Synthesis and Single Crystal X-ray Studies of Cyclic Te(IV) Diiodide

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Abstract. The cyclic tellurium(IV) diiodide, 2-Methyl-1,1-diiodo-1-telluracyclopentane, was prepared in good yields at room temperature by the incorporation of tellurium powder across Carbon–Iodine bond in presence of sodium iodide and acetone. The cyclic tellurium(IV) diiodide compound has been established by proton and ¹³carbon NMR spectroscopy along with elemental analysis. This compound was further characterized by ¹²⁵Te NMR in DMSO. Molecular structures of cyclic tellurium(IV) diiodide was also established by single-crystal X-ray studies. In solid-state, molecular structures of cyclic tellurium(IV) diiodide possess scarcely observed Te···I secondary bonding interactions (SBIs) and two molecule are co-crystallized. Both molecules are interconnected with each other by Te···I secondary bonding interactions. The five-membered rings acquire a twist-boat shape structure. Observed C–Te–C bond angles for molecule A, and molecule B are 85.0(1)° & 85.4(2)° respectively. Similarly observed, I–Te–I bond angles for both molecule A & B are 174.5(1)° & 174.2(1)° respectively.

Keywords. Cyclic Tellurium Compound, Insertion Reactions, Secondary Bonding Interactions.

1. Introduction
Available synthetic routes to organotellurium(IV) derivatives are oxidative addition reactions, electrophilic substitution reactions, and insertion reactions of elemental tellurium across the carbon–halogen bonds [1,2]. The oxidative addition of halogens with diorganoditellurides and diorganotellurides can afford ArTeX₃ and (Ar/R)₂TeX₂ (X = Cl₂, Br₂ & I₂) derivatives respectively (Ar = Aryl & R= Alkyl) [3-5]. In the case of electrophilic substitution reactions, TeCl₄/ArTeCl₃ can react with ArHgCl and acidic proton bearing organic moiety (e.g. ketones, anisole etc.) give rise to ArTeCl₃, ArTeCl₂Ar’ and ArTeCl₂CH₂(CO)R, (R = CH₃, CHMe₂, CMe₃, Phenyl etc.) tellurium(IV) derivatives respectively [1,6-8]. Insertion of elemental Tellurium across the C-halogen bond is the oldest methodology to get organotellurium derivatives [1-5] [1,9-13]. This methods can be employed as a direct and simple route to dialkyltellurium(IV) derivatives. Chauhan& co-workers have employed this route to get a series of functionalized bisorganotellurium(IV) derivatives (6a-6i) and unsymmetrical tellurium(IV) derivatives (7a-7j) [14-23]. Thereafter Singh and coworkers have designed the amino acid ligands bearing tellurium(IV) derivatives (8a-8c) by following the insertion route [24]. (Chart 1)
Molecule 1-5 can be synthesized by the insertion of tellurium powder into C-Cl/I bond in the presence of NaI by heating in 2-methoxyethanol[19-13]. First functionalized organotellurium(IV) derivative, [C6H5(CO)CH2]2TeBr2, 6a was reported by the reaction of tellurium powder with phenacyl bromide at ~60 °C[14]. Its para-substituted derivatives [p-yC6H5(CO)CH2]2TeBr2, (y =Me, 6b; MeO, 6c) can also be isolated through the similar route[15]. α-bromopincolone/α-iodopincolone reacted with Te powder at room temperature to give [t-Bu(CO)CH2]2TeBr2, 6d and [t-Bu(CO)CH2]2TeI2, 6d’ respectively[16]. Probably due to the inductive consequence of the t-butyl group and liquid state of α-halopincolone are responsible for room temperature reaction. However, iodoacetamide reacts withtellurium at 100 °C in toluene to give (NH2C(O)CH2)2TeI2, 6e, in good yield [17]. Amidomethylation of elemental tellurium established at 40–60°C for 24–36 h. It involves oxidative insertion of Te(0) into the C–Br bond of N-substituted α-bromoacetamides and afforded a crystalline amidomethyltellurium(IV) dibromides, (RCOCH2)2TeBr2 (R = EtN 6f), MePhN (6g), Me(c-Hex)N, (6h) and O(CH2CH2)2N, (6i) [18]. Similarly α-bromo-2,4,6-trimethylacetophenone, α-bromo-2-acetylthiophene, and α-bromo-3-acyl-2,5-dimethylthiophene react with tellurium powder to give (2,4,6-Me3C6H2COCH2)2TeBr2, (6j) [19], ((2-C4H3O)COCH2)2TeBr2 (6k) [20], (2-(C4H3S)COCH2)2TeBr2, (6l) [21], and (3-(2,5-Me2-C4HS)COCH2)2TeBr2, (6m) at ambient temperature respectively [22]. However, the reaction of α-bromoesters with elemental tellurium was failed up to 100 °C. The reaction takes place in the presence of NaI even at room temperature. In this report authors were able to characterize bis(alkoxy carbonylmethyl)TeI2, (RCOCH2)2TeI2 (R = MeO, 6n; t-BuO, 6o) in very good yields [23]. Simultaneously same group have also demonstrated the insertion of in situ prepared ArTeBr, (Ar = Mesityl, Mes; 1-Napthyl, Np) across the C-Br bond of RCOCH2Br, (R = t-Bu, Et2N, 2-Furon, 2-Thiophene, 2,5-Me2Thiophene) to get unsymmetrical Ar(RCOCH2)2TeBr2 derivatives (7a-7j) [16,18,20-22]. Later Singh et al. have designed the development of (CH3OC(O)CH(CH3)NHCOCH2)2TeBr2, 8a, (CH3OC(O)CH(R)NHCOCH2)2TeI2, (R = H 8b and CH2Phenyl (8c) derivatives by the treatment of Te powder with MeO(CO)CH(R)NH(CO)CH2Br (R = H, Me, CH2Ph) in presence/absence of NaI[24]. Among these observations, only insertion of Te takes place at room temperature without NaI with α-halopincolone, α-bromo-2-acetyl furan, and MeOC(O)CH(Me)NHCOCH2Br. An interesting feature is observed that all three reactants exist in liquid state with carbonyl functional group.

On the basis of these observations, we envisaged that the without functional group alky halide can also react with elemental tellurium at room temperature in presence of NaI and acetone. Since liquid state ligands with sodium iodide are capable of inserting Te(0) across C-Br/I bond at room temperature. With these ideas, we have chosen the ligands 1,4-dibromopentane. Herein, we report the synthesis and single crystal x-ray studies of cyclic chiral center bearing tellurium(IV) diiodide.
2. Result and Discussion

The cyclic tellurium(IV) diiodide was prepared in excellent yield at room temperature by treatment of tellurium powder with 1,3-dibromopropane in presence of sodium iodide and acetone. The molecule was isolated as bright red powdered solids. The powder cyclic tellurium(IV) diiodide dissolve in chloroform and allow to slow evaporation to give rise a red needle shaped crystal. The cyclic tellurium(IV) diiodide has been characterized by $^1$H, $^{13}$C, $^{125}$Te NMR spectroscopy, and elemental analysis. Molecular structure was further confirmed by single-crystal X-ray studies (vide infra). The $^1$H NMR spectrum of the molecule reveal the CH$_3$ proton as a doublet with a coupling constant of 5.6 Hz, & six sets of multiplets for the three methylene and one CH protons. Its $^{13}$C NMR spectrum shows the following 5 peaks: 19.7 Me, 32.1 CH$_2$, 43.1 CH$_2$, 46.6 CH$_2$Te & 55.8 for CHTe ppm. Its $^{125}$Te NMR shows a single peak at 1026 ppm that indicates it is stable in solution.

2.1. Molecular Structures of cyclic tellurium(IV) diiodide

Single crystal x-ray data and structure refinement details formolecule are given in table 1-3. ORTEPobservation of their molecular structures is depicted in figure 2. Its most important bond length and bond angles relevant to its geometry are shown in captions. The cyclic tellurium(IV) diiodide, crystallizes in a monoclinic crystal system with the $P_21/c$ space group. In crystal packing diagram each unit cell contain eight molecules. Each molecule are interconnected through C–H–I intermolecular hydrogen bonding and Te–I secondary bonding interactions. (Shown in figure 3) In this report we are able to observed better refinement data than the earlier reported value. However observed R value (3.68) is slightly higher than the previous reported value (3.37)[13]. Asymmetric unit of this molecule consists of two formula units and therefore, there are two crystallographically unique (but chemically similar). The geometry around the tellurium atom in themolecululesistrigonalbipyramidal. In whicha lone pair and two carbon atoms are located at equatorial positionand the iodine atoms are situated at the axial site. The five-membered rings acquire twist-boat shape structure. It should be well-known that the C–Te–C bond angles are 85.0(1)$^\circ$& 85.4(2)$^\circ$ for molecule A, and molecule B respectively. Similarly observed, I–Te–I bond angles both molecule are 174.5(1)$^\circ$&174.2(1)$^\circ$. 

Figure 1. Representatives of bis(organo)tellurium(IV) species.
2.2. Chemicals and experimental methodology employed
All experiment was carried out using syringe septa techniques under inert (N₂ gas) atmosphere. Acetone, chloroform and other solvents employed in this experiment were freshly distilled and used. 1,3-dibromopropane, and tellurium powder was purchased from Sigma Aldrich and used as received. Elemental analysis of the tellurium molecule was carried out on Perkin-Elmer 2400 elemental instrument. Proton and ¹³Carbon NMR spectra were recorded on Bruker 400 MHz apparatus at ambient temperature and the chemical shifts were measured in ppm relative to Me₄Si for proton and ¹³Carbon NMR. The ¹²⁵Tellurium NMR spectrum was recorded on Bruker 400 Megahertz instruments. In this experiment dimethyl telluride (Me₂Te) was employed as reference.

2.3. Synthesis of cyclic tellurium(IV) diiodide.
A solution of 1,4-dibromopentane, (1.36 ml, 10.0 mmol) in freshly distilled dry acetone (3 ml) was stirred at room temperature with a two-fold excess of NaI for 1 h. After 1 h, tellurium powder (1.27 g, 10 mmol) was added to the reaction mixture in two portions over a period of 30 minute at room temperature. After 24 h stirring, the reaction mixture was turned to a dark red colour solid. The product was dissolved in 150 ml chloroform and filtered. The filtrate was evaporated under vacuum to give a red colour crystalline solid of 14, which was recrystallized from chloroform. Yield: 1.73 g (38 %), mp 112 °C (lit 110-112 °C) [11]. Anal. Calcd. For C₅H₁₀TeI₂: C, 13.30; H, 2.23. Found: C, 13.60, H 2.49.¹H NMR (400 MHz, DMSO-d₆): δ 1.86 (d, 3H- CH₃), 2.34 (m, 1H), 2.54 (m, 1H), 2.96 (m 2H), 3.51 (m, 1H), 3.87 (m, 1H), 4.03 (m, 1H). ¹³C NMR (400 MHz, DMSO-d₆): δ 19.7, 32.1, 43.0, 46.6, 55.8. ¹²⁵Te NMR (126.3 MHz, DMSO-d₆): δ 1026.

3. Single Crystal X-ray Crystallographic Studies
The collected crystal data and structure refinement for cyclic tellurium(IV) diiodide are exhibited in table 1-3. Suitable size of single crystal was selected under an optical microscope and attached on the top of a glass fiber for data collection. Intensity data of the molecule was recorded by the use of MoKα (λ=0.71073 Å) radiation on a Bruker SMART APEX diffractometer operational with CCD area detector at 100(2)K. The facts combination and reduction were completed by the use of SAINT software [25]. An experimental absorption modification was engaged to the collected reflections with SADABS [26]. The structure was confirmed by direct methods using SHELXTL and was refined on F2 by the full-matrix least-squares procedure using the program SHELXL-97 [27,28]. All non-hydrogen atoms were refined with anisotropic dislocation parameters. All H atoms were positioned geometrically and refined with relative isotropic dislocation parameters.
Figure 2. ORTEP diagram of cyclic tellurium(IV) diiodide exhibiting 50% probability dislodgment ellipsoids with the atom numbering method. Most important bond distances (Å) and angles (°): molecule A:, Te1–C1A 2.158(4), Te1–C4A 2.206(4), Te1–I11 2.834(2), Te1–I12 3.037(4), C1A–Te1–C4A 85.0(1), C1A–Te1–I11 91.3(1), C4A–Te1–I11 92.7(1), C1A–Te1–I12 84.1(1), C4A–Te1–I12 89.8(1), I11–Te1–I12 174.5(1), C2A–C1A–Te1 105.3(2); molecule B: Te2–C1B 2.153(4), Te2–C4B 2.188(4), Te2–I21 = 2.830(4), Te2–I22 = 3.010(4), C1B–Te2–C4B 85.4(2), C1B–Te2–I21 88.0(1), C4B–Te2–I21 91.6(1), C1B–Te2–I22 87.1(1), C4B–Te2–I22 90.8(1), I21–Te2–I22 174.2(1), C2B–C1B–Te2 105.5(3).

Figure 3. Supramolecular synthon in crystal lattices of cyclic tellurium(IV) diiodides showing 2d synths associated with the help of C-H---I and Te---I interactions.
Table 1. Single crystal-ray data and structure refinement for cyclic tellurium(IV) diiodide

| Molecular formula | C₅H₁₀I₂Te | Theta for utilized data collection | 2.771 – 36.360° |
|-------------------|------------|-----------------------------------|-----------------|
| Formula weight    | 451.53     | Index ranges                      | -16<=h<=16, -16<=k<=17, -31<=l<=29 |
| Temperature       | 100(2) K   | Reflections collected              | 9323            |
| Wavelength        | 0.71073 Å  | Independent reflections            | 9323 [R(int) = 0.0311] |
| Crystal system    | Monoclinic | Completeness to theta = 25.242°    | 99.7 %          |
| Space group       | P 2₁/c     | Absorption correction              | Semi-empirical from equivalents |
| Unit cell dimensions | a = 9.9539(4) Å, α = 90°. | Max. and min. transmission | 0.7471 and 0.4984 |
|                   | b = 10.2698(4) Å, β = 98.196(2)°. |                               |                 |
|                   | c = 19.0228(8) Å, γ = 90°. |                               |                 |
| Volume            | 1924.74(14) Å³ | Refinement method | Full-matrix least-squares on F² |
| Z                 | 8          | Data/restraints/parameters         | 9323 / 0 / 147 |
| Density (calc.)   | 9.428 mm⁻¹| Goodness-of-fit on F²              | 1.228           |
| F(000)            | 1584       | R indices                          | R1:0.0368, wR2 : 0.0684 |
|                   |            |                                   | R1:0.0467, wR2: 0.0718 |
| Crystal size      | 0.40 x 0.35 x 0.21 mm³ | Biggest diff. peak & hole | 3.051 & -2.475 e.Å⁻³ |

Table 2. Atomic coordinates (x 10⁴) and corresponding isotropic dislodgment data (Å² x 10³) for cyclic tellurium(IV) diiodide. U(eq) is defined as one third of the trace of the orthogonalized U_ij tensor.

|     | x    | y    | z    | U(eq)  |
|-----|------|------|------|--------|
| Te(1) | 816(1) | 1705(1) | 4264(1) | 11(1)  |
| I(11) | 763(1) | 1542(1) | 2773(1) | 23(1)  |
| I(12) | 613(1) | 1742(1) | 5842(1) | 14(1)  |
| C(1A) | -1369(4) | 1834(4) | 4143(2) | 15(1)  |
| C(2A) | -1676(4) | 3257(4) | 4277(2) | 14(1)  |
| C(3A) | -720(4) | 4136(4) | 3938(2) | 14(1)  |
| C(4A) | 756(4) | 3852(4) | 4246(2) | 12(1)  |
| C(5A) | 1799(4) | 4500(5) | 3860(2) | 20(1)  |
| Te(2) | 4526(1) | 3711(1) | 907(1) | 11(1)  |
| I(21) | 4155(1) | 988(1) | 755(1) | 20(1)  |
| I(22) | 5175(1) | 6573(1) | 1007(1) | 15(1)  |
| C(1B) | 6683(4) | 3371(4) | 1050(2) | 17(1)  |
| C(2B) | 7054(4) | 2941(5) | 1823(3) | 22(1)  |
| C(3B) | 6239(4) | 3689(5) | 2309(2) | 21(1)  |
Table 3. Anisotropic limitation (Å² x 10³) was employed for cyclic tellurium(IV) diiodide. The anisotropic dislodgment factor exponent utilized the following form: 

\[-2p^2 a^* U_{11} + \ldots + 2hk a^* b^* U_{12}\]

| C(4B) | 4718(4) | 3568(5) | 2065(2) | 17(1) |
|-------|---------|---------|---------|-------|
| C(5B) | 3821(5) | 4503(5) | 2398(2) | 22(1) |

4. Conclusion
In conclusion we have reported synthesis and single crystal x-ray studies of cyclic tellurium(IV) diiodide, 2-Methyl-1,1-diiodo-1-telluracyclopentane in good yield at room temperature. We hope the developed methodology can be employed for synthesis of a series of chalcogenated heterocyclic derivatives. Our new single crystal x-ray studies provide monoclinic crystal system, space group P2₁/c with cell dimensions a = 9.9539(4) Å, b = 10.2698(4) Å, c = 19.0228(8) Å and α = 90°, β = 98.196(2)°, γ = 90°. The geometry about the central tellurium atoms adopt trigonal bipyramidal. In which a lone pair and two carbon atoms are located at equatorial position and the iodine atoms are situated at the axial site. The crystal packing of the 2-Methyl-1,1-diiodo-1-telluracyclopentane, reveal each unit cell contain eight molecules and each molecule are interconnected through C–H---I intermolecular hydrogen bonding and Te---I secondary bonding interactions.

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