Synthesis and Single Crystal X-ray Studies of Dimesityl Ditelluride: \([2,4,6-\text{Me}_3\text{C}_6\text{H}_2\text{Te}]_2\)

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Abstract. The reaction of freshly prepared mesityl magnesium bromide with tellurium powder in anhydrous THF provided the dimesityl ditelluride: \([2,4,6-\text{Me}_3\text{C}_6\text{H}_2\text{Te}]_2\). A suitable needle-shaped crystal of dimesityl ditelluride was developed by evaporation of a solution in chloroform. The Te compound was developed with the orthorhombic space group \(Iba_2\) with \(a = 15.2916(7)\) Å, \(b = 15.7225(7)\) Å, \(c = 14.5272(7)\) Å and \(\alpha, \beta, \gamma = 90^\circ\). The geometry about the central tellurium atoms adopt a bent-shaped geometry with torsion angle \(C_{10} - \text{Te}_2 - \text{Te}_1 - C_{1} = 87.0(3)^\circ\) and this may be considered a cisoid conformation. Intermolecular C–H····Te interactions give rise to a two-dimensional supramolecular synthons in its crystalline state. The crystal packing diagram shows Te····H [Te1····H5A, 3.2557(5) Å & Te1····H8C, 3.2578(5) Å] hydrogen-bonding interactions which are responsible for associative forces.

Keywords. Crystal Structure; Mesityl ditelluride; Mesityl magnesium bromide; Supramolecular synthons;

1. Introduction
Organotellurium compounds have attracted several research groups of academia and industry in the context of organic transformation reactions [1], ligand chemistry [2], biochemistry [3], and metal organic chemical vapor deposition process such as a precursor for semiconducting materials [4]. The organotellurium compounds are usually stable in I, II & IV oxidation states. In I & II oxidation state tellurium derivatives are commonly known as ditelluride and telluride respectively. A very interesting feature i.e. a labile Te–Te bond is existing only in case of ditellurides. Due to this diaryl ditellurides have been employed by several research groups as initial precursors for developing mixed ligand organotellurium derivatives. Chauhan’s group have reported, Mes(RCOCH_2)TeCl_2 (Mes = Mesityl, 2,4,6-Me_3C_6H_2) derivatives through electrophilic substitution reactions of RCOCH_3 (R = t-Bu, i-Pr, Mes) with Mes-TeCl_2 [5]. The same group has also established a new route to isolate Mes(RCOCH_2)TeBr_2 (R = t-Bu, Et_2N) derivatives via the incorporation of [MesTeBr] across the Carbon-Bromine bond of α-bromo-N,N-diethylacetamide/α-bromopinacolone [5a,5d]. Beckman and co-workers have reported a series of mesityltellurenylcations. These cations were stabilized by triphenylphosphorous, triphenylarsenic, triphenyantimony and
triphenylbismuth ligands [6]. In these derivatives, mesityl ligands are playing a significant role in the isolation of the novel derivatives. In 1998 Jeske et al. have published the molecular structure of dimesityl diselenide and bis(2,4,6-trisopropylphenyl) diselenide [7]. Thereafter Singh and co-workers have designed the synthesis of bis[2,5-dimethyl-4-tert-butylphenyl] diselenide [8a] and bis(4-(tert-butyl)-2,6-dimethylphenyl) ditellurides by following the Grignard route [8b]. In the later report, authors have demonstrated that both dichalcogenides are inactive catalysts compare to the analogous dichalcogenides in the reduction of H2O2 by using thiophenol as a thiol co-substrate [8b].

In this manuscript, we report an easiest methodology for synthesis and characterizaton of Mes2Te2 (I) bearing sterically hindered mesityl ligand. The ditellurides can be prepared by the treatment of activated tellurium powder with freshly prepared Grignard reagents, various organolithium compounds, and reduction of respective aryl telluriumtrihalides. Among these, the Grignard reagents and various organolithium compounds have been used extensively for the synthesis of aromatic ditellurides by hydrolysis and followed by air oxidation according to Scheme 1.

**Scheme 1** Synthesis of diarylditellurides (Ar = Aryl).

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2. Experimental
The reactions were carried out under Nitrogen/Argon atmosphere. Tellurium Powder (Fluka) and Bromomesitylene, (E. Merck), Iodine and Ammonium Chloride (S D Fine) was employed as procured from the supplier. THF was purified and dried on sodium metal in presence of benzyolperoxide [9].

2.1. Synthesis of Mes2Te2 (I)
Magnesium turnings (0.51 g, 21 mmol), 2-3 very small granules of iodine and 25 mL of anhydrous THF were added in a 250 mL round bottom two-necked flask under inert atmosphere. 2-Bromomesitylene (3.06 mL, 20 mmol) was added slowly with stirring at room temperature. The resulting solution was stirred continued for 5-10 minutes. Elemental Te(0) powder (2.55 g, 20 mmol) was further added to the reaction mixture at ambient temperature. After 3 h stirring, the resulting reaction mixture was turned to a dark red solution. The solution was poured into a 250 mL aqueous solution of NH4Cl and kept for 3 h. The product was separated with diethyl ether (3 x 50 mL). The diethyl ether solution was twice treated with water, and dried over anhydrous Na2SO4. Organic layer was filtered and evaporated to give a red colour crystalline solid of Mes2Te2. The red colour crystalline solid of Mes2Te2 was recrystallised in hot ethanol at 0 °C to provide a red needle shape crystals of Mes2Te2. Yield: 3.50 g (71 %), mp 128/128 °C (lit 125-127°(C) [10].

Analytical Calculation For C18H22Te2: C, 43.67; H, 4.54. Observed: C, 43.80, H 4.49. 1H NMR (300 MHz, CDCl3): δ2.31 (s, 3H- p-CH3), 2.36 (s, 6H-o-Me), 6.87 (s, 2H-aryl).
2.2. Crystal Structure Determinations

The diffraction measurement for molecule Mes₂Te₂ was performed on a Bruker APEX-II CCD diffractometer using graphite monochromated Mo Kα radiation (λ = 0.7107 Å) at 100(2) K. Absorption correction was carried out by a multi-scan technique employed in SADABS [11]. The molecular arrangement was confirmed by typical heavy atom methodology by the employment of SHELXS 2018/3 [12] and Fourier methods. The structure was also refined by complete-matrix least-square with the anisotropic other than hydrogen atoms. However H-atoms was fixed with static isotropic thermal parameter of 0.07 Å² using the SHELXL 97 program [13]. The H-atoms were moderately to be detected through the difference electron density maps, and the rest were fixed by predestined location. Scattering factors were from a common source [14].

Crystal data collection and refinement parameters are shown in Table 1-4 for Mes₂Te₂. CCDC 2018231 contains the supplementary information data for this paper. These data can be accessed without any cost from ‘The Cambridge Crystallographic Data Centre’ via www.ccdc.cam.ac.uk.

Table 1. Crystal information collection & refinement parameters for the structure of Mes₂Te₂

| Parameter                  | Value                                      |
|----------------------------|--------------------------------------------|
| Molecular formula          | C₁₈H₂₂Te₂                                  |
| Molecular weight           | 493.55                                     |
| Temp.                      | 100(2) K                                   |
| λ                          | 0.71073 Å                                  |
| Crystal system             | Orthorhombic                               |
| Space group                | I b a 2                                    |
| Cell Dimensions            |                                           |
| a                          | 15.2916(7) Å                               |
| b                          | 15.7225(7) Å                               |
| c                          | 14.5272(7) Å                               |
| α, β, γ angles             | 90°                                        |
| Vol.                       | 3492.7(3) Å                                |
| Z                          | 8                                          |
| Density                    | 1.877 Mg/m³                                 |
| Absorption coefficient     | 3.331 mm⁻¹                                  |
| F(000)                     | 1872                                       |
| Size of crystal            | 0.450 x 0.310 x 0.250 mm³                  |
| Range of θ                | 3.234 to 36.379°                           |
| Reflections collected      | 8408                                       |
| Completeness to θ = 25.242°| 99.8 %                                     |
| Data / restraints / parameters| 8408 / 1 / 187                           |
| Goodness-of-fit on F²      | 1.266                                      |
| Final R indices [I>2sigma(I)] | R1 = 0.0636, wR2 = 0.0910              |
| R indices (all data)       | R1 = 0.0999, wR2 = 0.1017                |
| Absolute structure parameter | -0.04(2)                                |
| Largest diff. peak and hole | 2.116 and -1.470 e.Å⁻³                  |
Table 2. Atomic coordinates ($x \times 10^4$) and corresponding isotropic displacement measurements ($\text{Å}^2 \times 10^3$) for Mes$_2$Te$_2$. $U(eq)$ is defined as 1/3 rd of the trace of the orthogonalized $U_{ij}$ tensor.

|        | x     | y     | z     | $U(eq)$ |
|--------|-------|-------|-------|---------|
| Te(1)  | 3004(1)| 8573(1)| 4679(1)| 16(1)   |
| Te(2)  | 4602(1)| 8558(1)| 5492(1)| 19(1)   |
| C(1)   | 2415(4)| 7579(4)| 5472(7)| 16(1)   |
| C(2)   | 2006(5)| 7758(5)| 6303(5)| 16(1)   |
| C(3)   | 1646(5)| 7089(5)| 6812(6)| 18(1)   |
| C(4)   | 1693(5)| 6246(5)| 6498(6)| 17(2)   |
| C(5)   | 2091(5)| 6087(5)| 5655(6)| 19(2)   |
| C(6)   | 2456(5)| 6741(5)| 5130(5)| 17(1)   |
| C(7)   | 1941(6)| 8645(5)| 6688(6)| 22(2)   |
| C(8)   | 1320(6)| 5527(6)| 7063(6)| 24(2)   |
| C(9)   | 2869(6)| 6510(6)| 4220(7)| 26(2)   |
| C(10)  | 5194(4)| 7603(4)| 4663(7)| 16(1)   |
| C(11)  | 5190(5)| 6746(5)| 4947(5)| 17(1)   |
| C(12)  | 5572(5)| 6142(5)| 4370(6)| 19(2)   |
| C(13)  | 5933(5)| 6350(6)| 3512(6)| 19(2)   |
| C(14)  | 5946(5)| 7199(6)| 3263(6)| 21(2)   |
| C(15)  | 5586(5)| 7834(5)| 3813(6)| 20(1)   |
| C(16)  | 4785(6)| 6473(6)| 5848(6)| 23(2)   |
| C(17)  | 6296(6)| 5666(6)| 2897(7)| 27(2)   |
| C(18)  | 5648(7)| 8749(6)| 3492(7)| 28(2)   |

Table 3. Anisotropic displacement data employed ($\text{Å}^2 \times 10^3$) for Mes$_2$Te$_2$. The anisotropic dislodgment aspect exponent takes the form: $-2\pi^2[ h^2 a^* 2U_{11} + ... + 2 h k a^* b^* U_{12} ]$

|        | $U_{11}$ | $U_{22}$ | $U_{33}$ | $U_{12}$ | $U_{13}$ | $U_{23}$ |
|--------|----------|----------|----------|----------|----------|----------|
| Te(1)  | 13(1)    | 17(1)    | 19(1)    | 2(1)     | 0(1)     | 0(1)     |
| Te(2)  | 14(1)    | 22(1)    | 22(1)    | -5(1)    | -2(1)    | -2(1)    |
| C(1)   | 13(3)    | 18(3)    | 16(3)    | -4(3)    | 2(3)     | -1(2)    |
| C(2)   | 16(3)    | 17(3)    | 15(3)    | -1(3)    | -1(3)    | -2(3)    |
| C(3)   | 18(3)    | 23(4)    | 13(3)    | -1(3)    | -2(3)    | -1(3)    |
3. Results and Discussion

The molecule Mes₂Te₂ was prepared by the treatment of freshly prepared MesMgBr with tellurium powder in anhydrous THF. Suitable single crystals of Mes₂Te₂ were grown by slow evaporation of a solution in CHCl₃. ORTEP observation of the molecule Mes₂Te₂ was revealed in Figure 1. Its most important bond lengths and bond angles relevant to the primary geometry are shown in captioned of Figure 1. The tellurium compound grown as single crystal in the orthorhombic space group Iba₂ with a = 15.2916(7) Å, b = 15.7225(7) Å, c = 14.5272(7) Å and α,β,γ = 90°. Earlier reported crystal data and refinement parameters for this compound are slightly different than the reported data in this article. However the observed R value and independent reflection [R = 0.0636 with observed independent reflection 6354] is slightly higher than the earlier reported value [R = 0.030 and observed independent reflection 2051] [15].

The preferred geometry around the Te atoms adopt a bent-shaped with torsion angle C10–Te2–Te1–C1 = 87.0(3)° and this may be considered a cisoid conformation. The asymmetric unit of Mes₂Te₂ contains eight molecules in the crystal structure. The observed Te–Te bond length (2.7133(6) Å) in the molecule Mes₂Te₂ is almost very close to that for the (1-C₁₀H₇)Te₂ [16a], cis and trans form of (2-C₁₀H₇)Te₂, 2.7110(6), 2.7089 (7) and 2.7179 (6) Å respectively [16b]. The above observation is slightly stronger than that in bis[(N,N-dimethyl)-1-naphthyl] ditelluride [Te–Te, 2.765 (1) Å], probably due to presence of a strong N····Te secondary bonding interactions and the geometry about all tellurium atoms is T-shaped [17]. C₁0–Te2–Te1–C₁ torsion angle for I, is 87.0(3)° and that is very close to a cisoid orientation (C–Te–Te–C < 90°). The C–Te–Te–C torsion angle for (1-C₁₀H₇)₂Te₂, trans and cis form of (2-C₁₀H₇)₂Te₂ have 97.96 (9°), 105.2 (3°) and 78.6 (2°) respectively. Intermolecular C–H····Te interactions give rise to a two-dimensional supramolecular synthons in its crystalline state as shown in Figure 2. Hydrogen-bond geometry is summarized in Table 2. The packing diagram shows Te····H [Te1····H5A, 3.2557(5) Å & Te1····H8C,
3.2578(5) Å] hydrogen bonding communications which are lesser than the sum of related van der Waals radii (3.55 Å).

**Figure 1.** ORTEP diagram of Mes₂Te₂, viewing 50% probability along with the atomic numbering. Most Important bond lengths (Å) and angles (°): Te₁–C₁ = 2.140(8), Te₁–Te₂ = 2.7133(6), Te₂–C₁₀ = 2.126(8); C₁–Te₁–Te₂ = 98.0(2), C₁₀–Te₂–Te₁ = 98.2(2).

**Figure 2.** A view of the two-dimensional supramolecular motif, showing the Te⋯H interactions (indicated as dashed lines).

| D–H⋯A | D–H (Å) | H⋯A(Å) | D⋯A(Å) | D–H⋯A(°) |
|-------|---------|--------|--------|----------|
|       |         |        |        |          |
4. Conclusions
We have reported synthesis and single crystal x-ray studies of dimesityl ditellurides, (2,4,6-Me3C6H2Te)2, which can be chlorinated to meistyltellurium trichloride, 2,4,6-Me3C6H2TeCl3 in hexane solvent at room temperature in excellent yield. These derivatives can be employed as starting materials for mixed organotellurium (IV) derivatives as well as starting materials for the semiconductor materials. Our new single crystal x-ray studies provide orthorhombic space group Iba2 with cell dimensions a = 15.2916(7) Å, b = 15.7225(7) Å, c = 14.5272(7) Å and \( \alpha = 90^\circ \), \( \beta = 90^\circ \), \( \gamma = 90^\circ \). The geometry about the central tellurium atoms adopt a bent-shaped geometry with torsion angle C10–Te2–Te1–C1 = 87.0(3)° and this may be considered a cisoid conformation. The crystal packing of the dimesityl ditellurides, reveal the domination of C–H······Te hydrogen bonding interactions. We hope this interpretation can be employed in the field of crystal engineering.

5. References
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