

Molecular and crystal structure of *ortho*-tellurated azomethines with intramolecular N → Te coordination

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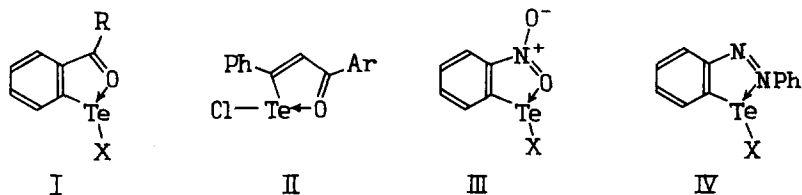
Abstract

Novel reactions have been discovered and studied of C_{aliph.}-Te bond scission in *o*-butyltellurobenzalanilines under the action of halogens, which afford 2-halogenotellurenyl- and 2-trihalogenotellurobenzalanilines in high yields. The series of azomethines have been synthesized with different tellurium-containing groups in *o*-positions with respect to the C=N bond. The effects of structural factors upon the length of N → Te intramolecular coordination bonds have been studied by the following methods: X-ray structural determinations, dipole moments, ¹H and ¹²⁵Te NMR spectroscopy and IR spectroscopy. In Te^{II} derivatives, the shortest intramolecular N → Te contact (2.23 Å) is formed in 2-chlorotellurenyl derivatives XIIIb. Bis(2-formylphenyl)tellurium imines XIVa exist in the crystal form as 10-Te-3 telluranes, in which long intramolecular fractional N → Te bonds (2.70–2.72 Å) have been detected, with the basicity of the imine N atom no practical effect on their length. The ¹²⁵Te NMR spectrum of the ¹⁵N labelled bis[2-(phenyl)iminomethylphenyl]telluride shows that in solutions of this compound a very fast (on an NMR timescale), Te–N and Te ← N bond scrambling occurs owing to a dynamic equilibrium between the topomeric 10-Te-3 structures that apparently takes place via the 12-Te-4 tellurane intermediates. The intramolecular coordination bond in the Te^{IV} derivative, (2-phenyliminomethylphenyl)butylmethyl telluronium perchlorate, belongs to the longest Te → N bonds (2.75 Å). For the first time, the ¹²⁵Te–¹⁵N spin–spin coupling constants are reported for a number of *o*-tellurated azomethines.

Introduction

In recent years interest has grown in compounds in which intramolecular coordination (secondary) bonds O → Te and N → Te are formed, with the participating Te atom in various degrees of oxidation; analogues of these bonds are well documented in the organic chemistry of sulfur and selenium [1,2]. The presence of such bonds considerably strengthens the thermal and hydrolytic stability of organic derivatives of tellurium and permits access to some novel types of tellurium organic compounds. Thus, among the organytellurenyl halogenides RTeHal, only

those compounds are stable, both in the crystalline state and in solution, which contain, in the *ortho*-position relative to the TeHal groups, atoms or groups that are capable of coordination with the Te atom, such as COR [3-7], NO₂ [8] or N=N [9-11] (I-IV).



R=H, NH₂, NHCH₃;

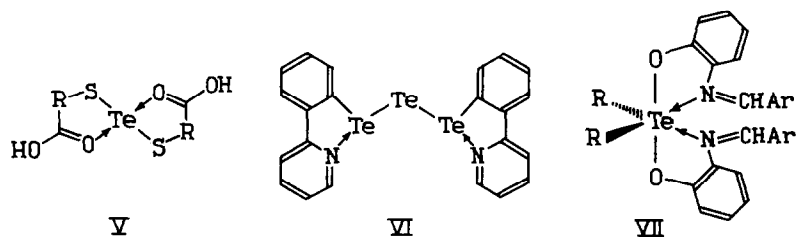
X=Cl, Br

X=Cl, OCOCH₃,

SCN, SC(S)NMe₂

Another example of the stabilizing effect of intramolecular coordination with the participation of a Te atom is given by bis(organylthio)tellurides (RS)₂Te. Bis(arythio)tellurides (ArS)₂Te decompose even at room temperature to produce diaryldisulfides and elemental tellurium [12]. On the other hand, bis(carboxyorganylthio)tellurides V in which, judging from the IR spectroscopy data, there occurs a strong noncovalent Te ← O=C interaction, are stable crystalline compounds. The presence of a strong intramolecular coordination bond N → Te whose length (2.70 Å) is 1 Å less than the sum of the Van der Waals radii of Te and N, which amounts to 3.70 Å [13], ensures the stability of bis[2-pyridyl]phenyl]triteluride VI [14]. Diorganyl(diaryloxy)telluranes VII that we have recently described [15,16] are not subject to hydrolysis even after a prolonged contact with water, whereas diaryl(dialkyloxy)telluranes Ar₂Te(OR)₂, which do not contain N → Te bonds, are hydrolyzed instantaneously even by exposure to air moisture [17]. Some other examples of the stabilizing effect of N → Te coordination may be found in our recently published paper [18].

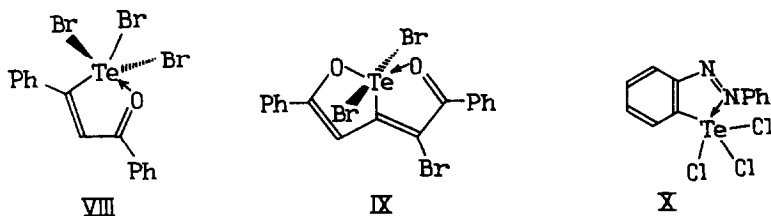
The structure of Te^{II} derivatives that contain a carbonyl [3-7] or an azo group [9-11] in *ortho*-positions relative to the tellurium atom has been examined by several authors. For these compounds in the crystalline form, the *s-cis* conformation is realized with the secondary X → Te (X = O, N) bonds, which in some cases are similar in their characteristics to the respective single covalent bonds. The structure



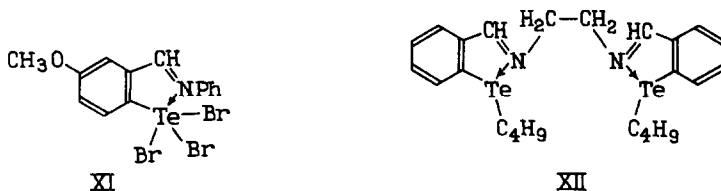
R=-CH₂-, -CH(CH₃)-,
-(CH₂)₂-, o-C₆H₄

of these compounds and of their structural analogs II corresponds, according to the N-X-L nomenclature [19], to 10-Te-3 telluranes.

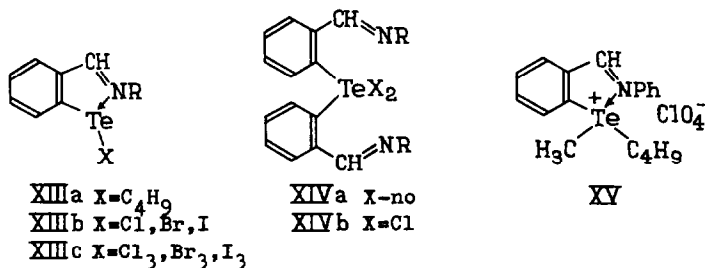
Intramolecular coordination bonds have also been found in Te^{IV} derivatives. Thus, according to the X-ray structural data [20,21], the O → Te bonds in the 12-Te-5 pertelluranes VIII (l = 2.362 Å) and IX (l = 2.153 Å) obtained via oxidative addition of bromine to oxatellurolium halogenides or dioxatellurapentalenes are only slightly longer than single covalent Te-O bonds [22–24]. In *o*-trichlorotelluroazobenzene X the length of the intramolecular coordination N → Te bond is 2.417 Å [25].



Literature data on the intramolecular coordination of tellurium by azomethine functions are scanty. In the case of the *ortho*-tellurated azomethine XI [26], the conclusion as to the presence of the secondary N → Te bond was based solely on IR spectroscopic data. A more clear-cut proof of the presence of such bonds has followed from an X-ray structural study of 1,6-bis(*o*-butyltellurophenyl)-2,5-diazahexa-1,5-diene XII, from which the length of this bond was found to be 2.77 Å [27].



The present paper reports the synthesis, structure and some reactions of *o*-tellurated azomethines XIII–XV.



Results and discussion

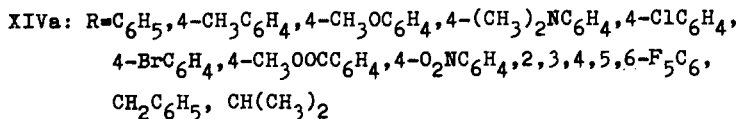
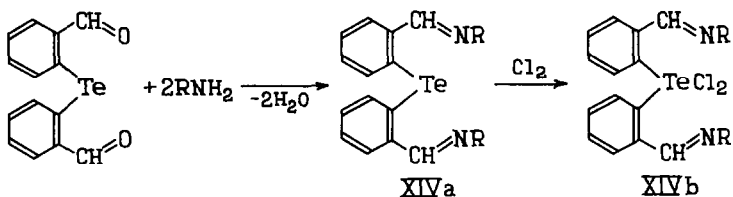
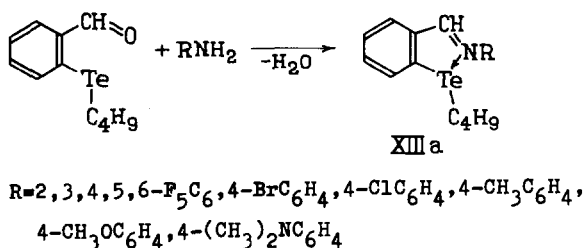
Synthesis and reactions of *o*-tellurated azomethines

Compounds XIIIa [28,29] and XIVa [30,31] have been obtained by usual methods, viz., through the reaction of *o*-butyltellurobenzaldehyde [32] or bis(*o*-formylphenyl)telluride [33] with primary amines.

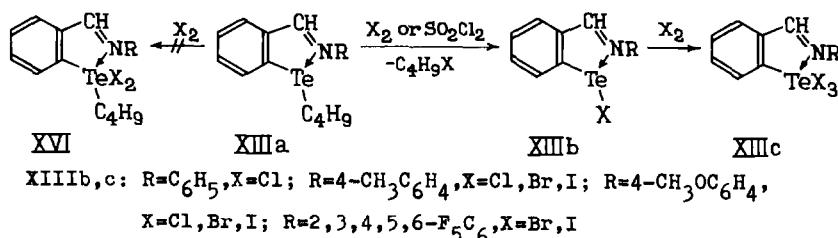
o-Butyltellurobenzalanilines XIIIa are crystalline compounds with colours ranging from yellow to orange, readily soluble in most usual organic solvents. The valence vibration frequency of the azomethine bond observed in the IR spectra lies in the 1600–1619 cm^{-1} range; the methine proton signals are seen in the ^1H NMR spectra as sharp singlets at 8.50–8.57 ppm [29].

Bis-imines XIVa are yellow crystals soluble in polar solvents. The valence vibration frequency of the C=N bond lies in the range 1598–1640 cm^{-1} , and the methine proton signals are observed in the ^1H NMR spectra at 8.47–9.13 ppm, being shifted 1.0–1.6 ppm upfield in comparison with the signal of the formyl proton in the initial bis(2-formylphenyl)telluride (10.13 ppm [33]).

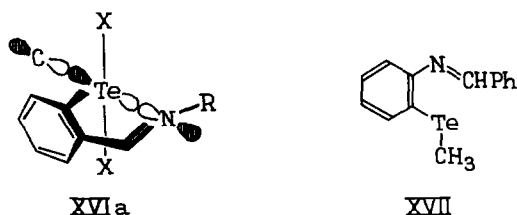
Of particular interest is the synthesis of *o*-halogenotellurenylbenzalanilines XIIIb and *o*-trihalogenotellurobenzalanilines XIIIc, since it clearly illustrates the effect the $\text{N} \rightarrow \text{Te}$ coordination has on the reactions of organotellurium compounds. These compounds have been prepared starting from *o*-butyltellurobenzalanilines XIIIa [28,29]. Judging from the behaviour of other arylalkyltellurides [34], it would be expected that the reaction of the compounds XIIIa with halogens or sulfuryl chloride should give *o*-dihalogenotellurobutylbenzalanilines XVI. In practice, upon the treatment of imines XIIIa with halogenating reagents, fission of the $\text{C}_{\text{aliph.}}-\text{Te}$ bonds takes place and, depending on the stoichiometric ratio between the reactants, either the tellurenyl XIIIb or the trihalogenotelluro derivatives XIIIc are obtained. It should be noted that the oxidation reactions of tellurides XIIIa proceed via the intermediate σ -telluranes XVI, which exist in solution only at low temperature, as shown by the ^1H NMR spectra measured for the mixture of reactants in the course of the reaction. When the temperature of the solution is raised to room temperature,



an elimination of butyl halogenide molecules occurs, resulting in the transformation of XVI to XIIIb in high yield.

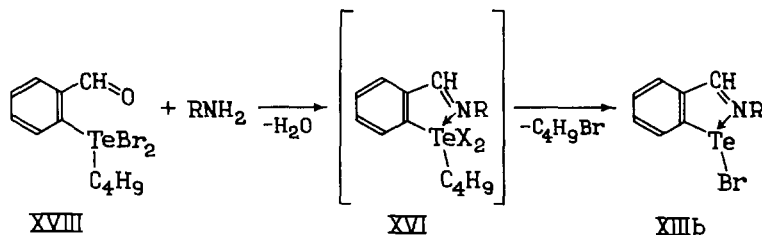


This reaction, at first sight unexpected, can be accounted for by two factors: a) the strong stabilization of the 10-Te-3 structures XIIIb due to the coordination of the azomethine nitrogen atom to the tellurium atom, and b) by the favourable steric conditions for nitrogen-tellurium $n(\text{N}) \rightarrow \sigma^*(\text{Te}-\text{C}_4\text{H}_9)$ electron delocalization in the intermediate XVI. As seen from the orbital interaction pattern shown in XVIa, such delocalization will lead to a strong weakening of the Te-C bond expected to be virtually aligned with the N → Te fractional bond, both bonds taking equatorial positions in the Te^{IV} trigonal bipyramid.



There are ample examples of reactions facilitating X-C bond rupture reactions that occur when interacting fragments meet each other in appropriate steric positions providing a large n_o or $N_N-\sigma^*(\text{X}-\text{C})$ overlap and, consequently, a partial population of the antibonding $\sigma^*(\text{X}-\text{C})$ orbital [35]. Indeed, benzal-2-methyltelluroaniline XVII, in which the N → Te coordination is sterically unrealizable, forms the corresponding tellurodihalogenides under the same conditions.

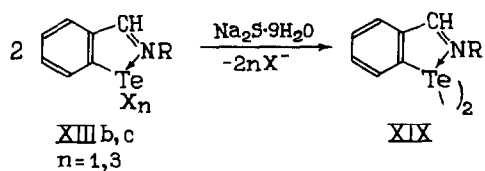
It is noteworthy that *o*-halogenotellurenylbenzalanilines XIIIb rather than azomethines XVI are also formed when *o*-dibromotellurobutylbenzaldehyde XVIII reacts with primary amines upon heating. The compounds XVI forming as intermediates readily eliminate a molecule of butyl bromide. This procedure for the preparation tellurenylbromides, also apparently applicable in the synthesis of other tellurenyl halogenides XIIIb, possesses an advantage over the formerly described halogenolysis of *o*-butyltellurobenzalanilines XIIIa in that it is not accompanied by the formation of tribromotelluro derivatives XIIIc as by-products.



It should be noted that prior to the present work only one method has been described for the preparation of type XIIIc *o*-tellurated azomethines used in the synthesis of 5-methoxy-2-tribromotellurobenzalaniline XI. This was based on the reaction of the corresponding *o*-chloromercurobenzalaniline with tellurium tetrabromide [26]. There are, however, certain shortcomings inherent in that method, namely: 1) it requires the synthesis of chloromercuro derivatives which are not readily accessible and can apparently only be obtained on the condition that the *o*-position (relative to the azomethine group) is activated by donor substituents; 2) only the synthesis of tribromotelluro derivatives XIIIc can be undertaken by this method since with TeCl_4 or TeI_4 no target compounds can be obtained. Thus, we have found a fission reaction of the $\text{C}_{\text{aliph.}}-\text{Te}$ bonds, previously unknown in the series of organotellurium compounds, which makes it possible to synthesize under mild conditions practically any azomethine of types XIIIb,c in high yield.

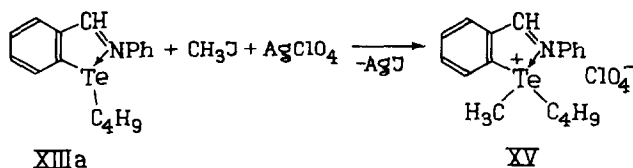
The *o*-tellurated azomethines XIIIb,c are crystalline compounds which, depending on the nature of the halogen attached to the tellurium atom, are coloured from yellow to violet. The trihalogenotelluro derivatives have a more intense colour than the monohalogeno derivatives. The latter are readily soluble in polar solvents, whereas the XIIIc compounds have high melting points and are poorly soluble. In the IR spectra, the valence vibration frequency of the azomethine bond lies in the $1560-1604\text{ cm}^{-1}$ range for tellurenyl halogenides XIIIb and in the $1593-1613\text{ cm}^{-1}$ range in the case of trihalogenotelluro derivatives.

Unlike tellurenyl halogenides and trihalogenotelluro compounds, which do not contain the $\text{N} \rightarrow \text{Te}$ coordination bonds [34], the azomethines XIIIb,c require more severe conditions for their reduction to the ditellurides XIX: this can take place only when they are heated for 2–3 h in the melt of a 4–6-fold excess of $\text{Na}_2\text{S} \cdot 9\text{H}_2\text{O}$ [29]. The stability of these compounds against reduction is apparently associated with the influence of the $\text{N} \rightarrow \text{Te}$ intramolecular coordination bond, since the $n(\text{N}) \rightarrow \sigma^*(\text{Te}-\text{X})$ interaction leads to an additional splitting of these energy levels, thus raising the energy of antibonding MO [35].



Bis(2-aryliminomethinyl)phenyl ditellurides XIX are orange crystalline substances that are readily soluble in polar solvents [29].

Like other derivatives of dicoordinate tellurium [34], arylimines of *o*-butyltellurobenzaldehyde can be alkylated at a Te atom by their treatment with methyl iodide in the presence of an equimolar amount of silver perchlorate, leading to the corresponding telluronium salt [36].



Molecular and crystal structure of *o*-tellurated azomethines

To reveal unequivocally the presence of the intramolecular coordination of the imine nitrogen atom with the tellurium atom in *o*-tellurated azomethines and to study the effect of the nature of substituents upon the length of the secondary Te ← N bonds, X-ray structural determinations, dipole moment measurements and ^1H and ^{125}Te NMR spectral investigations have been carried out.

1. *2-Halogenotellurenyl-, 2-acetatotellurenyl- and 2-butyltellurobenzalanilines.* The X-ray structural data for type XIIIb *o*-tellurated azomethines are exemplified by the case of 2-chlorotellurenyl-4'-methylbenzalaniline XIIIb1 (Fig. 1), whose structure has been described in detail [29]. The characteristic feature of this molecule is the strong attractive N → Te interaction, with the distance between these atoms being quite short (close to the sum of the covalent radii for Te in the axial direction and N, which equals 2.24 Å) [37], namely, 2.218 and 2.239 Å in two crystallographically independent molecules. Owing to this interaction, the Te atom has a T-shaped configuration (the angles N...Te-Cl are 168.0° and 168.7°) supplemented to a square-planar coordination by a weak intermolecular Te...Cl contact with a distance of 3.746 Å between these centres. In the almost planar bicyclic system of XIIIb1 a certain equalization of the bond lengths is observed in the azomethine fragments as compared to the standard values for the C-C and C=N bonds.

There is practically no difference between this structure and that of 2-acetatotellurenyl-4'-methylbenzalaniline XX (for the synthesis see ref. [18]) described in the present work. The stereoview of the molecule, as well as the important bond lengths and valence angles in XX, are shown in Fig. 2. The rest of the lengths and angles are characterized in Tables 1 and 2, respectively.

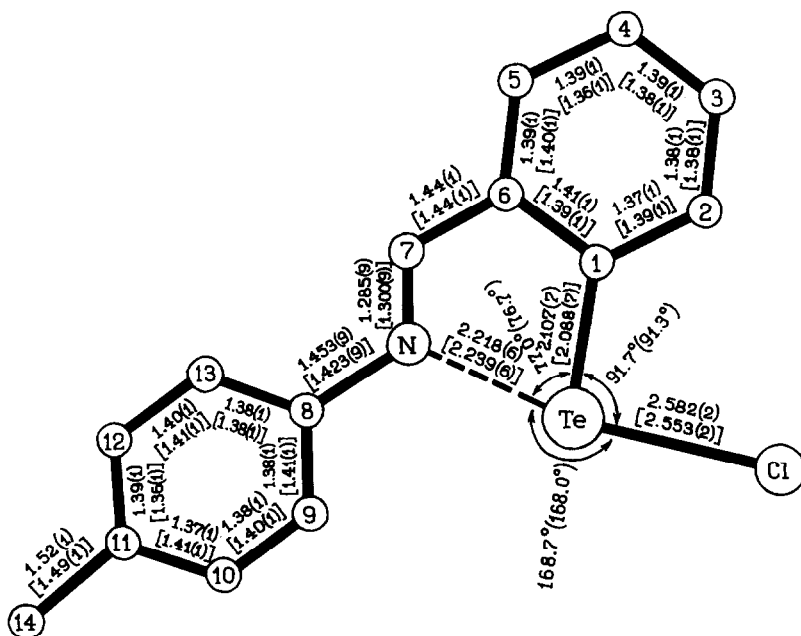


Fig. 1. The molecular geometry of 2-chlorotellurenyl-4'-methylbenzalaniline XIIIb1.

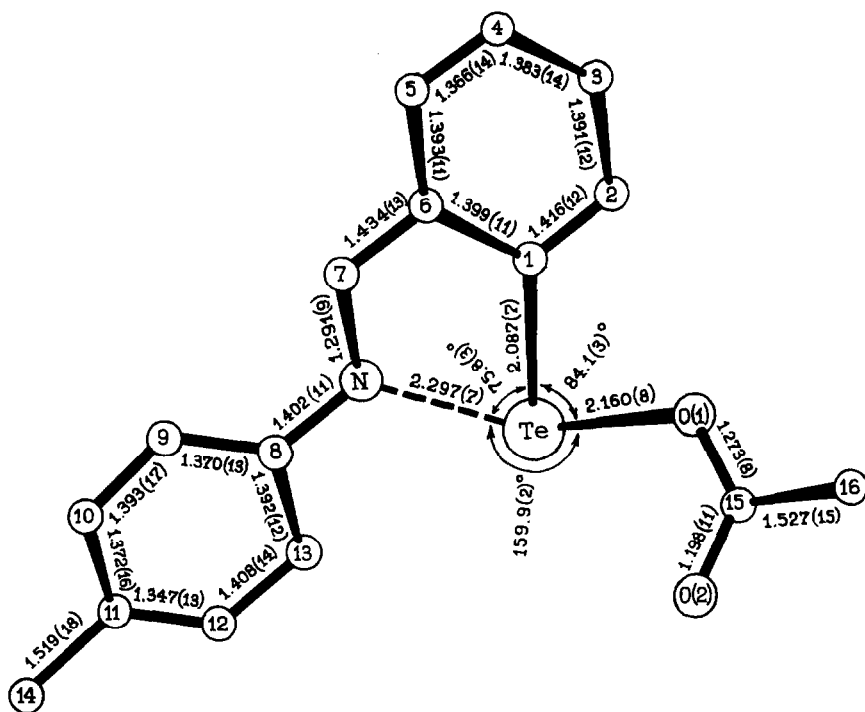


Fig. 2. The molecular geometry of 2-acetatellurenyl-4'-methylbenzalaniline XX.

Like azomethine XIIIb1, in this case, when the $N \rightarrow Te$ contact is taken into account (the distance between the atoms being 2.297(7) Å), the Te atom has a somewhat distorted T-shaped configuration (the angles $N \cdots Te-O(1)$, $N \cdots Te-C(1)$ and $O(1)-Te-C(1)$ are 159.9(2), 75.8(3) and 84.1(3)°, respectively). The atom O(1) lies almost in the plane of the bicyclic system (declination from the $Te(1)C(1)C(7)N$ plane, $\Delta = 0.018(6)$ Å), the atom O(2) is somewhat further out of this plane ($\Delta = 0.630(7)$ Å), while the declination of the N atom from the $TeC(7)C(8)$ plane is 0.059(5) Å, practically coinciding with the $Te \leftarrow N$ straight line, with the angle $C(7)-N \cdots Te$ equalling 112.5(5)° (in XIIIb1 this angle is 114.5 and 113.2°). Apart from the $N \rightarrow Te$ distance being close to that found in tellurenyl chloride XIIIb1, similar values are also found for the bond lengths of 1.291(9) Å for $C(7)=N$ and 1.434(13) Å for $C(6)-C(7)$ (in the compound XIIIb1 the respective bond lengths

Table 1

Bond lengths (Å) in compound XX

Te-O(1)	2.160(8)	C(1)-C(6)	1.399(11)	C(8)-C(13)	1.392(12)
Te-N	2.297(7)	C(2)-C(3)	1.391(12)	C(9)-C(10)	1.393(17)
Te-C(1)	2.087(7)	C(3)-C(4)	1.383(14)	C(10)-C(11)	1.372(16)
O(1)-C(15)	1.273(10)	C(4)-C(5)	1.366(14)	C(11)-C(12)	1.347(13)
O(2)-C(15)	1.198(11)	C(5)-C(6)	1.393(11)	C(11)-C(14)	1.519(18)
N-C(7)	1.291(9)	C(6)-C(7)	1.434(13)	C(12)-C(13)	1.408(14)
N-C(8)	1.402(11)	C(8)-C(9)	1.370(13)	C(15)-C(16)	1.527(15)
C(1)-C(2)	1.416(12)				

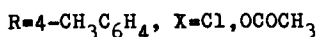
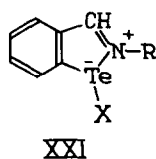
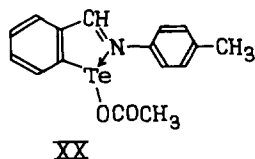
Table 2
Valence angles (degrees) in compound XX

O(1)TeN	159.9(2)	C(2)C(3)C(4)	122.6(8)	C(8)C(9)C(10)	119.2(10)
O(1)TeC(1)	84.1(3)	C(3)C(4)C(5)	119.2(8)	C(9)C(10)C(11)	121.4(10)
NTeC(1)	75.8(3)	C(4)C(5)C(6)	120.9(8)	C(10)C(11)C(12)	119.6(9)
TeO(1)C(15)	116.1(6)	C(1)C(6)C(5)	119.9(7)	C(10)C(11)C(14)	121.9(10)
TeNC(7)	112.5(5)	C(1)C(6)C(7)	117.9(7)	C(12)C(11)C(14)	118.5(9)
TeNC(8)	125.8(5)	C(5)C(6)C(7)	122.2(7)	C(11)C(12)C(13)	120.6(9)
C(7)NC(8)	121.3(7)	NC(7)C(6)	118.1(7)	C(8)C(13)C(12)	119.3(8)
TeC(1)C(2)	124.5(6)	NC(8)C(9)	120.8(8)	O(1)C(15)O(2)	124.8(8)
TeC(1)C(6)	115.7(5)	NC(8)C(13)	119.3(7)	O(1)C(15)C(16)	113.6(8)
C(2)C(1)C(6)	119.7(7)	C(9)C(8)C(13)	119.8(8)	O(2)C(15)C(16)	121.5(8)
C(1)C(2)C(3)	117.6(8)				

are 1.285, 1.300 Å and 1.436, 1.440 Å in two crystallographically independent molecules).

In structure XX, one more "shortened" contact for the Te atom has been found: the Te...O(2) distance is 3.060(8) Å, with the sum of the Van der Waals radii of Te and O being 3.6 Å [13], although this configuration of bonds at the Te atom can hardly be assigned to the square plane (the angles O(2)...Te ← N and O(2)...Te-C(1) equal 152.8(2) and 127.6(3)°, respectively). An analogous distorted square-planar configuration with the "fourth" intramolecular contact is characteristic of compounds of type IV with X = OCOCH₃ and SC(S)N(CH₃)₂ [10,11]. Thus, the molecular structures of the tellurenyl derivatives XIIIb1 and XX in the crystalline form are very similar to each other, and are equally similar to the structure of the tellurenyl azobenzenes IV [9–11]. In all these compounds that contain the electronegative groups Cl, OCOCH₃ or SC(S)N(CH₃)₂ attached to the Te^{II} centre the latter has a slightly distorted T-shaped configuration with a narrow range of values of the angle N → Te-R (159–170°) as well as of the N → Te bond length (2.19–2.34 Å).

For some Te^{II} derivatives, 2-halogenotellurenyl benzaldehydes I and oxatellurolium chlorides II [7], whose crystalline structure is analogous to that of the azomethines XIIIb1 and XX with a T-shaped configuration around the Te atom, the linear Hal-Te-O fragment can be described as a hypervalent three-centre, four-electron bond. Such a description may also be applied to the structure of the abovementioned azomethines, in which the N → Te distance is close to the length of the single covalent bond (2.02–2.10 Å [38,39]). This suggests the possibility of considering these compounds as heterocycles that are derivatives of benzoisotellurazole XXI. This suggestion is in line with the structure proposed by Detty [7] for the description of oxatellurolium chloride II.



The question of whether N → Te coordination bonds exist in solution was addressed by a ^{125}Te NMR spectral study of ^{15}N -labelled (50% enrichment) 2-halogenotellurenyl benzalanilines. If these coordination bonds do exist, a doublet should have been detected in the ^{125}Te NMR spectra due to ^{15}N - ^{125}Te spin-spin coupling, along with a singlet corresponding to the ^{125}Te nuclei linked to the ^{14}N centre. However, owing to quadrupolar effects that resulted in broadening induced by the halogen attached to the ^{125}Te centre, only poorly resolved multiplets could be observed in the spectra.

^{125}Te NMR spectroscopy was successfully used in a straightforward proof of the existence of N → Te coordination bonds in solutions of 2-butyltellurobenzalanilines XIIIa and bis(2-aryliminomethinyl)phenyl ditellurides XIX. In the ^{125}Te NMR spectra of these compounds containing the ^{15}N isotope (50% enrichment), the anticipated singlet and doublet signals of the ^{125}Te nuclei (formally a triplet signal with a 1 : 2 : 1 intensity ratio) have been observed, indicating the presence of N → Te coordination bonds. Some data on the ^1H and ^{125}Te NMR spectra of these compounds, as well as of the telluronium salt XV, are given in Table 3.

2. *Bis-imines of bis(2-formylphenyl)telluride.* Whereas in 2-halogenotellurenyl benzalanilines XIIIb only one coordination bond involving the participation of a tellurium atom is possible, in the bis-imines of bis(2-formylphenyl)telluride XIVa, owing to the presence of two monodentate ligands, it is possible that either one or two N → Te coordination bonds may be formed. In the former case the structure would correspond to 10-Te-3 tellurane, while in the latter to 12-Te-4 tellurane.

To clarify this uncertainty, an X-ray structural study of bis{2-[(4'-methoxyphenyl)iminomethinylphenyl]}telluride XIVa1 (Fig. 3) described elsewhere [31] was conducted.

As may be seen from Fig. 3, two chemically equivalent 4'-methoxyphenyliminomethinyl fragments of the molecule in question are differently positioned about the bonds Te-C(1), Te-C(15) and C(6)-C(7), C(20)-C(21). The N(1) atom lies almost in the plane of the C(1), Te, C(15) atoms at a distance of only 0.31 Å in the direction of the Te-C(15) bond, close (2.702 Å) to the Te atom [31]. The angle

Table 3

^{125}Te chemical shifts and ^{125}Te - ^{15}N spin-spin coupling constant values in ^{125}Te NMR spectra of *o*-tellurated azomethines enriched with the ^{15}N isotope

Compound type	R	^{125}Te ^a (ppm)	$J(^{125}\text{Te}-^{15}\text{N})$ (Hz)
XIIIa	C ₆ H ₅	483.0 ^b	101.4
XIIIa	4-BrC ₆ H ₄	484.8 ^b	102.0
XIX	C ₆ H ₅	1027.0 ^b	135.3
XIX	4-BrC ₆ H ₄	1036.0 ^b	141.4
XIIIb	C ₆ H ₅ (X = Cl)	1355.0 ^b	^c
XIIIb	C ₆ H ₅ (X = Br)	1316.0 ^b	^c
XIIIb	C ₆ H ₅ (X = I)	1187.0 ^b	^c
XV		641.5 ^b	62.4
XIVa	C ₆ H ₅	600.0 ^d	61.0
XIVb		636.0 ^d	122.0

^a ^{125}Te NMR spectra were recorded in CDCl₃ solutions; chemical shift values were measured upfield from (CH₃)₂Te. ^b 50% ^{15}N isotope enrichment. ^c ^{125}Te - ^{15}N spin-spin coupling is shown as poorly resolved multiplets owing to quadrupole effects of the halogen atoms. ^d 98% ^{15}N isotope enrichment.

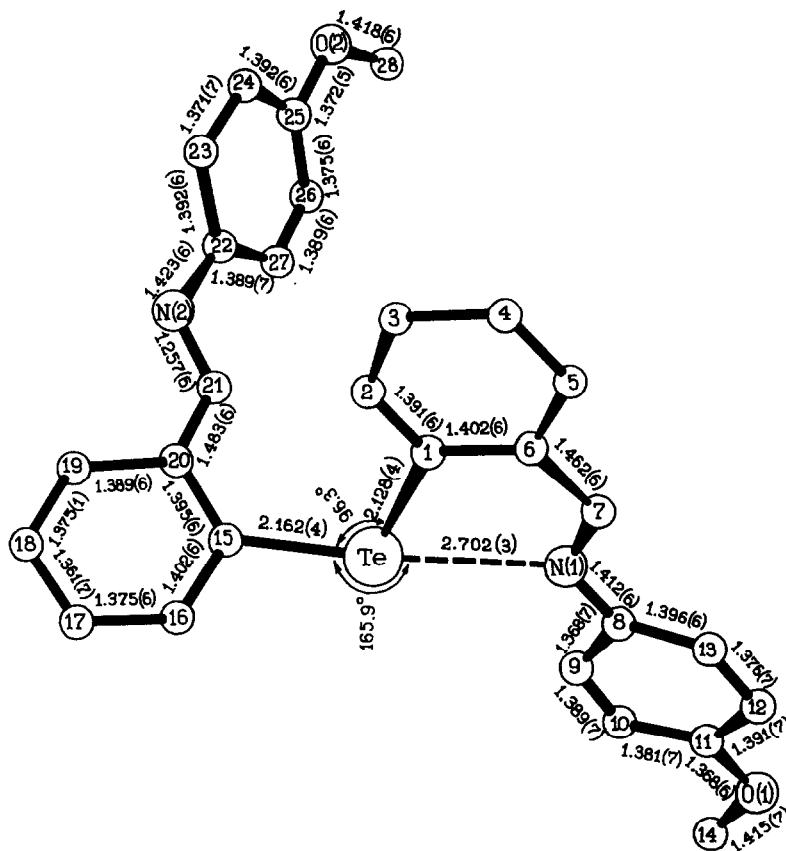


Fig. 3. The molecular geometry of bis[2-(4'-methoxyphenyl)iminomethylphenyl]telluride XIVA1.

C(15)–Te ← N(1) is 165.9° . The atom N(2), on the other hand, is declined from the C(1)TeC(15) plane by 3.3 \AA and lies at a considerable distance from the Te centre. Thus the geometry of the molecule indicates the presence in the crystal of one only attractive interaction, i.e., it corresponds to the structure of 10-Te-3 telluranc.

A similar structure, with an intramolecular N → Te contact close to that found in compound XIVA1 (2.77 \AA) was earlier described in the case of 1,6-bis(*o*-butyltellurophenyl)-2,5-diazahexa-1,5-diene XII [27]. In other words, in the azomethines XIVA1 and XII the N → Te bonds are appreciably longer than those in compounds XIIIb1 and XX, which also have a T-shaped configuration at the Te centre, but also possess electronegative substituents attached in a *trans* position to the N atom. At the same time, in the imines XII, XIVA1 the intramolecular N → Te contacts are much shorter than in tellurane VII (2.92 \AA) [16], thus having intermediate lengths between those found for the last-mentioned azomethine and the derivatives of the azobenzene IV, and the imines XIIIb1 and XX.

Even though the N(1) → Te distance in the azomethine XIVA1 considerably exceeds the sum of the covalent radii of Te and N, their interaction substantially affects the structure of the ligands. In the “chelated” fragment of the XIVA1 molecule, there occurs an equalization of the bond lengths C(6)–C(7), C(7)–N(1)

and N(1)–C(8) (1.462, 1.276 and 1.412 Å, respectively), a flattening of the ligand framework and an increase in the angle C(7)–N(1)–C(8) to 123.9° in comparison with the corresponding values in the “nonchelated” fragment: the lengths of the bonds C(20)–C(21), C(21)–N(2) and N(2)–C(22) are, respectively, 1.483, 1.257 and 1.423 Å, while the angle at the N atom is 118.7° [31]. In the imine molecule VII, however (where, according to the data of an X-ray study [16], the tellurium atom forms coordination bonds with both N atoms), the structures of the ligand moieties are practically identical.

To elucidate the effect of the basicity of the imine N atom on the length of the N → Te coordination bond, a study has been conducted on the crystal structure of the bis-imine derived from the aliphatic amine bis[(2-isopropyliminomethyl)phenyl]telluride XIVa2 [40]. A stereoview of the molecule, the lengths of the principal bonds and the valence angles of this compound are given in Fig. 4. Despite the large basicity of the imine nitrogen in this compound, in comparison with its aryl analogue XIVa1 [31], the structures of both compounds are quite similar. In both compounds only one N atom serves as the donor centre coordinated to Te, and the length of the N → Te bond (2.72 Å) is nearly the same as in the imine XIVa1. The bond configuration at the tellurium atom is T-shaped and the angle C(11)–Te–N(1) is 164.7° (in the imine XIVa1 it is 165.9°).

Thus, for the crystalline bis-imines of bis(2-formylphenyl)telluride the 10-Te-3 structure with one nonvalent N → Te interaction is realized regardless of the nature of the substituents at the nitrogen atom.

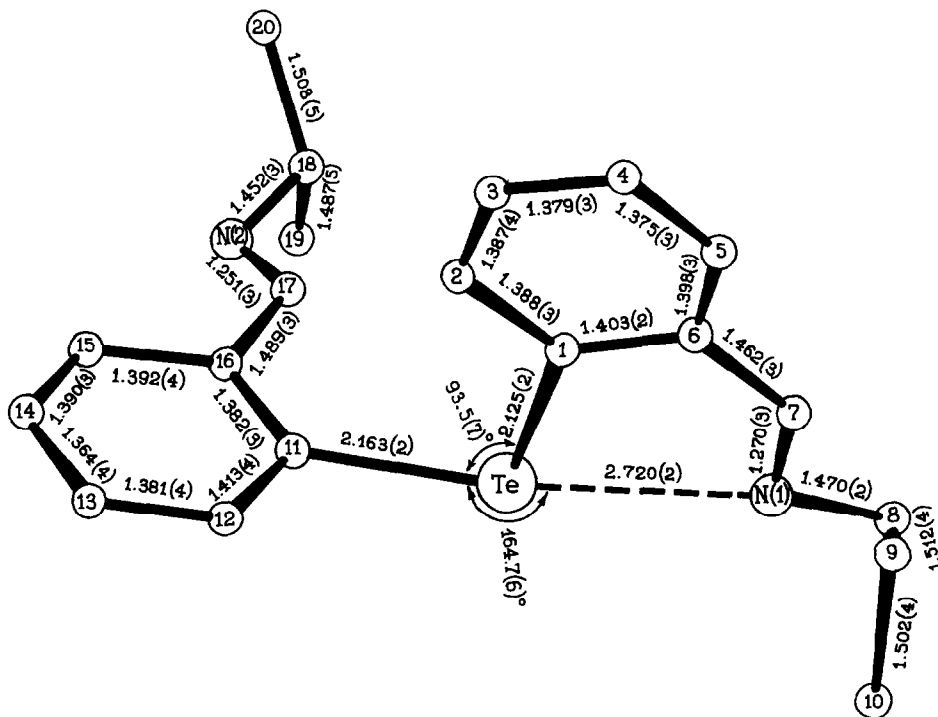
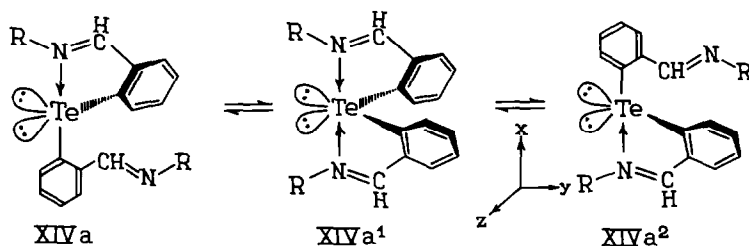


Fig. 4. The molecular geometry of bis(2-isopropyliminomethylphenyl)telluride XIVa2.

In the ^1H NMR spectra of the bis-imines XIVa, the signals of the methine protons are seen as singlets [30,31] (or as a doublet in the case of compound XIVa3 containing the ^{15}N isotope, with $\text{R} = \text{Ph}$); this indicates either (i) the existence of these compounds in one form or (ii) a very fast (on an NMR timescale) process of equilibration among the forms XIVa, XIVa¹ and XIVa² [31]. In the solutions of the imines VII a similar equilibrating process can be inferred from the doubling of the methine proton signals in the ^1H NMR spectra [16], which is thought to be associated with the rupture of the coordination bonds and the appearance in solution of several conformational forms that are close in energy.

The character of intramolecular coordination in the compounds XIVa in solution has been investigated by ^{125}Te NMR spectroscopy. In the ^{125}Te NMR spectrum of the ^{15}N -labelled compound XIVa3 (98% enrichment), the signal of the ^{125}Te nuclei in CDCl_3 is manifested as a triplet with a ^{125}Te - ^{15}N spin-spin coupling constant of 61 Hz [30,31]. This is approximately half the values of the ^{125}Te - ^{15}N spin-spin coupling constant for the imines XIIIa and XIX (see Table 3). Both the form of the signal and the spin-spin coupling constant indicate the presence in a solution of XIVa3 of a very fast (on an NMR timescale) equilibration $\text{XIVa} \rightleftharpoons \text{XIVa}^2$, where XIVa¹ may serve either as an intermediate or a transition state for which the lifetime of the 10-Te-3 isomers (XIVa, XIVa²) is so short that it does not lead to the reorientation of spins in the process of transition into the structure XIVa¹.



Similar manifestations of fast dynamic intramolecular bond migration in ^{15}N - $\text{H} \cdots ^{15}\text{N}$ triads (a triplet signal with a half-value of an apparent spin-spin coupling constant ^{15}N - ^1H) are well known in porphyrins and their analogues [41].

As in the spectrum of the telluride XIVa3, in the ^{125}Te NMR spectrum of the ^{15}N -labelled tellurium dichloride XIVb a triplet signal is observed with a ^{125}Te - ^{15}N spin-spin coupling constant (122 Hz) substantially exceeding the analogous value for the telluride [30,31].

Confirmation of the conclusion drawn from the ^{125}Te NMR spectra of the bis-imines XIVa was obtained by studying the dipole moments of compounds XIVa, the data for which are given in Table 4 [31].

If in solution stable structures were realized with two intramolecular $\text{N} \rightarrow \text{Te}$ coordination bonds (XIVa¹), their dipole moments would be determined (in the presence in para positions of N-aryl nuclei of regular substituents, i.e. those which bond or group moments aligned with the $\text{C}_{\text{Ar}}-\text{R}$ bond) by the projections onto the X and Y axes (m_x , m_y) only (for axis notation see form above). In such a case, the projections of the moments of individual bonds onto the X axis cancel out, and consequently the projection m_x is equal to zero. Therefore, the vector of the dipole moment of a compound containing an N-phenyl group that is equal to its value

Table 4

Dipole moments of compounds XIVa (in benzene at 25 °C)

No.	R	α	β	$P_{2\infty}(\text{cm}^3)$	$P_e(\text{cm}^3)$	$\mu_{\text{exp}}(D)$	$\mu_{\text{calc}}(D)$
1	C_6H_5	5.77	2.30	297.7	139.8	2.78	2.78
2	$4\text{-CH}_3\text{C}_6\text{H}_4$	5.47	2.30	297.1	149.9	2.68	2.14
3	$4\text{-CH}_3\text{OC}_6\text{H}_4$	8.97	2.44	421.1	153.9	3.61	—
4	$4\text{-(CH}_3)_2\text{NC}_6\text{H}_4$	20.02	2.10	667.7	168.6	4.94	—
5	$4\text{-ClC}_6\text{H}_4$	8.98	2.92	411.6	150.4	3.57	5.50
6	$4\text{-CH}_3\text{COOC}_6\text{H}_4$	10.03	2.90	452.0	164.4	3.75	—
7	$4\text{-NO}_2\text{C}_6\text{H}_4$	31.06	3.07	1151.2	157.1	6.89	9.71
8	$2,3,4,5,6\text{-F}_5\text{C}_6$	13.10	4.05	556.7	137.2	4.53	—
9	$\text{CH}_2\text{C}_6\text{H}_5$	6.02	2.74	303.8	149.9	2.74	—
10	$\text{CH}(\text{CH}_3)_2$	6.26	1.72	306.2	117.4	3.04	—
11	$-\text{CH}_2\text{CH}_2-$	2.45	2.08	149.9	94.7	1.64	—

(2.78 D) must be directed only along the Y axis relative to the tellurium atom. When this assumption, as well as the standard values of the bond moments of the substituents R, is used [42], the calculated dipole moments of compounds with regular para substituents (compounds 2, 5 and 7 in Table 4) differ substantially from the experimental values. Hence, the assumption of stable structures of type XIVa¹ with two N → Te coordination bonds is not borne out by the data on dipole moments.

Thus, in Te^{II} derivatives the length of the intramolecular N → Te coordination bonds is determined, in the first place, by the nature of the substituents at the Te atom. When this atom is linked with electronegative groups, short N → Te intramolecular bonds are realized in the corresponding azomethines that are similar in length (2.22–2.30 Å) to normal covalent N-Te bonds. When, however, the Te atom is linked with relatively electropositive *sp*³- or *sp*²-hybridized carbon atoms, then longer intramolecular N → Te contacts are found in the molecules under study.

3. *The telluronium salt XV.* We intended to carry out an X-ray structural study of compounds XIIIc, XIVb and XV, in which the Te atom has the formal oxidation number IV. Unfortunately, attempts to prepare appropriate crystal samples of XIIIc and XIVb were unsuccessful.

The molecular structure of the cation XV in the crystalline form, as well as the principal bond lengths and valence angles [36], is given in Fig 5. In the structure of XV, the atoms C(1)–C(7), N and Te lie, within 0.04 Å, in the same plane, while the phenyl ring C(8)–C(13) is somewhat turned out from this plane, with the torsion angle C(7)NC(8)C(9) being 22.8°. As in other telluronium salts [43–46], the configuration of primary bonds formed by the Te⁺(III) centre is represented by a trigonal pyramid.

Proceeding from electrostatic considerations, one might assume that the presence of a positive charge at the Te atom in the cation XV should result in an appreciable shortening of the N → Te bond. However, the N → Te distance in XV (2.75 Å), although much smaller than the sum of the Van der Waals radii of Te and N, practically coincides with the analogous distance in the Te^{II} derivatives XIVa1 (2.702 Å) [31] and XIVa2 (2.72 Å) [40]. This may be regarded as evidence that the length of coordination bonds depends in an essential manner on the valence state of the Te atom, and that only compounds of the same type of structure may be

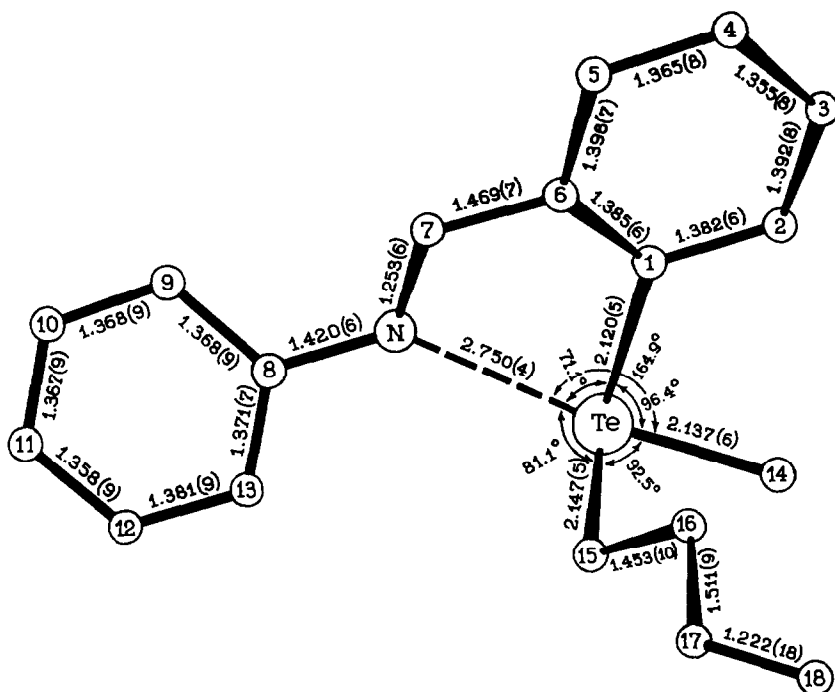


Fig. 5. The molecular geometry of methylbutyl(2-phenyliminomethinylphenyl) telluronium perchlorate XV.

compared. The same conclusion is suggested by the data on *o*-tellurated azobenzenes IV and X, which contain the atoms Te^{II} and Te^{IV} , respectively. The length of the $\text{N} \rightarrow \text{Te}$ coordination bond in tellurenyl chloride IV is 2.19–2.23 Å [9], while in tellurium trichloride X it is 2.417 Å [25]. Also, an elongation of the $\text{S}^{\text{IV}} \cdots \text{O}$ distance in comparison with that of $\text{S}^{\text{II}} \cdots \text{O}$ has been predicted by theoretical SCF calculations [47] and experimental findings in methyl-2-sulphonate and 2-nitrobenzenylsulphenyl chloride, which have a similar intramolecular $\text{S} \cdots \text{O}$ interaction [48].

In the crystal, very weak intermolecular contacts between the Te atom and the O atoms of perchlorate anions lying within 3.33–3.56 Å, and thus quite close to the sum of the Van der Waals radii (3.60 Å), are realized in XV. These contacts, linking the molecules to the centrosymmetric dimers, form a distorted pentagonal bipyramid around the Te atom of XV. These $\text{Te} \cdots \text{O}$ contacts are, however, of little importance for the bonding pattern, and the true coordination number of the Te atom is determined by the presence of a strong $\text{N} \rightarrow \text{Te}$ coordination bond. It is known that the coordination around Te in the telluronium salts $\text{R}_3\text{Te}^+\text{X}^-$ is strongly affected by the nature of the X^- anions. In triorganyl telluronium salts with anions of low nucleophilicity, e.g. $\text{Me}_3\text{Te}^+\text{BPh}_4^-$ [43], telluronium cation species have been detected containing a tricoordinated Te atom. Salts with highly nucleophilic anions (Hal^-) exist, owing to secondary interactions between these and the cations R_3Te^+ , either as dimers in which the pentacoordinated Te atom has a distorted square-pyramidal geometry ($\text{Ph}_3\text{Te}^+\text{Cl}^-$ [44], $\text{Et}_3\text{Te}^+\text{I}^-$ [45]) or as cubane-like tetramers with a hexacoordinated Te centre ($\text{Et}_3\text{Te}^+\text{Cl}^-$ [45], $\text{Et}_3\text{Te}^+\text{Br}^-$

[46]). In this case, the secondary Te...Hal bonds are close in length to ordinary bridge bonds. In the cation XV the pyramidal configuration of the Te atom is supplemented by the strong N → Te intramolecular interaction, giving rise to a trigonal-bipyramidal configuration at the Te atom characteristic of σ -telluranes (RTeHal₃, R₂TeHal₂): the angles C(14)–Te...N, C(1)–Te...N, C(15)–Te...N and C(1)–Te–C(15) are in this case 164.9, 71.1, 81.1 and 97.8° [36].

The intramolecular N → Te coordination bonds are also retained in the solution of the cation XV in CDCl₃. In the ¹²⁵Te NMR spectrum of the ¹⁵N-labelled compound XV (50% enrichment), in addition to a singlet corresponding to the ¹⁴N-linked ¹²⁵Te centre, a doublet signal has been observed due to ¹²⁵Te–¹⁵N spin–spin coupling ($J(^{125}\text{Te}-^{15}\text{N}) = 61$ Hz, see Table 3).

Experimental

The synthesis of compounds 1) XIIIa–c, XIX; 2) XIVa,b; 3) XV and 4) XX was carried out using procedures described in, respectively, Refs. [29], [31], [36] and [18].

The X-ray structural study of compound XX

The C₁₆H₁₅NO₂Te crystals are monoclinic, $a = 10.284(1)$, $b = 14.585(1)$, $c = 10.585(2)$ Å, $\beta = 105.98(1)^\circ$, $V = 1526(3)$ Å³, $Z = 4$, space group $P2_1/a$.

The intensity of 3311 reflections for $I > 2\sigma$ were measured on an Enraf-Nonius CAD-4 automatic four-circle diffractometer ($\lambda(\text{Cu-K}\alpha)$, the ratio of scanning rates was $\omega/\theta = 1.2/1$, $\theta < 75^\circ$).

The structure was studied by the heavy-atom method and refined by the least-squares method using a block-diagonal anisotropic approximation from 2640

Table 5

Atomic coordinates of Te and non-hydrogen atoms ($\times 10^4$) in compound XX

Atom	<i>x</i>	<i>y</i>	<i>z</i>
Te	1798(1)	2979(1)	3702(1)
O(1)	2705(8)	3287(4)	2137(6)
O(2)	3086(9)	4690(4)	2883(8)
N	985(6)	2141(4)	5158(6)
C(1)	2069(7)	1618(5)	3222(7)
C(2)	2699(8)	1341(6)	2251(8)
C(3)	2837(9)	405(6)	2071(9)
C(4)	2390(9)	–249(6)	2800(9)
C(5)	1796(8)	28(6)	3742(8)
C(6)	1644(7)	956(5)	3979(8)
C(7)	1082(8)	1268(5)	5001(8)
C(8)	575(7)	2497(6)	6218(7)
C(9)	928(11)	2071(7)	7418(10)
C(10)	544(11)	2463(9)	8461(10)
C(11)	–203(8)	3255(7)	8304(9)
C(12)	–550(8)	3677(7)	7127(9)
C(13)	–156(8)	3312(6)	6057(8)
C(14)	–606(12)	3698(11)	9439(12)
C(15)	3138(8)	4102(5)	2108(8)
C(16)	3828(10)	4264(8)	1021(10)

reflections with $F^2 > 8\sigma$. The positions of the hydrogen atoms were determined geometrically and included in the refinement using isotropic heat parameters. The absorption was taken into account by means of the program DIFABS [49]. The final value of the R -factor was 0.076 and $R_w = 0.080$. The computations were performed using the SHELX-76 program complex [50]. The atomic coordinates are given in Table 5.

The dipole moments were measured and calculated according to an earlier procedure [31]. ^1H NMR spectra were recorded on a Tesla-BS-487C (80 MHz) instrument, using HMDS as an internal standard in CDCl_3 solution. ^{125}Te NMR spectra were recorded on a Bruker CXP-300 spectrometer operating at 94.77 and 21.68 MHz with frequency alteration 90° , impulse 0.5 and 50 Hz. Chemical shifts on the scale were measured downfield to $(\text{CH}_3)_2\text{Te}$.

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