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Dimethyl tellurium (IV) derivatives: synthesis, spectroscopic characterisation and structures of Me_2TeBr_2 and $Me_2Te(OCOC_6H_5)_2$

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Abstract

The comparative solution ^1H-NMR spectra and solid state crystal structures of dimethyltellurium dihalides, Me_2TeX_2 (X = CI, Br, I) are described. The dimethyltellurium dicarboxylates, $Me_2TeX'_2$ (X′ = $OCOC_6H_5$, $OCOCH_3$, OCO) were obtained from the reactions of Me_2TeI_2 with silver carboxylates. They were characterised by IR, ^1H- and ^{13}C-NMR spectroscopy. The structures of Me_2TeBr_2 and $Me_2Te(OCOC_6H_5)_2$ were established by single crystal X-ray diffraction studies. Both possess immediate distorted trigonal bipyramidal geometries with a stereochemically active electron lone pair and the latter contains weak intermolecular C–H···O interactions. © 1999 Elsevier Science S.A. All rights reserved.

Keywords: Tellurium; Bromide; Carboxylate

1. Introduction

Vernon [1], on the basis of chemical work, suggested that dimethyl tellurium dihalides Me_2TeX_2 (X = Cl, Br, I) existed in α and β forms and subsequent investigations [2,3] revealed that α-Me_2TeI_2 was covalent whereas β-Me_2TeI_2 was ionic $(Me_3Te)^+$ $(Me_2TeI_4)^-$. The covalent Me_2TeI_2 [4–7], Me_2TeCl_2 [8,9] have been subject of spectroscopic and structural investigations but no report on Me_2TeBr_2 has appeared. As part of our contribution in hypervalent tellurium (+4) compounds [10] we were the first to report dimethyl tellurium dicarboxylates [11]. We predicted tentative geometry of dimethyltellurium dicarboxylates on the basis of IR and ^1H-NMR data. In order to compliment and extend the studies on dimethyltellurium derivatives, we now report the X-ray structure determination of Me_2TeBr_2 and compare it with related structures along with comparative solution ^1H-NMR study of Me_2TeX_2 (X = Cl, Br, I) and some new $Me_2TeX'_2$ [X′ = $OCOC_6H_5$, $OCOCH_3$, OCO] and their characterisation through IR, (^1H, ^{13}C) NMR data and X-ray structure of $Me_2Te(OCOC_6H_5)_2$.

While Te···halogen, Te···O secondary bonds are common place in organotellurium compounds [12,13], there is none on intermolecular C–H···O interactions. It was of interest to look for possible C–H···O interactions.

Currently C–H···O interactions are one of the main topics of hydrogen bond research [14–16] particularly in supramolecular chemistry, molecular crystal engineering [17] and in organometal crystals [18–20].

2. Experimental section

2.1. Physical measurements

Elemental analyses for C and H were carried out on Elemental Analyser Heraeus Carlo Erba 1108. IR spectra were recorded using Shirnadzu 8210 PC FTIR

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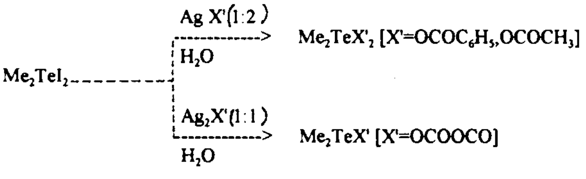
Table 1
Crystal data and refinement details for compounds **1** and **2**

	1	**2**
Empirical formula	$C_6H_6Br_2Te$	$C_{16}H_{16}O_4Te$
Formula weight	317.48	399.89
Temperature (K)	1 53(2)	213(2)
Crystal system	Monoclinic	Monoclinic
Space group	$P2_1/n$	Cc
a (Å)	10.91(3)	9.595(2)
b (Å)	6.56(2)	29.000(6)
c (Å)	11 27(3)	11.333(2)
β (°)	117 9(2)	90.02(3)
V (Å^3)	713(4)	3153.5(11)
Z	4	8
$D_{calc.}$ (mg m^{-3})	2.958	1.685
μ (mm^{-1})	15.252	1.899
$F(000)$	560	1568
h, k, l ranges	−11 to 11, −7 to 7, −12 to 12	−10 to 10, −10 to 31, −12 to 12
Reflections collected	1683	3029
Independent reflections	336 ($R_{int} = 0.0385$)	3026($R_{int} = 0.0055$)
Final R indices $[I > 26(I)]$	$R_1 = 0.0525$, $wR_2 = 0.1405$	$R_1 = 0.0226$, $wR_2 = 0.0603$
R indices (all data)	$R_1 = 0.0555$, $wR_2 = 0.1587$	$R_1 = 0.0235$, $wR_2 = 0.0664$

spectrometer in the frequency range 4000–350 cm^{-1} with the samples in the KBr disc. The (^1H and ^{13}C) NMR spectra were recorded on Bruker WM400 (400 MHz) FT NMR spectrometer in $CDCl_3$ using TMS as an internal standard. The single crystal X-ray diffraction studies were carried out at Anorganische Chemie der Institut, Göttingen, Germany.

2.2. Synthesis

Me_2TeI_2 was prepared in sealed tube (from Te and CH_3I) by literature method [1] and recrystallised from $CHCl_3$/Benzene (1:1) solvent mixture. It was converted into Me_2TeCl_2 [1] and Me_2TeBr_2 **1** [1]. Bis(benzoato)dimethyltellurium **2**, bis(acetato)dimethyltellurium **3** and dimethyl(oxalato)tellurium **4** were prepared by grinding Me_2TeI_2 with freshly prepared silver carboxylates by reaction 1. Previously we [11] prepared dimethyl tellurium dicarboxylates [$Me_2TeX'_2$ (X = CH_2ClOCO, $CHCl_2OCO$, CCl_3OCO, p-$OCH_3C_6H_4OCO$, C_6H_5–CH=CHOCO, 3,5-$(NO_2)_2C_6H_5OCO$ and p-$NH_2C_6H_4OCO$)] by the reaction of Me_2TeI_2 with carboxylic acids in presence of Ag_2O in chloroform/Pet.ether.



(1)

To dimethyl tellurium diiodide (4.12 g, 10 mmol), was added freshly prepared silver benzoate (4.58 g, 20 mmol), silver acetate (3.34 g, 20 mmol), silver oxalate (3.04 g, 10 mmol) in a mortar and ground with a little amount of water to make a thin paste. It was ground for 45 min more, after the red crystals of dimethyl tellurium diiodide disappeared. The paste was filtered with hot water. The filtrate was reduced to give compounds **2**–**4**. Compound **2** Yield: 3.40 g (85%), m.p. 150°C, Anal. Found: C, 48.00; H, 3.96; Te, 31.88. ($C_{16}H_{16}O_4Te$) Anal. Calc.: C, 48.05, H, 4.00; Te, 31.93%. Compound **3** Yield: 2.18 g (79%), m.p. 190°C, Anal. Found: C, 26.02; H, 4.12; Te, 46.10 ($C_6H_{12}O_4Te$) Anal. Calc.: C, 26.12; H, 4.35; Te, 46.29%. Compound **4** Yield: 1.85 g (75%), m.p. 320°C (decomp.), Anal. Found: C, 19.50; H, 2.32; Te, 51.82 ($C_4H_6O_4Te$) Anal. Calc.: C, 19.54; H, 2.44; Te, 51.95%.

2.3. X-ray measurements

The X-ray measurements for compound **1** and compound **2** were performed at 153(2) K and 213(2) K, respectively. The structure of **1** was solved in space group $P2_1/n$ and that of **2** in space group Cc (two independent molecules in the cell). It was not possible

Table 2
Atomic coordinates (×10^4) and equivalent isotropic displacement parameters (Å^2 × 10^3) for **1**[a]

	x	y	z	U_{eq}
Te(1)	584(1)	684(1)	2368(1)	23(1)
Br(1)	946(1)	−2552(2)	1056(1)	38(1)
Br(2)	49(1)	3564(2)	3705(1)	39(1)
C(1)	1648(11)	−957(15)	4168(10)	36(2)
C(2)	−1405(10)	−570(16)	1857(13)	45(3)

[a] U_{eq} is defined as one third of the trace of the orthogonalised U_{ij} tensor.

Table 3
Bond lengths [Å] and angles [°] for **1**[a]

Te(1)–C(1)	2.101(11)	Te(1)–C(2)	2.133(11)
Te(1)–Br(2)	2.647(5)	Te(1)–Br(1)	2.720(6)
C(1)–Te(1)–C(2)	95.5(5)	C(1)–Te(1)–Br(2)	89.2(4)
C(2)–Te(1)–Br(2)	87.8(4)	C(1)–Te(1)–Br(1)	88.3(4)
C(2)–Te(1)–Br(1)	86.6(3)	Br(2)–Te(1)–Br(1)	173.56(4)

[a] Symmetry transformations used to generate equivalent atoms.

to solve the structure of **2** in $C2_{lc}$ and in orthorhombic *Cmca* space groups. The data on the light yellow crystals ($0.70 \times 0.50 \times 0.20$ mm) of compound **1** and colourless crystals ($0.70 \times 0.70 \times 0.40$ mm) of compound **2** collected in the θ range 3.56–22.55° correspond to monoclinic cells whose dimensions are given in Table 1. The structures were solved by Patterson method and refined with SHELXL-93 [21] against F^2. Goodness-of-fit (GOF) on $F^2 = 1.085$ for **1** and 1.056 for **2**. Refinement by anisotropic factors for nonhydrogen atoms and isotropic factors for hydrogen resulted in final R indices $[1 > 2\sigma(1)]$, $R1 = 0.0525$, $wR2 = 0.1405$ for **1** and $R1 = 0.0226$, $wR2 = 0.0603$ for **2** and R indices (all data) $R1 = 0.0555$, $wR2 = 0.1587$ and $R1 = 0.0235$, $wR2 = 0.0664$ for **2** (R factors defined in ref. [21]). Intermolecular distances from Te to Br of other molecules are 3.539 and 3.626 Å in **1** and intermolecular Te···O, O···H(C) and Te···H(C) distances between the nearest molecules in **2** were found to be 2.224, 2.556, and 3.08 Å, respectively. Atomic coordinates for **1** are listed in Table 2; selected bond lengths and bond angles in Table 3 and atomic coordinates for **2** are listed in Table 4; selected bond lengths and bond angles in Table 5 and H– coordinates in Table 6. The crystal structure of **1** is shown in Fig. 1. The solid state molecular structure of **2** is shown in Fig. 2; the packing plot of **2** without hydrogen atoms is shown in Fig. 3, and with hydrogen atoms is shown in Fig. 4. Atomic coordinates, thermal parameters and bond lengths and angles have been deposited at the Cambridge Crystallographic Data Centre.

Table 4
Atomic coordinates [$\times 10^4$] and equivalent isotropic displacement parameters [$Å^2 \times 10^3$] for **2**[a]

	x	y	z	U_{eq}
Se(1)	−658(1)	−6700(1)	5958(1)	32(1)
O(1)	−2863(4)	−6109(2)	5141(4)	47(1)
O(2)	−1371(4)	−6035(1)	6621(3)	38(1)
O(3)	87(4)	−1394(1)	5781(3)	37(1)
O(4)	−1485(4)	−7408(2)	4315(3)	46(1)
C(1)	−2371(6)	−5882(2)	5966(4)	37(1)
C(2)	−2940(6)	−5415(2)	6263(5)	37(1)
C(3)	−4108(6)	−5253(2)	5664(5)	43(2)
C(4)	−4682(8)	−4833(2)	5950(6)	56(2)
C(5)	−4101(8)	−4572(3)	6811(7)	61(2)
C(6)	−2946(8)	−4726(3)	7399(6)	61(2)
C(7)	−2348(7)	−5141(2)	7144(5)	45(2)
C(8)	623(7)	−6700(2)	7459(6)	43(2)
C(9)	−2412(6)	−6982(2)	6795(5)	42(1)
C(10)	−510(8)	−7587(3)	4855(6)	39(2)
C(11)	67(6)	−8045(2)	4513(5)	36(1)
C(12)	1227(7)	−8238(2)	5095(6)	38(1)
C(13)	1727(8)	−8666(3)	4783(5)	54(2)
C(14)	1067(9)	−8911(2)	3903(6)	63(2)
C(15)	−72(8)	−8720(3)	3310(6)	56(2)
C(16)	−575(10)	−8293(3)	3616(9)	42(2)
Te(2)	4342(1)	−6699(1)	4700(1)	32(1)
O(5)	2137(4)	−6106(2)	5510(4)	51(1)
O(6)	3636(4)	−6030(1)	4046(3)	39(1)
O(7)	5086(4)	−7392(1)	4884(3)	38(1)
O(8)	3525(4)	−7411(2)	6339(3)	48(1)
C(17)	2615(5)	−5885(2)	4694(4)	34(1)
C(18)	2056(6)	−5418(2)	4398(5)	36(1)
C(19)	887(6)	−5255(2)	5003(5)	42(2)
C(20)	318(8)	−4841(3)	4740(6)	58(2)
C(21)	887(8)	−4569(3)	3855(7)	62(2)
C(22)	2046(8)	−4720(3)	3251(6)	56(2)
C(23)	2653(7)	−5153(2)	3510(5)	47(2)
C(24)	5629(8)	−6700(2)	3190(6)	46(2)
C(25)	2577(6)	−6975(2)	3871(5)	42(1)
C(26)	4483(8)	−7591(2)	5809(6)	32(2)
C(27)	5076(6)	−8045(2)	6137(4)	34(1)
C(28)	6219(7)	−8229(2)	5573(6)	42(2)
C(29)	6718(8)	−8657(3)	5891(5)	54(2)
C(30)	6048(9)	−8910(3)	6771(6)	61(2)
C(31)	4933(8)	−8727(3)	7343(6)	61(2)
C(32)	4435(12)	−8294(3)	7046(9)	52(3)

[a] U_{eq} is defined as one third of the trace of the orthogonalized U_{ij} tensor.

3. Results and discussion

Repeated crystallisation of **1** from $CHCl_3$ and recrystallisation of **2** from $CHCl_3$/benzene yielded crystals of Me_2TeBr_2 and $Me_2Te(OCOC_6H_5)_2$ suitable for single crystal X-ray diffraction studies.

3.1. Spectroscopic characterisation

Spectroscopic data for **1**–**4** are given in Table 7. The IR spectra of **1**–**4** contain ν (Te–CH_3) in the range 505 ± 10 cm^{-1} [22,23]. In the dimethyl tellurium dicarboxylates **2**–**4** ν (asym COO) and ν (sym COO) are in the range of 1590–1630 cm^{-1} and 1280–1360 cm^{-1}, respectively. $\Delta\nu$ (ν (asym COO)–ν (sym COO)) $\approx$ 252–310 indicates unidentate nature of carboxylate groups in **2**, **3** [24] except in the case of **4** which appears to contain bidentate oxalate group [25].

In the ^{1}H-NMR spectra of Me_2TeX_2 (X = Cl, Br, I), the signal due to CH_3–Te (H^1) appear as a singlet flanked by satellite bands. The coupling constants ($^2J_{TeCH}$) of dimethyltellurium dihalides [Me_2TeX_2; X = CI, Br, I] are in the range 23.0–26.0 (Table 7). In ^{1}H-NMR spectra of **2**–**4**, the singlet for the proton of the methyl group attached to tellurium appears in the range 2.63–3.27 ppm. The phenyl group protons ap-

Table 5
Bond length [Å] and angles [°] for **2**[a]

Te–(1)–C(9)	2.098(5)	Te(1)–C(8)	2.098(6)
Te(1)–O(3)	2.146(4)	Te(1)–O(2)	2.181(4)
O(1)–C(1)	1.238(7)	O(2)–C(1)	1.291(7)
O(3)–C(10)	1.321(8)	O(4)–C(10)	1.232(8)
C(1)–C(2)	1.497(9)	C(2)–C(3)	1.393(8)
C(2)–C(7)	1.397(8)	C(3)–C(4)	1.376(9)
C(4)–C(5)	1.354(10)	C(5)–C(6)	1.365(11)
C(6)–C(7)	1.364(10)	C(10)–C(11)	1.489(10)
C(11)–C(16)	1.390(11)	C(11)–C(12)	1.410(9)
C(12)–C(13)	1.378(9)	C(13)–C(14)	1.375(10)
C(14)–C(15)	1.397(11)	C(15)–C(16)	1.373(10)
Te(2)–C(25)	2.095(5)	Te(2)–C(24)	2.110(6)
Te–(2)–O(7)	2.142(4)	Te(2)–O(6)	2.184(4)
O(5)–C(17)	1.215(7)	O(6)–C(17)	1.295(6)
O(7)–C(26)	1.329(7)	O(8)–C(26)	1.215(8)
C(17)–C(18)	1.497(8)	C(18)–C(23)	1.389(5)
C(18)–C(19)	1.397(8)	C(19)–C(20)	1.350(10)
C(20)–C(21)	1.388(11)	C(21)–C(22)	1.377(11)
C(22)–C(23)	1.414(10)	C(26)–C(27)	1.482(9)
C(27)–C(28)	1.377(9)	C(27)–C(32)	1.402(11)
C(28)–C(29)	1.378(9)	C(29)–C(30)	1.396(10)
C(30)–C(31)	1.359(11)	C(31)–C(32)	1.385(11)
C(9)–Te(1)–C(8)	95.9(2)	C(9)–Te(1)–O(3)	86.7(2)
C(8)–Te–(1)–O(3)	83.1(2)	C(9)–Te–(1)–O(2)	84.5(2)
C(8)–Te–(1)–O(2)	84.5(2)	O(3)–Te(1)–O(2)	165.21(13)
C(1)–O(2)–Te(1)	109.8(3)	C(10)–O(3)–Te(1)	109.1(4)
O(1)–C(1)–O(2)	122.3(5)	O(1)–C(1)–C(2)	120.8(5)
O(2)–C(l)–1(2)	116.9(5)	C(3)–C(2)–C(7)	118.9(6)
C(3)–C(2)–C(1)	119.3(5)	C(7)–C(2)–C(1)	121.8(5)
C(2)–C(3)–C(4)	120.4(6)	C(5)–C(4)–C(3)	120.0(7)
C(4)–C(5)–C(6)	120.2(7)	C(5)–C(6)–C(7)	121.7(7)
C(6)–C(7)–C(2)	118.9(6)	O(4)–C(10)–O(3)	123.0(7)
O(4)–C(10)–C(11)	122.0(6)	O(3)–C(10)–C(11)	115.0(6)
C(16)–C(11)–C(12)	119.1(6)	C(16)–C(11)–C(10)	119.2(6)
C(12)–C(11)–C(10)	121.7(5)	C(13)–C(12)–C(11)	120.8(6)
C(14)–C(13)–C(12)	119.4(7)	C(13)–C(14)–C(15)	120.2(7)
C(16)–C(15)–C(14)	120.7(7)	C(15)–C(16)–C(11)	119.8(8)
C(25)–Te(2)–C(24)	96.3(3)	C(25)–Te(2)–O(7)	87.4(2)
C(24)–Te(2)–O(7)	83.3(2)	C(25)–Te(2)–O(6)	86.4(2)
C(24)–Te(2)–O(6)	84.7(2)	O(7)–Te(2)–O(6)	165.77(13)
C(17)–O(6)–Te(2)	109.3(3)	C(26)–O(7)–Te(2)	109.8(4)
O(5)–C(17)–O(6)	123.1(5)	O(5)–C(17)–C(18)	120.9(5)
O(6)–C(17)–C(18)	116.0(5)	C(23)–C(18)–C(19)	120.1(6)
C(23)–C(18)–C(17)	121.0(5)	C(19)–C(18)–C(17)	119.0(5)
C(20)–C(19)–C(18)	121.1(6)	C(19)–C(20)–C(21)	120.3(7)
C(20)–C(21)–C(22)	119.8(7)	C(21)–C(22)–C(23)	120.8(7)
C(18)–C(23)–C(22)	118.0(6)	O(8)–C(26)–O(7)	122.3(6)
O(8)–C(26)–C(27)	123.2(6)	O(7)–C(26)–C(27)	114.5(5)
C(28)–C(27)–C(32)	119.3(7)	C(28)–C(27)–C(26)	122.3(5)
C(32)–C(27)–C(26)	118.3(6)	C(29)–C(28)–C(27)	120.4(6)
C(28)–C(29)–C(30)	120.0(7)	C(31)–C(30)–C(29)	119.9(7)
C(30)–C(31)–C(32)	120.6(7)	C(31)–C(32)–C(27)	119.7(9)

[a] Symmetry transformations used to generate equivalent atoms.

pear as multiplets in **2** at 7.57–7.60 ppm. In **3**, OCH_3 protons appear as singlet at 3.18 ppm. The peak areas in **2** and **3** are consistent with the proposed stoichiometry of the complexes.

In ^{13}C-NMR spectra of **2** Te–CH_3(C) appears at 21.00 ppm and C_6H_5(C) appear in the range 128.52–133.84 ppm, CO(C) is present at 172.43 ppm.

3.2. Crystal and molecular structures of *1* and *2*

Componud **1** possesses distorted trigonal bipyramidal geometry (tbp) with Te at the centre, Br atoms at the axial position and of the three equitorial positions, two are occupied by two methyl groups and the third position is presumably occupied by the unshared elec-

Table 6
Hydrogen coordinates ($\times 10^4$) and isotropic displacement parameters ($Å^2 \times 10^3$) for **2**

	x	y	x	U_{eq}
H(3A)	−4508(6)	−5432(2)	5060(5)	52
H(4A)	−5477(8)	−4727(2)	5549(6)	67
H(5A)	−4492(8)	−4285(3)	7004(7)	73
H(6A)	−2554(8)	−4541(3)	7994(6)	73
H(7A)	−1551(7)	−5241(2)	7553(5)	55
H(8A)	1133(30)	−6988(6)	7499(19)	65
H(8B)	52(8)	−6666(13)	8160(6)	65
H(8C)	1276(27)	−6445(8)	7412(17)	65
H(9A)	−2726(27)	−7251(9)	6360(22)	63
H(9B)	−3151(16)	−6755(5)	6819(33)	63
H(9C)	−2168(13)	−7072(14)	7593(13)	63
H(12A)	1666(7)	−8072(2)	5704(6)	46
H(13A)	2510(8)	−8790(3)	5167(5)	64
H(14A)	1383(9)	−9208(2)	3702(6)	75
H(15A)	−498(8)	−8885(3)	2694(6)	67
H(16A)	−1351(10)	−8170(3)	3221(9)	50
H(19A)	490(6)	−5436(2)	5603(5)	50
H(20A)	−467(8)	−4737(3)	5159(6)	69
H(21A)	485(8)	−4283(3)	3669(7)	75
H(22A)	2438(8)	−4534(3)	2660(6)	67
H(23A)	3438(7)	−5259(2)	3093(5)	56
H(24A)	6208(30)	−6974(7)	3193(19)	69
H(24B)	6217(30)	−6428(7)	3197(19)	69
H(24C)	5053(8)	−6698(14)	2487(6)	69
H(25A)	2719(18)	−7302(4)	3729(33)	63
H(25B)	2424(26)	−6819(10)	3126(18)	63
H(25C)	1770(10)	−6933(13)	4376(17)	63
H(28A)	6660(7)	−8062(2)	4968(6)	50
H(29A)	7510(8)	−8779(3)	5514(5)	65
H(30A)	6367(9)	−9207(3)	6968(6)	74
H(31A)	4495(8)	−8896(3)	7967(6)	73
H(32A)	3671(12)	−8168(3)	7453(9)	63

tron pairs (Fig. 1, Table 3) in accordance with the valence shell electron pair repulsion (VSEPR) model [26–29]. In the packing plot the intermolecular Te···Br secondary bonds (3.539 and 3.626 Å) as proposed by Alcock [12], are shorter than combined van der Waals radii of 4.15 Å ([35]b) for tellurium and bromine and longer than the combined covalent radius of 2.51 Å ([35]a) for Te and Br. These give Tellurium^{IV} a six coordinate distorted octahedral geometry (figure is withheld for the sake of brevity). The comparative bond lengths and bond angles data of Me_2TeX_2 (X = Cl, Br, I) (Table 8) shows that Te–I > Te–Br > Te–Cl and Te···I > Te···Br > Te···Cl. The comparative solid state structural study of Me_2TeX_2 with Me_2SeX_2 (X = Cl, Br, I) indicates that all these compounds possess distorted tbp geometry except Me_2SeI_2 which possess molecular charge transfer spoke structure Me_2Se–I–I [30].

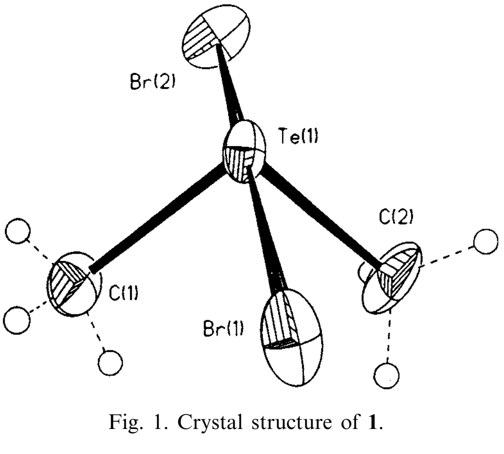


Fig. 1. Crystal structure of **1**.

The solid state molecular structure of **2** (Fig. 2) contains two independent molecules with identical structures, having benzoate groups as unidentate ligands bound to Te through one of the oxygens. It also possesses distorted tbp geometry with two methyl groups and an electron pair presumably occupying equatorial positions and the oxygen atoms are at the axial positions as per VSEPR model [26–29] (Table 5). The O–Te–O angles are 165°. This fairly large deviation from linearity in O–Te–O angle has also been observed in diaryl tellurium dicarboxylates [31–33] and may be attributed to the presence of Te···O secondary bonds which bring up the coordination of Te to octahedral. These Te···O secondary bonds [12] join the molecules in trimeric and dimeric units (Fig. 3) as envisaged by King et al. [13] for the structure of Ph_3TeSCN [34] where dimeric and tetrameric units, connected through Te···S and Te···N secondary bonds, are present. The Te···O distance is 2.224 Å appreciably shorter than the sum of van der Waals radii (3.60 Å) ([33], [35]b) and longer than the sum of covalent radii (2.03 Å) ([35]a) of Te and O and thus corresponds to secondary bond [12]. Te···O distances are (2.95–3.02 Å) in $(p\text{-}MeOC_6H_4)_2Te(CH_3COO)_2$ [31] and (2.99–3.03 Å) in $(C_6H_5)_2Te(CF_3COO)_2$ [33]. Thus Te···O secondary bonds, observed in the present case, are stronger in comparison to other diaryltellurium dicarboxylates [31,33]. In the packing plot of **2** with hydrogen atoms (Fig. 4) one of the CH_3 groups attached to Te enters into weak intermolecular C–H···O interaction and the observed values of C–H···O is 2.556 Å as against the sum of van da Waals radii of CH_3 group and O (3.40 Å) ([35]b) C–H···O in the range of 2.0–3.0 Å is present in a variety of organic compounds [14,15,18] and organometallic compounds [19]. This is so far the first report of intermolecular C–H···O interactions in organotellurium compound. Our recent structure on cyclic tellurium compound

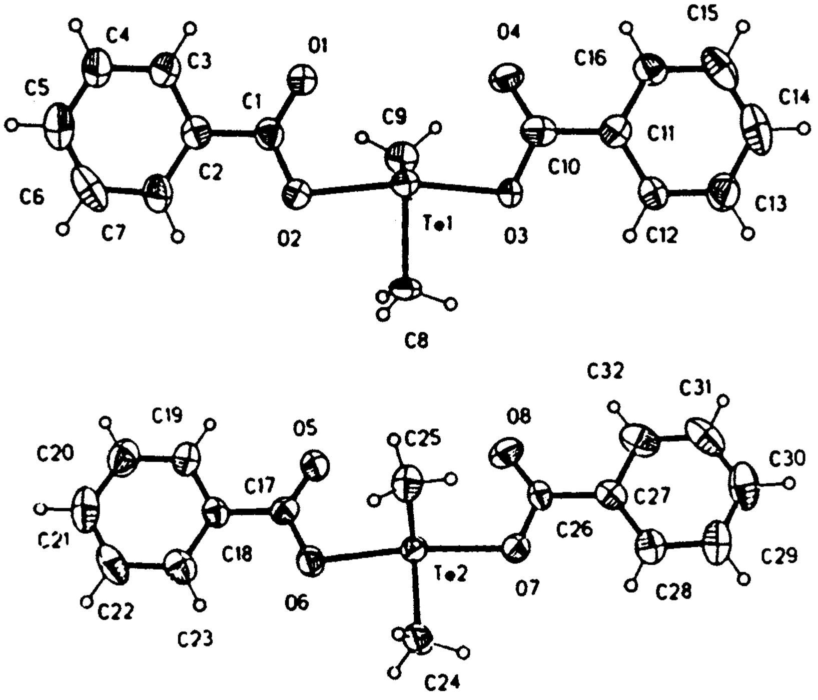


Fig. 2. ORTEP plot of **2** showing two independent molecules and atom labelling scheme.

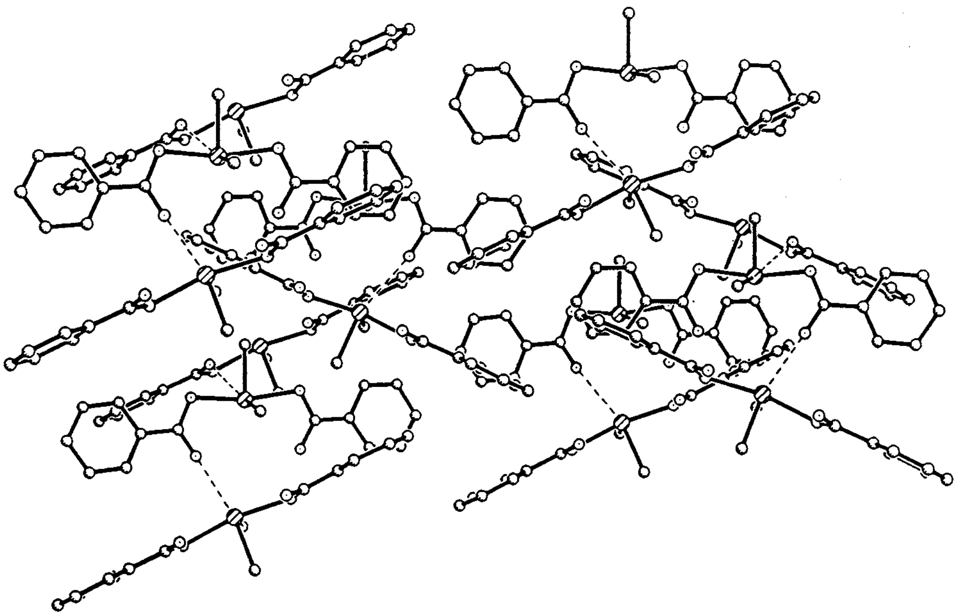


Fig. 3. Packing plot of **2** without hydrogen atoms showing the inter molecular Te···O secondary bonds (dashed) containing dimeric and trimeric units.

containing CH_2 and O is devoid of such C–H···O interactions [36].

The observed value of (C)H···Te is 3.08 Å against the sum of van der Waals radii of CH_3 group and Te (4.20 Å) ([35]b) indicates reduced value but it is more ikely close (C)H···Te contact because of incidental consequence of the Te···O secondary bonds (Fig. 4).

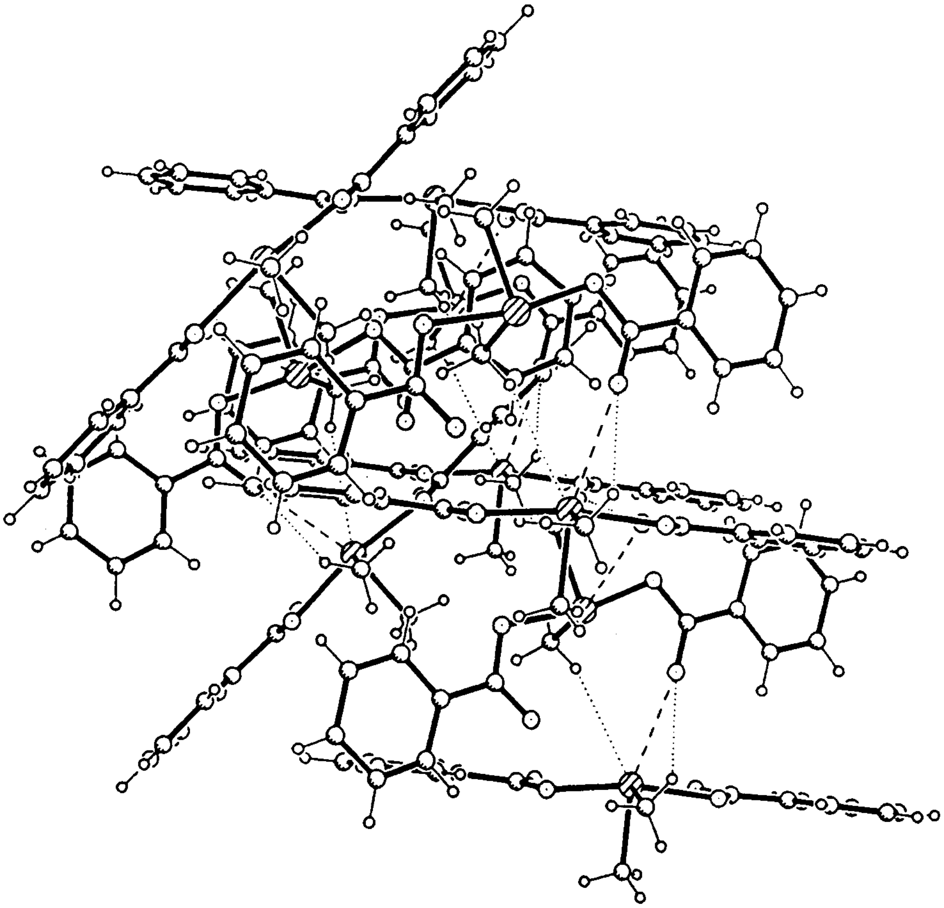


Fig. 4. Packing plot of **2** with hydrogen atoms showing intermolecular (C)H···O interactions/(C)H···Te contacts (dotted) and Te···O secondary bonds (dashed).

Table 7
Spectroscopic data for **1**–**4**[a]

Compound	IR(KBr) (cm^{-1})	^{1}H-NMR ($CDCl_3/CCl_4$) (ppm)	^{13}C-NMR ($CDCl_3$) (ppm)
1	515 ($TeCH_3$)	3.25(s) ($TeCH_3$)	
2	1590(asymCO)	3.27(s) ($TeCH_3$)	21.00($TeCH_3$)
	1280(symCO)	7.57–7.60(m) (C_6H_5)	128.52, 129.39, 130.26
	655(OCO)		133.84[(C_6H_5)(C)]
	1565(TeO		172.43(CO)
	495($TeCH_3$)		
3	1630(asymCO)	2.63(s) ($TeCH_3$)	–
	1332(symCO)	3.18(s) ($COCH_3$)	
	648(OCO)		
	510 ($TeCH_3$)		
4	1612(asymCO)	2.71(s) ($TeCH_3$)	–
	1360(symCO)		
	645(OCO)		
	500($TeCH_3$)		

[a] Me_2TeCl_2 [σ, 3.10; $^2J_{TeCH}$ (Hz) 23 0], Me_2TeBr_2 [$^2J_{TeCH}$ (Hz) 25.2 [present work], Me_2TeI_2 [σ 3.37; $^2J_{TeCH}$ (HZ) 26.0], [7, present work].

Table 8
Comparative bond lengths (Å) and angles (°) of Me_2TeX_2 (X = Cl, Br, I)

Compound	Te–C	Te–X	Te···X	∠XTeX	∠CTeX	∠CTeC	Reference
Me_2TeCl_2	2.11	2.49–2.54	3.41–3.47	172.44	86.50–82.29	96.63	[9]
Me_2TeBr_2	2.10–2.13	2.64–2.72	3.54–3.62	173.56	86.6–89.2	95.50	Present work
Me_2TeI_2	2.10–2.16	2.85–2.94	3.65–4.02	177.3–178.3	87–91	95–97	[4]

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