3.13
Two Adjacent Heteroatoms with at least One Selenium or Tellurium

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3.13.1 INTRODUCTION

Five-membered monocyclic rings containing one selenium or one tellurium atom and another adjacent heteroatom (oxygen, sulfur, selenium, tellurium, or nitrogen) form different ring systems, including the less saturated systems summarized in Scheme 1.

\[
\begin{align*}
\text{Se} & \quad \text{Te} \\
1,2-\text{Chalcogenaselenolane} & \quad 1,2-\text{Chalcogenatellurolane} \\
\text{Se} & \quad \text{Te} \\
1,2-\text{5H-Chalcogenaselenol} & \quad 1,2-\text{5H-Chalcogenatellurole} \\
\text{Se} & \quad \text{Te} \\
1,2-\text{3H-Chalcogenaselenol} & \quad 1,2-\text{3H-Chalcogenatellurole} \\
\text{Se} & \quad \text{Te} \\
1,2-\text{Chalcogenaselenolylium} & \quad 1,2-\text{Chalcogenatellurolylium} \\
\end{align*}
\]

\[
\begin{align*}
\text{Te} & \quad \text{Te} \\
1,2-\text{Tellurazolidin} & \quad 2\text{H,5H-1,2-Tellurazoline} \\
\text{Te} & \quad \text{Te} \\
2\text{H,3H-1,2-Tellurazoline} & \quad 4\text{H,5H-1,2-Tellurazoline} \\
\end{align*}
\]

\[
\begin{align*}
\text{Te} & \quad \text{Te} \\
1,2-\text{Tellurazole} & \quad 2\text{H,5H-1,2-Tellurazoline} \\
\end{align*}
\]

\[
\begin{align*}
\text{X} & = \text{O, S, Se or Te} \\
\end{align*}
\]

Scheme 1

Many of these systems still remain unknown. For the systems which are known, many of the parent systems, as well as derivatives including benzo-fused analogues, have been prepared.

Whereas the 1,2-dithiole system has been known for a long time and a detailed literature exists for this system (<82AH(31)63, 84CHEC-I(6)1049, 93HOU(E8a)470, 95SR173>, the literature is far less detailed for the 1,2-diselenolane first reported in 1890 (<1890CB1090> and the 1,2-ditellurole reported in 1977 (<77JA255>, the literature of the mixed systems being even less. A number of studies have focused mostly on organic conductors and hypervalent compounds. A systematic classification scheme which includes a concise description of such type of hypervalent bonding has been devised (<80JA7753>.

1,2-Ditelluroles and 1,2-tellurazoles as well as 1,2-oxatellurole derivatives have been reviewed (<85SR15, 93AH(58)48>. A review on 1,2-ditelluroles has been published (<91KGS291> as well as a review on synthetic methods (<90HOU(E12b)775>. The subject of this chapter was treated in the first edition of Comprehensive Heterocyclic Chemistry (CHEC-I) together with the isomeric 1,3-compounds (<84CHEC-I(6)947>.
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3.13.2 MOLECULAR STRUCTURE

3.13.2.1 X-ray Diffraction

The x-ray structure of the ditellurolane compound (1) has been reported. The small dihedral angle (8.5°) found in (1) results in a considerable overlap of the two tellurium lone-pair $p$ orbitals which gives rise to the doubly occupied $\pi$ and $\pi^*$ orbitals $<93JA885>$. 

\[ \text{Te-Te} \]

(1)

The structure of 5,6-diseleno-11,12-ditellurotetracene, DSeDTeT (2) has been determined for the bromine salt (DSeDTeT)$_2$Br $<86MI313>$. 

\[ \begin{array}{c}
\text{Se-Se} \\
\text{Te-Te}
\end{array} \]

(2)

The DSeDTe units form a uniform column along the $c$ axis. The normal of the molecular plane largely tilts from the $c$ axis (48.2°).

Analogous studies have been carried out on dichalcogen-bridged acenaphthenes (3). The crystal structure was determined for the complex with TCNQ. Both acceptor and donor were found to take planar conformations. They form unusual modified, mixed stacking columns along the [1.1.1] direction. A pair of donors and a pair of acceptors make an alternately stacking column $<88BCJ2013>$. 

\[ \text{Te-Te} \]

(3)

The structure of the 5,6:11,12-bis(ditelluro)tetracene (4) was reported. The structure shows rather short interstack Te—Te contacts of 37.01 nm $<82MCLC(86)79, 82OM739>$. 

\[ \text{Te-Te} \]

(4)

The structure of the oxatellurole compound (5) has been reported $<83JA875>$. Compound (5) shows a nearly linear (170°) arrangement of Cl—Te—O; a three-center–four-electron bond is proposed for this arrangement. The structure determination of benzocondensed compounds has also been reported $<90ZOB2764>$. 

\[ \begin{array}{c}
\text{Cl} \\
\text{Te-O} \\
\text{Ph-Te-Ph}
\end{array} \]

(5)
Bromine compounds like (6) were described. In this case three-center–four-electron bonds were also proposed \(^{(86JOC1692)}\).

\[
\begin{align*}
\text{Br} & - \text{Te} - \text{O} \\
\text{Ph} & - \text{Ph}
\end{align*}
\]

(6)

Pertelluranes like (7) were prepared and the structure given.

\[
\begin{align*}
\text{F}_3\text{C} & - \text{O} - \text{O} - \text{CF}_3 \\
\text{Te} & - \text{R}
\end{align*}
\]

(7)

The intermolecular Te—O distances (35.59–35.86 nm) are very close to the sum of the van der Waals’ radii for Te and O \(^{(84JA7529)}\).

No structures of simple 1,2-tellurazoles are reported; however, structures of hypervalent compounds which can be considered either as hypervalent tellurazoles or compounds with an extraordinary strong Te—N co-ordination resulting in a short tellurium–nitrogen distance have been reported. Such compounds are derived from azomethinimines \(^{(88ZOB1176, 90JOM(390)29, 91JOM(402)331, 93JCS(D)619)}\), from pyridines \(^{(91JOM(420)327)}\), or from quinolines (Scheme 2) \(^{(88JOM(356)159)}\).

\[
\begin{align*}
\begin{array}{c}
\text{NMe}_2 \\
\text{S}
\end{array}
\end{align*}
\]

Scheme 2

The structure of 2,5-diphenyl-1,6-dioxa-6\(\alpha\ \delta\)-tellurapentalene (8) has been recorded \(^{(83JOC5149)}\). The bicyclic system is planar as reported for the corresponding thiyapentalene case and the dioxa-thiapentalene \(^{(77ACS(31)711, 79JCS(P2)1521, 81JST(75)327)}\).

\[
\begin{align*}
\text{Ph} & - \text{O} - \text{Te} - \text{O} - \text{Ph}
\end{align*}
\]

(8)

Structure determination of selenium compounds is much more abundant. The structure of penta-carbonyltungsten-coordinated 1,2-diselenolanes (9) has been reported \(^{(92CC1050)}\).
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The structure of condensed compounds like 4,4'-diphenyl-2,3-diselenabicyclo[3.3.0]oct-7-ene (10) has been established (94JCS(P1)2151).

![Structure 10](image)

1,5,9,13-Tetraselenacyclohexadecane (16Se₄) forms a dication [16Se₄]²⁺([SO₃CF₃]⁻). The structure of this dication has been determined and displays a linear Se—Se—Se arrangement with nearly equal Se—Se distances 26.69 and 25.92 nm comparable to reported distances in 1,6,6a⁺-triselenapentalene 25.48–25.83 nm suggesting a weak bonding between the selenium atoms (90JA3706).

Structures of derivatives of 1-oxa-6,6a⁺-diselena-2-azapentalene, 1-thia-6,6a⁺-diselena-3-azapentalene and 1,6-dithia-6a⁺-selena-3-azapentalene have been reported. The three chalcogen atom arrangement in all three cases forms an angle of approximately 170° (87CC967).

The structure of the thiazafulvalene analogue 6,7-dihydro-2-phenyl-5H-2a⁺-thia-2-selena-1,2-diazacyclopent[cd]indene (11) was reported. The tricyclic frame of the molecule is almost planar (91AX(C)759).

![Structure 11](image)

The x-ray structure determination of 7-nitro-2,1-benzothiaselenol-3-one has been carried out (89AX(C)489). The structure of the analogous 7-nitro-2,1-benzoxaselenol-3-one was reported too (88AX(C)340). The structure of benzo-1,2-thiaselenol-3-thione was reported (82H(19)657).

The Fischer carbene complex (W(CO)₅COEtPh) reacts with PhCCSeLi and Se₈ to give (12) and (13), the structure of both is reported (88OM1853).

![Structures 12 and 13](image)

The observation that peri-dichalcogen-bridged polyacenes are superior electron donors for constructing organic conductors has resulted in several papers dealing with the structure of this class of compounds. A survey of structural aspects of one-dimensional conductors based on tetra-thiatetracene is found in (82MI 313-02). In connection with the telluro compounds, the mixed seleno and telluro compound (2) has already been mentioned. Other seleno-bridged tetracenes like (14) have been studied (82MCLC79, 82OM739).

![Structure 14](image)

Anthracene bridged derivatives like (15) and (16) have been studied too. Dimethyl and tetramethyl derivatives like (17) were further included in the studies. (82AX(B)2855, 91BCJ2091).
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3.13.3 EXPERIMENTAL STRUCTURAL METHODS

3.13.3.1 Mass Spectrometry

Mass spectra have been used intensively for structure elucidations and for characterization of many of the compounds dealt with in this chapter. However, if no systematic treatment was made of the mass spectrometric data, they will not be mentioned separately in this section.

The intensities of peaks with an abundance of more than 2% of the molecular ion clusters of (3) have been observed and compared to calculated intensities (<80TL4565>).

3.13.3.2 Ultraviolet–Visible Spectroscopy

In the same way as in Section 3.13.3.1, only papers dealing with more systematic discussion of UV–VIS spectra will be mentioned here.

The UV–VIS spectrum of fluorantheno[3,4-cd]-1,2-ditellurole (18) and its diselena analogue have been recorded. In contrast to fluoranthene itself which has no absorption above 800 nm, compound (18) shows a strong absorption at 503 nm (log ε 4.54) (<86TL2011, 87SM(19)595>).

Te–Te

(18)

The UV–VIS spectrum of (19) itself together with the iodine-doped compound has been recorded (<91MI 313-01>).

Se–Se

(19)

The electronic spectrum of (14) and its isomer (20) which both form highly conductive complexes with TCNQ and analogous acceptors have been reported (<90BCJ2441>). The solvatochromic behavior of the ditellurides (1), (21), and (22) has also been discussed (<93JA885>).
3.13.3.3 Nuclear Magnetic Resonance Spectroscopy

The isotopes $^{77}\text{Se}$ and $^{125}\text{Te}$, which give rise to NMR signals, both have a natural abundance of ca. 7% which opens the possibility to obtain NMR spectra of both nuclei in natural abundance. Enriched mixtures of both elements are also available for synthesis of enriched compounds.

3.13.3.3.1 Proton NMR spectroscopy

Dynamic nuclear magnetic resonance studies were carried out on mononuclear complexes of type (23). Detailed variable temperature NMR studies established the existence of pyramidal inversion about the coordinated selenium ligand atom and an intramolecular 1,2-metal shift between adjacent chalcogen ligand atoms $<85\text{JCS(D)1569}>$.  

$$\begin{align*}
\text{Se} & \quad \text{Se} \\
\text{M(CO)}_3 \\
(23) \quad \text{M} = \text{Cr, Mo or W}
\end{align*}$$

Based on a detailed discussion of the $^1\text{H}$ NMR spectra from the oxidation products of (24), it was concluded that the oxidation products consisted of 60% of (25) and 40% of (26) $<88\text{JOC2435}>$.  

(24)  

(25)  

(26)

3.13.3.3.2 Carbon-13 NMR spectroscopy

Carbon-13 NMR spectra of compounds of type (27) were reported. It was observed that the chemical shift of the four C-atoms, which were not part of the heterocyclic ring, was only a little dependent on the nature of X $<86\text{SA(A)57}>$.  

(27) $X = \text{Se or S}$

Based on $^1J (^{77}\text{Se}—^{13}\text{C})$ values, it is concluded that the equilibrium in Equation (1) is on the right side in solution favoring the cyclic selenurane structure (28) whereas the sodium salt has the acyclic structure (29). The values of the coupling constants are in the range of 61–65 Hz for selenuranes and 77–81 Hz for selenoxides. The observed 65.1 Hz for (29) and 81.4 Hz for (28) are in the typical regions for a selenurane and selenoxide, respectively $<81\text{CL1353}, 82\text{OMR}(20)117>$.  

(29)  

(28)  

$$
\text{HO} \quad \text{Se} \quad \text{Me} \\
\text{CO}_2 \quad \text{O} \\
\text{Me} \quad \text{Se} \\
(29) \quad \text{O} \quad \text{O} \\
\quad \text{HO} \quad \text{Me} \\
(28)
$$

The structure of the tellurane (5) and the pertelluranes of structure (6) were discussed based on $^{13}\text{C}$ NMR spectra compared to model substances $<86\text{JOC1692}>$.  

\[ \text{HO} \quad \text{Se} \quad \text{Me} \]

\[ \text{CO}_2 \quad \text{O} \quad \text{Me} \]

\[ \text{Se} \quad \text{Me} \]

\[ \text{HO} \quad \text{Me} \]

\[ \text{O} \quad \text{O} \]
3.13.3.3 Selenium-77 and Tellurium-125 NMR spectroscopy

The $^{77}\text{Se}$—$^{13}\text{C}$ coupling constants are used in the discussion of selenoxide–selenurane equilibrium in Equation (1) $^{(81}\text{CL}1353, 82\text{OM}(20)117}$. 

The presence of a three-center–four-electron bonding in compounds like (5) and (8) is discussed based on a comparison of the $^{125}\text{Te}$ NMR chemical shifts and the Te(3d$_{5/2}$) binding energies obtained by x-ray photon spectroscopy. It is suggested that the net bonding interaction for the two groups of compounds may be represented by (30) and (31). It is concluded that $^{125}\text{Te}$ NMR spectra are a valuable tool for such studies, as the chemical shifts are sensitive to geometry, oxidation state of tellurium, and the electronic environment of tellurium $^{(89}\text{OM}866}$.

![Chemical structures](image)

3.13.3.4 Photoelectron Spectroscopy

The photoelectron spectra of (4), (14), (24), (32), and (33) were discussed and compared with the corresponding sulfur compounds. It was observed that the energies of the HOMOs, determining the $\pi$-donor properties of dichalcogeno- and tetrachalcogenonaphthalenes as well as tetrachalcogeno-naphthacenes, are practically independent of the nature of the heteroatoms (S, Se or Te) $^{(90}\text{ZOB}421}$.

![Chemical structures](image)

3.13.4 THERMODYNAMIC ASPECTS

3.13.4.1 Electrochemistry and Conductivity

Being candidates for donors in organic conductors, the electrochemistry of peridichalcogeno-bridged polyacenes has, in particular, attracted interest. A survey of the electrochemistry and conductivity of cation-radical salts based on tetrascelenotetraene and tetrathiotetraene is found in Scheme 3 $^{(82}\text{MI}313-01}$.

Cyclic voltammograms of tetrachalcogenoanthracenes of type (15) all show two reversible one-electron redox waves. Introduction of methyl groups lowers the oxidation potentials. Substitution of tellurium for selenium results in a considerable lowering of both the first and second oxidation potentials. The electrochemistry of complexes with TCNQ and analogues of TCNQ is also included $^{(90}\text{CL}567, 91\text{BCJ}2091}$. See Tables 1 and 2 for physical constants of donors and complexes with various acceptors.

Similar results were obtained for the tetracene derivatives (14) and (20) with the tendency that the tetracene derivatives have stronger donating abilities than the anthracene counterparts $^{(90}\text{BCJ}2441, 91\text{SM}2389}$. The tetratelluro analogue of (14) has been studied and shows a similar behaviour $^{(82}\text{OM}739}$.

Electrochemistry and ESR spectra of (20) and its tetratelluro analogue have been reported $^{(83}\text{MI}313-01}$.

Tetrasceleno- and tetratelluronaphthalenes (32) and (33) exhibited two reversible oxidation waves. The donor character is strengthened by introduction of tellurium $^{(87}\text{CL}315}$. Analogous results were obtained from compounds of type (34) $^{(88}\text{SMB}509}$.
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Donors

<table>
<thead>
<tr>
<th>Donor</th>
<th>Formula</th>
</tr>
</thead>
<tbody>
<tr>
<td>TSN</td>
<td>X-X</td>
</tr>
<tr>
<td>TSA</td>
<td>X-X</td>
</tr>
<tr>
<td>TST</td>
<td>X-X</td>
</tr>
<tr>
<td>TTeT</td>
<td>X-X</td>
</tr>
<tr>
<td>TMTSA</td>
<td>X-X</td>
</tr>
</tbody>
</table>

TSN, X = Se
TMTTeN, X = Te

2,3-DMTSA, X = Se
2,3-DMTTeA, X = Te

6,7-DMTSA, X = Se

TMTTeA, X = Te

Acceptors

<table>
<thead>
<tr>
<th>Acceptor</th>
<th>Formula</th>
</tr>
</thead>
<tbody>
<tr>
<td>TCNQ</td>
<td>R¹ = R² = H</td>
</tr>
<tr>
<td>TCNQF₂</td>
<td>R¹ = R² = F</td>
</tr>
<tr>
<td>DMTCNQ</td>
<td>R¹ = Me, R² = H</td>
</tr>
<tr>
<td>DMOTCNQ</td>
<td>R¹ = OMe, R² = H</td>
</tr>
</tbody>
</table>

Scheme 3

Table 1 Half-wave oxidation potentials of peri-chalcogen donors <91BCJ2091>.

<table>
<thead>
<tr>
<th>Compound*</th>
<th>$E_{1/2}(1)/V$</th>
<th>$E_{1/2}(2)/V$</th>
<th>$\Delta E/V$</th>
</tr>
</thead>
<tbody>
<tr>
<td>TSA</td>
<td>0.35</td>
<td>0.71</td>
<td>0.36</td>
</tr>
<tr>
<td>2,3-DMTSA</td>
<td>0.31</td>
<td>0.72</td>
<td>0.41</td>
</tr>
<tr>
<td>2,3-DMTTeA</td>
<td>0.20</td>
<td>0.63</td>
<td>0.43</td>
</tr>
<tr>
<td>6,7-DMTSA</td>
<td>0.30</td>
<td>0.68</td>
<td>0.38</td>
</tr>
<tr>
<td>TMTSA</td>
<td>0.26</td>
<td>0.68</td>
<td>0.42</td>
</tr>
<tr>
<td>TMTTeA</td>
<td>0.16</td>
<td>0.55</td>
<td>0.39</td>
</tr>
</tbody>
</table>

*For the acronyms used cf. Scheme 3.
Table 2 Charge transfer complexes of peri-dichalcogenide anthracens \(<91BCJ2091>\).

<table>
<thead>
<tr>
<th>Complex*</th>
<th>(D : A)</th>
<th>(CT) band (\times 10^3) cm(^{-1})</th>
<th>(\Delta E_{\text{red}})^{\text{a}} (V)</th>
<th>(\sigma) (S) cm(^{-1})</th>
</tr>
</thead>
<tbody>
<tr>
<td>2,3-DMTSA · TCNQ</td>
<td>1:2</td>
<td>2.8, 9.9, 11.4</td>
<td>0.12</td>
<td>1.2</td>
</tr>
<tr>
<td>2,3-DMTSA · TCNQ</td>
<td>1:1</td>
<td>10.2</td>
<td>0.01</td>
<td>5.3 (\times 10^{-6})</td>
</tr>
<tr>
<td>6,7-DMTSA · TCNQ</td>
<td>1:1</td>
<td>3.2, 11.5</td>
<td>0.11</td>
<td>2.0</td>
</tr>
<tr>
<td>TMTSA · TCNQ</td>
<td>1:2</td>
<td>6.1, 10.0, 11.5</td>
<td>0.07</td>
<td>2.7 (\times 10^{-1})</td>
</tr>
<tr>
<td>TMTSA · TCNQ</td>
<td>1:1</td>
<td>10.0</td>
<td>-0.03</td>
<td>1.8 (\times 10^{-6})</td>
</tr>
<tr>
<td>2,3-DMTSA · TCNQ</td>
<td>1:1</td>
<td>11.2</td>
<td>-0.29</td>
<td>5.4 (\times 10^{-6})</td>
</tr>
<tr>
<td>2,3-DMTSA · TCNQ</td>
<td>1:1</td>
<td>10.5</td>
<td>-0.40</td>
<td>1.8 (\times 10^{-7})</td>
</tr>
<tr>
<td>6,7-DMTSA · TCNQ</td>
<td>1:1</td>
<td>11.0</td>
<td>-0.30</td>
<td>8.8 (\times 10^{-5})</td>
</tr>
<tr>
<td>TMTSA · TCNQ</td>
<td>1:1</td>
<td>11.1</td>
<td>-0.34</td>
<td>5.2 (\times 10^{-7})</td>
</tr>
<tr>
<td>2,3-DMTSA · DMTCNQ</td>
<td>2:1</td>
<td>4.6, 11.3, 12.6</td>
<td>0.19</td>
<td>5.3 (\times 10^{-1})</td>
</tr>
<tr>
<td>2,3-DMTSA · DMTCNQ</td>
<td>2:1</td>
<td>10.2</td>
<td>0.08</td>
<td>1.2 (\times 10^{-3})</td>
</tr>
<tr>
<td>6,7-DMTSA · DMTCNQ</td>
<td>2:1</td>
<td>5.4, 11.6</td>
<td>0.18</td>
<td>2.7 (\times 10^{-8})</td>
</tr>
<tr>
<td>TMTSA · DMTCNQ</td>
<td>2:1</td>
<td>11.5</td>
<td>0.14</td>
<td>1.2 (\times 10^{-5})</td>
</tr>
<tr>
<td>TMTSA · DMTCNQ</td>
<td>2:1</td>
<td>10.2</td>
<td>0.04</td>
<td>4.6 (\times 10^{-2})</td>
</tr>
<tr>
<td>2,3-DMTSA · DMTCNQ</td>
<td>1:1</td>
<td>6.9</td>
<td>0.32</td>
<td>5.0 (\times 10^{-7})</td>
</tr>
<tr>
<td>2,3-DMTSA · DMTCNQ</td>
<td>1:1</td>
<td>10.3</td>
<td>0.19</td>
<td>3.2 (\times 10^{-2})</td>
</tr>
<tr>
<td>6,7-DMTSA · DMTCNQ</td>
<td>2:1</td>
<td>non</td>
<td>0.29</td>
<td>1.9 (\times 10^{-9})</td>
</tr>
<tr>
<td>TMTSA · DMTCNQ</td>
<td>2:1</td>
<td>non</td>
<td>0.25</td>
<td>1.0 (\times 10^{-8})</td>
</tr>
<tr>
<td>TMTSA · DMTCNQ</td>
<td>2:1</td>
<td>non</td>
<td>0.15</td>
<td>1.1 (\times 10^{-7})</td>
</tr>
<tr>
<td>2,3-DMTSA · TNAP</td>
<td>1:1</td>
<td>3.5, 8.9</td>
<td>0.10</td>
<td>2.6 (\times 10^{-2})</td>
</tr>
<tr>
<td>2,3-DMTSA · TNAP</td>
<td>1:1</td>
<td>8.5, 10.2</td>
<td>-0.01</td>
<td>4.9 (\times 10^{-3})</td>
</tr>
<tr>
<td>TMTSA · TNAP</td>
<td>1:1</td>
<td>8.8, 10.0</td>
<td>0.05</td>
<td>9.2 (\times 10^{-3})</td>
</tr>
<tr>
<td>TMTSA · TNAP</td>
<td>1:1</td>
<td>8.8, 10.3</td>
<td>-0.05</td>
<td>6.0 (\times 10^{-1})</td>
</tr>
</tbody>
</table>

*For the acronyms used cf. Scheme 3. \(^{a}\)\(\Delta E_{\text{red}} = E_{1/2}(D) - E_{1/2}(A)\).

The cyclic voltammogram of fluorantheno[3,4-cd]-1,2-ditellurole \((18)\), as well as its diseleno analogue, exhibited one reversible oxidation wave, the donor character being most pronounced for the tellurium compound \(\langle86TL2011, 87SM(19)595\rangle\).

The electrochemistry of \(\sigma\)-bonded heteroatom dications \((35)\) has been studied by cyclic voltammetry in acetonitrile. Only a one-reversible reduction peak was observed at \(+0.11\) V \(\langle90TL6375\rangle\).

\[
\begin{align*}
\text{(35)}
\end{align*}
\]

The electrochemical oxidation of \((36)\) suggests the intermediate formation of dication \((37)\), which is also observed from the chemical oxidation \(\langle91TL4345\rangle\).

Cyclic voltammograms were obtained from \((38)\) to study the formation of dication \((39)\) which can also be obtained by oxidation with 2 equivalents of the one-electron oxidizing agent NO\(^{+}\)PF\(_6\)^{−} \(\langle90TL2307\rangle\).

It is observed that the selenuran \((40)\) undergoes facile electrochemical reduction in acetonitrile at \(-0.10\) V \(\langle92JA3117\rangle\).

### 3.13.5 Reactivity

Generally speaking, the chemical reactivity of the known systems has not been studied much, the physico-chemical properties being more intensively investigated.
Two Adjacent Heteroatoms with at least One Selenium or Tellurium

3.13.5.1 Thermal and Photochemical Reactions Involving No Other Species

3.13.5.1.1 Thermolysis

It is observed that (41) isomerizes to (42) in 68% yield at 120 °C whereas the reverse isomerization does not take place (Equation (2)) \( \langle 82 \text{H(19)657} \rangle \). The analogous thermal scrambling of sulfur in 1,2-dithiole-3-thione has been studied by mass spectrometry using \(^{34}\text{S}\) labeled compounds \( \langle 91 \text{JCR(S)226} \rangle \).

\[
\begin{array}{c}
\text{(41)} \\
\searrow 120 \degree C \\
\text{(42)}
\end{array}
\]

The selenurate (43) was transformed into 2-(phenylseleno)benzophenone upon heating at 195 °C for 10 minutes \( \langle 90 \text{CPB874} \rangle \).

\[
\begin{array}{c}
\text{(43)}
\end{array}
\]

It is observed that the pertellurate (44) upon heating at 60 °C in 3 days isomerizes to (45). The kinetics of the isomerization was studied \( \langle 84 \text{JA7529} \rangle \).

\[
\begin{array}{c}
\text{(44)} \\
\text{(45)}
\end{array}
\]

3.13.5.2 Reactions with Electrophiles

3.13.5.2.1 Reactions involving protons or Lewis acids

The 1,2-diselenol-3-one (46) is easily protonated in trifluoroacetic acid, which results in a shift of the protons to lower field in the \(^1\text{H}\) NMR spectrum \( \langle 87 \text{KGS855} \rangle \).
The ditelluroles (1) and (21) react with triflic acid in methylene chloride to give (1:1) salts \langle93JA885\rangle.

3H-1,2-Benzothiaselenol-3-one reacts as a selenium-transferring reagent for the conversion of nucleoside \(H\)-phosphonates and nucleoside \(H\)-phosphonothioate diesters into the corresponding seleno analogues \langle92TL7255\rangle.

Oxidation of naphtho[1,8-\(cd\)]-1,2-diselenol with \(m\)-chloroperbenzoic acid results in the formation of (25) and (26) \langle88JOC2435\rangle.

10-Chloro-10,9-epoxy-9-phenylselenoxanthen (47) derives from the reaction of 9-phenylselenoxanthen-9-ol with \(N\)-chlorosuccinimide \langle84H(22)1473, 90CPB874\rangle.

2,5-Diphenyl-1,6-dioxaselenapentalene (8) is oxidized at low temperature by chlorine or bromine to pertelluranes (48) and (49), which are reduced by hydrazine to give the dioxa-tellurapentalene (50) \langle83JOC5149\rangle.

1,2-Oxatellurulylium and 1,2-oxaselenolylium salts are oxidized by bromine and chlorine to trihalogenopertelluranes of the same type as (69) \langle82USP4329284, 85EUP138220\rangle.

### 3.13.5.2.2 Reactions involving carbenes

1,3-Diselenanes are formed from 1,2-diselenolanes and dimethyl diazomethanephosphonate according to Equation (3) \langle91TL4189\rangle.

### 3.13.5.3 Reactions with Nucleophiles

#### 3.13.5.3.1 Reaction with bases

Compound (51) is extremely water sensitive and loses the \(t\)-butyl group to give (52) \langle81TL4241, 82JOC2275\rangle.

The dication (35) is reduced to the cation radical (53) in the reaction with fluorenyllithium, the same was observed with ferrocene \langle90TL6375\rangle, which indicates that the fluorenyl carbanion acts as a one-electron donor.

The dication (54) reacts with water to give the selenoxide (55) \langle91TL4345\rangle.
Two Adjacent Heteroatoms with at least One Selenium or Tellurium

3.13.5.3.2 Reaction with aromatics

Dication (35) reacted with aniline and \( N,N \)-dimethylaniline according to Scheme 4. Aliphatic amines like diisopropylamine did not react. Thiophenol was oxidized by (35) to diphenyl disulfide; the difference is probably due to difference in oxidation potentials \( \langle 90\text{CL393}\rangle \).

\[
\begin{align*}
\text{Scheme 4}
\end{align*}
\]

3.13.6 REACTIVITY OF SUBSTITUENTS ATTACHED TO RING CARBON ATOMS

4,5-Diphenyl-1,2-diselenol-3-one and thiophosgene reacted with the formation of 3-chloro-4,5-diphenyl-1,2-diselenolylidium chloride which was further reduced by Zn to 3,3′-bis(4,5-diphenyl-1,2-diselenolylidene), (1,2-TSeF) according to Scheme 5 \( \langle 88\text{BSF101}\rangle \), 1,2-TSeF is one of the few known TSeFs \( \langle 93\text{SR245}\rangle \).

\[
\begin{align*}
\text{Scheme 5}
\end{align*}
\]

3-Methyl-5-aryl-1,2-oxatellurolylium chlorides (56) react with acid chlorides in the presence of an amine base or pyridine to give 1,6-dioxa-6a\( \lambda^4 \)-tellurapentalenes like compound (48) (Scheme 6) \( \langle 87\text{OM1597}\rangle \).
Two Adjacent Heteroatoms with at least One Selenium or Tellurium

3.13.7 SYNTHESIS

The synthesis of five-membered heterocycles containing one selenium or tellurium atom and another heteroatom adjacent can be classified in three groups, according to the number of building blocks required in a one-step reaction: (i) one-component synthesis, in which the starting molecule is cyclized by joining two heteroatoms or by joining one heteroatom and one carbon atom; (ii) \([2 + 3]\) two-component synthesis, in which a two-atom unit is joined with a three-atom unit; (iii) multicomponent synthesis, in which the heterocyclic ring is formed from nonisolated intermediates formed in a reaction of more than two building blocks.

3.13.7.1 One Component Synthesis

Naphtho[1,8-\(b,c\)]-1,2-diselenole (24) is formed by the oxidation of 1,8-bis(methylseleno) naphthalene with benzoyl peroxide \(<92CL1437>\).

2-Oxa-6,7-ditelluraspiro[3,4]octane (1) and 6,7-ditelluraspiro[3,4]octane (21) were both prepared from the corresponding bistellurocyanatomethyl compounds by heating \(<93JA885>\).

The tetraselenaperylene derivative (57) was prepared by reacting (24) with AlCl\(_3\) in nitrobenzene \(<84EUP107392>\).

1,2-Diselenolane (58) has been prepared from 1,3-bis(selenocyanato)propane and KOH \(<93T1605>\).

A series of hypervalent diselenide and ditelluride dications of the same type as (35) have been described \(<B-93MI 313-01>\).

1,5-Diselenoniabicyclo[3.3.0]octane hexafluorophosphates were prepared by reaction of 1,5-diselenacyclooctane with nitronium hexafluorophosphate \(<89CC1789, 90TL6375>\). 2,2,8,8-Tetraduterated salts have also been synthesized \(<93T1605>\).

1,5-Ditelluroniabicyclo[3.3.0]octane hexafluorophosphate could be prepared in an analogous way \(<91TL4537>\).
Benz-condensed systems like (59) have been described formed by the reaction of \(5H,7H\)-dibenzo[\(b,g\)]-1,5-diselenocine Se-oxide with silyl triflate \(<92\text{JCS(P1)2247}\>.

\[
\begin{array}{c}
\text{Se} \\
\text{Se} \\
\text{OH} \\
\text{(59)}
\end{array}
\]

The transient existence of dication (54) formed from dinaphtho[1,8-\(b,c\)]-1,5-diselenocine has been reported \(<91\text{TL}4345>\).

Tellur analogues of (59) were prepared from the corresponding dibenzo[\(b,g\)]-1,5-ditellurocin by reaction with iodine which gave the hypervalent diiodo compound (60). Mixed Se and Te compounds like (61) and (62) were also described \(<93\text{CL}263>\). If 1,5-ditellurocyclooctane was reacted with two equivalents of iodine, the dimer (63) could be isolated in quantitatively yield \(<92\text{JCS(P1)2583}\>.

\[
\begin{array}{cccc}
\text{Te} & \text{Te} \\
\text{I} & \text{I} \\
\text{(60)} & \\
\text{Te} & \text{Te} \\
\text{Se} & \text{Br} \\
\text{(61)} & \\
\text{Br} & \text{Te} \\
\text{Se} & \text{(62)} \\
\text{I-Te-Te-Te-Te-I} & \text{(63)}
\end{array}
\]

1,1-(Methanoselenomethano)-5\(H,7H\)-dibenzo[\(b,g\)]-1,5-diselenocine (64) is oxidized by concentrated sulfuric acid or 2 equivalents of nitronium hexafluorophosphate to the hypervalent selenenane (40) (Equation (4)) \(<92\text{JA}3117>\).

\[
\begin{array}{c}
\text{Se} \\
\text{Se} \\
\text{(64)} \\
\text{Se} \\
\text{Se} \\
\end{array}
\begin{array}{c}
+ \\
\text{NOPF}_{6}
\end{array}
\begin{array}{c}
\text{(40)}
\end{array}
\]

1,2-Oxatellurolylium compounds are formed by isomerization of 2-chlorocarbonylthene-1-yl aryl tellurium derivatives in dichloromethane in the presence of Lewis acids such as aluminum chloride according to Scheme 6 \(<83\text{JA}875, 83\text{JA}883, 88\text{OM}2188>\). The analogous 1,2-oxaselenolyl compounds could be prepared in the same way from 2-chlorocarbonylthene-1-yl aryl selenium derivatives \(<83\text{JA}883>\).

1-Bromo-1-butyl-3\(H\)-2,1-benzoxatellurole has been prepared from \(\alpha\)-(dibromobutyltelluro)benzyl alcohol and triethylamine \(<90\text{ZOB}471>\).

3.13.7.2 \([2 + 3]\) Two Component Synthesis

The method of synthesis, which is depicted generally in Equation 5, has been utilised for the synthesis of a great number of peridichalcogen-bridged polyacenes which are used as the donor part in organic conductors.

\[
\begin{array}{c}
\text{Cl} & \text{Cl} \\
\text{Cl} & \text{Cl} \\
\text{Cl} & \text{Cl} \\
\end{array}
\begin{array}{c}
\text{Na}_2X
\end{array}
\begin{array}{c}
\text{X} = \text{Se or Te}
\end{array}
\]

\[
\begin{array}{c}
\text{X} & \text{X} \\
\text{X} & \text{X}
\end{array}
\]
5,6-Dihydroacenaphtho[5,6-d]-1,2-diselenolene (65) was prepared from 5,6-dibromoacenaphthene via the dilithio derivative \(80\text{TL}4565, 88\text{BCJ}2013\). The ditelluride compound (3), however, could not be prepared by this method but was synthesized by reaction of sodium ditelluride with 5,6-dichloroacenaphthene in HMPA \(88\text{BCJ}2013\).

![Diagram](image)

The tetramethyl derivatives of (32) and (33) were prepared from the corresponding tetrachloro compounds \(87\text{CL}315, 88\text{SM}B509, 92\text{EUP}503113\).

Naphthaceno[1,12-c,d:4,5-c’,d’]bis[1,2]diselenolene (20) was prepared both from 1,4,5,12-tetrachloronaphthacene and from 1,4,5,12,12-hexachloronaphthacene \(90\text{BCJ}2441, 92\text{JAP}(K)0449274\).

The synthesis of naphthaceno[5,6-c,d:11,12-c’,d’]bis[1,2]diselenolene (14) has been described \(87\text{GEP}(O)3635124\). Derivatives have also been prepared from 5,12-diacetoxynaphthacene and selenium \(89\text{EUP}434111\).

Naphthaceno[5,6-c,d:11,12-c’,d’]bis[1,2]ditelluride, the tellurium analogue of (14), was prepared by the reaction of the corresponding tetrachlorotetracene with a new sodium telluride reagent formed directly from the elements in a 1:1 atomic ratio \(82\text{OM}739\). The synthesis of derivatives with functional groups has been described \(85\text{GEP}(O)3510090, 88\text{MIP}664154\).

Anthraceno[1,9-c,d:4,10-c’,d’]bis[1,2]diselenolene (15) was synthesized from 1,4,9,10-tetraloranthracene and sodium and selenium in DMF in 20% yield \(82\text{CL}1841, 83\text{MI}313-01\). Dimethyl and tetramethyl derivatives of (15) were prepared from appropriate tetrachloro compounds. The analogue tetratelluride compounds were also synthesized \(90\text{CL}567, 91\text{BCJ}2901\).

Fluorantheno[3,4-c,d]-1,2-ditelluride (18) and the analogue fluorantheno[3,4-c,d]-1,2-diselenolene were prepared from the corresponding dichloro compound and \(\text{Na}_2\text{Te}_2\) and \(\text{Na}_2\text{Se}_2\) respectively \(86\text{TL}2011, 87\text{SM}(19)599\).

The parent 1,2-diselenolene and 4,4-dimethyl-1,2-diselenolene were prepared from the corresponding dibromo compounds and lithium diselenide in THF \(88\text{TL}6119\). 1,2-Diselenolene-4-ol was synthesized from 1,3-dibromoprop-2-ol and sodium hydrogenselenide \(83\text{AJC}815\).

It has been reported that the reaction of phenylethylene with elemental tellurium at 60–100 °C gave rise to the formation of 3-benzylidene-4-phenyl-1,2-ditelluride \(85\text{SUL}13, 86\text{ZOR}220\). It has, however, since been proved that the product from this reaction is a 1:1 mixture of cis and trans-2-benzylidene-5-phenyl-2H-1,3-ditelluride (66) \(89\text{TL}441\).

![Diagram](image)

1,2-Diseleno[3,4-b]quinolines were prepared from 2-chloro-3-vinylquinolines and sodium hydrogenselenide in ethanol \(81\text{JJC}174\).

### 3.13.7.3 Multicomponent Synthesis

From the Fischer carbene complex \(\text{W(CO)}_2\text{COEiPh}\) derivatives of 1,2-selenathioc, 1,2-diselenene, and 1,2-dithiole have been prepared as complexes with \(\text{W(CO)}_3\) according to Scheme 7 \(84\text{CC}634, 88\text{OM}1853\).

The gas-phase reaction of dimethylselenide with propargyl alcohol at 450 °C gave 1,2-diselenol-3-one (46) \(87\text{KGS}855\). Compound (46) was also formed from diphenylselenide and propargyl alcohol at 450–600 °C. But, 1,2-ditelluril-3-one was not formed from diphenylditelluride and propargyl alcohol under the same conditions \(90\text{MI}313-01\)
Treatment of diphenylmethyltriphenylphosphonium bromide with butyllithium and elemental selenium followed by cyclopentadiene gave (67). The reaction could also be carried out with other substituted phosphonium salts (90H(31)2107, 94JCS(P1)2151).

Pentacarbonyltungsten coordinated selenetanes react with seleno- and tellurocyanates by insertion of the chalcogen atom in the Se—C bond of the selenetane to give 1,2-diselenolanes and 1,2-selenatellurolane, respectively, according to Scheme 8. The analogous reaction with the corresponding thietane gave 1,2-thiatellurolane (92CC1050).

If 1,3-ditelluroles, with at least one hydrogen present on the ring, are treated in MeCN with triphenylcarbenium tetrafluoroborate, the \(^1\)H NMR spectra of the solution show the formation of 1,3-ditellurolylium ions. The spectrum, however, quickly changes showing the formation of 1,2-ditellurolylium ions instead (82TL1531).

3,5-Dialkylamino-substituted 1,2-diselenolylum cations have been prepared from 1,3-bis(dialkylamino)-1,3-dichloropropenylum chloride by treatment with sodium hydrogen selenide and subsequent oxidation with hydrogen peroxide or \(m\)-chloroperbenzoic acid (87BCJ2686). These salts were also prepared by reaction with sodium diselenide in ethanol (86MCLC333).

If 2-methylseleno-3-nitrobenzoic acid is reacted with bromine in dichloromethane containing pyridine, 7-nitro-2,1-benzoxaselenol-3-one is formed in 75% yield. If this product is refluxed in thionyl chloride, 7-nitro-2,1-benzothiaselenol-3-one is formed in 92% yield (91T9053).
Two Adjacent Heteroatoms with at least One Selenium or Tellurium

The reaction of 2-methylselenobenzoic acid with 1,1'-carbonyldiimidazole followed by addition of t-butyl hydroperoxide gave the cyclic selenurane (68) \( 81TL2441 \), \( 82JOC2275 \).

![Structure of 68](image)

S-Methyl-1,2-benzodithiolium iodide reacted with sodium hydrogenselenide to give 1,2-benzo-thiaseleleno-3-thione (42) \( 82H(19)657 \).

The reaction of a silyloxypropyne with tellurium(IV)chloride resulted in formation of (69) in high yield \( 91TL229 \).

![Structure of 69](image)

Compounds like (56) were also prepared in a multistep reaction starting from tellurochroman-4-one \( 90ZOB2764 \).

Simple 1,2-tellurazoles are a class of compounds relatively sparsely described. They may be formed in low yields, often not exceeding 10%, from complex reaction mixtures consisting of \( \alpha \)-alkynic ketones, hydroxylamine \( O \)-sulfonic acid, sodium acetate, and potassium telluride \( 83S824 \), \( 87H(26)1587 \).

A series of compounds which can be considered hypervalent 1,2-tellurazoles have been prepared and the structures have been given (see Section 3.13.2.1) (Scheme 2). Such compounds have also been reported without structure determinations \( 85JCS(D)821 \), \( 85SRH043 \), \( 86EUP192466 \), \( 88KGS1426 \), \( 88MI313-01 \), \( 88ZOB1684 \), \( 89MI313-01 \), \( 89MI313-02 \), \( 90JOM(391)179 \), \( 90JOM(397)153 \).

3,4-Dimethyl-1,6-dioxa-6a\( \lambda^4 \)-selena-2-azapentalene (71) was formed in high yield when the diselena compound (70) reacted with mercury(II)acetate in boiling acetic acid (Equation (6)) \( 81JCS(P1)1596 \).

![Structure of 69](image)

\[
\text{(70)} \qquad \text{Hg(OAc)}_2, \text{AcOH} \quad \text{(71)}
\]

The salts (72) and (73) in DMF gave, on treatment with aqueous potassium selenosulfate, the thiaselenadiazapentalenes (74) and (75), respectively (Equations (7) and (8)) \( 83JCS(P1)777 \).
Two Adjacent Heteroatoms with at least One Selenium or Tellurium

Thiadiselenazapentalenes (76) and (77) are formed when 3,4-dimethyl-1-oxa-6,6α4-diselena-2-azapentalene reacts with phosphorus pentasulfide \( \langle 87 \text{CC967} \rangle \).

![Diagram of molecules](image)

Compounds of the same type as (74) and (75) were formed from (78) by the reaction with phenylselenophosphonic dichloride and triethylamine. If oxadithiapentalenes reacted with phenyl-selenophosphonic dichloride, selenadithiapentalenes were formed \( \langle 88 \text{CC1494} \rangle \).

![Diagram of molecule](image)

3.13.8 APPLICATIONS

Peridi- or tetrachalcogen-bridged polyacenes have been claimed in the patent literature for the preparation of electrical conducting materials \( \langle 88 \text{EUP285564, 93EUP521826} \rangle \). They have also been claimed as copolymers for the preparation of radiation sensitive polymers \( \langle 90 \text{EUP362143} \rangle \).

1,6-Dioxo-6α2-selena(tellura) pentalenones have been claimed for use as sensitizers in electrophotogenic compounds \( \langle 84 \text{USP4450217} \rangle \).

4,4-Disubstituted-1,2-diselenoles and telluroles have been proposed as fog inhibitors for silver halide photographic materials \( \langle 89 \text{USP4861703} \rangle \).