

Synthesis and reactivity of *para*-substituted benzoylmethyltellurium(II and IV) compounds: observation of intermolecular C–H–O hydrogen bonding in the crystal structure of $(p\text{-MeOC}_6\text{H}_4\text{COCH}_2)_2\text{TeBr}_2$

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Abstract

Bis(*p*-substituted benzoylmethyl)tellurium dibromides, $(p\text{-YC}_6\text{H}_4\text{COCH}_2)_2\text{TeBr}_2$, (Y = H (**1a**), Me (**1b**), MeO (**1c**)) can be prepared either by direct insertion of elemental Te across C_{Rf}–Br bonds (where C_{Rf} refers to α -carbon of a functionalized organic moiety) or by the oxidative addition of bromine to $(p\text{-YC}_6\text{H}_4\text{COCH}_2)_2\text{Te}$ (Y = H (**2a**), Me (**2b**), MeO (**2c**)). Bis(*p*-substituted benzoylmethyl)tellurium dichlorides, $(p\text{-YC}_6\text{H}_4\text{COCH}_2)_2\text{TeCl}_2$ (Y = H (**3a**), Me (**3b**), MeO (**3c**)), are prepared by the reaction of the bis(*p*-substituted benzoylmethyl)tellurides **2a–c** with SO₂Cl₂, whereas the corresponding diiodides $(p\text{-YC}_6\text{H}_4\text{COCH}_2)_2\text{TeI}_2$ (Y = H (**4a**), Me (**4b**), MeO (**4c**)) can be obtained by the metathetical reaction of **1a–c** with KI, or alternatively, by the oxidative addition of iodine to **2a–c**. The reaction of **2a–c** with allyl bromide affords the diorganotellurium dibromides **1a–c**, rather than the expected triorganotelluronium bromides. Compounds **1–4** were characterized by elemental analyses, IR spectroscopy, ¹H, ¹³C and ¹²⁵Te NMR spectroscopy (solution and solid-state) and in case of **1c** also by X-ray crystallography. $(p\text{-MeOC}_6\text{H}_4\text{COCH}_2)_2\text{TeBr}_2$ (**1c**) provides, a rare example, among organotellurium compounds, of a supramolecular architecture, where C–H–O hydrogen bonds appear to be the non-covalent intermolecular associative force that dominates the crystal packing.

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1. Introduction

Organotellurium compounds containing RCOCH₂ group have received considerable attention due to their application in non-silver imaging [1] and as synthons for α -haloketones [2,3]. Bis(aroilmethyl)- and arylaroilmethyl tellurium dichlorides obtained earlier [2–7] by the electrophilic substitution reaction of aroilmethyl ketones with air/moisture sensitive TeCl₄ or ArTeCl₃, have recently [8] also been synthesized by the use of potas-

sium telluracyanate, KTeCN, prepared from KCN and Te powder. The corresponding Te(II) compounds are reported to be formed either by the reduction of their parent dichlorides [7] or by the reaction between lithium enolate of a methylketone and PhTeI, prepared in situ [9]. Although many of these compounds have been characterized spectroscopically, only little information is available on their solid-state structures. The role of non-covalent secondary bonding, a characteristic feature of organotellurium compounds, is currently being investigated in the context of supramolecular chemistry principles. Among organotellurium halides, Te–X secondary interactions are responsible for the formation of either supramolecular arrays or oligomeric supermolecules,

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Table 1
Selected IR and NMR data for compounds **1–4**

Compound	IR ν_{CO} (cm^{-1})	NMR chemical shifts (in ppm) in CDCl_3		
		^1H (CH_2)	^{125}Te	^{125}Te (δ_{iso})
$(\text{PhCOCH}_2)_2\text{TeCl}_2$ (3a)	1662 ^a	5.46 ^c		
$(\text{PhCOCH}_2)_2\text{TeBr}_2$ (1a)	1659 ^b	5.45 ^b	672	635
$(\text{PhCOCH}_2)_2\text{TeI}_2$ (4a)	1645 ^b	5.43 ^b		
$(p\text{-MeC}_6\text{H}_4\text{COCH}_2)_2\text{TeCl}_2$ (3b)	1654	f		
$(p\text{-MeC}_6\text{H}_4\text{COCH}_2)_2\text{TeBr}_2$ (1b)	1646	5.41	681	667
$(p\text{-MeC}_6\text{H}_4\text{COCH}_2)_2\text{TeI}_2$ (4b)	1649	5.45		
$(p\text{-MeOC}_6\text{H}_4\text{COCH}_2)_2\text{TeCl}_2$ (3c)	1645	f		
$(p\text{-MeOC}_6\text{H}_4\text{COCH}_2)_2\text{TeBr}_2$ (1c)	1638	5.45	675	661
$(p\text{-MeOC}_6\text{H}_4\text{COCH}_2)_2\text{TeI}_2$ (4c)	1636	5.41		
$(\text{PhCOCH}_2)_2\text{Te}$ (2a)	1642 ^d	4.26 ^e		
$(p\text{-MeC}_6\text{H}_4\text{COCH}_2)_2\text{Te}$ (2b)	1656	4.4		
$(p\text{-MeOC}_6\text{H}_4\text{COCH}_2)_2\text{Te}$ (2c)	1647	4.22		
PhCOCH_2Br	1693	4.46		
$p\text{-MeC}_6\text{H}_4\text{COCH}_2\text{Br}$	1685	4.44		
$p\text{-MeOC}_6\text{H}_4\text{COCH}_2\text{Br}$	1684			

^a (Lit. [6], 1660).

^b (Earlier work [12]).

^c (Lit. [6], 5.45, [8], 4.75).

^d (Lit. [7], 1640).

^e (Lit. [7], 4.26, [8], 4.53).

^f Poor solubility.

tellurium(IV) in **1a** (26.7 ppm) [12], is in accordance with the expected enhanced shielding of the methylene carbon in **2a**. As such the previously reported signal at 35.8 ppm for the methylene carbon atom in **2a** is in contradiction with the enhanced shielding.

The proton-decoupled ^{125}Te NMR solution spectra of the three bis(*p*-substituted benzoylmethyl)tellurium dibromides **1a–c** display a single resonance at δ 672, 681 and 675, respectively. The chemical shifts are considerably upfield as compared to those of the corresponding bis(*p*-substituted phenyl)tellurium dichlorides (δ 919–931 ppm) [15]. The enhanced shielding may be due to (i) intramolecular coordination of the carbonyl oxygens to the tellurium atoms, (ii) the change from Te–aryl to Te–alkyl and (iii) the difference between Te–Cl and Te–Br. The ^{125}Te MAS NMR chemical shifts of **1a–c** (δ 635, 667 and 661, respectively) compare reasonably well with the values observed in CDCl_3 solution. It is interesting to note that the isotropic chemical shifts are accompanied by only one set of small spinning sidebands on each

side. A possible explanation for this observation is the high (pseudo) symmetrical environment around the tellurium atoms, which is substantiated by X-ray crystallography for **1a** [12] and **1c**. In addition, for all three cases the ^{125}Te MAS NMR signals are subject to second order quadruple coupling with the bromine atoms. However, due to the presence of two magnetically inequivalent bromine atoms and two different isotopomers the extraction of coupling constants was not attempted.

Single crystal X-ray structures of **1a** and **4a** have been reported previously by us [12]. Attempts to grow single crystals of the remaining compounds described in this work were only successful in the case of compound **1c**. The crystals obtained of the diorganotellurides **2a–c** crumble as soon as they are separated from the mother-liquor. The ORTEP view and atom numbering of the molecular structure of **1c** is presented in Fig. 1 and selected bond lengths, bond angles and torsion angles are given in Table 2. (*p*-MeOC₆H₄COCH₂)₂TeBr₂ (**1c**) crystallizes in the orthorhombic crystal system and the

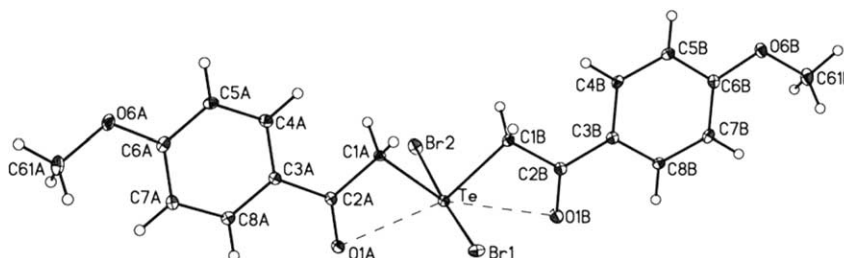


Fig. 1. Crystal structure of **1c**.

Table 2
Selected bond lengths and angles for (*p*-MeOC₆H₄COCH₂)₂TeBr₂

Bond lengths (Å)		Bond angles (°)		
Te–C(1B)	2.132(4)	C(1B)–Te–C(1A)	95.35(13)	
Te–C(1A)	2.140(3)	C(1B)–Te–Br(1)	87.52(10)	
Te–Br(1)	2.6532(5)	C(1A)–Te–Br(1)	88.09(10)	
Te–Br(2)	2.6710(5)	C(1B)–Te–Br(2)	88.29(10)	
Te–O(1A)	2.840(3)	C(1A)–Te–Br(2)	88.76(10)	
Te–O(1B)	2.830(3)	Br(1)–Te–Br(2)	174.500(15)	
O(1A)–C(2A)	1.211(4)	C(6A)–O(6A)–C(61A)	117.2(3)	
O(1B)–C(2B)	1.227(4)	C(6B)–O(6B)–C(61B)	116.7(3)	
		C(2A)–C(1A)–Te	104.4(2)	
		C(2B)–C(1B)–Te	105.1(2)	
Torsion angles (°)		O(1A)–C(2A)–C(3A)	122.6(3)	
C(1B)–Te–C(1A)–C(2A)	–168.0(2)	O(1A)–C(2A)–C(1A)	119.7(3)	
C(1A)–Te–C(1B)–C(2B)	170.1(2)	C(3A)–C(2A)–C(1A)	117.7(3)	
Te–C(1A)–C(2A)–O(1A)	4.1(4)	O(1B)–C(2B)–C(3B)	122.2(3)	
Te–C(1B)–C(2B)–O(1B)	–0.9(4)	O(1B)–C(2B)–C(1B)	118.5(4)	
O(1A)–C(2A)–C(3A)–C(8A)	–2.4(5)	C(3B)–C(2B)–C(1B)	119.3(3)	
C(1A)–C(2A)–C(3A)–C(8A)	177.9(3)			
O(1A)–C(2A)–C(3A)–C(4A)	177.1(3)			
C(1A)–C(2A)–C(3A)–C(4A)	–2.6(5)			
O(1B)–C(2B)–C(3B)–C(8B)	0.6(5)			
C(1B)–C(2B)–C(3B)–C(8B)	–178.9(3)			
O(1B)–C(2B)–C(3B)–C(4B)	–179.6(4)			
C(1B)–C(2B)–C(3B)–C(4B)	0.9(5)			
Hydrogen bond parameters				
D–H···A	<i>d</i> (D–H) (Å)	<i>d</i> (H···A) (Å)	<i>d</i> (D···A) (Å)	∠(DHA) (°)
C(61A)–H(61C)···O(1A)#1	0.98	2.45	3.289(5)	143.1
C(61B)–H(61E)···O(1B)#2	0.98	2.48	2.984(5)	111.9
C(61A)–H(61B)···O(6B)#3	0.98	2.47	3.319(5)	145.4
C(61B)–H(61F)···O(6A)#3	0.98	2.68	3.499(5)	141.8

Symmetry transformations used to generate equivalent atoms: #1: $x - 1/2, -y + 5/2, -z$; #2: $-x + 2, y + 1/2, -z - 1/2$; #3: $x + 1/2, -y + 7/2, -z$.

$P2_12_12_1$ space group (cf. (PhCOCH₂)₂TeX₂; X = Br, I; monoclinic crystal system with $P2_1/n$ space group) with four molecules per unit cell. The asymmetric unit reveals only one crystallographically independent molecule, which is consistent with the number of signals found in the ¹²⁵Te MAS NMR spectrum. In view of the steric demand of the active lone pair, the primary geometry of the tellurium atom may be described best as distorted trigonal bipyramidal. The distortion (though less than that observed in case of **1a**) is apparent from the reduced bond angles Br₁–Te–Br₂ (174.5°) and C1A–Te–C1B (95.35°) as against 180° and 120°, respectively, for the idealized trigonal bipyramidal geometry. The larger equatorial C–Te–C bond angle in (*p*-MeOC₆H₄COCH₂)₂TeBr₂ (**1c**) as compared to that of (PhCOCH₂)₂TeBr₂ (**1a**) (93.04°) indicates that Te–C bonds in the former have relatively poorer *p*-character. This would impart poorer *s*-character to the lone pair resulting in a deshielding of the Te nucleus in **1c** as compared to **1a** which is also corroborated by the appearance of downfield resonance signal in the solution as well as in the solid state ¹²⁵Te NMR spectra of **1c** when compared to that of **1a**. Tellurium, owing to its great propensity for secondary bonding, achieves higher

coordination number in organotellurium compounds with the help of inter- and intra-molecular Te–X (X = halogen, N, O, S) secondary interactions. Furthermore, it has been observed that the 5 + 2 coordination geometry (5 equatorial neighbours including the lone pair and 2 apical neighbours) about the central tellurium atom is the most frequently encountered amongst six coordinate diorganotellurium dihalides [11]. The geometry of **1c** is no exception to this showing intramolecular coordination of both carbonyl O atoms (Te–O distances: 2.840 and 2.830 Å), which are both longer than the sum of their covalent bond radii (2.03 Å) and significantly shorter than the sum of van der Waals radii (3.60 Å) [16]. Also, the tetrahedral bond angles Te–C1A–C2A and Te–C1B–C2B have been reduced to 104.4° and 105.1°. The shorter Te–O distances in **1c** compared to **1a** (2.938 and 2.917 Å) indicate a stronger Te–O interaction, which is also reflected in the lowering of carbonyl stretching frequency in **1c** compared to **1a**.

The intramolecularly bonded carbonyl O atoms are arranged *cis* to each other in the equatorial plane, both at an angle of 54.5° to the adjacent Te–C bonds, providing sufficient space for the lone pair (bond angle O1A–Te–O1B 149.6°). The octahedrally arranged six

ligand atoms and slight deviation of the two O atoms from the equatorial plane impart an almost perfect C_{2v} molecular geometry.

The remarkable feature of the solid-state structure of (*p*-MeOC₆H₄COCH₂)₂TeBr₂ (**1c**) is the presence of C–H–O bonding interaction having a considerable electrostatic contribution. Such interactions have been proposed to be the dominant factor in assembling the molecular units leading to a supramolecular structure in organic [17] and nonorganic [18] crystals as well as in crystalline organotellurium(IV) carboxylates [19]. The chemically meaningful H–O distance, which is the separation between CH of methoxy group (acting as H-bond donor) and the O atom of the carbonyl/methoxy group (H-bond acceptor) of neighboring molecules, lie in the range between 2.45 and 2.68 Å (Table 2). An H–O distances of 2.80 Å is taken as a cut off value for a bonafide C–H–O bond in the case of 3d transition metal carbonyl complexes [20]. The C–H–O hydrogen bonding interaction has significant implications in many diverse areas of structural chemistry and is, no longer, considered an exoteric phenomenon. However, for the first time such interactions among organotellurium halides are shown to be a significant factor in the self-organization of molecular units resulting in the supramolecular structure (Fig. 2). From the crystal packing pattern it is obvious that molecules of (*p*-MeOC₆H₄COCH₂)₂TeBr₂ (**1c**) are placed in pairs in such a way that the lone pairs on the Te atoms are facing opposite directions and the stacking of benzene rings becomes feasible, thereby providing an opportunity for attractive C–H–O hydrogen bonding as well as π – π interactions, resulting in the stabilization of the crystal lattice.

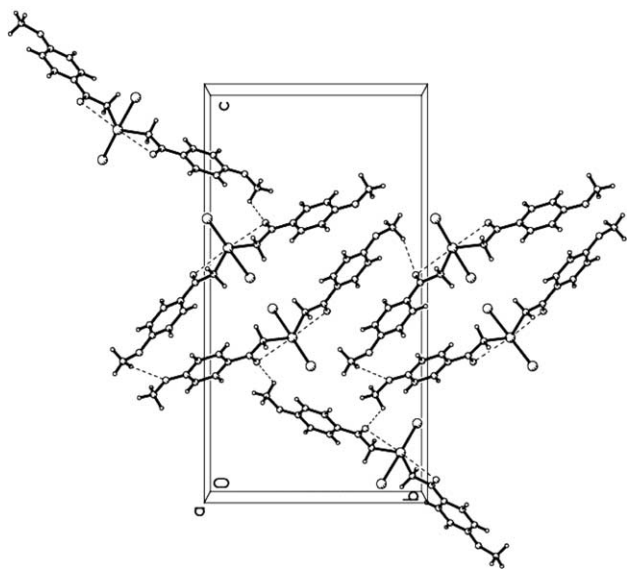


Fig. 2. Molecules of **1c** connected through C–H–O hydrogen bonds.

3. Experimental

3.1. General procedures

Benzoylmethyl bromides were prepared by bromination of the corresponding acetophenones in glacial acetic acid. The commercial tellurium powder (Fluka) was washed with concentrated HCl and water and dried at ~ 120 °C. It was ground for ~ 10 min just before use. Solvents were purified and dried by standard methods. Melting points were recorded in capillary tubes and are uncorrected. Wherever required the reactions were carried out under dry nitrogen gas. The ¹H and ¹³C NMR spectra were recorded at 300.13 and 50.32 MHz, respectively, in CDCl₃ on a Varian DRX 300 spectrometer using TMS as internal standard. Solution ¹²⁵Te NMR were measured in CDCl₃ at 85.2 MHz using a JEOL GX 270 MHz NMR spectrometer and referenced against Me₂Te. The ¹²⁵Te MAS NMR spectra were obtained at 126.2 MHz using a JEOL Eclipse Plus 400 MHz NMR spectrometer equipped with a high speed locked 4 mm Bruker Probe operating at spinning frequencies between 8 and 9 kHz. Experimental condition: pulse width 1 ms, relaxation delay 120 s, 400–900 transients. The isotropic chemical shifts were referenced against Me₂Te using solid Te(OH)₆ as the secondary reference (δ_{iso} 692.1, 685.5) [21]. IR spectra were examined as KBr pellets using a Perkin–Elmer RX1 spectrometer. Elemental carbon and hydrogen analyses were performed on a Carlo Erbra 1108 make analyzer. Tellurium was estimated volumetrically and the halogen content gravimetrically as silver halide.

3.1.1. Synthesis of (*p*-YC₆H₄COCH₂)₂TeBr₂ (Y = CH₃ (**1b**); OCH₃ (**1c**))

A mixture of tellurium powder (1.28 g; 10 mmol) and *p*-methylbenzoylmethyl bromide (4.69 g; 22 mmol) was heated (~ 60 °C) with stirring until the mixture solidified. Dichloromethane (10 ml) was added and reaction mixture heated to reflux for 2 h. The solid was filtered, washed with cold dichloromethane and extracted with hot alcohol free chloroform. Concentration of the extract and addition of pet-ether (40–60 °C) afforded crystalline **1b**, yield, 2.80 g, (49%); m.p. 195 °C; Anal. Calc. for C₁₈H₁₈O₂Br₂Te: C, 39.0; H, 3.3; Br, 28.9; Te, 22.9. Found C, 39.2; H, 3.1; Br, 28.7; Te, 21.9%. ¹H NMR (CDCl₃), (δ ppm) 7.97–7.84(d), 7.34–7.29(d), 5.41(s), 2.57(s); IR; $\nu(\text{CO})$, 1646 cm⁻¹.

1c was prepared similarly. Yield, 50%; m.p. 165 °C; Anal. Calc. for C₁₈H₁₈O₄Br₂Te: C, 36.8; H, 3.1; Br, 27.3; Te, 21.8. Found C, 37.1; H, 2.9; Br, 26.9; Te, 21.4%. ¹H NMR (CDCl₃), (δ ppm) 8.05–8.01(d), 7.04–6.99(d), 5.45(s), 3.73(s); IR; $\nu(\text{CO})$, 1638 cm⁻¹.

3.1.2. Reduction of (*p*-YC₆H₄COCH₂)₂TeBr₂ to (*p*-YC₆H₄COCH₂)₂Te, (Y=H (**2a**); CH₃ (**2b**); OCH₃ (**2c**))

A solution of **1b** (0.89 g, 1.6 mmol) in dichloromethane (50 ml) was shaken with an aqueous solution of Na₂S₂O₅ (0.38 g, 2 mmol) for a few minutes. The organic layer gradually turned yellow. It was separated and washed (3 × 20 ml) with water, dried over anhydrous Na₂SO₄ for about 10 min. Volatiles were removed under reduced pressure and the residue was crystallized from pet-ether to give yellow needles of **2b**, which are stable at low temperature. Yield, 2.39 g, (38%); m.p. 86 °C (Lit. [7] 95 °C); Anal. Calc. for C₁₈H₁₈O₂Te: C, 54.9; H, 4.6; Te, 32.4. Found C, 54.6; H, 4.3; Te, 33.3%. ¹H NMR (CDCl₃), (δ ppm) 8.05–8.02(d), 7.44–7.43(d), 4.40(s), 2.60(s).

2a and **2c** were prepared similarly. **2a**, Yield, (40%); m.p. 76 °C (Lit. [7], 79 °C); Anal. Calc. for C₁₆H₁₄O₂Te: C, 52.5; H, 3.9; Te, 34.9. Found C, 52.2; H, 3.7; Te, 34.5%. ¹H NMR (CDCl₃), (δ ppm) 7.98–7.96(d), 7.58–7.55(t), 7.50–7.45(t), 4.26(s); ¹³C NMR (CDCl₃), (δ ppm) 197.3, 135.0, 133.3, 128.6, 10.3. IR: ν(CO), 1642 cm⁻¹. **2c**, Yield (32%); m.p. 66 °C (Lit [7], 67 °C); Anal. Calc. for C₁₈H₁₈O₄Te: C, 50.8; H, 4.2; Te, 30.0. Found C, 50.6; H, 3.9; Te, 29.3%. ¹H NMR (CDCl₃), (δ ppm) 7.98–7.95(d), 6.95–6.92(d), 4.22(s), 3.88(s); IR: ν(CO), 1647 cm⁻¹.

3.1.3. Oxidation of (*p*-YC₆H₄COCH₂)₂Te (**2**) with Br₂, I₂ and SO₂Cl₂

- (a) Freshly prepared **2a** (0.35 g, 1 mmol) was dissolved in pet-ether (20 ml) and cooled at 0 °C. A solution of bromine (0.18 ml, 1.2 mmol) in CCl₄ was slowly added with stirring. After the complete addition, the reaction mixture was gradually warmed to room temperature and stirred for 2 h. A light yellow colored solid separated which was filtered, dried and recrystallized with CHCl₃/pet-ether to give **1a**. Yield, 0.43 g, (85%); m.p. 182 °C (Lit. [12], 182–184 °C), IR: ν(CO), 1659 cm⁻¹ (Lit. [12]), 1659 cm⁻¹. **1b** and **1c** were prepared similarly from **2b** and **2c**, respectively, and their melting points and IR spectra were similar to those obtained by method (Section 3.1.1).
- (b) Sulfuryl chloride (0.5 ml) was added dropwise with stirring to a solution of **2a** (0.35 g, 1 mmol) in dichloromethane at 0 °C. The reaction mixture was allowed to come to the room temperature and stirred for 15 min. Concentration under reduced pressure and addition of pet-ether afforded colourless crystalline **3a**. Yield, 0.33 g, (81%); m.p. 195 °C (Lit. [7,8], 195–197 °C). **3b**. Yield, 80%; m.p. 212–214 °C (Lit. [7], 213–215 °C) and **3c**. Yield, 75%; m.p. 195–196 °C (Lit. [7], 197 °C) were obtained similarly.
- (c) The iodides, **4a**, **4b** and **4c** were prepared by using iodine and the corresponding **2** as in Section 3.1.3a.

Their melting points and IR spectra were similar to those obtained by method (Section 3.1.4).

3.1.4. Halogen exchange/metathesis

A solution of **1b** (0.54 g, 1 mmol) in chloroform was stirred with 1.5-fold excess of KI for 2 h. The orange coloured reaction mixture was filtered. Concentration of the filtrate and addition of pet-ether afforded **4b** as red/brown crystals. Yield, 0.44 g, (70%); m.p. 145 °C; Anal. Calc. for C₁₈H₁₈O₂I₂ Te; C, 33.4; H, 2.8; I, 39.2; Te, 19.7. Found C, 33.1; H, 2.6; I, 39.1; Te, 19.0%. ¹H NMR (CDCl₃, δ ppm) 7.95–7.85(d), 7.36–7.30(d), 5.45(s), 4.36(s); IR: ν(CO), 1649 cm⁻¹.

4c was obtained similarly. Yield, (72%); m.p. 150 °C; Anal. Calc. for C₁₈H₁₈O₄I₂ Te; C, 31.8; H, 2.7; I, 39.2; Te, 19.6. Found C, 31.5; H, 2.7; I, 38.2; Te, 18.9%. ¹H NMR (CDCl₃, δ ppm) 8.03–8.01(d), 7.05–7.02(d), 5.41(s), 3.95(s); IR: ν(CO), 1636 cm⁻¹.

3.1.5. Attempted oxidative addition of allyl bromide to **2a**

Allyl bromide (1 ml) in pet-ether (10 ml) was added slowly to a stirred solution of freshly prepared **2a** (0.79 g; 2 mmol) in the same solvent (30 ml) with stirring. A white solid gradually formed, which after 2 h was collected by filtration, washed with pet-ether and characterized as **1a**. Yield: 1 g, (85%); m.p. 182 °C. Likewise **2b** and **2c** afforded **1b** and **1c**, respectively, in over 80% yield.

3.2. X-ray crystallography

Needle shaped white single crystals of (*p*-MeOC₆H₄COCH₂)₂TeBr₂ (**1c**) suitable for diffraction studies were obtained by slow cooling of its dichloromethane solution. The X-ray diffraction measurements were performed at 93(2) K Bruker P4S diffractometer employing graphite monochromated Mo Kα radiation (λ = 0.71073 Å) to a maximum of θ_{max} = 29.19° via ω scan (completeness 92.4% to θ_{max}). A total of 15,425 reflections were collected and the data were reduced and corrected for absorption using SADABS program. The structure was solved by direct methods and difference Fourier synthesis using SHELX-97 implemented in the WIN GX 2002 [22]. 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 and the final cycle of full-matrix least squares refinement based on 4878 independent reflections and 228 parameters converged with unweighted (R_1) and weighted (wR_2) agreement factors of 0.0255 and 0.0538, respectively. Flack parameter Lattice parameters and structure solution of the title compound are: C₁₈H₁₈Br₂O₄Te, $M = 585.74$, orthorhombic, $P2_12_12_1$, $a = 5.6210(7)$ Å, $b = 13.6545(17)$ Å, $c = 25.608(3)$ Å, $V = 1965.4(4)$ Å³, $Z = 4$, $D_x = 1.980$ M g/m³, $F(000) = 1120$, $\mu = 5.598$ mm⁻¹. The maximum and

minimum residual electron densities were 0.539 and $-0.753 \text{ e } \text{Å}^{-3}$ while the value for the Flack parameter is 0.0124 with 0.0074 esd.

4. Supplementary material

Crystallographic data for the structure analysis has been deposited with the Cambridge Crystallographic Data Center, CCDC No. 209756 for bis(4-methoxybenzoylmethyl)tellurium dibromide (**1c**). Copies of this information may be obtained free of charge from the Director, CCDC, 12 Union Road, Cambridge CB2 1EZ, UK. Fax: +44-1223-336-033; 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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References

- [1] (a) M. Lalental, H.J. Gysling, *J. Photogr. Sci.* 28 (1980) 209;
(b) H.J. Gysling, M. Lalental, M.G. Mason, L.J. Gerenser, *J. Photogr. Sci.* 30 (1982) 55.
- [2] N. Petragnani, *Tetrahedron* 12 (1961) 219.
- [3] (a) H.A. Stefani, A. Chieffi, J.V. Comasseto, *Organometallics* 10 (1991) 1178;
(b) H.A. Stefani, J.V. Comasseto, N. Petragnani, *Synth. Commun.* 17 (1987) 443.
- [4] E. Rust, *Ber. Dtsch. Chem. Ges.* 30 (1987) 2828.
- [5] (a) G.T. Morgan, O.C. Elvins, *J. Chem. Soc.* (1925) 2625;
(b) G.T. Morgan, H.D.K. Drew, *J. Chem. Soc.* (1920) 1456.
- [6] D.G. Marsh, J.Y.C. Chu, J.W. Lewicki, J.L. Weaver, *J. Am. Chem. Soc.* 98 (1975) 8432.
- [7] L. Engman, *Organometallics* 6 (1986) 427.
- [8] A.Z. Al-Rubaie, L.Z. Yousif, A.K. Al-Ba'aj, *J. Organomet. Chem.* 673 (2003) 40.
- [9] T. Hiroyo, N. Kambe, A. Ogawa, N. Mioyoshi, S. Mrai, N. Sonada, *Synthesis* (1987) 1096.
- [10] I. Haiduc, R.B. King, H.B. Newton, *Chem. Rev.* 1094 (1994) 301.
- [11] I. Haiduc, J. Zuckerman-Schpector, *Phosphorous, Sulfur and Silicon* 171 (2001) 171.
- [12] A.K.S. Chauhan, A. Kumar, R.C. Srivastava, R.J. Butcher, *J. Organomet. Chem.* 658 (2002) 169.
- [13] (a) A.Z. Al-Rubaie, W.R. McWhinnie, S. Chapelle, *J. Organomet. Chem.* 234 (1982) 287;
(b) R.H. Jones, T.A. Hamor, *J. Organomet. Chem.* 234 (1982) 299.
- [14] T.N. Srivastava, R.C. Srivastava, V.K. Srivastava, *Ind. J. Chem.* 22A (1983) 503.
- [15] J. Beckmann, D. Dakternieks, A. Duthie, N.A. Smith, *J. Organomet. Chem.* 669 (2003) 149.
- [16] H.J. Gysling, H.R. Luss, S.A. Gardner, *J. Organomet. Chem.* 184 (1980) 417.
- [17] (a) G.R. Desiraju, *Acc. Chem. Res.* 24 (1991) 290;
(b) V.R. Pedireddi, W. Jones, A.P. Chorlton, R. Docherty, *Chem. Commun.* (1997) 997.
- [18] D. Braga, F. Grepioni, *Acc. Chem. Res.* 33 (2000) 601.
- [19] (a) P.C. Srivastava, S. Bajpai, R. Lath, C. Ram, S. Bajpai, R.J. Butcher, M. Zimmer, M. Veith, *J. Organomet. Chem.* 649 (2002) 70;
(b) P.C. Srivastava, A. Sinha, S. Bajpai, H.G. Schmidt, M. Noltemeyer, *J. Organomet. Chem.* 575 (1999) 261.
- [20] (a) D. Braga, F. Grepioni, P. Sabatino, G.R. Desiraju, *Organometallics* 13 (1994) 3532;
(b) D. Braga, F. Grepioni, K. Biradha, V.R. Pedireddi, G.R. Desiraju, *J. Am. Chem. Soc.* 117 (1995) 3156;
(c) D. Braga, F. Grepioni, K. Biradha, V.R. Pedireddi, G.R. Desiraju, *J. Am. Chem. Soc.* 98 (1975) 8432.
- [21] M.J. Collins, J.A. Ripmeester, J.F. Sawyer, *J. Am. Chem. Soc.* 109 (1987) 4113.
- [22] L.J. Farrugia, *J. Appl. Crystallogr.* 20 (1997) 565.