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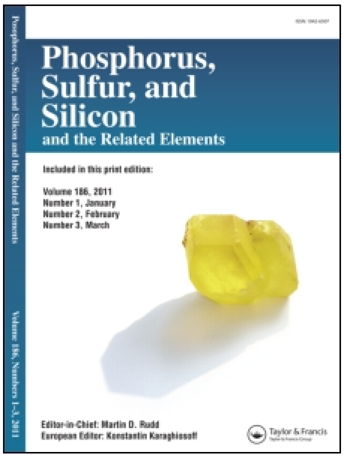

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DISELENIDES AND IODINE: INFLUENCE OF SOLUTION EQUILIBRIA BETWEEN COVALENT COMPOUNDS AND CHARGE – TRANSFER COMPLEXES

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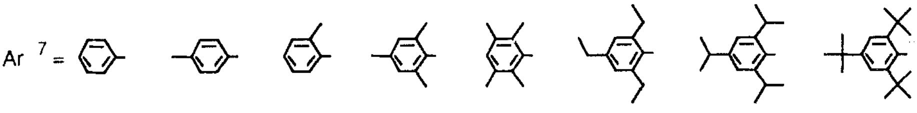
Abstract: Substitution of diselenides with sterically crowded groups enable the formation of iodoselanes, compounds with covalent Se–I bonds. With less bulky substituents, charge–transfer complexes become the predominant species. Conditions, causing the formation either of iodoselanes Ar–Se–I (**2d–h**) or charge–transfer complexes (**2a, b**) were investigated by the reaction of diaryl diselenides **1a–h** with iodine.

INTRODUCTION

Transitions between compounds with covalent Se–I bonds and charge–transfer complexes can be observed, when diaryl diselenides react with iodine. Transitions of this kind are also presumably involved in processes iodine–catalysed crystallization of elemental selenium [1-3] . The influence of the substituents shows the lower tendency of dialkyl selenides to form charge–transfer complexes in the reaction with iodine by enlargement of the substituents [4] . The isolation of Ph_2Se_2 / I_2 (**2a**) as a cyclic charge–transfer complex [5] and the synthesis of 2,4,6–tri–*tert*–butylphenyliodoselane (**2h**), the first stable uncharged iodoselane [6] , point to a connection between sterical demands of bulky substituents and activation of Se – Se bonds regarding to their cleavage by molecular iodine.

For this reason, we examined diaryl diselenides containing substituents with increasingly sterical demands, starting with diphenyl diselenide.



Ph- ; p-Tol- ; o-Tol- ; Mes- ; TMP- ; TEP- ; TIP- ; SM-
a **b** **c** **d** **e** **f** **g** **h**

N.m.r. - spectroscopic observation (^{1}H, ^{13}C, ^{77}Se) of reactions of diaryl diselenides **1a–h** with iodine shows in the case of Ph_2Se_2 (**1a**)and *p*-Tol_2Se_2 (**1b**) charge-transfer complexes, independently of the iodine concentration in solution, to be in equilibrium with the educts (fast process on the n.m.r. time scale) (eq I) .

$$\underset{\textbf{1a, b}}{Ar-Se-Se-Ar} \quad + \quad I_2 \quad \rightleftarrows \quad \underset{\textbf{2a, b}}{Ar-Se-Se-Ar \quad I_2} \qquad (\mathrm{I})$$

In crossing experiments species with covalent Se – I bonds could be excluded by the detection of separate signals for the system Ph-Se-Se-*p*-Tol / I_2 (table 1) .

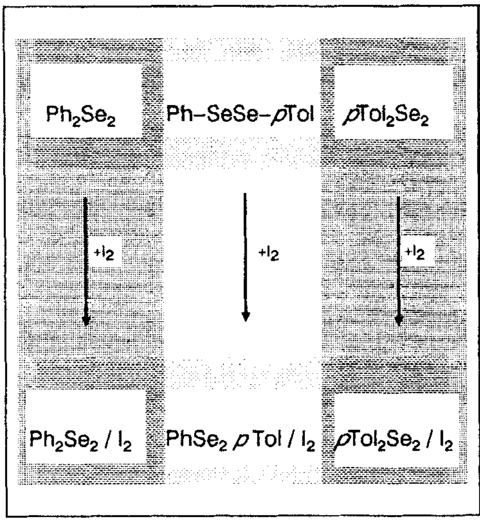


Table 1

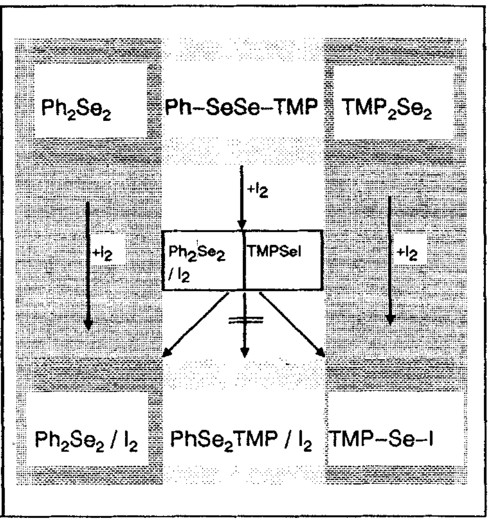


Table 2

Alkylation in *o*-position of the aromatic group appears to activate adjacent Se – Se bonds. Compounds **1d** – **h** show a quick adjustment of equilibria between diaryl diselenide, iodine and iodoselane **2d** – **h** by the reaction with iodine (eq II) .

$$\underset{\textbf{1d - h}}{Ar-Se-Se-Ar} \quad + \quad I_2 \quad \rightleftarrows \quad \underset{\textbf{2d - h}}{2\ Ar-Se-I} \qquad (\mathrm{II})$$

In this case crossing experiments reveal the formation of iodoselanes. Asymmetric species, as they are formed in solution by scrambling reactions of pure diselenides, were no longer observed after reaction with stoichiometric amounts of iodine (table 2) .

Raising the iodine concentration yields quantitativly the corresponding iodoselanes **2d** – **h** (table 3) .

Diselenide	∂ [ppm]	pure	$+I_2$ [a])		$+I_2$ [b])
$(C_6H_5)_2Se_2$	(**1a**)	460	478		8)
(*p*-$CH_3(C_6H_4))_2Se_2$	(**1b**)	473	488		495
(*o*-$CH_3(C_6H_4))_2Se_2$	(**1c**)	403	415	449	495
$((CH_3)_3C_6H_2)_2Se_2$	(**1d**)	368	370	401	403
$((CH_3)_4C_6H)_2Se_2$	(**1e**)	386	389	423	424
$((C_2H_5)_3C_6H_2)_2Se_2$	(**1f**)	370	372	386	388
((*iso*-$C_3H_7)_3C_6H_2)_2Se_2$	(**1g**)	359	359	371	373
((*tert*-$C_4H_9)_3C_6H_2)_2Se_2$	(**1h**)	515		518	8)

Table 3 : [a]) separate signals for educts 1d–h and products 2d–h [b]) with exess iodine

^{77}Se – n.m.r. chemical shift

Bruker AM 300 / 57.24 MHz / (CH_3)$_2$Se (ext.) standard / C_6D_6

From equimolar mixtures of bis(2,4,6-triisopropylphenyl) diselenide (**1g**) with iodine in inert solvents crystallization occurs with loss of iodine leading to **3g** , a charge-transfer complex with 2 : 1 composition [9]. X-ray structure determination shows the "intercalation" of one iodine molecule between the units of two diselenides (fig 1) .

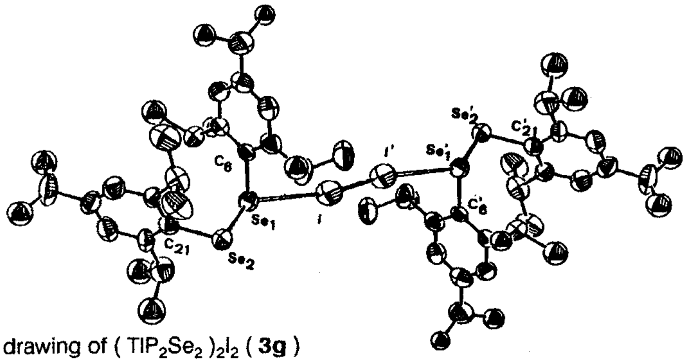


Figure 1: ORTEP drawing of (TIP_2Se_2)$_2I_2$ (**3g**)

Dihalogen molecules tend to give 2:1 complexes only with very weak donors. Quite typical for such adducts, the arrangement Se– I – I –Se of **3g** (< Se – I – I = 169.1 °) is not far from linear [10]. Remarkably different is the behavior of the selenium atoms of **3g** in comparison to the cyclic charge – transfer complex **2a** , where three – coordinated selenium atoms act as donor (8–Se–3) as well as acceptor (10–Se–3) [6, 9] .

Surprisingly, from the reaction of less bulky bis(2,3,5,6-tetramethylphenyl) diselenide (**1e**) with iodine, the product crystallizes as iodoselane (fig 2) .

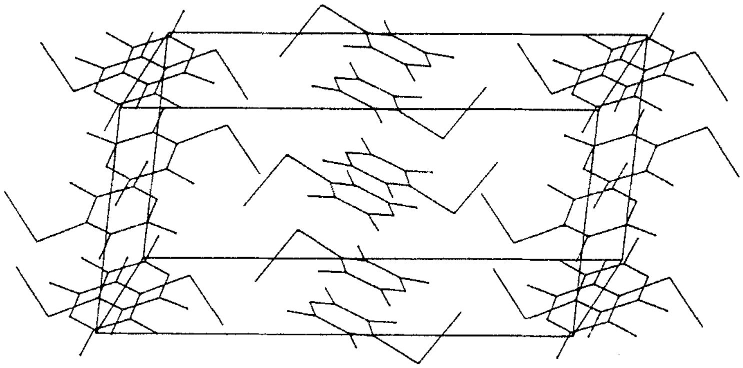


Figure 2 : Cell – Plot , based on x-ray structure determination of TMPSeI (**2e**)

A quite high packing density becomes possible by arrangement of the iodoselane molecules in layers. The shortest intermolecular I – I distances (437 pm) are comparable to interactions between the layers of molecular iodine. Transformation barriers between in solution predominant iodoselanes and charge-transfer complexes are so low, that slight energy differences can be surmounted by packing forces.

In the presence of tetraethylammonium iodide, charge-transfer complexes as well as aryl(iodo)selanes **2a – h**, **3g** are decomposed with the formation of triiodide I_3^- and the corresponding diselenides **1a – h** , (eq III) .

$$\left.\begin{array}{ll} [\,Ar_2Se_2 -\!- I_2\,] & \mathbf{2a,\ b} \\ 2\,Ar - Se - I & \mathbf{2d - h} \\ (\,Ar_2Se_2\,)_2I_2 & \mathbf{3g} \end{array}\right\} + \ I^- \ \rightleftarrows \ \underset{\mathbf{1a-h}}{Ar_2Se_2} \ + \ I_3^- \qquad (\,\mathrm{III}\,)$$

The structurally related 2,4,6-triisopropylphenyliodotellane (**4g**) reacts under appropriate conditions to a stable hypervalent anion $TIP\text{-}TeI_2^-$ (**5g**) with triiodide-like linear arrangement I-Te-I (< I-Te-I = 180 °), ($C_6H_5TeI_2^-$, < I-Te-I = 178 °) [11] (eq IV) .

$$\underset{\mathbf{4g}}{TIP - Te - I} \ + \ I^- \ \rightleftarrows \ \underset{\mathbf{5g}}{TIP - Te - I_2^-} \qquad (\,\mathrm{IV}\,)$$

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   o–Tol– = 2–methylphenyl– ; (*ortho*–**tol**yl–)
   Mes– = 2,4,6–trimethylphenyl– ; (**mes**ityl–)
   TMP– = 2,3,5,6–**t**etra**m**ethyl**p**henyl–
   TEP– = 2,4,6–**t**ri**e**thyl**p**henyl–
   TIP– = 2,4,6–**t**ri**i**sopropyl**p**henyl–
   SM– = 2,4,6–tri–*tert*–butylphenyl– ; (**s**uper**m**esityl–)
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