

# Synthesis and structure of *N*-arylimines of $\beta$ -tellurocyclohexenals with the intramolecular coordination N $\rightarrow$ Te bonds

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## Abstract

A series of *N*-arylimines of  $\beta$ -tellurocyclohexenals **11** have been synthesized and the molecular and crystal structures of the compounds **11a–e** and also  $\beta$ -(dimethyltelluronium)cyclohexenal perchlorate **12** studied by X-ray crystallography. All the compounds contain strong intramolecular coordination N  $\rightarrow$  Te (O  $\rightarrow$  Te) bonds of the hypervalent type. In **11a–e**, the lengths of the N  $\rightarrow$  Te bonds are within the range of 2.690–2.147 Å and are 1.0–1.5 Å shorter than the sum of the van der Waals radii of respective atoms. In the *N*-arylimines **11b–e** with the electronegative groups attached to the tellurium center, the lengths of the N  $\rightarrow$  Te bonds are very close to that characteristic of a standard covalent N–Te bond. The experimental observed geometries are well reproduced by the DFT calculations performed at B3LYP/LanL2DZ level of approximation. The energies of the intramolecular coordination N  $\rightarrow$  Te bonds vary from 23 kJ mol<sup>-1</sup> for **11a** to 119 kJ mol<sup>-1</sup> for **11e**. The calculated energy of the O  $\rightarrow$  Te bond in **12** was found to be 50 kJ mol<sup>-1</sup>. The <sup>125</sup>Te NMR chemical shifts of compounds **11** span the wide range of 734.3–1622.4 ppm. The largest downfield <sup>125</sup>Te NMR chemical shifts are observed in the case of the compounds **11e, f** in which the most electronegative atoms are attached to the tellurium centers.

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**Keywords:**  $\beta$ -Tellurocyclohexenals;  $\beta$ -(Dimethyltelluronium)cyclohexenal perchlorate; Intramolecular N  $\rightarrow$  Te and O  $\rightarrow$  Te coordination; Quantum chemical calculations; X-ray structures; <sup>1</sup>H, <sup>125</sup>Te NMR spectra

## 1. Introduction

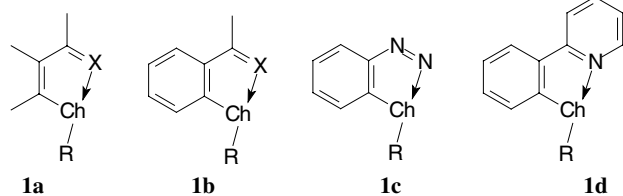
Recent years have seen a rapidly growing interest in gaining a deeper insight into the nature, chemical, and

structural consequences of the non-covalent attractive interaction between chalcogen atom and other electron abundant main group centers [1,2]. Intramolecular and intermolecular interactions of this type define the preferred conformations of organochalcogen compounds, the secondary and tertiary structure of many biologically important compounds such as thiazole and selenazole nucleosides [3] and angiotensin II receptor

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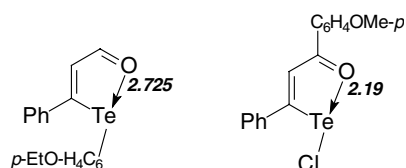
antagonists [4], the crystal structure and packing features of organic and inorganic chalcogen-containing compounds [1,2,5] and their chemical reactivity [1,6]. Special attention has been given to the intramolecular coordination  $O(N) \rightarrow \text{Chalc}$  bonds existing in the appropriately functionalized organochalcogen compounds [1,7–12]. According to the estimates based on ab initio and DFT quantum chemical calculations [11,12] and dynamic NMR studies [10,13] the energies of these bonds cover the wide range of values between 20 and 125  $\text{kJ mol}^{-1}$ . The largest values approach those of a covalent bond and characterize the intramolecular coordination  $O(N) \rightarrow \text{Chalc}$  bonds constituting a part of the conjugated five-membered rings in type **1a–1d** compounds. The strength of the bonds increases along the sequence  $\text{Ch} = \text{S}, \text{Se}, \text{Te}$  and with an increase in electronegativity of a substituent  $R$  attached to the chalcogen atom.



$\text{Ch} = \text{S}, \text{Se}, \text{Te}; \text{X} = \text{O}, \text{NR}';$   $\text{R} = \text{Alk}, \text{Ar}, \text{OR}''$ , Hal

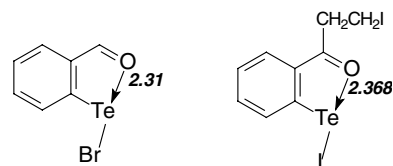
A clear manifestation of these trends is given by X-ray structural determination of a broad series of type **1a–1d** compounds, see [1,14–16] for reviews. In all the compounds, the secondary  $\text{Chalc} \cdots \text{O(N)}$  bonds are significantly shorter than the sum of the van der Waals radii of the respective atoms and in some of the organotellurium compounds, e.g., **3**, **4**, **7**, **9**, are almost indistinguishable in length from the corresponding covalent two-center, two-electron bonds (2.11 Å for both  $\text{Te}-\text{O}$  and  $\text{Te}-\text{N}$  bonds). In these compounds, the covalency factor  $\chi$  of the intramolecular coordination  $\text{Te} \cdots \text{O(N)}$  bonds calculated by the Eq. (1) [17] (where  $R$  and  $r$  are the van der Waals and covalent radii; respectively, and  $d$  is the distance between the interacting centers) achieves 90% which points to the dominant contribution of  $n_{\text{X}} \rightarrow \sigma_{\text{TeR}}^*$  charge transfer in the intramolecular  $\text{Te} \cdots \text{X}$  bonding. The intramolecular  $\text{X} \rightarrow \text{Te}$  coordination provides for the T-shaped configuration of tellurium centers with nearly linear arrangements of the  $\text{X}-\text{Te}-\text{R}$  bonds (for compounds **1**, the angles  $\text{XTeR}$  are found within the range of 157–179°)

$$\chi = \frac{(R_{\text{Te}} + R_{\text{X}})_{\text{vdW}} - d_{\text{TeX}}}{(R_{\text{Te}} + R_{\text{X}})_{\text{vdW}} - (r_{\text{Te}} + r_{\text{X}})_{\text{cov}}} \quad (1)$$



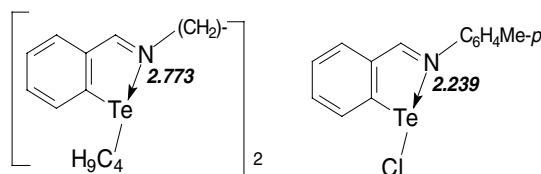
**2** [6] ( $\chi = 0.58$ )

**3** [8] ( $\chi = 0.92$ )



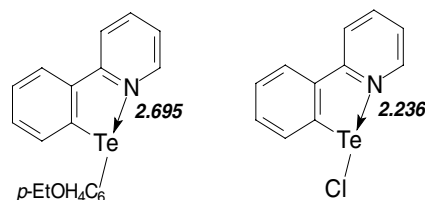
**4** [18] ( $\chi = 0.90$ )

**5** [19] ( $\chi = 0.81$ )



**6** [20] ( $\chi = 0.57$ )

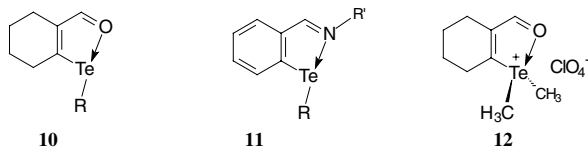
**7** [13] ( $\chi = 0.91$ )



**8** [21] ( $\chi = 0.62$ )

**9** [22] ( $\chi = 0.91$ )

Recently the data on intramolecular  $\text{O} \rightarrow \text{Te}$  coordination have been supplemented with our X-ray structural determinations of  $\beta$ -(alkyl/aryl)tellurocyclohexenals **10** in which *cis*-configuration of the vicinal aldehyde and telluro groups is rigidly fixed by insertion of the double bond into a cyclohexene ring [23]. The main goal of the work reported here was the synthesis of imino derivatives of  $\beta$ -tellurocyclohexenals and the structural characterization of the intramolecular coordination  $\text{N} \rightarrow \text{Te}$  bonds in the compounds **11** with substituents at the tellurium centers covering a wide range of electronegativity from carbon to fluorine. In order to compare the lengths and strengths of the intramolecular coordination  $\text{O} \rightarrow \text{Te}$  bonds in 10-Te-3 (see [24] for the nomenclature) compounds **10** with those of a 12-Te-4 derivative we have also prepared a compound **12** and studied its structure by X-ray crystallography



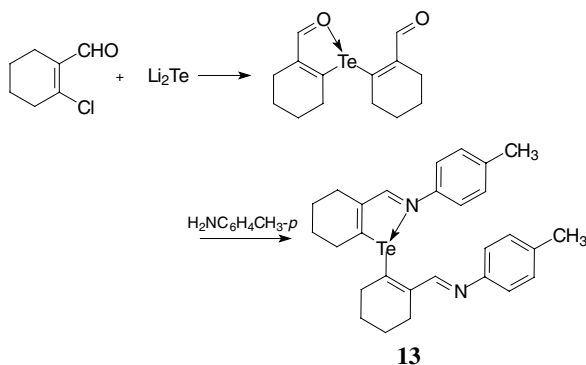
- a** R=Me ( $d_{\text{TeO}}$  2.692 Å [23]); **a** R= C<sub>6</sub>H<sub>4</sub>OEt-*p*, R' = C<sub>6</sub>H<sub>4</sub>Me-*p*;  
**b** R=C<sub>6</sub>H<sub>4</sub>OEt-*p* ( $d$  2.657 Å [23]); **b** R=OC(=O)Me, R' = C<sub>6</sub>H<sub>3</sub>Me<sub>2</sub>-2,6;  
**c** R=1-(2-formyl)cyclohexenyl ( $d$  2.657 Å [23]); **c** R=Br, R' = C<sub>6</sub>H<sub>4</sub>Me-*p*;  
**d** R=Br, R' = C<sub>6</sub>H<sub>3</sub>Me<sub>2</sub>-2,6;  
**e** R=F, R' = C<sub>6</sub>H<sub>3</sub>Me<sub>2</sub>-2,6;  
**f** R=F, R' = C<sub>6</sub>H<sub>4</sub>Me-*p*

The structural information is discussed in parallel with data obtained by <sup>125</sup>Te and <sup>1</sup>H NMR spectroscopy of compounds **10**, **11** and their derivatives and with results of density functional theory (DFT) quantum mechanical calculations on compounds **11** (R' = C<sub>6</sub>H<sub>5</sub>) and **12**.

## 2. Results and discussion

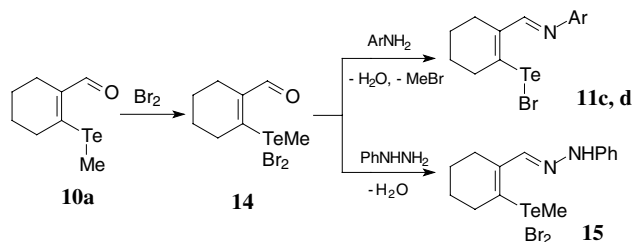
### 2.1. Synthesis of β-tellurocyclohexenals and their *N*-arylimines

β-(Methyltelluro)cyclohexenal **10a** was prepared in 54% yield using the previously described method of coupling β-chlorocyclohexenal with lithium methyltelluroate generated by the reaction of methyl lithium and elemental tellurium in tetrahydrofuran [6,25]. When lithium methyltelluroate was substituted in this reaction by lithium 4-ethoxyphenyltelluroate prepared by the reduction of di-(*p*-ethoxyphenyl) ditelluride by lithium in tetrahydrofuran in the presence of catalytic amounts of naphthalene, β-(*p*-ethoxyphenyltelluro)cyclohexenal **10b** [6,26] was obtained in 37% yield. In a similar way, the reaction of β-chlorocyclohexenal with lithium telluride affords di-(2-formylcyclohexen-1-yl) telluride in 60% yield [6,26], which reacts with *p*-toluidine to give the diimine **13**



β-(Dimethyltelluronium)cyclohexenal perchlorate **12** was prepared in 91% yield by treatment of the aldehyde **10a** with an equivalent amount of methyl iodide and silver perchlorate.

*N*-(*p*-tolylimino)-β-(*p*-ethoxyphenyltelluro)cyclohexenal **11a** was obtained by refluxing an ethanol solution of equivalent amounts of **10b** with *p*-toluidine. For the synthesis of *N*-arylimines of β-(bromotellurenyl)cyclohexenal **11c** and **11d** a combination of oxidation-addition and alkyl halide elimination reactions specific for organotellurium chemistry was employed. The first reaction occurs in benzene at room temperature to give dibromide **14** in quantitative yield [6,25] and the subsequent transformation proceeds smoothly under refluxing methanol solution of **14** and the corresponding arylamine. In contrast with the reaction of **14** with arylamines, no elimination of methyl bromide occurs when coupling **14** with phenylhydrazine. The phenylhydrazone **15** was obtained in 84% yield



When treated with silver acetate or silver fluoride in chloroform, the imines **11c**, **d** readily undergo the anion exchange reaction to give the compounds **11b** and **11e**, **f**, respectively.

### 2.2. Molecular and crystal structure of *N*-arylimines of β-tellurocyclohexenals **11**

The X-ray determined molecular structures of compounds **11 a–e** are shown in Figs. 1–5<sup>1</sup>. Data on the important bond lengths and angles are collected in Tables 1–5. The principal crystallographic data are given in Table 6.

In all the compounds **11** the five-membered cycles closed by the intramolecular coordination N → Te bonds are virtually planar. The tellurium atoms are deflected out of the plane by ca. 0.01–0.04 Å. The lengths of the Te–C bonds in the cycle cover a relatively narrow range of values as indicated in Table 6. As for compounds 2–9, the intramolecular X → Te coordination warrants T-shaped configuration of the tellurium centers

<sup>1</sup> Results of a preliminary structural study of compounds **11a**, **c** were presented in a paper [23].

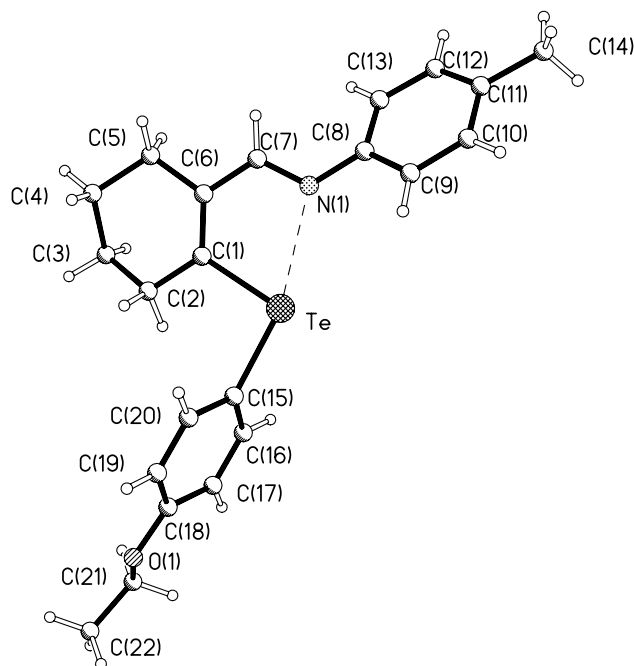


Fig. 1. Molecular structure of  $\beta$ -(*p*-ethoxyphenyltelluro)cyclohexenylidene-(*p*-toluidine) **11a**.

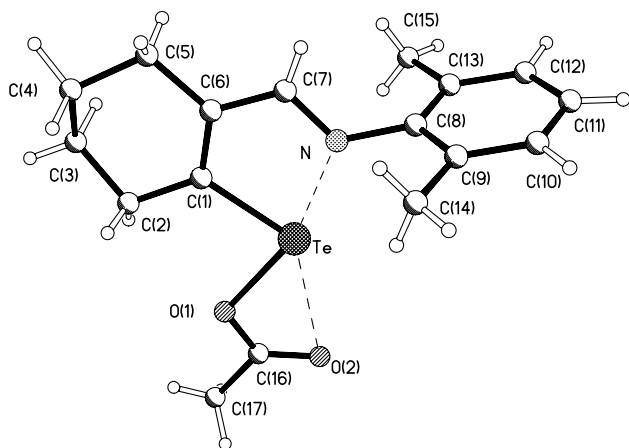


Fig. 2. Molecular structure of  $\beta$ -(acetoxytellurenyl)cyclohexenylidene-(2,6-dimethylaniline) **11b**.

and nearly linear arrays of the XTeR triad in **11a–e** (the N–Te–R' angles are in the range 162.2–171.0°). The angles of turn of *N*-aryl rings around the N–C bond in the imines **11a** and **11c** are 36.3° and 21.7°, respectively, whereas in the imines **11b**, **11d**, **e** the aryl rings bearing two *o*-methyl groups are nearly orthogonal to the plane of the rest of the molecules. The principal structural feature of the *N*-arylimines **11** is the very close proximity of the two closed electron shell nitrogen and tellurium centers. In the compounds **11b–e** which contain the highly electronegative groups R attached to the tellurium atom the N...Te distances differ from the length of a standard covalent N–Te bond, e.g., 2.11 Å in benzoisotellurazole

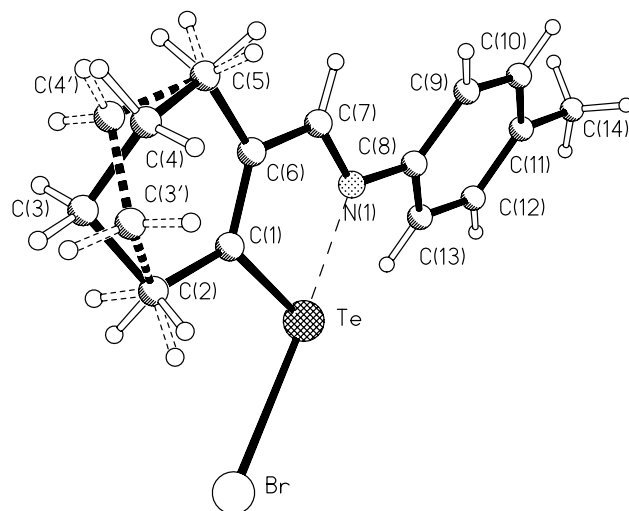


Fig. 3. Molecular structure of  $\beta$ -(bromotellurenyl)cyclohexenylidene-(*p*-toluidine) **11c**.

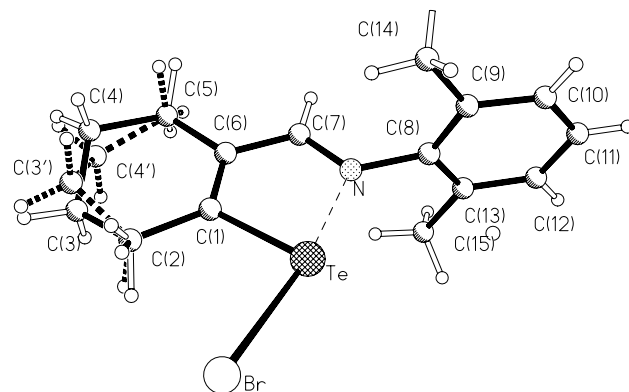


Fig. 4. Molecular structure of  $\beta$ -(bromotellurenyl)cyclohexenylidene-(2,6-dimethylaniline) **11d**.

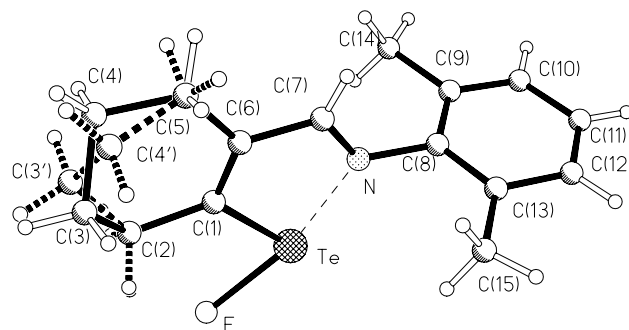


Fig. 5. Molecular structure of  $\beta$ -(fluorotellurenyl)cyclohexenylidene-(2,6-dimethylaniline) **11e**.

[28], or less than 0.1 Å and their calculated covalency factors are close to 100%. The well established origin of this effect is in the lowering energy levels of vacant  $\sigma_{\text{Te-R}}^*$  orbitals which provides for significant narrowing of the gap between those and the donating  $n_{\text{N}}$  orbitals

Table 1  
Bond lengths (Å) and angles (°) in  $\beta$ -(*p*-ethoxyphenyltelluro)cyclohexenylidene-(*p*-toluidine) **11a**

Te–C(1)	2.131(8)	C(8)–C(9)	1.393(12)
Te–C(15)	2.130(9)	C(9)–C(10)	1.383(15)
O(1)–C(18)	1.332(13)	C(10)–C(11)	1.368(15)
O(1)–C(21)	1.443(14)	C(11)–C(12)	1.379(14)
N(1)–C(7)	1.292(12)	C(11)–C(14)	1.475(17)
N(1)–C(8)	1.392(13)	C(12)–C(13)	1.362(15)
C(1)–C(6)	1.345(12)	C(15)–C(20)	1.392(13)
C(1)–C(2)	1.469(14)	C(15)–C(16)	1.408(13)
C(2)–C(3)	1.541(11)	C(16)–C(17)	1.354(16)
C(3)–C(4)	1.537(14)	C(17)–C(18)	1.382(14)
C(4)–C(5)	1.523(17)	C(18)–C(19)	1.411(13)
C(5)–C(6)	1.496(12)	C(19)–C(20)	1.349(15)
C(6)–C(7)	1.411(15)	C(21)–C(22)	1.442(19)
C(8)–C(13)	1.390(13)		
C(1)–Te–C(15)	94.6(3)	C(11)–C(10)–C(9)	122.4(9)
C(18)–O(1)–C(21)	118.2(9)	C(10)–C(11)–C(12)	118.0(10)
C(7)–N(1)–C(8)	122.2(9)	C(10)–C(11)–C(14)	120.3(11)
C(6)–C(1)–C(2)	122.4(7)	C(12)–C(11)–C(14)	121.7(11)
C(6)–C(1)–Te	120.4(7)	C(13)–C(12)–C(11)	121.2(9)
C(2)–C(1)–Te	117.3(6)	C(12)–C(13)–C(8)	120.9(9)
C(1)–C(2)–C(3)	114.2(8)	C(20)–C(15)–C(16)	116.6(9)
C(4)–C(3)–C(2)	106.1(8)	C(20)–C(15)–Te	121.9(7)
C(5)–C(4)–C(3)	112.7(8)	C(16)–C(15)–Te	121.3(7)
C(6)–C(5)–C(4)	112.0(8)	C(17)–C(16)–C(15)	121.8(9)
C(1)–C(6)–C(7)	122.8(8)	C(16)–C(17)–C(18)	121.2(8)
C(1)–C(6)–C(5)	123.2(9)	O(1)–C(18)–C(17)	125.9(8)
C(7)–C(6)–C(5)	114.0(8)	O(1)–C(18)–C(19)	116.8(8)
N(1)–C(7)–C(6)	121.8(9)	C(17)–C(18)–C(19)	117.4(9)
N(1)–C(8)–C(13)	123.2(8)	C(20)–C(19)–C(18)	121.2(8)
N(1)–C(8)–C(9)	118.1(8)	C(19)–C(20)–C(15)	121.7(8)
C(13)–C(8)–C(9)	118.5(9)	C(10)–C(9)–C(8)	118.8(9)
O(1)–C(21)–C(22)	108.8(11)		

Table 2  
Bond lengths (Å) and angles (°) in  $\beta$ -(acetoxyltellurenyl)cyclohexenylidene-(2,6-dimethylaniline) **11b**

Te–C(1)	2.074(4)	C(5)–C(6)	1.509(6)
Te–O(1)	2.197(3)	C(6)–C(7)	1.414(6)
Te–N	2.202(3)	C(8)–C(9)	1.388(5)
N–C(7)	1.294(5)	C(8)–C(13)	1.389(5)
N–C(8)	1.436(5)	C(9)–C(10)	1.393(5)
O(1)–C(16)	1.284(5)	C(9)–C(14)	1.498(6)
O(2)–C(16)	1.209(6)	C(10)–C(11)	1.361(7)
C(1)–C(6)	1.356(5)	C(11)–C(12)	1.393(7)
C(1)–C(2)	1.505(5)	C(12)–C(13)	1.389(6)
C(2)–C(3)	1.505(8)	C(13)–C(15)	1.490(6)
C(3)–C(4)	1.482(10)	C(16)–C(17)	1.509(6)
C(4)–C(5)	1.508(7)		
C(1)–Te–O(1)	85.75(12)	N–C(7)–C(6)	118.3(3)
C(1)–Te–N	76.64(12)	C(9)–C(8)–C(13)	122.5(3)
O(1)–Te–N	162.30(11)	C(9)–C(8)–N	118.3(3)
C(7)–N–C(8)	122.6(3)	C(13)–C(8)–N	119.1(4)
C(7)–N–Te	112.5(2)	C(8)–C(9)–C(10)	117.5(4)
C(8)–N–Te	124.3(2)	C(8)–C(9)–C(14)	121.7(4)
C(16)–O(1)–Te	113.0(2)	C(10)–C(9)–C(14)	120.7(4)
C(6)–C(1)–C(2)	122.2(3)	C(11)–C(10)–C(9)	121.4(5)
C(6)–C(1)–Te	115.0(2)	C(10)–C(11)–C(12)	120.2(4)
C(2)–C(1)–Te	122.8(3)	C(13)–C(12)–C(11)	120.3(4)
C(1)–C(2)–C(3)	111.9(4)	C(12)–C(13)–C(8)	118.1(4)
C(4)–C(3)–C(2)	112.6(5)	C(12)–C(13)–C(15)	120.3(4)
C(3)–C(4)–C(5)	111.5(5)	C(8)–C(13)–C(15)	121.6(4)
C(6)–C(5)–C(4)	113.3(4)	O(2)–C(16)–O(1)	124.4(4)
O(1)–C(6)–C(7)	117.3(3)	O(2)–C(16)–C(17)	121.3(4)
C(1)–C(6)–C(5)	122.3(3)	O(1)–C(16)–C(17)	114.3(4)
C(7)–C(6)–C(5)	120.4(4)	C(8)–C(13)–C(12)	118.1(4)

and, thus, enhancing attractive two-electron orbital interaction [2,12]. Due to partial population of the antibonding  $\sigma_{\text{Te-R}}^*$  orbitals the shortening of the Te...N distances in compounds **11** is attended with elongation of the Te–R bonds (Table 6), which reaches a maximum at the tellurenyl bromides **11c, d**. These structural features allows the formulation of the bonding in compounds **11** within the framework of a hypervalent three-center, four-electron model. Therefore, the structures of these molecules correspond to aromatic heterocycles **16a** as was first suggested by Detty [8] for the case of oxatellurolium chlorides **17**. The elongated Te–R bonds and the proneness of the tellurenyl halides **11c, d** to anionic exchange reactions evidence a significant contribution of the ion pair structure **16b** to the resonance hybrid. Substantially longer than in **11b–e**, although almost 1 Å shorter than the van der Waals contact, is the Te...N distance in **11a** in which the tellurium center is attached with a less electronegative aryl substituent. The values of the lengths of the intramolecular coordination N  $\rightarrow$  Te bonds and their covalency factors in **11a** and a structurally analogous compound **10b** practically coincide. Although the  $n_{\text{N}} \rightarrow \sigma_{\text{Te-R}}^*$  charge transfer interaction in the imines somewhat ex-

Table 3  
Bond lengths (Å) and angles (°) in  $\beta$ -(bromotellurenyl)cyclohexenylidene-(*p*-toluidine) **11c**

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(10)
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)	1.378(5)
C(1)–Te–N(1)	77.91(11)	C(1)–C(6)–C(5)	122.5(3)
C(1)–Te–Br	91.95(9)	C(7)–C(6)–C(5)	119.4(3)
N(1)–Te–Br	168.70(7)	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	113.4(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 4

Bond lengths (Å) and angles (°) in  $\beta$ -(bromotellurenyl)cyclohexenyldiene-(2,6-dimethylaniline) **11d**

Te–C(1)	2.093(7)	C(3)–C(2)	1.526(10)
Te–N	2.147(6)	C(4')–C(3')	1.513(16)
Te–Br	2.760(1)	C(8)–C(13)	1.394(9)
N–C(7)	1.291(9)	C(8)–C(9)	1.398(9)
N–C(8)	1.454(8)	C(9)–C(10)	1.389(10)
C(1)–C(6)	1.325(11)	C(9)–C(14)	1.496(11)
C(1)–C(2)	1.518(9)	C(10)–C(11)	1.370(11)
C(6)–C(7)	1.405(9)	C(11)–C(12)	1.365(11)
C(6)–C(5)	1.514(9)	C(12)–C(13)	1.386(10)
C(5)–C(4)	1.517(10)	C(13)–C(15)	1.500(10)
C(4)–C(3)	1.502(15)		
C(1)–Te–N	77.0(2)	C(3)–C(2)–C(1)	111.3(8)
C(1)–Te–Br	94.1(2)	N–C(7)–C(6)	119.3(7)
N–Te–Br	171.0(1)	C(13)–C(8)–C(9)	122.9(6)
C(7)–N–C(8)	124.0(6)	C(13)–C(8)–N	118.8(6)
C(7)–N–Te	112.4(4)	C(9)–C(8)–N	118.1(6)
C(8)–N–Te	123.6(5)	C(10)–C(9)–C(8)	116.6(7)
C(6)–C(1)–C(2)	125.5(7)	C(10)–C(9)–C(14)	120.6(7)
C(6)–C(1)–Te	114.1(5)	C(8)–C(9)–C(14)	122.7(6)
C(2)–C(1)–Te	120.3(6)	C(11)–C(10)–C(9)	122.1(7)
C(1)–C(6)–C(7)	117.1(6)	C(10)–C(11)–C(12)	119.3(7)
C(1)–C(6)–C(5)	121.2(6)	C(11)–C(12)–C(13)	122.3(7)
C(7)–C(6)–C(5)	121.7(7)	C(12)–C(13)–C(8)	116.7(7)
C(4)–C(5)–C(6)	112.7(8)	C(12)–C(13)–C(15)	121.4(7)
C(3)–C(4)–C(5)	113.0(9)	C(8)–C(13)–C(15)	121.8(6)
C(4)–C(3)–C(2)	111.6(9)		

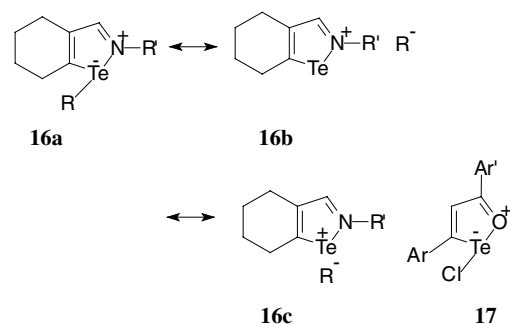
ceeds that of  $n_{\text{O}} \rightarrow \sigma_{\text{Te-R}}^*$  in *o*-tellurocarbonyl compounds, and despite *cis-s-cis*-configurations of the imines being more stabilized with respect to their

Table 5

Bond lengths (Å) and angles (°) in  $\beta$ -(fluorotellurenyl)cyclohexenyldiene-(2,6-dimethylaniline) **11e**

Te–C(1)	2.052(7)	C(3')–C(4')	1.565(17)
Te–F	2.063(5)	C(6)–C(7)	1.443(9)
Te–N	2.185(6)	C(8)–C(13)	1.372(12)
N–C(7)	1.302(8)	C(8)–C(9)	1.393(12)
N–C(8)	1.447(9)	C(9)–C(10)	1.365(12)
C(1)–C(6)	1.339(10)	C(9)–C(14)	1.501(15)
C(1)–C(2)	1.519(8)	C(10)–C(11)	1.385(16)
C(2)–C(3)	1.498(11)	C(11)–C(12)	1.348(16)
C(3)–C(4)	1.580(17)	C(12)–C(13)	1.439(12)
C(4)–C(5)	1.504(12)	C(13)–C(15)	1.482(13)
C(5)–C(6)	1.513(9)		
C(1)–Te–F	87.5(2)	C(7)–C(6)–C(5)	119.0(6)
C(1)–Te–N	76.2(2)	N–C(7)–C(6)	115.5(6)
F–Te–N	163.7(2)	C(13)–C(8)–C(9)	123.0(7)
C(7)–N–C(8)	121.6(6)	C(13)–C(8)–N	118.8(7)
C(7)–N–Te	114.4(5)	C(9)–C(8)–N	118.1(7)
C(8)–N–Te	123.9(4)	C(10)–C(9)–C(8)	118.5(10)
C(6)–C(1)–C(2)	121.7(6)	C(10)–C(9)–C(14)	119.8(10)
C(6)–C(1)–Te	116.5(4)	C(8)–C(9)–C(14)	121.7(8)
C(2)–C(1)–Te	121.8(5)	C(9)–C(10)–C(11)	121.1(10)
C(3)–C(2)–C(1)	111.4(7)	C(12)–C(11)–C(10)	120.0(9)
C(2)–C(3)–C(4)	107.7(9)	C(11)–C(12)–C(13)	121.5(10)
C(5)–C(4)–C(3)	108.5(9)	C(8)–C(13)–C(12)	116.0(8)
C(4)–C(5)–C(6)	111.8(8)	C(8)–C(13)–C(15)	122.8(7)
C(1)–C(6)–C(7)	117.3(6)	C(12)–C(13)–C(15)	121.2(9)
C(1)–C(6)–C(5)	123.7(6)		

unstrained *trans-s-trans* isomers than *o*-tellurocarbonyl compounds [12], this is compensated in the latter by stronger electrostatic attractive forces between the interacting centers. In **11b**, the distance between the carbonyl O(2) atom of the acetyl group and the Te atom is about 0.6 Å closer than the respective van der Waals contact, which points to additional attractive interaction between these atoms. This interaction is, most probably, of electrostatic origin, since the geometry of the formed four-membered cycle TeO(2)C(16)O(1) is not favorable for the overlap of valence orbitals of the considered centers



As seen from Figs. 3–5, the X-ray determined structures of compounds **11** display a disordering of C(3), C(4) atoms of the cyclohexene rings. This effect is definitely associated with the extremely high conformational flexibility peculiar to cyclohexene and its derivatives. The inversion barriers for the parent compound and its derivatives fall into the narrow range of 0.4–24 kJ mol<sup>-1</sup> [29]. It should be noted that the occupancies of the two possible positions for the atoms C(3), C(4) and C(3'), C(4') in the aliphatic moieties of compounds **11c**, **11d**, **11e** differ in the proportion 4:1, 3:2 and 1:1, respectively.

The perchlorate **12** is the first structurally characterized  $\beta$ -tellurovinylcarbonyl compound with a formally tricoordinated tellurium atom involved in intramolecular O  $\rightarrow$  Te interaction. Its molecular and crystal structures are depicted in Figs. 6 and 7. In spite of a substantial positive charge at the tellurium atom (+1.15, Fig. 9) the length of the intramolecular coordination Te...O bond in **12** (2.631 Å) is only slightly shorter than those in the aldehydes **10a–c**. The calculated covalency factor for the Te...O bond in **12** is 0.64. In the crystal, stereochemical configuration of the tellurium in telluronium salts is known to be defined by the nature of counterions. Discrete telluronium cations with tricoordinated tellurium were observed for the salts with low nucleophilic anions as is the case of Me<sub>3</sub>Te<sup>+</sup> BPh<sub>4</sub><sup>-</sup> [30]. With nucleophilic anions the secondary Te...Hal interactions lead to the formation of dimeric structures with pentacoordinated square-pyramidal tellurium centers (Ph<sub>3</sub>Te<sup>+</sup> Cl<sup>-</sup> [31], Et<sub>3</sub>Te<sup>+</sup> I<sup>-</sup> [32])

Table 6

Geometry parameters of the five-membered cycles closed by the intramolecular coordination  $N \rightarrow Te$  bonds in compounds **11** and the covalency factors of  $N \rightarrow Te$  bonds (calculated based on the Bondi vdW radii [27])

Compound	$d(Te-C(1))$ (Å)	$\angle N-Te-R'$ (°)	$\angle C(6)-C(7)-N$ (°)	$d(Te-R)$ (Å) <sup>a</sup>	$d(N \rightarrow Te)$ (Å)	$\chi$
<b>11a</b>	2.127	165.1	121.9	2.129 (0.01)	2.690	0.62
<b>11b</b>	2.073	162.2	118.2	2.197 (0.12)	2.202	0.93
<b>11c</b>	2.077	168.7	118.5	2.774 (0.28)	2.170	0.95
<b>11d</b>	2.093	171.0	119.3	2.760 (0.27)	2.147	0.97
<b>11e</b>	2.052	163.7	115.5	2.063 (0.01)	2.185	0.95

<sup>a</sup> The elongation of a bond relative to the sum of covalent radii of the corresponding atoms is given in parentheses.

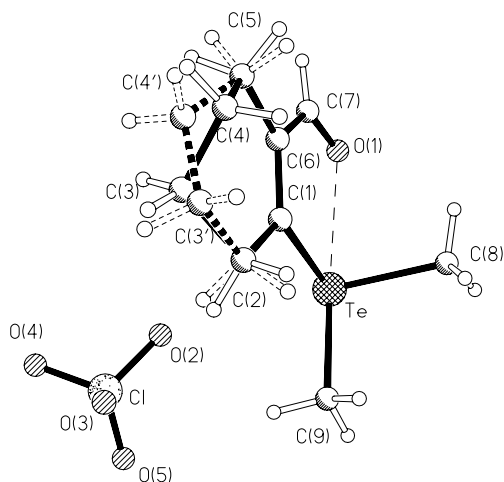


Fig. 6. Molecular structure of  $\beta$ -(dimethyltelluronium)cyclohexenal perchlorate **12**.

or of cubane-like tetramers with hexacoordinated tellurium centers ( $Et_3Te^+ Cl^-$  [32],  $Et_3Te^+ Br^-$  [33]). Our previous X-ray study [34] of the structure of Te-methyl, Te-butyl-(2-phenyliminomethinyl)telluronium perchlorate showed that the secondary  $Te \cdots O$  bonds involving the perchlorate anion are very weak (3.33–3.56 Å), the type of coordination at the tellurium atom is determined by solely intramolecular  $N \rightarrow Te$  bond (2.750 Å,  $\chi = 0.58$ ) and the tellurium atom in the solid acquires trigonal bipyramidal configuration typical of  $\sigma$ -tellura-

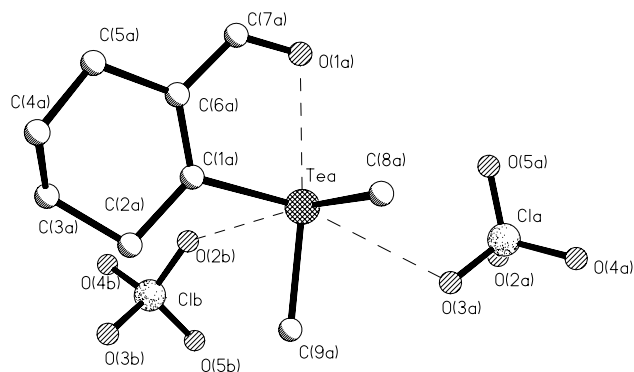


Fig. 7. The nearest vicinity of the Te atom in the crystal of **12** (without the hydrogen atoms and the disordered aliphatic atoms C(3'a) and C(4'a)).

nes  $R_2TeX_2$  [35] and  $RTeX_3$  [36]. The crystal packing of **12** is different (Fig. 7) revealing much stronger intermolecular secondary  $Te \cdots O$  interactions ( $Te \cdots O$  distances are 3.118 and 3.129 Å and the respective covalency factors are 0.32 and 0.31). With the account taken for these interactions the stereochemical configuration of tellurium in **12** may be described as a distorted octahedron (see Table 7).

### 2.3. Quantum chemical calculations

The total gain in energy due to the formation of the secondary  $Te \cdots N$  bonds of the hypervalent type in the compounds **11** was evaluated as the energy difference ( $\Delta E$ ) between the ring-closed *s-cis*- and ring-opened *s-trans*-isomers of the compounds **18** differing from **11** by only the absence of one or two methyl groups in the *N*-aryl substituent. Results of the calculations performed with the use of density functional theory B3LYP/LanL2DZ level of approximation successfully employed in a number of previous theoretical studies of organotellurium compounds [37,38] are depicted in Fig. 8 and are given in Table 8 where comparison is also made between computationally predicted and X-ray determined structural parameters for the proper pairs of the compounds **18** and **11**. Fig. 9 and Table 9 contains similar data for the telluronium salt **12** and its conformers. As is clear from the calculations, the conformations **18** containing the intramolecular coordination  $N \rightarrow Te$  bonds are substantially stabilized relative to the free of strain *s-trans* conformers **19**. In the case of the *N*-arylimines **18b–d** containing strong electronegative substituents at the tellurium centers the energy differences ( $\Delta E$ ) between the two forms approach the value of 125  $\text{kJ mol}^{-1}$  which corresponds to the highest known energy for attractive closed-shell interactions [2,12] and is comparable with the energies of three-center, four-electron  $Y-X-Y$  bonds in trichalcapentalenes and 1,6-dioxo-6 $\lambda$ -chalcapentalenes [12,39]. The  $\Delta E$  value drastically decreases when passing to the compound **18a** with a less electronegative carbon-centered substituent at the tellurium. This trend is well explained by the much greater contribution of the orbital interaction energy between the nitrogen lone pairs ( $n_N$ ) and the anti-bonding orbital ( $\sigma_{TeX}^*$ ) in compounds **18b–e** (310–448  $\text{kJ mol}^{-1}$ ) as

Table 7

Bond lengths (Å) and angles (°) in  $\beta$ -(dimethyltelluronium)cyclohexenal perchlorate **12**

Te–C(1)	2.118(14)	C(1)–C(6)	1.39(2)
Te–C(9)	2.125(17)	C(1)–C(2)	1.53(2)
Te–C(8)	2.130(18)	C(2)–C(3)	1.56(3)
Cl–O(5)	1.385(17)	C(3)–C(4)	1.48(3)
Cl–O(4)	1.392(16)	C(4)–C(5)	1.50(3)
Cl–O(3)	1.405(14)	C(5)–C(6)	1.53(2)
Cl–O(2)	1.417(13)	C(3')–C(4')	1.47(3)
O(1)–C(7)	1.190(19)	C(6)–C(7)	1.43(2)
Te–O(1)	2.631(16)		
C(1)–Te–C(9)	97.5(7)	C(6)–C(1)–Te	116.7(10)
C(1)–Te–C(8)	97.7(6)	C(2)–C(1)–Te	118.5(10)
C(9)–Te–C(8)	97.3(7)	C(1)–C(2)–C(3)	101.4(17)
O(5)–Cl–O(4)	111.4(14)	C(4)–C(3)–C(2)	113(2)
O(5)–Cl–O(3)	108.3(11)	C(3)–C(4)–C(5)	102(2)
O(4)–Cl–O(3)	110.2(12)	C(4)–C(5)–C(6)	113.3(16)
O(5)–Cl–O(2)	111.2(12)	C(1)–C(6)–C(7)	122.5(15)
O(4)–Cl–O(2)	108.5(10)	C(1)–C(6)–C(5)	120.6(14)
O(3)–Cl–O(2)	107.2(9)	C(7)–C(6)–C(5)	116.9(15)
C(6)–C(1)–C(2)	124.7(13)	O(1)–C(7)–C(6)	122.0(16)
O(1)–Te–C(9)	167.1(10)		

against **18a** (58.5 kJ mol<sup>-1</sup>) determined by natural bond orbital (NBO) second-order perturbation analysis.

The calculations reproduce well the principal structural effects of the formation of the N  $\rightarrow$  Te bond,

i.e., a sharp shortening of the N...Te distance relative to the van der Waals contact and the trend to alignment of the N...Te–R triad. As seen from Table 8, the B3LYP/LanL2DZ computed N...Te bond lengths are only 0.06–0.09 Å longer than those found using X-ray crystallography. It has been shown that a very careful account for the effects of electron correlation is critical for an adequate reproduction of the structural consequences of closed-shell interactions [2,11]. Therefore, in accordance with results of more sophisticated calculations on tellurium-containing compounds [12,40] one may expect that even better matching calculated and experimental geometries may be achieved when using more extended basis sets for tellurium. The Te–R, Te–C bond lengths, N...Te–R angles and other geometric parameters obtained by the calculations for compounds **18** are in good agreement with those determined by X-ray studies for their structural analogues (Table 8, Figs. 1–5, 8). The B3LYP/LanL2DZ calculations afford also a correct prediction of the preferred conformation of the acetoxy group in the imine **11b** to be compared with **18b**. This conformation is stabilized by the formation of a moderately strong secondary O...Te bond closing a planar TeOCO four-membered ring. Although both experimental and computed geometries of the compounds **11** witness the T-shaped configuration of their R–Te–N triads,

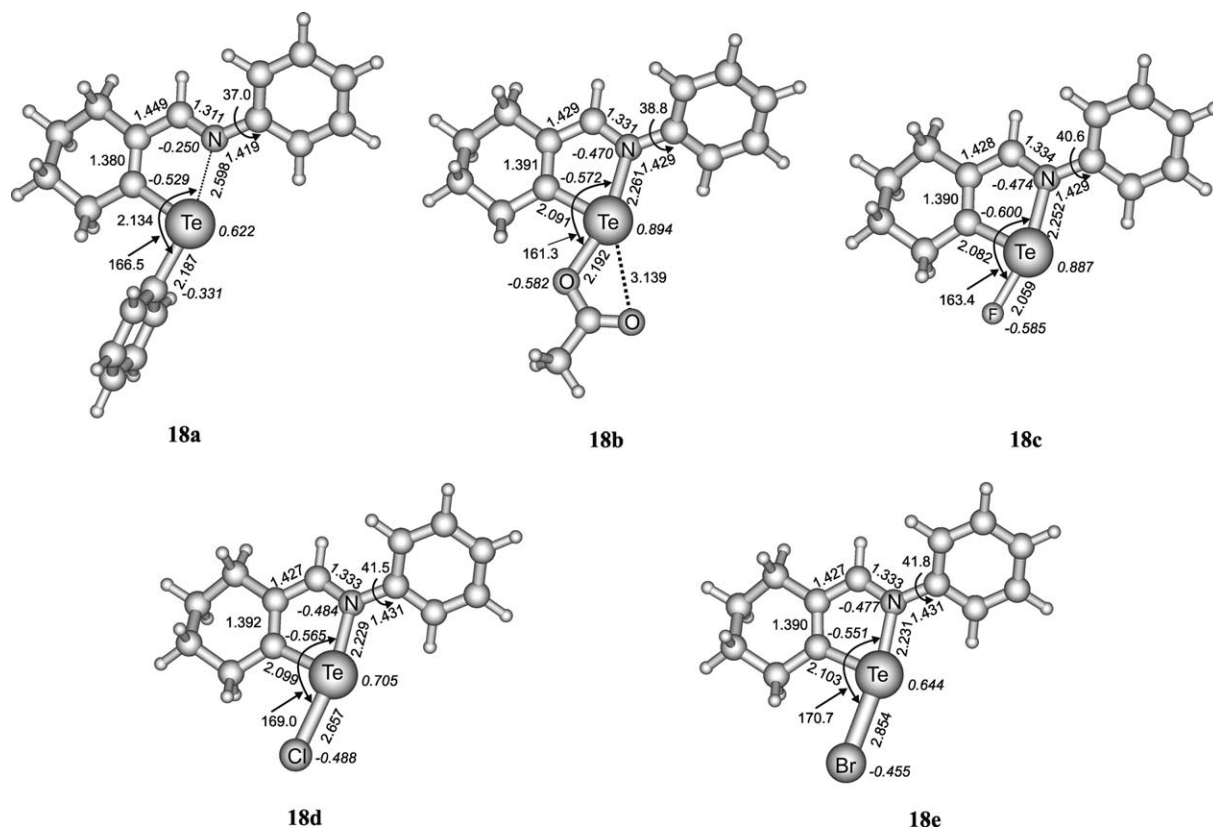


Fig. 8. Optimized geometries of *N*-phenylimines of  $\beta$ -tellurocyclohexenals **18a–e** calculated using B3LYP/LanL2DZ method.



Table 8

Stabilization of the conformations **18** of  $\beta$ -tellurocyclohexaldimines relative to their ring-opened isomers **19**, Mulliken electron populations ( $P$ ) of the intramolecular coordination Te...N and Te–R bonds and structural parameters calculated by B3LYP/LanL2DZ method in comparison with X-ray determined values (in parentheses)<sup>a</sup>

Property	R = Ph (a)	R = OCOMe (b)	R = Br (c)	R = Cl (d)	R = F (e)
<b>18</b> $E_{\text{tot}}$ (a.u.)	–798.112665	–794.988020	–579.718450	–581.499554	–666.396749
<b>19</b> $E_{\text{tot}}$ (a.u.)	–798.103608	–794.947149	–579.676893	–581.455154	–666.349935
$\Delta E_{\text{tot}}$ (kJ mol <sup>–1</sup> )	5.7	25.7	26.1	27.9	29.4
$\Delta(E_{\text{tot}} + \text{ZPE})^{\text{b}}$ (kJ mol <sup>–1</sup> )	23.8	103.8	105.4	112.5	118.8
$P(\text{Te} \dots \text{N})$	0.145	0.334	0.366	0.370	0.357
$P(\text{Te}–\text{R})$	0.720	0.368	0.610	0.568	0.457
$d(\text{Te} \dots \text{N})$ (Å)	2.598 (2.690)	2.261 (2.202)	2.230 (2.170)	2.220 (2.229)	2.252 (2.185)
$d(\text{Te}–\text{R})$ (Å)	2.180 (2.129)	2.192 (2.197)	2.850 (2.774)	2.660 (2.567)	2. (2.063)
$d(\text{Te}–\text{C})$ (Å)	2.130 (2.127)	2.091 (2.073)	2.100 (2.077)	2.090 (2.097)	2.080 (2.052)
$\angle \text{N}–\text{Te}–\text{R}$ (°)	167.3 (165.1)	161.3 (162.2)	170.7 (168.7)	169.0 (168.3)	163.2 (163.7)

<sup>a</sup> The structural parameters calculated for compound **18a** (R = Ph) are correlated with those of **11a**, **18b** with **11b**, **18c** with **11c**, **18d** with **7**, **18e** with **11e** selected as the presently studied most closed analogues.

<sup>b</sup> Energy differences accounting for ZPE.

and thus point to the dominant contribution of the structure **16a** to the resonance hybrid, the total electron distribution dictated primarily by the effects related to differences in electronegativity on the adjacent atoms is characterized by large positive charges at the tellurium centers (Fig. 8). The increase in the net charges in the sequence of compounds from **11a** to **11e** is indicative of increased ionic bonding

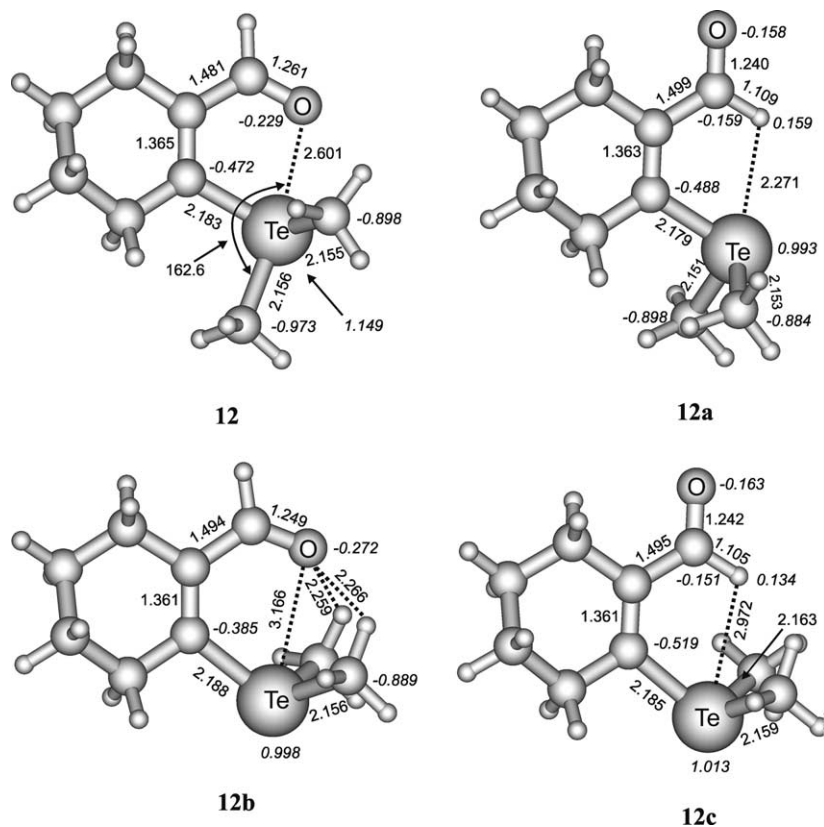
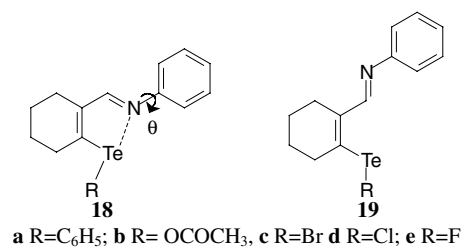


Fig. 9. Optimized geometries of the conformers of  $\beta$ -(dimethyltelluronium)cyclohexenal cation calculated using B3LYP/LanL2DZ method.

Table 9

Energy characteristics of the conformations of  $\beta$ -dimethyltelluroniumcyclohexenal cation shown in Fig. 9

Conformation	$E_{\text{tot}}$ (a.u.)	$\Delta E_{\text{tot}}$ (kJ mol <sup>-1</sup> )	$\Delta(E_{\text{tot}} + \text{ZPE})^{\text{a}}$ (kJ mol <sup>-1</sup> )
<b>12</b>	-434.933789	0	0
<b>12a</b>	-434.913685	52.7	49.8
<b>12b</b>	-434.921486	32.2	30.5
<b>12c</b>	-434.908674	66.1	62.8

<sup>a</sup> Energy differences accounting for ZPE.

As shown by the calculations, the *s-cis*-conformation of the  $\beta$ -(dimethyltelluronium)cyclohexenal cation **12** with the intramolecular coordination O  $\rightarrow$  Te bond is also strongly stabilized relative to the *s-trans* isomer **12a** possessing no such bond (Table 9). Along with the most stable T-shaped conformation **12** the DFT calculations predict the existence of another conformation **12b** formed from **12** by a turn of the dimethyltelluro group. The TeCCCO quasi-ring in **12b** is almost planar and the Te...O distance is  $\sim 0.5$  Å shorter than the van der Waals contact. Due to this relatively weak intramolecular coordination **12b** is energy preferred compared with the free of strain *s-trans* conformation **12a**. The calculated Te...O distance in **12** (Fig. 9) is in reasonably good agreement (the difference is only 0.03 Å) with that determined by X-ray crystallography (Fig. 6). As expected for the compounds with 12-Te-4 configurations of three-center, four-electron bonds formed by tellurium [1] this bond is longer than those in the compounds exhibiting 10-Te-3 coordination. In the cations **12** the positive charge is concentrated at the low electronegative tellurium atoms. In the conformation **12** the Mulliken charge is calculated to be larger than +1 (Fig. 9).

#### 2.4. <sup>125</sup>Te and <sup>1</sup>H NMR spectra

All newly synthesized compounds were characterized by <sup>125</sup>Te and <sup>1</sup>H NMR spectroscopy, the former being known for extreme sensitivity to the geometry and the electronic environment of tellurium [1,9,13,41–44]. The  $\delta^{125}\text{Te}$  and  $\delta^1\text{H}$  chemical shift data are listed in Table 10. The  $\delta^{125}\text{Te}$  values for the compounds **10–15** cover a wide range 537.7–1622.4 ppm. The largest downfield <sup>125</sup>Te NMR chemical shifts are observed in the case of the compounds **11e, f** with the most electronegative atoms attached to the tellurium centers and where the geometries at these centers most closely approach trigonal bipyramidal (an electron pair at tellurium is a phantom ligand) configuration. As was previously argued [9] these are the two principal factors governing the degree of deshielding of a tellurium nucleus occurring in parallel with an increase in the strength of three-center, four-electron bonding. Another important factor is net charge at a tellurium center. However, as seen from a comparison of the  $\delta^{125}\text{Te}$  values of **10a** (537.7 ppm) with the cation **12** (623.1 ppm), the effect caused by

the increase in the positive charge is substantially lower than that determined by the electronegativity of a substituent at tellurium: from 734.3 ppm in **11a** up to 1622.4 ppm in **11e**. The latter effect is also illustrated by the downfield shift of the <sup>125</sup>Te NMR chemical shift on passing from the imine **11a** (734.3 ppm) to its oxygen analogue **10b** (821.6 ppm). The <sup>125</sup>Te NMR chemical shifts in tellurenyl fluorides **11e, f** reach the maximal values currently known for these types of 10-Te-3 compounds. On diluting chloroform solutions of tellurenyl fluorides **11e, f** to a concentration lower than 5 weight per cent, doubling of both <sup>125</sup>Te and <sup>1</sup>H NMR spectral signals was observed which is indicative of the existence of two different forms of the compounds. Similar concentration effects interpreted as a result of dissociation of the intramolecular coordination N  $\rightarrow$  Te bonds were previously observed in the cases of the trichloromercurate **20** [45] derived from **8** and Te, Te-dimethyl-bis[2-(R<sup>2</sup>-benzylideneimino)-R<sup>1</sup>-phenoxy]telluranes **21** [43]. The origin of the effect is not fully understood. The current interpretation is not in accord with the very high sensitivity of <sup>125</sup>Te NMR chemical shifts to the type of coordination at tellurium centers which drastically changes upon dissociation of the N  $\rightarrow$  Te bonds. Another possible explanation of the splitting of the NMR spectral signals on dilution of solutions of compounds **11e, f**, **20**, **21** may be associated with establishing an equilibrium between associated (concentrated solutions) and monomeric (diluted solutions) forms of the compounds. Doubling not only <sup>125</sup>Te but also <sup>1</sup>H NMR spectral signals in solutions of **11e, f** indicates that by contrast with **21**, in which the <sup>1</sup>H NMR spectra measured at room temperature are averaged over two interconverting forms, the chemical exchange of these forms of **11e, f** is a relatively slow process.

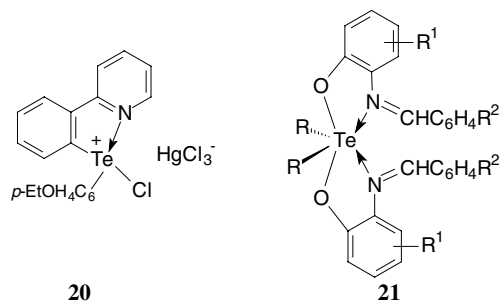
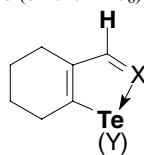


Table 10

<sup>125</sup>Te NMR and <sup>1</sup>H NMR chemical shifts of the methine protons (chloroform-d<sub>6</sub>) in compounds

Compound			$\delta$ <sup>125</sup> Te (ppm) <sup>a</sup>	$\delta$ <sup>1</sup> H (ppm) (CH=O, CH=N)
Structure	X	Y		
<b>10a</b>	O	CH <sub>3</sub>	537.7	9.63
<b>10b</b>	O	C <sub>6</sub> H <sub>4</sub> OEt- <i>p</i>	821.6	9.69
<b>10c</b>	O	TeC <sub>6</sub> H <sub>8</sub> CHO	737.6	9.90
<b>14</b>	O	CH <sub>3</sub> Br <sub>2</sub>	770.5	9.60
<b>12<sup>b</sup></b>	O	(CH <sub>3</sub> ) <sub>2</sub> ClO <sub>4</sub>	623.1	9.46
<b>11a</b>	NC <sub>6</sub> H <sub>4</sub> CH <sub>3</sub> - <i>p</i>	C <sub>6</sub> H <sub>4</sub> OEt- <i>p</i>	734.3	8.21
<b>11b</b>	NC <sub>6</sub> H <sub>4</sub> (CH <sub>3</sub> ) <sub>2</sub> -2,6	OC(=O)CH <sub>3</sub>	1491.7	8.43
<b>11c</b>	NC <sub>6</sub> H <sub>4</sub> CH <sub>3</sub> - <i>p</i>	Br	1424.4	8.68
<b>11d</b>	NC <sub>6</sub> H <sub>4</sub> (CH <sub>3</sub> ) <sub>2</sub> -2,6	Br	1426.7	8.48
<b>11e</b>	NC <sub>6</sub> H <sub>4</sub> (CH <sub>3</sub> ) <sub>2</sub> -2,6	F	1605.2, 1622.4 <sup>c</sup>	8.62, 8.65
<b>11f</b>	NC <sub>6</sub> H <sub>4</sub> CH <sub>3</sub> - <i>p</i>	F	1604, 1621.8 <sup>c</sup>	8.40, 8.42
<b>15</b>	NNHC <sub>6</sub> H <sub>5</sub>	CH <sub>3</sub> Br <sub>2</sub>	774.9	7.98

<sup>a</sup> Relative to dimethyl telluride (CH<sub>3</sub>)<sub>2</sub>Te.<sup>b</sup> Solvent is DMSO-d<sub>6</sub>.<sup>c</sup> For a diluted solution (less than 5% of **11** by weight).

### 3. Experimental

<sup>1</sup>H NMR spectra were recorded on a Varian Unity 300 spectrometer (300 MHz) using CDCl<sub>3</sub> or DMSO-d<sub>6</sub> as solvents and tetramethylsilane as internal reference. The solvents used were dried and distilled in accordance with the standard procedure. <sup>125</sup>Te NMR spectra were recorded on the same spectrometer at 94.74 MHz with a 5 mm broad-band probe (60–80 mg of sample/0.7 ml of solvent, 20 °C). Samples were referenced to <sup>125</sup>Te(C<sub>6</sub>H<sub>5</sub>)<sub>2</sub> relative to <sup>125</sup>Te(CH<sub>3</sub>)<sub>2</sub> at  $\delta$  0.0 as an external standard run as a chloroform solution [41]. The spectra were collected over 1000–2000 transients by using a 100 000 Hz sweep width, with a pulse time of 8  $\mu$ s and a delay time of 1.0 s. The spectra were proton decoupled with WALTZ decoupling by using 1.5 W of power centered at 5 ppm in the proton window.

Quantum chemical calculations have been carried out using the DFT B3LYP method which combines Becke's three-parameter non-local hybrid exchange potential [46] with the non-local correlation functional of Lee, Yang and Parr [47]. Geometries obtained with this method are, in general, in fairly good agreement with experimental values [48,49]. All calculations were performed using GAUSSIAN-98 program package [50]. The force constant matrices were calculated at the same (B3LYP/LanL2DZ) level of approximation used for geometry optimization to verify that the optimized structures correspond to local minima on the respective potential energy surfaces and to evaluate the zero-point energies (ZPE). The orbital interaction energies as well as atomic charges were calculated by natural bond orbi-

tal method [17] at the B3LYP/LanL2DZ level. Bond orders *P*, given in Table 8, were calculated with SBKJ basis set of orbitals [51] using GAMESS program package [52].

#### 3.1. X-ray crystallographic studies of the compounds **11a–e** and **12**

The X-ray diffraction data sets for compounds **11a–e**, **12** 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 [53]. The principal crystallographic characteristics are given in Table 11. Most of the H atoms were located from difference Fourier syntheses. The remaining H atoms were placed in geometrically calculated positions. For the structures **11b** and **11c**, the coordinates and isotropic thermal parameters of the H atoms were refined with the exception of the H atoms attached to the disordered carbon atoms, which were refined using the “riding” model. Positions of the H atoms for other structures were also refined using this model [53].

#### 3.2. Synthesis

##### 3.2.1. $\beta$ -(Dimethyltelluronium)cyclohexenal perchlorate **12**

To a solution of  $\beta$ -(methyltelluro)cyclohexenal **10b** (0.563 g, 0.00397 mol) in acetonitrile (10 ml) a solution of AgClO<sub>4</sub>·3CH<sub>3</sub>CN (1.31 g, 0.00397 mol) in acetonitrile

(5 ml) was added dropwise under stirring. The mixture was stirred at room temperature for 15 min and the precipitate of AgI filtered off. Ether (15 ml) was added to the filtrate and the mixture was kept at  $-15\text{ }^{\circ}\text{C}$  for 1 h. The precipitate of perchlorate **12** was filtered off, washed with a small portion of ether and dried to give **12** (1.32 g, 91% yield) as colorless crystals; m.p.  $142\text{--}143\text{ }^{\circ}\text{C}$  (with decomposition).  $^1\text{H NMR}$  (DMSO- $d_6$ ),  $\delta$ , ppm: 1.85–2.70 (m, 8H,  $(\text{CH}_2)_4$ ); 2.30 (s, 6H,  $2\text{CH}_3$ ); 9.51 (s, 1H, CHO). Found %: C, 29.38; H, 4.06.  $\text{C}_9\text{H}_{15}\text{ClO}_5\text{Te}$ . Calculated %: C, 29.51; H, 4.14.

### 3.2.2. $\beta$ -(*p*-Ethoxyphenyltelluro)cyclohexenylidene-(*p*-toluidine) **11a**

A solution of  $\beta$ -(*p*-ethoxyphenyltelluro)cyclohexenal **10b** (3.58 g, 0.01 mol) and *p*-toluidine (1.07 g, 0.01 mol) in ethanol (40 ml) was refluxed and then cooled. The precipitate was filtered off and dried to give **11a** (3.76 g, 84%) as yellow crystals; m.p.  $122\text{--}123\text{ }^{\circ}\text{C}$  (from toluene/hexane, 1:1).  $^1\text{H NMR}$  ( $\text{CDCl}_3$ ),  $\delta$ , ppm: 1.40 (t, 3H,  $\text{OCH}_2\text{CH}_3$ ); 1.58–2.60 (m, 8H,  $(\text{CH}_2)_4$ ); 2.35 (s, 3H,  $\text{CH}_3$ ); 4.05 (q, 2H,  $\text{OCH}_2\text{CH}_3$ ); 6.80 (d, 2H, arom.); 7.72 (d, 2H, arom.); 8.20 (s, 1H,  $\text{CH}=\text{N}$ ). Found %: C, 58.97; H, 5.58.  $\text{C}_{22}\text{H}_{25}\text{NOTe}$ . Calculated %: C, 59.11; H, 5.64.

### 3.2.3. $\beta$ -(Acetoxyltelluro)cyclohexenylidene-(2,6-dimethylaniline) **11b**

To a suspension of silver acetate (0.397 g, 0.0238 mol) in acetonitrile (5 ml) a solution of  $\beta$ -(bromotellurenyl)cyclohexenylidene-(2,6-dimethylaniline) **11d** (1.0 g, 0.00238 mol) in acetonitrile (15 ml) was added under

stirring (in dark). The mixture was then stirred at room temperature for 1 h, the precipitated AgBr filtered off and the solvent evaporated to give **11b** (0.81 g, 85%) as light yellow crystals; m.p.  $157\text{--}158\text{ }^{\circ}\text{C}$  (from toluene/hexane, 1:1).  $^1\text{H NMR}$  ( $\text{CDCl}_3$ ),  $\delta$ , ppm: 1.81–3.10 (m, 8H,  $(\text{CH}_2)_4$ ); 2.03 (s, 3H,  $\text{OCOCH}_3$ ); 2.08 (s, 6H,  $2\text{CH}_3$ ); 7.10–7.25 (m, 3H, arom.); 8.47 (s, 1H,  $\text{CH}=\text{N}$ ). Found %: C, 49.97; H, 5.24.  $\text{C}_{17}\text{H}_{21}\text{NO}_2\text{Te}$ . Calculated %: C, 51.18; H, 5.31.

### 3.2.4. $\beta$ -(Bromotellurenyl)cyclohexenylidene-(*p*-toluidine) **11c**

A solution of  $\beta$ -(methylbromotelluro)cyclohexenal **14** (4.12 g, 0.01 mol) and *p*-toluidine (1.07 g, 0.01 mol) in methanol (20 ml) was refluxed and then cooled. The precipitate was filtered off, washed by ether and dried to give **11c** (3.53 g, 87%). Yellow crystals with m.p.  $136\text{--}137\text{ }^{\circ}\text{C}$  (from methanol).  $^1\text{H NMR}$  ( $\text{CDCl}_3$ ),  $\delta$ , ppm: 1.88–3.17 (m, 8H,  $(\text{CH}_2)_4$ ), 2.40 (s, 3H,  $\text{CH}_3$ ), 7.16–7.27 (m, 4H, arom.), 8.76 (s, 1H,  $\text{CH}=\text{N}$ ). Found %: C 41.31, H 3.89.  $\text{C}_{14}\text{H}_{16}\text{BrNTe}$ . Calculated %: C 41.44, H 3.98.

### 3.2.5. $\beta$ -(Bromotellurenyl)cyclohexenylidene-(2,6-dimethylaniline) **11d**

Obtained in the same way as **11c** in 92% yield. Light-yellow crystals; m.p.  $235\text{--}237\text{ }^{\circ}\text{C}$  (from chloroform/methanol, 1:3).  $^1\text{H NMR}$  ( $\text{CDCl}_3$ ),  $\delta$ , ppm: 1.81–3.21 (m, 8H,  $(\text{CH}_2)_4$ ); 2.10 (s, 6H,  $2\text{CH}_3$ ); 7.05–7.21 (m, 3H, arom.); 8.48 (s, 1H,  $\text{CH}=\text{N}$ ). Found %: C, 42.69; H, 4.22.  $\text{C}_{15}\text{H}_{18}\text{BrNTe}$ . Calculated %: C, 42.92; H, 4.32.

Table 11  
Main crystallographic parameters for compounds **11a–e**, **12**

Compound	<b>11a</b>	<b>11b</b>	<b>11c</b>	<b>11d</b>	<b>11e</b>	<b>12</b>
Formula	$\text{C}_{22}\text{H}_{25}\text{NOTe}$	$\text{C}_{17}\text{H}_{21}\text{NO}_2\text{Te}$	$\text{C}_{14}\text{H}_{16}\text{BrNTe}$	$\text{C}_{15}\text{H}_{18}\text{BrNTe}$	$\text{C}_{15}\text{H}_{18}\text{FNTe}$	$\text{C}_9\text{H}_{15}\text{ClO}_5\text{Te}$
Weight	447.03	398.95	405.79	419.81	358.90	366.26
Crystal system	Monoclinic	Monoclinic	Triclinic	Monoclinic	Monoclinic	Monoclinic
Space group	$P2_1/c$	$P2_1/c$	$P\bar{1}$	$P2_1/a$	$P2_1/c$	$P2_12_12_1$
<i>a</i> (Å)	8.100(2)	8.358(2)	9.397(4)	9.217(2)	12.904(3)	7.839(2)
<i>b</i> (Å)	16.766(3)	13.493(3)	9.184(2)	20.432(3)	8.705(2)	9.407(2)
<i>c</i> (Å)	16.544(3)	14.914(3)	9.934(2)	8.678(3)	14.726(3)	17.859(4)
$\alpha$ (°)	90	90	78.36(3)	90	90	90
$\beta$ (°)	117.41(3)	90.58(3)	67.49(3)	104.18(3)	115.59(3)	90
$\gamma$ (°)	90	90	66.87(3)	90	90	90
<i>V</i> (Å <sup>3</sup> )	1994.6(7)	1681.8(6)	727.0(4)	1584.5(7)	1491.9(6)	1316.9(5)
<i>Z</i>	4	4	2	4	4	4
<i>D</i> (g/m <sup>3</sup> )	1.489	1.576	1.854	1.760	1.598	1.847
$\mu$ (mm <sup>-1</sup> )	1.5	1.77	4.77	4.38	1.99	2.46
$\theta$ range	2.43–33.08	2.04–35.06	2.22–30.08	1.99–35.14	1.75–30.11	2.28–35.02
Unique observed reflections	5014	5708	4192	5817	3979	2.405
Observed reflections with $I > 2\sigma(I)$	2381	2908	2845	2063	1532	901
Parameters	226	275	198	182	182	165
<i>R</i>	0.072	0.037	0.027	0.057	0.045	0.072
<i>R</i> $\omega$	0.152	0.135	0.066	0.204	0.182	0.211
Radiation	Mo(K $\alpha$ )	Mo(K $\alpha$ )	Mo(K $\alpha$ )	Mo(K $\alpha$ )	Mo(K $\alpha$ )	Mo(K $\alpha$ )
Gof	0.966	0.857	0.982	0.913	0.864	0.960

### 3.2.6. $\beta$ -(Fluorotellurenyl)cyclohexenylidene-(2,6-dimethylaniline) **11e**

To a solution of **11d** (1.0 g, 0.00238 mol) in chloroform (15 ml) 5 ml of a water solution of silver fluoride (0.31 g, 0.0238 mol) was added dropwise under intense stirring at room temperature. The precipitate of AgBr was filtered off, the chloroform layer separated, washed with water, dried over sodium sulfate and the solvent evaporated. The solid residue was crystallized from toluene/hexane (1:1) to give **11e** (0.80 g, 94%) as light-yellow crystals. m.p. 147–149 °C.  $^1\text{H NMR}$  ( $\text{CDCl}_3$ , 80 mg of **11e** in 1 ml of the solvent),  $\delta$ , ppm: 1.81–3.05 (m, 8H,  $(\text{CH}_2)_4$ ); 2.08 (s, 6H,  $2\text{CH}_3$ ); 7.08–7.18 (m, 3H, arom.); 8.40 (s, 1H,  $\text{CH}=\text{N}$ ). Found %: C, 50.01; H, 4.98.  $\text{C}_{15}\text{H}_{18}\text{FNTe}$ . Calculated %: C, 51.18; H, 5.31.

### 3.2.7. $\beta$ -(Fluorotellurenyl)cyclohexenylidene-(*p*-toluidine) **11f**

Prepared similarly to **11e** in 92% yield starting from **11c**. Light-yellow crystals; m.p. 126–128 °C (from toluene/hexane, 1:1).  $^1\text{H NMR}$  ( $\text{CDCl}_3$ , 50 mg of **11f** in 1 ml of the solvent),  $\delta$ , ppm: 1.81–3.18 (m, 8H,  $(\text{CH}_2)_4$ ); 2.36 (s, 3H,  $\text{CH}_3$ ); 7.12 (d, 2H, arom.); 7.21 (d, 2H, arom.); 8.65 (s, 1H,  $\text{CH}=\text{N}$ ). Found %: C, 48.54; H, 4.59.  $\text{C}_{14}\text{H}_{16}\text{FNTe}$ . Calculated %: C, 48.76; H, 4.68.

### 3.2.8. Di-[2-cyclohexenylidene-(*p*-toluidin)-1-yl] telluride **13**

A solution of di-(2-formylcyclohexen-1-yl) telluride **10c** (1.73 g, 0.005 mol) and *p*-toluidine (1.07 g, 0.01 mol) in ethanol (50 ml) was refluxed for 5 h and then cooled. The precipitate was filtered off and dried to give **13** (1.28 g, 49%) as orange-yellow crystals; m.p. 141–142 °C (from hexane).  $^1\text{H NMR}$  ( $\text{CDCl}_3$ ),  $\delta$ , ppm: 1.60–2.70 (m, 16H,  $2(\text{CH}_2)_4$ ); 2.15 (s, 6H,  $2\text{CH}_3$ ); 7.05 (d, 4H, arom.); 7.15 (d, 4H, arom.); 8.51 (s, 2H,  $\text{CH}=\text{N}$ ). Found %: C, 63.83; H, 6.02.  $\text{C}_{28}\text{H}_{32}\text{N}_2\text{Te}$ . Calculated %: C, 64.16; H, 5.15.

### 3.2.9. $\beta$ -(Methyldibromotelluro)cyclohexenal phenylhydrazone **15**

Obtained in 84% yield similarly to **11c**, **d** starting from **14** and phenylhydrazine. Light-yellow crystals; m.p. 172–173 °C (from toluene).  $^1\text{H NMR}$  ( $\text{CDCl}_3$ ),  $\delta$ , ppm: 1.70–2.81 (m, 8H,  $(\text{CH}_2)_4$ ); 2.91 (s, 3H,  $\text{CH}_3$ ); 6.91–7.30 (m, 6H, arom. + NH); 7.98 (s, 1H,  $\text{CH}=\text{N}$ ). Found %: C, 33.41; H, 3.40.  $\text{C}_{14}\text{H}_{18}\text{Br}_2\text{N}_2\text{Te}$ . Calculated %: C, 33.51; H, 3.62.

## 4. Supplementary material

CCDC–233752 (**11a**), 233753 (**11b**), 233754 (**11c**), 233755 (**11d**), 233756 (**11e**) and 233757 (**12**) contain

the supplementary crystallographic data for this paper. These data can be obtained free of charge from the Cambridge Crystallographic Data Centre: 12, Union Road, Cambridge CB2 1EZ, UK [fax: (internat.) +44-1223/336-033; e-mail: deposit@ccdc.cam.ac.uk].

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