Synthesis and structure of diorganyldiaryloxytelluranes with intramolecular Te ⋯ N coordination bonds

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Abstract

A wide series of diorganyldiaryloxytelluranes having an azomethine function in the position *ortho* to the tellurium atom have been synthesized by the reaction of diorganyldimethoxytelluranes with benzylidene-*o*-aminophenols. The X-ray structural investigation of the dimethylbis[2-(4-nitrobenzylideneimino)phenyloxy]tellurane indicates the presence of an intramolecular coordination bond Te ⋯ N. According to the dipole moment data and the ^{1}H, ^{125}Te, ^{14}N NMR spectra, in compounds VII, excluding those having nitro groups in the position *para* to the CH=N bond, the Te ⋯ N coordination is retained in a non-polar solvent (benzene).

Introduction

In recent years there has been a growing interest in the study of the effects of intramolecular coordination in organotellurium compounds. A number of Te^{II} compounds bearing a carbonyl [1–5], azo [6,7] or azomethine [8] function in the *o*-position with respect to the tellurium atom have been shown to possess the *s-cis*-configuration I with the Te ⋯ X bonds which are close in their characteristics to a covalent Te–X bond. The structure of such compounds and of their analogs such as II [5,9] corresponds to that of the 10-Te-3 telluranes [10] with a three-center four-electron bond in the Z–Te–X fragments. The Pauling bond order [11] of the Te–O bond attains the value of 0.5–0.6 [5,9] in compounds II.

The propensity for intramolecular coordination is also retained for the derivatives of Te^{IV}. According to the X-ray structural data [9,12], the 12-Te-5 pertelluranes III and IV obtained via oxidative addition of bromine to the oxatellurolylium halides

(I)   (II)
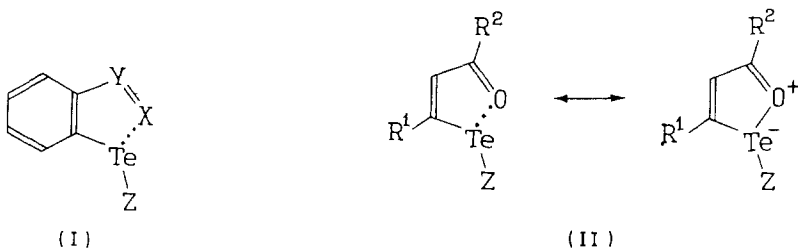
(Z = Y = C(R)═O , N═NPh , CH═N ;

  Z = Hal , Alk)

[9] or to the dioxatellurapentalenes [12] possess Te $\cdots$ O bonds whose lengths are only slightly greater than the ordinary Te–O bond [13–15].

(III)   (IV)
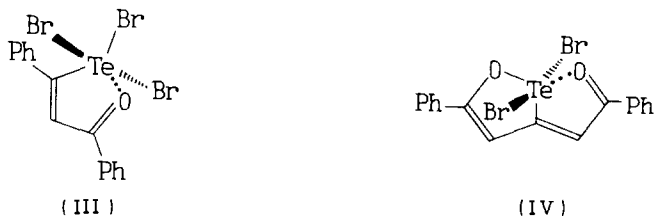
(l(Te—O) 2.362 Å)   (l(Te—O) 2.135 , 2.171 Å)

Still scarce are data for Te^{IV} compounds intramolecularly coordinated to a nitrogen function. In the case of o-tellurated azomethines and phenylhydrazones (V), the formation of a Te $\cdots$ N bond was inferred from the IR data (a $10\text{–}30\ cm^{-1}$ shift of the C=N bond towards the longer wavelength region) [6]. A more exact proof of the existence of this bond was provided on the basis of an X-ray structural investigation of the compound VI obtained by the interaction of $TeCl_4$ with 2,6-diacetylpyridine [16]. In this compound the tellurium atom possesses two coordination bonds, though the Te $\cdots$ N bond length slightly exceeds the sum of the covalent radii of tellurium and nitrogen.
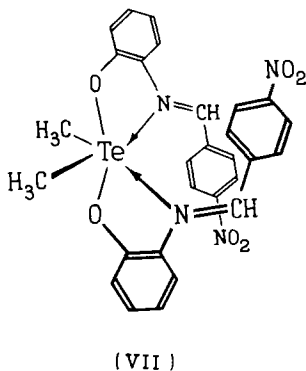

(VI)

(V : R = Ph , NHPh)

(l(Te—O) 2.878 Å)

l(Te—N) 2.402 Å)

In compound VI the tellurium atom, unlike that in pertelluranes III and IV, is hexacoordinated. The authors [16] describe the structure of VI as a pentagonal

(VII)

bipyramid in which one of the equatorial positions is occupied by the stereochemically active electron lone pair. Using the N–X–L nomenclature [10] compound VI would belong to the 14-Te-6 group.

The present work describes the synthesis and structure of a novel group of Te^{IV} compounds of type VII where the central tellurium atom could possess two additional intramolecular Te $\cdots$ N coordination bonds and thus belong to the 14-Te-6 type. A capacity for such coordination has been rendered by the structure of two bidentate ligands linked with Te^{IV} which bring the azomethine groups into positions sterically accessible for coordination.

Results and discussion

Synthesis

The compounds VII (Table 1) were synthesized by an exchange reaction of the diorganyldimethoxytelluranes (VIII), themselves obtained via treatment of the corresponding diorganyltellurium dibromides or diiodides with two equivalents of sodium methoxide in toluene, with the benzylidene-*o*-aminophenols (IX) [17]. Yields of the compounds VII are almost quantitative.
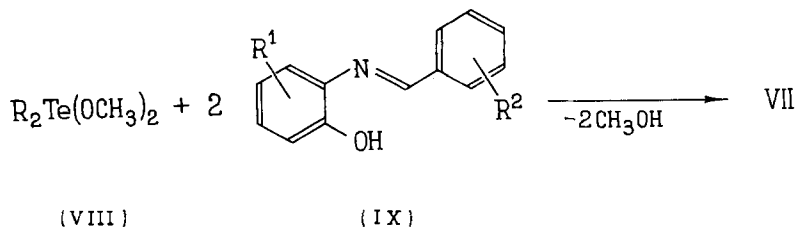
Similarly, ^{15}N-labeled dimethylbis[2-(4-methoxybenzylidenimino)-4′-methylphenyloxy]tellurane (compound No. 24, Table 1) (R = CH_3, R^1 = 4-CH_3, R^2 = 4-OCH_3) has been synthesized by reaction of ^{15}N-2-(4′-methoxybenzylidenimino)-4-methylphenol with dimethyldimethoxytellurane.

The compounds VII are brightly colored crystalline substances with melting points in the range of 110–220°C. Unlike diaryldialkoxytelluranes of type VIII which are readily hydrolyzed even by atmospheric moisture [18], the compounds VII

Table 1

M.p. and spectral characteristics of the compounds VII

No.	R	R^1	R^2	M.p. [a] (°C)	ν(C=N) [b] (cm^{-1})
1	CH_3	H	4-NO_2	182	1600 (1633)
2	CH_3	H	3-NO_2	116	1608 (1633)
3	CH_3	H	4-Br	133–135	1610 (1633)
4	CH_3	H	H	113	1613 (1628)
5	CH_3	H	4-CH_3	141	1600 (1627)
6	CH_3	H	4-OCH_3	142–144	1605 (1630)
7	CH_3	H	4-$N(CH_3)_2$	151–153	1612 (1613)
8	CH_3	4-NO_2	4-Br	124	1609 (1627)
9	CH_3	4-NO_2	3-F	156–157	1600 (1627)
10	CH_3	4-NO_2	H	158–160	1607 (1630)
11	CH_3	4-NO_2	4-CH_3	135	1609 (1632)
12	CH_3	4-NO_2	4-OCH_3	151–152	1607 (1629)
13	CH_3	4-NO_2	4-$N(CH_3)_2$	195	1602 (1618)
14	CH_3	5-NO_2	4-Br	185	1607 (1627)
15	CH_3	5-NO_2	H	152	1604 (1628)
16	CH_3	5-NO_2	4-$N(CH_3)_2$	220 (dec.)	1619 (1619)
17	CH_3	4-NO_2,6-Cl	4-OCH_3	174	1593
18	CH_3	4-NO_2,6-Cl	4-$N(CH_3)_2$	210 (dec.)	1586
19	$CH_2C_6H_5$	H	4-OCH_3	122	1600 (1630)
20	$CH_2C_6H_5$	H	H	122	1620 (1628)
21	4-$CH_3C_6H_4$	H	4-NO_2	174	1595 (1633)
22	4-$CH_3C_6H_4$	H	4-CH_3	135	1605 (1627)
23	4-$CH_3C_6H_4$	H	4-OCH_3	162–164	1600 (1630)
24 [c]	CH_3	4-CH_3	4-OCH_3	148–150	–

[a] Elemental (C, H, N, Te) analyses correspond to structure VII for all the compounds. [b] ν(C=N) values are shown for compounds IX in brackets. [c] Compound contains the ^{15}N isotope with 50% enrichment.

do not undergo hydrolysis even upon prolonged contact with water at ambient temperature. Such a considerable stability of these compounds to hydrolysis may apparently be due to coordination of the azomethine nitrogen atoms which prevents access of nucleophilic reagents to the latter.

A comparison of the ν(C=N) in the IR spectra of complexes VII with those of the ligands IX indicates a negative shift of 15–35 cm^{-1} in the frequency of the C=N stretching vibrations as compared to IX. Compounds of the type V, exhibit an analogous spectral shift, which was ascribed to the formation of the Te $\cdots$ N coordination bonds [6]. At the same time, in the ^{1}H NMR spectra of compounds VII the methine proton resonances are observed in a stronger field ($\sim$ 0.4 ppm) as compared to the similar protons of the free ligands (IX) (See Table 5).

X-ray structural study of dimethylbis[2-(4-nitrobenzylidenimino)phenyloxy]tellurane (VII, R = CH$_3$, R^1 = H, R^2 = 4-NO$_2$)

The crystals of dimethylbis[2-(4-nitrobenzylidenimino)phenyloxy]tellurane (Compound No. 1 in Table 1) were chosen for the X-ray structural investigation as they appeared to be most suitable for this purpose, though the presence of a strong electron-withdrawing nitro group in the *p*-position to the azomethine function is bound to weaken considerably the donor properties of the imine nitrogen.
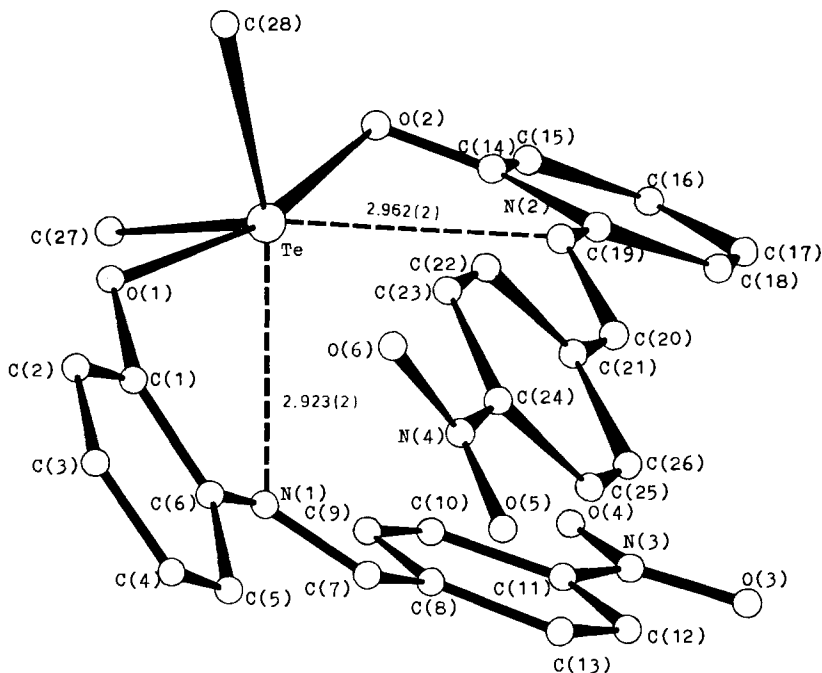
Fig. 1. The geometry of the molecule of dimethylbis[2-(4-nitrobenzylidenimino)phenyloxy]tellurane (compound No. 1) and numeration of atoms in the molecule.

The molecular structure of tellurane No. 1 in the crystal and the numeration of the atoms are presented in Fig. 1. The bond lengths and valence angles are given in Tables 2 and 3, respectively.

The coordinational geometry of tellurium in the compound under study may be treated on the grounds of distorted trigonal bipyramidal configuration of four

Table 2

Bond lengths d (Å) in compound No. 1

Bond	d	Bond	d	Bond	d
Te–O(1)	2.129(2)	N(2)–C(20)	1.269(3)	C(12)–C(13)	1.365(3)
Te–O(2)	2.100(2)	N(3)–C(11)	1.462(3)	C(14)–C(15)	1.400(3)
Te–C(27)	2.100(3)	N(4)–C(24)	1.469(3)	C(14)–C(19)	1.396(3)
Te–C(28)	2.092(3)	C(1)–C(2)	1.396(3)	C(15)–C(16)	1.367(4)
Te···N(1)	2.923(3)	C(1)–C(6)	1.418(3)	C(16)–C(17)	1.364(4)
Te···N(2)	2.962(3)	C(2)–C(3)	1.378(4)	C(17)–C(18)	1.378(3)
O(1)–C(1)	1.340(3)	C(3)–C(4)	1.358(4)	C(18)–C(19)	1.399(3)
O(2)–C(14)	1.336(3)	C(4)–C(5)	1.389(3)	C(20)–C(21)	1.467(3)
O(3)–N(3)	1.235(3)	C(5)–C(6)	1.384(3)	C(21)–C(22)	1.391(3)
O(4)–N(3)	1.210(3)	C(7)–C(8)	1.468(3)	C(21)–C(26)	1.399(3)
O(5)–N(4)	1.199(3)	C(8)–C(9)	1.385(3)	C(22)–C(23)	1.379(3)
O(6)–N(4)	1.218(3)	C(8)–C(13)	1.391(3)	C(23)–C(24)	1.381(3)
N(1)–C(6)	1.413(2)	C(9)–C(10)	1.375(3)	C(24)–C(25)	1.386(3)
N(1)–C(7)	1.269(3)	C(10)–C(11)	1.376(3)	C(25)–C(26)	1.372(3)
N(2)–C(19)	1.415(2)	C(11)–C(12)	1.381(3)		

Table 3

Valence angles α (in degrees) in compound No. 1

Angle	α	Angle	α
O(1)TeO(2)	164.9(1)	C(14)C(15)C(16)	121.5(3)
O(1)TeC(27)	85.3(1)	C(15)C(16)C(17)	120.6(2)
O(1)TeC(28)	85.7(1)	C(16)C(17)C(18)	119.5(3)
O(2)TeC(27)	85.3(1)	C(17)C(18)C(19)	121.0(3)
O(2)TeC(28)	83.7(1)	N(2)C(19)C(14)	117.2(2)
C(27)TeC(28)	96.9(2)	N(2)C(19)C(18)	123.4(2)
TeO(1)C(1)	121.8(1)	C(14)C(19)C(18)	119.4(2)
TeO(2)C(14)	123.6(1)	N(2)C(20)C(21)	121.6(2)
C(6)N(1)C(7)	120.5(2)	C(20)C(21)C(22)	122.0(2)
C(19)N(2)C(20)	120.1(2)	C(20)C(21)C(26)	119.1(2)
O(3)N(3)O(4)	122.1(2)	C(22)C(21)C(26)	118.8(2)
O(3)N(3)C(11)	117.8(2)	C(21)C(22)C(23)	121.2(2)
C(2)C(3)C(4)	121.5(2)	O(4)N(3)C(11)	120.0(2)
C(3)C(4)C(5)	119.0(3)	O(5)N(4)O(6)	124.0(2)
C(4)C(5)C(6)	121.2(3)	O(5)N(4)C(24)	118.8(2)
N(1)C(6)C(1)	116.7(2)	O(6)N(4)C(24)	117.2(2)
N(1)C(6)C(5)	123.8(2)	O(1)C(1)C(2)	118.9(2)
C(1)C(6)C(5)	119.5(2)	O(1)C(1)C(6)	123.3(2)
N(1)C(7)C(18)	121.4(2)	C(2)C(1)C(6)	117.8(2)
C(7)C(8)C(9)	121.8(2)	C(1)C(2)C(3)	120.9(3)
C(7)C(8)C(13)	119.4(2)	N(3)C(11)C(10)	118.7(2)
C(9)C(8)C(13)	118.8(2)	N(3)C(11)C(12)	119.4(2)
C(8)C(9)C(10)	121.2(2)	C(10)C(11)C(12)	122.0(2)
C(9)C(10)C(11)	118.3(2)	C(11)C(12)C(13)	118.8(2)
C(8)C(13)C(12)	120.9(2)	N(1) · · · TeO(1)	64.8(2)
O(2)C(14)C(15)	118.7(2)	N(1) · · · TeO(2)	128.0(2)
O(2)C(14)C(19)	123.4(2)	N(1) · · · TeC(27)	96.2(2)
C(15)C(14)C(19)	117.9(2)	N(1) · · · TeC(28)	146.6(2)
C(22)C(23)C(24)	118.1(2)	N(1) · · · TeN(2)	85.9(2)
N(4)C(24)C(23)	119.6(2)	N(2) · · · TeO(1)	129.1(2)
N(4)C(24)C(25)	118.0(2)	N(2) · · · TeO(2)	64.1(2)
C(23)C(24)C(25)	122.5(2)	N(2) · · · TeC(27)	141.3(2)
C(24)C(25)C(26)	118.4(2)	N(2) · · · TeC(28)	102.3(2)
C(21)C(26)C(25)	121.0(2)		

valence bonds with oxygen atoms in axial positions and two methyl groups as well as an electron lone pair in the equatorial positions. The angle between the axial bonds O(1)–Te–O(2) (164.9°) fully coincides with the analogous angle in diphenyltellurium bis(trifluoroacetate) [15]. Such a geometry is typical for σ-telluranes R_2TeX_2 (X = Hal, OCOR) [13–15,24,25]. The lengths of the Te–O bonds (2.100(2) and 2.129(2) Å) and of the Te–C bonds (2.092(3) and 2.100(3) Å) are normal for these compounds as the range for the axial Te–O bond lengths lies between 2.07 and 2.18 Å [13–15,24,25] and for the equatorial Te–C bonds it is between 2.09 and 2.15 Å.

Additional intramolecular coordination of tellurium by imine nitrogen atoms can optimally be realized in the *cis*-configuration (VII) where Te · · · N bonds are nearly in a *trans*-position reactive to the Te–CH$_3$ groups. As is evident from Table 3, the angles N(1)–Te–C(28) and N(2)–Te–C(27) in compound No. 1 are 146.6° and

141.3°, respectively, both of which practically coincide with the angle of 144° expected for the pentagonal-bipyramidal configuration in the equatorial plane. Despite the possibility of a relatively free rotation of the ligands about the O(1)–C(1) and O(2)–C(14) bonds leading to a "transoid" configuration, such rotations are inhibited. Conversely, the torsion angles Te–O(1)–C(1)–C(6) and Te–O(2)–C(14)–C(19) of 36.3° and 37.6° respectively, appear to be close in their values to the minimum possible ones which could be accounted for by steric repulsion of the ligands. Thus in the real conformation in the crystal of compound No. 1, the distance between atoms of the ligands are close to the sum of their Van der Waals' radii, particularly the distances C(7) ⋯ C(20), C(11) ⋯ C(17), C(9) ⋯ C(19), C(4) ⋯ C(24) and C(6) ⋯ C(22), which are 3.456(2), 3.693(3), 3.876(3), 3.731(3) and 3.677(2) Å respectively. The ligand fragments being brought close together are nearly parallel to each other with angles between the planes of six-membered rings C(1)–C(6) and C(21)–C(26) being 5.9° and C(8)–C(13) and C(14)–C(19) being 3.3°. Such a conformation of the molecule No. 1 renders the distances of 2.923(2) and 2.926(2) Å for Te ⋯ N(1) and Te ⋯ N(2), respectively, limited by those allowable by the structure of the ligands. The distances are smaller than the sum of the Van der Waals' radii of Te and N (3.7 Å), but they are considerably greater than either the sum of the covalent radii (2.07 Å) or the valence bond lengths of Te^{II}–N (2.02–2.10 Å) found in benzoisotellurazole and 1,2,5-telluradiazole [26,27].

The short intramolecular Te ⋯ N contacts found in compound No. 1 correspond to the Pauling bond order of merely 0.04, reflecting the weak attractive interaction arising out of stabilization of the observed "cisoid" conformation. A stronger intramolecular coordination bond Te^{IV} ⋯ N exists in compound VI [16] (bond order 0.28). In compounds of the Te^{II} the intramolecular coordination Te ⋯ N was also detected by an X-ray structural investigation on 1,6-bis[2-butyltellurophenyl-2,5-diazahexa-1,5-diene] [8], where the intramolecular distance Te^{II} ⋯ N amounts to 2.773 Å (bond order 0.07) and in bis[2-(2-pyridyl)phenyl]tritelluride (with Te^{II} ⋯ N bond length of 2.554 Å and Pauling bond order of 0.16) [28]. A stronger Te ⋯ N interaction in compound No. 1 is impeded by steric inaccessibility of the equatorial plane TeC(1)C(2) to the nitrogen atoms, which otherwise would have resulted in a distorted octahedral (or pentagonal-bipyramidal if the phantom ligand, the electron lone pair was taken into account) configuration as in compound VI [16]. In compound No. 1 the planes O(1)TeO(2) and C(27)TeC(28) are nearly perpendicular (dihedral angle of 89.3°) and the plane N(1)TeN(2) makes an angle of 38.8° with the former and an angle of 50.6° with the latter (Fig. 2). The angles around tellurium atom are shown in Table 3 taking into account the coordination of the nitrogen atoms. But seemingly, for the weak Te ⋯ N bonds the direction of coordinative interaction is not rigidly fixed. Thus, in tellurane $(C_6H_{12}O_2)_2Te$,
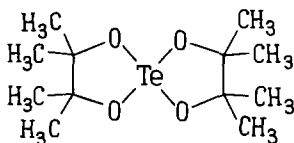
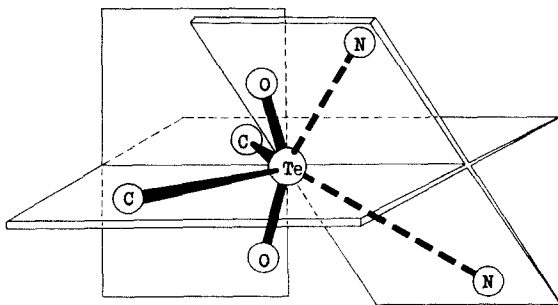where bisphenoid coordination of tellurium is supplemented by two intermolecular

Fig. 2. Environment of the central tellurium atom in compound 1 (VII R = CH$_3$, R^1 = H, R^2 = 4-NO$_2$).

O $\cdots$ Te contacts, the observed configuration of the tellurium atom (with these contacts considered) is similar to that found in compound No. 1.

The dipole moments

The dipole moment values for the series of telluranes VII in benzene solution at 25 °C are presented in Table 4.

Assuming the nearly identical conformation of the C, N-diarylazomethine fragment for compounds VII, with R^2 = H and 4-Br (compounds No. 3 and 4 in Table 4) and suggesting that the angle O(1)TeO(2) is of the same value (165°) as that in tellurane No. 1 (R^2 = 4-NO$_2$) with the valence angles in the aromatic ligands being close to the standard value of near 120° (see Table 3), the angles between the projections of the Te $\cdots$ N bonds on the equatorial H$_3$C–Te–CH$_3$ plane can be calculated by means of the additive vector scheme [29] (the dipole moment of the C–Br bond is taken as equal to 1.57 D). In the C$_2$-symmetrical compounds VII with regular substituents, for which a direction of the dipole moment of a group R coincides with that of the Ar–Te bond, the vector of the dipole moment is directed along the x-axis (zero projections onto the y, z axis). This implies that the angle θ is bounded by the range of values 60–75°, which, as in the crystalline phase, is considerably less than the expected value for a conformation with unhindered rotation about the Te–O(1), Te–O(2) bonds.

In Table 4, experimental values of the dipole moments for compounds VII are compared with those calculated by the vector addition of group dipole moments under assumption of approximate constance of the angle θ for various substituents in the C- and N-aryl nuclei of the ligands. The calculation of the dipole moments of the compounds with irregular substituents (whose vector of the dipole moment does not coincide with the bond direction) has been carried out using the formula of Gilman [30]).

A sufficiently good agreement between the calculated and experimental values of the dipole moments for most of the compounds VII indicates that the sterically constrained conformation of these compounds caused by intramolecular Te $\cdots$ N coordination of two imine nitrogen atoms is retained in solutions as well. However, in the case of compounds Nos. 1, 12–18, 21 (Table 4) containing a nitro group in the aryl moieties, the calculated dipole moments for the conformation VII are considerably lower than the corresponding experimental values. This probably indicates that for these compounds the C$_2$-conformation, perceivable in the crystal-

Table 4

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

No.	R	R^1	R^2	α	β	$P_{2\infty}$ (cm^3)	$P_3 = 1.1R_D$	μ_{exp} (D)	μ_{calc} (D)
1	CH$_3$	H	4-NO$_2$	10.65	5.324	432.2	159.7	3.54	1.4
2	CH$_3$	H	3-NO$_2$	14.19	3.766	591.0	159.7	4.50	4.0
3	CH$_3$	H	4-Br	4.17	4.245	267.3	164.0	2.06	2.06 [a]
4	CH$_3$	H	H	4.95	2.626	282.6	148.5	2.41	2.41 [a]
5	CH$_3$	H	4-CH$_3$	6.17	2.489	336.4	157.7	2.82	2.49
6	CH$_3$	H	4-OCH$_3$	7.91	3.275	385.0	161.0	3.19	3.08
7	CH$_3$	H	4-N(CH$_3$)$_2$	14.44	2.454	632.9	174.8	4.64	4.45 [b]
8	CH$_3$	4-NO$_2$	4-Br	20.39	2.468	880.9	175.2	5.80	5.62 [b]
9	CH$_3$	4-NO$_2$	3-F	16.19	3.494	677.3	159.5	4.95	4.94 [b]
10	CH$_3$	4-NO$_2$	H	17.84	3.529	719.6	159.7	5.15	5.24 [b]
11	CH$_3$	4-NO$_2$	4-CH$_3$	16.79	2.956	708.6	168.9	4.05	5.17 [b]
12	CH$_3$	4-NO$_2$	4-OCH$_3$	18.16	4.143	734.6	172.2	5.16	– [c]
13	CH$_3$	4-NO$_2$	4-N(CH$_3$)$_2$	21.65	3.320	880.7	186.0	5.75	– [c]
14	CH$_3$	5-NO$_2$	4-Br	14.91	3.349	679.1	175.2	4.87	3.16 [b]
15	CH$_3$	5-NO$_2$	H	21.71	3.376	852.0	149.7	5.75	3.51 [b]
16	CH$_3$	5-NO$_2$	4-N(CH$_3$)$_2$	26.13	5.526	991.6	186.0	6.20	– [c]
17	CH$_3$	4-NO$_2$,6-Cl	4-OCH$_3$	16.64	3.737	717.3	181.9	5.02	– [c]
18	CH$_3$	4-NO$_2$,6-Cl	4-N(CH$_3$)$_2$	13.72	4.033	1145.6	195.8	6.74	– [c]
19	CH$_2$C$_6$H$_5$	H	4-OCH$_3$	9.88	3.966	483.6	209.2	3.52	3.08
21	4-CH$_3$C$_6$H$_4$	H	4-NO$_2$	13.52	3.352	631.3	207.9	4.43	1.4
22	4-CH$_3$C$_6$H$_4$	H	4-CH$_3$	6.43	3.157	483.6	205.9	2.73	2.49

[a] Taken as found experimentally and used for the calculation of dipole moments of the other compounds. [b] Group moments of the N(CH$_3$)$_2$ and NO$_2$ groups equally +0.8 D [29] are added to the interaction moments directed along the Ar–N bond line. [c] With the presence of two substituents possessing the strong cumulative electron-donating and electron-accepting effects in different aryl nuclei the μ values remain uncertain.

line phase, is not the most stable on in solution. Considering the high value of the nitro group dipole moment, it might be assumed that even slight non-symmetrical deformations in the C_2-conformation could give rise to noted deviations.

The main reason for the destabilization of the conformation VII in compound No. **1, 12–18, 21** (Table 4) probably lies in a sharp decrease in the donor ability of the imine nitrogen, because the strong electron-withdrawing substituent (nitro group) in the aryl nuclei of these compounds is in a conjugational position with respect to the imine nitrogen atom. The energy of the weak intramolecular Te $\cdots$ N bond observed in the crystalline state seems to be insufficient for maintaining the sterically constrained conformation VII (Fig. 1) in solution.

^1H, ^{125}Te and ^{14}N NMR spectra

^{1}H, ^{125}Te and ^{14}N NMR spectral data for the compounds VII are given in Table 5.

In the ^{1}H NMR spectra the most characteristic chemical shifts are those of the methine protons and the protons of the Te-methyl groups. In deuterochloroform solutions, resonance of these protons, excluding compound No. **1** appear as sharp singlet peaks. Methine protons resonate in the region of 7.82–8.49 ppm and they are shifted towards a stronger field by 0.2–0.6 ppm as compared to the analogous resonances in the ligands IX. Resonances of the Te-methyl protons appear in the region of 2.48–2.72 ppm. These data indicate the presence of only one structural form of compounds VII in this solvent. But with the presence of such a strong electron-withdrawing substituent as a nitro group in the position para to the azomethine bond (compound No. **1**), the methine and Te-methyl protons each show two distinct signals. One of the methine proton signals is close in its position to that of the methine proton in the ligand IX. In such strong donor solvents as DMSO or DMF, for compounds VII having *p*-nitro groups, the above protons appear as double (compound No. **17**) or even triple resonance signals (compound No. **12**). The multiplying of resonance peaks of compounds (VII) in the above solvents has been observed in the ^{13}C NMR spectra as well. On changing over to DMSO-d_6 from deuterochloroform, the number of signals in the ^{13}C NMR spectra become doubled (compound No. **12**). Probably in solvents such as DMSO, the compounds VII might exist in two or even three conformational isomeric forms resulting from the rupture of weak Te $\cdots$ N coordination bonds.

At the same time, in the ^{125}Te NMR spectra (in CDCl$_3$) of the compounds VII, two different ^{125}Te resonances revealing the existence of the two structural forms in the solution are observed. In this case the *p*-substituent in the aldehyde fragment of the ligands does not markedly affect the values of the ^{125}Te chemical shift. In the case of the derivatives of arylidene-2-aminophenol, ^{125}Te chemical shifts lie in the range of 1055–1107 ppm while in the derivatives of arylidene-2-amino-4-nitrophenol they cover the region of 998–1179 ppm. It must be noted however, that the values of ^{125}Te chemical shifts in σ-telluranes R$_2$TeX$_2$ (X = Cl, Br, I) are rather sensitive to the nature of the halogen as well as to organic groups bonded to the tellurium atom and cover a region of 550 ppm (700–1250 ppm) [31–35]. In the case of tetraalkoxytelluranes Te(OR)$_4$ too, the ^{125}Te chemical shifts lie in the region of 1390–1600 ppm [36]. So that, on the basis of the ^{125}Te chemical shift values, unambigous conclusions as to the type of coordination in compounds VII around the central tellurium atom can hardly be achieved.

Table 5

^{1}H, ^{125}Te and ^{14}N NMR chemical shifts of compounds VII

No.	R	R^1	R^2	Solvent	δ(C=N) (ppm)[a]	δ(Te–CH$_3$) (ppm)	δ(^{125}Te) (ppm)[b]	δ(^{14}N) (ppm)[c]
1	CH$_3$	H	4-NO$_2$	CDCl$_3$	8.44, 8.74 (8.75)	2.59, 2.79	1056, 1076, 1104[d]	−6
2	CH$_3$	H	3-NO$_2$	DMSO-d_6	9.10	2.49	1055, 1112[d]	−7.3
3	CH$_3$	H	4-Br	CDCl$_3$	8.17	2.48	1056, 1102[d]	−7.2
4	CH$_3$	H	H	CDCl$_3$	8.25 (8.42)	2.50	1057, 1105[d]	−78
5	CH$_3$	H	4-CH$_3$	CDCl$_3$	8.17 (8.40)	2.49	1055, 1108[d]	−81
	CH$_3$	H	4-CH$_3$	C$_6$H$_6$	–	–	1100[e]	–
6	CH$_3$	H	4-OCH$_3$	CDCl$_3$	8.17	2.51	1056, 1107[d]	−88
7	CH$_3$	H	4-N(CH$_3$)$_2$	DMF-d_7	8.36	2.51	1056, 1105[d]	−93
8	CH$_3$	4-NO$_2$	4-Br	CDCl$_3$	8.23	2.62	–	–
9	CH$_3$	4-NO$_2$	3-F	CDCl$_3$	8.32	2.62	–	–
11	CH$_3$	4-NO$_2$	4-CH$_3$	CDCl$_3$	8.12 (8.69)	2.60	1104, 1179[d]	–
12	CH$_3$	4-NO$_2$	4-OCH$_3$	DMSO-d_6	8.55, 8.84 / 10.02 (10.03)	2.57, 2.68	998, 1111, 1122[d]	–
13	CH$_3$	4-NO$_2$	4-OCH$_3$	CDCl$_3$	8.49	2.99	1103, 1178[d]	–
14	CH$_3$	4-NO$_2$	4-N(CH$_3$)$_2$	CDCl$_3$	7.94 (8.56)	2.59	–	–
15	CH$_3$	5-NO$_2$	4-Br	CDCl$_3$	8.24 (8.61)	2.60	–	–
16	CH$_3$	5-NO$_2$	H	CDCl$_3$	8.27 (8.70)	1.60	–	–
17	CH$_3$	4-NO$_2$,6-Cl	4-OCH$_3$	DMF-d_7	8.30, 9.64	2.58	–	–
18	CH$_3$	4-NO$_2$,6-Cl	4-N(CH$_3$)$_2$	CDCl$_3$	7.96	2.72	–	–
19	CH$_2$C$_6$H$_5$	H	4-OCH$_3$	CCl$_4$	7.82	–	–	–
22	4-CH$_3$C$_6$H$_4$	H	4-CH$_3$	CCl$_4$	8.03 (8.40)	–	–	–
23	4-CH$_3$C$_6$H$_4$	H	4-OCH$_3$	CDCl$_3$	8.04	–	–	–
24	CH$_3$	4-CH$_3$	4-COH$_3$	CD$_2$Cl$_2$	8.23[f]	–	1100, 1052[d] / 1089[d]	–

[a] In brackets are shown chemical shift values of the methine proton in corresponding Schiff bases IX. [b] ^{125}Te chemical shifts are relative to (CH$_3$)$_2$Te. [c] ^{14}N chemical shifts are relative to NO$_3^-$. [d] Spectra are recorded in CHCl$_3$. [e] Spectra are recorded in C$_6$H$_6$. [f] Doublet (J(^{1}H–^{15}N) 3.6 Hz).

The presence of two well-defined resonance peaks in the ^{125}Te NMR spectra of compounds VII as distinct from one common CH signal in the ^{1}H NMR spectra may be explained by the appreciably broader interval of ^{125}Te chemical shifts as compared to that of ^{1}H [37]. These spectral patterns lead to a conclusion in favor of sufficiently rapid chemical exchange between two isomeric forms of compounds VII existing in the CDCl$_3$ solution. The exchange appears to be slow enough on the ^{125}Te NMR time scale, thus allowing one to observe separate resonance signals of both interconvertible isomers, presumably the structure VII with the intramolecular Te $\cdots$ N coordination and a conformer with broken Te $\cdots$ N bond(s). On the other hand, the chemical exchange is fast at ambient temperature on the ^{1}H NMR time scale giving rise to the appearance of averaged signals of isomers.

It is noteworthy that in benzene solution only single ^{125}Te resonances are observed (compound No. 5 in Table 5). This indicates the presence of a single isomeric form of compounds VII in benzene solution which provides support from the above interpretation of the dipole moment values.

On account of the strong influence of solvents on the conformational equilibria of compounds VII evidenced by their ^{125}Te spectral pattern it may be concluded that intramolecular Te $\cdots$ N coordination in these is weak and easily disturbed by solvation in polar solvents. No ^{15}N–^{125}Te coupling was observed in the ^{15}N and ^{125}Te NMR spectra of dimethylbis[2-(4-methoxybenzylidenimino)-4'-methylphenyl-oxy]tellurane (compound No. 24 in Table 5) enriched in ^{15}N in chloroform solution which confirms the weakness of the Te $\cdots$ N coordination bond. On the contrary, in compounds X and XI which we have recently prepared [38] ^{15}N–^{125}Te coupling was found to be rather effective resulting in $^1J(^{15}$N–^{125}Te) values of 61 Hz and 122 Hz, respectively.

(X)   (XI)
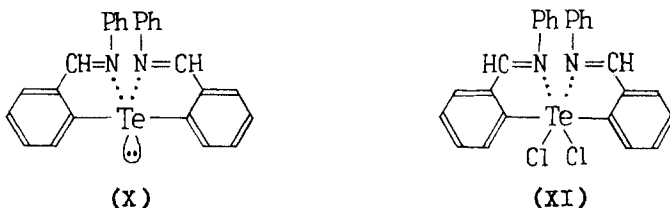
Experimental

Synthesis

Dimethyltellurium diiodide and di-*p*-tolyltellurium dibromide were prepared in accordance with reported methods [39,40]. Schiff bases were synthesized by the condensation of *o*-aminophenols with aromatic aldehydes and their constants verified from literature data.

The following general procedure was employed for the synthesis of compounds VII [17]: to a solution of 8.23 g (20 mmol) dimethyltellurium diiodide or 9.40 g (20 mmol) di-*p*-tolyltellurium dibromide in 50 cm^3 of dry toluene, a solution of sodium methoxide prepared from 0.95 g (40 mmol) sodium metal in 30 cm^3 of absolute methanol was added under stirring. Methanol was distilled off until the temperature of the vapors reached 110 °C and large crystals of NaI (NaBr) were precipitated. Sodium halogenide was filtered off and the colorless filtrate, i.e. a solution of

diorganylmethoxytellurane, was added to a solution of 40 mmol of the corresponding Schiff base in 50 cc of dry toluene under stirring. Most of the toluene was removed under vacuum from the reaction mixture obtained and an equal volume of absolute there was added to the concentrated remainder ($\sim$ 30 cm^3). Then the flask was cooled to $-5\,°$C, crystals of product were filtered off, dried and recrystallized from an appropriate solvent (usually hexane or a mixture of hexane and toluene or CCl$_4$).

X-Ray structural analysis of compound No. 1

Crystals of the compound C$_{28}$H$_{24}$N$_4$O$_6$Te (No. 1) are monoclinic. At $20\,°$C a 7.557(1), b 27.002(5), c 13.176(2) Å, β 100.21(1)$\,°$, V 2646.1(2) Å^3, $Z = 4$, D_c 1.61 g/cm^3, space group $P2_1/c$.

Table 6

Atomic coordinates of Te ($\times 10^5$), non-hydrogen atoms ($\times 10^4$) and hydrogen atoms ($\times 10^3$) in compound No. 1

Atom	x	y	z	Atom	x	y	z
Te	50253(2)	29639(1)	30237(2)	C(23)	6402(4)	4119(1)	5750(2)
O(1)	7172(3)	2710(1)	4176(2)	C(24)	7566(4)	4516(1)	5926(2)
O(2)	2661(3)	3024(1)	1921(2)	C(25)	7719(4)	4863(1)	5172(2)
O(3)	4512(4)	4558(1)	−1843(2)	C(26)	6693(4)	4803(1)	4212(2)
O(4)	4292(4)	3774(1)	−2073(2)	C(27)	5536(5)	2328(2)	2203(3)
O(5)	9763(4)	4911(1)	7075(2)	C(28)	3329(5)	2627(1)	3913(3)
O(6)	8396(4)	4305(1)	7634(2)				
N(1)	8495(3)	3439(1)	3008(2)	H(2)	876(5)	270(1)	601(3)
N(2)	3473(3)	3971(1)	2700(2)	H(3)	1090(4)	320(1)	679(2)
N(3)	4826(4)	4128(1)	−1543(2)	H(4)	1212(4)	377(1)	589(2)
N(4)	8669(4)	4585(1)	6962(2)	H(5)	1108(4)	393(1)	422(2)
C(1)	8494(4)	3012(1)	4614(2)	H(7)	898(4)	415(1)	289(2)
C(2)	9228(5)	2948(1)	5655(3)	H(9)	742(4)	318(1)	112(2)
C(3)	10555(4)	3259(2)	6144(2)	H(10)	576(4)	333(1)	−48(2)
C(4)	11228(4)	3630(2)	5630(2)	H(12)	629(3)	474(1)	−17(2)
C(5)	10567(4)	3694(1)	4585(2)	H(13)	781(4)	469(1)	150(2)
C(6)	9211(3)	3395(1)	4070(2)	H(15)	121(4)	304(1)	16(2)
C(7)	8535(3)	3851(1)	2550(2)	H(16)	43(5)	366(1)	−102(3)
C(8)	7692(3)	3914(1)	1465(2)	H(17)	97(4)	444(1)	−47(2)
C(9)	7078(4)	3513(1)	846(2)	H(18)	218(4)	456(1)	120(2)
C(10)	6172(4)	3578(1)	−146(2)	H(20)	463(3)	459(1)	248(2)
C(11)	5861(4)	4054(1)	−506(2)	H(22)	370(4)	382(1)	471(2)
C(12)	6508(4)	4461(1)	78(2)	H(23)	638(5)	388(1)	623(2)
C(13)	7413(4)	4388(1)	1059(2)	H(25)	834(4)	509(1)	530(2)
C(14)	2241(3)	3421(1)	1323(2)	H(26)	685(4)	500(1)	377(2)
C(15)	1397(4)	3351(1)	298(2)	H(271)	547(5)	246(1)	153(3)
C(16)	910(4)	3743(2)	−349(2)	H(272)	449(6)	215(2)	199(3)
C(17)	1237(4)	4217(1)	−12(2)	H(273)	649(6)	224(2)	255(3)
C(18)	2074(4)	4301(1)	990(2)	H(281)	283(5)	272(2)	430(3)
C(19)	2604(3)	3906(1)	1665(2)	H(282)	376(6)	241(2)	424(3)
C(20)	4490(4)	4342(1)	2349(2)	H(283)	256(6)	247(2)	356(3)
C(21)	5507(3)	4403(1)	3998(2)				
C(22)	5379(4)	4066(1)	4780(2)				

Cell parameters and intensity for 5818 reflections with $I > 2\sigma$ were collected on an Engraf-Nonins CAD 4 diffractometer (λ(Mo-K_α), scan speed ratio $\omega/\theta = 1.2/1$, $2° < \theta < 28°$).

The structure was solved by a direct method and full-matrix least squares refinement based on 4291 reflections with $F > 5\sigma$. All non-hydrogen atoms were refined with anisotropic thermal parameters and hydrogen atoms located in difference Fourier synthesis were refined with isotropic thermal parameters. Final agreement factor $R = 0.029$, $R_w = 0.042$.

Atomic coordinates are given in Table 6.

All calculations were performed on a PDP-11 computer using SDP-PLUS [41].

Dipole moments

The molar polarization for compounds VII in benzene solutions at 25°C at infinite dilution, $P_{2\infty}$ was calculated using Hedestrand's formula [42]. Values of the electronic polarizability P_e were taken as equal to those of the refraction R_D. These were calculated as the sum of the atomic refractions using Eisenlor's increments [43]. Atomic polarization values (P_a) were taken as 10% of the electronic polarization.

NMR and IR spectra

^{1}H NMR spectra were recorded on a Tesla-BS-487C (80 MHz) instrument, using HMDS as internal standard in CDCl$_3$ or DMSO-d_6 solutions, and ^{13}C NMR spectra on a Varian XL-100 spectrometer using the Fourier transform technique in the same solvents (with deuterochloroform lock). ^{125}Te and ^{14}N 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, respectively. Cr(Acac)$_3$ was used as a relaxation agent. Chemical shifts on the δ scale were measured downfield to (CH$_3$)$_2$Te (^{125}Te) and NO$_3^-$ (^{14}N). IR spectra were recorded on a Specord 75 IR spectrophotometer in Nujol.

Acknowledgement

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