

Account

Tuning selenium–iodine contacts: from secondary soft–soft interactions to covalent bonds

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Abstract

Selenium to iodine contacts ranging from the sum of the Se and I van der Waals distances to strong covalent bonds are reviewed with the help of recent structural determinations of compounds exhibiting Se–I distances from 384 to 244 pm, with emphasis on ‘less clear-cut’ cases, in terms of different extents of ‘hypervalent’ 3c–4e (10–Se–3) and (10–I–2) interactions. Within a continuum of Se–I interactions from undisturbed single bonds via $n \rightarrow \sigma^*(\text{Se–I})$ interactions and typical 3c–4e X–Se–I or Se–I–X systems to van der Waals contacts, any desired Se–I distances can be tuned by an appropriate choice of the particular substituents and ligands attached to the Se–I moiety. © 2001 Elsevier Science B.V. All rights reserved.

Keywords: Selenium; Iodine; Hypervalency; Supramolecular structures; Soft–soft interactions

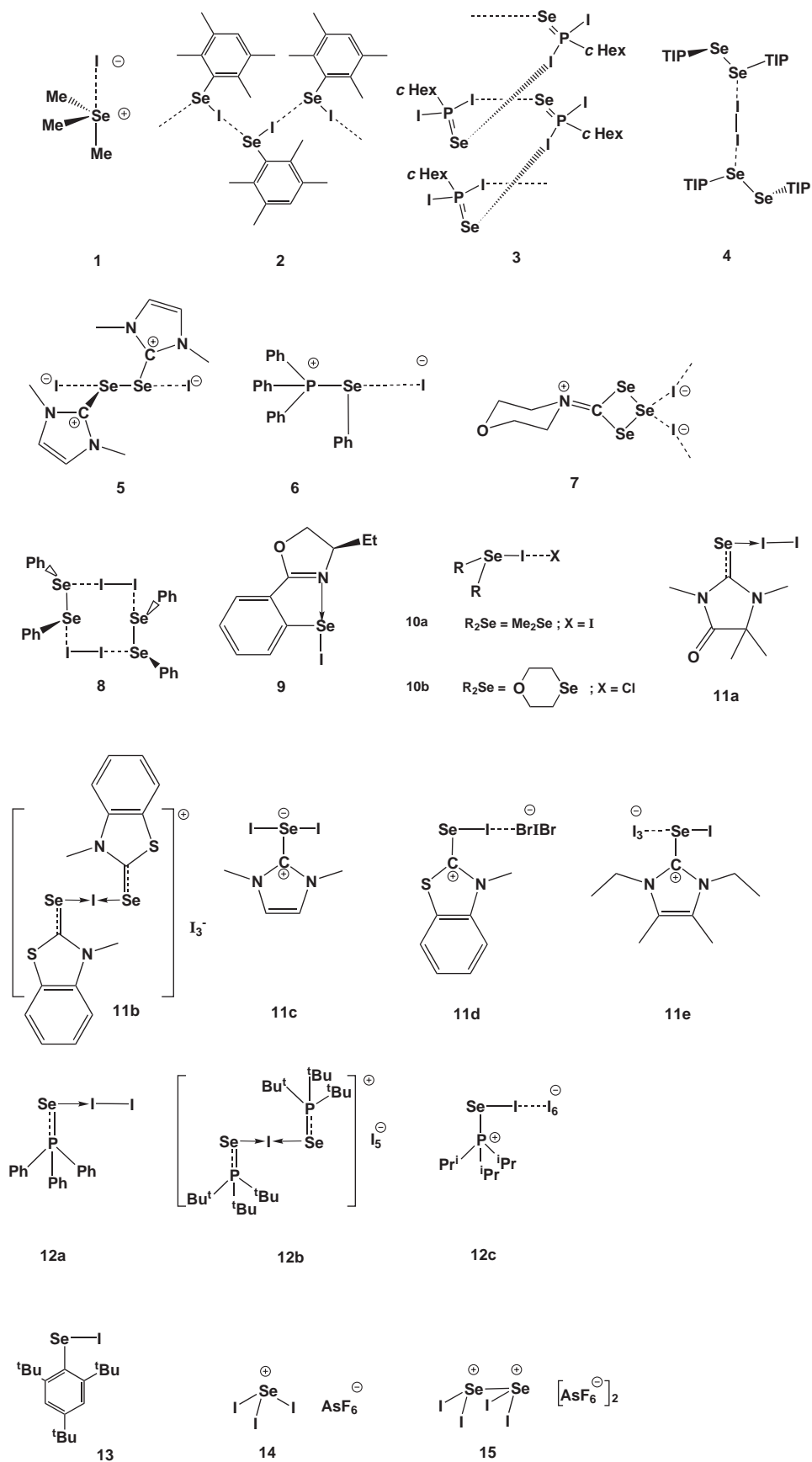
1. Introduction

For a long time, uncharged covalent selenium iodides have been regarded as non-existent [1,2]. Intermediate Se–I compounds had been postulated as early as 1953, when the impact of iodine on the rate of conversion of amorphous into crystalline selenium had been studied in context with early industrial applications of selenium [3]. It was also recognized that organic selenides may act as donors towards molecular iodine and certain iodine compounds leading to ‘charge–transfer complexes’ which are generally more stable than those of the corresponding sulfur ligands [4–6]. A major breakthrough was the isolation of stable solid $\text{SeI}_3^+ \text{AsF}_6^-$ [7]. ‘Stabilization by crystal lattice energy’ [2,7] has subsequently allowed the preparation of a large number of stable cationic Se–I (and various related cationic S–I) compounds [2]. At present, fully characterized un-

charged covalent Se–I compounds with 2c–2e bonds are still extremely rare, but basic conditions for the existence of Se–I compounds are now well-understood [2,8,9]. The observation that the in vivo deiodination of the prohormone thyroxine (T4) to the biologically active 3,5,3'-triiodothyronine (T3) implies a selenoenzyme, and the postulate of some kind of Se–I interaction in the enzyme–substrate complex [10,11] has stimulated further interest to improve understanding of the interactions of selenium nucleophiles with molecular iodine [12] or iodine compounds.

In this overview, the state of knowledge about different kinds of selenium–iodine interactions will be reviewed by using a series of selected compounds with different Se–I distances representing a ‘continuum of Se–I interactions’ ranging from about 390 pm (slightly less than the sum of Se and I van der Waals radii) to 244 pm (shorter than a single bond). Between these extremes, all kind of ‘transitions’ are known (for the selected examples see Table 1, Scheme 1). Many of the Se–I distances that are longer than those of covalent

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Scheme 1. Topology of Se-I interactions in compounds 1–15 from Table 1.

two center–two electron (2c–2e) bonds (about 252 pm) can be regarded as implying ‘valence shell expansion’ at Se or at I leading to an increase in the number of electron pairs and of the coordination number at Se (typically 10–Se-3) and/or at I (10–I-2) [13].

Although ‘sharp lines’ between different extents of Se–I overlap cannot be drawn, we will use the following idealized cases as a rough concept for the classification of Se–I interactions:

1. ‘Secondary bonds’, i.e. weak interactions that involve Se–I distances which are significantly longer than those of typical 3c–4e Se–I systems (about 265–300 pm) but shorter than the sum of the Se and I van der Waals distances (\leq about 390 pm). These Se \cdots I secondary bonds play a very important role in determining the crystal packing of the various products. Whenever the case, we will point out the importance of these interactions also during the discussion of compounds belonging to the classes II and III.
2. Typical ‘three center–four electron’ bonds, i.e. triiodide-like bonding, that involves a ‘hypervalent’ central atom with, in a symmetrical case, two bonds of bond order 0.5 each. Typical Se–I bond lengths in compounds involving the Se–I bond order 0.5 are close to 276 pm (about 265–295 pm).
3. Predominantly ‘covalent’ bonds, i.e. bonds that can be described satisfactorily by two center–two electron overlap leading to Se–I bond orders close to 1;

typical Se–I single bond distances are close to 250 pm.

2. Weak Se \cdots I interactions [secondary bonds, $d(\text{Se–I}) > 300$ pm]

The ‘nonexistence’ of solid binary Se–I compounds has been associated with the very similar electronegativity of these two elements, i.e. the lack of ion-covalence resonance energy in covalent Se–I bonds. Weak ‘soft–soft interactions’ between selenium and iodine, related to those in both elements (between selenium chains in grey selenium [344 pm] and between iodine molecules within layers of solid iodine: [348 pm]), do not depend on differences in electronegativity. Yet polar contributions like cation–anion attractions may add to intrinsic soft–soft interactions. A considerable number of structures of iodides and triiodides of selenium-containing cations exhibit Se \cdots I cation–anion contacts in the range of 390 to even less than 320 pm. Among such cations are triorganylselenonium cations (Section 2.1) [15,34], cationic di- and oligoselenides (see Sections 2.5 and 2.7; Se \cdots I 308–380 pm) [18,20,35–37], selenodiazolium and diselenodiazolium cations (Se \cdots I 342–384 pm) [38,39], seleno-substituted tetrathiofulvalene cations (Se \cdots I 364–389 pm) [40,41], a selenophosphonium cation (see Section 2.6) [19], a tris(thioseleno)-bridged molybdenum cluster cation $\{\text{Mo}_3(\mu_3\text{-S})(\mu_2\text{-SSe})_3[\text{S}_2\text{P}(\text{OEt})_2]_3\}^+$

Table 1
Se–I distances of selected compounds

Compound (Ref.)		Se–I distance (pm)	Comment
$\text{Me}_3\text{Se}^+\text{I}^-$ 1 [15]		378	Ion pair (10–Se–4)
DurSeI 2 [14]	(Intermolecular)	367	Intermolecular Se–I contacts
	(Intramolecular)	253.4	Covalent bond
c-HexP(Se)I ₂ 3 [16]		347.6	Intermolecular (10–I–2)
(TIP ₂ Se ₂) ₂ I ₂ 4 [17]		348.3	‘Iodine intercalation’
$[(\text{C}_5\text{H}_8\text{N}_2\text{-Se})_2]^{2+}$, 2I [–] 5 [18]		341.0, 333.0	Cation–anion (n[I]–> σ^* [SeSe])
Ph ₃ PSe(Ph)I 6 [19]		325.6	Ion pair (n[I]–> σ^* [SeP]) (10–Se–3)
[O(C ₂ H ₄) ₂ NCSe ₂]SeI 7 [20]	Molecule 1	318, 315	Ion chain (n[I]–> σ^* [SeSe])
	Molecule 2	308	Ion chain (n[I]–> σ^* [SeSe])
[Ph ₂ Se ₂ I–I] ₂ 8 [21]	(Shorter Se–I)	299	3c–4e (10–I–2)
	(Longer Se–I)	358	(n[I]–> σ^* [SeSe]) (10–Se–3)
<i>o</i> -Oxaz-C ₆ H ₄ SeI 9 [22]		286.2	Internally chelated 3c–4e (10–Se–3)
Me ₂ SeI–I 10a [23]		276.8	3c–4e (10–I–2)
[(BenzSe) ₂ I ⁺] ₃ [–] 11b [24]		280.0, 271.9	3c–4e (10–I–2)
C ₅ H ₈ N ₂ –SeI ₂ 11c [25]		288.6, 273.8	3c–4e (10–Se–3)
Ph ₃ PSeI–I 12a [26]		280.3	3c–4e (10–I–2)
[(<i>t</i> -Bu ₃ PSe) ₂ I] ₅ 12b [27]		276.7, 273.7	3c–4e (10–I–2)
CO–imidSeI–I 11a [28]		269.9	3c–4e (10–I–2)
O(C ₂ H ₄) ₂ SeI Cl 10b [29]		263.0	Ion pair (10–I–2)
Et/Me–imidSeI ⁺ I ₃ [–] 11e [30]		259.1, 341.7	Covalent Se–I, with cation–anion contacts (10–Se–3)
BenzSeI ⁺ I Br ₂ [–] 11d [31]		256.4	Covalent Se–I with cation–anion contacts (10–I–2)
<i>i</i> -Pr ₃ PSeI ⁺ I ₆ [–] 12c [27]		256.3	Covalent Se–I with cation–anion contacts (10–I–2)
2,4,6- <i>t</i> -Bu ₃ C ₆ H ₂ SeI 13 [32]		252.9	Covalent
SeI ₃ ⁺ AsF ₆ [–] 14 [7]		251.0, 251.3	Covalent; weak AsF \cdots I–Se contacts
Se ₂ I ₄ ²⁺ (AsF ₆ [–]) ₂ 15 [33]		243.6–245.7	Covalent (σ and π overlap)

Table 2
Structures with types of cation–anion Se–I contacts that are not covered in the following chapters

CSD ref	Compound	Literature	d(Se–I) (pm)
Cinpaq	Bis-(tetraselenatetracene)-bis(μ_2 -iodo)-tetra-iodo-di-mercury	[35]	379.7, 375.1, 366.2, 362.5, 353.2
Cofmuf10	2,1,3-Benzoselenadiazole-2,1,3-benzoselenadiazolium penta-iodide	[38]	373.7
Fobcee	Bis(μ_2 -iodo)-bis(ethyleneselenourea-Se)-tellurium)-di-iodide	[43]	371.5
Fezhat	Bis(μ_2 -iodo)-di-iodo-bis(tetramethylselenourea-Se)-di-tellurium(II)	[44]	378.3
Gastav	Di-iodo-bis(tetrahydroselenophene-Se)-mercury(II)	[45]	389.2, 387.5
Hegvuk	4-Phenyl-1,2,3,5-diselenadiazolium 4-phenyl-1,2,3,5-diselenadiazolyl tri-iodide	[47]	359.3, 355.6, 356.6, 352.3, 351.5, 351.1
Hazford	(μ_2 -Cycloheptaselenido-Se,Se')-bis(μ_2 -iodo)-hexacarbonyl-di-rhenium heptane solvate	[46]	368.5, 387.0
Iseute	Iodo-(ethylselenourea)-phenyl-tellurium	[48]	384.6
Kernea	Tetrakis(methylseleno)tetrathiafulvalenium tri-iodide	[40]	389.3, 385.2, 375.6
Kernea01	Tetrakis(methylseleno)tetrathiafulvalenium tri-iodide	[40]	383.7, 379.7, 372.7, 364.5
Ritzid	Tetraethylammonium (μ_2 -seleno)-(μ_2 -iodo-mercury)-nonacarbonyl-tri-iron	[49]	364.5
Seskuw	Bis(bis(ethylenediseleno)tetrathiafulvalene) tri-iodide	[41]	389.2
Seslad	Bis(bis(ethylenediseleno)tetrathiafulvalene) di-iodo-gold	[41]	379.7
Teocex	1,4-Bis(1,2,3,5-diselenadiazol-4-yl)benzene-iodide	[39]	374.8, 370.8
Teocib	1,3-Bis(1,2,3,5-diselenadiazol-4-yl)benzene-iodide	[39]	382.4, 374.3, 349.7
Teocoh	1,4-Bis(1,2,3,5-diselenadiazol-4-yl)benzene-iodide tri-iodide	[39]	377.5, 356.0, 352.3, 347.9, 342.7, 335.8
Oadhos	((μ_2 -Sulfido)-tris(μ_2 -sulfidoselenido)-(diethyldithiophosphato)-molybdenum) iodide	[42]	386.7, 359.0, 349.8

with 3 Se \cdots I $^-$ contacts (Se \cdots I 311.4, 316.6 and 316.7 pm) [42] and other coordination compounds with selenium ligands [43–49] (Tables 1 and 2).

A typical feature of many compounds that contain ‘rather strong’ Se–I bonds (with intramolecular distances of less than 300 pm) is their tendency to exhibit further intermolecular or cation–anion secondary Se \cdots I interactions in the 350–390 pm range.

2.1. Cation–anion contacts in triorganylselenonium iodides

In crystalline Me₃SeI (**1**), the classic compound with Se \cdots I cation–anion interaction, there are pairs of pyramidal Me₃Se⁺ cations and iodide anions. The Se \cdots I distance (378 pm) is shorter than the sum of Se and I van der Waals distances (415 pm) and the S \cdots I distance in the sulfur analogue (389 pm). The Se–I contact and one of the Se–C bonds are almost collinear i.e. the coordination environment of Se can be regarded as ψ -trigonal-bipyramidal [15]. This ion pair has also been described as a charge–transfer complex [15]. Compared with **1**, Ph₃SeI exhibits a slightly shorter Se \cdots I contact (372.2 pm) [34].

2.2. Intermolecular interactions in solid areneselenenyl iodides [11]

With iodine, dimesityldiselenide provides mesityleneselenenyl iodide (2,4,6-Me₃C₆H₂SeI (**16**)), that is slightly less predominant in solution in equilibrium with

its diselenide and iodine [32] compared with 2,4,6-*i*-Pr₃C₆H₂SeI [17], but in the solid state pure mesitylene selenenyl iodide is present. The X-ray crystal structure determination of **16** reveals that in a first approximation the selenenyl iodide may be described as a monomeric molecular compound. Intermolecularly, a network of weak Se \cdots I and I \cdots I interactions resembles the L-shaped motive of I₂ \cdots I₂ interactions within the sheets of solid iodine. Bands of soft–soft interactions are surrounded by staples of the aromatic substituents (Fig. 1). The orientation of the molecules within the crystal allows each selenium atom to approach one iodine atom (383.9 pm) from a neighboring molecule within a staple. Each iodine atom is also in contact with two iodine atoms (384 pm) from neighboring molecules of an adjacent staple. Including these interac-

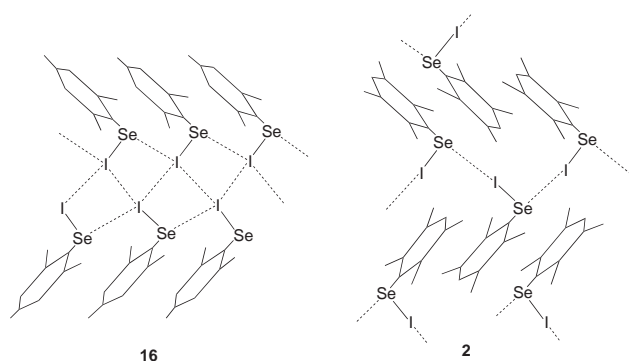


Fig. 1. Intermolecular interactions in solid 2,4,6-(CH₃)₃C₆H₂SeI (**16**) (left) and 2,3,5,6-(CH₃)₄C₆HSeI (**2**) (right).

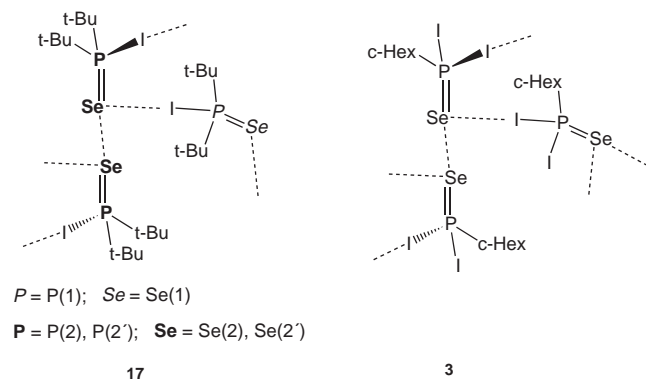


Fig. 2. Intermolecular interactions in solid **17** (left) and **3** (right).

tions, the Se environment can be classified as (10-Se-3), whereas the iodine atoms exhibit one primary (covalent) and three secondary contacts with the description (12-I-4).

The molecular structure of monomeric 2,3,5,6-Me₄C₆HSeI (dureneseleenyliodide, **2**) is closely related to that of 2,4,6-Me₃C₆H₂SeI. Its columnar structure is quite different as far as soft–soft interactions are concerned (Fig. 1). Channels of weak soft–soft interactions between the Se–I moieties of the molecules are bridged by staples of aromatic rings. These are arranged in slipped-sandwich-type pairs. The two Se–I groups of such a pair of molecules are directed to two different soft channels. These channels are made up from zigzag chains that consist of approximately linear sequences of covalent Se–I bonds and secondary Se...I contacts (10-I-2). These contacts (367 pm), however, are significantly shorter than those in **16** which correlates well with the lower coordination number 2 of iodine in **2**.

2.3. Intermolecular donor–acceptor interactions in solid iodophosphane selenides [16]

Iodine atoms adjacent to $\sigma^4\lambda^5$ -phosphonium centers behave as soft electrophiles. With iodide anions as nucleophiles, anion–cation donor–acceptor I...I interactions of I[−] with electrophilic I atoms of iodophosphonium ions R_nPI_{4−n}⁺ lead, depending on the number of iodine atoms bonded to phosphorus, to ion pairs with approximately linear P–I...I units ($n = 3$; R₃PI₂), to rings, helices and zigzag chains ($n = 2$, R₂PI₃), or to interpenetrating puckered layers and 3D networks ($n = 1$, RPI₄) [50]. This kind of cation–anion soft–soft donor–acceptor interactions leads to novel kinds of base pairing building blocks for supramolecular chemistry when soft donor and acceptor functions are expressed in one type of molecule. Because phosphane selenides R₃P=Se are known to coordinate fairly with molecular iodine, phosphane selenide (P=Se) functions were chosen to coordinate to electrophilic iodine atoms bonded to P($\sigma^4\lambda^5$).

The simplest combination of a $\sigma^4\lambda^5$ -P–I acceptor function with a P=Se donor function within one molecule is expressed in iodophosphane selenides R_nP(=Se)I_{3−n}. [16].

Iodophosphane selenide [(*t*-C₄H₉)₂P(=Se)I] (**17**) crystallizes with two independent molecules. Bond angles and distances within the two molecules of **17** are very similar; the most significant deviation between molecules I and II of **17** is the slightly larger P–Se distance in molecule II. (P1–Se1: 210.4(2) pm, P2–Se2: 212.1(2) pm). Compound **17** can be described as a helical chain-like polymer when intermolecular P–Se...I–P contacts are taken into consideration (Fig. 2).

These secondary Se...I contacts (Se1–I2' 369.04(9) and Se2–I1 384.38(9) pm) are only slightly shorter than the sum of the van der Waals radii of Se and I. However, the L-shaped geometry of the P=Se...I–P bridges, with the iodine atoms being approximately linearly coordinated, is consistent with the expectations for typical Se(donor)→I (acceptor) interactions [$< P1–I1–Se2$ 158.62(4)°, $< P2–I2–Se1'$ 167.68(4)°].

A surprising feature of the structure of **17** is the additional intermolecular contacts between the two symmetry-equivalent Se atoms Se2 and Se2' (Se2...Se2' 359.4(2) pm; symmetry operator: $-x, y+1, -z+1$); the P–Se...Se–P arrangement is not far from linear [$< P–Se–Se$ 173.73(6)°]. This additional secondary cross-link between the chains arising from PSe...IP interactions is associated with the above-mentioned slight elongation of d(P2–Se2) compared with d(P1–Se1): Se1 does not participate in intermolecular Se...Se interactions (Fig. 2). Cross-linking of the PSe...IP chains by PSe...SeP interactions leads to layers that are separated by regions containing the *t*-butyl groups from adjacent layers.

Like **17**, the related diiodophosphane selenide *c*-HexP(=Se)I₂ (**3**) contains a P=Se donor function; however, two electrophilic iodine atoms are attached to the phosphorus atom of **3**. As in compound **17**, L-shaped P–Se...I–P donor–acceptor interactions (Se...I: 347.59(8) pm) form one motif of the supramolecular structure of **3** and P–Se...Se–P contacts (361.23(14) pm) the other (Fig. 2). The Se...I distance in **3** is comparable to those in the adduct of 1,4-diselenane with triiodomethane (351.2 and 346.5 pm) [5].

Interconnection of two stacks of molecules of **3** by L-shaped P–Se...I–P bridges leads to staircase-like helices; layers are built up by connection of these helices through Se...Se contacts.

In contrast to **17**, all Se atoms of **3**, but only one I atom of each molecule participate in building up layers from helices. The stacking of these layers allows cyclohexyl groups and iodine atoms from 'terminal' P–I groups to approach in a herringbone pattern, creating domains of iodine atoms and of cyclohexyl groups from two adjacent layers.

Both iodophosphane selenides exhibit intermolecular L-shaped P–Se⋯I–P donor–acceptor interactions; these interactions, however, do not lead to base-pair-like dimers but to helices.

2.4. Iodine intercalation in a solid organic diselenide [17]

Attempts to draw crystals of the bulky areneselenenyl iodide 2,4,6-*i*-Pr₃C₆H₂SeI led to a great surprise. The selenenyl iodide, that is the predominant species in solution, decomposes upon evaporating or cooling the solution in favor of a completely different crystalline compound [(TIP₂Se₂)₂I₂] (4) [17]. It contains two equivalents of the diselenide starting material and one equivalent of iodine. This solid may be regarded as an ‘intercalation compound’ of the solid diselenide with 1/2 equivalent of iodine. The iodine molecule is in contact (348.3 pm) with the selenium atoms of two different diselenide molecules (related to each other by a center of inversion). They appear to be undisturbed by the weak interaction with iodine; their Se–Se bond length (235.3 pm) is only slightly longer than that of the non-coordinated diselenide (233.9 pm) [51]. Even the CSeSeC torsion angles are very similar (73.4° in the diselenide, 72.9° in the intercalation compound with iodine). In the solid diselenide the shortest intermolecular Se⋯Se distances between two diselenide molecules are 770.6 and 778.1 pm (Se1⋯Se'2, Se1⋯Se'1); in the *z*-axis, however, exists another Se1⋯Se'1 distance (right across a center of inversion) of 946.1 pm. This distance suggests the existence of a favorable site for iodine intercalation if the arrangement Se⋯I–I⋯Se is not completely linear. In the X-rayed intercalation compound the sum of 2 × 348.3 pm (Se⋯I) plus 272.2 pm (I–I) is indeed only about 2% longer than 946.1 pm.

2.5. I⋯Se–Se⋯I Cation–anion interactions in Se–Se-bridged dications

Starting from 4-imidazoline-2-selones and 4-imidazolidine-2-selones, salts of Se–Se bridged dications with

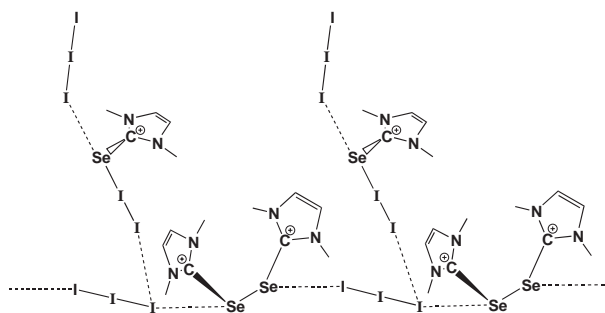
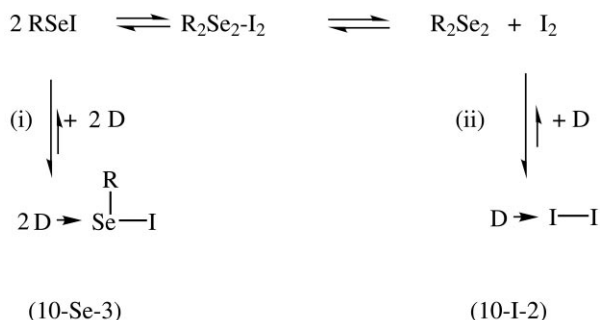


Fig. 3. Se⋯I and I⋯I interactions in solid $\{[(C_5H_{10}N_2-Se)_2]^{2+}, 2 I_3^-, C_5H_{10}N_2-Se-I_2\}$.

halide or interhalide anions can be obtained under certain conditions. In the solid salts, Se–Se bridged dications exhibit significant interactions with their anions, depending on the number and the soft nucleophilicity of the anions. An increasing extent of cation–anion interactions correlates fairly with Se–Se bond expansion as a consequence of the population of the $\sigma^*[\text{SeSe}]$ orbital. The ionic compound $[(C_5H_8N_2-Se)_2]^{2+}, 2 I^-$ (5) [18], prepared by the reduction of $(C_5H_8N_2)-SeI_2$ (11c) with tellurium, contains an almost linear I⋯Se–Se⋯I fragment ($\angle \text{ISeSe } 165.78$ and 176.00°) with Se⋯I contacts of 341.0 and 333.0 pm and an Se–Se bond of 243.4 pm. The corresponding dibromide $[(C_5H_8N_2-Se)_2]^{2+}, 2 Br^-$, obtained from selone and IBr [18], exhibits a slightly shorter Se–Se bond (240.9 pm).

In both structures, additional secondary contacts (Se⋯Br 350.6 pm and Se⋯I 362.7 pm) determine a tetracoordination at the corresponding selenium atom and the formation of chains parallel to the *b* axis.

A number of related dications with different extents of cation–anion ($n \rightarrow \sigma^*[\text{SeSe}]$) overlap have been characterized [36]. A very interesting compound containing a Se–Se-bridged dication has been obtained by reacting *N,N'*-dimethylimidazolidine-2-selone with iodine in CCl₄ in a 1:1 molar ratio. The asymmetric unit contains a iodine C.T. adduct of the selenium donor molecule and the dication $[(C_5H_{10}N_2-Se)_2]^{2+}$ balanced by two I_3^- ions. The crystal packing features chains of dications asymmetrically bridged by one I_3^- (see Fig. 3) (Se⋯I 359.0 and 349.8 pm). The bridging I_3^- interacts at one end with the terminal iodine atom of the charge–transfer adduct unit by I⋯I long–range interactions of 419.3 pm. On the basis of structural data, the I₂ adduct unit (Se–I 268.3 pm, I–I 302.5 pm) can also be seen as deriving from the donor–acceptor interaction between a $[\text{RSe-I}]^+$ fragment and a iodide atom ($n[I^-] \rightarrow \sigma^*[\text{Se-I}]$, see Section 3.4). A further contact exists between the second molecule of I_3^- and the selenium atom of the adduct unit (386.7 pm) which determines the formation of an almost linear $I(I_3^-) \cdots [\text{RSe-I}]^+ \cdots I^-$ system. This formally resembles the $X^- \cdots [\text{RSe-SeR}]^{2+} \cdots X^-$ (X = I, Br) systems discussed above, the $I(I_3^-) \cdots [\text{RSe-SeR}]^{2+} \cdots I(I_3^-)$ fragment in the chain and the linear I_4^{2-} ($I^- \cdots I-I \cdots I^-$). All these linear arrangements can be seen as 4c–4e systems in which the central acceptor is only slightly perturbed by the interaction with the terminal halides. In fact, in the present structure (see Fig. 3) the Se–Se (237.2 pm) and the Se–I (268.3 pm) bonds in the acceptors are slightly longer than those of non-coordinated diselenides (233.9 pm) [51] and typical Se–I single bonds, respectively. This structure represents the only example of a dication obtained by direct oxidation of a selonic compound with iodine. The analogous reaction of the corresponding imidazoline-2-selone derivative gives the hyperva-



Scheme 2. Dismutation and coordination equilibria of RSeI with donors D.

lent (10-Se-3) selenium compound **11c** (see Section 3.4.3).

2.6. The adduct of benzene selenenyl iodide with triphenylphosphane (6): ion pairs from selenophosphonium cations interacting with iodide anions [19]

Stabilization of an organic selenenyl iodide requires avoiding the dismutation into diselenide and iodine (Scheme 2) either by disfavoring the diselenide (see Section 4) or by favoring the species containing a Se–I bond.

Such Se–I bond stabilization with respect to the above decomposition by dismutation can be achieved by an adduct formation with an appropriate donor that coordinates with selenium leading to a 3-center–4-electron situation, which implies significant weakening of the Se–I bond. Donors that are suitable to trap RSeI disturb the equilibrium according to Eq. (i), Scheme 2, but however, will also be potential donors towards molecular iodine. D–>I–I coordination (Eq. (ii), Scheme 2) would trap iodine, disturbing the equilibrium and thus favor the decomposition of RSeI.

Arenetellurenyl iodides (R₂TeI; R = Ph [52] or TIP [53]) are known to add iodide anions to provide stable aryldiiodotellurate(II) salts; the attempted use of iodide anions (from *n*-Bu₄N⁺I[−]) as donors towards TIPSeI (see Section 2.4) led to complete decomposition of the arene selenenyl iodide providing diselenide (TIP₂Se₂) and the triiodide anion [9]. Towards iodide ions, I₂ is apparently a better acceptor than TIPSeI.

This base-induced decomposition of arene selenenyl iodides can be avoided by use of internal chelating donor functions (see Section 3.2). The first successful case of RSeI coordination with a donor, that is not internally chelating, was confirmed recently by structure determination of Ph₃PSe(Ph)I (**6**) [19]. This adduct was prepared by the addition of Ph₃P to Ph₂Se₂I₂ in dichloromethane solution. By adduct formation with Ph₃P, the (hypothetic) covalent Se–I single bond of Ph–Se–I (that should be shorter than 260 pm) is ex-

panded to 325.6 pm (Se–I bond order << 0.5) in solid **6**. The P–Se distance in **6**, however, (225.8 pm) is still longer than that in the related cation of [Ph₃PSeMe]⁺ (P–Se 220.4 pm) that is rather well separated from its [ClO₄][−] counteranion [54].

The weak Se–I interactions in solid **6** allow us to describe the compound as an ion pair [Ph₃PSe(Ph)⁺⋯I[−]], in which the electrophilic Se atom adjacent to the phosphonium center is attacked by the nucleophilic iodide anion. This *n*[I[−]]->σ*[Se–P] interaction explains the P–Se bond expansion in **6** compared with [Ph₃PSeMe]⁺[ClO₄][−] [54].

2.7. N-Morpholinocarbodiselenatoselenium iodide (7): a chain structure made from Se–I cation–anion interactions [20]

Well documented cases of Se–Se bond cleavage with molecular iodine are still rare. An early example is the reaction of bis(morphinoselenocarbonyl)triselenide with iodine [20]. In the first stage of this reaction, a (RR'C=Se–>I–I) charge transfer complex of the triselenide with iodine can be detected by UV–Vis spectroscopy. Subsequently, Se–Se bond cleavage occurs and the solid crystalline compound (*N*-morpholinocarbodiselenato)selenium(II)iodide (**7**) can be isolated [18]. Solid **7** is not an open chain selenenyl iodide [O(C₂H₄)₂NC(=Se)SeSeI], but it consists of chains from cationic moieties [O(C₂H₄)₂N=CSe₃]⁺ that are μ₂-bridged through the central selenium atom by iodide anions. The cation of **7** may be described as containing a triselenetane ring or as a Se²⁺ cation that is chelated by a [O(C₂H₄)₂N=CSe₂][−] (morpholinodiselenocarbamate) ligand. Within an isolated [O(C₂H₄)₂N=CSe₃]⁺ cation, all selenium atoms would adopt 8-electron shells (8-Se-2); the central selenium atom of the cyclic triselenide moiety, however, allows cation–anion like contacts with two μ₂-bridging iodide anions thus determining a trapezoidal coordination around it and a roughly planar structure. Within the chain structure there are two crystallographically different types of cations. Those with the longer Se⋯I contacts (318 pm)

exhibit Se–Se bond lengths of 236 and 239 pm (longer than average Se–Se distances); the other type of cations allows closer Se⋯I contacts (304, 308 pm) that correlate well with increasing expansion of the adjacent Se–Se bonds (238, 244 pm). These Se–Se bond expansions suggest site-dependent extent of the ($n[\text{I}^-] \rightarrow \sigma^*[\text{Se–Se}]$) overlap on formation of the polymeric chains of ions. Each I^- acts as a donor towards two neighboring cations in a bent $\text{Se}\cdots\text{I}^-\cdots\text{Se}$ sequence. The $\text{Se}\cdots\text{I}$ bond distances in **7** are considerably shorter than those found in the compound previously described in Section 2.1 where the $\text{Se}\cdots\text{I}$ interaction is mainly ionic. A related chain-like dithiocarbamatosenium iodide with μ_2 -bridging iodide ions (Se–I 312.4 pm) has been reported recently [37].

3. 'Typical' three center–four electron Se–I bonds [300 pm > d(Se–I) > 260 pm]

3.1. The diphenyldiselenide–iodine adduct (**8**) [21]

Addition of one equivalent of iodine to a mixture of diphenyldiselenide and di-*p*-tolylidisele- nide leads to a very broad ^{77}Se signal covering the complete range from 468 to 489 ppm, whereas the products from the single diselenides 1:1 with iodine would give resonance at 468 ppm ($\text{Ph}_2\text{Se}_2\text{–I}_2$) and 488 ppm ($p\text{-Tol}_2\text{Se}_2\text{–I}_2$) [14]. It appears that in the mixture of diselenides, iodine will be coordinated to symmetric and to unsymmetric diselenides, but iodine will also catalyze diselenide scrambling. $\text{Ph}_2\text{Se}_2\text{–I}_2$ acts as source of molecular Ph–Se–I [19,55,56], but in the solid state it exists as a dimeric diselenide–diiodine complex. One selenium atom of each diselenide is a donor towards molecular iodine (Se–I 299.2 pm, I–I 277.5 pm), whereas the other selenium atom behaves as a very weak acceptor (Se–I 358.8 pm). Formation of the 'square' dimer ($\text{Ph}_2\text{Se}_2\text{I}_2$)₂ allows donor and acceptor selenium and iodine atoms to fulfill the geometric predictions from VSEPR theory (like linear bridging 'hypervalent' (10-I-2) iodine atoms and bent bridging (8-I-2) iodine atoms). In the crystal the squares of ($\text{Ph}_2\text{Se}_2\text{I}_2$)₂ are connected by I⋯I contacts (412.7 pm) [8,21] in the range of the van der Waals distance.

3.2. Internally chelated arenesele- nyl iodides

Donors can stabilize selenenyl iodides, when competing coordination of the same donor with molecular iodine (which is a product from the decomposition of selenenyl iodides, see Scheme 2) is avoided.

Internal amino [57] or imino [22,58,59] chelate functions are a very useful tool to achieve this type of selenenyl iodide stabilization. The Se–I bonds are weakened (kinetically activated) by this type of thermody-

amic stabilization, because coordination leads to 3c–4e Se–I bonding systems (10-Se-3) involving T-shaped selenium environments (**9** and related compounds). Depending on the nature of the chelating function, Se–I distances range from 274.2 pm (in the *N*, *N*-dimethylnaphthylamine derivative [57]) to 286.1 pm (in solid **9**). 2-(4,4-Dimethyl-2-oxazoliny)benzenesele- nyl iodide [59] exhibits weak intermolecular Se⋯I contacts (372.5 pm) leading to a centrosymmetric dimer with longer N→Se bonds (213.3 pm) and shorter Se–I bonds (277.7 pm) compared to the strictly monomeric 4-ethyl-substituted isomer **9** (Se–N 207.4) [22].

3.3. Adducts of diorganylselenides with I₂, IBr and ICl

Diorganylsulfides and selenides react with molecular iodine providing charge transfer complexes [4,6]. These can also be classified as two-coordinate iodine(I) complexes with competing halogen and chalcogen ligands [12]. In general, the formation of a charge transfer complex between a sulfur or selenium donor (D) and an I–X acceptor occurs by mixing of the HOMO of the donor with the σ^* antibonding LUMO of the I–X bond. This implies a transfer of a fractional negative charge on the acceptor with a consequent lowering of the I–X bond order, i.e. the stronger the D→I–X interaction the larger the I–X bond distance with a consequent decrease of the D–I distance. In general, on the basis of the strength of these donor–acceptor interactions, three categories of adducts can be roughly identified: [18] (1) weak or medium weak molecular adducts for which the D–I bond order is lower than 0.4; (2) 'strong adducts' in which the D–I and I–X bond orders range between 0.4 and 0.6; (3) very strong adducts for which the D–I bond order is higher than 0.6, in this case the compound can be envisaged as an $[\text{D–I}]^+$ cation interacting with the X^- anion.

Diorganylselenides interact with I–X acceptors (X = I, Br, Cl) generally giving charge transfer adducts belonging to the last two categories. In 1:1 adducts the Se⋯I–X arrangement is essentially linear, the deviation from the linearity being mainly due to other interactions in the crystal packing. For example, in the selenide adducts $\text{R}_2\text{Se–I–I}$, iodine–iodine distances are in the range of those of symmetric or only slightly disturbed triiodide anions (290–295 pm); i.e. the I–I and Se–I bond orders in these approximately symmetric 3c–4e-systems are both close to 0.5 ('strong adducts'). In the tetrahydroselenophene–diiodine adduct, weak contacts between the 'outer' iodine atom (having acquired donor properties) and the Se atom of a neighboring molecule (Se⋯I 364 pm) were observed (Fig. 4) [60]. Comparing $\text{Me}_2\text{Se–I–I}$ (**10a**) [23] [d(Se–I) 276.8 pm, bond order close to 0.5] and related compounds [4,60,61] with the structures of the IBr adduct $\text{Me}_2\text{Se–I–Br}$ [62] [d(Se–I) 266.4 pm] and of the ICl

adduct $\text{O}(\text{C}_2\text{H}_4)_2\text{Se}-\text{I}-\text{Cl}$ (**10b**) [29] [$d(\text{Se}-\text{I})$ 263.0 pm] reveals that the increased polarity of the $\text{I}-\text{X}$ bonds or the lower nucleophilicity of X^- [63] correlate well with increasing $\text{Se}-\text{I}$ bond strengths. Due to its very unsymmetrical 3c–4e system, compound **10b** can also be regarded as ion pair with weak ($n[\text{Cl}^-] \rightarrow \sigma^*[\text{I}-\text{Se}]$) interaction. The crystal structure of the complexes between iodine and 1,4-diselenane ($[\text{6]aneSe}_2 \cdot 2\text{I}_2$, $\text{Se}-\text{I}$ 282.9, $\text{I}-\text{I}$ 287.0 pm, $\text{Se}-\text{I}-\text{I}$ 180.0°) [4] and 1,3,5-triselenane ($[\text{6]aneSe}_3 \cdot \text{I}_2$, $\text{Se}-\text{I}$ 273.4, $\text{I}-\text{I}$ 294.4 pm, $\text{Se}-\text{I}-\text{I}$ 179.3°) [61] show discrete molecular units of the adducts held together by $\text{Se} \cdots \text{I}$ contacts (ranging from 388.9 to 402.2 pm for $[\text{6]aneSe}_2 \cdot 2\text{I}_2$ and from 376.4 to 395.0 pm for $[\text{6]aneSe}_3 \cdot \text{I}_2$) which contribute to the crystal packing together with several $\text{I} \cdots \text{I}$ long range interactions. A slightly stronger $\text{Se} \cdots \text{I}$ [370.8 pm] secondary interaction is also a determinant for the crystal packing of $[\text{6]aneOSe} \cdot \text{I}_2$ [4]. On the other hand, the related adducts of 1,4-diselenane with triiodomethane ($\text{Se} \cdots \text{I}$ 351.2 and 346.5 pm), tetraiodoethylene ($\text{Se} \cdots \text{I}$ 341 pm) and diiodoacetylene ($\text{Se} \cdots \text{I}$ 333.6 pm) (Fig. 4) [5] are cases of weak ($n[\text{Se}] \rightarrow \sigma^*[\text{I}-\text{C}]$) interactions between uncharged molecules.

In $\text{Ph}_2\text{Se}-\text{I}-\text{Br}$ [56] [$d(\text{Se}-\text{I})$ 280.9 pm] the $\text{Se}-\text{I}$ and $\text{I}-\text{Br}$ bond orders are close to 0.5 (classifying this compound as a ‘strong adduct’) because Ph_2Se and Br^- are both comparably weak donors towards the central iodine cation.

3.4. The wide range of ‘adducts’ of selenocarbonyl functions with I_2 , IBr and ICl

Molecular coordination compounds of thio- and selenocarbonyl derivatives with iodine have been known for as long as ‘charge transfer complexes’. All the studies on the reaction between selenocarbonyl derivatives and iodine in solution have shown that the equilibrium constants of selenium ligand complexes with iodine are larger than those of related sulfur ligands [58,64] and also larger than those reported for diorganylselenides [64]. Generally, 1:1 charge transfer complexes between donors containing the selenocarbonyl function and $\text{I}-\text{X}$ ($\text{X} = \text{I}, \text{Br}, \text{Cl}$) are stronger than those reported with selenides, and the formation of the $[\text{RSe}-\text{I}]^+$ cation is more likely to occur.

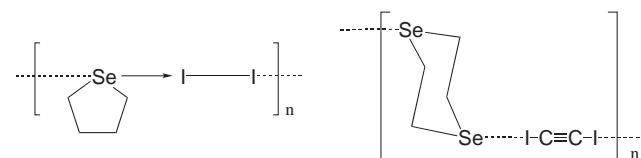


Fig. 4. $\text{Se}-\text{I}$ interactions in tetrahydroselenophene-diiiodine (left) and in the 1,4-diselenan-diiiodoacetylene adduct (right).

Starting from 4-imidazoline-2-selones and 4-imidazolidine-2-selones or related heterocyclic selenourea derivatives, slight variations in the nature of the $\text{C}=\text{Se}$ functions as well of the stoichiometry and other reaction conditions can influence the structure of the final solid products being

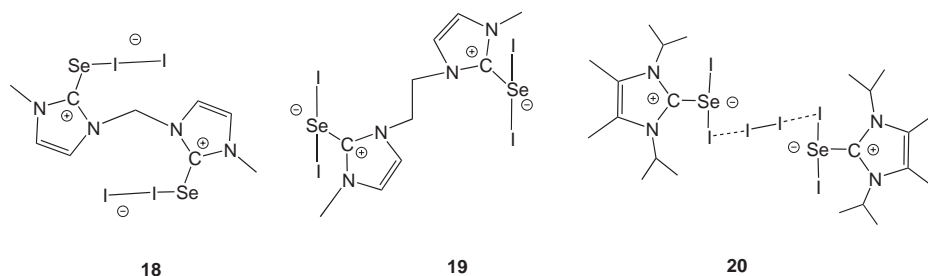
1. molecular (10-I-2) adducts $[\text{RR}'\text{C}=\text{Se} \rightarrow \text{I}-\text{I}]$ [28,65],
2. ionic (10-I-2) compounds $[(\text{RR}'\text{C}=\text{Se})_2\text{I}]^+ \text{I}_n^-$ [24],
3. molecular (10-Se-3) compounds $[\text{RR}'\text{CSeI}_2]$ [25,30,36,65,66] or
4. ionic compounds with (2c-2e) $\text{Se}-\text{I}$ bonds in cations $[\text{RR}'\text{CSeI}]^+$ that exhibit a certain degree of $\text{I} \cdots \text{I}$ $n \rightarrow \sigma^*[\text{I}-\text{Se}]$ interactions [31] or
5. ionic compounds with (2c-2e) $\text{Se}-\text{I}$ bonds in cations $[\text{RR}'\text{CSeI}]^+$ that exhibit a certain degree of $\text{I} \cdots \text{Se}$ $n \rightarrow \sigma^*[\text{Se}-\text{I}]$ interactions [30] with their polyiodide or interhalogen anions, or
6. dicationic diselenides $[(\text{RR}'\text{CSe})_2]^{2+}$ (that were covered in Section 2.5).

The latter can be formed by oxidative coupling of two $\text{RR}'\text{C}=\text{Se}$ functions with iodine [36] or other oxidants [18] or by the reduction of $[\text{RR}'\text{CSeI}_2]$ compounds with elemental tellurium [18]. A unique tetraselenium dication $[(\text{RR}'\text{CSe})_4\text{Se}]^{2+}$ with a planar Se_5 framework was isolated by electrochemical oxidation of *N*-methylbenzothiazole-2(3*H*)-selone [67].

Characteristic structural and bonding features of 3c–4e bonding systems with $\text{C}=\text{S}$ and $\text{C}=\text{Se}$ ligands have been covered recently by a comprehensive review [12].

3.4.1. Molecular (10-I-2) adducts $[\text{RR}'\text{C}=\text{Se} \rightarrow \text{I}-\text{I}]$

The reaction of 5,5-dimethyl-2-selenoximidazoline-4-one with iodine provided the first structurally characterized compound of the type $[\text{RR}'\text{C}=\text{Se} \rightarrow \text{I}-\text{I}]$ (**11a**) [28]. The $\text{Se}-\text{I}$ bond is shorter (269.9 pm) and the $\text{I}-\text{I}$ contacts are longer (296.2 pm) than in 1:1 adducts of dialkylselenides with iodine; the rather strong $\text{Se}-\text{I}$ bond in **11a** is consistent with the high stability constant of this complex in solution [68]. Subsequent structural analyses of 1:1 discrete charge–transfer complexes of selenic donors with $\text{I}-\text{X}$ ($\text{X} = \text{I}, \text{Br}, \text{Cl}$) acceptors have shown that their structural features resemble those discussed for diorganylselenide donors, the main difference being a stronger donor–acceptor interaction with a consequent further lengthening of the $\text{I}-\text{X}$ bond and strengthening of the $\text{Se}-\text{I}$ bond. As expected on passing from I_2 to IBr and ICl the interaction strength increases for a fixed donor molecule. For example the $\text{Se}-\text{I}$ bond is 272.6 pm in $\text{tzseMe} \cdot \text{I}_2$ and shortens to 268.9 pm in $\text{tzseMe} \cdot \text{IBr}$ ($\text{tzseMe} = N$ -methyl-1,3-thiazolidine-2(3*H*)-selone) [31], whereas the shortest $\text{Se}-\text{I}$ bond distance in such adducts has been observed in $\text{btseMe} \cdot \text{ICl}$ [about 262 pm] ($\text{btseMe} = N$ -methylbenzothiazole-2(3*H*)-selone) [69]. The high polarization of the $\text{I}-\text{X}$ bond (see Section 3.3) in this compound suggests that this is, like compound **10b**, a borderline case between a C.T. com-

Fig. 5. Constitution of **18–20**.

plex and an ion pair $[RSe-I]^+ \cdots [X-A]^-$ with secondary $I \cdots X$ interaction. A clear example of the latter case is represented by the 1:2 donor–acceptor adduct between btseMe with IBr **11d** which will be discussed in Section 3.4.4.

The comparison of the reactions of 1,3-dimethyl-4-imidazoline-2-selone, 1,1'-bis-(3-methyl-4-imidazoline-2-selone)methane, and 1,2-bis-(3-methyl-4-imidazoline-2-selone)ethane [25] revealed that only the CH_2 -bridged bidentate ligand gives an iodine adduct **18** (Fig. 5) with Se–I–I moieties (Se–I 271.6 and 277.6 pm, I–I 291.2 and 299.5 pm), whereas the monodentate selone and the ethylene-bridged bidentate ligand add iodine oxidatively to their selenium atoms of the $C=Se$ functions providing compounds **11c** and **19** (10-Se-3, see Section 3.4.2).

The above and further studies [24,31,36] indicate that the nature of the adducts as well as Se–I and I–I distances in the adducts depend, obviously in subtle ways, on the donor properties of the selenourea-related function of the particular $RR'C=Se$ ligands and on steric, conformational and lattice effects.

3.4.2. The ionic (10-I-2) species $[(RR'C=Se)_2I]^+$ in compound (**11b**)

The difference in energy between $[RR'C=Se \rightarrow I]$ and other kinds of iodine adducts is small. In the case of *N*-methylbenzothiazole-2(3*H*)-selone, one equivalent of iodine provides a molecular adduct in dichloromethane solution [70]; crystallization however, leads to a ionic compound **11b** of the type $[(RR'C=Se)_2I]^+ I_3^-$ [24]. This compound is the only one reported in the literature featuring a two coordinated iodine(I) complex with two donor molecules containing selenocarbonyl groups. The X-ray crystal structure shows two molecules of btseMe linearly coordinated to a central I^+ ion to give a slightly asymmetric Se–I–Se arrangement [Se–I 280.0, 271.9 pm, Se–I–Se 178.0°]. The unit cell contains two of these cations centrosymmetrically related and balanced by two I_3^- ions. Other compounds featuring the $RSe-I^+-SeR$ system will be discussed later (see Section 4.2).

3.4.3. Molecular (10-Se-3) compounds $[RR'CSeI_2]$

Molecular compounds $[RR'CSeI_2]$ containing hypervalent selenium (10-Se-3) and featuring the I–Se–I system may be formally regarded as adducts of the SeI_2 molecule (acceptor) with a nucleophilic carbene ligand as the donor. An alternative description would be the inner salt of an organyldiiodoselenate(II) $RR'C^+-SeI_2^-$. First structurally known examples of this kind were products from the iodination of 1,3-dimethyl-4-imidazoline-2-selone (**11c**) [25], of 1,2-bis-(3-methyl-4-imidazoline-2-selone)ethane (**19**) [25] and of 1,3-diisopropyl-4,5-dimethyl-4-imidazolin-2-selone [65]. The I–Se–I fragments for the three compounds are asymmetric and roughly linear [I–Se–I ranging from 175.4 to 178.6 pm] and the $CSeI_2$ moieties adopt T-shaped geometries (Se–C single bonds, Se–I bond orders close to 0.5, like those of internally chelated selenenyl iodides). In **11c** and **19** the Se atom shows roughly square planar coordination if the contact $Se \cdots I$ ($x, 1/2 - y, 1/2 + z$) 354.8 pm, which determines chain formation in the direction of c in **11c**, and the contact $Se \cdots I$ ($-x, 1 - y, 1 - z$) 364.5 pm in the direction of c in **19**, are considered. In **19**, as a consequence of these weak $Se \cdots I$ interactions, a four-membered square-planar ring with the $-SeISeI-$ sequence are formed through a symmetry center.

Compounds **11c**, **19**, and related I–Se(R)–I (10-Se-3) compounds as well as adducts $R_nSe-I-I$ (10-I-2) can be considered as pseudo-triiodides. In fact, these three systems show a strict analogy in their vibrational behavior particularly in their Raman spectra in the low frequency region. Generally it is very difficult to distinguish between the three classes of compounds using only the Raman technique [25].

With 1,3-diisopropyl-4,5-dimethyl-4-imidazoline-2-selone and a slight excess of iodine an adduct (**20**) of the composition $(RR'CSeI_2 \cdot 0.5 I_2)$ was obtained (see Fig. 5). In this centrosymmetric compound, an iodine molecule (I–I 276.6 pm) is intercalated (I \cdots I 345.1 pm) between two T-shaped $CSeI_2$ functions [30]. The Se–I bonds that participate in I_2 intercalation are longer (285.1 pm) than the terminal ones (275.6).

From 1,1'-bis-(3-methyl-4-imidazoline-2-selone)-methane with iodine bromide, a solid compound

containing disordered molecules with T-shaped CSeI_2 functions (unlike compound **18**) and with T-shaped Br-Se(C)-I functions in the same crystal was isolated. From 1,2-bis-(3-methyl-4-imidazoline-2-selone)ethane with iodine bromide, a solid compound containing a molecular species **21** with two (non-disordered) T-shaped Br-Se(C)-I functions (related to compound **19**) was recently characterized by a crystal structure determination [66]. Interestingly in **21** the Se–I bond distances (260.6, 262.9 pm) are shorter than the Se–Br ones (289.7, 276.6). Therefore the compound can be regarded as being derived from donor–acceptor interactions between Br^- anions and the Se atoms of $[\text{Se-I}]^+$ fragments.

3.4.4. Iodoselenocarbenium salts exhibiting $\text{I}\cdots\text{X}$ cation–anion interactions (10-I-2): (**11d**)

As mentioned in Section 3.4.1, when the interaction between a selenium donor molecule and the linearly coordinated I-X ($\text{X} = \text{I}, \text{Br}, \text{Cl}$) acceptor is particularly strong, a remarkable fractional negative charge is induced on the terminal X atom which can behave as donor towards another I-X acceptor molecule [28,31,70]. In the limit case an ionic $[\text{RSe-I}]^+\cdots[\text{X-I-X}]^-$ system can be formed. This situation is well documented by compound **11d** in which the first IBr molecule is so strongly bonded to the selenium atom that the Se–I distance (256.4 pm) can be formally regarded as a covalent single bond slightly perturbed by anion(donor)–cation(acceptor) interactions (see Section 4.3). On the other hand, the elongation of the IBr molecule to the value of 312.9 pm and the strong interaction of Br^- with a second IBr molecule leads to the formation of an asymmetric IBr_2^- anion [I-Br 280.3 and 264.5 pm] similar to that reported for CsIBr [I-Br 278.0 and 262.0 pm]. In this case, on the basis of the structural features, the ionic formulation $[\text{RSe-I}]^+\cdots[\text{Br-I-Br}]^-$ is in accordance with FT-Raman spectra in the low frequency region, which shows peaks typical of authentic IBr_2^- ions. The same *N*-methylbenzothiazole-2(3*H*)-selone (btseMe) donor molecule gives a 1:2 molecular adduct with I_2 (**22**) (see Fig. 6). The structural features of the resulting $\text{btseMe}\cdots\text{I}_2\cdots\text{I}_2$ bent shaped compound do not agree with ionic pair description as for $\text{btseMe}\cdot 2\text{IBr}$. In fact, in $\text{btseMe}\cdot 2\text{I}_2$ the

strong interaction with the selenium atom [Se-I mean value 267.4 pm] lengthens the I-I bond to 303.0 pm (mean value). The further interaction of the terminal iodine atom of the Se-I_2 system with the second I_2 molecule [$\text{I}\cdots\text{I}_2$ mean value 319.2 pm] is not strong enough to form a triiodide ion. This system can be better described as $\text{RSe-I}^+\cdots\text{I}^-\cdots\text{I}_2$ which resembles that observed in ‘V-shaped’ pentaiodides in which an I^- ion binds two low perturbed diiodine molecules $\text{I}_2\cdots\text{I}^-\cdots\text{I}_2$. The case of $\text{btseMe}\cdot 2\text{I}_2$ (**22**) resembles that of $(\text{Me}_2\text{N})_3\text{PSe}\cdot 2\text{I}_2$ (**23**) which will be discussed in Section 3.5.3.

3.4.5. Iodoselenocarbenium salts exhibiting $\text{Se}\cdots\text{I}$ cation–anion interactions (10-Se-3): (**11e**)

When the site of the nucleophilic $n-\sigma^*$ [Se-I] attack of a polyiodide anion is the Se atom of a $\text{RR}'\text{CSeI}^+$ cation, linear asymmetric $3c-4e$ $\text{I-Se}\cdots\text{I}_n$ moieties (10-Se-3) are generated [30]. Like in the previous case, Se–I bond distances/bond strengths in the cations depend on the nucleophilicity of the anion.

3.5. Adducts of phosphane selenides with iodine

The reactions of phosphane selenides with iodine [71] are in many respects related to those of selenocarbonyls (see Section 3.4.5), however, 1,1-additions of iodine to the selenium atom of P=Se double bonds leading to (10-Se-3) species have not yet been observed.

3.5.1. Molecular compounds with hypervalent iodine(10-I-2): (**12a**)

The reaction of tri-*t*-butylphosphane selenide with one equivalent of iodine leads to a solid product that contains both a molecular 1:1 adduct ($t\text{-Bu}_3\text{PSe-I-I}$) and a ionic species ($t\text{-Bu}_3\text{PSe}_2\text{I}^+\text{I}_3^-$) in the same crystal [9,22]. Both kinds of species exhibit Se–I distances of about 276 pm that indicate bond orders of 0.5. In other molecular adducts $\text{R}_3\text{PSe-I-I}$, more electron-releasing substituents (like dialkylamino groups) lead to stronger Se–I bonds which correlate with decreasing bond orders within the P-Se and within the $\text{I}\cdots\text{I}$ moieties. More electron-withdrawing substituents (like $\text{R} = \text{Ph}$, **12a**) have the opposite effect on the P-Se-I-I moieties [16,26].

3.5.2. Ionic compounds with hypervalent iodine (10-I-2): (**12b**)

The solid 1:1 adduct of $i\text{-Pr}_3\text{P=Se}$ with I_2 is ($i\text{-Pr}_3\text{PSe}_2\text{I}^+\text{I}_3^-$). The reaction of tri-*t*-butylphosphane selenide with 1.5 equivalents of iodine leads to a solid product that contains pairs of $(t\text{-Bu}_3\text{PSe})_2\text{I}^+$ cations intercalated between corrugated layers of the polymeric I_5^- anions. The $(t\text{-Bu}_3\text{PSe})_2\text{I}^+$ cation pairs are well separated from the pentaiodide layers; they exhibit, however, pairs of $\text{Se}\cdots\text{Se}$ contacts within the cation pairs [27].

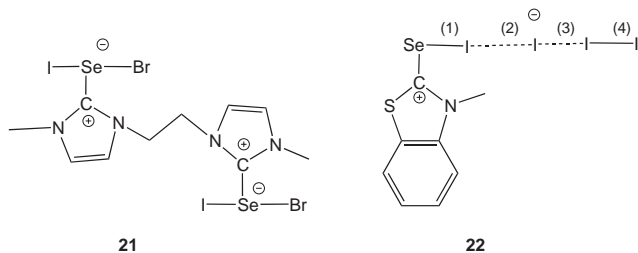
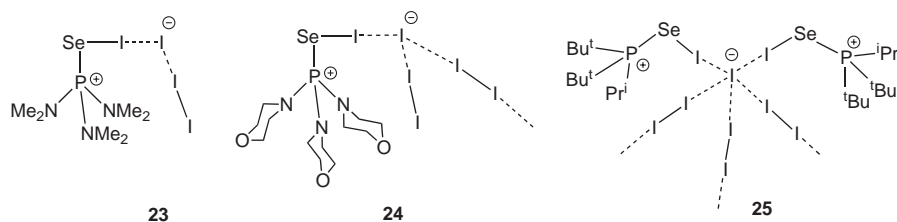


Fig. 6. Constitution of **21** and **22**.

Fig. 7. Cation–anion contacts in **23**–**25**.

3.5.3. Iodoselenophosphonium salts with cation–anion contacts; (**12c**)

With two or more equivalents of iodine, phosphane selenides can furnish iodoselenophosphonium salts $R_3PSeI^+I_n^-$ that exhibit certain degrees of cation–anion $I \cdots I$ interactions. Reacting $(Me_2N)_3PSe$ and $(Morph)_3PSe$ (Morph = morpholino) with two equivalents of iodine provides the solid compounds $(Me_2N)_3PSeI_4$ (**23**) and $(Morph)_3PSeI_5$ (**24**) [12]; *i*- Pr_3PSe and *t*- Bu_2i - $PrPSe$ with excess iodine provides *i*- Pr_3PSeI_7 (**12c**) and *t*- Bu_2i - $PrPSeI_7$ (**25**) [27]. These compounds are examples of $[R_3PSeI]^+$ cations with different extents of cation–anion interactions. The nucleophilicity of the iodide anion is suppressed by its coordination with increasing amounts of iodine; the decreasing nucleophilicity ($I^- \cdot I_2$, $2I^- \cdot 3I_2 > 2I^- \cdot 5I_2$) correlates with increasing covalent Se–I bond orders, indicated by Se–I distances [**23** and **24**: Se–I about 259 pm, **12c** and **25**: about 256 pm] that are influenced by the different extents of $(n[I_x^-] > \sigma^*[Se-I])$ overlap.

The slight steric differences between the alkyl groups of the cations lead to quite different far orders of their polyiodide anion structures. In solid *t*- Bu_2i - $PrPSeI_7$ (**25**) (Fig. 7), one iodide anion bridges two of the *t*- Bu_2i - $PrPSeI^+$ cations and is in further contact with three I_2 molecules; the other I^- anion is in contact with five I_2 molecules [27]. In solid **12c**, one I^- is surrounded by two cations and four I_2 molecules (when one 368 pm distance is included), two (5-coordinated) I^- are in contact with one cation and four I_2 molecules, and the fourth I^- is surrounded by five I_2 molecules [27].

4. Predominantly covalent Se–I single bonds [$d(Se-I) < 260$ pm]

4.1. Uncharged compounds with covalent Se–I single bonds

The lack of polarity, i.e. of ion-covalence resonance energy, in covalent Se–I bonds may explain, that there is no intrinsic tendency to make covalent Se–I bonds from Se–Se and I–I bonds. This argument provides, however, not an intrinsic reason why in solution Se–Se bonds and I–I bonds should avoid reacting with each

other in a kind of statistic dismutation providing certain amounts of Se–I bonded species in equilibria. If a particular Se–Se bond would be higher in energy than an average Se–Se bond, for instance, due to a sterically enforced less favorable conformation of the X–Se–Se–X moiety, the dismutation of this Se–Se bond with molecular iodine forming two Se–I bonds will be favored by the relief from the above strain. The expectation of such a slight thermodynamic destabilization of strained diselenides, i.e. the hypothesis of ‘steric activation’ of homonuclear single bonds [8,9] gave reason to study the reactions of various bulky diselenides with molecular iodine.

Introducing two alkyl substituents into the *ortho*-positions of diaryldiselenides changes their behavior towards iodine completely: ^{77}Se -NMR spectra indicates the presence of areneselenenyl iodides $Ar-Se-I$ in solution [14,32] accompanied by minor amounts of the unconsumed diselenides. Increasing α -branching of the *ortho* and *para* substituents of 2,4,6- $R_3C_6H_2$ groups (from R = methyl to ethyl, isopropyl, *tert*-butyl) improves the position of the equilibria slightly in favor of the Se–I compounds [14]. From such an equilibrium mixture in solution, the strictly monomeric areneselenenyl iodide 2,4,6-*t*- $Bu_3C_6H_2SeI$ (**13**) was obtained as crystalline compound [32]. The Se–I bond length of 252.9 pm meets the sum of covalent radii of selenium and iodine. The *ortho-tert*-butyl groups lead to a rather typical distortion of the aromatic ring system; they also force the iodine atom (i.e. the Se–I bond) out of the aromatic ring plane.

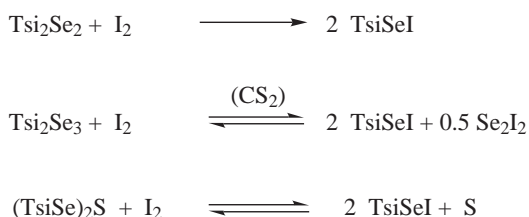
Attempts to draw crystals of the related slightly less bulky areneselenenyl iodide 2,4,6-*i*- $Pr_3C_6H_2SeI$ led to the intercalation compound **4** from two equivalents of the diselenide and one equivalent of iodine (see Section 2.4, [17]).

The structures of bis(2,4,6-triisopropylphenyl)diselenide, of its iodine intercalation derivative **4**, and of less bulky bis(2,4,6-trimethylphenyl)diselenide (dimesityl)diselenide do not indicate significant ‘steric activation’ of the Se–Se bonds. Solid mesitylene selenenyl iodide exhibits, however, extended intermolecular interactions (see Section 2, [14]).

All diaryldiselenide–iodine reactions studied provide equilibrium mixtures in solution. Obviously, the bulki-

ness of these *ortho*-disubstituted aryls is not sufficient to force diaryldiselenides into really unfavorable conformations. A molecule with such conformation is Tsi_2Se_2 (Tsi = tris(trimethylsilyl)methyl). The Se–Se bond of this crowded *trans*-dialkyldiselenide is significantly longer than Se–Se bonds of common diorganyldiselenides [9,72]. Thus Tsi_2Se_2 accepts Se–Se bond breaking by molecular iodine as relief from severe steric strain. The cleavage of the Se–Se bond of Tsi_2Se_2 with iodine provides (Scheme 3) pure black–violet TsiSeI in quantitative yield (crystal data is not available) [73]. This monomeric selenenyl iodide allowed studies on the reactivity of a well-defined molecule with a Se–I bond [74].

The Se–I bond of TsiSeI is reactive towards both, elemental sulfur and elemental selenium [74]. In each case, the formation of iodine is observed while Se–Se and Se–S bond formation lead to the trichalcogenides $(\text{TsiSe})_2\text{Se}$ and $(\text{TsiSe})_2\text{S}$. The reactions, however, are incomplete and lead to equilibria. This was confirmed by verifying the reverse reactions, i.e. cleavage of the trichalcogenides with iodine. The cleavage of $(\text{TsiSe})_2\text{S}$ with iodine leads to TsiSeI , sulfur, and minor amounts of the tetrachalcogenide $(\text{TsiSe})_2\text{S}_2$. Cleavage of $(\text{TsiSe})_2\text{Se}$ with iodine leads to formation of TsiSeI and precipitation of selenium. The extent of Se–Se bond cleavage of the triselenide with iodine is solvent-dependent: the reaction is incomplete in toluene; in carbon disulfide, however, and in the presence of excess iodine, the triselenide is completely consumed in favor of the selenenyl iodide TsiSeI ($\delta^{77}\text{Se} + 674$ ppm) and of Se_2I_2 ($\delta^{77}\text{Se} + 916$ ppm) [74,75].



Scheme 3. Reactions involving tris(trimethylsilyl)methaneselenenyl iodide (TsiSeI).

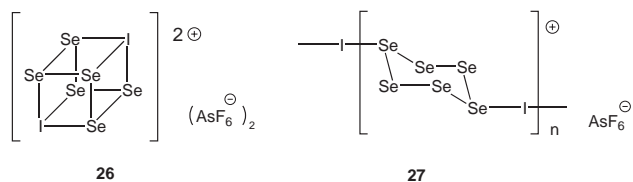


Fig. 8. Iodycyclohexaselenonium cations **26**, **27**.

4.2. Inorganic iodoselenonium cations

Oxidation of selenium in the presence of iodine or reactions of selenium dications like Se_2^{2+} with iodine and the use of non-nucleophilic anions like AsF_6^- allowed us to isolate a number of salt-like compounds with selenium–iodine cations. This class of compounds was covered by excellent reviews a decade ago [2].

In most of these compounds, terminal iodine atoms are bonded to positively (formally) charged three-coordinated selenium atoms. In $[\text{SeI}_3]^+ [\text{AsF}_6]^-$ **14**, the Se–I distances (251.0–251.3 pm) [7] are just like those expected for covalent Se–I single bonds. In the dication $\text{Se}_2\text{I}_4^{2+}$, that can be understood as being derived from $\pi^*-\pi^*$ interactions between two 19-electron SeI_2^+ cations in compound **15**, even shorter Se–I distances of about 245 pm exist [33]. In the polynuclear dication $\text{Se}_6\text{I}_2^{2+}$, that can be described as a distorted cube or unsymmetrically bicapped Se_6 chair structure, each of the iodine atoms is connected to the centrosymmetric Se_6 moiety by one short Se–I bond (245.4 pm) and two further contacts (370.9 and 371.9) [76]. The ‘less oxidized’ species $1/n [\text{Se}_6\text{I}]_n^+$ [77] with 1,4 axial Se–I bonds of bond order 0.5 (10-I-2) is related to compound **11b** (see Section 3) (see Fig. 8).

4.3. The role of anions for the structures of iodoselenoimidazolium and iodoselenophosphonium ions: tuning Se–I contacts

Uncharged compounds with 2c–2e Se–I bonds involving two-coordinated selenium require steric stabilization to avoid dismutation into iodine and diselenides; cationic species with 2c–2e Se–I bonds, however, can be stable, even when the substituents bonded to selenium are not very bulky. Such (iodoseleno)phosphonium ($\text{R}_2\text{R}'\text{P}-\text{Se}-\text{I}^+$) cations and related (iodoseleno)carbenium ($\text{RR}'\text{C}-\text{Se}-\text{I}^+$) cations are soft electrophiles that are susceptible to nucleophilic attack. Such kind of attack at Se or I may lead to decomposition; weakening of Se–I bonds by formation of 3c–4e bonding systems, however, can also be a way of stabilization, like in the case of internally chelated arene selenenyl iodides.

By appropriate choice of their anions, Se–I distances of $[\text{R}_2\text{R}'\text{P}-\text{Se}-\text{I}]^+$ and $[\text{RR}'\text{C}-\text{Se}-\text{I}]^+$ cations can be ‘tuned down’ from about 275 pm (Se–I bond order 0.5) to 256.4 pm, whereas cation–anion Se–I contacts can be ‘tuned up’ to about 350 pm (Section 3.4.4, see Table 1). Compared with uncharged R–Se–I species (Se–I 253 pm) [14,32], all Se–I distances of the yet identified $[\text{R}_2\text{R}'\text{P}-\text{Se}-\text{I}]^+$ and $[\text{RR}'\text{C}-\text{Se}-\text{I}]^+$ cations with polyhalide anions are longer, what is fairly explained by the $n-\sigma^*$ nature of their anion to cation donor–acceptor interactions involving σ^* orbitals of covalent Se–I bonds. We expect that, like in the case of Passmore’s

inorganic Se–I cations, the use of counteranions of very low nucleophilicity will provide general access to ‘undisturbed’ halogenoseleno-substituted onium ions with covalent Se–I bonds.

5. Summary

Uncharged covalent Se–I compounds with Se–I bond orders close to one will have to rely on stabilization methods that prevent their dismutation into diselenides and iodine or into diselenide–iodine adducts. Useful concepts will be steric destabilization of the diselenides, (like *trans*-Tsi₂Se₂ [72]), or bowl-shaped environments (like that of stable RSeOH and RSI compounds [78]). Stabilization by coordination is an alternative which implies a loss of Se–I bond order due to the presence of ‘hypervalent’ 3c–4e (X–Se–I) bonding systems. Such easily accessible hypervalent states allow rapid Se–I bond making–bond breaking equilibration reactions without the need of formation of radicals.

Within a continuum of interactions [79,80] from undisturbed Se–I single bonds via $n \rightarrow \sigma^*(\text{Se}-\text{I})$ interactions and typical 3c–4e X–Se–I or Se–I–X systems to van der Waals contacts, any desired Se–I distances can be tuned by an appropriate choice of the particular substituents, ligands and charges at the Se–I moieties.

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