1-Naphthyl- and mesityltellurium(IV, II) derivatives of small bite chelating organic ligands: Effect of steric bulk and intramolecular secondary bonding interaction on molecular geometry and supramolecular association

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Abstract

The synthesis and characterization of unsymmetric diorganotellurium compounds containing a sterically demanding 1-naphthyl or mesityl ligand and a small bite chelating organic ligand capable of $1,4$-Te$\cdots$N(O) intramolecular interaction is described. The reaction of ArTeCl$_3$ (Ar = 1-C$_{10}$H$_7$, Np; 2,4,6-Me$_3$C$_6$H$_2$, Mes) with (SB)HgCl [SB = the Schiff base, 2-(4,4'-NO$_2$C$_6$H$_4$CH=NC$_6$H$_3$-Me)] or a methyl ketone (RCOCH$_3$) afforded the corresponding dichlorides (SB)ArTeCl$_2$ (Ar = Np, **1Aa**; Mes, **1Ba**) or (RCOCH$_2$)ArTeCl$_2$ (Ar = Np; R = Ph (**2Aa**), Me (**3Aa**), Np (**4Aa**); Ar = Mes, R = Ph (**2Ba**)). Reduction of **1Aa** and **1Ba** by Na$_2$S$_2$O$_5$ readily gave the tellurides (SB)ArTe (Ar = Np (**1A**), Mes, (**1B**)) but that of dichlorides derived from methylketones was complicated due to partial decomposition to tellurium powder and diary[ditelluride (Ar$_2$Te$_2$), resulting in poor yields of the corresponding tellurides **2A**, **2B** and **3A**. Oxidation of the isolated tellurides with SO$_2$Cl$_2$, Br$_2$ and I$_2$ yielded the corresponding dihalides. All the synthesized compounds have been characterized with the help of IR, ^{1}H, ^{13}C, and ^{125}Te NMR and in the case of **2Aa**, and **2Ba** by X-ray crystallography. Appearance of only one ^{125}Te signal indicated that the unsymmetric derivatives were stable to disproportionation to symmetric species. Intramolecular $1,4$-Te$\cdots$O secondary bonding interactions (SBIs) are exhibited in the crystal structures of both the tellurium(IV) dichlorides, **2Aa**, and **2Ba**. Steric repulsion of the mesityl group in the latter dominates over lone pair–bond pair repulsion, resulting in significant widening of the equatorial C–Te–C angle. This appears to be responsible for the lack of Te$\cdots$Cl involved supramolecular associations in the crystal structure of **2Ba**.
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Keywords: Sterically hindered organotelluriums; Supramolecular association; Intramolecular coordination; Secondary bonding interactions

1. Introduction

Secondary bonding interactions (SBIs) among the electron-rich p-block elements [1] affect the stability and reactivity of molecules and also influence the 'chemistry beyond molecules'. These non-covalent associative forces, besides the widely recognized hydrogen bonds, play a crucial role in the activity of biological macromolecules as well as the observed electro-optical properties of crystalline molecular materials. For this reason, theoretical and experimental structural studies on organotellurium compounds that possess suitably placed nucleophilic atoms as potential donors for intra- and/or inter-molecular Te$\cdots$O/N/X SBI have gained impetus in the last few years [2] as they allow heuristic conclusions to be drawn for designing model molecules with desired functionality. Recently, we carried out aryltelluration of 4-nitro-4'-methylbenzalideneaniline (NMBA)

and examined solid state structures of the resulting diaryltellurides as well as some of their mercury(II) halide complexes [3] with the view that intramolecular 1,4-Te···N SBI in the geometrically constrained orthotellurated species or the metal-assisted C–H···X interactions could lead to non-centrosymmetric supramolecular structures. Such solids might possess non-zero second-order susceptibility imparting thereby linear and non-linear electro-optic properties similar to those observed for the monoclinic crystal modifications of the organic substrate, NMBA.

Though the influence of intramolecular SBIs on the molecular and crystal structures of organotellurium compounds has been studied considerably, the role of sterically demanding groups in this respect have received limited attention. Whereas the isolation of tellurols RTeH at low temperatures and that of monomeric volatile metal tellurolates $M(TeR)_2$ (M = Zn, Cd, Hg) at room temperature could be realized by incorporating the bulky 2,4,6-triorganophenyl [4], sitel $[Si(SiMe_3)_3]$ [5] or 2-[1-(3,5-dimethylphenyl)-2-naphthyl]-4,5-dihydro-4,4-dimethyloxazole [6] groups, steric crowding around central tellurium atom has made the isolation of mesityltellurium triiodide hitherto impossible [7]. However, simultaneous effects of intramolecular coordination to Te as well as the steric bulk of the organic ligands on the molecular geometry and crystal packing of organotelluriums has not been examined, even though organotelluriums containing a sterically hindered organic group which is also capable of forming 1,5-Te···N SBI have been prepared [2n]. We report here the synthesis

and characterization together with single crystal structural determination of some unsymmetric diorganotellurium compounds. Acylmethyl ligands, $RCOCH_2–$ (R = Ph, Me, Np) or the Schiff base, 2-(4,4'-$NO_2C_6H_4CH=NC_6H_3$-Me), capable of forming strained four-membered intramolecular rings via Te···O/N coordination were chosen as one of the organic ligands attached to tellurium, while 2,4,6-$Me_3C_6H_2$ (Mes) or 1-$C_{10}H_7$ (Np) were employed as the other ligand due to their steric and electronic effects as well as their ability to cause various conformations and cell packings.

2. Results and discussion

Interesting unsymmetric diorganotellurium compounds containing one sterically demanding group and another capable of 1,4-intramolecular Te···N/O interaction have been prepared by the interaction of $ArTeCl_3$ (Ar = Np, Mes) with (SB)HgCl [SB = 2-(4,4'-$NO_2C_6H_4CH=NC_6H_3$-Me)] or an acylmethyl ketone (Scheme 1).

Reduction of the diorganotellurium dichlorides **1Aa** and **1Ba** with $Na_2S_2O_5$ affords the tellurides **1A** and **1B**, which in turn can be oxidized to **1Ab** and **1Bb**, **1Ac** and **1Bc** or back to **1Aa** and **1Ba** by Br_2, I_2, or SO_2Cl_2, respectively. Reductions of the acylmethyl derivatives **2Aa**, **2Ba** and **3Aa** are complicated and afford the tellurides, **2A**, **2B** and **3A** in low yields along with the tellurium powder and the ditellurides, Ar_2Te_2. Similar decomposition is reported in the preparation of several other alkylaryl tellurides [8]. Reduction of the dibromides **2Ab**, **2Bb** and **3Ab** (vide infra)
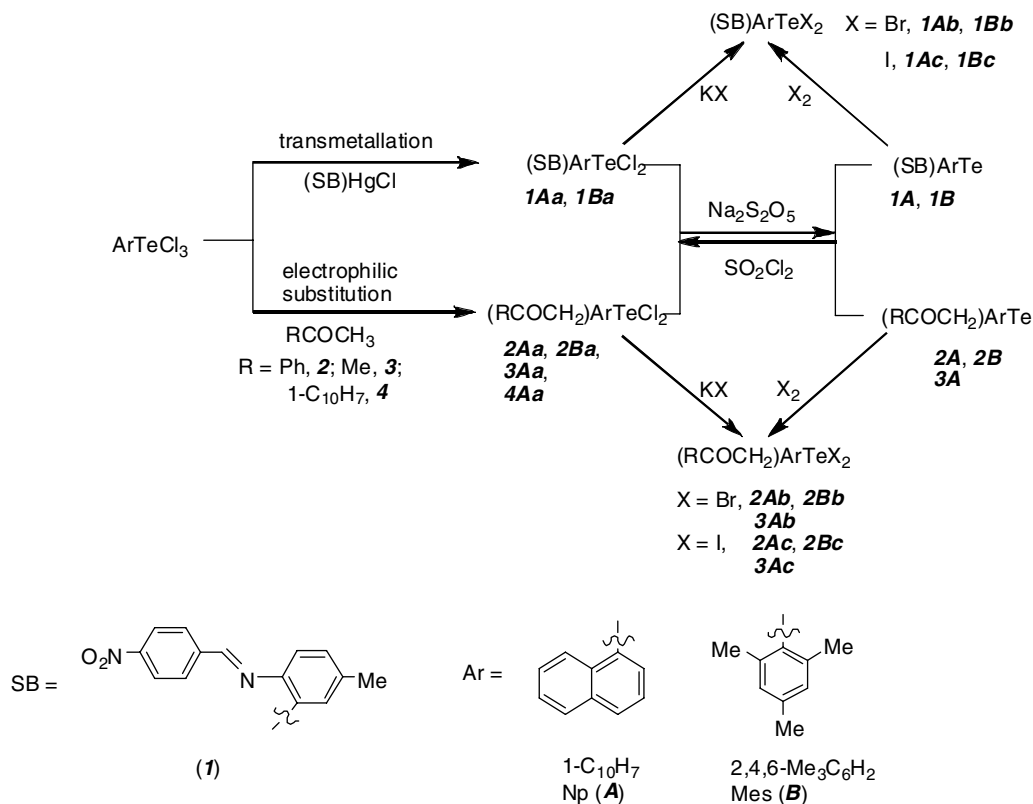
Scheme 1.

interestingly affords better yields of the tellurides on reduction. Oxidation of these tellurides **2A**, **2B** and **3A** also afforded the corresponding dihalides. The dibromides and diiodides were also obtained by the metathetical reaction of KBr and KI with the corresponding dichlorides.

The unsymmetric dihalides (SB)ArTeX$_2$ and (RCO-CH$_2$)ArTeX$_2$ are quite stable to decomposition to the symmetric species. All the compounds are crystalline solids soluble in dichloromethane and chloroform. It is interesting to note that among the dihalides the naphthyl derivatives have comparatively higher melting points than their mesityl analogues. Greater steric requirement of the mesityl group probably allows less compact packing of the molecules in the crystal lattice. The IR spectra of the Schiff base derivatives show v(C=N) at 1590–1645 cm^{-1} the values for the tellurides are higher than those for the dihalides. In the spectra of the acylmethyl derivatives, v(CO) shows a negative shift with respect to the parent ketone (**2–4**) which is indicative of intramolecular Te$\cdots$OC interaction. In the ^{1}H NMR spectra of the Schiff base derivatives the azomethine proton appears downfield, as expected, at ~8.9 ppm while a singlet for the methylene protons is observed at ~5.8 ppm in the acylmethyl derivatives. The 2,4,6-substituted methyl protons in the mesityl derivatives appear as singlets in the ratio 1(*para*):2(*ortho*).

The ^{125}Te NMR chemical shifts of some representative compounds have been measured in solution as well as in solid state and have been found to be quite sensitive to the nature of the halogen and the oxidation state of tellurium. Enhanced deshielding is observed in the order I < Br < Cl and Te^{II} < Te^{IV} for the compounds. The ^{125}Te chemical shifts for the mesityl tellurium(II,IV) derivatives of the Schiff base are nearly 100 ppm downfield to their corresponding naphthyl analogues but are close to those for other aryl analogues, (SB)Ar'Te (Ar' = Ph, 4-MeOC$_6$H$_4$, 4-MeC$_6$H$_4$) [3] which may be due to the greater Te$\cdots\pi$ interaction, even in solution, of the naphthalene ring compared to the benzene rings.

2.1. Crystal and molecular structure of 2Aa and 2Ba

Compounds **2Aa** and **2Ba** crystallize in the triclinic crystal system where the primitive lattice in both the compounds bears a center of symmetry. Asymmetric units consist of only one molecule in **2Aa** and two independent molecules in **2Ba**. The Te^{IV} atom in the molecules of these compounds presents a primary pseudo-trigonal-bipyramidal configuration in complete agreement with the VSEPR model. The axial Te–Cl bond lengths differ slightly and the unequal equatorial Te–C distances (Te–C$_{sp3}$ > Te–C$_{sp2}$) are well within the range commonly observed in other R^{F}ArTeCl$_2$ compounds (R^F is an organic ligand suitably functionalized to bear a nucleophilic atom A, viz. O, N, S or Cl that involves Te in the intramolecular 1,4-Te$\cdots$A SBI) [9,10]. Formation of four-membered rings by means of Te$\cdots$O SBIs in **2Aa** and **2Ba** is evident from interatomic distances [2.862(4) in **2Aa**, 2.890(2) and 2.846(2) Å in **2Ba**]

that are significantly shorter than the sum of their van der Waals radii (3.58 Å).

In the crystal packing of the naphthyl derivative, **2Aa**, besides the carbonyl oxygen, the Cl2 atom of a neighboring molecule also comes sufficiently close to the Te^{IV} atom by means of intermolecular Te$\cdots$Cl SBI [Te$\cdots$Cl2 = 3.622(1) Å < 3.83 Å, the sum of their van der Waals radii] to be considered as part of the coordination sphere. The Te$\cdots$Cl2 SBI is cooperated with a metal assisted C–H$\cdots$Cl interaction (C8B–H8BA$\cdots$Cl2–Te^{IV}) in giving rise to centrosymmetric dimeric supramolecules. These dimeric units are oriented in a parallel fashion by means of another intermolecular metal assisted C–H$\cdots$Cl interaction (C8A–H8AA$\cdots$Cl2–Te^{IV}) resulting in a one-dimensional supramolecular architecture. It brings all the Te and Cl atoms in to a plane (r.m.s. deviation of Te and Cl atoms from the mean plane = 0.0834 Å), forming an elegant doubly-bridged (TeCl$_2$)$_n$ polymeric ribbon flanked with organic ligand on both sides. The antiparallel consecutive Cl1–Te–Cl2 units in the polymeric chain confer greater stability to the motif by alternating the local dipole moment. Such 1-D arrays achieved by (A1–Te–A2)$_n$ synthons are ubiquitous among organotelluriums containing nucleophilic atoms one or two bonds from tellurium. The potential of Te$\cdots$A recognition pattern to give rise to (A1–Te–A2)$_n$ supramolecular synthons has been recognized in crystal engineering [2i,2j]. It implies that SBI based synthons are as effective as those which involve conventional H-bond or C–H$\cdots$A interactions, which are quite common among organic compounds. In the case of **2Aa**, the metal assisted C–H$\cdots$Cl interactions appear to be strong enough to bring all the Te and Cl atoms in the plane of the polymeric ribbon, in spite of the involvement of only one of the Cl atoms in SBI.

The steric repulsion of the mesityl group is quite evident in the crystal structure of **2Ba** and is stronger than lone pair-bond pair repulsions as it causes angular distorsion, at least equatorial, of the primary geometry around Te^{IV}. The observed C1–Te–C9 bond angles in **2Ba** [108.0(1) and 107.9(1) for the two independent molecules] are unusually large in comparison to the average value of 96(3)° found for C–Te–C in the CSD [11] but not uncommon for aryltelluranes [12] that possess at least one 2,6-disubstituted aryl ligand attached to Te^{IV}. It may be inferred that the steric repulsion of ligands in the primary sphere of Te(IV) affects molecular geometry considerably, albeit, steric congestion due to the presence of nucleophilic atoms attached to Te(IV) through SBIs is insignificant as evident from the C–Te–C angle values in such compounds [9] which vary over the range 93.1(1)–99.1(1)°. The crystal packing of **2Ba** differs from that of **2Aa**. The bulky mesityl group inhibits intermolecular Te$\cdots$Cl SBI and 1-D arrays formed by ($\cdots$Cl–Te–Cl$\cdots$)$_n$ supramolecular synthon, present in **2Aa**, is not realized in the crystalline state of **2Ba**. Instead, interplay of C–H$\cdots$O and C–H$\cdots$Cl interactions (Table 1) in the self assembly of **2Ba** results in three-dimensional centrosymmetric supramolecular motif.

Table 1
Hydrogen bond parameters[a,b]

	D–H···A	d(D–H) (Å)	d(H···A) (Å)	d(D···A) (Å)	<(DHA) (°)
2Aa	C8–H8···Cl1[i]	0.95	3.783(5)	2.854(2)	166.3
	C14–H14···Cl2[ii]	0.95	3.765(5)	2.898(1)	152.5
	C17–H17···Cl2[iii]	0.95	3.732(6)	2.845(2)	155.7
	C11–H11···O[iv]	0.95	3.314(7)	2.604(5)	131.8
2Ba	C17A–H17A···O1A[v]	0.98	2.699(1)	3.641(2)	161.4
	C4A–H4AA···Cl2A[vi]	0.95	2.779(1)	3.586(3)	143.4
	C5A–H5AA···Cl2A[vii]	0.95	2.880(1)	3.602(3)	133.7
	C11B–H11B···Cl1A[viii]	0.95	2.864(2)	3.636(3)	139.2
	C16B–H16E···Cl1A[ix]	0.98	2.836(1)	3.469(3)	123.0
	C13B–H13B···O1B[x]	0.95	2.590(1)	3.476(3)	155.4
	C1B–H1BA···Cl1B[vi]	0.99	2.741(1)	3.620(3)	148.2
	C8B–H8BA···O1B[xi]	0.95	2.484(1)	3.370(3)	155.6

[a] Symmetry operations used to generate equivalent atoms: (i) $-x, -y, -z$; (ii) $-x, 1-y, -1-z$; (iii) $-x, -y, -1-z$; (iv) $x, 1-y, z$; (v) $-1+x, y, z$; (vi) $-x, 2-y, 1-z$; (vii) $-x, 1-y, 1-z$; (viii) $x, -1+y, z$; (ix) $1-x, 2-y, -z$; (x) $1+x, y, z$; (xi) $-1-x, 2-y, 1-z$.

[b] The term "hydrogen bond" for such interactions has been discouraged recently (P. Munshi, T.N.G. Row, J. Phys. Chem. A 109 (2005) 659) in favour of weak van der Waals interactions.

3. Experimental

3.1. General

Preparative work was performed under dry nitrogen. Melting points were recorded in capillary tubes and are uncorrected. The starting material [{2-(4-nitrobenzylideneamino)-5-methyl}phenyl]mercury chloride was prepared according to literature method [10]. 1-Naphthyl- and mesityltellurium trichlorides were prepared by the chlorination of their corresponding ditellurides. 1-Acetonaphthone was prepared by the reaction of 1-naphthylmagnesium bromide with acetyl chloride in THF. Commercial acetophenone and acetone were used after purification by standard method. ^{1}H NMR spectra were recorded at 300.13 MHz in CDCl$_3$ on a Varian DRX 300 Spectrometer using TMS as internal standard. Solution ^{13}C (100.54 MHz) and ^{125}Te (126.19 MHz) NMR spectra were recorded in CDCl$_3$ on a JEOL Eclipse Plus 400 NMR spectrometer, using Me$_4$Si and Me$_2$Te as internal standards. ^{125}Te CP-MAS NMR spectra were obtained using the same spectrometer equipped with a 6 mm rotor operating at spinning frequencies between 8 and 10 kHz. A 60 s recycle delay was used and typically 1000–5000 transitions were accumulated to obtain adequate signal-to-noise ratios. The isotropic chemical shifts δ_{iso} were determined by comparison of two acquisitions measured at sufficiently different spinning frequencies and were referenced against Me$_2$Te using solid Te(OH)$_6$ as the secondary reference (δ_{iso} 692.2/685.5). IR spectra were recorded as KBr pellets using a Perkin–Elmer RX1 Spectrometer. Microanalyses were carried out using a Carlo Erba 1108 make analyzer. Tellurium was estimated volumetrically and the halogen content gravimetrically as silver halide.

3.2. Syntheses

3.2.1. Transmetallation reaction: synthesis of *1Aa and 1Ba*
A suspension of (SB)HgCl (2.37 g, 5.00 mmol) and NpTeCl$_3$ (1.80 g, 5.00 mmol) in dry dioxane (40 ml) was heated under reflux until a clear solution was obtained. After cooling and evaporation to ~10 ml, diethyl ether (5 ml) was added. The solution was decanted off from a sticky mass which was extracted with ether (3 × 10 ml) and hot chloroform (2 × 10 ml). Volatiles were removed from the combined extract and the residue was dissolved in chloroform (20 ml) and filtered to remove the solid, if any. Concentration of the filtrate, addition of pet ether (~5 ml) and cooling to 0 °C afforded yellow crystalline **1Aa**. Yield: (1.27 g, 45%); mp 200 °C. Anal. Calc. for C$_{24}$H$_{18}$N$_2$O$_2$Cl$_2$Te: C, 51.03; H, 3.21; N, 4.96; Cl, 12.55; Te, 22.59. Found: C, 51.22; H, 3.33; N, 5.05; Cl, 12.00; Te, 23.03%. IR (cm^{-1}): 1595.5 ($v_{CH=N}$). ^{1}H NMR (ppm): δ 2.46 (s, Me), 7.26–8.43 (m, aryl), 8.92 (s, CH=N). ^{125}Te NMR: δ 802.0. ^{125}Te CP-MAS: δ 830. ^{13}C NMR, (δppm): 21.58 (Me), 116.51, 124.27, 124.29, 127.13, 127.25, 127.3, 127.92, 129.51, 130.21, 130.47, 132.73, 133.05, 133.3, 134, 135.53, 145.27, 149.2 (CH=N), 156.57, 140.02, 140.47, 140.85, 140.98.

Compound **1Ba** was prepared similarly. Yield: (42%); mp 170 °C. Anal. Calc. for C$_{23}$H$_{22}$N$_2$O$_2$Cl$_2$Te: C, 49.60; H, 3.98; N, 5.03; Cl, 12.73; Te, 22.91. Found: C, 49.21; H, 3.92; N, 5.22; Cl, 12.22; Te, 23.51%. IR (cm^{-1}): 1590.1 ($v_{CH=N}$). ^{1}H NMR (ppm): δ 2.25–2.73 (s, Me), 7.00–8.05 (m, aryl), 8.88 (s, CH=N).

The yield was comparatively low when these reactions were carried out in chloroform instead of dioxane.

3.3. Electrophilic substitution reaction: synthesis of *2Aa–4Aa and 2Ba*

A mixture of 1-naphthyltellurium trichloride (3.61 g, 10.0 mmol) and acetophenone (2.34 mL, 20.0 mmol) were stirred slowly at room temperature under the flow of dry nitrogen for about 15 h until the evolution of HCl ceased. The resulting white paste was washed with pet-ether (3 × 10 mL) and triturated with diethyl ether and filtered to remove excess of acetophenone. Recrystallization from dichloromethane yielded colourless needles of **2Aa**. Yield: (3.60 g, 81%); mp 188 °C. Anal. Calc. for C$_{18}$H$_{14}$OCl$_2$Te:

C, 48.60; H, 3.17; Cl, 15.94; Te, 28.69. Found: C, 48.32; H, 3.11; Cl, 16.33; Te, 28.00%. IR (cm^{-1}): 1660 ($\nu_{C=O}$). ^{1}H NMR (ppm): δ 5.71 (s, CH$_2$), 7.43–8.11 (m, aryl). ^{125}Te NMR: δ 761.6. ^{125}Te CP-MAS: δ 798. ^{13}C NMR, (δ ppm): 191.9 (CO), 67.1 (CH$_2$).

Compounds **2Ba** and **4Aa** were prepared similarly.

Compound **2Ba**: Yield: (72%); mp 148 °C. Anal. Calc. for C$_{17}$H$_{18}$OCl$_2$Te: C, 46.74; H, 4.15; Cl, 16.23; Te, 29.21. Found: C, 46.51; H, 3.99; Cl, 16.39; Te, 28.64%. IR (cm^{-1}): 1650 ($\nu_{C=O}$). ^{1}H NMR (ppm): δ 5.65 (s, CH$_2$), 2.32–2.81 (s, 3Me), 6.98–8.04 (m, aryl). ^{125}Te NMR: δ 781.2. ^{125}Te CP-MAS: δ 814. ^{13}C NMR, (δ ppm): 192.27 (CO), 63.45 (CH$_2$), 20.99, 23.55, 24.17 (3Me).

Compound **4Aa**: Yield: (62%); mp 208 °C. Anal. Calc. for C$_{22}$H$_{16}$OCl$_2$Te: C, 53.40; H, 3.26; Cl, 14.33; Te, 25.78. Found: C, 53.12; H, 3.35; Cl, 13.98; Te, 25.22%. IR (cm^{-1}): 1654 ($\nu_{C=O}$). ^{1}H NMR (ppm): δ 5.89 (s, CH$_2$), 7.55–9.00 (m, aryl). ^{125}Te NMR: δ 765. ^{13}C NMR, (δ ppm): 194.48 (CO), 69.66 (CH$_2$).

Compound **3Aa**: 1-naphthyltellurium trichloride (1.80 g, 5.00 mmol) was dissolved in an excess of dry acetone ($\sim$10 mL) and stirred vigorously. White solid of **3Aa** separated slowly (15 min) which was filtered, washed with cold ether and recrystallized with chloroform. Yield: (1.62 g, 85%); mp 157 °C. Anal. Calc. for C$_{13}$H$_{12}$OCl$_2$Te: C, 40.80; H, 3.16; Cl, 18.53; Te, 33.34. Found: C, 40.56; H, 3.36; Cl, 18.10; Te, 33.87%. IR (cm^{-1}): 1656 ($\nu_{C=O}$). ^{1}H NMR (ppm): δ 5.12 (s, CH$_2$), 2.5 (s, Me), 7.59–8.16 (m, aryl). ^{125}Te NMR: δ 801.8. ^{13}C NMR, (δ ppm): 200.06 (CO), 67.78 (CH$_2$), 29.74 (Me).

3.4. Reduction reactions: synthesis of 1A–3A, 1B and 2B

A solution of **1Aa** (1.13 g, 2 mmol) in dichloromethane ($\sim$50 ml) was shaken with an aqueous solution of Na$_2$S$_2$O$_5$ (0.57 g, 3 mmol) for 15 min. The organic layer gradually turned red. It was separated, washed (4 $\times$ 50 ml) with water and dried over anhydrous Na$_2$SO$_4$ overnight. Volatiles were removed under reduced pressure and the residue crystallized from CHCl$_3$/Et$_2$O to give red needles of **1A**. Yield: (0.63 g, 64%); mp 148 °C. Anal. Calc. for C$_{24}$H$_{18}$N$_2$O$_2$Te: C, 58.35; H, 3.67; N, 5.67; Te, 25.83. Found: C, 58.43; H, 3.42; N, 5.74; Te, 26.42%. IR (cm^{-1}): 1639.5 ($\nu_{CH=N}$). ^{1}H NMR: δ 2.18 (s, Me), 6.78–8.54 (m, Aryl), 8.87 (s, CH=N). ^{125}Te NMR: δ 471.0. ^{13}C NMR, (δ ppm): 20.95 (Me), 115.53, 122.42, 124, 126.04, 126.39, 126.59, 127.22, 127.39, 128.29, 128.82, 129.38, 130.14, 130.39, 133.19, 136.87, 146.72, 149.2 (CH=N), 156.46, 139.13, 140.42, 140.51, 140.91, 141.33, 142.24.

Compound **1B** was prepared similarly from **1Ba**. Yield: (68%); mp 180 °C. Anal. Calc. for C$_{23}$H$_{22}$N$_2$O$_2$Te: C, 56.84; H, 4.56; N, 5.76; Te, 26.25. Found: C, 56.53; H, 4.67; N, 5.55; Te, 26.58%. IR (cm^{-1}): 1644.1 ($\nu_{CH=N}$). ^{1}H NMR (ppm): δ 2.31–2.20 (s, Me), 6.81–8.34 (m, aryl), 8.57 (s, CH=N). ^{125}Te NMR: δ 575.6. ^{13}C NMR, (δ ppm): 21.05 (Me, NMBA), 21.43 (2, o-Me-Mes), 29.5 (p-Me-Mes), 115.49, 122.91, 124.16, 126.06, 128.23, 129.38,

130.02, 130.6, 130.67, 130.81, 133.74, 135.41, 138.87, 140.43, 141.41, 154.19 (CH=N), 156.52, 149.69.

Accordingly colourless compounds **2A**, **2B** and **3A** were obtained by the reduction of their corresponding dibromides (**2Ab**, **2Bb** and **3Ab**).

Compound **2A**: Dichloromethane solution (25 mL) of **2Ab** (1.07 g, 2 mmol) was shaken vigorously in a seperatory funnel for 10 min with an aqueous solution of (50 mL) of Na$_2$S$_2$O$_5$ (0.5 g, 2.6 mmol). The yellow organic phase was separated, washed once with water, and dried for 5 min over Na$_2$SO$_4$. The solution gradually changed to orange with slight separation of elemental tellurium. Evaporation to dryness and fractional crystallization of the residue afforded red coloured bis(1-naphthyl)ditelluride (0.16 g, 30% of **2Ab** converted) and **2A**: Yield: (0.45 g, 61%); mp 103 °C. Anal. Calc. for C$_{18}$H$_{14}$OTe: C, 57.82; H, 3.77; Te, 34.13. Found: C, 57.61; H, 3.83; Te, 34.68%. IR (cm^{-1}): 1648 ($\nu_{C=O}$). ^{1}H NMR (ppm): δ 5.72 (s, CH$_2$), 7.55–8.31 (m, aryl). ^{13}C NMR, (δ ppm): 192.02 (CO), 67.19 (CH$_2$).

Compound **2B**: Yield: (53%); mp 98 °C. Anal. Calc. for C$_{17}$H$_{18}$OTe: C, 55.80; H, 4.96; Te, 34.87. Found: C, 55.50; H, 5.05; Te, 35.30%. IR (cm^{-1}): 1650 ($\nu_{C=O}$). ^{1}H NMR (ppm): δ 5.66 (s, CH$_2$), 2.33–2.83 (s, 3 Me), 7.00–8.05 (m, aryl).

Compound **3A**: Yield: (56%); mp 137 °C. Anal. Calc. for C$_{13}$H$_{12}$OTe: C, 50.07; H, 3.88; Te, 40.92. Found: C, 50.24; H, 3.56; Te, 40.52%. IR (cm^{-1}): 1648 ($\nu_{C=O}$). ^{1}H NMR (ppm): δ 5.29 (s, CH$_2$), 2.53 (s, Me), 7.58–8.15 (m, aryl).

3.5. Oxidative addition reaction of 1A–3A, 1B and 2B with Br$_2$, I$_2$ and SO$_2$Cl$_2$

a. Compound **1A** (1.00 g, 2.00 mmol) was dissolved in carbon tetrachloride (25 mL) and a solution of bromine (0.12 mL, 4.40 mmol) in the same solvent was slowly added with stirring at 0 °C. A light coloured solid separated which was filtered, dried and recrystallized with CHCl$_3$ to give the corresponding dibromide, **1Ab**. Yield: (0.94 g, 72%); mp 190 °C. Anal. Calc. for C$_{24}$H$_{18}$N$_2$O$_2$Br$_2$Te: C, 44.09; H, 2.77; N, 4.28; Br, 24.44; Te, 19.52. Found: C, 44.33; H, 2.56; N, 4.35; Br, 25.03; Te, 19.22%. IR (cm^{-1}): 1590 ($\nu_{CH=N}$). ^{1}H NMR (ppm): δ 2.35 (s, Me), 6.84–7.83 (m, aryl), 8.89 (s, CH=N).

Similarly **2A**, **3A**, **1B** and **2B** yielded their corresponding dibromides.

Compound **2Ab**: Yield: (74%); mp 159 °C. Anal. Calc. for C$_{18}$H$_{14}$OBr$_2$Te: C, 40.51; H, 2.64; Br, 29.94; Te, 23.91. Found: C, 40.32; H, 2.52; Br, 30.22; Te, 24.35%. IR (cm^{-1}): 1655 ($\nu_{C=O}$). ^{1}H NMR (ppm): δ5.72 (s, CH$_2$), 7.54–8.31 (m, aryl). ^{125}Te NMR: δ 693.0. ^{13}C NMR, (δ ppm): 191.89 (CO), 67.09 (CH$_2$).

Compound **3Ab**: Yield: (90%); mp 163 °C. Anal. Calc. for C$_{13}$H$_{12}$OBr$_2$Te: C, 33.11; H, 2.56; Br, 33.88; Te, 27.05. Found: C, 33.54; H, 2.46; Br, 33.72; Te, 27.43%. IR (cm^{-1}): 1650 ($\nu_{C=O}$). ^{1}H NMR (insufficient solubility).

Compound **1Bb**: Yield: (76%); mp 178 °C. Anal. Calc. for $C_{23}H_{22}N_2O_2Br_2Te$: C, 42.77; H, 3.43; N, 4.34 Br, 24.74; Te, 19.76. Found: C, 42.58; H, 3.65; N, 4.41; Br, 23.42; Te, 21.02%. IR (cm^{-1}): 1592 ($\nu_{CH=N}$). ^{1}H: δ 2.51–2.21 (s, Me), 6.87–8.34 (m, aryl), 8.58 (s, CH=N).

Compound **2Bb**: Yield: (70%); mp 121 °C. Anal. Calc. for $C_{17}H_{18}OBr_2Te$: C, 38.84; H, 3.45; Br, 30.40; Te, 24.27. Found: C, 39.10; H, 3.61; Br, 31.00; Te, 24.52%. IR (cm^{-1}): 1657 ($\nu_{C=O}$). ^{1}H NMR (ppm): δ5.76 (s, CH$_2$), 2.34–2.89 (s, 3Me), 7.01–8.10, (m, aryl).

b. Iodine (0.26 g, 2 mmol) in CCl$_4$ (15 mL) was added dropwise to the solution of **1A** (0.5 g 1 mmol) in the same solvent at 0 °C. The resulting mixture was concentrated till some solid started to precipitate, the amount increasing on adding pet-ether (40–60 °C). It was filtered and recrystallized from dichloromethane to give the corresponding diiodide, **1Ac**. Yield: (0.52 g, 68%); mp 172 °C. Anal. Calc. for $C_{24}H_{18}N_2O_2I_2Te$: C, 38.55; H, 2.43; N, 3.75; I, 33.94; Te, 17.06. Found: C, 38.72; H, 2.54; N, 3.43; I, 34.22; Te, 17.63%. IR (cm^{-1}): 1592 ($\nu_{CH=N}$). ^{1}H NMR (ppm): δ 2.62 (s, Me), 6.95–7.98 (m, aryl), 8.86 (s, CH=N).

Similarly **2A**, **3A**, **1B** and **2B** gave their corresponding diiodides.

Compound **2Ac**: Yield: (80%); mp 122 °C. Anal. Calc. for $C_{18}H_{14}OI_2Te$: C, 34.44; H, 2.25; I, 40.43; Te, 20.33. Found: C, 34.53; H, 2.32; I, 40.10; Te, 20.76%. IR (cm^{-1}): 1649 ($\nu_{C=O}$). ^{1}H NMR (ppm): δ 5.91 (s, CH$_2$), 7.31–8.50 (m, aryl). ^{125}Te NMR: δ 599.8. ^{13}C NMR, (δ ppm): 192.28 (CO), 62.72 (CH$_2$).

Compound **3Ac**: Yield: (40%); mp 138 °C. Anal. Calc. for $C_{13}H_{12}OI_2Te$: C, 27.60; H, 2.14; I, 44.87; Te, 22.56. Found: C, 27.36; H, 2.36; I, 45.00; Te, 22.31%. IR (cm^{-1}): 1653 ($\nu_{C=O}$). ^{1}H NMR (ppm): δ5.31 (s, CH$_2$), 2.52 (s, Me), 7.49–8.34 (m, aryl).

Compound **1Bc**: Yield: (73%); mp 162 °C. Anal. Calc. for $C_{23}H_{22}N_2O_2I_2Te$: C, 37.34; H, 3.00; N, 3.79 I, 34.31; Te, 17.25. Found: C, 37.66; H, 3.20; N, 3.71; I, 34.04; Te, 17.61%. IR (cm^{-1}): 1597 ($\nu_{CH=N}$). ^{1}H NMR (insufficient solubility).

Compound **2Bc**: Yield: (50%); mp 102 °C. Anal. Calc. for $C_{17}H_{18}OI_2Te$: C, 32.95; H, 2.93; I, 40.95; Te, 20.59. Found: C, 32.77; H, 3.02; I, 41.31; Te, 20.37%. IR (cm^{-1}): 1658 ($\nu_{C=O}$). ^{1}H NMR (ppm): δ 5.57 (s, CH$_2$), 2.23–2.75 (s, 3 Me), 6.2–7.93 (m, aryl).

c. Sulfuryl chloride (0.5 ml) was added dropwise with stirring to a solution of the telluride (**1A–3A**, **1B** and **2B**) (1 mmol) in dichloromethane at 0 °C. The reaction mixture was allowed to come to the room temperature and stirred for 15 min. Concentration under reduced pressure and addition of pet-ether afforded the corresponding dichlorides. **1Aa**, yield, 82%; **2Aa**, yield, 92%; **3Aa**, yield, 82%; **1Ba**, yield, 80%; **2Ba**, yield, 81% (authentic TLC and Mp).

3.6. Halogen exchange reaction of 1Aa–3Aa, 1Ba and 2Ba with KBr and KI

a. A solution of the dichloride in chloroform was stirred with a two-fold excess of KBr for ∼8 h. A colour change from yellow to red occurred. The mixture was filtered and the filtrate reduced to approximately one fifth *in vacuo*. Addition of petroleum ether 40–60 °C (10 mL) induced crystallization, providing the corresponding dibromides (**1Ab–3Ab**, **1Bb** and **2Bb**) in good yields. Their melting points and TLC were similar to those obtained by the method D(a).

b. Iodides **1Ac** and **1Bc** were also prepared by using two-fold excess of KI and the solution of the corresponding dichlorides (**1Aa** and **1Ba**) in dichloromethane at room temperature.

In the preparation of **2Ac** slow decomposition was observed and the reaction was not continued for completion. Immediately it was filtered and the filtrate was concentrated to obtain reddish solid. The pure diiodide **2Ac** was obtained by fractional crystallization in ∼40% yield.

Compound **2Bc**: A solution of **2Ba** (1.75 g, 4 mmol) in CHCl$_3$ (10 mL) was added to a suspension of KI (three-fold excess) in CHCl$_3$ under stirring at 0 °C. The resulting greenish-brown solution was stirred for 15 min and filtered to remove the potassium salts. The solvent was removed from the filtrate and the residue, upon fractional crystallization, afforded **2Bc** (0.74 g, 30% based on **2Ba**) and the adduct Mes$_2$Te · MesTeI (0.4 g, 40% based on **2Ba**), mp 88 °C, (lit. 85.9–87.7 [7]). Anal. Calc. for $C_{27}H_{33}ITe_2$: C, 43.84; H, 4.50; I, 17.16; Te, 34.50. Found: C, 43.71; H, 4.37; I, 17.43; Te, 34.11%.

The melting points and IR spectra of the diiodides were similar to those obtained by oxidative addition of iodine to the tellurides (method 2.D.b).

Table 2
Crystal data and structure refinement

| Parameter	2Aa	2Ba
Crystal size (mm^3)	$0.52 \times 0.22 \times 0.20$	$0.19 \times 0.25 \times 0.42$
Crystal system	Triclinic	Triclinic
Space group	$P\bar{1}$	$P\bar{1}$
a (Å)	9.371(2)	9.019(2)
b (Å)	9.888(2)	14.093(3)
c (Å)	10.962(2)	14.723(4)
α (°)	65.673(3)	70.840(4)
β (°)	78.647(3)	78.203(8)
γ (°)	66.141(3)	83.120(9)
V (Å^3)	846.0(3)	1727.6(6)
Z	2	4
D_{calcd} (Mg m^{-3})	1.746	1.679
T (K)	93(2)	173(2)
θ Range (°)	2.04–28.37	1.77–30.17
Completeness to θ_{max} (%)	91.5	84.7
$R_1(F)$ $(I > 2\sigma(I))$	0.0460	0.0293
$wR_2(F)$ $(I > 2\sigma(I))$	0.1275	0.0719
R_1 (all data)	0.0482	0.0381
wR_2 (all data)	0.1300	0.0761
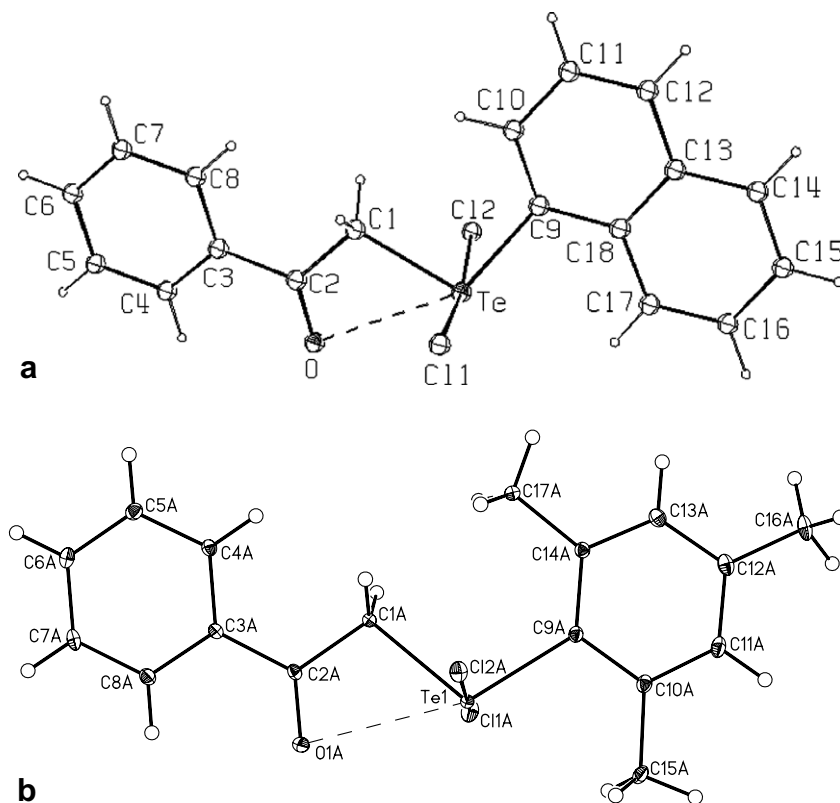
Fig. 1. ORTEP diagram showing 30% probability displacement ellipsoids and the crystallographic numbering scheme with relevant bond parameters for (a) **2Aa** d(Å) [Te–C1, 2.125(3); Te–C9, 2.118(4); Te–Cl1, 2.5120(11); Te–Cl2, 2.5174(10)]; <(°) [C1–Te–C9, 98.38(14); Cl1–Te–Cl2, 173.09(3)] and (b) **2Ba** d(Å) [Te–C1, 2.138(3), 2.141(3); Te–C9, 2.127(3), 2.121(3); Te–Cl1, 2.4819(8), 2.4753(8); Te–Cl2, 2.5081(8), 2.5517(9)]; <(°) [C1–Te–C9, 107.99(10), 107.87(10); Cl1–Te–Cl2, 173.23(3), 170.90(2)].

4. Crystallography

Single crystals of **2Aa** and **2Ba** suitable for X-ray crystallography were obtained by slow evaporation of their chloroform solutions. Intensity data were collected on a Bruker PS4 diffractometer with graphite-monochromated Mo Kα (0.7107 Å) radiation. Data were reduced and corrected for absorption using the programs SAINT and SADABS [13]. The structures were solved by direct methods and difference Fourier synthesis using SHELXS-97 implemented in the program WINGX 2002 [14]. Full-matrix least-squares refinements on F^2, using all data, were carried out with anisotropic displacement parameters applied to all non-hydrogen atoms. Hydrogen atoms were included in geometrically calculated positions using a riding model and were refined isotropically. Crystallographic parameters and details of the data collection and refinement are given in Table 2. ORTEP diagrams for compounds **2Aa** and **2Ba** are presented in Fig. 1.

Acknowledgement

Appendix A. Supplementary material

CCDC 608672 and 608671 contain the supplementary crystallographic data for **2Aa** and **2Ba**. These data can be obtained free of charge via htpp://www.ccdc.cam.ac.uk/conts/retrieving.html, or from the Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; fax: (+44) 1223-336-033; or e-mail: deposit@ccdc.cam.ac.uk.

[125]Te NMR spectra and figures depicting supramolecular architectures in the crystal packings of compounds **2Aa** and **2Ba** are provided as Supplementary material. Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.jorganchem.2006.09.050.

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