

Synthesis and characterization of monomeric diorganotellurium dihalides: crystal and molecular structures of diphenacyltellurium dibromide and -diiodide

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Abstract

Tellurium, but not selenium, reacts with phenacyl bromide (ω -bromoacetophenone) to give diphenacyltellurium dibromide $(\text{PhCOCH}_2)_2\text{TeBr}_2$ (**1**), which represents the first example of a functionally substituted organotellurium halide to have been prepared directly from elemental tellurium and an organic halide. Metathesis of **1** with KI affords the crystalline diiodide, $(\text{PhCOCH}_2)_2\text{TeI}_2$ (**2**), but halide–pseudohalide exchange does not proceed with KSCN or AgN_3 . Compounds **1** and **2** have been characterized by elemental analyses, IR, ^1H - and ^{13}C -NMR and mass spectrometry. Coordinative interaction of both the carbonyl groups in **1** and **2**, in solid state as well as in solution, is indicated by IR spectra. Crystal and molecular structures of the dihalides were determined by X-ray diffraction method. Compounds **1** and **2** are isostructural and crystallize in the monoclinic system with space group $P2_1/n$. The primary geometry about the central Te atom in both the compounds is Ψ -trigonal-bipyramidal with axial halogens. Stereochemically active lone pair of electrons occupies the equatorial plane along with methylene C atoms of the organic ligands. The $\text{Te}\cdots\text{O}$ intramolecular attractive interactions, though weak [$\text{Te}\cdots\text{O}(1)$, $\text{Te}\cdots\text{O}(2)$: 2.938, 2.912 Å in **1** and 2.877, 2.818 Å in **2**] appear to saturate tellurium(IV) atom coordinatively so as to prevent intermolecular $\text{Te}\cdots\text{Br/I}$ interactions. However, there is evidence of weak intermolecular $\text{Te}\cdots\text{Br}\cdots\text{H}(\text{methylene})$ secondary interactions in compound **1**, leading to the formation of supramolecular assemblies. © 2002 Elsevier Science B.V. All rights reserved.

Keywords: Secondary bonding; Organotellurium halides; Intramolecular coordination

1. Introduction

The ubiquitous nature of intermolecular and intramolecular attractions is a characteristic feature of chalcogen chemistry and owes to the hypervalent nature of the elements. Such secondary interactions have attracted considerable interest in the last two decades due to their role in the (a) conformation of biological macromolecules [1], (b) stabilization of otherwise unstable organoselenium–tellurium compounds [2], (c) catalytic mechanism of glutathione peroxidase-like anti-oxidant activity [3], (d) activity of the therapeutic agents [1b,4] and (e) supramolecular association [5,6]. Systematic structural investigations on the origin and magnitude

of such interactions that involve sulfur and selenium have been carried out in detail [1a,7]. Among organotellurium compounds, the kinetic stability of organytellurenyl halides RTeX is enhanced when the functionalized organic ligand provides an opportunity for intramolecular coordination through one of its nucleophilic atoms A, to the central tellurium(II) and a nearly linear $\text{X}\cdots\text{Te}\cdots\text{A}$ arrangement is attained [8,9].

Organotellurium(IV) halides in general, and diorganotellurium(IV) dihalides in particular, have been shown to involve intermolecular $\text{Te}\cdots\text{X}$ and $\text{I}\cdots\text{I}$ secondary bonds that lead to molecular association giving rise to dimeric, two-dimensional zigzag ribbon like or three-dimensional polymeric structures in the solid state [5,9,10]. However, when the organic ligand is functionalized and possesses a nucleophilic atom N or O in close proximity to tellurium(IV), intramolecular $\text{Te}\cdots\text{N/O}$ bonding is expected to discourage intermole-

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cular $\text{Te} \cdots \text{X}$ secondary bonding. Organotellurium(IV)-trichlorides and -tribromides that involve intramolecular coordination through carbonyl oxygen [11,12] or pyridyl [13,14], azo [15], imino [16] and amino [8,17] nitrogen as well as intermolecular $\text{Te} \cdots \text{X}$ secondary bond (though weak and only one) are accessible either via transmetallation using the organomercury derivative and TeCl_4 or by orthotelluration of the appropriate organic substrate using *n*-butyllithium and elemental tellurium followed by halogenolysis reaction with sulphuryl chloride or bromine [18]. The diorganotellurium(IV) dihalides that have been studied for intramolecular coordination are of $\text{RR}'\text{TeX}_2$ stoichiometry, where only one organic ligand is functionalized [19]. All such intramolecularly coordinated organotellurium(IV) halides belong to 12–Te–5 class and always involve molecular association through intermolecular, though weak, $\text{Te} \cdots \text{X}$ secondary bonding in solid state.

We report here the first examples of structurally characterized diorganotellurium(IV) dihalides in which, both the functionalized organic ligands are involved in intramolecular coordination through carbonyl O atoms and the resulting 14–Te–6 system is devoid of any intermolecular $\text{Te} \cdots \text{X}$ secondary interaction. It also appears to be the first report on oxidative addition of a functionalized alkyl halide to elemental tellurium, though the addition of simple alkyl iodides–bromides to Te to give dialkyltellurium dihalides has been known since long.

2. Results and discussion

2.1. Synthesis and spectral characterization

The freshly activated tellurium powder reacts with phenacyl bromide under mild condition to afford colorless **1**. However, neither the ethylene ketal of phenacyl bromide nor *p*-bromophenacyl bromide reacted with tellurium powder even when heated up to their melting points. While the former case is not entirely unexpected the latter case is surprising as both phenacyl bromide and *p*-bromophenacyl bromide react with Ph_3P with equal ease to give the corresponding phosphonium salts [20]. The reason is probably electronic and not steric. Metathetical reaction of **1** with an excess of KI in chloroform yielded red needles of **2** but halide–pseudohalide exchange reactions with KSCN and AgN_3 failed, as did the reaction of Se powder with phenacyl bromide. Both **1** and **2** are moderately soluble in chloroform and dichloromethane and are stable to air.

2.2. IR and NMR spectroscopic studies

The IR spectra of **1** and **2** show absorption due to $\nu(\text{CO})$ at lower wave number $\sim 1650 \text{ cm}^{-1}$ compared

with that appearing at 1693.4 cm^{-1} in case of phenacyl bromide. This negative shift [$\Delta\nu(\text{CO}) = 34.7 \text{ cm}^{-1}$ for **1** and 48.2 cm^{-1} for **2**] is indicative of the involvement of carbonyl oxygens in coordination to Te (IV). Larger value of $\Delta\nu(\text{CO})$ for **2** suggests comparatively stronger coordinative interaction of CO groups to Te(IV) in **2** compared with **1**. Coordinative saturation of Te(IV) in **1** and **2** is also evident from the fact that both the compounds failed to form anionic complexes with Me_4NI which readily forms complexes with organotellurium(IV) halides that are devoid of any intramolecular coordinative interactions [21].

The ^1H -NMR spectra of **1** and **2** consist of a multiplet for the phenyl ring protons and a singlet for the methylene protons which is shifted downfield compared with the signal for the same protons in phenacyl bromide. This deshielding of the methylene protons is probably caused, at least in part, due to coordinative interaction of the carbonyl groups. The signal for the methylene protons is flanked by two ^{125}Te satellites with $^2J(^{125}\text{Te}-^1\text{H})$ value of 6.9 Hz for **1** and 6.3 Hz for **2**.

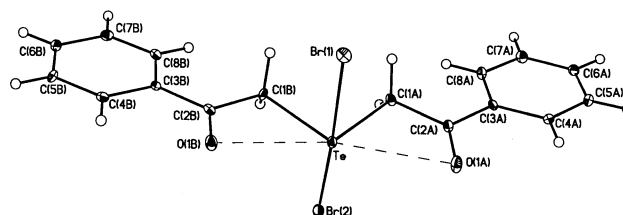
The ^{13}C -NMR spectra of the dihalides exhibit signals due to carbon atom of CO group at $\sim 193 \text{ ppm}$ and methylene group at $\sim 27.7 \text{ ppm}$ in addition to signals for the phenyl ring carbon atoms at their usual places.

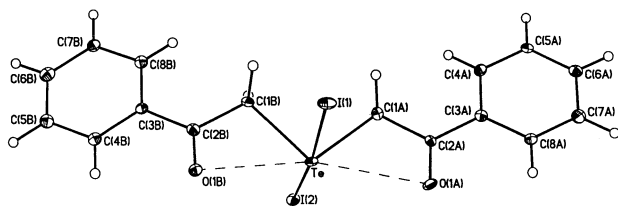
The mass spectrum of **1** does not show the molecular ion peak but shows fragmentation peaks at m/z 105, 77 and 51 due to $\text{C}_6\text{H}_5\text{CO}^+$, C_6H_5^+ and C_4H_3^+ characteristic of the fragmentation of the aromatic ketones. The FAB mass spectrum consists of the base peak at m/z 447 corresponding to $[\text{M}^+ - \text{Br}]$ for ^{130}Te and another peak at m/z 367 corresponding to $[\text{M}^+ - 2\text{Br}]$ for ^{130}Te .

2.3. Description and discussion of the structures of **1** and **2**

The molecular structures of **1** and **2** with atom numbering are presented in Figs. 1 and 2, respectively. Crystal data and numerical details of the data collection and refinement are given in Table 1 and selected bond lengths and angles in Table 2. Torsion angle values that are significant to illustrate distortion from coplanarity of the atoms around the central Te atom are given in Table 3.

Both the compounds crystallize in the monoclinic system with four molecules per unit cell. The primary



Fig. 2. ORTEP view of compound **2**.Table 1
Crystal data and structure refinement details for compounds **1** and **2**

	Compound 1	Compound 2
Empirical formula	C ₁₆ H ₁₄ Br ₂ O ₂ Te	C ₁₆ H ₁₄ I ₂ O ₂ Te
Formula weight	525.69	619.67
Temperature (K)	93(2)	93(2)
Wavelength (Å)	0.71073	0.71073
Crystal system	Monoclinic	Monoclinic
Space group	<i>P</i> 2 ₁ / <i>n</i>	<i>P</i> 2 ₁ / <i>n</i>
Crystal size (mm)	0.15 × 0.35 × 0.98	0.12 × 0.35 × 0.96
Unit cell dimensions		
<i>a</i> (Å)	5.8385(7)	5.7920(5)
<i>b</i> (Å)	10.4127(13)	7.4170(7)
<i>c</i> (Å)	27.656(3)	40.914(4)
α (°)	90	90
β (°)	91.166(2)	90.520(2)
γ (°)	90	90
Volume (Å ³)	1681.0(4)	1757.6(3) <i>g</i> = 90°
<i>Z</i>	4	4
Absorption coefficient (mm ^{−1})	6.524	5.207
Index ranges	−6 ≤ <i>h</i> ≤ 6, −12 ≤ <i>k</i> ≤ 12, −32 ≤ <i>l</i> ≤ 31	−6 ≤ <i>h</i> ≤ 6, −8 ≤ <i>k</i> ≤ 8, −47 ≤ <i>l</i> ≤ 48
Reflections collected	8879	9583
Independent reflections	2864 [<i>R</i> _{int} = 0.0295]	2977 [<i>R</i> _{int} = 0.0766]
Absorption correction	SADABS	SADABS
Data/restraints/parameters	2864/0/191	2977/96/191
Goodness-of-fit on <i>F</i> ²	1.000	1.367
Final <i>R</i> indices	<i>R</i> ₁ = 0.0261, <i>wR</i> ₂ = 0.0572	<i>R</i> ₁ = 0.0767, <i>wR</i> ₂ = 0.1883
[<i>I</i> > 2σ(<i>I</i>)] ^a		
<i>R</i> indices (all data)	<i>R</i> ₁ = 0.0336, <i>wR</i> ₂ = 0.0594	<i>R</i> ₁ = 0.0834, <i>wR</i> ₂ = 0.1915
Extinction coefficient	0.00040(15)	0.0027(4)
Largest difference peak and hole (e Å ^{−3})	1.00 and −0.706	3.748 and −2.567

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

geometry about the central Te atom in these compounds is Ψ-trigonal-bipyramidal with apical positions occupied by the more electronegative halogen atoms whereas the methylene C atoms are at equatorial corners. The lone pair of electrons at the third equatorial position is stereochemically active as it reduces bond angles X(1)–Te–X(2) (172.5° in **1** and 172.6° in **2**) and C(1A)–Te–C(1B) (93.0° in **1** and 95.8° in **2**) considerably. The distances Te–C(1A) and Te–C(1B) being 2.139(4) and 2.134(4) Å in **1** and 2.131(15) Å each in **2** are insignificantly shorter than the sum of Pauling's single

Table 2
Bond lengths (Å) and angles (°) for **1** and **2**

	1 (X = Br)	2 (X = I)
<i>Bond lengths</i>		
Te–X(1)	2.6459(5)	2.8808(14)
Te–C(1B)	2.134(4)	2.131(15)
C(1B)–C(2B)	1.515(5)	1.54(2)
C(2B)–C(3B)	1.482(5)	1.48(2)
O(1B)–C(2B)	1.224(4)	1.208(19)
Te–O(1A)	2.938	2.877
Te–X(2)	2.6927(5)	2.9345(14)
Te–C(1A)	2.139(4)	2.131(15)
C(1A)–C(2A)	1.509(5)	1.50(2)
C(2A)–C(3A)	1.486(5)	1.48(2)
O(1A)–C(2A)	1.226(4)	1.217(18)
Te–O(1B)	2.917	2.818
<i>Bond angles</i>		
C(1B)–Te–C(1A)	93.04(14)	95.8(6)
C(1B)–Te–X(1)	87.56(10)	88.3(4)
C(1A)–Te–X(1)	89.13(10)	88.7(4)
C(2B)–C(1B)–Te	107.4(2)	103.6(10)
O(1B)–C(2B)–C(3B)	122.3(3)	123.0(14)
O(1B)–C(2B)–C(1B)	119.1(4)	117.5(14)
C(3B)–C(2B)–C(1B)	118.6(3)	119.5(13)
C(4B)–C(3B)–C(2B)	118.8(3)	117.7(14)
C(8B)–C(3B)–C(2B)	122.0(3)	121.7(14)
O(1B)–Te–C(1B)	53.2	54.7
O(1B)–Te–C(1A)	145.5	149.9
O(1A)–Te–O(1B)	160.7	152.7
X(1)–Te–X(2)	172.474(15)	172.64(5)
C(1B)–Te–X(2)	86.52(10)	85.1(4)
C(1A)–Te–X(2)	86.54(10)	88.7(4)
C(2A)–C(1A)–Te	107.8(2)	106.6(10)
O(1A)–C(2A)–C(3A)	121.9(4)	121.4(13)
O(1A)–C(2A)–C(1A)	119.8(3)	119.1(13)
C(3A)–C(2A)–C(1A)	118.2(3)	119.4(13)
C(8A)–C(3A)–C(2A)	121.8(4)	119.6(14)
C(4A)–C(3A)–C(2A)	118.6(3)	121.2(14)
O(1A)–Te–C(1A)	52.9	53.5
O(1A)–Te–C(1B)	145.8	147.6

Table 3
Significant torsion angles (°) for **1** and **2**

	1	2
C(1B)–Te–C(1A)–C(2A)	−176.7(3)	168.0(10)
Te–C(1A)–C(2A)–O(1A)	−2.6(4)	1.4(17)
Te–C(1A)–C(2A)–C(3A)	178.9(3)	−176.7(11)
O(1A)–C(2A)–C(3A)–C(8A)	167.4(4)	−1(2)
C(1A)–C(2A)–C(3A)–C(8A)	−14.2(6)	177.4(14)
O(1A)–C(2A)–C(3A)–C(4A)	−12.9(5)	177.9(15)
C(1A)–C(2A)–C(3A)–C(4A)	165.6(3)	−4(2)
C(1A)–Te–C(1B)–C(2B)	−174.6(3)	178.9(10)
Te–C(1B)–C(2B)–O(1B)	4.7(4)	16.4(17)
Te–C(1B)–C(2B)–C(3B)	−175.3(3)	−163.7(12)
O(1B)–C(2B)–C(3B)–C(4B)	3.9(6)	−9(2)
C(1B)–C(2B)–C(3B)–C(4B)	−176.1(3)	171.5(14)
O(1B)–C(2B)–C(3B)–C(8B)	−175.1(4)	173.3(16)
C(1B)–C(2B)–C(3B)–C(8B)	4.8(5)	−7(2)

bond covalent radii [22] of tellurium and sp^3 hybridized carbon atoms (2.142 Å) and may be compared with the typical values found in dialkyl- [5c], alkylaryl- [19,23] and cycloalkyl-tellurium dihalides [5c,5d]. The phenyl rings are planar and its bond lengths and angles are as expected.

Molecular association is a characteristic feature of organotellurium(IV) halides where the central Te atom attains six coordination via intermolecular $Te \cdots X$ secondary interactions. The $Te \cdots Br$ distances 2.6459(5) and 2.6927(5) Å in **1** are longer than the sum of covalent radii of Te (1.37 Å) and Br (1.13 Å) [22] but are typical of the reported Te–Br bond lengths when the Br atom is not involved in intermolecular $Te \cdots Br$ secondary interactions [9,17]. Longer Te–Br bond distances, viz. 2.758(2) Å for [2-(dimethylamino-methyl)phenyl]tellurium(IV) tribromide [17] and 2.71(1) Å for 2-(2'-pyridyl)phenyltellurium(II) bromide [24] have been observed and in the case of the former elongation of Te–Br bonds has been attributed to the involvement of this Br atom in intermolecular $Te \cdots Br$ secondary interaction.

The apical Te–I bond lengths 2.8808(14) and 2.9345(14) Å in compound **2** are typical of organotellurium diiodides that are reported to possess nearly linear I–Te–I system with two unequal Te–I distances; the shorter in the range 2.85–2.90 Å and the longer in the range 2.91–3.01 Å [5d,5e]. The pair of bonds, each of order ca. 1/2, has been described as three center-four electron bond where lengthening of one through intermolecular secondary bonding of the iodine atom to a Te or I atom in neighboring molecules shortens the other bond of the pair. Compound **2** is the first structurally characterized organotellurium(IV) iodide where six coordination around the Te atom is achieved by intramolecular secondary interactions and intermolecular $Te \cdots I$ or $I \cdots I$ secondary interactions are absent. The explanation given above for the elongation of one of the Te–X bond in intermolecularly bonded organotellurium halides is not applicable for **2** and may not be the only factor for elongation in the former cases as well. There is evidence of intermolecular $Te-Br \cdots H$ secondary bonding in **1** [$Br \cdots H$, 2.951 Å ($0.5-x$, $0.5+y$, $-0.5-z$) and $Te-Br-H$ angle, 164.3°]. One of the Br atoms of one molecule bridges two H atoms, one from each methylene groups of the neighboring molecule simultaneously (Fig. 3), leading to the formation of molecular assemblies with staircase like structure.

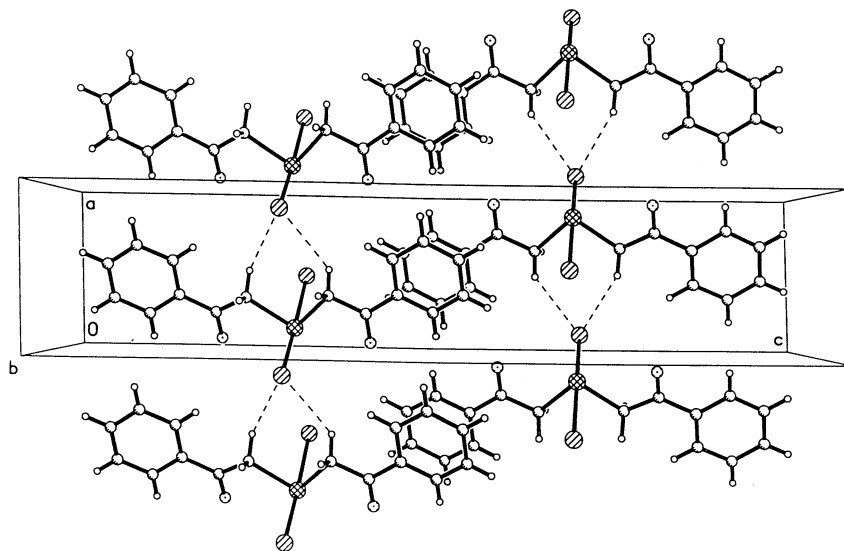
Involvement of both the carbonyl O atoms to the central Te atom is evident from the Te–O distances 2.938 and 2.917 Å in compound **1** and 2.877 and 2.818 Å in compound **2** which are shorter than the sum of the van der Waals radii (3.58 Å) of the two atoms. Comparatively smaller $Te \cdots O$ interatomic distances in **2** indicate stronger intramolecular interaction and is in accordance with the larger value for $\Delta\nu(CO)$ for **2** than

1. This may be attributed to steric factors as longer Te–I bonds in **2** would permit closer approach of the carbonyl oxygens to the central Te atom. The $Te \cdots O$ interactions appear to be weak in comparison to those reported for other intramolecularly bonded organotellurium compounds [11,12,25–27], where the observed Te–O distances fall in the range 2.13–2.57 Å {except in the case of 2-(butyldichlorotelluro)benzaldehyde [19], where it is 2.839 Å}. All such compounds consist of less strained five membered intramolecular heterocyclic ring. However, the two organic bidentate chelating ligands with a smaller bite present in molecules **1** and **2**, that belong to 14–Te–6 class, form four-membered heterocyclic rings. The strong intramolecular interactions leading to close $Te \cdots O$ contacts seem to be impeded by steric limitations imposed by the tetrahedral and trigonal angles at the carbon atoms of the methylene and the carbonyl groups, respectively. As a consequence, all the atoms that constitute heterocyclic rings due to intramolecular coordination around Te atom in each of the compound **1** and **2** deviate marginally from coplanarity as is obvious from the torsion angle values given in Table 3. Analogous weak intramolecular secondary interactions with $Te \cdots O$ distances 2.953 Å for acetato(2-phenylazophenyl)-C,N'-tellurium(II) [28] and 2.988 Å for diacetatobis(*p*-methoxyphenyl)tellurium(IV) [29] have been observed earlier and support our conclusion. It is therefore, interesting to note that Te(IV) atom prefers intramolecular $Te \cdots O$ interactions to complete its six coordination to intermolecular $Te \cdots X$ secondary interactions even when it leads to the formation of the strained four-membered rings. The molecules of compound **1** and **2** acquire cisoidal conformation of the organic ligands, though there exists an opportunity for the Te atom to attain six coordination in each molecule via intramolecular $Te \cdots O$ secondary interaction by adopting transoid ligand conformations by means of free rotations about Te–C(methylene) or C(methylene)–C(carbonyl) bonds, which is probably prohibited by the presence of stereochemically active lone pair on the Te atom.

3. Experimental

3.1. General procedures

All reactions were carried out under dry nitrogen gas. Solvents were purified and dried by standard methods. The commercial tellurium powder (Fluka) was activated by washing with conc. HCl and water and drying at ~ 120 °C. It was grinded for 15 min just before use. Phenacyl bromide was prepared by bromination of acetophenone in glacial acetic acid and its ethylene ketal by azeotropic distillation with ethylene glycol. Melting points were recorded in capillary tubes and are

Fig. 3. Unit cell structure of compound **1**.

uncorrected. ^1H - and ^{13}C -NMR spectra were recorded at 300.13 and 75.46 MHz, respectively, in CDCl_3 or $\text{DMSO}-d_6$ on a Varian DRX 300 Spectrometer using TMS as internal standard. IR spectra of solid samples were examined as KBr pellets as well as chloroform solution using a Perkin–Elmer RX1 Spectrometer. Elemental carbon and hydrogen analyses were performed on a Carlo Erba 1108 make analyzer. Tellurium was estimated volumetrically and the halogen content gravimetrically as silver halide. Fast atom bombardment (FAB) mass spectrum of **1** was recorded on a JEOL SX 102/DA-6000 Mass Spectrometer/Data System using Argon/Xenon (6 kV, 10 mA) as the FAB gas. The accelerating voltage was 10 kV and *m*-nitrobenzyl alcohol was used as the matrix.

3.1.1. Synthesis of $(\text{PhCOCH}_2)_2\text{TeBr}_2$ (**1**)

A mixture of tellurium powder (1.28 g, 10 mmol) and phenacyl bromide (4.38 g, 22 mmol) was heated to $\sim 60^\circ\text{C}$ with stirring for 5 h. Dichloromethane (10 ml) was added and the reaction mixture was refluxed for 2 h. The resulting green solid was filtered and washed with cold dichloromethane (2×5 ml). It was extracted with hot chloroform. Concentration of the chloroform solution and addition of pet-ether ($40\text{--}60^\circ\text{C}$) afforded colorless crystal of **1**. Yield 2.6 g, (50%); m.p. $182\text{--}184^\circ\text{C}$; Anal. Found: C, 36.56; H, 2.72; Cl, 30.35; Te, 20.43. Calc. for $\text{C}_{16}\text{H}_{14}\text{O}_2\text{Br}_2\text{Te}$: C, 36.56; H, 2.68; Br, 30.40; Te, 20.50%. ^1H -NMR (CDCl_3), δ (ppm) 8.03(d), 7.70 (t), 7.55 (t), 5.45 (s). ^{13}C -NMR ($\text{DMSO}-d_6$), δ (ppm) 198.8, 137.72, 134.05, 129.56, 129.01, 27.57; IR: $\nu(\text{CO})$, 1658.7 cm^{-1} .

3.1.2. Synthesis of $(\text{PhCOCH}_2)_2\text{TeI}_2$ (**2**)

An excess of potassium iodide was added to a solution of **1** (0.53 g, 1.0 mmol) in chloroform (20 ml) and the

mixture was stirred vigorously for 5 h. After filtering off the potassium halide, the red solution was concentrated to give red needles of **2**. Yield: 0.40 g (65%); m.p. 134°C ; Anal. Found: C, 31.24; H, 2.40; I, 41.22; Te, 20.35. Calc. for $\text{C}_{16}\text{H}_{14}\text{O}_2\text{I}_2\text{Te}$: C, 31.01; H, 2.28; I, 40.96; Te, 20.59%. ^1H -NMR (CDCl_3), δ (ppm) 8.00 (d), 7.67 (t), 7.52 (t), 5.43 (s). ^{13}C -NMR ($\text{DMSO}-d_6$), δ (ppm) 190.0, 136.8, 133.2, 128.7, 128.1, 26.7; IR: $\nu(\text{CO})$, 1645.2 cm^{-1} .

3.1.3. Attempted reaction of **1** with Me_4NI , KCN or AgN_3

To a solution of **1** (0.26 g, 0.5 mmol.) in chloroform (10 ml) was added Me_4NI (0.24 g, 1.2 mmol). The reaction mixture was refluxed for 4 h, cooled and filtered. The filtrate was freed from solvent and the residue (0.23 g) was identified as unreacted **1** (authentic ^1H -NMR spectrum).

Compound **1** was recovered unchanged after stirring with an excess of potassium thiocyanate or silver azide in refluxing chloroform for 5 h.

3.1.4. Attempted reaction of tellurium with phenacyl bromide ethylene ketal or 4-bromophenacyl bromide

A mixture of tellurium powder (1.28 g, 10 mmol) and the ethylene ketal of phenacyl bromide (5.08 g, 25 mmol) was heated to $\sim 70^\circ\text{C}$ for 5 h Chloroform (10 ml) was added and the reaction mixture was refluxed for 2 h. Unreacted tellurium (1.26 g, 98%) was filtered off. The filtrate was freed from solvent to give unreacted ketal (4.83 g, 95.1%), m.p. 60°C (authentic IR and ^1H -NMR spectrum).

Reactants were similarly recovered unchanged when tellurium powder was heated with 4-bromophenacyl bromide at $\sim 100^\circ\text{C}$ for 5 h.

3.1.5. Attempted reaction of selenium powder with phenacyl bromide

Selenium powder (0.79 g, 10 mmol) and phenacyl bromide (4.38 g, 22 mmol) were heated together at $\sim 60^\circ\text{C}$ for 8 h. Chloroform (10 ml) was added and the reaction mixture was refluxed for 2 h. After cooling, the reaction mixture was filtered, washed with chloroform (2×5 ml) and dried. The non-aromatic residue (0.75 g; 95%) was unreacted selenium powder. The phenacyl bromide was recovered from the filtrate (authentic IR spectrum).

3.2. X-ray crystallographic studies

Diffraction quality transparent needle shaped crystals of compound **1** were obtained by allowing a saturated acetone solution to cool slowly at room temperature. Reddish–orange fine needle shaped crystals of **2** were obtained by keeping the concentrated filtrate obtained from the reaction of **1** with KI in chloroform overnight at room temperature. The X-ray diffraction measurements were performed at 93(2) K for both the compounds on a Bruker P4S diffractometer employing graphite monochromated Mo– K_α radiation ($\lambda = 0.71073 \text{ \AA}$). The lattice parameters were determined from 25 randomly selected reflections using the automatic search index and least-squares routines. A total of 8879 reflections over a θ range from 2.09 to 24.76° for the compound **1** and 9583 reflections over a θ range from 1.00 to 24.71° for the compound **2** were collected using ω – 2θ scan technique and the data were corrected for Lorentz and polarization effects. An empirical absorption correction was applied to the data using SADABS program. The maximum transmission value of the correction factor for both the compounds was 1.000000 while the minimum values were 0.565707 and 0.287325 for compound **1** and **2**, respectively. Two standard reflections were monitored after every 60 min of X-ray exposure time in each case, to check electronic reliability and crystal stability and no abnormalities were found. The structures were solved by the routine heavy-atom method using SHELXS-86 program and difference Fourier syntheses yielded the position of all non hydrogen atoms. The non-hydrogen atoms were refined anisotropically while the hydrogen atoms introduced on calculated positions were refined isotropically. An acceptance criterion of $I > 2\sigma(I)$ was used in determining the reflection to be used in least-squares refinement. The final cycle of full-matrix least-squares refinement based on 191 variable parameters and 2864 and 2977 observed reflections for compound **1** and **2**, respectively, converged with unweighted (R_1) and weighted (wR_2) agreement factors of 0.0261 and 0.0594 for compound **1** and 0.0767 and 0.1883 for the compound **2**.

4. Supplementary material

Crystallographic data for the structure analyses have been deposited with the Cambridge Crystallographic Data Center, CCDC no.179339 for diphenacyltellurium dibromide (**1**) and CCDC no. 179340 for diphenacyltellurium diiodide (**2**). Copies of this information may be obtained free of charge from The Director, CCDC, 12 Union Road, Cambridge CB2 1EZ, UK (Fax: +44-1223-336033; or e-mail: deposit@ccdc.cam.ac.uk or [www: http://www.ccdc.cam.ac.uk](http://www.ccdc.cam.ac.uk)).

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