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Intramolecular O→Te and N→Te coordination bonds in molecules of β-tellurocyclohexenals and their nitrogen analogs

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The structures of β-tellurocyclohexenals and their nitrogen analogs, *viz.*, β-methyltellurocyclohexenal (**6**), β-(4-ethoxyphenyltelluro)cyclohexenal (**7**), di(2-formylcyclohexen-1-yl) telluride (**8**), β-(4-ethoxyphenyltelluro)cyclohexenylidene(4´-methylaniline) (**9**), β-bromotellurenylcyclohexenylidene(4´-methylaniline) (**10**), and β-bromotellurenylcyclohexenal (4-methylbenzoyl)hydrazone (**11**), were studied by X-ray diffraction analysis. Compounds **6—11** have a *Z* configuration at the double bond, which provides the formation of intramolecular O→Te or N→Te coordination bonds. The bonds about the Te atom have a T-shaped configuration. There is only one of two possible O→Te coordination bonds in dialdehyde **8** and, consequently, this compound belongs to the 10-Te-3-tellurane structural type. Hydrazone **11** possesses both N→Te and O→Te intramolecular coordination bonds. Taking into account these interactions, the coordination polyhedron of the tellurium atom can be considered as a trigonal bipyramid. The intramolecular O→Te or N→Te coordination bond lengths in compounds **6** (2.692 Å), **7** (2.657 Å), **8** (2.657 Å), and **9** (2.690 Å) are 0.9—1.0 Å smaller than the sums of the van der Waals radii of the corresponding atoms. These bond lengths in compounds **10** (2.170 Å) and **11** (2.203 Å) are almost equal to the standard covalent bond length.

Key words: intramolecular O→Te and N→Te coordination bonds, crystal and molecular structures, β-bromotellurenylcyclohexenal (4-methylbenzoyl)hydrazone, synthesis, β-tellurocyclohexenals, β-tellurocyclohexynilidene(4´-methylanilines), X-ray diffraction analysis.

Noncovalent binding interactions between chalcogen atoms and electron-excessive centers containing O and N atoms have received considerable recent attention. These interactions give rise to a virtually linear arrangement of the O(N)...M—X centers (M is chalcogen and X is a substituent at the chalcogen atom) and lead to a substantial shortening of the O(N)...M distances compared to the sums of the corresponding van der Waals radii.[1—5] According to the results of quantum-chemical calculations,[4,5] the strength of the intramolecular O→M and N→M coordination bonds in an analogous environment increases in the series $S < Se < Te$ and their energies can be as high as 20—25 kcal mol^{-1}.

For organotellurium compounds, such bonds were studied, primarily, in aromatic derivatives, in which various tellurium-containing groups (TeHal, TeOR, TeOCOR, TeSCN, TeR, $Te(R)Hal_2$, $TeHal_3$, *etc.*; Hal is halogen) are in the *ortho* positions with respect to substituents containing the sp^2- or sp^3-hybridized oxygen or nitrogen atoms (CHO, COR, CO_2R, NO_2, N=N, CH=N, or CH_2NR_2). The intramolecular O→Te or N→Te coordination (hereinafter, O(N)→Te) stabilizes various organotellurium compounds, primarily, two-coordinate tellurium derivatives, which are thermodynamically and kinetically unstable in the absence of such bonds, and has a substantial effect on their reactivity. Aryltellurenyl halides,[1,2,6,7] azides,[1,7] acylates,[1,6,7] and alkoxy derivatives[1,7] can be prepared in pure form only if these compounds contain the O(N)→Te coordination bonds. Compounds in which either *ortho*-formyltellurobenzene or related azomethines serve as tellurium-containing substituents are the only presently known tellurium-containing cyclopentadiene complexes.[8]

The O(N)→Te coordination bond lengths vary over a wide range, sometimes approaching the usual covalent bond lengths, which indicates that the covalent compo-

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nent makes a substantial contribution to the energy of an intramolecular coordination bond. This contribution is quantitatively estimated by the covalency factor (χ), which is calculated by the equation[9]

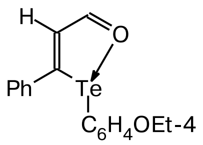
$$\chi = [(R_A + R_B) - d_{A,B}]/[(R_A + R_B) - (r_A + r_B)],$$

where R and r are, respectively, the van der Waals and covalent radii of the A and B atoms involved in the coordination bond and $d_{A,B}$ is the distance between these atoms. Evidently, the shorter the bond, the larger χ.

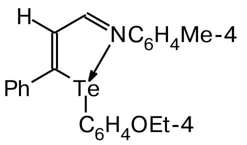
X-ray diffraction data for β-tellurovinylcarbonyl compounds and their nitrogen analogs, unlike those for aromatic derivatives, are scarce.

Earlier,[10] we have studied the structures of β-(4′-ethoxyphenyltelluro)-β-phenylvinylaldehyde (**1**) and its arylimine (**2**) and demonstrated that the intramolecular O→Te and N→Te coordination bond lengths in these compounds are intermediate between the sums of the van der Waals radii and the covalent bond lengths. These data add to the earlier information on the structures of three β-tellurovinyl ketones **3—5**.[11—13] The main conclusion is that the electronegativity of the substituent at the Te atom has a substantial effect on the length and strength of the O→Te bond.

The intramolecular O(N)→Te interatomic distances and the calculated covalency factors for compounds **1—5** are given below.



1



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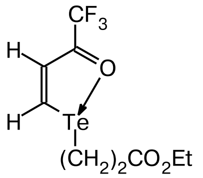

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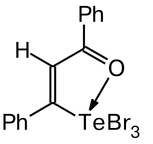

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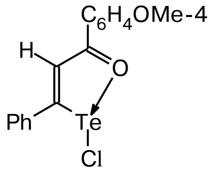


5

	1	2	3	4	5
O(N)→Te/Å	2.725[10]	2.771[10]	3.22[11]	2.362[12]	2.19[13]
χ	0.58	0.57	0.25	0.81	0.93

In the present study, the structures of six β-tellurocyclohexenal derivatives, which have the *cis* configuration at the double bond containing coordinated groups, were established by X-ray diffraction analysis. The aims of the study were (1) to compare the effects of the carbon substituents at the Te atom on the length and, consequently, the strength of the intramolecular O→Te coordination bond based on the data for compounds **6—8**; (2) to examine the possibility of double O→Te coordination in symmetrical telluride **8** and determine which of two alternative structures, 10-Te-3 or 12-Te-4, of tellurane (see Ref. 14 for the N-X-L nomenclature accepted for a series of chalcogenouranes) is preferable; (3) to reveal the influence of the nature of electron-donating centers on the O(N)→Te coordination bond lengths based on the data for compounds **7** and **9** as well as for compounds **1** and **2** studied earlier, which differ from each other only by the nature of the electron-donating center (CH=O or CH=NR); (4) to characterize the influence of electronegativity of the substituent at the Te atom on the intramolecular N→Te coordination bond length using *N*-aryl-β-tellurocyclohexenyl aldimines **9** and **10** as examples; (5) to study the structure of a representative (**11**) of previously unknown *N*-aroylhydrazones and reveal the possibility of the double O→Te and N→Te coordination in this compound.

Results and Discussion

The structures of compounds **6—11** are shown in Figs. 1—6, respectively. Their bond lengths and bond angles are given in Tables 1—6.

Structural data. Compounds **6—11** have a *Z* configuration at the double bond, which provides the formation of intramolecular O(N)→Te coordination bonds. The molecules of compounds **6—11** contain the nearly planar five-membered heterocyclic fragments involving the C(1), C(6), C(7), O(N), and Te atoms (atomic numbering

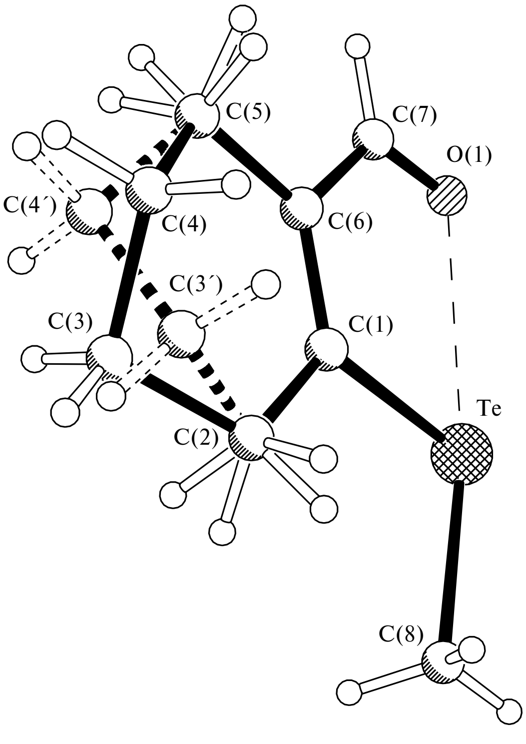


Fig. 1. Overall view of molecule **6**.

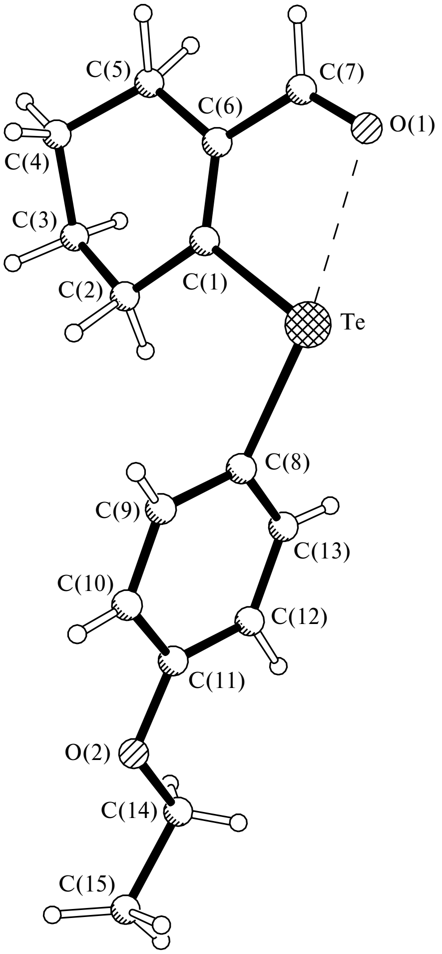


Fig. 2. Overall view of molecule **7**.

scheme corresponds to those presented in Figs. 1—6). The C—Te bond lengths vary over a narrow range (2.077—2.129 Å) and are close to the standard values.[15] The O—CH—C angles in aldehydes **6—8** are virtually independent of the nature of the substituent at the Te

Table 1. Selected bond lengths (*d*) and bond angles (ω) in molecule **6**

Bond	*d*/Å	Angle	ω/deg
Te—C(1)	2.086(3)	C(1)—Te—C(8)	96.3(1)
Te—C(8)	2.154(4)	C(2)—C(1)—C(6)	121.7(3)
C(1)—C(6)	1.350(4)	C(6)—C(1)—Te	121.0(2)
C(6)—C(7)	1.453(5)	C(2)—C(1)—Te	117.3(2)
C(6)—C(5)	1.512(6)	C(1)—C(6)—C(7)	120.1(3)
C(5)—C(4)	1.517(7)	C(7)—C(6)—C(5)	117.2(3)
C(4)—C(3)	1.511(9)	C(6)—C(5)—C(4)	112.3(4)
C(3)—C(2)	1.519(6)	C(3)—C(4)—C(5)	109.9(5)
C(1)—C(2)	1.506(4)	C(4)—C(3)—C(2)	109.2(5)
C(4´)—C(3´)	1.510(9)	C(1)—C(2)—C(3)	112.5(4)
C(7)—O(1)	1.209(6)	O(1)—C(7)—C(6)	124.3(4)

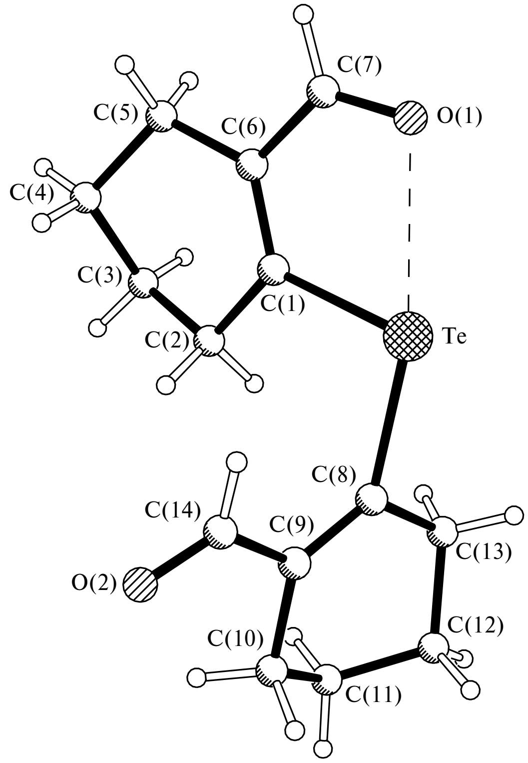


Fig. 3. Overall view of molecule **8**.

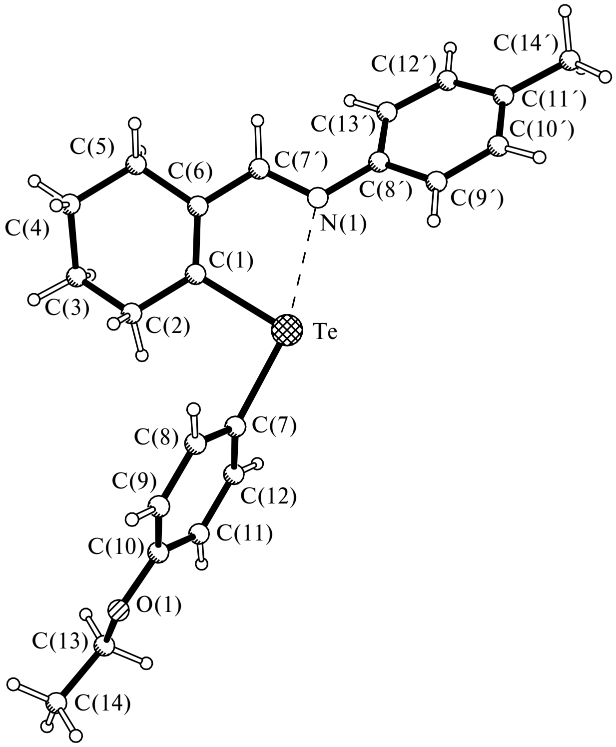


Fig. 4. Overall view of molecule **9**.

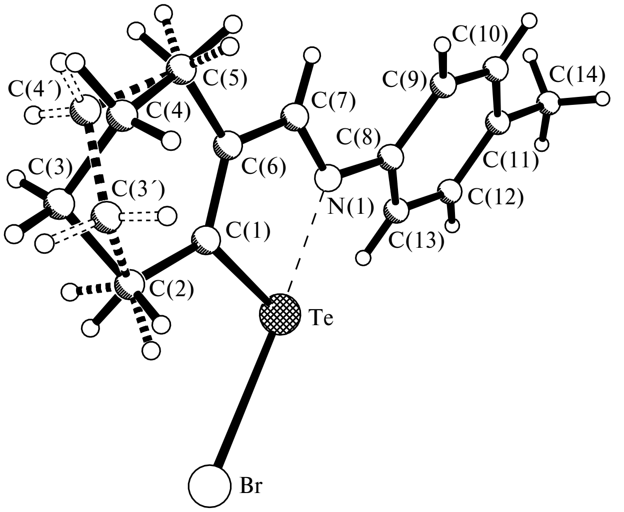


Fig. 5. Overall view of molecule **10**.

atom and are in the range of 124.3—125.2°, whereas the N—CH—C angles in aldimines **9—11** (113.0—121.9°) depend on the nature of the substituents at the N and Te atoms. The Te atoms deviate from the plane of the heterocyclic fragment by 0.01—0.04 Å. Taking into account the intramolecular O(N)→Te coordination bonds, the coordination polyhedra about the Te atoms have slightly distorted T-shaped configurations. The X—Te—R angles

Table 2. Selected bond lengths (*d*) and bond angles (ω) in molecule **7**

Bond	*d*/Å	Bond	*d*/Å
Te—C(1)	2.108(4)	O(2)—C(11)	1.375(6)
Te—C(8)	2.135(5)	O(2)—C(14)	1.406(8)
C(1)—C(6)	1.342(6)	C(9)—C(10)	1.354(7)
C(1)—C(2)	1.500(6)	C(11)—C(12)	1.379(8)
O(1)—C(7)	1.226(8)	C(11)—C(10)	1.390(8)
C(6)—C(7)	1.441(7)	C(5)—C(4)	1.501(9)
C(6)—C(5)	1.509(7)	C(12)—C(13)	1.401(8)
C(8)—C(13)	1.374(8)	C(3)—C(4)	1.501(9)
C(8)—C(9)	1.385(7)	C(14)—C(15)	1.524(9)
C(2)—C(3)	1.523(7)		

Angle	ω/deg	Angle	ω/deg
C(1)—Te—C(8)	96.5(2)	C(10)—C(9)—C(8)	121.7(5)
C(6)—C(1)—C(2)	122.5(4)	O(2)—C(11)—C(12)	124.8(5)
C(6)—C(1)—Te	119.9(3)	O(2)—C(11)—C(10)	115.1(5)
C(2)—C(1)—Te	117.6(3)	C(12)—C(11)—C(10)	120.1(5)
C(1)—C(6)—C(7)	120.2(5)	O(1)—C(7)—C(6)	124.9(5)
C(1)—C(6)—C(5)	122.7(4)	C(4)—C(5)—C(6)	112.7(4)
C(7)—C(6)—C(5)	117.0(4)	C(11)—C(12)—C(13)	118.7(5)
C(13)—C(8)—C(9)	118.3(5)	C(8)—C(13)—C(12)	121.3(5)
C(13)—C(8)—Te	120.1(4)	C(4)—C(3)—C(2)	112.2(5)
C(9)—C(8)—Te	121.2(4)	C(9)—C(10)—C(11)	120.0(5)
C(1)—C(2)—C(3)	113.3(4)	C(3)—C(4)—C(5)	111.4(5)
C(11)—O(2)—C(14)	118.8(5)	O(2)—C(14)—C(15)	107.1(7)

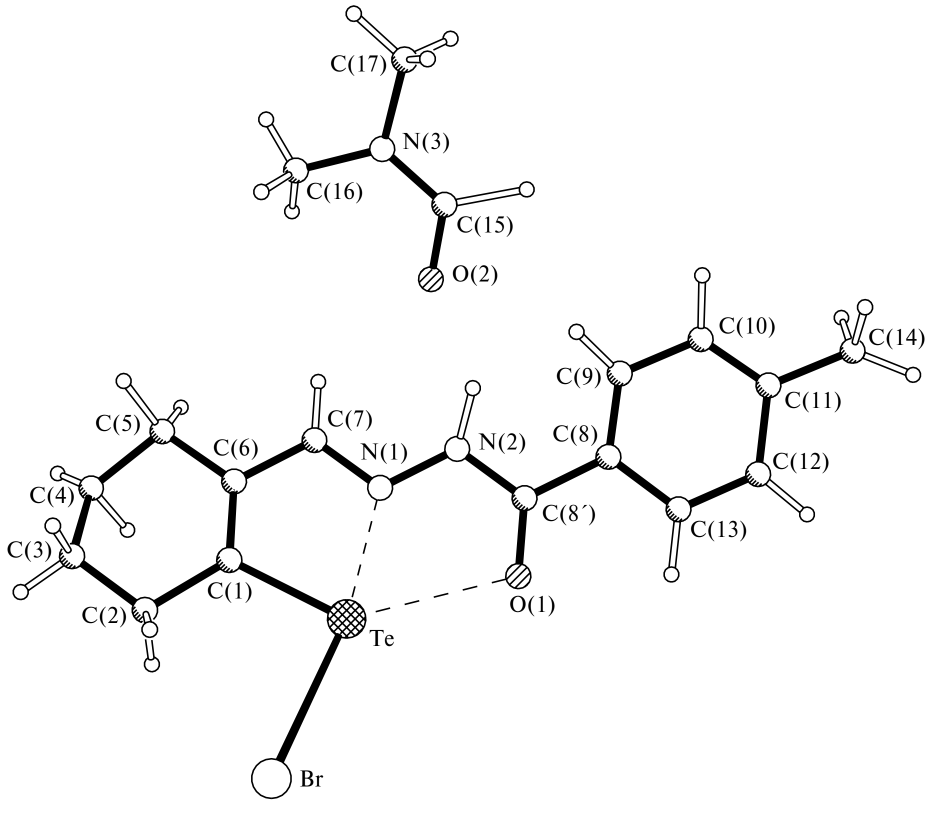


Fig. 6. Overall view of molecule **11**.

Table 3. Selected bond lengths (*d*) and bond angles (ω) in molecule **8**

Bond	*d*/Å	Bond	*d*/Å
Te—C(1)	2.103(6)	C(6)—C(1)	1.341(9)
Te—C(8)	2.147(7)	C(6)—C(7)	1.444(9)
O(1)—C(7)	1.233(9)	C(6)—C(5)	1.514(9)
C(8)—C(9)	1.321(9)	C(5)—C(4)	1.529(9)
C(8)—C(13)	1.515(9)	C(3)—C(4)	1.493(9)
C(9)—C(14)	1.472(9)	C(10)—C(11)	1.500(9)
C(9)—C(10)	1.517(9)	C(13)—C(12)	1.542(9)
C(2)—C(1)	1.500(9)	C(11)—C(12)	1.454(9)
C(2)—C(3)	1.526(9)	O(2)—C(14)	1.161(9)

Angle	ω/deg	Angle	ω/deg
C(1)—Te—C(8)	95.8(3)	C(4)—C(3)—C(2)	110.9(8)
C(9)—C(8)—C(13)	122.8(7)	C(6)—C(1)—C(2)	121.6(6)
C(9)—C(8)—Te	125.6(6)	C(6)—C(1)—Te	120.6(5)
C(13)—C(8)—Te	111.7(5)	C(2)—C(1)—Te	117.8(4)
C(8)—C(9)—C(14)	122.0(8)	C(9)—C(10)—C(11)	113.2(7)
C(8)—C(9)—C(10)	121.9(7)	C(3)—C(4)—C(5)	109.5(7)
C(14)—C(9)—C(10)	116.2(7)	C(8)—C(13)—C(12)	111.6(8)
C(1)—C(2)—C(3)	112.6(6)	O(1)—C(7)—C(6)	125.2(7)
C(1)—C(6)—C(7)	119.5(7)	C(12)—C(11)—C(10)	111.1(9)
C(1)—C(6)—C(5)	123.4(7)	C(11)—C(12)—C(13)	111.1(9)
C(7)—C(6)—C(5)	117.1(7)	O(2)—C(14)—C(9)	124.1(9)
C(6)—C(5)—C(4)	112.1(6)		

Table 4. Selected bond lengths (*d*) and bond angles (ω) in molecule **9**

Bond	*d*/Å	Angle	ω/deg
Te—C(7)	2.127(9)	C(7)—Te—C(1)	94.7(3)
Te—C(1)	2.129(8)	C(6)—C(5)—C(4)	112.1(8)
C(5)—C(6)	1.49(1)	C(1)—C(6)—C(7′)	122.7(8)
C(5)—C(4)	1.52(2)	C(1)—C(6)—C(5)	123.2(9)
C(6)—C(1)	1.34(1)	C(7′)—C(6)—C(5)	114.1(8)
C(6)—C(7′)	1.41(1)	C(7′)—N(1)—C(8′)	122.5(8)
N(1)—C(7′)	1.29(1)	N(1)—C(7′)—C(6)	121.9(9)
N(1)—C(8′)	1.39(1)	C(8)—C(7)—C(12)	116.6(9)
C(7)—C(8)	1.39(1)	C(8)—C(7)—Te	121.8(7)
C(7)—C(12)	1.41(1)	C(12)—C(7)—Te	121.4(7)
C(1)—C(2)	1.47(1)	C(6)—C(1)—C(2)	122.2(7)
C(2)—C(3)	1.54(1)	C(6)—C(1)—Te	120.5(7)
C(8)—C(9)	1.35(1)	C(2)—C(1)—Te	117.3(6)
C(8′)—C(13′)	1.38(1)	C(1)—C(2)—C(3)	114.2(8)
C(8′)—C(9′)	1.39(1)	C(9)—C(8)—C(7)	121.5(8)
C(12)—C(11)	1.35(1)	C(13′)—C(8′)—N(1)	122.8(8)
O(1)—C(10)	1.32(1)	C(13′)—C(8′)—C(9′)	119.0(9)
O(1)—C(13)	1.42(1)	N(1)—C(8′)—C(9′)	118.0(8)
C(9′)—C(10′)	1.38(1)	C(11)—C(12)—C(7)	122.0(8)
C(11′)—C(10′)	1.37(1)	C(10)—O(1)—C(13)	118.7(9)
C(11′)—C(12′)	1.37(1)	C(10′)—C(9′)—C(8′)	118.6(9)
C(11′)—C(14′)	1.48(1)	C(10′)—C(11′)—C(12′)	118(1)
C(9)—C(10)	1.41(1)	C(10′)—C(11′)—C(14′)	120(1)
C(13)—C(14)	1.44(1)	C(12′)—C(11′)—C(14′)	121(1)
C(11)—C(10)	1.38(1)	C(8)—C(9)—C(10)	121.4(8)
C(3)—C(4)	1.52(1)	O(1)—C(13)—C(14)	109(1)
C(12′)—C(13′)	1.36(1)	C(12)—C(11)—C(10)	121.0(8)
		C(4)—C(3)—C(2)	106.4(8)
		O(1)—C(10)—C(11)	125.6(8)
		O(1)—C(10)—C(9)	117.1(8)
		C(11)—C(10)—C(9)	117.3(9)
		C(5)—C(4)—C(3)	112.7(8)
		C(13′)—C(12′)—C(11′)	120.9(9)
		C(12′)—C(13′)—C(8′)	120.7(8)
		C(11′)—C(10′)—C(9′)	122.3(9)

(X is the electron-donating center and R is the substituent at the Te atom) vary over a relatively narrow range (165.1—169.2°) (Table 7).

Intramolecular O(N)→Te coordination bonds. The lengths of the bonds involving the Te atoms, among them the intramolecular O(N)→Te bond lengths, and the calculated covalency factors χ are given in Table 7.

The intramolecular O→Te coordination bond length in aldehyde **6** is 2.692 Å (χ = 0.60), which is 0.9 Å smaller than the sum of the van der Waals radii of the corresponding atoms involved in the interaction (3.60 Å).[16]

The replacement of the Me group at the Te atom (compound **1**) by the aryl substituent (aldehyde **7**) has virtually no effect on the structure and influences only slightly the O→Te coordination bond length.

In aldehydes **6** and **7**, only one intramolecular O→Te coordination bond can exist. By contrast, either one or two O→Te coordination bonds can occur in dialdehyde **8** due to the presence of two monodentate ligands. In these two cases, the molecular structures correspond to 10-Te-3 and 12-Te-4 telluranes, respectively.

As can be seen from Fig. 3, two chemically equivalent formylcyclohexene fragments differ substantially in the arrangement about the Te—C(1) and Te—C(8) bonds. The O(1) atom lies in the plane of the five-membered heterocycle involving the C(1), C(6), C(7), O(1), and Te atoms and forms a coordination bond with the Te atom. The intramolecular coordination bond length in this compound is 2.657 Å (χ = 0.62). The second formylcyclohexene fragment is twisted about the Te—C(8) bond, and the O(2) atom is far removed from the Te atom. Therefore, the structure of dialdehyde **8** in the crystal corresponds to 10-Te-3 tellurane.

The results of X-ray diffraction study show that the intramolecular O→Te coordination bond lengths in β-tellurovinylaldehydes **6—8** depend only slightly on the nature of the carbon substituent at the Te atom. In these aldehydes, the O→Te coordination bonds are relatively long (2.657—2.692 Å, χ = 0.60—0.62).

The intramolecular N→Te coordination bond length in aldimine **9** (2.690 Å, χ = 0.62) is virtually equal to the analogous distance in the aromatic derivative, *viz.*, 4-ethoxyphenyl-2-(2-pyridyl)phenyl telluride (2.695 Å, χ = 0.6).[17]

A comparison of the O→Te bond length in aldehyde **7** (2.657 Å) and the N→Te bond length in its nitrogen

Table 5. Selected bond lengths (*d*) and bond angles (ω) in molecule **10**

Bond	*d*/Å	Bond	*d*/Å
Te—C(1)	2.077(3)	C(5)—C(6)	1.507(5)
Te—N(1)	2.170(2)	C(3´)—C(4´)	1.518(9)
Te—Br	2.774(1)	C(6)—C(7)	1.413(4)
N(1)—C(7)	1.300(4)	C(8)—C(9)	1.379(4)
N(1)—C(8)	1.421(4)	C(8)—C(13)	1.383(4)
C(1)—C(6)	1.357(4)	C(9)—C(10)	1.365(5)
C(1)—C(2)	1.485(4)	C(10)—C(11)	1.380(5)
C(2)—C(3)	1.538(5)	C(11)—C(12)	1.385(4)
C(3)—C(4)	1.510(7)	C(11)—C(14)	1.502(5)
C(4)—C(5)	1.520(6)	C(12)—C(13)	1.387(5)

Angle	ω/deg	Angle	ω/deg
C(1)—Te—N(1)	77.9(1)	C(1)—C(6)—C(5)	122.5(3)
C(1)—Te—Br	91.9(1)	C(7)—C(6)—C(5)	119.4(3)
N(1)—Te—Br	168.7(1)	N(1)—C(7)—C(6)	118.5(3)
C(7)—N(1)—C(8)	122.9(2)	C(9)—C(8)—C(13)	118.9(3)
C(7)—N(1)—Te	112.2(2)	C(9)—C(8)—N(1)	122.1(3)
C(8)—N(1)—Te	124.7(2)	C(13)—C(8)—N(1)	119.1(2)
C(6)—C(1)—C(2)	123.2(3)	C(10)—C(9)—C(8)	120.3(3)
C(6)—C(1)—Te	113.3(2)	C(9)—C(10)—C(11)	122.0(3)
C(2)—C(1)—Te	123.5(2)	C(10)—C(11)—C(12)	117.5(3)
C(1)—C(2)—C(3)	111.9(3)	C(10)—C(11)—C(14)	121.1(3)
C(4)—C(3)—C(2)	110.4(4)	C(12)—C(11)—C(14)	121.5(3)
C(3)—C(4)—C(5)	110.3(4)	C(13)—C(12)—C(11)	121.2(3)
C(6)—C(5)—C(4)	112.3(3)	C(12)—C(13)—C(8)	120.2(3)
C(1)—C(6)—C(7)	118.1(3)		

Table 6. Selected bond lengths (*d*) and bond angles (ω) in molecule **11**

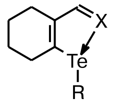
Bond	*d*/Å	Bond	*d*/Å
Te—C(1)	2.10(1)	C(6)—C(7)	1.46(2)
Te—N(1)	2.20(2)	C(8´)—C(8)	1.49(2)
Te—Br	2.74(3)	C(8)—C(9)	1.34(2)
O(1)—C(8´)	1.24(2)	C(8)—C(13)	1.41(2)
N(1)—C(7)	1.35(2)	C(9)—C(10)	1.40(2)
N(1)—N(2)	1.39(2)	C(10)—C(11)	1.32(2)
N(2)—C(8´)	1.34(2)	C(11)—C(12)	1.44(2)
C(1)—C(6)	1.33(2)	C(11)—C(14)	1.48(2)
C(1)—C(2)	1.52(2)	C(12)—C(13)	1.40(2)
C(2)—C(3)	1.47(3)	O(2)—C(15)	1.26(2)
C(3)—C(4)	1.45(3)	N(3)—C(15)	1.33(2)
C(4)—C(5)	1.51(2)	N(3)—C(16)	1.47(2)
C(5)—C(6)	1.49(2)	N(3)—C(17)	1.48(3)

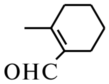
Angle	ω/deg	Angle	ω/deg
C(1)—Te—N(1)	75.9(6)	O(1)—C(8´)—N(2)	121(1)
C(1)—Te—Br	93.7(5)	O(1)—C(8´)—C(8)	120(1)
N(1)—Te—Br	169.2(4)	N(2)—C(8´)—C(8)	117(1)
C(7)—N(1)—N(2)	115.3(9)	C(9)—C(8)—C(13)	118(1)
C(7)—N(1)—Te	115.3(9)	C(9)—C(8)—C(8´)	124(1)
N(2)—N(1)—Te	129(1)	C(13)—C(8)—C(8´)	117(1)
C(8´)—N(2)—N(1)	116.4(9)	C(8)—C(9)—C(10)	121(1)
C(6)—C(1)—C(2)	120.9(9)	C(11)—C(10)—C(9)	122(1)
C(6)—C(1)—Te	116.2(9)	C(10)—C(11)—C(12)	118(1)
C(2)—C(1)—Te	122.3(9)	C(10)—C(11)—C(14)	124(1)
C(3)—C(2)—C(1)	113(1)	C(12)—C(11)—C(14)	117(1)
C(4)—C(3)—C(2)	117(1)	C(13)—C(12)—C(11)	119(1)
C(3)—C(4)—C(5)	114(1)	C(12)—C(13)—C(8)	119(1)
C(6)—C(5)—C(4)	110(1)	C(15)—N(3)—C(16)	123(1)
C(1)—C(6)—C(7)	119(1)	C(15)—N(3)—C(17)	116(1)
C(1)—C(6)—C(5)	125(1)	C(16)—N(3)—C(17)	120(1)
C(7)—C(6)—C(5)	115(9)	O(2)—C(15)—N(3)	121(1)
N(1)—C(7)—C(6)	113(1)		

analog **9** (2.690 Å) shows that in the compounds possessing the same carbon skeleton and the substituent at the Te atom, the nature of the electron-donating center (CH=O or CH=NR) influences, although weakly, the lengths of the coordination bonds involving the Te atom. This is evidenced also by the O→Te bond length in aldehyde **1** (2.725 Å) and the N→Te bond length in azomethine **2** (2.771 Å).

In compounds containing the same electron-donating centers and substituents at the Te atom, the O(N)→Te

Table 7. Intramolecular X→Te coordination bond lengths and Te—C and Te—R bond lengths (*d*), covalency factors (χ), and X—Te—R bond angles in compounds **6—11**

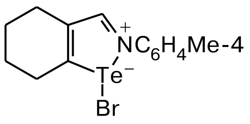


Compound	R	X	*d*/Å			χ	Angle X—Te—R /deg
			Te—C	Te—R	X...Te		
6	Me	O	2.086	2.154	2.692	0.60	168.4
7	C_6H_4OEt-4	O	2.108	2.135	2.657	0.62	167.8
8	 OHC	O	2.103	2.147	2.657	0.62	167.3
9	C_6H_4OEt-4	NC_6H_4Me-4	2.127	2.129	2.690	0.60	165.1
10	Br	NC_6H_4Me-4	2.077	2.774	2.170	0.95	168.7
11	Br	$NNHC(O)C_6H_4Me$-4	2.10	2.74	2.20	0.94	169.2

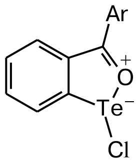
coordination bond lengths are strongly influenced by the nature of the carbon fragment. In β-tellurocyclohexenal **7**, the O→Te bond length is 2.657 Å, whereas this bond length in its analog **1** is 2.725 Å.[10] In the corresponding aldimines **9** and **2**, the N→Te distances are 2.690 and 2.771 Å, respectively.

As might be expected from the results of X-ray diffraction studies of structurally similar derivatives[1,2,6,13,17,18] and quantum-chemical calculations,[3—5] the intramolecular N→Te coordination bond in aldimine **10** containing the TeBr substituent in the β position is the shortest one in the series of compounds under consideration. This bond length (2.170 Å, $\chi = 0.95$) is close to the N—Te bond lengths in 2-halogenotellurenylbenzalanilines[6] and [(2-pyridyl)phenyl]tellurenyl halides.[18] The intramolecular N→Te coordination bond lengths are 2.223 and 2.236 Å in 2-chlorotellurenylbenzal-4´-methylaniline and [(2-pyridyl)phenyl]tellurenyl bromide, respectively.

In oxatellurolium chlorides **12**,[12] whose structures in the crystals are analogous to that of aldimine **10**, the nearly linear O—Te—Cl fragment contains a three-center four-electron bond. Apparently, this approach is also applicable for describing the structure of compound **10**. Since the N→Te distance in tellurenyl bromide **10** (2.170 Å) is close to the standard N—Te covalent bond length (2.11 Å in benzoisotelluroazole[19]), the structure of **10** can be described as a heterocyclic compound, *viz.*, isotelluroazole derivative **13**, structurally similar to heterocycles **14**, which were proposed[13] for the description of oxatellurolium chlorides **12**.[12]



13



14

In spite of substantial differences in the structures of the substituents R at the sp^2-hybridized N atom (R = C_6H_4Me-4 in aldimine **10** and R = $NHCOC_6H_4Me$-4 in hydrazone **11**), the intramolecular N→Te coordination bond in **11** (2.20 Å, $\chi = 0.94$) is only 0.03 Å longer than the analogous bond in aldimine **10**.

Up to now, 2,6-diacetylpyridinetellurium trichloride has been the only known compound containing simultaneously the intramolecular N→Te and O→Te coordination bonds.[20] Taking into consideration these bonds, this compound has a distorted pentagonal-pyramidal structure unusual for organyltellurium trichloride $RTeCl_3$. Hydrazone **11** contains the N→Te coordination bond along with a rather short O...Te contact (2.831 Å, $\chi = 0.51$). The C(1)—Te...O(1) angle in **11** is 136°. Taking into account both types of interactions, the coordination polyhedron of the Te atom in hydrazone **11** can be considered as a distorted trigonal bipyramid, whose axial positions are occupied by the N(1) and Br atoms and the

Table 8. Principal X-ray diffraction data for compounds **6—11**

Parameter	**6**	**7**	**8**	**9**	**10**	**11**
M	251.78	357.89	345.88	447.03	405.79	448.82
Space group	$P\bar{1}$	$P2_1/c$	$P\bar{1}$	$P2_1/c$	$P\bar{1}$	$P\bar{1}$
a/Å	10.120(4)	7.887(1)	8.382(4)	8.100(1)	9.397(4)	9.308(6)
b/Å	5.803(2)	9.717(3)	11.023(2)	16.766(3)	9.184(2)	14.376(5)
c/Å	7.945(2)	19.057(5)	8.064(2)	16.544(3)	9.934(2)	7.772(5)
α/deg	106.39(3)	90	95.45(3)	90	78.36(3)	87.92(2)
β/deg	92.74(3)	94.41(2)	100.03(3)	117.41(3)	67.49(3)	84.68(2)
γ/deg	90.74(3)	90	109.64(3)	90	66.87(3)	76.10(2)
V/Å^3	446.9(3)	1456.2(6)	681.5(4)	1994.6(7)	727.0(4)	1005(1)
Z	2	4	2	4	2	2
d_{calc}/g cm^{-3}	1.871	1.632	1.686	1.489	1.854	1.725
μ/mm^{-1}	3.3	2.0	2.17	1.5	4.77	3.48
θ/deg	3.26—30.06	1.07—30.10	1.99—30.07	2.43—33.08	2.22—30.08	1.46—30.09
Total number of reflections	2499	4262	3402	5014	4192	2729
Number of reflections with $I > 2\sigma(I)$	1873	2254	2385	2381	2845	896
Number of parameters in refinement	120	163	154	226	198	226
R	0.027	0.041	0.049	0.072	0.027	0.054
wR_2	0.047	0.109	0.081	0.152	0.066	0.26
Radiation	Mo-Kα	Mo-Kα	Mo-Kα	Mo-Kα	Mo-Kα	Mo-Kα
GOF	1.048	0.993	1.037	0.966	0.982	0.983

equatorial plane is formed by the C(1) and O atoms and the lone electron pair of the Te atom.

On the whole, the degree of coordination interaction between the lone electron pair of the O(N) atoms and the σ* orbital of the Te—R bond (n—σ* interaction) depends on the nature of the substituent at the Te atom. In the presence of carbon substituents, the intramolecular O(N)→Te coordination bond lengths are in the range of 2.6—2.7 Å. The presence of electronegative substituents (Hal or OCOMe) at the Te atom leads to a sharp shortening of the O(N)→Te distances (2.14—2.20 Å), which is consistent with the results of quantum-chemical calculations.

Experimental

Compounds **6**,[10,21,22] **7**,[10,21] **8**,[10,21] **9**,[10] and **10** [10,22] were prepared according to known procedures. The ^{1}H NMR spectra were recorded on a Varian Unity instrument (300 MHz) using residual H atoms of the solvent as the internal standard.

β-Bromotellurenylcyclohexenal (4-methylbenzoyl)hydrazone (11). A mixture of β-methyldibromotellurocyclohexen-1-al[22] (4.12 g, 10 mmol) and 4-methylbenzoic hydrazide (1.50 g, 10 mmol) in MeOH (35 mL) was refluxed for 30 min until hydrazone **11** precipitated. The reaction mixture was cooled. The precipitate was filtered off and dried. Compound **11** was obtained in a yield of 3.46 g (77%) as bright-yellow crystals, m.p. 264 °C (from a 1 : 2 toluene—hexane mixture). Found (%): C, 39.92; H, 3.62; N, 6.14. $C_{15}H_{17}BrN_2OTe$. Calculated (%): C, 40.09; H, 3.79; N, 6.24. ^{1}H NMR (DMSO-d_6), δ: 1.80—3.00 (m, 8 H, $(CH_2)_4$); 2.40 (s, 3 H, Me); 7.22—7.80 (m, 4 H, C_6H_4); 8.46 (s, 1 H, CH=N); 9.82 (s, 1 H, NH).

X-ray diffraction analysis. The X-ray diffraction data sets for compounds **6—11** were collected on an automated four-circle KUMA diffractometer at T = 293 K. The structures were solved by direct methods and refined anisotropically by the least-squares method using the SHELX-97 program package.[23] For compounds **6** and **10**, semiempirical absorption corrections were applied.[24] The principal crystallographic characteristics are given in Table 8. A number of H atoms were located from difference Fourier syntheses. The remaining H atoms were placed in calculated positions. For the structure of **7**, the coordinates and isotropic thermal parameters of the H atoms were refined. For all other structures, the positions of the H atoms were refined using the riding model.[23] In compounds **6** and **10**, the aliphatic C(3) and C(4) atoms are disordered over two equally probable positions with respect to the C(2) and C(5) atoms in ratios of 1 : 1 and 2 : 3, respectively. Analysis of intermolecular interactions in these and other tellurium compounds, which we have studied earlier, shows that the above-mentioned disorder is not accounted for by the packing mode.

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