linear disposition of the N and Se atoms. The chelate bite angles at both the rings are also similar [N(1)–Se(1)–C(1) 73.9(1), N(2)–Se(2)–C(10) 74.2(1)°].

Crystal structure of compound 4

Very few examples of structurally characterised arylselenium halides are known.[25,44-47] The molecular structure of compound **4** is shown in Fig. 2. Table 6 gives the bond distances and angles. The structure shows a discrete monomer with eight molecules per unit cell. Compounds **3** and **4** are isostructural and a typical 10–Se–3 selane, T-shaped geometry around Se is found with strong non-valent Se · · · N interaction. Atoms Se, C(1), C(6) and C(7) are coplanar and the nitrogen atom is displaced by 0.7 Å from their plane. The three-co-ordinate Se is bonded to a carbon atom, a bromine atom and shows a N · · · Se separation of 2.143(6) Å, well within the sum of van der Waals

Table 6 Bond lengths (Å) and angles (°) with e.s.d.s in parentheses for compound **4**

C(1)–C(2)	1.38(1)	Se–Br	2.634(1)
C(1)–C(6)	1.38(1)	Se–C(1)	1.929(7)
C(2)–C(3)	1.40(1)	Se–N	2.143(6)
C(3)–C(4)	1.36(1)	C(7)–N	1.47(1)
C(4)–C(5)	1.38(1)	N–C(8)	1.49(1)
C(5)–C(6)	1.36(1)	N–C(9)	1.48(1)
C(6)–C(7)	1.50(1)		
Se–C(1)–C(2)	124.7(6)	Br–Se–N	177.6(3)
Se–C(1)–C(6)	113.8(5)	C(1)–Se–N	81.4(4)
C(1)–C(2)–C(3)	117.1(6)	C(1)–Se–Br	96.3(3)
C(1)–C(6)–C(5)	119.4(6)	C(6)–C(7)–N	106.7(6)
C(1)–C(6)–C(7)	116.9(6)	C(7)–N–C(8)	111.9(6)
C(2)–C(1)–C(6)	121.4(6)	C(7)–N–C(9)	112.1(6)
C(2)–C(3)–C(4)	121.8(7)	C(8)–N–C(9)	110.4(6)
C(3)–C(4)–C(5)	119.2(7)	C(7)–N–Se	103.5(5)
C(4)–C(5)–C(6)	121.0(7)	C(8)–N–Se	109.5(5)
C(5)–C(6)–C(7)	123.6(6)	C(9)–N–Se	109.1(6)

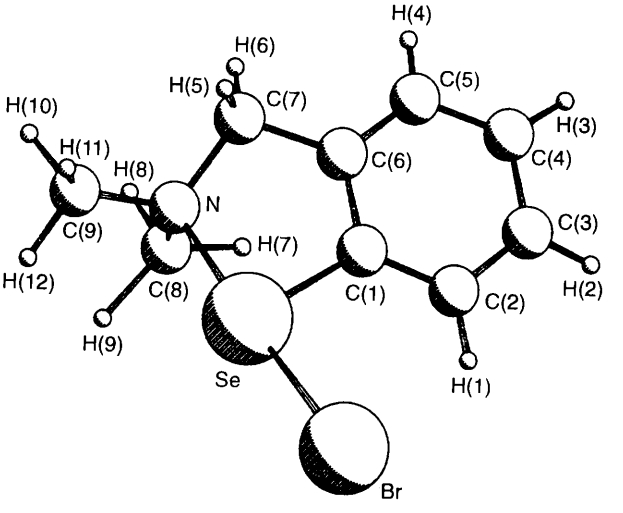


Fig. 2 Molecular structure of $(2\text{-}Me_2NCH_2C_6H_4)SeBr$ **4**

radii for N and Se (N, 1.5; Se, 2.00 Å) as reported by Pauling.[43] This distance is shorter then the Se · · · O distance reported for the *ortho*-substituted benzene derivative, $MeOC_6H_4SeBr$ [Se · · · O 2.305(19) Å].[46] Since the covalent radius of oxygen is shorter than that of nitrogen the Se · · · N interaction in **4** can be considered to be stronger than the Se · · · O interaction. This distance is also shorter than the average Se–N distance [2.859(4) Å] in the diselenide (see above), but longer than in a recently reported aryl dicopper(II) complex (2.191 Å).[47] The Se–Br distance of 2.634(1) Å is also longer than the sum of single-bond covalent radii for Se and Br (2.31 Å) but significantly shorter than the sum of the van der Waals radii (3.95 Å). The increase is probably due to the presence of a Br atom in *trans* position relative to N in the X–Se · · · N fragment. The N and Br atoms occupy the axial positions and the angle N–Se–Br is

roughly linear [177.6(3)°]. The co-ordination geometry around the Se is entirely consistent with the presence of two stereochemically active lone pairs of electrons. The Se–C(1) bond distance [1.929(7) Å] is as expected.

Experimental

Materials and methods

The reactions of 2-lithio-*N*,*N*-dimethylbenzylamine were performed under N_2 by modified Schlenk techniques. Reactions were monitored using TLC techniques. All chemicals were of reagent grade used as received. Solvents were purified by standard techniques.[48] Melting points were recorded in capillary tubes and are uncorrected. Proton (299.94 MHz), ^{13}C (75.42 MHz) and ^{77}Se (57.22 MHz) NMR spectra were recorded on a Varian VXR 300S spectrometer at the indicated frequencies. Chemical shifts are cited with respect to $SiMe_4$ as internal (^1H and ^{13}C) and Me_2Se (^{77}Se) as the external standard; s = singlet, d = doublet, t = triplet, q = quartet, br = broad. Carbon atoms are numbered as in Table 2. Elemental analyses were performed on a Carlo-Erba model 1106 elemental analyzer. Infrared spectra were recorded in the range 4000–600 cm^{-1}, neat for liquid samples between NaCl plates on a Perkin-Elmer 681 spectrometer. In the range 450–100 cm^{-1} they were recorded as solid samples in polyethylene pellets on a Bruker IFS 66V FT-IR spectrometer. The Fourier-transform Raman spectrum was recorded for a crystalline sample on a Dilor Z24 spectrometer. Excitation was achieved using an Argon laser at 514.5 nm, with a laser power of 10 mW. Only a single scan was recorded. The UV/VIS spectra in solution (chloroform) were recorded on a Shimadzu UV-260 spectrometer. Fast atom bombardment mass spectra were recorded at room temperature on a JEOL SX 102/DA-6000 mass spectrometer/data system using xenon (6 kV, 10 mV) as the FAB gas; accelerating voltage 10 kV, *m*-Nitrobenzyl alcohol was used as the matrix with positive-ion detection. In case of an isotopic pattern the value given is for the most intense peak. The GC analyses were performed on a Shimadzu GC 15-A instrument fitted with a 15% OV-17 capillary column.

Syntheses of organoselenium compounds (see Scheme 1)

Bis[2-(dimethylaminomethyl)phenyl] diselenide 3. A stirred solution of *N*,*N*-dimethylbenzylamine (1.53 cm^3, 1.37 g, 10.2 mmol) in dry diethyl ether (50 cm^3) was treated dropwise with a 1.6 mol dm^{-3} solution of *n*-butyllithium in hexane (6.4 cm^3, 10.2 mmol) *via* a syringe. On stirring for 24 h at ambient temperature a white slurry of the lithiated product was obtained. Selenium powder (0.80 g, 10.2 mmol) was added under a brisk flow of N_2 gas and stirring continued for half an hour. All the selenium was found to be consumed immediately to give compound **2**. The reaction mixture was then detached from the nitrogen line, poured into a beaker containing aqueous $NaHCO_3$ and oxygen passed at a moderate rate for half an hour. The organic phase was separated, dried over anhydrous Na_2SO_4 and filtered. The filtrate was evaporated to dryness to give a yellow oil. To this was added methanol (5 cm^3) and the solution allowed to diffuse slowly. After 2 d a precipitate was obtained. This was removed with a spatula, rinsed with ether and dried. Seeding of the remaining viscous oil with this precipitate gave crystals of compound **3** in a few hours. It was recrystallised from methanol, yield 1.7 g (79%), m.p. 74 °C [Found: C, 50.2; H, 5.65; N, 6.6% *m/z* 427 (M^+). $C_{18}H_{24}N_2Se_2$ requires C, 50.7; H, 5.6; N, 6.5%; *M*, 426]; $\tilde{\nu}_{max}/cm^{-1}$ 432m, 403w, 292s, 263m, 218m, 169s and 121m (polyethylene); FT Raman $\tilde{\nu}_{max}/cm^{-1}$ 300m, 271 and 181; *m/z* 427 (M^+, 18), 214 ($SeC_6H_4CH_2NMe_2$, 100), 171 ($SeC_6H_4CH_2$, 10), 134 ($C_6H_4CH_2NMe_2$, 12), 91 (C_7H_7, 5), 58 (CH_2NMe_2, 15) and 44 (NMe_2, 5%).

[2-(Dimethylaminomethyl)phenyl]selenium bromide 4. A cold stirred solution of compound **3** (0.511 g, 0.12 mmol) in chloroform (25 cm^3, 0 °C) was treated dropwise with a solution of bromine (0.19 g, 0.12 mmol) in chloroform (25 cm^3). The reaction mixture was stirred at 0 °C for half an hour and then allowed to come to room temperature. The solution obtained was concentrated and cooled to give a yellow crystalline product **4**. This was recrystallised from chloroform, yield 0.60 g (85%), m.p. 149 °C [Found: C, 36.6; H, 4.5; N, 4.1%; *m/z* 294 (M^+). $C_9H_{12}BrNSe$ requires C, 36.9; H, 4.1; N, 4.8%; *M*, 293]; $\tilde{\nu}_{max}/cm^{-1}$ 406w, 375w, 302m, 237w, and 197m (polyethylene); *m/z* 294 (M^+, 10), 214 ($SeC_6H_4CH_2NMe_2$, 100), 170 ($SeC_6H_4CH_2$, 10), 134 ($C_6H_4CH_2NMe_2$, 42), 91 (C_7H_7, 15), 77 (C_6H_5, 12), 58 (CH_2NMe_2, 10) and 44 (NMe_2, 5%).

[2-(Dimethylaminomethyl)phenyl]selenium iodide 5. The compound was synthesised by a method similar to that for **4** but using a solution of iodine (0.30 g, 0.12 mmol) in chloroform (25 cm^3). The reaction mixture was stirred at 0 °C for 1 h and at room temperature for 2 h. The solution obtained was evaporated to dryness to give a red solid which was recrystallised from a dichloromethane–hexane mixture to give brick red crystals of compound **5** (0.69 g, 84%), m.p. 152 °C [Found: C, 32.4; H, 3.7; N, 4.05%; *m/z* 341 (M^+). $C_9H_{12}INSe$ requires C, 31.8; H, 3.5; N, 4.1%; *M*, 341]; *m/z* 341 (M^+, 3), 214 ($SeC_6H_4CH_2NMe_2$, 100), 170 ($SeC_6H_4CH_2$, 8) 134 ($C_6H_4CH_2NMe_2$, 42), 91 (C_7H_7, 15), 77 (C_6H_5, 12), 58 (CH_2NMe_2, 15) and 44 (NMe_2, 5%).

[2-(Dimethylaminomethyl)phenyl]selenium tribromide 6. A similar experiment as described above starting with compound **3** (0.21 g, 0.50 mmol) and an excess of bromine (0.25 g, 3.0 mmol) in chloroform (25 cm^3) gave a yellow precipitate. This was filtered off, washed with additional $CHCl_3$, dried and weighed (0.34 g, 72%), m.p. 163 °C (Found: C, 24.7; H, 2.4; N, 2.8. $C_9H_{12}Br_3NSe$ requires C, 23.9; H, 2.7; N, 3.1%); $\tilde{\nu}_{max}/cm^{-1}$ 388w, 298m, 265m, 199s, 176.6m, and 138.9m (polyethylene); *m/z* 429 [$(SeC_6H_4CH_2NMe_2)_2$, 38], 294 ($BrSeC_6H_4CH_2NMe_2$, 100), 214 ($SeC_6H_4CH_2NMe_2$, 72), 198 ($SeC_6H_4CH_2NMe$, 90), 170 ($SeC_6H_4CH_2$, 18), 134 ($C_6H_4CH_2NMe_2$, 35), 91 (C_7H_7, 15), 77 (C_6H_5, 12), 58 (CH_2NMe_2, 12) and 44 (NMe_2, 15%).

2,2′-Methylenediselenobis[(*N*,*N*-dimethylaminomethyl)benzene 7. To a solution of compound **3** (0.20 g, 0.46 mmol) in dry ether at 0 °C was added an excess of diazomethane in ether. The diazomethane (2–3 cm^3) was added in portions until the evolution of N_2 was seen. After 45 min the yellow diselenide had disappeared. The reaction mixture was stirred at 0 °C for 2 h after which diazomethane was removed by bubbling nitrogen through the solution and the volatile materials were removed under reduced pressure. The resulting crude oil was chromatographed with ethyl acetate to give the desired compound as a pale yellow oil (0.08 g, 40%) (Found: C, 51.0; H, 5.1; N, 5.9. $C_{19}H_{26}N_2Se_2$ requires C, 51.8; H, 5.9; N, 6.4%).

2,2′-Diselenobis[*N*,*N*-dimethylaminomethyl)benzene]dihydrochloride 8. Diselenide **3** (0.43 g, 1 mmol) was dissolved in ethanol and treated with HCl solution and worked up following the literature procedure[18] to give a yellow solid (0.30 g, 60%) m.p. 224 °C (lit.,[18] 219 °C) [Found: C, 42.7; H, 5.3; N, 5.0%; *m/z* 507 (M^+) $C_{18}H_{26}Cl_2N_2Se_2$ requires C, 43.3; H, 5.2; N, 5.6%; *M* 500]; $\tilde{\nu}_{max}/cm^{-1}$ 420m, 395s, 349m, 299s, 265w, 218s and 164m (polyethylene); *m/z* 507(M^+, 10), 465 (M^+ – Cl, 10), 429 [$(SeC_6H_4CH_2NMe_2)_2H^+$, 80], 293 ($SeSeC_6H_4CH_2NMe_2$, 10), 230 ($SeC_6H_4CH_2NMe$, 10), 214 ($SeC_6H_4CH_2NMe_2$, 100), 170 ($SeC_6H_4CH_2$, 12), 137 ($C_6H_4CH_2NMe_2$, 60), 89 (C_7H_7, 20) and 44 (NMe_2, 10%).

Table 7 Crystal data and refinement details for compounds **3** and **4***

	3	**4**
Molecular formula	$C_{18}H_{24}N_2Se_2$	$C_9H_{12}BrNSe$
M	426.3	293.05
Crystal size/mm	0.2 × 0.15 × 0.12	0.12 × 0.13 × 0.12
a/Å	8.895(1)	7.929(1)
b/Å	22.849(4)	10.872(1)
c/Å	18.805(4)	23.399(1)
U/Å^3	3821.85	2017.04
D_c/g cm^{-3}	1.48	1.93
$F(000)$	1712	1136
μ/cm^{-1}	37.8	75
Reflections collected	2839	2984
No. reflections with $I > 3\sigma(I)$	1843	1895
No. parameters refined	272	145
R	0.031	0.062
R'	0.031	0.081
Residual electron density $(\Delta\rho)_{max}$/e Å^{-3}	0.3	2.1(1 Å from Se)
$(\Delta/\sigma)_{max}$	0.18	0.14

* Details in common: orthorhombic, space group *Pbca*; $Z = 8$; $2 < \theta < 25°$.

Catalytic reactions

Oxidation of olefins, unoptimised conditions (general procedure). The diselenide **3** (0.1 mmol) and copper(II) nitrate trihydrate (0.1 mmol) were dissolved in acetic acid (3 cm^3) and the mixture was stirred at room temperature for 0.5 h. A dark green solution was obtained which, on further stirring, gave a bluish green precipitate. Molecular sieves were added to the reaction mixture. Then an excess of alkene (1 mmol) and $Na_2S_2O_8$ (1 mmol) were added successively. After stirring for 3 d, the mixture was filtered with suction through a sintered crucible containing a layer of Celite (5–10 mm). The Celite layer was washed successively with pentane–ether (1:1, 50 cm^3) and water (50 cm^3). The organic phase was separated and the aqueous phase extracted with aliquots of pentane–ether (1:1), 3 × 50 cm^3. The combined organic phases were finally dried over anhydrous $MgSO_4$. After evaporation of the solvent, the product was purified by flash chromatography. Time was optimised for the individual reactions. Gas chromatography was performed on the crude sample to calculate the yield.

Cyclohex-2-en-1-yl acetate **12**.[49] R_2Se_2 **3** (0.46 g, 1.1 mmol), $Cu(NO_3)_2{\cdot}3H_2O$ (0.26 g, 1.1 mmol), acetic acid (3 cm^3), C_6H_{10} (2.2 cm^3, 21.8 mmol) and $Na_2S_2O_8$ (5.0 g, 21.8 mmol). Reaction time 48 h, 27 °C, (yield 72%); $\tilde{\nu}_{max}$/cm^{-1} 1738 and 1230 (neat); $\delta_H(CDCl_3)$ 5.99–5.90 (m, 1 H), 5.73–5.67 (br d, 1 H), 5.24 (br s, 1 H), 2.05 (s, 3 H) and 2.10–1.45 (m, 6 H); $\delta_C(CDCl_3)$ 170.96, 132.8, 125.95, 68.34, 28.52, 25.08, 21.54 and 19.09.

Cyclooct-2-en-1-yl acetate **13**.[50] R_2Se_2 **3** (0.10 g, 0.25 mmol), $Cu(NO_3)_2{\cdot}3H_2O$ (0.06 g, 0.25 mmol), acetic acid (3 cm^3), C_8H_{14} (0.38 g, 0.32 cm^3, 2.45 mmol) and $Na_2S_2O_8$ (0.57 g, 2.45 mmol). Reaction time 72 h, 27 °C, yield 0.236 g, (57%); $\tilde{\nu}_{max}$/cm^{-1} 1740, 1230 and 750 (neat); $\delta_H(CDCl_3)$ 5.65 (m, 2 H), 5.45 (m, 1 H), 2.24 (m, 1 H), 2.10 (m, 1 H), 2.03 (s, 3 H), 1.89 (m, 1 H) and 1.73–1.32 (m, 7 H); $\delta_C(CDCl_3)$ 170.38, 130.64, 129.64, 72.28, 35.05, 28.73, 26.28, 25.77, 23.31 and 21.33; GC showed 28.2% of the diacetate **14**.

Cyclododec-2-en-1-yl acetate **15**.[50] R_2Se_2 **3** (0.39 g, 0.91 mmol), $Cu(NO_3)_2{\cdot}3H_2O$ (0.22 g, 0.91 mmol), acetic acid (5 cm^3), $C_{12}H_{22}$ (1.67 g, 1.73 cm^3, 9.06 mmol) and $Na_2S_2O_8$ (2.1 g, 9.06 mmol). Reaction time 72 h, 27 °C, yield 1.0128 g (54.65 or 85% based on unreacted cyclododecene recovered); $\tilde{\nu}_{max}$/cm^{-1} 1740, 1230 and 750; δ_H 5.70 (ddd, 1 H), 5.38 (ddt, 1 H), 5.17 (d, apparent t, 1 H), 2.02 (s, 3 H) and 2.3–1.2 (m, 18 H); δ_C 170.14, 130.4, 129.11, 75.8, 31.97, 31.56, 25.74, 25.48, 24.78 (2C), 24.44, 24.22, 22.21 and 21.38.

Crystallography

All measurements were performed at room temperature (295 K) on an Enraf-Nonius CAD4 diffractometer using graphite-monochromated Mo-Kα radiation ($\lambda = 0.7107$ Å) employing the ω–2θ scan technique. The unit cell was determined from 25 randomly selected reflections using the automatic search index, and the least-squares routine. Two standard reflections monitored at regular intervals to check the stability of the crystal showed insignificant variation. The data were corrected for Lorentz-polarisation factors and also for absorption effects, employing the ψ-scan technique at $\chi = 90°$ (for every 10°). However, for compound **4** the final data continued to suffer from some absorption effect. The maximum and minimum values of the transmission factors for **3** were 0.999 and 0.779 and for **4** were 0.999 and 0.323 respectively.

Both structures were solved by routine heavy-atom methods (using the SHELXS 86 program)[51] and Fourier methods and refined on F by full-matrix least squares with the non-hydrogen atoms anisotropic and hydrogens with fixed thermal parameters of 0.07 Å^2 using the SHELX 76 program.[52] The molecular plots were obtained using the PLUTO program.[53] Details of the crystal and experimental parameters are given in Table 7.

For compound **3** all the hydrogens were located from the difference map whereas for **4** they were partially located from difference electron-density maps and the rest were fixed at the calculated positions. The weighting scheme employed was of the form $w = K/[\sigma^2(F) + gF^2]$ where K and g refined to 2.59 and 0.000 26 for **3** and to 2.19 and 0.002 725 for **4**. The scattering factors of Se and Br were from ref. 53, while those for the remaining atoms were as incorporated in the SHELX 76 program. All calculations were carried out on an ND-500 computer.

Atomic coordinates, thermal parameters and bond lengths and angles have been deposited at the Cambridge Crystallographic Data centre (CCDC). See Instructions for Authors, *J. Chem. Soc., Dalton Trans.*, 1996, Issue 1. Any request to the CCDC for this material should quote the full literature citation and the reference number 186/57.

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