

The interplay of secondary Te···N, Te···O, Te···I and I···I interactions, Te··· π contacts and π -stacking in the supramolecular structures of [2-(4-nitrobenzylideneamino)-5-methyl}phenyl](4-methoxyphenyl)tellurium dihalides

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Abstract

The unsymmetrically substituted diorganotellurium dihalides [2-(4,4'-NO₂C₆H₄CHNC₆H₃Me)R]TeX₂ (R = 4-MeOC₆H₄, X = Cl, **1a**; Br, **1b**; I, **1c**; R = 4-MeC₆H₄; X = Cl, **2**; R = C₆H₅, X = Cl, **3**) were prepared in good yields and characterized by solution and solid-state ¹²⁵Te NMR spectroscopy, IR spectroscopy and X-ray crystallography. In the solid-state, molecular structures of **1a** and **1c** possess scarcely observed 1,4-type intramolecular Te···N secondary interaction. Crystal packing of these compounds show an unusually rich diversity of intermolecular secondary, Te···O, Te···I and I···I interactions, Te··· π contacts as well as extensive π -stacking of the organic substituents.

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1. Introduction

The crystal structures of most diorganotellurium dihalides are characterized by the presence of considerably longer intermolecular Te···X secondary bonds. The number and directionality of these interactions and the influence on the geometry of the tellurium atoms in diorganotellurium dihalides has been thoroughly investigated [1]. By contrast the less commonly observed

secondary Te··· π [2] interactions remain comparatively less understood. On the other hand secondary Te···N, Te···O interactions have mostly been identified to exist intramolecularly [3]. The formation of, in general, a five-membered ring by chelation through secondary Te···N(O) interaction is reported to modulate the stability and reactivity of organotellurium derivatives with important consequences upon their applications [4]. We have recently reported [5] the existence of strained four-membered rings formed by 1,4-type intramolecular secondary Te···O interaction among diorganotellurium dihalides and their influence on the intermolecular secondary Te···X interaction.

We now describe the synthesis and full characterization of five unsymmetrically substituted diorganotellu-

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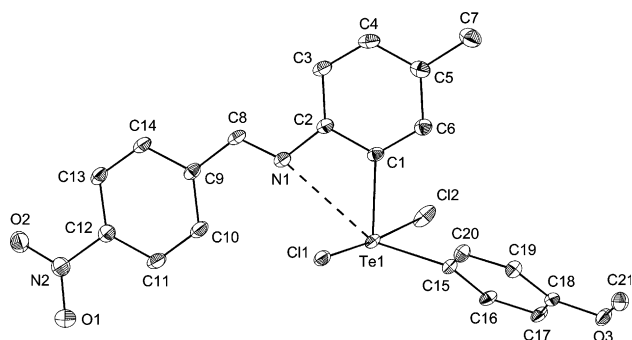


Fig. 1. Molecular structure of **1a** showing 30% probability displacement ellipsoids and the crystallographic numbering scheme.

tion. In contrast to many other diorganotellurium dichlorides, compound **1a** shows no secondary $\text{Te} \cdots \text{Cl}$ interactions [1]. Also there is no evidence for secondary $\text{Cl} \cdots \text{Cl}$ interactions in the crystal structure of **1a**; the

shortest distance between two Cl atoms in the crystal structure is 4.416(2) Å (between Cl1 and Cl2 of an adjacent molecule). However, the proximity of the tellurium to a methoxy group of an adjacent molecule suggests that a $\text{Te} \cdots \pi$ interaction is operative (Fig. 2). The $\text{Te} \cdots \pi$ and $\pi (\text{C}=\text{Y}) \cdots \pi (\text{C}=\text{Y})$ contacts associated with quinoid electron delocalization across the *para*-methoxy phenyl as well as the NMBA fragments appear to be the intermolecular associative forces in absence of $\text{Te} \cdots \text{Cl}$ and $\text{Cl} \cdots \text{Cl}$ interactions. In the solid-state, compound **1c** contains two crystallographically independent, yet similar conformers featuring Te1A and Te1B (Fig. 4). Besides the intramolecular N-coordination, the secondary coordination spheres of Te1A and Te1B are defined by a secondary $\text{Te} \cdots \text{O}$ interaction of 3.258(9) Å (O1A of an adjacent nitro group; symmetry operation: $1-x, 2-y, 3-z$) and a secondary $\text{Te} \cdots \text{I}$ interaction of 3.927(8) Å (I2B of an adjacent molecule; symmetry

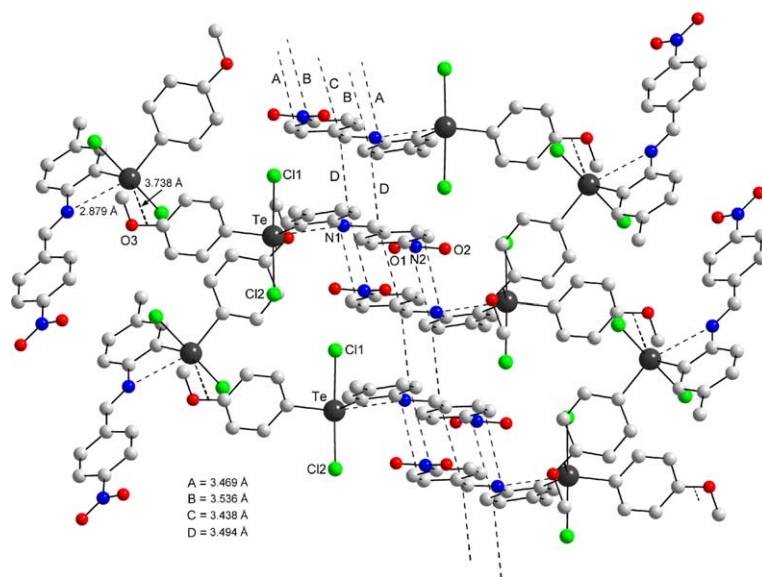


Fig. 2. Crystal structure of **1a**, viewed along the *a*-axis.

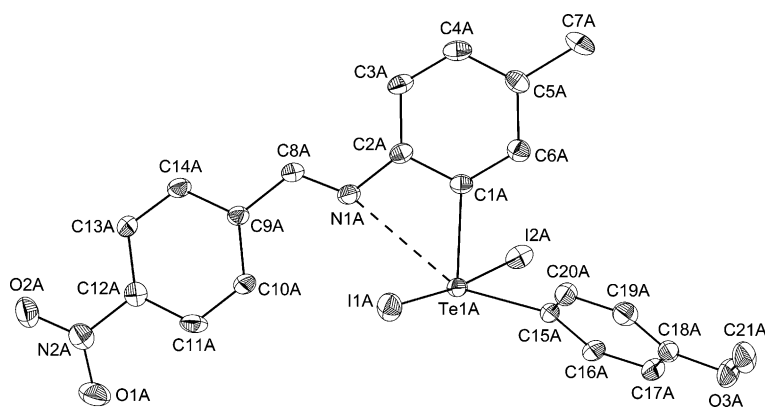
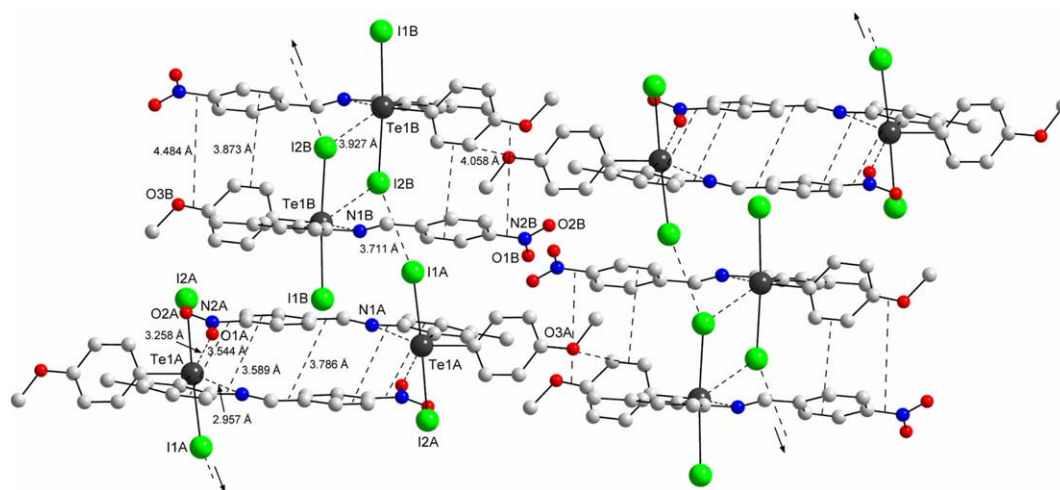


Fig. 3. Molecular structure of one of the two crystallographically independent conformers of **1c** showing 30% probability displacement ellipsoids and the crystallographic numbering scheme.

Fig. 4. Crystal structure of **1c**, viewed along the *a*-axis.Table 1
Crystal data and structure refinement for **1a** and **1c**

	1a	1c
Formula	C ₂₁ H ₁₈ Cl ₂ N ₂ O ₃ Te · 0.5CHCl ₃	C ₂₁ H ₁₈ I ₂ N ₂ O ₃ Te
Formula weight (g mol ⁻¹)	604.56	727.77
Crystal system	Monoclinic	Triclinic
Crystal size, mm	0.25 × 0.30 × 0.55	0.08 × 0.40 × 0.95
Space group	C2/c	P $\bar{1}$
<i>a</i> (Å)	24.501(3)	10.0878(17)
<i>b</i> (Å)	7.6443(10)	15.491(3)
<i>c</i> (Å)	25.868(4)	16.247(3)
α (°)	90	77.616(3)
β (°)	101.421(2)	82.594(3)
γ (°)	90	86.944(4)
<i>V</i> (Å ³)	4748.8(11)	2458.2(7)
<i>Z</i>	8	4
<i>D</i> _{calc} Mg m ⁻³	1.691	1.966
<i>T</i> (K)	103(2)	148(2)
μ (mm ⁻¹)	1.673	3.744
<i>F</i> (000)	2376	1360
Number of reflections collected	17616	12756
Number of independent reflections/ <i>R</i> _{int}	5787	8498
Number of reflections observed with (<i>I</i> > 2σ(<i>I</i>))	4900	7017
<i>R</i> ₁ (<i>F</i>)(<i>I</i> > 2σ(<i>I</i>))	0.022	0.046
<i>wR</i> ₂ <i>F</i> ² (all data)	0.065	0.127
(Δ/σ) _{max}	0.00010(4)	0.00078(18)
Largest difference peak/hole (e Å ⁻³)	0.551/−0.446	1.367 (near Te)/−1.390 (near Te)

operation: $1 - x, 3 - y, 1 - z$, respectively. In the crystal structure of **1c** there is also a secondary I···I contact of 3.711(5) Å between I1A and I2B (symmetry operation: $1 - x, 3 - y, 2 - z$), which is comparable to those reported previously for other diorganotellurium diiodides [13]. Compounds **1a** and **1c** crystallize in centrosymmetric space groups and in their crystal lattice symmetry-related *N*-(4-methylphenyl)-4-nitrobenzylideneimine moieties are associated by extensive π -stacking and adopt head-to-tail conformations similar to the NMBA molecules in the triclinic modification (Figs. 2 and 4). Consequently, all putative second-order NLO effects are expected to be nullified [6].

3. Experimental

3.1. General

Preparative work was performed under dry nitrogen. The starting materials [{2-(4-nitrobenzylideneamino)-5-methyl}phenyl]mercury chloride and aryltellurium trichlorides were prepared according to literature methods [9,14]. Solution ¹H (300.13 MHz), ¹³C (75.47 MHz) and ¹²⁵Te (85.29 MHz) NMR spectra were recorded in CDCl₃ on Varian 300 DRX, 300 Unity Plus and JEOL GX 270 NMR spectrometers, using Me₄Si and Me₂Te as internal standards. Solid-state ¹²⁵Te (126.2 MHz)

Table 2
Selected bond parameters (Å, °) for **1a** and **1c**

	1a (X = Cl)	1c (X = I)	
		Molecule A	Molecule B
Te1–X1	2.507(1)	2.933(3)	2.993(2)
Te1–X2	2.475(1)	3.022(3)	2.953(2)
Te1–N1	2.879(2)	2.958(7)	2.888(7)
Te1–C1	2.107(3)	2.159(7)	2.152(7)
Te1–C15	2.104(3)	2.172(7)	2.174(7)
X1–Te1–X2	175.04(2)	174.97(2)	170.41(2)
X1–Te1–N1	81.44(5)	79.17(9)	84.78(10)
X1–Te1–C1	87.65(6)	90.94(17)	84.44(17)
X1–Te1–C15	89.89(6)	92.04(17)	93.74(17)
X2–Te1–N1	96.58(5)	95.89(9)	85.67(10)
X2–Te1–C1	87.52(7)	85.33(17)	89.21(17)
X2–Te1–C15	89.67(6)	91.79(17)	94.17(17)
N1–Te1–C1	53.61(8)	53.79(19)	54.13(19)
N1–Te1–C15	150.48(8)	149.37(19)	151.24(19)
C1–Te1–C15	98.12(9)	97.61(23)	97.12(23)

CP MAS NMR spectra were acquired using a JEOL Eclipse Plus 400 NMR spectrometer equipped with a high speed locked 4 mm 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 are referenced against Me₂Te using solid Te(OH)₆ as the secondary reference (δ_{iso} 692.1, 685.5) [15]. Definitions δ_{iso} (ppm) = $-\sigma_{iso} = -(\sigma_{11} + \sigma_{22} + \sigma_{33})/3$; ζ (ppm) = $\sigma_{33} - \sigma_{iso}$ and $\eta = (\sigma_{22} - \sigma_{11})/(\sigma_{33} - \sigma_{iso})$ where σ_{11} , σ_{22} and σ_{33} (ppm) are the principal tensor components of the shielding anisotropy (SA), sorted as follows $|\sigma_{33} - \sigma_{iso}| > |\sigma_{11} - \sigma_{iso}| > |\sigma_{22} - \sigma_{iso}|$. IR spectra were recorded as KBr pellets using a Perkin–Elmer RX1 Spectrometer. Microanalyses were carried out using a Carlo Erba 1108 make analyzer. Tellurium was estimated volumetrically and the halogen content gravimetrically as silver halide [16].

3.2. Synthesis of (4-methoxyphenyl)[{2-(4-nitrobenzylideneamino)-5-methyl}phenyl]tellurium dichloride (**1a**)

A solution of [{2-(4-nitrobenzylideneamino)-5-methyl}phenyl]mercury chloride (2.37 g, 5.00 mmol) and 4-methoxyphenyltellurium trichloride (1.70 g, 5.00 mmol) in chloroform (250 ml) was heated under reflux for 20 h. Precipitated HgCl₂ was filtered off and the solvents reduced to approximately one fifth in vacuo. Addition of petroleum ether (b.p. 40–60 °C) (50 mL) induced the precipitation of solid, which was recrystallized twice from CHCl₃ to give yellow crystals of **1a**. Yield: (1.88 g, 66%); m.p. 220 °C. Anal. Found: C, 42.68; H, 3.06; N, 4.80; Cl, 20.03; Te, 20.87. Calcd. for C₂₁H₁₈N₂O₃Cl₂·Te · 0.5CHCl₃ (604.61): C, 42.71; H, 3.08; N, 4.63; Cl, 20.52; Te, 21.11. IR (cm⁻¹): 1623.5 ($\nu_{CH=N}$). ¹H NMR: δ 2.36 (s), 3.94 (s), 7.15–8.41 (m), 8.88 (s). ¹³C NMR: δ 21.56, 55.63, 115.75, 116.49, 118.75, 124.29,

130.11, 130.54, 133.86, 137.27, 144.22, 156.65, 162.38. ¹²⁵Te NMR: δ 886.2. ¹²⁵Te MAS NMR: δ_{iso} 882.4 (η : 0.45 ζ : 313; σ_{11} : -1110, σ_{22} : -969, σ_{33} : -570).

Compounds **2** and **3** were prepared similarly. For (4-methylphenyl)[{2-(4-nitrobenzylideneamino)-5-methyl}phenyl]tellurium dichloride, **2**, Yield: (63%); m.p. 230 °C. Anal. Found: C, 47.47; H, 3.21; N, 5.46; Cl, 13.07; Te, 25.07. Calcd. for C₂₁H₁₈N₂O₂Cl₂Te (528.89): C, 47.69; H, 3.43; N, 5.30; Cl, 13.41; Te, 24.12. IR (cm⁻¹): 1624.0 ($\nu_{CH=N}$). ¹H NMR: δ 2.38 (s), 2.56 (s), 7.42–8.40 (m), 8.88 (s). ¹³C NMR: δ 21.47, 76.58, 116.42, 124.21, 130.05, 130.63, 130.83, 133.78, 135.42, 140.44, 141.13, 142.49, 156.56. ¹²⁵Te NMR: δ 880.0. For (phenyl)[{2-(4-nitrobenzylideneamino)-5-methyl}phenyl]tellurium dichloride, **3**, Yield: (55%); m.p. 252 °C. Anal. Found: C, 45.88; H, 3.32; N, 5.18; Cl, 14.00; Te, 25.12. Calcd. for C₂₀H₁₆N₂O₂Cl₂Te (514.86): C, 46.65; H, 3.13; N, 5.44; Cl, 13.77; Te, 24.78. IR (cm⁻¹): 1621.5 ($\nu_{CH=N}$). ¹H NMR: δ 2.356 (s), 7.428–8.417 (m), 8.897 (s). ¹³C NMR: δ 21.62, 77.09, 116.58, 124.37, 129.97, 130.18, 130.58, 131.91, 134.00, 135.68, 140.51, 141.36, 156.75. ¹²⁵Te NMR: δ 881.1.

3.3. Synthesis of (4-methoxyphenyl)[{2-(4-nitrobenzylideneamino)-5-methyl}phenyl]tellurium dibromide (**1b**) and diiodide (**1c**)

A solution of **1a** (550 mg, 1.00 mmol) in chloroform (50 mL) was stirred with a twofold excess of KI for 12 h. A colour change from yellow to red occurred. The mixture was filtered and the solvents reduced to approximately one fifth in vacuo. Addition of petroleum ether 40–60 °C (10 mL) induced crystallization, providing red/brown crystals of **1c**. Yield (611 mg, 84%); m.p. 196 °C. Anal. Found: C, 34.88; H, 2.54; N, 4.03; I, 34.52; Te, 17.07. Calcd. for C₂₁H₁₈N₂O₃I₂Te (727.82): C, 34.66; H, 2.42; N, 3.84; I, 34.87; Te, 17.53. IR (cm⁻¹): 1615.5 ($\nu_{CH=N}$). ¹H NMR: δ 2.39 (s), 3.93 (s), 7.03–8.43 (m), 8.90 (s). ¹³C NMR: δ 21.56, 55.62, 115.83, 116.57, 124.29, 131.10, 130.13, 133.86, 138.73, 144.18, 156.46, 162.31. ¹²⁵Te NMR: δ 840.7.

1b was prepared similarly from **1a** and KBr. Yield: (82%); m.p. 180 °C. Anal. Found: C, 39.73; H, 2.64; N, 4.60; Br, 24.10; Te, 21.07. Calcd. for C₂₁H₁₈N₂O₃Br₂Te (633.79): C, 39.80; H, 2.86; N, 4.42; Br, 25.21; Te, 20.13. IR (cm⁻¹): 1620.5 ($\nu_{CH=N}$). ¹H: δ 2.355 (s), 3.935 (s), 7.154–8.407 (m), 8.881 (s). ¹³C NMR: δ 21.54, 55.59, 116.11, 116.77, 124.34, 130.18, 132.19, 133.71, 140.46, 144.12, 156.07, 162.15. ¹²⁵Te NMR: δ 777.1.

4. Crystallography

Single crystals of **1a** and **1c** suitable for X-ray crystallography were obtained by slow evaporation of

chloroform solutions. Intensity data were collected on a Bruker PS4 diffractometer with graphite-monochromated Mo K α (0.7107 Å) radiation. Data were reduced and corrected for absorption using the programs SAINT and SADABS [17]. The structures were solved by direct methods and difference Fourier synthesis using SHELXS-97 implemented in the program WINGX 2002 [18]. Full-matrix least-squares refinements on F^2 , using all data, were carried out with anisotropic displacement parameters applied to all non-hydrogen atoms. Hydrogen atoms were included in geometrically calculated positions using a riding model and were refined isotropically. Crystallographic parameters and details of the data collection and refinement are given in Table 1. Figures were created using DIAMOND [19].

5. Supplementary material

Crystallographic data for the structure analysis have been deposited with the Cambridge Crystallographic Data Center, CCDC No. for **1a** 246743 and for **1c** is 246745. Copies of this information may be obtained free of charge from the Director, CCDC, 12 Union Road, Cambridge CB2 1EZ, U.K. Fax: +44-1223-336-033; or E-mail: deposit@ccdc.cam.ac.uk or [www://www.ccdc.cam.ac.uk](http://www.ccdc.cam.ac.uk).

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