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# Synthesis of intramolecularly coordinated heteroleptic diorganotellurides and diorganotelluroxides: Isolation of monomeric diorganotelluroxide [{2,6-$(Me_2NCH_2)_2C_6H_3$}$_2$TeO] and diorganohydroxytelluronium chloride [{2,6-$(Me_2NCH_2)_2C_6H_3$}$_2$Te(OH)]Cl

Anand Gupta [a], Rajesh Deka [a], Saravanan Raju [a], Harkesh B. Singh [a, *], Ray J. Butcher [b]

[a] Department of Chemistry, Indian Institute of Technology Bombay, Mumbai, 400076, India
[b] Department of Chemistry, Howard University, Washington, DC, 20059, USA

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ABSTRACT

A series of heteroleptic diorganotellurides (2-$NMe_2CH_2C_6H_4$)(R)Te, where R = $C_6H_5$ (**5**), 2-$MeC_6H_4$ (**6**), 2,6-$MeC_6H_3$ (**7**) and 2,6-$^iPrC_6H_3$ (**8**) was synthesised from *N,N*-dimethylbenzylamine via the *ortho*-lithiation route. Reactions of **5**–**8** with $SO_2Cl_2$ followed by alkaline hydrolysis afforded diorganotelluroxides (2-$NMe_2CH_2C_6H_4$)(R)TeO, where R = $C_6H_5$ (**10**), 2-$MeC_6H_4$ (**11**), 2,6-$MeC_6H_3$ (**12**) and 2,6-$^iPrC_6H_3$ (**13**) respectively. A similar alkaline hydrolysis of homoleptic diorganotellurides, {2,6-$(Me_2NCH_2)_2C_6H_3$}$_2$Te (**9**), afforded a co-crystal of [{2,6-$(Me_2NCH_2)_2C_6H_3$}$_2$TeO] (**14a**) and disordered [{2,6-$(Me_2NCH_2)_2C_6H_3$}$_2$Te(OH)]Cl (**14b**) or a completely ordered diorganohydroxytelluronium chloride [{2,6-$(Me_2NCH_2)_2C_6H_3$}$_2$Te(OH)]Cl (**14c**). Heteroleptic diorganotellurides **7**–**8** and telluroxides **10**–**14a-b** and diorganohydroxytelluronium chloride **14c** were characterised by single crystal X-ray diffraction studies. In the molecular structures, the N-donor substituent made five membered chelating ring with the tellurium atom via Te···N secondary bonding interactions. Diorganotelluroxide **10** existed in dimeric form exhibiting both intramolecular Te···N and intermolecular Te···O secondary interactions. Due to the strong intramolecular Te···N secondary bonding interactions from the three N-donor substituents, diorganotelluroxide **14a** was stabilised in the monomeric form. This is, in fact, the only second example of a discrete monomeric diorganotelluroxide. Again, because of the presence of intramolecular Te···N secondary bonding interactions, the diorganotelluroxides **10**–**14a-b** and diorganohydroxytelluronium chloride **14c** exhibited downfield $^{125}$Te NMR chemical shift as compared with the earlier reported oligomeric or polymeric diorganotelluroxides.



## 1. Introduction

Organotelluroxanes, a class of tellurium derivatives containing Te–O covalent bond, have become an important research area in organometallic chemistry with respect to their promising applications in various aspects such as in, catalysis [1–3], oxygen transfer reactions [4–6], developing supramolecular synthons [7–9], synthesis of biologically active compounds [10–13], and $CO_2$ fixation [14,15] to name a few. Within this broad context, diorganotelluroxide ($R_2TeO$), a class of tellurium(IV) compounds have gained significant attention with respect to their structural heterogeneity [16–19], stabilisation by intramolecular secondary bonding interactions [20,21] and more importantly with their diverse reactivity [1,2,4–6,14,15,22,23]. Due to the presence of polar Te=O bond, one of the promising reactions of diorganotelluroxide in organometallic chemistry is the oxidation reaction, where it acts as a mild oxidant. In particular, the oxidizing properties of various diorganotelluroxides towards the conversion of different alcohols, xanthates, phosphines, thiobezoates, *etc.* to their corresponding oxo derivatives have been comprehensively studied in literature [22,24–28].

Although, the synthesis of first diorganotelluroxide, $Ph_2TeO$ was

* Corresponding author.
*E-mail address:* chhbsia@chem.iitb.ac.in (H.B. Singh).

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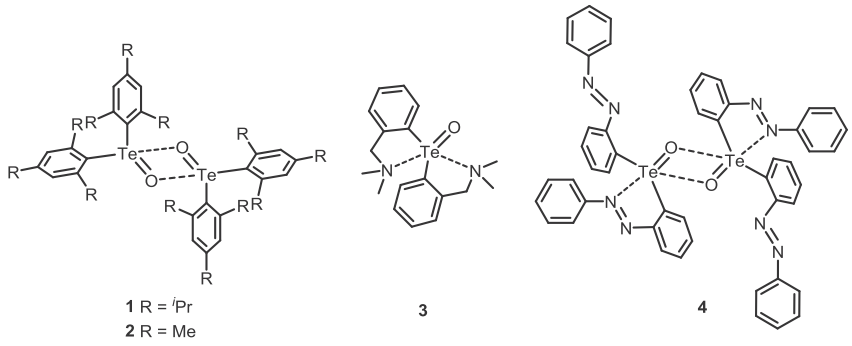


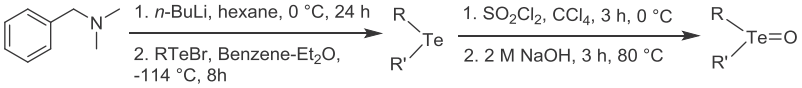

**Chart 1.** Examples of monomeric and dimeric diorganotelluroxides.

reported in 1894 [29], its structural elucidation remained elusive for a long time, until Alcock et al. reported the molecular structure of $Ph_2TeO$ in dimeric form [16]. In fact, it is worth noting that most of diorganotelluroxides exist in aggregated form (dimer or polymer) in their solid states, which is accountable to their polar Te=O bonds [16–19,21,30]. Oba et al. have incorporated bulky aryl groups namely, 2,4,6-triisopropylphenyl (Tip) and 2,4,6-trimethylphenyl (Mes) and reported the synthesis of diorganotelluroxides, $Tip_2TeO$, **1** and $Mes_2TeO$, **2** (Chart 1) [30]. (Chart 1 should be ideally placed before Scheme 1.) Diorganotelluroxides **1** and **2** exist in the dimeric form originating from the intermolecular Te···O secondary interactions. Klapötke et al., fortuitously, isolated the first monomeric telluroxide, $(2\text{-}Me_2NCH_2C_6H_4)_2TeO$, **3** stabilised by intramolecular Te···N secondary bonding interactions from the N donor atoms of the side arms to the Te atom [20]. Recently, our group has reported the synthesis of bis(2-phenylazophenyl-C,N')tellurium(IV) oxide, **4** by alkaline hydrolysis of bis(2-phenylazophenyl-C,N')tellurium(IV) dichloride in ethanolic solution [21]. Due to the steric constraints from the bulky azo groups, only one of the two $sp^2$ N-donor substitutions was involved in secondary bonding interactions to the tellurium atom. Consequently, telluroxide **4** was stabilized in dimeric form consisting of both intramolecular Te···N and intermolecular Te···O secondary interactions. Interestingly, when (2-phenylazophenyl-C,N')tellurium(IV) trichloride was subjected to alkaline hydrolysis in THF solution, it underwent condensation to afford heptatellurium covalent cluster stabilized by extensive Te···N secondary bonding interactions [31]. One of the interesting aspects of diorganotelluroxide ($R_2TeO$) is that, due to the polar and basic nature of Te=O bond, it readily undergoes hydrolysis in presence of moisture to afford diaryltellurium dihydroxide, $[R_2Te(OH)_2]$ [32–34]. The diaryltellurium dihydroxide, being unstable by nature, can further undergo dissociation resulting in the formation of diarylhydoxytelluronium(IV) cation, $[R_2Te(OH)]^+$. Beckmann et al. have synthesized intramolecularly coordinated diorganotelluroxide, $(8\text{-}Me_2NC_{10}H_6)_2TeO$ and reacted with triflic acid ($HO_3SCF_3$). It was observed that diorganotelluroxide $(8\text{-}Me_2NC_{10}H_6)_2TeO$ underwent protonation and afforded diarylhydroxytelluronium triflate, $[(8\text{-}Me_2NC_{10}H_6)_2Te(OH)](O_3SCF_3)$ [33]. Similar results were also observed when $(p\text{-}MeOC_6H_4)TeO$ was treated with $HO_3SCF_3$ or diphenylphosphinic acid ($HO_2PPh_2$) [34].

From the literature studies, it is perceived that most of the diorganotelluroxides reported so far are 'homoleptic' *i.e.*, both the 'R' group in $R_2TeO$ are identical. Herein, in the present work, we report the synthesis of a series of intramolecular interaction stabilized 'heteroleptic' diorganotelluroxides, **10**–**13**, where one of the 'R' groups contains 'one coordinating group' with $sp^3$ N- donor atom. Recently we have reported the ligation behavior of homoleptic diorganotelluride namely bis[{2,6-(dimethylamino)methyl}phenyl]telluride, **9** containing four coordinating $sp^3$ N-donor atoms [35]. In this paper, we envisaged to explore the oxidation reaction of **9** and report the synthesis of the 'second' example of a monomeric diorganotelluroxide, **14a** and its protonated derivatives **14b-c**. The structures of the synthesized diorganotelluroxides, **10**–**14a-b** and diorganohydroxytelluronium chloride **14c** were thoroughly studied both in solution states as well as solid states (telluroxide **10** and **14a-b** and diorganohydroxytelluronium chloride **14c**) and are compared with the similar reported diorganotelluroxides and diorganohydroxytelluronium salts.

## 2. Results and discussion

In order to synthesize diorganotelluroxides **10**–**13**, first diorganotellurides **5** [36]-**8** were synthesized by the *otho*-lithiation route as reported in the literature (Scheme 1) [36,37]. In particular, *N,N*-dimethylbenzylamine was treated with *n*-BuLi to afford the aryllithium intermediate. When aryltelluryl bromides, RTeBr (generated *in situ* by slow addition of dry benzene solution of $Br_2$ to the $Et_2O$ solution of $R_2Te_2$ at −114 °C; R = $C_6H_5$, 2-$MeC_6H_4$, 2,6-$MeC_6H_3$, 2,6-$^iPrC_6H_3$) were added to the lithiated intermediates, nucleophilic substitution reactions took place at the tellurium centers to afford diorganotellurides, **5**–**8**. Diorganotellurides **5**–**8** were purified by column chromatography using petroleum ether (60–80%) as eluent. The first fraction was isolated as the corresponding diorganoditellurides ($R_2Te_2$) and the second fraction obtained was the desired diorganotellurides **5**–**8**. The yield of the diorganotellurides ranged from 42 to 45% in all the cases. It is




**5** R = 2-$Me_2NCH_2C_6H_4$; R' = $C_6H_5$
**6** R = 2-$Me_2NCH_2C_6H_4$; R' = 2-$MeC_6H_4$
**7** R = 2-$Me_2NCH_2C_6H_4$; R' = 2,6-$Me_2C_6H_3$
**8** R = 2-$Me_2NCH_2C_6H_4$; R' = 2,6-$^iPr_2C_6H_3$

**10** R = 2-$Me_2NCH_2C_6H_4$; R' = $C_6H_5$
**11** R = 2-$Me_2NCH_2C_6H_4$; R' = 2-$MeC_6H_4$
**12** R = 2-$Me_2NCH_2C_6H_4$; R' = 2,6-$Me_2C_6H_3$
**13** R = 2-$Me_2NCH_2C_6H_4$; R' = 2,6-$^iPr_2C_6H_3$

**Scheme 1.** Synthesis of diorganotellurides **5**–**8** and diorganotelluroxides **10**–**13**.

worth-mentioning that the formation of corresponding ditellurides significantly reduced the yield of the desired tellurides. Diorganotelluride, **9** was synthesized from 2-bromo-1,3-bis[(dimethylamino)methyl]benzene by the treatment of *n*-BuLi followed by addition of Te(dtc)$_2$ (dtc = diethyldithiacarbamate) [35]. The synthesis of diorganotelluroxides **10**–**13** from the corresponding diorganotellurides **5**–**8** was achieved by chlorination followed by alkaline hydrolysis. In detail, when tellurides **5**–**8** were chlorinated by $SO_2Cl_2$, the corresponding diorganyltellurium(IV) chlorides were obtained. The diorganyltellurium(IV) chlorides on alkaline hydrolysis by NaOH afforded the desired diorganotelluroxides **10**–**13** (Scheme 1).

Interestingly, the oxidation reaction of **9** with $SO_2Cl_2$/NaOH was not as straightforward and provided varied oxidized products from preparation to preparation (Scheme 2). The initial oxidation experiment provided a co-crystal of novel monomeric telluroxide **14a** and zwitterionic telluroxane **14b** (as evident by single crystal X-ray diffraction studies, *vide infra*). In order to check the reproducibility of the experiments, when the experiment was repeated, it offered completely ordered diorganohydroxytelluronium chloride **14c** (*vide infra*).

The $^1$H NMR spectra of diorganotellurides **5**–**8**, recorded in $CDCl_3$ at room temperature, showed sharp singlet at ~2.2 ppm corresponding to the -N($C\underline{H}_3$)$_2$ protons from the *N,N*-dimethylbenzylamine moiety. The benzylic protons attached to the -N($CH_3$)$_2$ showed a sharp singlet at ~ 3.4 ppm for all the tellurides. The aromatic protons and the protons corresponding to the substituent(s) on the ancillary phenyl ring showed resonances in the expected regions with appropriated integration values (*vide infra*). Interestingly, in the corresponding $^1$H NMR spectra of telluroxides **10**–**13**, due to the geminal coupling, the two benzylic protons resolved in to two discrete diastereotopic signals. The splitting of the benzylic protons in the telluroxides in comparison to that of the corresponding tellurides might be attributed to the more restricted rotation of the side arms around the tellurium center due to the presence of Te=O bond.

The $^{125}$Te NMR chemical shifts for the synthesized tellurium derivatives are given in Table 1. The $^{125}$Te NMR spectra of all the synthesized tellurium derivatives exhibited single resonance signals suggesting the desired purity and stability of the compounds. In particular, the $^{125}$Te NMR signals for tellurides **5**–**9** appeared in the region 633-350 ppm (Table 1). These chemical shifts are considerably downfield shifted in comparison to other related diorganotellurides which lacked intramolecular coordinating N-donor substituents [38]. The $^{125}$Te NMR signals for the telluroxanes **10**–**14a-c** were significantly downfield shifted in comparison to the corresponding tellurides and appeared in the region 1223–1256 ppm. The significant downfield shifts of the telluroxanes **10**–**14** in comparison to that of the tellurides, **5**–**9,** are attributed to the presence of polar Te=O bonds in the former. These chemical shifts in **10**–**14** are in agreement with the values reported in the literature for similar telluroxides. For example, telluroxide **4** exhibited $^{125}$Te NMR chemical shift at 1228 ppm [21]. Similarly (8-$Me_2NC_{10}H_6$)$_2$TeO exhibited chemical shift at 1255 ppm (in $CD_3OD$) and 1272 ppm (in $CDCl_3$) [33].

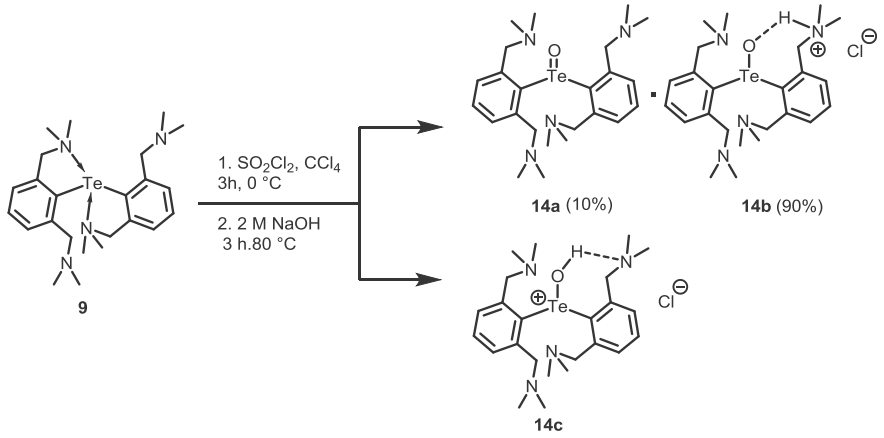
**Table 1**
$^{125}$Te NMR chemical shifts for tellurides **5**–**9** and telluroxides **10**–**14**.

| $^{125}$Te NMR of tellurium compounds | | | |
|---|---|---|---|
| Telluride | Chemical shift ($\delta$) in ppm | Telluroxide | Chemical shift ($\delta$) in ppm |
| **5** | 633 | **10** | 1223 |
| **6** | 549 | **11** | 1214 |
| **7** | 410 | **12** | 1240 |
| **8** | 350 | **13** | 1256 |
| **9** [37] | 367 | **14** | 1119 |

The High Resolution Electrospray Ionization Mass Spectrometry (HRMS) also aided validation of the synthesized tellurides **5**–**9** and telluroxanes **10**–**14**. In the mass spectra taken in the positive ion mode, the molecular ion peaks at *m*/z 342.0495 (Calc. 342.0497 [M+H]$^+$) (**5**), 356.0654 (Calc. 356.0653 [M+H]$^+$) (**6**), 370.0811 (Calc. 370.0810 [M+H]$^+$) (**7**), 426.1436 (Calc. 370.1436 [M+H]$^+$) (**8**) substantiated the formation of the tellurides. Similarly, in cases of the mass spectra of telluroxides **10**–**14**, the molecular ion peaks at *m*/z 358.0445 (Calc. 358.0446 [M+H]$^+$) (**10**), 372.0601 (Calc. 372.0602 [M+H]$^+$) (**11**), 386.0758 (Calc. 386.0759 [M+H]$^+$) (**12**), 442.1388 (Calc. 442.1385 [M+H]$^+$) (**13**) confirmed the formation of the respective compounds. It is worth noting that the observed patterns in HRMS of all the compounds were in agreement with the simulated isotopic patterns.

Interestingly, in the $^{125}$Te NMR spectrum of telluroxide **14a-b**, a single resonance was observed at 1119 ppm. This observation is probably due to the fluxional behavior of the proton between the two compounds, **14a** and **14b**. In the HRMS spectra of **14a-b** and **14c**, the molecular ion peak at *m*/z 529.2183 (for **14a-b**) and 529.2188 (for **14c**) was assigned to the [**14a** + H]$^+$, [**14b**]$^+$ and [**14c**]$^+$ (Calc. 529.2182) species respectively. The observed patterns in HRMS perfectly matched with the theoretical isotopic patterns. Again, the absence of any promising peaks with characteristic Te-isotopic pattern in the *m*/z range 0–1400 of the spectrum further substantiated the absolute formation of telluroxide **14a-b** and **14c**.

In the $^1$H NMR spectrum of **14a** and **14b**, all the signals appeared




**Scheme 2.** Synthesis of monomeric diorganotelluroxides **14a-b** and diorganohydroxytelluronium chloride **14c**.

broad, which in turn, could not be adequately integrated. The broadening of the signal could be probably due to the fluxional nature of the proton and interconversion of **14a** ↔ **14b** in the solution state. In fact, from the solid state structural analysis, it was revealed that in compound **14b**, another equilibrium is present where **14b** and **14c** existed as tautomer in the ratio 72.2(1):27.8(1) (*vide infra*). Such broadening of signals in $^1$H spectrum of **14a-b** is not unusual, as similar complexity in $^1$H spectra of intramolecularly coordinated diorganotelluroxanes has been observed in the literature [33,34], as these molecules are prone to fluxional behavior in solution state. In comparison to the $^1$H NMR spectrum of **14a**-**b**, the corresponding $^1$H NMR spectrum of **14c** was well-resolved. The aromatic protons showed resonances in the range 7.1–8.1 ppm. The chemical shifts for the benzylic protons were observed in the range 2.5–4.5 ppm. Out of the four methylene groups one showed AB pattern and appeared in the down field region. This might be due to the interactions of the corresponding nitrogen atom to the tellurium center. In the IR spectrum of compound **14c**, the absorption at $\bar{\upsilon} = 3417\ cm^{-1}$ corresponded to the O–H stretching vibration involved in hydrogen bonding interactions. It is worth mentioning that the formation of diorganotelluroxides **14a**-**b** and diorganohydroxytelluronium chloride **14c** from telluride under similar conditions might be attributed to the generation of varying amounts of HCl during hydrolysis. Interestingly, in both the reactions only one HCl molecule is trapped.

## 3. Crystal structures

To confirm the proposed formulations of the synthesized compounds, we obtained single crystals for X-ray diffraction experiments. The molecular structure of monotelluride **7** is shown in [Fig. 1a]. In the molecular structure, the unit cell contains two molecules of compound **7**. The spatial arrangement around Te atom is distorted T-shaped, taking the Te···N intramolecular interaction in to account. The tellurium atom is bonded to two carbon atoms with Te1–C1 and Te1–C10 distances of 2.123(4) Å and 2.156(5) Å respectively. It is worth mentioning that due to the hypervalent interaction, the Te1–C10 bond, which *trans* to the amino group, is elongated in comparison to that of Te1–C1 bond. These distances are in the agreement with the sum of the single bonded covalent radii for Te–C (2.11 Å) bond, as suggested by Pauling [39]. The N1···Te1–C10 bond angle 165.1(1)° deviates from linearity, whereas N1···Te1–C1 angle is 71.2(1)°. The intramolecular Te1···N1 bond lengths of 2.786 (4) Å is much shorter than Σ $r_{vdw}$ (Te, N) *i.e.* 3.58 Å but are longer than Σ $r_{cov}$ (Te, N) *i.e.* 2.09 Å [39,40]. This Te···N bond distance is in close agreement with the values observed in telluride **5** [36] and other related compounds, namely bis[2-(phenylazo)phenyl-C,N']telluride [2.62(2) Å] [21], bis[2-(4′-methoxyphenyl)iminomethinylphenyl]telluride [2.702(3) Å] [41], bis(2-isopropyl-iminomethinylphenyl)telluride) [2.720(2) Å] [41], 8-(dimethylamino)naphthylphenyltelluride [2.713(1) Å] [42]. The C1–Te1–C10 angle is 93.93 (16)° and is close to the related diorganotellurides [21, 36, 41–42].

The molecular structure of compound **8** [Fig. 1b] is similar to that of **7**, except the fact that in the place of phenyl ring, diisopropylphenyl unit is bonded to the tellurium atom. The intramolecular Te1···N1 distance is 2.844 (2) Å, is slightly longer than that observed for compound **7**. The N1···Te1–C10, N1···Te1–C1, C1–Te1–C10 bond angles are 165.91 (7)°, 70.64 (7)° and 95.41 (8)° respectively. All these bond angles are in line with that of the previous structure, **7**. Again, Te1–C1 and Te1–C10 distances of 2.122(2) Å and 2.167(2) Å respectively closely resemble with the respective bond distances observed in compound **7**.

The molecular structure of telluroxide **10** is shown in Fig. 2. In the unit cell of telluroxide **10**, two asymmetric units are connected to a water solvent molecule via H-bonding. Compound **10** exists as a dimer consisting of a $Te_2O_2$ core with two different Te–O distances, one characteristic Te–O double bond and other one is elongated coordinative bond. The structure of the compound essentially resembles to that of the previously reported dimeric diaryltellurium(IV) oxides [16–18,30]. The geometry around each tellurium atom is distorted square pyramidal. The Te–O double

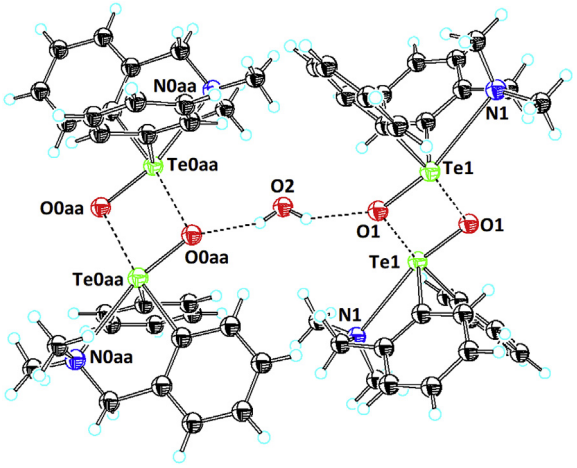



**Fig. 2.** Molecular structure of dimeric telluroxide, **10** at 50% probability level.

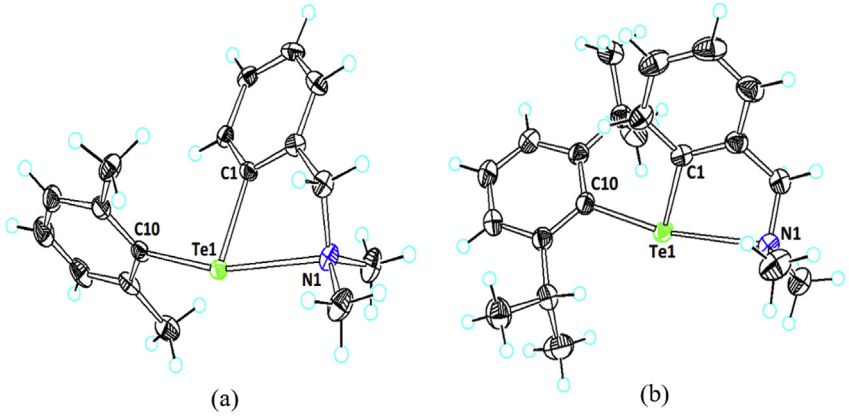



**Fig. 1.** Molecular structures of (a) **7** and (b) **8** at 50% probability level.

bond distance is 1.872 (3) Å, which is in agreement with the corresponding Te–O bond distances observed in similar dimeric telluroxides such as $Ph_2TeO$ [1.871(2) Å] [16], $(C_6F_5)_2TeO$ [1.872 (2)/ 1.87(1) Å] [17,18], **1** [1.853(5)], **2** [1.855(4)] [30], **4** [1.864 (12) Å] [21]. Similarly, the secondary intermolecular Te···O distance of 2.525(3) Å is close to that observed for $Ph_2TeO$ [2.563(21), 2.545(22) Å] [16], **1** [2.536(5) Å, 2.518(4) Å], **2** [2.613(4) Å, 2.647(4) Å] [30] and **4** [2.623(12) Å] [21]. The intramolecular Te···N secondary bonding distance of 2.819(3) Å is considerably longer than that of **3** [2.755(6) and 2.565(4) Å] [20], **4** [2.714(1) Å] [21]. The C1–Te1–C10 bond angle in **10** is 94.27(16)°, which is again in the same range of the corresponding bond angles found in $Ph_2TeO$ [90.6(6)°, 91.8(6)°] [16], **1** [94.7(2)°], **2** [94.1(2)°, 96.8(2)°] [30] and **4** [90.69(6)°] [21].

The title compound **14** was a co-crystal of a salt, $[C_{24}H_{39}N_4OTe]^+Cl^-$ (**14b**) and the neutral molecule, $[C_{24}H_{38}N_4OTe]$ (**14a**) as well as a water solvent molecule at full occupancy. The occupancy factors were 0.9059(7) for the salt and 0.0941(7) for the neutral molecule (Fig. 3). Each component will be discussed separately but it is notable that both contain rare examples of a monomeric telluroxide moiety. Even in the major component, *i.e.*, in **14b**, the H-atom is distributed between the telluroxide O-atom and the proximal N-atom. In the major component, it is attached to N1B with occupancy of 0.6545(15) and in the minor component it is attached to O1A with occupancy of 0.2514(15) [both values add up to 0.9059 which is the occupancy of the major component overall and the ratio between the major component and minor component within **14b** is 72.2(1):27.8(1)]. For the major tautomer, there is a very strong hydrogen bond between N1B and O1A [N1B···O1A separation of only 2.621(4)]. In the major component, i.e., the salt **14b** (Fig. 3a), the central Te is six coordinate with a coordination sphere made up of a terminal Te–O (with H delocalized between O1A and N1B), 2 C donors from two phenyl rings and three of the possible 4 N donor atoms. This results in a very distorted octahedral arrangement where the *trans* angles range from 156.74(11)° to 174.30(8)° and the *cis* angles range from 69.48(8)° to 116.97(9)°. In the coordination sphere, the terminal Te–O bond at 1.943(3) Å is longer than that observed in previous telluroxides containing Te=O bonds [16–21] while the Te–C distances at 2.1229(18) Å and 2.1756(18) Å are in the normal range. The Te–N distances at 2.665(3) Å, 2.676(3) Å and 2.755(3) Å, while longer than typical Te–N single bonds, are much shorter than the sum of the van der Waals radii for these atoms [40]. The two phenyl rings occupy *cis* position in the Te coordination sphere and are twisted with respect to each other making a dihedral angle of 60.0(1)°.

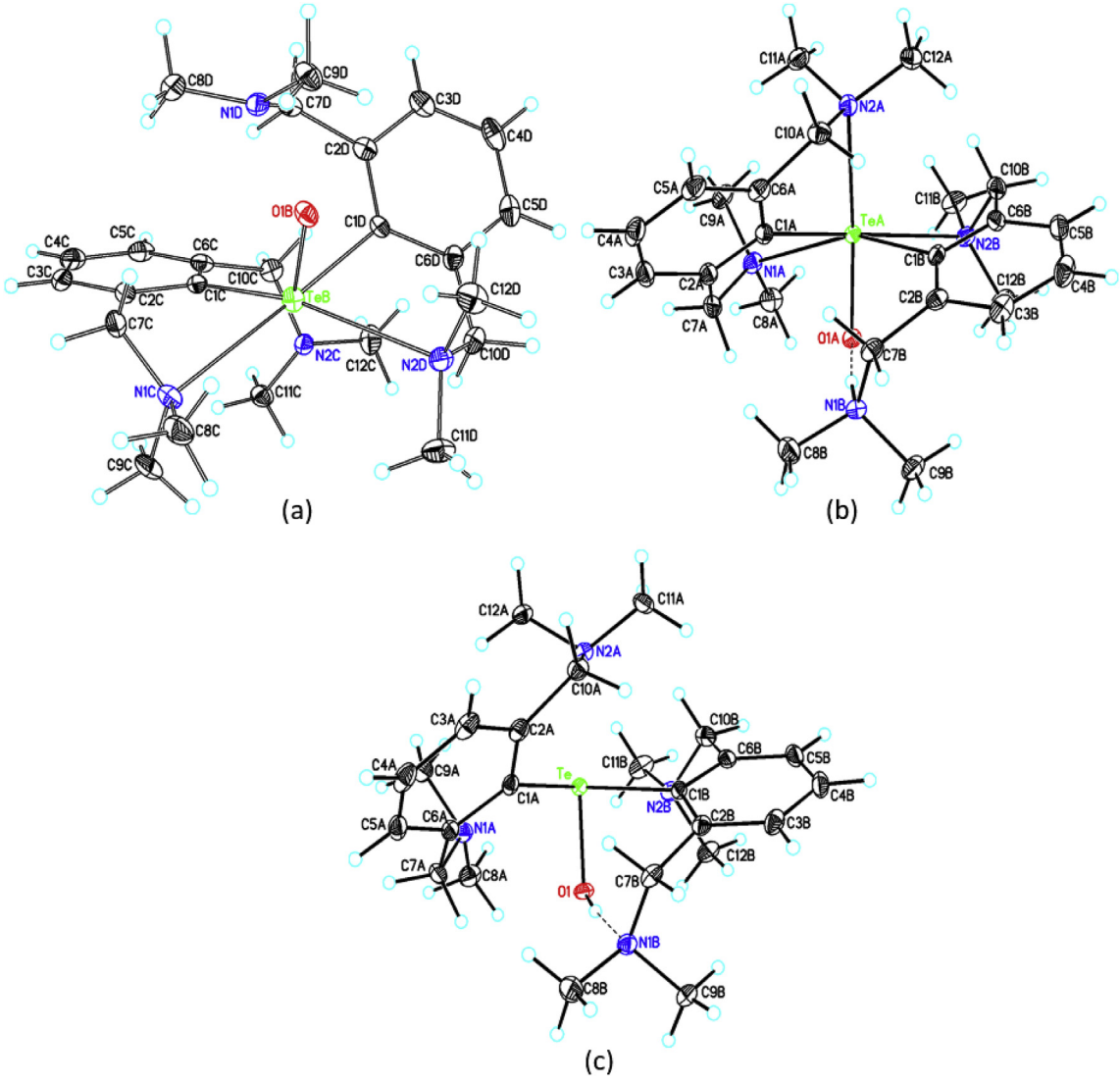



**Fig. 3.** Molecular structures of (a) **14a** and (b) cation of **14b**(major tautomer only) and (c) cation of **14c**.

There is no evidence of either π… π stacking or C–H… π interactions, thus the major influence on the packing arrangement is a hydrogen bonding scheme (see in Supporting Information, Fig. S36) which involves both intra- and interspecies hydrogen bonds. There is a strong intra-species hydrogen bond involving the $N^+$-H and the Te–O moieties [N….O distance of 2.626(5) Å and N–H···O angle of 174.3(4)°]. The major influence in the packing results from the cations, chloride anion and water molecules linked into ribbons in the 1 0 1 direction by O–H···Cl, C–H···Cl and O–H···O hydrogen bonds. In the minor tautomer the O–H group forms a weaker hydrogen bond with N1A.

The minor component, [$C_{24}H_{38}N_4OTe$], **14a** is only at 0.0941(7) occupancy and thus the esd's on its metrical parameters are significantly larger than those of the major component. In addition, the coordination sphere about the central Te is significantly different from that in the cation as in this case the Te is five coordinate with a distorted square pyramidal geometry ($\tau = 0.287$) (Fig. 3b). The coordination sphere is made up of the terminal O, 2 C donors from two phenyl rings and two N donors (one each from the two ligands). The terminal Te=O distance is 1.83(3) Å, a value which is much closer to those found in other telluroxides [16–21] and significantly shorter than that observed in the cation, **14b**. The Te–C [2.084(5) Å, 2.222(5) Å] and Te–N [2.678(5) Å, 2.763(5)Å] distances are similar to those observed in the cation. As is observed for the cation, the two phenyl donors occupy *cis* positions in the coordination sphere and are significantly twisted with a dihedral angle of 57.1(1)°.

Obviously the packing arrangement for the neutral molecule cannot be the exactly the same as that observed for the salt. However, since they are co-crystals (or alternatively considered as a 9% doping into the major lattice), the packing arrangement looks quite similar as observed from an examination of the two packing diagrams (see in Supporting Information, Fig. S37). There is no $N^+$-H group or $Cl^-$ anion but the $H_2O$ molecule is still present and dominates the packing arrangement. The major packing interactions involve O–H···O(terminal) and C–H···O(water) within the stoichiometric unit with no interactions between units. Thus in the absence of both the $N^+$-H group and $Cl^-$ anion there are no ribbons in the 1 0 1 direction.

In order to test the reproducibility of this reaction, it was repeated under identical conditions and new crystals were obtained. Even though the cell constants for the new sample were identical to those previously obtained (within experimental errors), a new structure was obtained (**14c**). In this case there was no disorder, no minor component, and no minor tautomer and only the salt was obtained, which had metrical parameters which were identical to the major component in **14b** but with a better overall result (i.e. lower esd's). Unlike the previous case, in **14b** where the H was only partially attached to O (ca. 27.8%) in **14c** it is completely localized on O confirming that both **14a-b** and **14c** are hydroxytelluronium cations (for these metrical parameters for both **14b** and **14c** along with figures of all species present see ESI). Thus **14c** can be considered to be a pseudo-polymorph as well as a tautomer of **14b**.

## 4. Conclusion

As an extension of our previous work for the synthesis of diorganotelluroxides stabilized by secondary bonding interactions [21], here we have reported the synthesis of a series of intramolecularly coordinated heteroleptic diorganotelluroxides. To overcome the steric constraints observed in the previous work due to the presence of two bulky azo groups, in the present work we have used heteroleptic diorganotellurides as a precursors that contain flexible $sp^3$ N-donor arm(s). When diorganotellurides with one coordinating group are used, similar to our earlier observations, we have obtained dimeric diorganotelluroxides stabilized by both intramolecular Te···N and intermolecular Te···O secondary interactions. However, when a pincer type substrate is used where each aryl substrate contains two coordinating groups, we have succeeded in isolating the second example of monomeric, homoleptic diorganotelluroxide, **14a** and its protonated derivative **14b**. Interestingly, in order to check the reproducibility of the reaction, when the oxidation of **9** was carried out under identical conditions, the tautomer of **14b**, where the proton was located on oxygen was isolated and the structure was completely orders. In diorganotelluroxide, **14** the N-donor substituents offered extensive intramolecular Te···N secondary bonding interactions to the Te atom and thereby sufficing the coordination environment around Te center. This results in the isolation of a monomeric telluroxide entity.

## 5. Experimental section

### 5.1. Materials and methods

All manipulations were performed under a $N_2$ atmosphere using standard Schlenk techniques. Solvents were dried by following standard methods. The starting materials and solvents were purchased from commercial sources. $^1$H (400 and 500 MHz), $^{13}$C (100 and 125 MHz) and $^{125}$Te (126 MHz, 158 MHz) NMR spectra were recorded on Bruker AV 400 MHz and Bruker AV 500 MHz spectrometers at 25 °C. Chemical shifts cited were referenced to TMS ($^1$H, $^{13}$C) as internal and $Me_2Te$ ($^{125}$Te) as external standard. Electron spray mass spectra (ESI-MS) were performed on a Q-Tof micro (YA-105) mass spectrometer. Melting points were recorded in capillary tubes on a Veego VMP-1 instrument and are uncorrected.

### 5.2. General procedure for synthesis of diaryltelluride (*5*–*8*)

A stirred solution of *N*,*N*-dimethylbenzylamine (1.95 mL, 1.78 g, 13.16 mmol) in dry $Et_2O$ (50 mL) was treated dropwise with 1.6 M solution of *n*-BuLi in hexane (8.23 mL, 13.16 mmol) at 0 °C under nitrogen atmoshphere for 30 min. The reaction mixture was allowed to stir for 24 h at room temperature to give a white suspension of the lithiated product. A solution of ArTeBr (Ar = $C_6H_5$, 2-$MeC_6H_4$, 2,6-$Me_2C_6H_3$, 2,6-$^i$Pr$MeC_6H_3$) was prepared *in situ* by slow addition of solution of $Br_2$ in benzene (10 mL) at −114 °C to the solution of $Ar_2Te_2$ (Ar = $C_6H_5$, 2-$MeC_6H_4$, 2,6-$Me_2C_6H_3$, 2,6-$^i$Pr-$MeC_6H_3$) in 150 mL of $Et_2O$. The solution was stirred for 30 min In an ice bath. The white suspension of the lithiated product was transferred *via* a cannula to the dark red RTeBr reagent at −114 °C and the resulting suspension was stirred for 2 h at the same temperature and at room temperature for 6 h. after completion of the reaction (monitored by TLC), saturated $NH_4Cl$ aqueous solution (100 mL) was added. The reaction mixture was extracted with $Et_2O$ (25 mL x 3) and the organic phase was washed with $H_2O$, dried over anhydrous $Na_2SO_4$ and concentrated over rotary evaporator. The resulting semi-solid was purified by column chromatography using petroleum ether (60–80%) as eluent. The first fraction isolated was $Ar_2Te_2$ and second fraction was desired diorganotellurides **5**–**8**

**Synthesis of 5** [36]. Reagents used were $C_6H_5TeBr$, prepared by $Br_2$ (1.05 g, 6.58 mmol), 1,2-diphenylditelluride (2.69 g, 6.58 mmol). A yellowish liquid which solidified upon cooling to give crystalline solids (yield: 0.75 g, 42%); m.p. 77–80 °C (lit 77 °C [36]). $^1$H NMR (400 MHz, $CDCl_3$): δ (ppm) 7.80 (d, 2H, Ar–H), 7.29–7.27 (m, 1H, Ar–H), 7.20–7.16 (m, 2H, Ar–H), 7.09 (d, 1H, Ar–H), 7.02–7.00 (d, 2H, Ar–H), 6.84 (t, 1H, Ar–H), 3.46 (s, 2H, $ArCH_2$), 2.18 (s, 6H, $NMe_2$). $^{13}$C NMR (100 MHz, $CDCl_3$): δ (ppm) 140.84, 140.53, 134.73, 129.32, 128.73, 128.01, 127.97, 125.94, 122.91, 121.11, 66.38, 43.89. $^{125}$Te NMR

(126 MHz, $CDCl_3$): δ (ppm) 633. ESI-MS (positive mode): $[M+H]^+$ $m/z = 342.0495$(observed), 342.0497 (calculated).

**Synthesis of 6.** Reagents used were 2-$MeC_6H_4TeBr$ (*in situ*) prepared by $Br_2$ (1.05 mL, 6.58 mmol), 1,2-di-o-tolylditelluride (2.88 g, 6.58 mmol). A Yellowish liquid which solidified upon cooling. yield: 0.80 g (45%). $^1H$ NMR (400 MHz, $CDCl_3$): δ (ppm) 7.88 (d, 1H, Ar–H), 7.20 (s, 2H, Ar–H), 7.00–6.94 (m, 4H, Ar–H), 6.81 (t, 1H, Ar–H), 3.43 (s, 2H, $ArCH_2$), 2.37 (s, 2H, Ar-$CH_3$), 2.17 (s, 6H, $NMe_2$). $^{13}C$ NMR (100 MHz, $CDCl_3$): δ (ppm) 144.59, 142.21, 141.07, 134.51, 129.09, 128.99, 128.81, 128.01, 126.60, 125.93, 124.13, 122.56, 66.55, 44.00, 27.22. $^{125}$TeNMR (126 MHz, $CDCl_3$): δ (ppm) 549. ESI-MS (positive mode): $[M+H]^+$ $m/z = 356.0654$ (observed), 356.0653(calculated).

**Synthesis of 7.** Reagents used were 2,6-$Me_2C_6H_3TeBr$ (*in situ*) prepared by $Br_2$ (1.05 mL, 6.58 mmol) [1,2-bis(2,6-dimethylphenyl) ditelluride] (3.06 g, 6.58 mmol). White solid, yield: 0.78 g (44%); m.p. 88–90 °C. $^1H$ NMR (400 MHz, $CDCl_3$): δ (ppm) 7.17–7.14 (m. 1H, Ar–H), 7.13–7.11 (m, 1H, Ar–H), 7.05 (d, 2H, Ar–H), 6.98 (t, 1H, Ar–H), 6.85 (t, 1H, Ar–H), 6.61 (d, 1H, Ar–H), 3.42 (s, 2H, Ar-$CH_2$), 2.35 (s, 6H, $CH_3$), 2.20 (s, 6H, $NMe_2$) $^{13}C$ NMR (100 MHz, $CDCl_3$): δ (ppm) 143.82, 138.74, 135.95, 132.55, 129.74, 129.35, 129.13, 128.90, 128.44, 128.00, 127.97, 125.24, 64.67, 45.07, 24.49. $^{125}$Te NMR (126 MHz, $CDCl_3$): δ (ppm) 410. ESI-MS (positive mode): $[M+H]^+$ $m/z = 370.0811$ (observed), 370.0810(calculated).

**Synthesis of 8.** Reagents used were 2,6-$^iPr_2C_6H_3TeBr$ (*in situ*) prepared by $Br_2$ (1.05 mL, 6.58 mmol) [1,2-bis(2,6-di*iso*propylphenyl)ditelluride] (3.80 g, 6.58 mmol), provided a white solid. Yield 0.76 mg (43%), m.p. 95–97 °C. $^1H$ NMR (400 MHz, $CDCl_3$): δ (ppm) 7.28 (t, 1H, Ar–H), 7.14 (t, 2H, Ar–H), 7.01 (d, 1H, Ar–H), 6.94 (t, 1H, Ar–H), 6.83 (d, 1H, Ar–H) 6.77–6.73 (m, 1H, Ar–H), 3.69 (sept, 2H, Ar-CH), 3.46 (s, 2H, Ar-$CH_2$), 2.21 (s, 6H, $NMe_2$), 1.05 (d, 12H, *iso*-propyl). $^{13}C$ NMR (100 MHz, $CDCl_3$): δ (ppm) 155.53, 140.91, 134.67, 129.77, 128.73, 128.68, 127.84, 125.60, 123.93, 122.93, 66.84, 44.20, 39.51, 24.83. $^{125}$Te NMR (126 MHz, $CDCl_3$): δ (ppm) 350. ESI-MS (positive mode): $[M+H]^+$ $m/z = 426.1436$ (observed), 426.1436 (calculated).

### 5.3. General procedure for the oxidation of tellurides **10**–**14** by halogenation followed by hydrolysis

A solution of tellurides **5**–**9** in $CCl_4$ (15 mL) was chlorinated by gradual addition of $SO_2Cl_2$ in $CCl_4$ solution (10 mL) at 0 °C under inert atmosphere and the solution was stirred for an additional 30 min and was then permitted to stir at room temperature for additional 3 h. The precipitate formed was filtered and washed with hexane (2x10 mL). The resulting solid was dried under vacuum to afford white solids of the corresponding diorganyltellurium(IV) chlorides and was used as such for the next step without any further purification. A suspension of the chlorinated compound in 2 M NaOH (10 mL) was refluxed for 3 h. A few drops of ethanol were added until the product had entirely dissolved and the solution was filtered in hot condition. The organic component was extracted with $CH_2Cl_2$ and the combined organic layer was dried over anhydrous $Na_2SO_4$ and concentrated by rotary evaporator to afford white solids. The white solids were washed with hexane (2x10 mL) to give the pure product in ~80% yield. Single crystals of **10** and **14** suitable for single-crystal diffraction analysis were obtained by slow diffusion of hexane in $CH_2Cl_2$ solution of the respective compounds at room temperature

**Synthesis of 10.** The reagents used are **5** (0.5 g, 1.47 mmol) in $CCl_4$ (10 mL), $SO_2Cl_2$ (0.2 g, 1.47 mmol, 119 μL) in $CCl_4$ (5 mL) and 2 M NaOH aqueous solution (5 mL). Yield 0.41 g (79%), $^1H$ NMR (400 MHz, $CDCl_3$): δ (ppm) 8.42 (d, 1H, Ar–H), 7.56 (d, 3H, Ar–H), 7.46 (t, 1H, Ar–H), 7.36 (d, 3H, Ar–H),7.18 (d, 1H, Ar–H), 3.56 (d, 1H, Ar-$CH_2$), 3.25 (d, 1H, Ar-$CH_2$), 2.06 (s, 6H, $NMe_2$). $^{13}C$ NMR (100 MHz, $CDCl_3$): δ (ppm) 140.46, 138.29, 134.95, 131.53, 131.08, 130.76, 129.49, 128.92, 128.17, 63.38, 44.33, 18.50. $^{125}$Te NMR (126 MHz, $CDCl_3$): δ (ppm) 1223. ESI-MS (positive mode): $[M+H]^+$ $m/z = 358.0445$ (observed), 358.0446 (calculated).

**Synthesis of 11.** The reagent used are **6** (0.5 g, 1.42 mmol) in $CCl_4$ (10 mL), $SO_2Cl_2$ (0.19 g, 1.42 mmol, 114 μL) in $CCl_4$ (5 mL) and 2 M NaOH aqueous solution (5 mL). Yield 0.39 g (76%),$^1H$ NMR (400 MHz, $CDCl_3$): δ (ppm) 8.36 (d, 1H, Ar–H), 7.57 (t, 1H, Ar–H), 7.46 (t, 1H, Ar–H), 7.23–7.26 (m, 4H, Ar–H),7.12 (t, 1H, Ar–H), 3.51 (d, 1H, Ar-$CH_2$), 3.34 (d, 1H, Ar-$CH_2$), 2.70 (s, 3H, Ar-$CH_3$), 2.07 (s, 6H, $NMe_2$). $^{13}C$ NMR (100 MHz, $CDCl_3$): δ (ppm) 140.48, 139.86, 139.27, 133.75, 131.81, 131.46, 131.16, 130.80, 130.16, 128.94, 128.28, 127.46, 63.37, 44.45, 23.34. $^{125}$Te NMR (126 MHz, $CDCl_3$): δ (ppm) 1214. ESI-MS (positive mode): $[M+H]^+$ $m/z = 372.0601$ (observed), 372.0602 (calculated).

**Synthesis of 12.** The reagent used are **7** (0.5 g, 1.36 mmol) in $CCl_4$ (10 mL), $SO_2Cl_2$ (0.18 g, 1.36 mmol, 110 μL) in $CCl_4$ (5 mL) and 2 M NaOH aqueous solution (5 mL). Yield 0.43 g (82%), $^1H$ NMR (400 MHz, $CDCl_3$):δ (ppm) 8.33 (d, 1H, Ar–H), 7.50 (t, 1H, Ar–H), 7.43 (td, 1H, Ar–H), 7.19 (d, 2H, Ar–H),7.01 (d, 2H, Ar–H), 3.33 (dd, 2H, Ar-$CH_2$), 2.42 (s, 6H, Ar-$CH_3$), 2.08 (s, 6H, $NMe_2$). $^{13}C$ NMR (100 MHz, $CDCl_3$): δ (ppm) 142.95, 140.75, 137.12, 133.72, 132.13, 130.80, 128.98, 128.94, 128.39, 63.55, 44.74, 22.99. $^{125}$Te NMR (126 MHz, $CDCl_3$): δ (ppm) 1240. ESI-MS (positive mode): $[M+H]^+$ $m/z = 386.0758$ (observed), 386.0759 (calculated).

**Synthesis of 13.** The reagent used are **8** (0.5 g, 1.18 mmol) in $CCl_4$ (10 mL), $SO_2Cl_2$ (0.16 g, 1.18 mmol, 96 μL) in $CCl_4$ (5 mL) and 2 M NaOH aqueous solution (5 mL). Yield 0.41 g (80%), $^1H$ NMR (400 MHz, $CDCl_3$): δ (ppm) 7.82 (d, 1H, Ar–H), 7.32–7.37 (m, 3H, Ar–H), 7.23 (d, 3H, Ar–H), 3.79 (d, 1H, Ar-$CH_2$),3.60 (sept, 2H, Ar-CH), 3.28 (d, 1H, Ar-$CH_2$), 2.20 (s, 6H, $NMe_2$), 1.23 (d, 6H, $CH_3$), 0.98 (d, 6H, $CH_3$). $^{13}C$ NMR (100 MHz, $CDCl_3$): δ (ppm) 154.50, 141.48, 138.40, 135.40, 132.55, 131.24, 130.67, 128.94, 128.55, 124.56, 63.04, 44.54, 32.75, 24.95, 24.81. $^{125}$Te NMR (126 MHz, $CDCl_3$): δ (ppm) 1256. ESI-MS (positive mode): $[M+H]^+$ $m/z = 442.1388$ (observed), 442.1385 (calculated).

**Synthesis of 14a·14b.** The reagents used are **9** [37] (0.75 g, 1.46 mmol) in $CCl_4$ (10 mL), $SO_2Cl_2$ (0.2 g, 1.47 mmol, 119 μL) in $CCl_4$ (5 mL) and 2 M NaOH aqueous solution (5 mL). $^1H$ NMR (400 MHz, $CDCl_3$): 8.1–8.0 (v br), 7.6–7.2 (v br), 4.8 (dd, br), 4.3 (dd, br), 3.6–3.1 (br), 3.0–2.8 (br), 2.4–2.0 (v br), 1.8–1.6 (v br), $^{125}$Te NMR (126 MHz, $CDCl_3$): δ (ppm) 1119. ESI-MS (positive mode): $[M+H]^+$ $m/z = 529.2183$ (observed), 529.2182 (calculated).

**Synthesis of 14c.** The reagents used are **9** [37] (0.75 g, 1.46 mmol) in $CCl_4$ (10 mL), $SO_2Cl_2$ (0.2 g, 1.47 mmol, 119 μL) in $CCl_4$ (5 mL) and 2 M NaOH aqueous solution (5 mL). Yield 0.65 g (76.2%), m.p. 194 °C. $^1H$ NMR (500 MHz, $CDCl_3$) δ (ppm) 8.11 (d, 1H, Ar–H), 8.05 (d, 1H, Ar–H), 7.49 (s, br, 1H, Ar–H), 7.38 (s, br, 1H, Ar–H), 7.33 (s, br, 1H, Ar–H), 7.21 (d, br, 1H, Ar–H), 4.64 (dd, 1H, Ar-$CH_2$), 4.13 (dd, 1H, Ar-$CH_2$), 3.38 (t, 1H, Ar-$CH_2$), 3.29 (d, 2H, Ar-$CH_2$), 3.20 (d, 1H, Ar-$CH_2$), 2.99 (d, 1H, Ar-$CH_2$), 2.79 (d, 1H, Ar-$CH_2$), 2.28 (s, br, 8H, $CH_3$), 2.09 (s, br, 4H, $CH_3$), 1.75 (s, br, 12H, $CH_3$), $^{125}$Te NMR (126 MHz, $CDCl_3$): δ (ppm) 1120, ESI-MS (positive mode): $[M]^+$ $m/z = 529.2188$ (observed), 529.2182 (calculated). Elemental analysis: Anal. Calcd. for $C_{24}H_{39}ClN_4OTe$: C, 51.23; H, 6.99; N, 9.96. Found: C, 51.1879; H, 6.3321; N, 8.8794. FTIR: ῡ (OH) 3417 $cm^{-1}$.

## 6. X-ray crystallographic study

The single crystal X-ray diffraction measurements were performed on a Rigaku Saturn 724 diffractometer and an Oxford Diffraction Gemini diffractometer. The data were corrected for Lorentz, polarization, and absorption effects. The structures were determined by routine direct methods using SHELXT [43] and Fourier methods and refined by full-matrix least squares with the

anisotropic non-hydrogen atoms and hydrogen atoms with fixed isotropic thermal parameters of 0.07 $Å^2$ using the SHELXL-2018 [44] program. The hydrogens were partially located from difference electron density maps, and the rest were fixed at predetermined positions. Scattering factors were from common sources [45]. For **14**, the metrical parameters of the minor component were constrained to be similar to those of the cation using the SAME command in Shelxl-2018. The occupancy within **14b** was refined using the SUMP command: sump 0.90595 .001 1 3 1 4; FVAR 1.02308 0.90595 0.25145 0.65448, free variable 3 and 4 refined with good esd's. [Final values were 0.251(1) for **14c** and 0.654(1) for **14b**. If these are expressed as percentages the values would be 27.8(1) % (**14c**) and 72.2(1) % (**14b**)]. X-ray structural parameters for compounds **7**, **8**, **10**, **14a-b** and **14c** are given in Supporting Information (Table S1). CCDC 1501265 (**7**), 1501266 (**8**), 1501267 (**10**), 1885841 (**14a-b**), and 1903831 (**14c**) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from 'The Cambridge Crystallographic Data Centre' via www.ccdc.cam.ac.uk/structures-beta/.

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## Appendix A. Supplementary data

Supplementary data to this article can be found online at https://doi.org/10.1016/j.jorganchem.2019.05.003.

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