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MOLECULAR STRUCTURE OF SELENOPHENES AND TELLUROPHENES. (REVIEW)

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The results of X-ray diffraction investigations of compounds containing selenophene and tellurophene fragments are reviewed and analyzed. The structural features of unsubstituted selenophene and tellurophene and their mono-, di-, tri-, and tetrasubstituted derivatives and also the structure of the complexes of selenophenes and tellurophenes with transition metals are discussed.

Keywords: selenium, selenophene, tellurium, tellurophene, molecular structure.

The increasing interest in the compounds of selenophene and tellurophene in recent years is explained by the discovery of a series of derivatives with clearly defined biological activity. The effect of a selenophene or tellurophene fragment in the porphyrin macrocycle on anticancer activity was studied, and it was established that the glycosylated derivatives of selenophene are inhibitors of inosine 5'-monophosphate dehydrogenase. Investigations in the region of organic π-conjugated oligomers containing selenophene or tellurophene fragments are of great interest for the production of prospective materials with semiconducting and optoelectronic characteristics. The biological activity and physicochemical properties of selenophenes and tellurophenes are determined primarily by their structural characteristics. The present review therefore covers the data from X-ray crystallographic analysis of selenophene and tellurophene derivatives.

1. SELENOPHENES

The results of numerous attempts to determine the geometric parameters and molecular structure of unsubstituted selenophene [1-4] are extremely contradictory. The largest differences entail the question of coplanarity. More recently microwave spectroscopy has been used to refine the parameters of the simplest unsubstituted selenophene (**1**). The microwave spectra of selenophene, 2,5-dideuteroselenophene, and tetradeuteroselenophene were recorded at 233 K [5]. The molecular structure of selenophene was determined by the method of Kraitchman and Costain [6, 7]. The bond lengths and angles of selenophene, calculated from the rotational constants, indicate a completely planar structure for the molecule (Table 1).

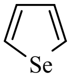

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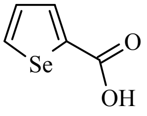
TABLE 1. The Geometric Parameters of Selenophene

Bond	Bond lenght, Å	Angle	
Se–C2	1.8547 ± 0.0009	C5–Se–C2	87°46' ± 4'
C2–C3	1.3695 ± 0.0012	Se–C2–C3	111°34' ± 8'
C3–C4	1.4332 ± 0.0030	C2–C3–C4	114°33' ± 6'
C2–H2	1.0700 ± 0.0013	Se–C2–H2	121°44' ± 3'
C3–H3	1.0792 ± 0.0011	C4–C3–H3	122°52' ± 5'

A special feature of the structure of selenophene-2-carboxylic acid (**2**) [8] is the fact that in the single crystal the molecule exists in the form of a dimer connected by hydrogen bonds (Table 2).

According to data from X-ray crystallographic analysis the pyrrole rings of 2,5-bis[(2-pyrrolyl)phenylmethyl]selenophene (**3**) [9] are in the *trans* position in relation to the selenophene ring. The planes of the central selenophene and terminal pyrrole rings form dihedral angles [31.3(6)° and 65.7(5)°] indicating that the molecule is spiral in form in the solid state (Table 2).

In the molecule of ethyl 2-β-*D*-ribofuranosylselenophene-4-carboxylate (**4**) [10] the selenophene ring is planar and coplanar with the ethoxycarbonyl group at position 4 of the heterocycle. As a result of intramolecular interaction between the selenium and the oxygen of the tetrahydrofuran ring these atoms are in the cisoid position in relation to each other. (The Se···O distance amounts to 3.12 Å.) Torsion angle O–C–C–Se in relation to glycoside bond C–C is 46.3°.



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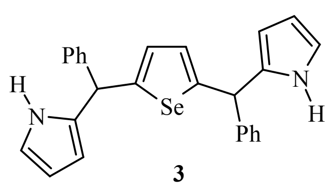

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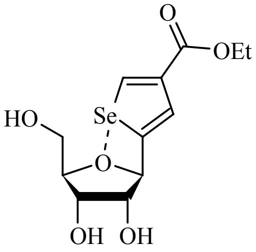

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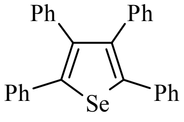
The Se–C bonds in 2,3,4,5-tetraphenylselenophene (**5**) [11] differ in length [1.82(3) and 1.92(3) Å] on account of the sterically bulky phenyl groups, arranged like a propeller in relation to the selenophene ring. In the molecule of tetramethoxycarbonylselenophene (**6**) [12] the steric hindrances are smaller, and the bonds are more equalized (Table 2).



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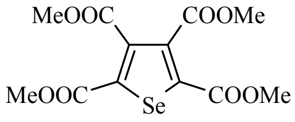

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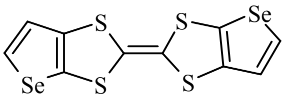
TABLE 2. The Geometric Parameters of the Selenophenes **2**, **3**, **5**, and **6**

Compound	Bond lenght, Å						*R*	References
	Se–C2	Se–C5	C2–C3	C3–C4	C4–C5	C2–Se–C5		
2	1.872(8)	1.850(12)	1.356(15)	1.421(17)	1.355(15)	87.6(2)	0.084	[8]
3	1.884(5)	1.880(4)	1.337(7)	1.429(7)	1.353(6)	87.8(2)	0.1042	[9]
5	1.92(3)	1.82(3)	1.35(4)	1.46(5)	1.38(2)	88.7(7)	0.092	[11]
6	1.866	1.880	1.385	1.417	1.374	87.71	0.054	[12]

In the crystalline state diselenolotetrathiafulvalene (**7**) [13] represents a mixture of transoid and cisoid isomers with different *cis*-(C_{2v}) and *trans*-(C_{2h}) symmetry. Both isomers are stable in the solid state. With tetracyanoquinodimethane compound **7** forms a charge-transfer complex **8** [14]. The distance between the molecules of the donor and the acceptor is ~3.5 Å, and the Se···Se contacts are 3.80 Å. It was only possible to crystallize the molecule of 2,2'-bi(selenolo[3,4-*b*]-1,3-dithiol-2-ylidene) (**9**) [14] in the form of a solvate complex (DMF) with nonachloropentathiahexarhenate. In the obtained cluster the distances between the selenium atoms of the adjacent molecules (Se···Se) did not exceed 3.80 Å. The selenophene heterocycle in the molecule of compound **10** [15] is condensed with two tetrathiafulvalene substituents. The C–Se–C angle in the molecule of the selenophene **10** is 85.48(6)°, which is almost 2° smaller than in free selenophene.



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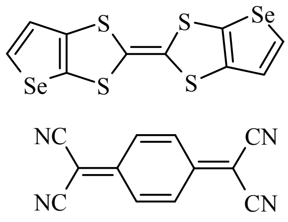

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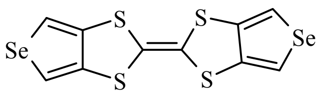

$Re_2S_5Cl_9$
2 DMF

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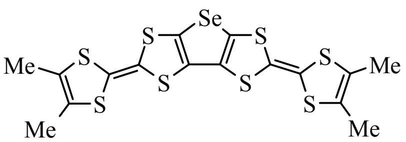

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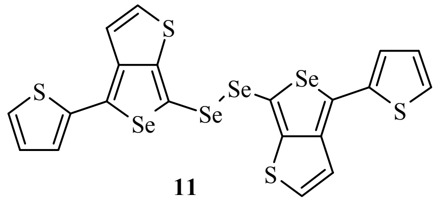

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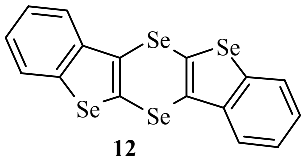
There are eight molecules in the molecular cell of bis{4-(2-thienyl)selenolo[3,4-*b*]thiophen-6-yl} diselenide (**11**) (*Z* = 8) [16]. The condensed selenolothiophene group is practically planar. The sulfur of the terminal thiophene ring and the selenium atom in the selenophene are in the transoid arrangement in relation to each other (torsion angle 170.3°). A distinctive feature of the structure is the fact that the two condensed parts of the molecule lie in different planes parallel to each other and are linked by a diselenide bridge [Se–Se = 2.390(2) Å]. The intramolecular separation between the selenophene selenium atoms (Se···Se) amounts to 3.620(1) Å.

The benzo[*b*]selenophene fragments of compound **12** [17] annellated with a six-membered 1,4-diselenin heterocycle have a substantial effect on the geometric parameters of the central ring. The diselenin ring assumes the almost ideal twisted boat conformation. The geometry of the selenophene rings in fact coincides with unsubstituted selenophene. The molecule as a whole has a V-shaped form (the butterfly conformation) bent along the Se–Se bond of the diselenin ring. The two halves of the molecule are practically planar, and the dihedral angle between them amounts to 123.5°. In the crystal of dibenzo[*b*]selenopheno[2,3-*b*:2,3-*e*]-1,4-diselenin (**12**) intermolecular Se···Se contacts shorter than twice the van der Waals radius of the selenium atom (4.0 Å) are observed. Thus, between the adjacent molecules, packed in stacks, the intermolecular Se···Se separations are 3.887(2) Å.



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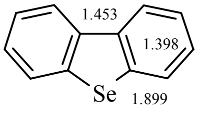
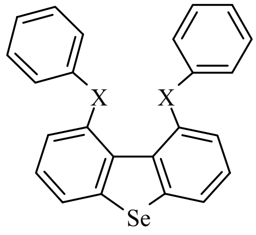


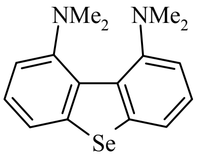
13

The five- and six-membered rings of the dibenzoselenophene (**13**) [18] are practically planar, and the dihedral angle between the benzene rings does not exceed 1.2°. The Se–C bond in dibenzoselenophene [1.889(5) Å] is elongated compared with unsubstituted selenophene. The intermolecular contact between the Se···Se selenium atoms of two adjacent molecules amounts to 3.887(2) Å.

The planarity of the selenophene rings in the isostructural 1,9-diphenylthio- and 1,9-diphenylselenodibenzoselenophenes (compounds **14** and **15**) [19] are somewhat distorted. The deformations are due to the bulky PhS and PhSe substituents, and the dihedral angles between the planes of the benzene rings are in the order of 6.6-8.5°. The shortened S···S interaction in compound **14** [2.973(1) Å] is smaller than for the Se···Se contact in the analog **15** [3.070(1) Å].



14 X = S, **15** X = Se



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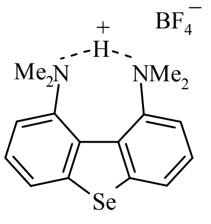
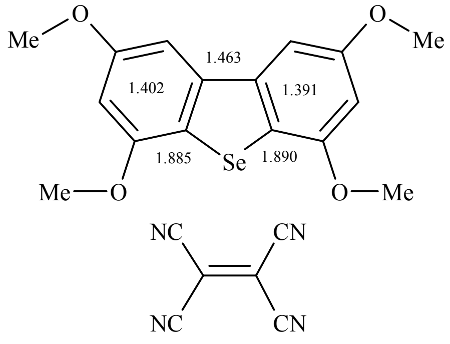


17

The condensed benzene rings of the 1,9-bis(dimethylamino)dibenzoselenophene (**16**) molecule [20] do not form the ideal plane with the selenophene heterocycle on account of the steric strain of the dimethylamino groups. The condensed system of dibenzoselenophene tetrafluoroborate **17** is more planar [20]. Protonation of the amino group reduces the distance between the nitrogen atoms N···N from 2.823 to 2.573 Å, and the N···H···N angle is 175°.

In the reaction of 2,4,6,8-tetramethoxydibenzoselenophene with tetracyanoethylene and tetracyanoquinodimethane the charge-transfer complexes **18** and **19** are formed [21]. The geometric parameters of these complexes differ very little from those of the dibenzoselenophene **13**.



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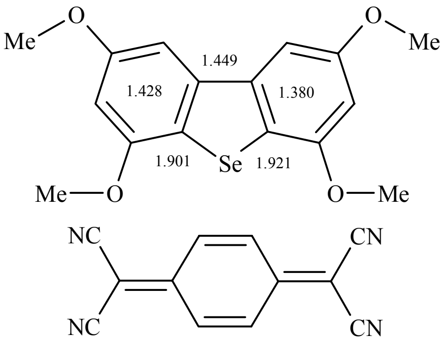

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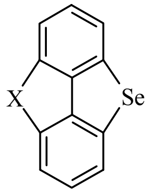
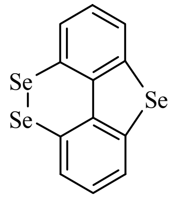
According to X-ray crystallographic analysis the molecules of dibenzo[*bc*,*fg*]selenathiapentalene (**20**) and dibenzo[*bc*,*fg*]diselenapentalene (**21**) [22] are absolutely planar. The Se–C bonds are elongated (1.911-1.930 Å) compared with dibenzoselenophene, but the selenophene C3–C4 bond is shorter (1.38 Å, **21**). The introduction of a second selenium atom into one of the heterocycles of the dibenzoselenapentalene system (compound **22**) leads to loss of planarity (torsion angle 13.9°). The length of the diseleno Se–Se bond is 2.32 Å.

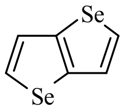


20 X = S; **21** X = Se



22

During comparison of the geometric parameters of selenolo[3,2-*b*]selenophene (**23**) [23] with the thienothiophene analog it was found that the lengths of the C–C bonds were similar but the C–Se–C angle was smaller [86.1(3)°] than C–S–C (91.2°) on account of the longer C–Se bonds [1.93(2) and 1.84(2) Å].



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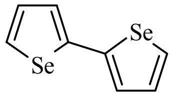

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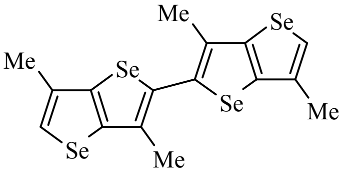
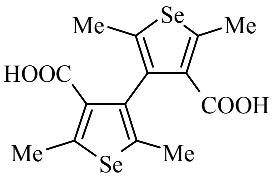
The molecule of 2,2'-biselenophene (**24**) [24] has a planar transoid conformation. The molecular layers in the crystal are packed in herring-bone form with an angle of 60.6°. As in bithiophene, in compound **24** there are no interatomic interactions between adjacent molecules.

Investigation of the structure of 2,2'-bi(3,6-dimethylselenolo[3,2-*b*]selenophene) (**25**) [25] showed that the molecule in the solid state is present in the *s-cis* conformation. The practically planar selenoloselenophene fragments form a dihedral angle (69.5°). Such a large dihedral angle is due to steric hindrances created by the two β-methyl groups. The bond between the selenoloselenophenes is shorter than an ordinary C–C bond, which makes it possible to suppose the presence of conjugation between the two aromatic groups.



25

The bond lengths and the angles of the heterocycle in the molecule of 4,4'-dicarboxy-2,2',5,5'-tetramethyl-3,3'-biselenophene **26** [26] do not differ from those described above. The planes of the two selenophene rings are practically orthogonal (dihedral angle 96°) with the carboxyl groups in the transoid position. All the molecules of the biselenophene **26** are linked by hydrogen bonds [~2.651(13) Å], formed by the carboxyl groups.



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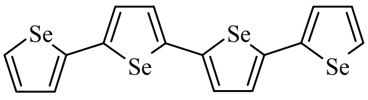
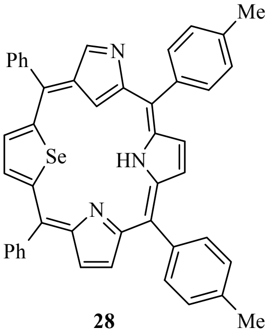


27

Extremely interesting is the structure of the α-quaterselenophene **27** [27]. The torsion angles (176.76, 180.0, and -176.76°) indicate that the molecule is practically planar. All the selenophene rings are in the transoid position. The C–C bond between the central selenophenes (1.405 Å) is shorter than the C–C bond with the terminal heterocycles (1.425 Å), while the C–Se–C angle in the terminal selenophenes is 1° smaller (88.13°) than in the inner selenophenes (89.29°).

In recent years a series of porphyrin derivatives in which one or several pyrrole heterocycles are replaced by selenophenes have been synthesized. The pyrrole rings of 5,20-diphenyl-10,15-bis(*p*-tolyl)-21-selenaporphyrin (**28**) [28] are disordered, and the selenophene heterocycle is not included in the delocalization of the macrocycle. In the stereoisomeric selenaporphyrin **29** [29] all the nitrogen atoms are turned inside the macrocycle. The lengths of the Se–C bonds in the selenaporphyrins **28** [1.893(8) Å] and **29** [1.850(7) Å and 1.868(7) Å] correspond to the values of the covalent Se–C bonds. The macrocycle **30** [30] is practically planar. One selenophene ring has the normal structure, while the other is characterized by the formation of a *meso* form. The imine hydrogen atom is delocalized among all the pyrrole rings, leading to disordering of the molecule. The distance between the imine hydrogen atom and the selenium atoms in the crystalline state amounts to 2.63(17) and 2.28(17) Å. The Se···Se distance in 22π-diselenaporphyrin **30** is 3.9315(8) Å.



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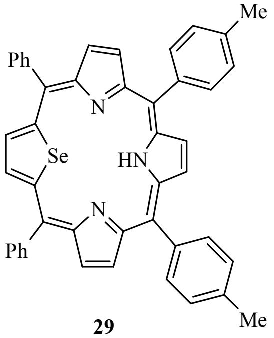

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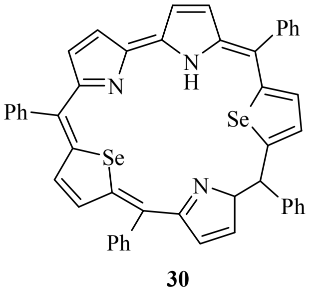

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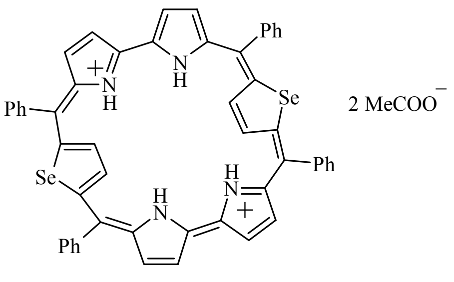

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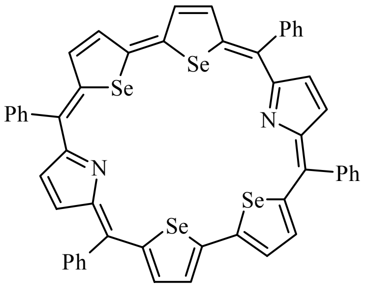
The molecular cell of 5,10,19,24-tetraphenyl-30,33-diselenarubyrin (**31**) [9] contains two independent molecules (*Z* = 2), one of which is solvated by methanol. As in the porphyrin **30**, one of the selenophenes exists in the *meso* form. The selenophene and mesoselenophene heterocycles are turned in such a way that the selenium atoms are directed toward the outside of the macrocycle. The dihedral angle between the planes of the selenophene and close-lying pyrrole amounts to 23.01°. The double bonds of the selenophene ring are equal to 1.381(14) and 1.390(13) Å, while the single bond is 1.412(13) Å. In the second heterocycle the lengths of the C2–C3 [1.409(14) and 1.414(14) Å] and C3–C4 [1.366(14) Å] bonds confirm the formation of the *meso* form.

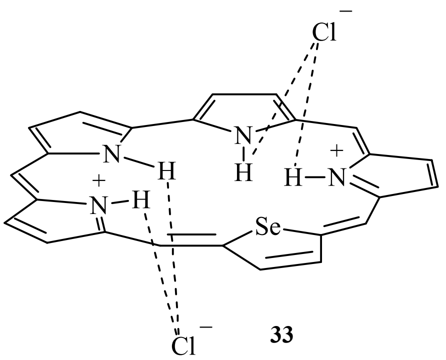
In the crystalline state the macrocycle of compound **32** [31] only departs slightly from planarity. One of the selenophene rings of biselenophene is rotated by 6.18° in relation to the other. The biselenophene fragments are in the *syn* conformation, due to which the distances between the selenium atoms in the biselenophene fragments are 3.468 (for mesoselenophene) and 3.566 Å (for selenophene).



32

The dihydrochloride of 2,8,17,23-tetramethyl-3,7,18,22-tetraethyl-27-selenasapphyrin (**33**) [32] represents a sapphyrin plane with two chloride anions projecting on different sides of the macrocycle. The distances between the chlorine and nitrogen atoms amount to 3.031(2) and 3.119(2) Å, and between the two chloride ions 5.337(2) Å. The selenophene heterocycle participates in the π-delocalization of the sapphyrin and exists in the meso form [C2–C3 1.419(4) Å, C3–C4 1.364(6) Å].

As in the dichloride, in the neutral iridium complex **34** [32] the metal atoms lie on different sides of the ring. The selenium atom does no participate in the coordination of the metal. The iridium atoms are only linked to the pyrrole nitrogen atoms of the macrocycle. The distance between the iridium atoms Ir···Ir amounts to 4.233(1) Å, while the Ir–N bonds are equal to 2.100(1) and 2.076(6) Å. The C–C carbon bonds of the selenophene fragment are practically identical [C2–C3, 1.42(10), C3–C4, 1.41(5) Å] on account of the high level of delocalization in the macrocycle **34**.



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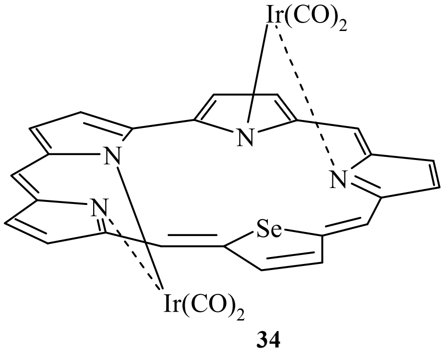
(For simplicity the alkyl groups are not indicated.)



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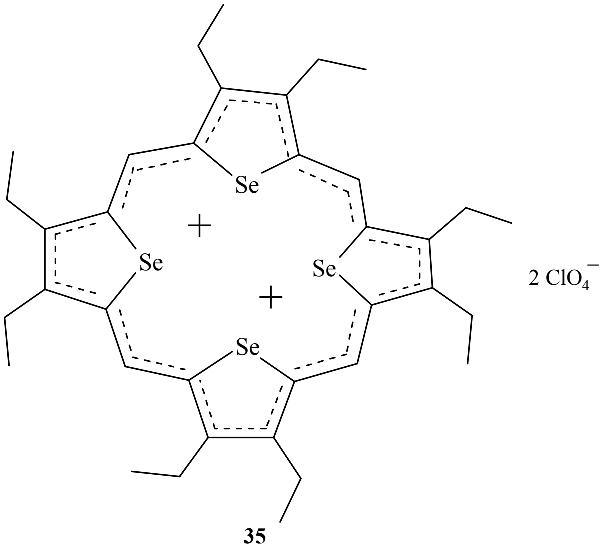
X-ray crystallographic analysis of the octaethyltetraselenaporphyrin perchlorate (**35**) molecule [33] showed that the macrocycle is not planar. However, since the molecule exists in the form of a dication it is centrosymmetric, and the planes of the selenophene rings form dihedral angles of 24.3 and 30.5° with each other. The 1.5-fold bonds C2–C3, C3–C4, and C4–C5 of the selenophenes are practically identical (in the order of 1.40-1.44 Å), and the shortest distance between the selenium atoms is 2.9 Å, which is 1.1 Å less than the sum of their van der Waals radii.

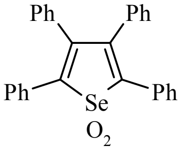


35

2. HYPERVALENT DERIVATIVES OF SELENOPHENE

2,3,4,5-Tetraphenylselenophene 1,1-dioxide (**36**) [34] is formed during oxidation of the initial selenophene with two equivalents of acetone peroxide. The five-membered ring is practically planar, but the lengths of the bonds (C2–C3 1.354, C3–C4 1.516, C4–C5 1.345 Å) indicate loss of aromaticity. All the phenyl groups are not coplanar but form a conformation of the propeller type with a five-membered ring. The C–Se–C angle is 91.1(2)°.

In the unit cell of bis(2,2'-biphenylene)-1,1-difluoroselenurane (**37**) [35] there are four molecules (*Z* = 4) together with four molecules of methylene chloride. The racemic mixture contains two types of selenium centers, having two biphenylylene ligands and two fluorine atoms. The selenium atom has a distorted octahedral geometry with two fluorine atoms in the cisoid position. The lengths of the Se–F bond [1.853(4) Å] and the covalent bond (1.88 Å) practically coincide.



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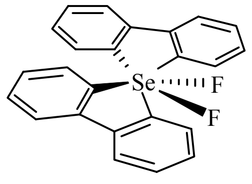
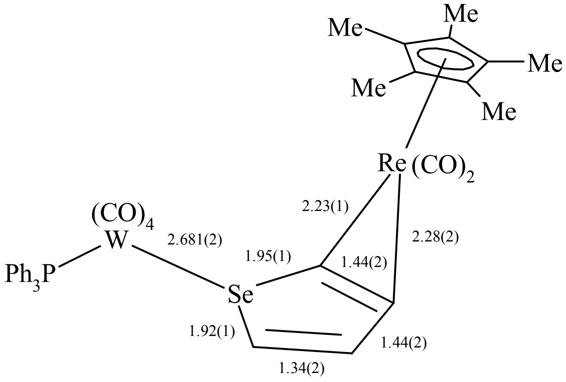


37

3. COMPLEXES OF SELENOPHENES WITH TRANSITION METALS

According to data from low-temperature X-ray crystallographic analysis (203 K) the selenophene ring of the tungsten-rhenium complex **38** is planar [36]. The C2–C3 bond [1.44(2) Å] coordinated with the rhenium and also the Se–C2 [1.95(1) Å] and Se–C5 [1.92(1) Å] bonds are rather longer than the bonds of free selenophene. The selenium atom in the molecule is pyramidal, while the structure of the selenophene ring is greatly changed on account of coordination with the two metals.



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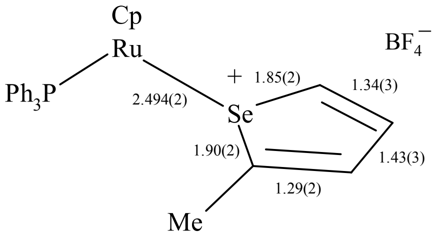

39

In the molecule of the 2-methylselenophene complex with ruthenium **39** [37] the selenophene ring is planar, and the deviation from the plane does not exceed 0.89°. The ruthenium atom is not connected to all the atoms of the selenophene ring but only to the selenium. The length of the Ru–Se bond is 2.494(2) Å, which is 0.102 Å longer than the Ru–S bond in the thiophene analog. The selenium atom has trigonal geometry. The C–Se–C angle is 88(1)°.

4. TELLUROPHENES

The geometric parameters of tellurophene **40** were first determined in 1973 by microwave spectroscopy [38]. More recently calculations based on the ^{1}H NMR spectrum in a nematophase solvent and X-ray diffraction data have been used to refine the structure of the heterocycle (Table 3) [39, 40]. The Te–C2 bond is somewhat longer than the Se–C2 bond in selenophene (1.8547 Å), while the C2–Te–C5 angle is smaller than the C2–Se–C5 angle of selenophene, since the tellurium atom is larger than the selenium atom.

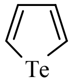

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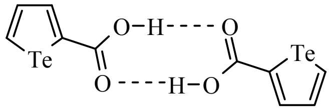
TABLE 3. The Geometric Parameters of Tellurophene

Bond	Bond lenght, Å	Angle	Deg.
Te–C2	2.046	C5–Te–C2	82.00
C2–C3	1.371	Te–C2–C3	111.83
C3–C4	1.478	C2–C3–C4	116.76
C2–H2	1.074	Te–C2–H2	122.93
C3–H3	1.079	C4–C3–H3	121.59

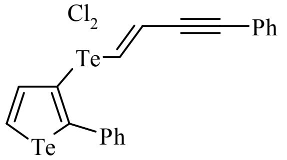
According to X-ray crystallographic analysis, the molecular cell of tellurophene-2-carboxylic acid (**41**) [41] consists of a dimer of two crystallographically non-equivalent molecules, linked to each other by hydrogen bonds. The two molecules of the dimer are slightly displaced in relation to each other, and the dihedral angle between the planes of the tellurophene rings amounts to 166.30°.



41

The tellurophene ring of compound **42** [42] is absolutely planar. The dihedral angle with the phenyl group amounts to 69.4(4)°, and the lengths of the Te–C bond [2.088(12), 2.140(2) Å] and the C–Te–C angle [82.6(5)°] in the heterocycle are similar to those in unsubstituted tellurophene.

In the unit cell of 3-iodo-2,5-diphenyltellurophene (**43**) [43] there are eight molecules (Z = 8). The tellurophene ring is planar, while the conjugated π system as a whole departs from coplanarity, and the phenyl groups are rotated by 126.0(2) and 29.2(5)° in relation to the plane of the tellurophene. The C–Te–C angle is 82.7(4)°.



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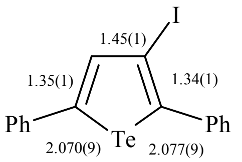

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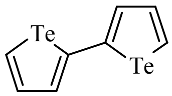
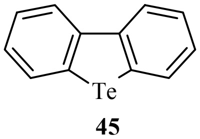


44

The molecular structure of 2,2'-bitellurophene (**44**) [44] was determined by X-ray crystallographic analysis. The tellurophene rings are in the transoidal position (torsion angle 180.0°). The length of the C–C bond between the tellurophenes amounts to 1.46(3) Å. The other bond lengths and the angles practically coincide with the analogous parameters of unsubstituted tellurophene. The molecular layers are packed in the crystal in herring-bone form with an angle of 74.0°, which is 13.4° larger than in the selenophene analog. There are no short interatomic contacts between the molecules of **44** in the parallel layers, but fairly strong Te···Te interactions (4.31 Å) exist between the tellurium atoms in the herring-bone.

The benzene rings of dibenzotellurophene (tellurane) (**45**) [45] are slightly deflected from the plane of the tellurophene ring [1.4(2) and 0.6(2)°]. The Te–C bond lengths are in the order of 2.084(5) and 2.089(5) Å, while the C–Te–C angle is 81.7(2)°. The shortest distance in the unit cell (Z = 4) between the tellurium atoms Te···Te is 4.056 Å, which is less than the sum of the van der Waals radii (4.40 Å).

On account of the large size of the tellurium atom [Te–C = 2.083(9), 2.065(9) Å] the macrocycle of 21-telluraporphyrin (**46**) [46] is somewhat distorted. The state of the tellurophene in the meso form is confirmed by the lengths of the bonds in the ring [C3–C4 1.37(2), C2–C3 1.42(2) Å]. Thus, in contrast to the selenaporphyrin analog, the tellurophene ring is involved in aromatic delocalization.



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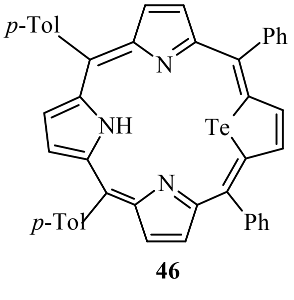
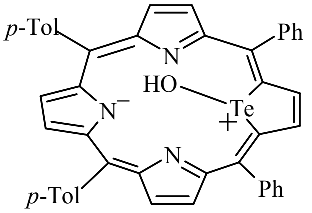


46

5. HYPERVALENT DERIVATIVES OF TELLUROPHENE

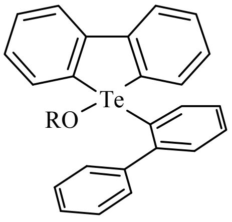
21-Telluraporphyrin Te-1-oxide was synthesized by oxidation of the initial macrocycle **46** with *m*-chloroperbenzoic acid. The oxygen at the tellurium deprotonates the pyrrole ring, forming a new compound of betaine type **47** [46] with a hydroxyl group at the tellurium atom.



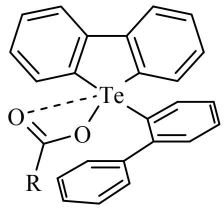
47

The most interesting structural feature of compound **47** is the fact that the hydroxyl group projects from the plane of the telluraporphyrin ring. The Te–O bond [1.916(4) Å] is an ordinary covalent bond. The distance between the proton of the hydroxyl group and the deprotonated nitrogen atom amounts to 2.243 Å.

The Te–C bonds in the phenoxytellurane **48** [47, 48] are not identical, but the lengths of the Te–O bond [2.29(4) Å] and the Te–O covalent bond coincide, which confirms the tetravalence of the tellurium (Table 4). If the phenoxy group is replaced by a *p*-nitrophenoxy group (R = 4-$O_2NC_6H_4$) the Te–O bond in compound **49** [47, 48] is elongated [2.762(2) Å] on account of the increase in the electronegativity of the substituent. In turn the 2,4,6-trichlorophenoxy derivative (R = 2,4,6-$Cl_3C_6H_3$) of tellurane **50** [47, 48] in the single crystal exists in the form of a solvated centrosymmetric O-bonded dimer (*Z* = 2). The Te–O bond is even more elongated [2.787(2) Å] but does not exceed the sum of the van der Waals radii (3.60 Å). With increase in the electronegativity of the substituent (R) the structure of the tellurane moves from the hypervalent state to an onium salt with a positive charge at the tellurium atom.



48–50



51, **52**

48, 51 R = Ph, **49** R = 4-$O_2NC_6H_4$, **50** R = 2,4,6-$Cl_3C_6H_2$, **52** R = Me

TABLE 4. The Geometric Parameters of the Telluranes **48-52***

Compound	Bond lenght, Å							Angle C2–Te–C5, deg.	*R*
	Te–C2	Te–C5	C2–C3	C3–C4	C4–C5	Te–O	Te···O		
48	2.174(5)	2.103(5)	1.391(7)	1.471(8)	1.398(7)	2.294(4)		79.7(2)	0.044
49	2.150(4)	2.102(4)	1.392(7)	1.462(8)	1.404(7)	2.461(3)		80.2(2)	0.031
50	2.119(4)	2.108(4)	1.399(5)	1.467(7)	1.394(5)	2.762(2)		81.3(2)	0.030
51	2.152(5)	2.116(5)				2.491(4)	3.181(4)	80.3(2)	0.027
52	2.131(5)	2.110(5)				2.469(3)	3.182(3)	80.9(1)	0.025

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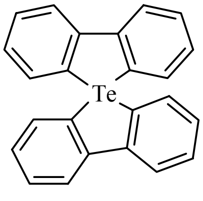
*Compounds **48-50**, data from [47, 48]; compounds **51**, **52**, data from [49].

In the molecule of benzoxytellurane **51** (R = Ph) [49] the covalent Te–O bond [2.469(3) Å] is longer than a normal Te–O bond (2.101 Å) (Table 4). The tellurium atom in the compound is tetravalent with distorted pseudotrigonal-bipyramidal geometry, since the tellurium atom is additionally coordinated with the oxygen atom of the carbonyl group [3.182(3) Å]. The molecules of the tellurane **51** are packed in the unit cell as monomeric independent molecules (*Z* = 2). The structures of the acetoxytellurane **52** [49] (R = Me) and compound **51** are similar, but the tellurium atom has trigonal-bipyramidal geometry. The differences in the packing of the molecules of the benzoic and acetic acid derivatives are due to the steric factors of the carboxyl substituent (*Z* = 16). The apical Te–C bonds in the molecule of bis(2,2'-biphenylylene)tellurane (**53**) [50] are longer [2.244(9), 2.235(9) Å] than the equatorial bonds [2.144(8), 2.137(9) Å]. The C–Te–C angles in the tellurophene rings amount to 77.8(3) and 90.3(3)°.

The tellurium atom in the molecule of tellurane 1,1-diiodide (**54**) [51] is attached to two carbon atoms [2.113(12), 2.111(4) Å], and the C–Te–C angle is 81.8(2)°. With the iodine atoms the tellurium forms axial bonds [2.994(1), 2.928(1) Å], and the I–Te–I angle in the tellurane **54** amounts to 178.47(1)°. In addition to the covalent bonds the tellurium atom forms coordination bonds Te···I [3.717(1) and 3.696(1) Å] with the iodine atoms of adjacent molecules. As a result of the additional bonds the tellurium atom acquires octahedral geometry. The dibenzotellurophene fragment in compound **54** is practically planar.



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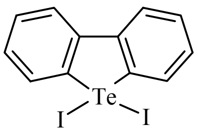
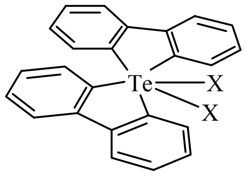


54

In the unit cell of bis(2,2'-biphenylylene)-1,1-difluorotellurane (**55**) [52] there are four molecules (*Z* = 4) together with two molecules of water of crystallization. The racemic mixture contains two types of tellurium centers, having two biphenylylene ligands and two fluorine atoms. The tellurium atom has distorted octahedral geometry with the two fluorine atoms in the cisoid position. The length of the Te–F bond (1.972 Å) coincides with the value for a covalent bond. In turn, the unit cell of bis(2,2'-biphenylylene)-1,1-dichlorotellurane (**56**) [52] apart from the four molecules of compound **56** contains four molecules of methylene chloride. The Te–Cl bond (2.530 Å) is longer than a covalent bond (2.31 Å) (Table 5).

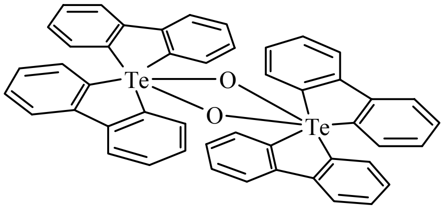


55 X = F, **56** X = Cl

TABLE 5. The Geometric Parameters of Dihalotelluranes **55** and **56** [52]

Compound	Bond lenght, Å						Angle C2–Te–C5, deg.	*R*
	Te–C2	Te–C5	C2–C3	C3–C4	C4–C5	Te–X		
55	2.12(3)	2.08(1)	1.38(1)	1.49(2)	1.43(2)	1.969(6); 1.975(6)	82.9(4)	0.025
56	2.130(3)	2.116(4)	1.404(5)	1.471(5)	1.400(5)	2.530(1)	82.7(1)	0.052

The tellurium atom in the dimer bis(2,2'-biphenylylene)tellurane 1-oxide (**57**) [53] has distorted octahedral geometry.

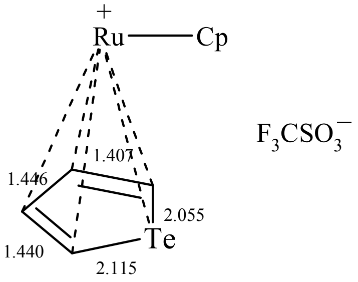


57

The lengths of the Te(VI)–C bonds in compound **57** lie in the range between 2.122(9) and 2.159(9) Å. However, the Te(VI)–O bonds [1.997(6)-2.019(6) Å] are significantly shorter than an ordinary Te–O bond (2.101 Å). The four-membered ring, consisting of two tellurium atoms and two oxygen atoms, is planar. It is interesting that the distance between the two tellurium atoms [3.1243(8) Å] is only 15% longer than a Te–Te covalent bond.

6. COMPLEXES OF TELLUROPHENES WITH TRANSITION METALS

The molecular structure of the ruthenium complex of tellurophene **58** [54] was determined by X-ray crystallographic analysis. Equalization of the C–C bonds in the tellurophene heterocycle is observed. The length of the coordinated Te···Ru bond amounts to 2.635 Å, while the length of the ruthenium–tellurophene ring bond is 1.809 Å.



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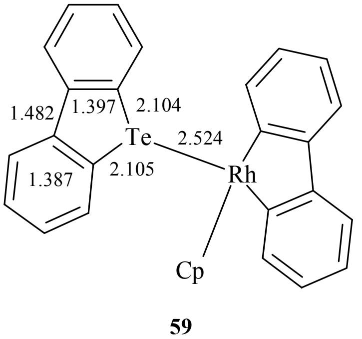

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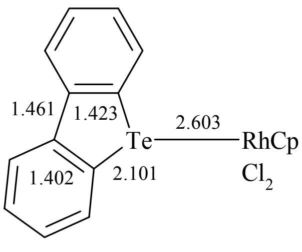

60

In the rhodium complexes of tellurane **59** and **60** [55] the rhodium atom is not attached to the aromatic π system but to the tellurium atom. The length of the Rh–Te bond lies in the range of 2.524-2.603 Å.

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