Influence of Both Steric Effects and Te···N Intramolecular Nonbonded Interactions on the Stabilization of Organotellurium Compounds Incorporating [2-[1-(3,5-Dimethylphenyl)-2-naphthyl]-4,5-dihydro-4,4-dimethyloxazole]

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A series of novel low-valent organotellurium compounds incorporating [2-[1-(3,5-dimethylphenyl)-2-naphthyl]-4,5-dihydro-4,4-dimethyloxazole] (**1**) stabilized by Te···N nonbonded interactions have been synthesized. The synthesis has been achieved by the ortholithium route. The lithium arenetellurolate **3** was obtained by direct metalation of **1** with 1.6 M of n-BuLi in hexane followed by the insertion of tellurium into the Li−C bond. Oxidation of **3** then afforded the desired ditelluride **4**. The reaction of **4** with a stoichiometric amount of sulfuryl chloride yielded stable tellurenyl(II) chloride **5**, whereas the addition of an excess sulfuryl chloride led to the formation of tellurium(IV) trichloride **6**. The stable bromo compound **7** was obtained by the controlled bromination of **4** with bromine. No tellurium tribromide formation was observed when the ditelluride was treated with an excess of bromine. Compound **4** underwent facile reaction with a stoichiometric amount of iodine to give a stable mono iodo compound (**8**). The phenyltelluride derivative **9** was obtained by the treatment of lithiated product **2** with PhTeBr at low temperature. Attempts to synthesize the symmetrical telluride of the type R_2Te (**10**) by the reaction of **2** with $Te(dtc)_2$ (dtc = diethyldithiocarbamate) or TeI_2 were unsuccessful. All compounds were characterized by elemental analysis, multinuclear (^1H, ^{13}C, ^{125}Te) NMR, and mass spectrometry techniques. The presence of strong Te···N intramolecular nonbonded interactions in all the compounds was confirmed by single-crystal X-ray crystallographic studies.

Introduction

It has long been recognized that the organotellurium species are efficient and versatile reagents in organic synthesis for various organic transformation reactions such as C−C bond formation, tellurium/metal exchange cross-coupling, radical-mediated cross-coupling, and "living" radical polymerization reactions.[1] In addition to organic synthesis, organotellurium compounds also have enormous applications in other fields such as in (a) metal−organic chemical vapor deposition (MOCVD) processes as single-source precursors,[2] (b) ligand chemistry,[3] and (c) biochemistry.[4] Although the organotellurium compounds find increasing applications, the synthesis of stable organotellurium compounds has been found to be very challenging due to their very unstable and highly reactive nature. In recent years there has been significant exploration of the concepts of intramolecular coordination and steric effects, as they proved to be a very effective and challenging strategy for the

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synthesis of stable organotellurium compounds, which are otherwise reactive and unstable. The sterically more hindered groups such as sitel (sitel = $-Si(SiMe_3)_3$),[5] mesityl, triisopropylphenyl, and tri-*tert*-butylphenyl groups[6] have been used in the literature for the synthesis of stable organotellurium compounds. In the past stable organotellurium compounds have also been synthesized successfully using intramolecularly coordinating ligands containing nitrogen donor atoms. McWhinnie et al.[7] reported the first examples of organotellurium(II) and -(IV) derivatives of azobenzene in 1979, and (2-phenylazophenyl-*C*,*N*′)-tellurium(II) chloride was one of the first compounds containing an intramolecular coordinate Te−N bond to be crystallographically characterized. This approach has been further extended to the synthesis of a range of *ortho*-tellurated derivatives of the same ligand[8] and to the other ligands carrying potentially chelating *ortho* substituents, such as 2-(2-pyridyl)phenyl,[9] azomethine,[10] and related systems[11] to isolate novel monomeric, stable organotellurium compounds and to study the nature of interactions between the tellurium and nitrogen atom. Minkin and coworkers[12] have extensively studied the synthesis, reactions, and structures of *ortho*-tellurated derivatives of azomethines with intramolecular tellurium−nitrogen coordinate bonds. The ligands bearing an oxygen donor atom have also been used for the synthesis of stable organotellurium compounds.[13] Our group has also been involved in the use of intramolecular coordination strategy to synthesize stable organotellurium compounds[14] and has reported intramolecularly stabilized organotellurium compounds incorporating *N*,*N*-dimethylbenzylamine,[15] 1-(*S*)-(dimethylamino)ethylbenzene,[15b] 1-(*N*,*N*-dimethylnaphthyl)amine,[16] 4,4-dimethyl-2-phenyloxazoline,[17] (*R*)-(4-ethyl)-2-phenyloxazoline,[4f] and *o*-bromobenzaldehyde.[18] Intramolecularly coordinating substrates having a nitrogen donor atom receive special attention, as their cyclometalation reaction to form a ring is facile and isolation of the products is relatively easy.

Furthermore, monomeric and stable metal thiolates[19] and selenolates[20] have been isolated using the intramolecular coordinating ligands. However, attempts to obtain crystals of group 12 tellurolates were unsuccessful due to the facile decomposition of the complexes in common solvents.[17] Although the use of either intramolecular coordinating groups or sterically more hindered groups has been successful to some extent in organotellurium chemistry, the isolation and structural characterization of very unstable compounds such as metal tellurolates and telluroles under ambient conditions remains a difficult task. In this context, we contemplated using the ligand that has both intramolecular coordinating and sterically more hindered groups. To our knowledge, there are no reports about the use of this type of ligand in organotellurium chemistry. This would also provide an opportunity to study Te···N interactions in the presence of sterically more hindered groups. Before attempting to isolate very unstable compounds such as telluroles and tellurolates, we have synthesized a series of stable organotellurium compounds to understand the stability and the nature of the Te···N intramolecular interactions.

In this paper we report the synthesis and characterization of some organotellurium compounds derived

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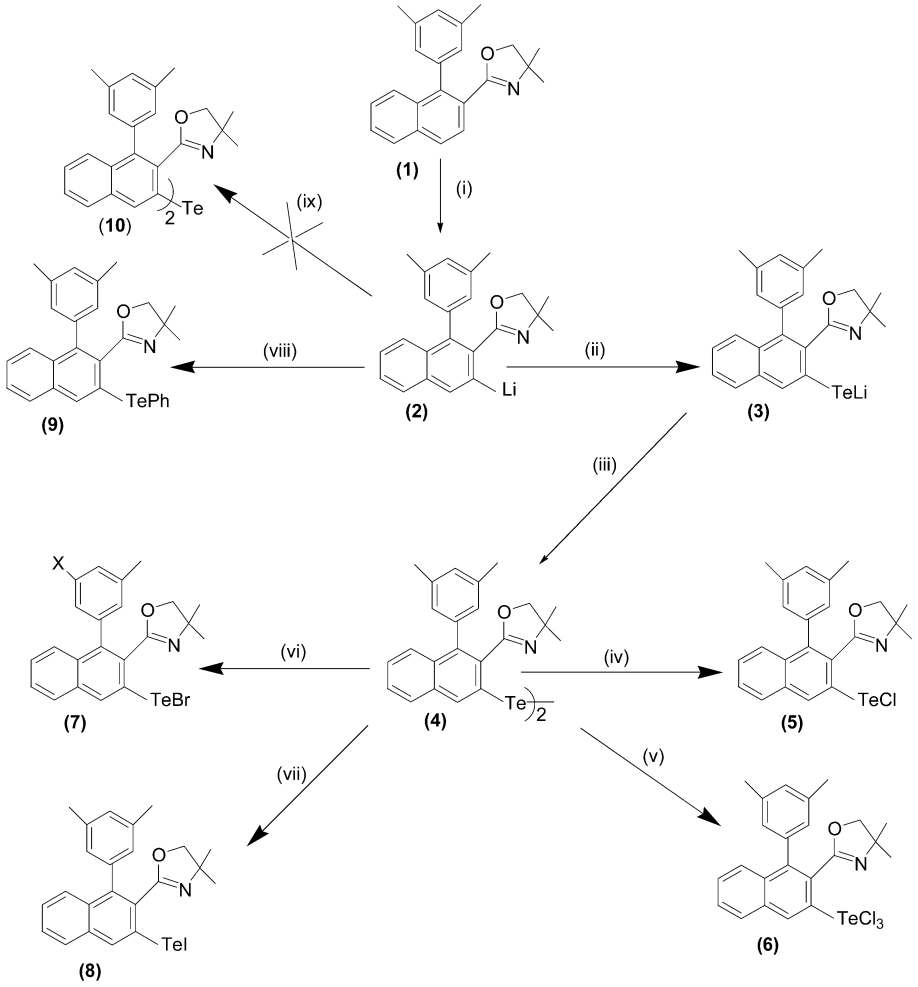
Scheme 1. Synthetic Routes for the Synthesis of Organotellurium Compounds[a]



[a] (i) n-BuLi, Et_2O, 0 °C, (ii) Te, 0 °C, (iii) [O]/H_2O, (iv) SO_2Cl_2, CCl_4, 0 °C, (v) excess SO_2Cl_2, CCl_4, rt, (vi) Br_2, CCl_4, 0 °C, (vii) I_2, CCl_4, 0 °C, (viii) PhTeBr, ether, 0 °C, (ix) $Te(dtc)_2$, 0 °C.

from [2-[1-(3,5-dimethylphenyl)-2-naphthyl]-4,5-dihydro-4,4-dimethyloxazole] (**1**) and compare the structural and spectroscopic behavior with related organotellurium compounds derived from the sterically less hindered ligands, in particular, with organotellurium compounds derived from 4,4-dimethyl-2-phenyloxazoline. The structural characterization of **4**−**8** has been undertaken to investigate the nature of Te···N interactions in the presence of sterically more hindered groups. This substrate has been synthesized as one of the intermediates in the preparation of mevanolactones, which are used as inhibitors in cholesterol biosynthesis.[21]

Results and Discussion

Synthesis. The reaction of lithiated compound **2** with well-ground tellurium powder followed by oxidative workup yielded the desired ditelluride (**4**). Tellurenyl(II) chloride **5** was prepared by the dropwise addition of an equimolar amount of sulfuryl chloride to the carbon tetrachloride solution of **4**. The excess of sulfuryl chloride led to the formation of colorless tellurium(IV) trichloride **6**. The reaction of a stoichiometric amount of bromine with **4** gave the stable bromo compound **7**. No tellurium tribromide formation was observed when an excess of bromine was reacted with the ditelluride. The orange-colored novel mono iodo compound **8** was obtained by slow addition of iodine into **4**. Phenyltelluride derivative **9** was prepared by the reaction of **2** with PhTeBr in ether at low temperature. PhTeBr was prepared in situ by the addition of a bromine of benzene to a solution of diphenylditelluride in dry ether. The reactions are shown in Scheme 1.

All compounds except **6** are highly soluble in common organic solvents such as dichloromethane, chloroform, and methanol. However, some decomposition was observed for **4** when it was kept in dichloromethane for crystallization. Compound **4** was, therefore, recrystallized from toluene. Compound **6** was soluble only in strongly coordinating solvents such as DMSO. All compounds are synthesized in good yields (40−85%). All are very stable toward air and moisture due to the presence of strong Te···N nonbonded interactions (vide infra). No visible decomposition was observed even upon prolonged exposure to the atmosphere.

The reaction of **2** with $Te(dtc)_2$ or TeI_2 was expected to give the novel telluride of the type R_2Te (**10**). However, all the attempts to synthesize the novel telluride were unsuccessful. It is worth mentioning that the reaction of 4,4-dimethyl-2-phenyloxazoline with $Te(dtc)_2$ gave the desired telluride.[22] Although the formation of benzyl telluride of the type $RTeCH_2Ph$ by the

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treatment of benzyl chloride with **3** was observed by ^{125}Te NMR spectroscopy, the compound slowly decomposed to give **4** rather than the coupled hydrocarbon product.[23] Attempts to prepare the tellurenyl sulfide derivative, RTeSPh, by the reaction of benzenethiol with **4** were also unsuccessful.

Spectroscopy. Compounds **4**−**9** were characterized by NMR spectroscopy to find out their stability in solution. On the basis of the trend in the chemical shifts of ^{1}H NMR, compounds **4**−**9** can be classified into two groups. Compounds **5**−**8** fall into the first category in which intramolecular Te···N interactions are very strong. These compounds show significant downfield shifts for $-CH_3$ (∼0.33 ppm) and $-CH_2$ (∼0.5 ppm) compared to the free ligand. The trend RTeCl > RTeBr > RTeI suggests that the Te···N interactions decrease as the electronegativity of the groups attached to the tellurium decreases. Compounds **4** and **9** fall into the second category in which the Te···N interactions are weak. In these compounds only slight downfield shifts are observed for methyl and methylene groups compared with the free ligand. The ^{13}C NMR spectra were not quite informative, as similar spectra were obtained for all the compounds and there were no marked shifts compared to each other.

^{125}Te NMR is one of the main characteristics to study the nature of the Te···N interactions in organotellurium compounds in solution. The downfield shift of the ^{125}Te NMR peaks as a result of strong Te···N nonbonding interaction is widely accepted, although the values for the shift do not correspond exactly with the strength of the Te···N interaction. The ^{125}Te NMR signal for **4** was observed at 421 ppm. The significant downfield shifts of **5**−**8** and compound **9** compared with the ditelluride support the presence of strong Te···N interactions in the halide derivatives. The ^{125}Te NMR shifts of halide derivatives decrease in the order $RTeCl_3$ (1418 ppm) > RTeCl (1163 ppm) > RTeBr (1124 ppm) > RTeI (996 ppm). This can be attributed to the enhanced electronegativity that will favor removal of nonbonded electron density from the tellurium atom. It is interesting to know that ^{125}Te NMR chemical shifts for compounds **7** and **8** are observed upfield from those of the corresponding derivatives of 1-(*N*,*N*-dimethylnaphthyl)amine[16b] and *N*,*N*-dimethylbenzylamine[15d] {[(2-dimethylamino)-naphthyl]tellurium bromide, 1511 ppm; [(2-dimethylamino)naphthyl]tellurium iodide, 1239 ppm; [(2-dimethylaminomethyl)phenyl]tellurium iodide, 1191 ppm]}, although Te···N nonbonded interactions are stronger for **7** and **8** (vide infra). For **9** the chemical shift (670 ppm) is close to that observed for [(2-dimethylaminomethyl)-phenyl]phenyl telluride (636 ppm) and [(2-dimethylamino)naphthyl]phenyl telluride (709 ppm), respectively.

Mass spectra for compounds **4**, **5**, and **9** were recorded to identify the constitution of the products under mass spectrometric conditions. The presence of eight stable isotopes of Te leads to a highly characteristic group of peaks for the tellurium-containing fragments. Molecular ion peaks were observed in very low intensities for all the compounds. In all the cases the base peak observed at m/e = 458 and m/e = 330 can be attributed to the RTe^+ and R^+ fragments, respectively. This clearly indicates the weakening of the Te−X (X = TeR, Ph) bond *trans* to the Te···N fragment.

Table 1. Important Bond Lengths (Å) and Bond Angles (deg) of Compounds 4−8

Compound **4**			
Te(1)−Te(1a)	2.7474(5)	Te(1a)···N(1a)	2.718(3)
C(1a)−Te(1a)	2.148(3)	C(19a)−O(1a)	1.338(5)
N(1a)−C(19a)	1.241(5)	O(1a)−C(20a)	1.423(7)
C(1a)−Te(1)−Te(1a)	101.44(9)	C(19a)−N(1a)−C(21a)	110.1(3)
C(1)−Te(1)−Te(1a)−C(1a)	91.87(12)		
Compound **6**			
N(1)···Te(1)	2.251(3)	Te−Cl(1)	2.5059(11)
Te−Cl(2)	2.4814(11)	Te−Cl(3)	2.4510(12)
N(1)···Te(1)−Cl(3)	166.60(8)	Cl(1)−Te(1)−Cl(2)	172.44(4)
N(1)···Te(1)−Cl(2)	87.19(8)	Cl(2)−Te(1)−Cl(3)	92.37(4)
N(1)···Te(1)−Cl(1)	86.41(8)	Cl(3)−Te(1)−Cl(1)	92.91(4)

	Compound **5** (X = Cl)	Compound **7** (X = Br)	Compound **8** (X = I)
Te(1)−N(1)	2.252(2)	2.252(4)	2.259(6)
Te(1)−X(1)	2.5284(11)	2.7468(7)	2.8519(8)
C(1)−Te(1)−N(1)	75.44(10)	75.00(14)	75.00(2)
C(1)−Te(1)−X(1)	91.80(8)	94.38(12)	94.36(17)
N(1)−Te(1)−X(1)	166.87(7)	167.84(9)	169.97(15)

Compounds **4**−**9** exhibited similar absorption spectra with a strong peak in the region 280−310 nm and the absorption maximum at 295 nm due to the ligand core. Fluorescence spectra for compounds **4**−**7** and free ligand **1** were recorded to probe their fluorescence emission properties in methanol at the excitation wavelength of 285 nm. The quantum yield of fluorescence emission was determined by using naphthalene (Φ_f = 0.23) as a standard.[24] From the quantum yield of the fluorescence emission of **4** (Φ_f = 0.04), **5** (Φ_f = 0.020), **6** (Φ_f = 0.022), and **7** (Φ_f = 0.020) compared to the fluorescence emission of free ligand **1** (Φ_f = 0.067) it is clear that the fluorescence emissions were quenched in compounds **4**−**7** compared to the free ligand **1** due to the substitution of heavy metal atoms.[25] In addition, compounds **5**−**7** are further quenched (∼50%) compared to **4** due to the presence of heavy halogen atoms in addition to tellurium.

In solid state FT IR spectral measurements (KBr), $\nu_{C=N}$ vibrations for the compounds **4**−**8** are found in the range 1590−1640 cm^{-1}, which are shifted ∼20−50 cm^{-1} to lower frequency compared to the free oxazoline ligand, indicating that nitrogen of the oxazoline ring is coordinated to the tellurium.

Crystal Structures. The important bond lengths and bond angles of all the compounds are summarized in Table 1. The molecular structure of **4** is shown in Figure 1. One disordered toluene molecule per dimer is located on a center of symmetry. The coordination geometry around the tellurium is distorted T-shaped, with each tellurium atom bonded to another tellurium, carbon, and a nitrogen atom. One of the characteristic features of this structure is the presence of strong Te(1)···N(1) (2.718(3) Å) intramolecular interaction. In all the reported intramolecularly stabilized ditellurides including the 4,4-dimethyl-2-phenyloxazoline, unequal Te(1)··· N(1) and Te(1)a···N(1)a distances were observed.[4f,16b,17,18a] The observed Te···N intramolecular distances (2.718-

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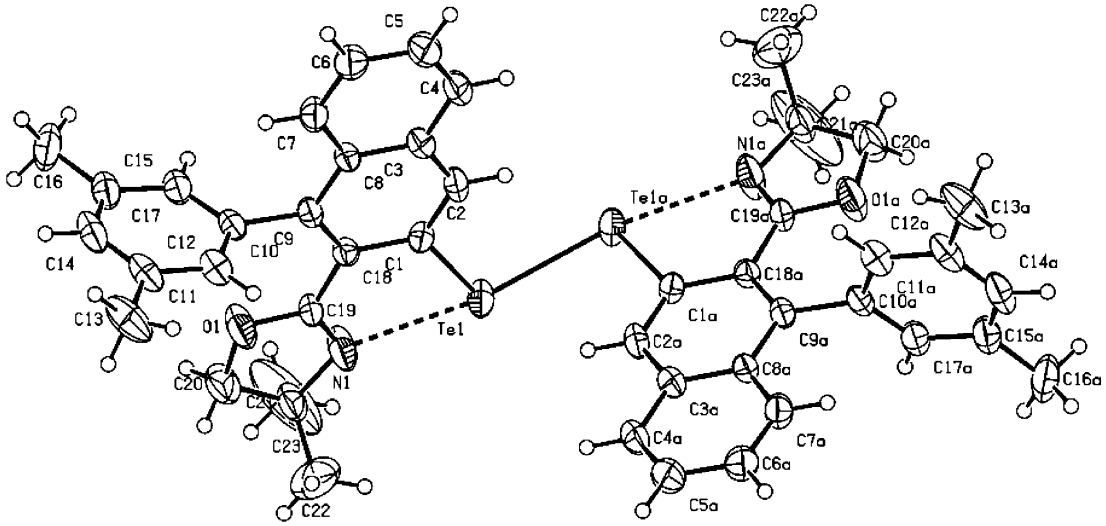

Figure 1. Molecular structure of **4**.

(3) Å) are equal and much shorter than the corresponding distances of bis[2-(4,4-dimethyl-2-phenyl)oxazolinyl]-ditelluride[17] (2.864 Å; 2.694 Å), (*R*,*R*)-bis[2-(4-ethyl-2-phenyl)oxazolinyl]ditelluride[4f] (2.792 Å; 2.755 Å), and bis[2-(hydroxyiminomethyl)phenyl]ditelluride[10c] (2.822(5) Å; 2.876(5) Å), where also the nitrogen is in sp^2 state. The distance is shorter than the respective distances of bis[(2-dimethylamino)formyl]ditelluride (3.019 Å)[26] and bis[(2-dimethylaminomethyl)phenyl]ditelluride (2.903 Å; 2.848 Å), where the nitrogen is in sp^3 state. The Te···N distance is, however, longer than the sum of the covalent radii (2.1 Å) but much shorter than the sum of van der Waals radii (3.65 Å).[27] The Te(1)−Te(1)a (2.7474(5) Å) distance is slightly longer than that in bis[2-(4,4-dimethyl-2-phenyl)oxazolinyl]ditelluride and close to the other reported ditellurides. It is known that diaryl ditellurides exhibit "conformational polymorphism" in the solid state.[28] The "cisoid" conformations show the torsion angle C−Te−Te−C to be <90°, and the "transoid" conformations show the torsion angle C−Te−Te−C to be >90°. In this structure, the torsion angle C(1)−Te(1)−Te(1)a−C(1)a is 91.87(12)°, and therefore, the conformation can be termed as "transoid". But in the case of bis[2-(4,4-dimethyl-2-phenyl)oxazolinyl]ditelluride the torsion angle C−Te−Te−C is −84.4° and, therefore, exhibits "cisoid" conformation. The shorter (strong) Te···N intramolecular interactions, slightly larger Te−Te distance, and the "transoid" conformation of this structure compared with the bis[2-(4,4-dimethyl-2-phenyl)oxazolinyl]ditelluride clearly suggest that the presence of sterically more demanding groups plays an important role in addition to the intramolecular coordination. The packing diagram shows weak intermolecular Te···H (Te1···H2_a, 2.9497 Å; Te1···H22A_c, 3.2475 Å; Te1···H16C_d, 3.1818 Å) interactions, which are shorter than the sum of respective van der Waals radii (3.55 Å). These intermolecular interactions may be a result of optimized dense packing of the molecules.

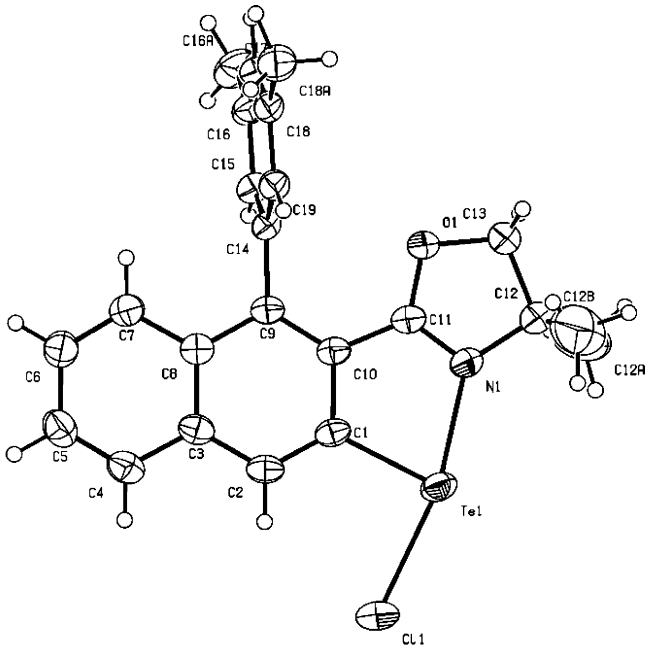

Figure 2. Molecular structure of **5**.

The molecular structure of **5** is shown in Figure 2. The T-shaped tellurium is formally bonded to a halogen atom and to an aromatic carbon atom, with an additional link to the nitrogen atom *trans* to the chlorine. The Te(1)···N(1) bond distance (2.252(2) Å) is close to the Te−N single bond covalent radii (2.1 Å), whereas the Te(1)−Cl(1) bond (2.5284(11) Å) is longer than the sum of the corresponding covalent radii (2.34 Å). The angle Cl(1)−Te(1)···N(1) [166.87(7)°] is very close to the linear arrangement. These parameters clearly indicate that the elongation of the Te(1)−Cl(1) bond that is in *trans* position relative to the N in the N(1)···Te(1)−Cl(1) fragment may be due to the result of strong Te(1)···N(1) interactions and approximately linear alignment of Cl(1)−Te(1)···N(1), which allows the effective orbital overlap between the nitrogen lone pair and the σ^* orbital of the Te(1)−Cl(1) bond. The Te(1)···N(1) and Te−Cl bond distances are somewhat longer and shorter than the corresponding distances of phenylazophenyl-

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(*C, N′*)tellurium chloride[7,8d] [Te···N, 2.210(7) and 2.23(2) Å; Te−Cl, 2.533(3) and 2.2552 Å], 2-(2-pyridyl)phenyltellurium chloride[9d,e] [Te···N, 2.205(11) Å; Te−Cl, 2.606(11) Å], and 2-chlorotellurenyl-4′-methylbenzalaniline[11d,f] [Te···N, 2.218 and 2.239 Å; Te−Cl, 2.582(2) and 2.553(2) Å], respectively. The Te(1)···N(1) and Te(1)−Cl(1) bond distances are very close to the respective distances in the related compound [2-(4,4-dimethyl-2-phenyl)oxazolinyl]tellurium chloride.[29] The Te−Cl bond distance is, however, longer than the respective distance in 3-phenyl-5-(4-methoxyphenyl)-1,2-oxatellurol-1-ium chloride, where tellurium is involved in an intramolecular interaction with the oxygen atom.[13e] Compound **5** can be considered as a five-membered heterocycle, as proposed by Detty et al.[13e] for oxatellurium chloride. The packing pattern of this structure is significantly different from the packing diagram of reported tellurium chloride derivatives. The Te···Cl intermolecular distance of [2-(4,4-dimethyl-2-phenyl)oxazolinyl] (2.5602 Å), phenylazophenyl(C,N′) (3.66 Å), and 2-(2-pyridyl)phenyl (3.92 Å) derivatives was shorter than the sum of their van der Waals radii (4.0 Å). However, in this structure, the shortest intermolecular distance between the tellurium and chlorine (5.077 Å) is much greater than the sum of their van der Waals radii (4.0 Å). The absence of intermolecular (secondary) interactions in this structure suggests that the sterically more demanding group may be preventing this type of intermolecular interaction to avoid steric crowding. Thus, this compound can be considered as an example of a true monomeric tellurenyl chloride. However, weak intermolecular Te···H (Te1···H12F, 3.4160 Å; Te1···H16A_a, 3.1443 Å) and Cl···H (Cl1···H19_b, 3.0006 Å) interactions exist in the packing diagram of **5**. Both the Te···H and Cl···H distances are shorter than the sum of the van der Waals radii, 3.55 and 3.45 Å, respectively. The weak Te···H intermolecular interactions may be as a result of optimized dense packing of the molecules.

The molecular structure of **6** is shown in Figure 3. The geometry around the tellurium is distorted trigonal bipyramidal with two chlorine atoms in axial positions and nitrogen, tellurium, and a chlorine atom in equitorial positions. The Te(1)···N(1) distance (2.251(3) Å) is much shorter than that in all other reported organotellurium trichloride derivatives.[8a,15b,30] Te−Cl distances [Te(1)−Cl(3), 2.4510(12) Å; Te(1)−Cl(2), 2.4814(11) Å; Te(1)−Cl(1), 2.5059(11) Å] are almost in the range of reported intramolecularly stabilized organotellurium trichlorides. However, these Te−Cl distances are slightly longer than that in the *trans*-2-ethoxy-cyclohexyltellurium(IV) trichloride and trichloro(2-chlorobicyclo[2.2.1]-hept-7-yl)-λ^4-tellurane.[31] The elongation of the *trans*-Te−Cl distance indicates the presence of a strong Te···N intramolecular interaction. The bond angle Cl(2)−Te(1)−Cl(1) (172.44(4)°) is close to the linear arrangement. The bond angle Cl(3)−Te(1)···N(1) (166.60(8)°) is also in good agreement with that of reported organotellurium trichlorides. In addition to weak Cl···H and Te···H intermolecular interactions, very weak Te···Cl

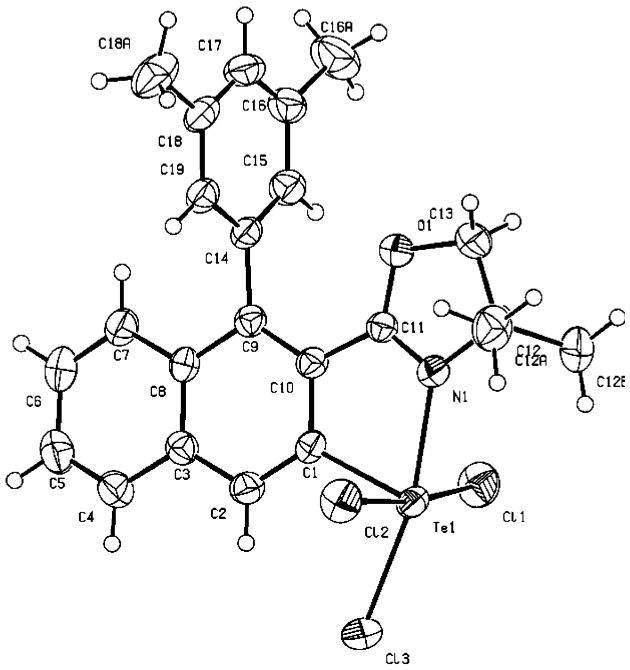

Figure 3. Molecular structure of **6**.

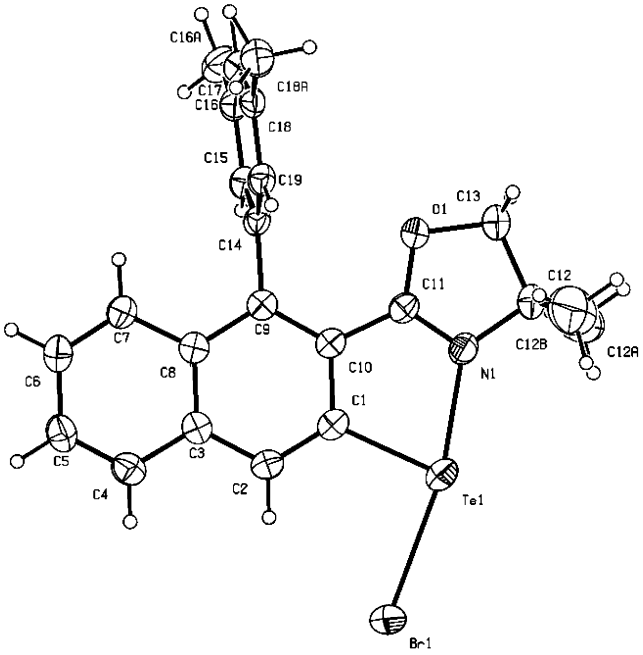

Figure 4. Molecular structure of **7**.

[Te1···Cl1_a, 3.9091(12) Å] intermolecular interactions that are shorter than the sum of the van der Waals radii, 4.0 Å, also exist in the packing diagram of **6**.

The molecular structure of **7** is shown in Figure 4. The Te(1)···N(1) distance (2.2520(4) Å) is shorter than the corresponding distances in [(2-dimethylamino)-naphthyl]tellurium bromide[16b] (2.395 Å) and slightly longer than in phenylazophenyl(*C,N′*)tellurium bromide (2.219(8) Å)[8d] and [2-(2-pyridyl)phenyltellurium bromide (2.236(11) Å).[9d] The Te(1)···N(1) distance is also longer than in 2-bromotelluro-*N*-(*p*-tolyl)benzylamine (2.375-(13) Å), where the sp^3 nitrogen atom present.[11d] The N(1)−Te(1)−Br(1) bond angle of 167.84(9)° is more deviated than in [(2-dimethylamino)naphthyl]tellurium bromide (∼3°), phenylazophenyl(*C,N′*)tellurium bro-

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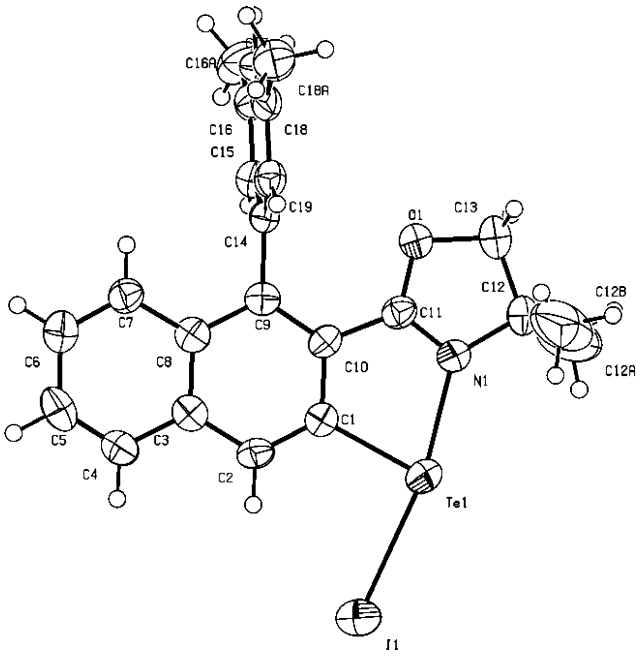

Figure 5. Molecular structure of **8**.

mide (~0.2°), and 2-(2-pyridyl)phenyltellurium bromide (~1.4°) and from the linear arrangement. However, elongation of the Te(1)−Br(1) distance (2.7468(7) Å) is still greater than those in [(2-dimethylamino)naphthyl]-tellurium bromide (2.672 Å), phenylazophenyl(*C,N′*)-tellurium bromide (2.698(1) Å), 2-(2-pyridyl)phenyltellurium bromide (2.707(11) Å), and 2-bromotelluro-*N*-(*p*-tolyl)benzylamine (2.663(3) Å). This may be due to the effect of sterically more demanding groups in association with the strong intramolecular coordination. Observation of Te···X intermolecular (secondary) interactions is very common in organotellurium halides.[7,8d,9de,29,32] However, in the structure **7** no such intermolecular (secondary) interactions between tellurium and bromine were observed. The shortest intermolecular Te···Br distance (4.917 Å) is longer than the sum of the van der Waals radii (4.1 Å). Again this clearly proves that the sterically demanding group present in this system prevents the formation of a weak dimer via intermolecular interactions. This structure also can be regarded as an example of a true monomeric tellurenyl bromide. However, in the packing diagram very weak intermolecular H···Br [Br1···H19_b, 3.1336 Å; Br1···H4_c, 3.1747 Å; Br1···H5_c, 3.1252 Å] and Te···H [Te1···H12A, 3.4093 Å; Te1···H16A_a, 3.3101 Å] interactions exist which are shorter than their sum of the van der Waals radii, 4.1 and 4.0 Å, respectively.

The molecular structure of **8** is given in Figure 5. Compound **8** is isostructural with **5** and **7**. Te−I (2.8519(8) Å) and Te···N (2.259(6) Å) distances are close to the respective distances in phenylazophenyl(*C,N′*)-tellurium iodide,[8d] [2-(2-pyridyl)phenyltellurium iodide,[9e] and 1-iodo-2-p-tolyl-1-tellura-2-azaindene,[10d] where sp^2 nitrogen donor atoms are involved. As expected, the Te···N distance is shorter than the respective distance in [(2-dimethylaminomethyl)phenyl]tellurium iodide[15d] (2.366 Å), where an sp^3 nitrogen donor atom is present. The Te−I bond distance of **8** is expected to be longer than the corresponding distance in [(2-dimethylaminomethyl)phenyl]tellurium iodide due to the *trans* effect

Chart 1. Postulated Contribution of Oxygen Atoms in Resonance Stabilization of Oxazoline Ring in Compounds 4−10

of the strong Te···N interaction. In contrast, the Te−I distance (2.8519 Å) of **8** is somewhat shorter than that in [(2-dimethylaminomethyl)phenyl]tellurium iodide (2.8982 Å). This unique observation may be explained by comparing the intermolecular interactions existing between tellurium and iodine in their packing diagrams. In the packing pattern of [(2-dimethylaminomethyl)-phenyl]tellurium iodide, weak Te···I intermolecular interactions (4.291 Å) exist. This is very close to the sum of the van der Waals radii (4.22 Å). However, no such intermolecular interactions between tellurium and iodine were observed in the packing diagram of **8**. The shortest intermolecular distance between tellurium and iodine is 4.904 Å, which is longer than the sum of the van der Waals radii (4.22 Å). The absence of Te···I intermolecular interactions may be attributed to the presence of a sterically bulkier group and the reason for the shorter Te−I distance in **8**. In addition, the absence of intermolecular interactions confirmed the formation of a true monomeric tellurium iodide. In this structure also weak intermolecular Te···H (Te1···H16A_d, 3.0878 Å) and I···H (I1···H19_a, 3.2068 Å; I1···H4_b, 3.2446 Å; I1···H5_b, 3.2489 Å; I1···H12E_c, 3.3181 Å) interactions between the tellurium and methyl group of the phenyl ring were observed. Both the Te···H and I···H distances are shorter than their sum of their van der Waals radii 4.1 and 3.57 Å, respectively.

Common Features. Compounds **4**−**8** crystallized in the monoclinic system with four molecules per unit cell. The strong Te···N interactions observed in the crystal structures of **4**−**8** are well supported by chemical shifts of multinuclear (^{1}H, ^{13}C, ^{125}Te) NMR studies. In all compounds the intramolecular interaction between tellurium and the nitrogen atom of the oxazoline ring led to the formation of another five-membered ring. However, there is no significant interaction between the tellurium and the oxygen atom of the oxazoline ring. The absence of significant Te···O interaction may be explained on the basis of the following reasons: (i) involvement of the lone pair of the oxygen atom in a resonance contribution with the π systems shown in Chart 1. This resonance contribution is also supported by the shorter C−O and C−N bond distances observed in the X-ray crystal structures of compounds **4**−**8**. The shorter bond distances of C(19)−O(1) (1.314−1.339 Å) and C(19)−N(1) (1.241−1.280 Å) of **4**−**8** compared to C(20)−O(1) (1.423−1.458 Å) and C(21)−N(1) (1.358−1.457 Å) single bond distances[33] suggest the presence of double-bond character in both C(19)−O(1) and C(19)−N(1) as shown in Chart 1. (ii) The rotamer with oxygen pointing toward tellurium is less preferred than the

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Table 2. ^{125}Te Chemical Shifts and Te···N Distances

compound	Te···N distance (Å)	^{125}Te NMR (ppm)	ref
5	2.252	1163	this work
6	2.251	1418	this work
7	2.252	1124	this work
8	2.259	996	this work
11[a]	2.395	1512	16b
12[b]	2.28	1221	18a
13[c]	2.241	1203	29
14[d]	2.366	1192	15d
15[e]	2.185	1332	18b
16[f]	2.252	990	8d
17[g]	2.219	983	8d

[a] [(2-Dimethylamino)naphthyl]tellurium bromide. [b] *o*-[2-Hydroxy-2-phenyl-1-methylethyl)iminomethinyl]phenyl tellurium(IV) tribromide. [c] [2-(4,4-Dimethyl-2-phenyl)oxazolinyl]tellurium chloride. [d] [(2-Dimethylaminomethyl)phenyl]tellurium iodide. [e] 1,6-Bis(2-chlorotellurophenyl)-2,5-diazahexa-1,5-diene. [f] Phenylazophenyl-(C,N′)tellurium(II) iodide. [g] Phenylazophenyl(C,N′)tellurium(II) bromide.

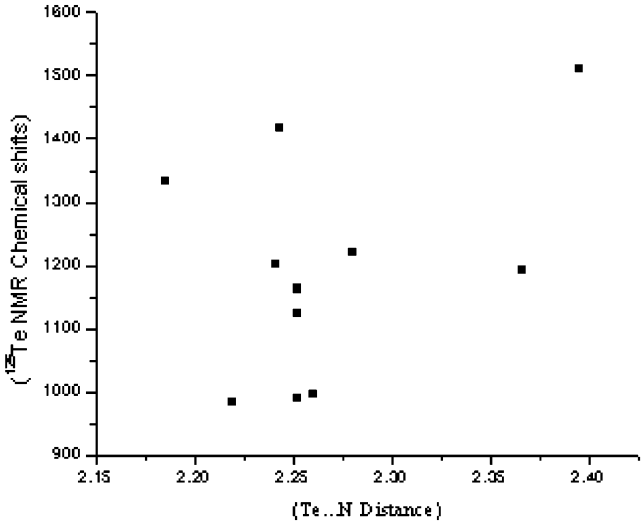

Figure 6. Correlation diagram between ^{125}Te NMR chemical shifts and Te···N distances.

rotamer with nitrogen pointing toward the tellurium due to the orientation of lone pairs on oxygen and nitrogen. The lone pairs on oxygen are out of plane, whereas in the case of nitrogen they lie in the ring plane. Thus for such a lone pair on oxygen pointing toward tellurium the ring must rotate out of the coplanar orientation with tellurium. Such a rotation elongates the distance between tellurium and oxygen, and as a result, the bond strength would be weaker than that of the corresponding Te···N interaction with the lone pair being in the ring plane. (iii) Nitrogen may prefer to coordinate with tellurium, as nitrogen is a softer base than oxygen.

The lengthening of Te−X (X = Cl, Br, and I) bond distances in compounds **5**−**8** is probably due to the *trans* influence of strong Te···N interactions.

Correlation between Te···N Interactions and ^{125}Te NMR Chemical Shifts. The ^{125}Te NMR chemical shifts are plotted against Te···N intramolecular distances (Table 2) of the organotellurium halides (Figure 6). We find that there is no systematic change in ^{125}Te NMR chemical shifts with Te···N distance.

Conclusion

The use of a sterically more hindered group in addition to the *ortho*-chelating group enhances the Te···N interactions and lengthens the *trans* Te−X (X = TeR, TePh, Cl, Br, I) bond compared to other reported organotellurium compounds. The elongation of the Te−X bond enhances the possibility of nucleophilic attack on the tellurium. In the packing diagram no Te···X (Cl, Br, I) intermolecular (secondary) interactions between the tellurium and the halogens were observed. The absence of Te···X intermolecular interactions may be due to the presence of a sterically more demanding group, and thus, these compounds represent the formation of true monomeric organotellurium halides. However, Te···H intermolecular interactions were observed in the packing diagram of structures **4**, **5**, and **8**. In addition, Cl···H intermolecular interactions were observed for the structure **5**. This kind of intermolecular interaction may be a result of optimized dense packing of molecules. A symmetrical monotelluride of the type R_2Te could not be isolated, although it was possible to isolate using the 4,4-dimethyl-2-phenyloxazoline ligand. From these observations, it is concluded that (i) the strength of Te···N interactions depends not only on the nature of the nitrogen atom used as an *ortho*-chelating group but also on the steric effect imposed by the substituents. (ii) The strength of Te···N interactions also depends on the electronegativity of the atom attached to the tellurium and the nature of the tellurium. (iii) The intermolecular (secondary) interactions between tellurium and halogens vanish due to the steric influence, and hence the synthesis of truly monomeric organotellurium halide derivatives was achieved using the sterically more demanding group in addition to the *ortho*-chelating group.

Experimental Section

General Procedures. All reactions were carried out in an inert atmosphere using nitrogen or argon with standard vacuum-line techniques. All solvents were purified by following literature methods and freshly distilled prior to use.[34] All the chemicals used, e.g., 2-[1-(3,5-dimethylphenyl)-2-naphthyl]-4,5-dihydro-4,4-dimethyloxazole (Aldrich) and *n*-butyllithium (E-Merck), were reagent grade and used as received. $Te(dtc)_2$ was prepared using a reported procedure.[35] Melting points were recorded in capillary tubes and are uncorrected. ^{1}H, ^{13}C, and ^{125}Te NMR were obtained at 300, 75.42, and 94.75 MHz, respectively, in $CDCl_3$ on a Varian VXR 300S spectrometer. Chemical shifts are cited with respect to $SiMe_4$ as internal (^{1}H and ^{13}C) and Me_2Te (^{125}Te) as external standard. Elemental analysis was determined with a Carlo-Erba model EA 1112 CHNS analyzer. Infrared spectra were recorded in the range 4000−400 cm^{-1} on a Nicolet Impact 400 FT-IR spectrometer. UV−vis spectra were recorded on a Shimadzu UV-160A spectrophotometer and fluorescence spectra on a Perkin-Elmer LS-55 luminescence spectrometer. ES-MS spectra were recorded at room temperature on a Q-Tof (YA-105) micro mass spectrometer. Fast atomic bombardment (FAB) mass spectra were recorded at room temperature on a JEOL SX 102/DA-6000 mass spectrometer/data system with xenon (6 kV, 10 mV) as the bombarding gas. The accelerating voltage was 10 kV. M-Nitrobenzyl alcohol was used as the matrix with cation detection. For isotopes the value given is for the most intense peak.

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Synthesis of Bis[2-[1-(3,5-dimethylphenyl)-2-naphthyl]-4,5-dihydro-4,4-dimethyloxazole] Ditelluride (4). Addition of a 1.6 M solution of n-BuLi in hexane (3.45 mL, 5.5 mmol) to the ether solution of **1** (1.647 g, 5 mmol) at 0 °C afforded a deep brown-colored solution of **2**. After 2 h finely ground tellurium powder (0.635 g, 5 mmol) was added at 0 °C. Stirring was continued for 30 min at this temperature and 3 h at room temperature. During this time almost all the tellurium powder reacted to give a brown-colored lithium arenetellurolate (**3**). The reaction mixture was then poured into a beaker containing cold aqueous sodium carbonate and oxidized by passing oxygen at a moderate rate for 30 min. The organic phase was washed three times with water, combined, and dried over Na_2SO_4. The filtrate was concentrated to give a yellow oil, which solidified upon addition of hexane. Pale yellow crystals were obtained by recrystallization from toluene. Yield: 1.0 g, 44%. Mp: >98 °C (dec). Anal. Calcd for $C_{53}H_{51}N_2O_2Te_2$: C, 63.46; H, 5.12; N, 2.79. Found: C, 63.20; H, 5.41; N, 2.72. IR (KBr, cm^{-1}): 1631 ($\nu_{C=N}$). λ_{max}/nm (methanol) 296 (ϵ/dm^3 mol^{-1} cm^{-1} 7857). ^{1}H NMR (300 MHz, $CDCl_3$): δ 1.21 (s), 2.36 (s), 3.73 (s), 7.00 (d), 7.49 (t), 7.51 (t), 7.73−7.75 (t), 7.85−7.88 (t). ^{13}C NMR (300 MHz, $CDCl_3$): δ 21.51, 28.12, 67.45, 79.47, 125.87, 125.98, 126.22, 126.58, 127.18, 127.25, 127.84, 127.91, 128.74, 132.03, 134.19, 138.97, 138.22, 140.23, and 163.69. ^{125}Te NMR (300 MHz, $CDCl_3$): δ 421 ppm. FAB-MS (*m*/*z*): 912 (M^+), 913 ($M^+ + 1$), 458 (RTe^+), 330 (R^+).

Synthesis of [2-[1-(3,5-Dimethylphenyl)-2-naphthyl]-4,5-dihydro-4,4-dimethyloxazole] tellurium(II) Chloride (5). To a solution of **4** (0.227 g, 0.25 mmol) in CCl_4 (~25 mL) was added a carbon tetrachloride solution of sulfuryl chloride (0.033 g, 0.25 mmol) at 0 °C. A yellow precipitate formed after the complete addition of sulfuryl chloride, and stirring was continued for an additional 30 min. The volatile impurities were removed by evaporation under reduced vacuum to give the desired chloro compound. Yellow crystals were obtained by recrystallization from the mixture of chloroform and toluene (2:1). Yield: 0.15 g, 76%. Mp: >216 °C (dec). Anal. Calcd for $C_{23}H_{22}NOTeCl$: C, 56.21; H, 4.51; N, 2.85. Found: C, 56.10; H, 4.36; N, 2.75. IR (KBr, cm^{-1}): 1596 ($\nu_{C=N}$). λ_{max}/nm (methanol): 292 (ϵ/dm^3 mol^{-1} cm^{-1} 16 710). ^{1}H NMR (300 MHz, $CDCl_3$): δ 1.54 (s), 2.40 (s), 4.25 (s), 6.90 (s), 7.10 (s), 7.47 (m), 7.95 (d), 9.10(s). ^{13}C NMR (300 MHz, $CDCl_3$): δ 21.48, 28.76, 65.47, 82.80, 119.11, 126.47, 127.60, 127.97, 128.80, 129.13, 129.55, 131.79, 132.85, 134.81, 137.11, 137.24, 145.35, 169.26. ^{125}Te NMR (500 MHz, $CDCl_3$): δ 1163 ppm. ES-MS (*m*/*z*): 491 (M^+), 493 ($M^+ + 2$), 458 (RTe^+), 330 (R^+).

Synthesis of [2-[1-(3,5-Dimethylphenyl)-2-naphthyl]-4,5-dihydro-4,4-dimethyloxazole]tellurium(IV) Trichloride (6). The compound was prepared by using the same method as described for **5**. Addition of excess sulfuryl chloride to the ditelluride afforded the desired product. Colorless crystals were obtained by recrystallization from toluene. Yield: 0.12 g, 54%. Mp: >228 °C (dec). Anal. Calcd for $C_{23}H_{22}NOTeCl_3$: C, 49.12; H, 3.94; N, 2.49. Found: C, 49.22; H, 3.80; N, 4.13. IR (KBr, cm^{-1}): 1599 ($\nu_{C=N}$). λ_{max}/nm (methanol): 294 (ϵ/dm^3 mol^{-1} cm^{-1} 19 920). ^{1}H NMR (300 MHz, DMSO-d_6): δ 1.60 (s), 2.50 (s), 4.60 (s), 7.00−8.00 (m), 9.23 (s). ^{125}Te NMR (500 MHz, DMSO-d_6): δ 1419 ppm.

Synthesis of [2-[1-(3,5-Dimethylphenyl)-2-naphthyl]-4,5-dihydro-4,4-dimethyloxazole] tellurium(II) Bromide (7). The procedure used for the preparation of **7** was similar to that used for the preparation of **5**. A solution of bromine (0.04 g, 0.25 mmol) in CCl_4 (25 mL) was treated with a carbon tetrachloride (25 mL) solution of the ditelluride (0.227 g, 0.25 mmol). Formation of a yellow precipitate was observed after the complete addition of bromine, and stirring continued for an additional 30 min. Usual workup of the product gave the yellow-colored desired product. Recrystallization from benzene afforded single X-ray quality crystals. Yield: 0.20 g, 78%. Mp: >292 °C (dec). Anal. Calcd for $C_{23}H_{22}NOTeBr$: C, 51.55; H, 4.14; N, 2.61. Found: C, 50.18; H, 4.04; N, 2.30. IR (KBr, cm^{-1}): 1604 ($\nu_{C=N}$). λ_{max}/nm (methanol): 296 (ϵ/dm^3 mol^{-1} cm^{-1} 25 334). ^{1}H NMR (300 MHZ, $CDCl_3$): δ 1.54 (s), 2.38 (s), 4.25 (s), 6.90 (s), 7.09 (s), 7.40−7.48 (m), 7.62 (d), 7.95 (d), 9.10 (s). ^{13}C NMR (300 MHz, $CDCl_3$): δ 21.57, 28.86, 65.42, 82.82, 118.87, 125.90, 126.37, 127.42, 127.77, 127.82, 128.67, 129.36, 131.77, 133.87, 134.64, 136.92, 137.05, 145.06, 168.58. ^{125}Te NMR (300 MHz, $CDCl_3$): δ 1124 ppm.

Table 3. Crystal Data and Structure Refinement for 4, 5, and 6

	4	**5**	**6**
empirical formula	$C_{53}H_{51}N_2O_2Te_2$	$C_{23}H_{22}ClNOTe$	$C_{23}H_{22}Cl_3NOTe$
fw	1003.16	491.47	562.37
cryst syst	monoclinic	monoclinic	monoclinic
space group	*C*2/*c*	$P2_1/c$	$P2_1/n$
a (Å)	26.369(2)	11.5012(8)	10.0971(9)
b (Å)	10.3905(6)	9.7805(7)	20.6226(14)
c (Å)	17.0929(15)	18.4007(14)	11.5861(9)
β (deg)	102.266(10)	93.532(9)	104.857(9)
V (Å^3)	4576.4(6)	2065.9(3)	2331.9(3)
Z	4	4	4
D(calcd) [Mg/m^3]	1.456	1.580	1.602
abs coeff (mm^{-1})	1.317	1.582	1.634
no. of obsd reflns [$I > 2\sigma(I)$]	4317	4387	4198
final $R(F)$ [$I > 2\sigma(I)$][a]	0.0325	0.0305	0.0290
$wR(F^2)$ [$I > 2\sigma(I)$]	0.0666	0.0701	0.0685
no. of data/ restraints/params	4317/11/276	4387/0/248	4198/0/266
goodness of fit on F^2	0.842	0.995	0.947

[a] Definitions: $R(F_o) = \sum||F_o| - |F_c||/\sum|F_o|$ and $wR(F_o^2) = \{\sum[w(F_o^2 - F_c^2)^2]/\sum[w(F_c^2)^2]\}^{1/2}$.

Synthesis of [2-[1-(3,5-Dimethylphenyl)-2-naphthyl]-4,5-dihydro-4,4-dimethyloxazole]tellurium(II) Iodide (8). A solution of iodine (0.062 g, 0.25 mmol) in carbon tetrachloride (20 mL) was treated with **4** (0.227 g, 0.25 mmol) in carbon tetrachloride (25 mL) at 0 °C, and stirring continued for an additional 0.5 h. The usual workup gave the desired orange-colored compound. The orange-colored crystals were obtained from the mixture of chloroform and toluene (2:1). Yield: 0.20 g, 70%. Mp: >196 °C (dec). Anal. Calcd for $C_{23}H_{22}NOTeI$: C, 47.39; H, 3.80; N, 2.40. Found: C, 47.97; H, 4.60; N, 2.56. IR (KBr, cm^{-1}): 1604 ($\nu_{C=N}$). λ_{max}/nm (methanol): 294 (ϵ/dm^3 mol^{-1} cm^{-1} 21 034). ^{1}H NMR (300 MHz, $CDCl_3$): δ 1.53 (s), 2.38 (s), 4.22 (s), 6.90 (s), 7.00−8.00 (m), 9.00 (s). ^{13}C NMR (300 MHz, $CDCl_3$): δ 21.58, 28.91, 65.36, 82.89, 120.00, 126.43, 127.40, 127.59, 127.85, 128.65, 129.34, 129.74, 131.13, 134.69, 136.92, 137.14, 140.27, 168.40. ^{125}Te NMR (300 MHz, $CDCl_3$): δ 996 ppm.

Synthesis of [2-[1-(3,5-Dimethylphenyl)-2-naphthyl]-4,5-dihydro-4,4-dimethyloxazole]phenyl Telluride (9). Compound **9** was prepared by the reaction of **2** with PhTeBr. A solution of PhTeBr was prepared in situ by the addition of an equimolar amount of Br_2 (0.82 g, 0.26 mL, 5.1 mmol) in benzene (12 mL) into a solution of Ph_2Te_2 (2.09 g, 5.1 mmol) in ether (125 mL) at −78 °C. This solution was stirred for 0.5 h in an ice bath, and the resulting suspension of red-colored PhTeBr was transferred into a ether solution of **2** at −78 °C. Stirring in an ice bath for 1 h and then 0.5 h at room temperature, followed by usual workup, gave the desired yellow compound. The yellow compound was purified by column chromatography with a petroleum ether (60−80 °C) and dichloromethane mixture (1:1). Yield: 0.34 g, 13%. Mp: 135−137 °C. Anal. Calcd for $C_{29}H_{27}NOTe$: C, 65.33; H, 5.10; N, 2.62. Found: C, 64.91; H, 5.02; N, 2.56. λ_{max}/nm (methanol): 294 (ϵ/dm^3 mol^{-1} cm^{-1} 9540). ^{1}H NMR (300 MHz, $CDCl_3$): δ 1.34 (s), 2.39 (s), 3.74 (s), 6.88 (s), 7.01 (s), 7.3−7.8 (m), 7.96 (d). ^{13}C NMR (300 MHz, $CDCl_3$): δ 21.43, 28.30, 67.45, 79.47, 110.70, 116.90, 117.37, 123.28, 126.15, 126.34, 126.98, 127.22, 127.30, 127.59, 127.87, 127.97, 128.62, 129.09, 129.49, 129.82, 131.28, 134.35, 134.82, 136.84, 137.24, 138.33, 140.41, 140.78, 164.10. ^{125}Te NMR (300 MHZ, $CDCl_3$): δ 670 ppm. ES-MS (*m*/*z*): 533 (M^+), 458 (RTe^+), 330 (R^+).

Table 4. Crystal Data and Structure Refinement for 7 and 8

	7	8
empirical formula	$C_{23}H_{22}BrNOTe$	$C_{23}H_{22}INOTe$
fw	535.93	582.92
cryst syst	monoclinic	monoclinic
space group	$P2_1/c$	$P2_1/c$
a (Å)	11.6776(9)	11.7944(10)
b (Å)	9.8397(6)	9.8566(6)
c (Å)	18.3471(12)	18.3522(15)
β (deg)	91.723(8)	90.962(10)
V (Å^3)	2107.2(2)	2133.2(3)
Z	4	4
D(calcd) [Mg/m^3]	1.689	1.815
abs coeff (mm^{-1})	3.320	2.854
no. of obsd reflns [$I > 2\sigma(I)$]	3991	4353
final $R(F)$ [$I > 2\sigma(I)$][a]	0.0351	0.0467
$wR(F^2)$ [$I > 2\sigma(I)$]	0.0801	0.1127
no. of data/restraints/params	3991/0/248	4353/0/248
goodness of fit on F^2	0.886	0.925

[a] Definitions: $R(F_o) = \sum||F_o| - |F_c||/\sum|F_o|$ and $wR(F_o^2) = \{\sum[w(F_o^2 - F_c^2)^2]/\sum[w(F_c^2)^2]\}^{1/2}$.

X-ray Structure Determination of Compounds 4−8. The diffraction measurements were performed in a STOE (Darmstadt, Germany) IPDS imaging plate single-crystal diffractometer at room temperature with graphite-monochromated Mo Kα radiation ($\lambda = 0.7107$ Å). The structures were solved by direct methods and full-matrix least-squares refinement on F^2 (program SHELXL-97).[36] Hydrogen atoms were localized by geometrical means. A riding model was chosen for refinement. The isotropic thermal parameters of the H atoms were fixed at 1.5 times (CH_3 groups) or 1.2 times U(eq) (Ar−H) of the corresponding C atom. Some details of the data collection and refinement are given in Tables 3 and 4.

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Supporting Information Available: Complete tables of crystallographic data, final atomic coordinates, bond lengths and angles, anisotropic displacement parameters, and hydrogen atom coordinates for **4**−**8**. This material is available free of charge via the Internet at http://pubs.acs.org.

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