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Synthesis, characterization and X-ray structures of bis(arytelluro)ethynes

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Abstract

Bis(aryltelluro)ethynes ArTeC≡CTeAr (Ar = C_6H_5 (**1**), *p*-MeC_6H_4 (**2**), *p*-$Me_2NC_6H_4$ (**3**), *p*-FC_6H_4 (**4**), *p*-ClC_6H_4 (**5**), *p*-BrC_6H_4 (**6**), *p*-IC_6H_4 (**7**), *p*-PhC_6H_4 (**8**), *p*-$PhOC_6H_4$ (**9**), α-$C_{10}H_7$ (**10**), β-$C_{10}H_7$ (**11**)) were prepared in 42–97% yields, by reacting BrMgC≡CMgBr with two equivalents of the corresponding ArTeX formed in situ. These organotellurium compounds were characterized by ^1H- and ^{13}C-NMR and IR spectroscopies. The X-ray crystal structures of **1**, **2**, **3**, **7** and **9** were determined, and showed that the TeC≡CTe moieties are ca. linear, while the coordination at the Te atoms is angular. The ranges of some geometric parameters are: Te–C(sp^2), 2.103(5)–2.142(6) Å; Te–C(sp), 2.021(6)–2.058(6) Å; C≡C, 1.166(12)–1.203(11) Å; C–Te–C, 94.2(3)–97.2(2)°. © 2002 Elsevier Science B.V. All rights reserved.

Keywords: Organotellurium; Telluroethynes; Grignard; Crystal structures; Molecular structures

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1. Introduction

Work on organic chemistry of tellurium, which initially was pursued as an extension of selenium and sulfur chemistry, attained relevance on its own in the 1970s [1,2]. The last two decades have seen a rapid development of this area of chemistry, as attested by the number of books and reviews published on the subject [3]. The growing interest in organotellurium compounds has been prompted, in part, by their occurrence in biological [4] and environmental [5] systems; but the investigative efforts were mainly done in areas such as synthesis [6], electrochemistry [7,8], MOCVD and MOCPE [9] and medicinal chemistry [10].

Many efforts have been done in order to synthesize compounds with a Te atom bonded to an unsaturated system. Some 160 compounds containing the Te–C≡C–R unit have been described in about 100 papers [11]. On the other hand, only a few compounds with a bistelluroethyne core, R–Te–C≡C–Te–R′, have been reported, all of them symmetric (R = R′): three alkyl (R = Me, Et, *i*-Pr) [8,12] and two aryl (R = Ph, *p*-$MeOC_6H_4$) derivatives [13,14]. Three η^2-bonded W complexes of the ethyl derivative have been also characterized [15].

As a part of our synthetic and structural studies on the organic chemistry of tellurium [16], we have devoted some efforts to the synthesis and structural characterization of several new symmetric bis(aryltelluro)ethynes. Here we report the syntheses of 11 bis(aryltelluro)ethynes, ArTeC≡CTeAr, viz. Ar = C_6H_5 (**1**), *p*-MeC_6H_4 (**2**), *p*-$Me_2NC_6H_4$ (**3**), *p*-FC_6H_4 (**4**), *p*-ClC_6H_4 (**5**), *p*-BrC_6H_4 (**6**), *p*-IC_6H_4 (**7**), *p*-PhC_6H_4 (**8**), *p*-$PhOC_6H_4$ (**9**), α-$C_{10}H_7$ (**10**), β-$C_{10}H_7$ (**11**), and the X-ray crystal structures of five of them (**1**, **2**, **3**, **7** and **9**).

2. Experimental

2.1. Syntheses

2.1.1. General comments

All reactions were carried out under purified nitrogen using standard Schlenk techniques. Organic solvents

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were distilled on sodium–benzophenone, under nitrogen. A low boiling point fraction (distilled below 40 °C) of petroleum ether was used throughout. Tellurium powder (200 mesh, 99.8%) was dried overnight at 110 °C. Solutions 1.0 M of EtMgBr and of t-BuLi in THF were purchased from Aldrich Chemical Co. Merck silica gel G 60 (70–230 mesh) was used for column chromatography.

The ArTeTeAr precursors of all compounds, except **3** and **10**, were synthesized via the ArHgCl compounds [17], which were treated with $TeCl_4$ in dioxane to afford the $ArTeCl_3$ derivatives [18]. To obtain the trichloride derivative for **3**, $TeCl_4$ in CCl_4 was treated directly with anisol [19], and for **10**, $TeCl_4$ in $CHCl_3$ was treated directly with Ph–O–Ph [20]. All the $ArTeCl_3$ derivatives were reduced with $Na_2S \cdot 9H_2O$ to produce the ArTeTeAr [21] precursors. $TeCl_4$ was prepared from Te^0 and Cl_2(g) [18]. BrMgC≡CMgBr was prepared by bubbling dry acetylene through an EtMgBr solution 1.0 M in THF, at 50 °C [22].

To prepare the ArTeX intermediates, a solution of the corresponding ArTeTeAr (3–5 mmol) in THF (40–120 ml) was treated dropwise with Br_2 or I_2 (3–5 mmol) in benzene (10–50 ml), at 0 °C, under N_2 [23]. To this solution was added BrMgC≡CMgBr (3–5 mmol) suspended in THF (5–15 ml). Gradual disappearance of the dark red color of the ArTeX solution was observed, and the slurry turned light reddish as the addition was completed. After stirring (30–60 min) at room temperature (r.t.), the solution was diluted with petroleum ether (50 ml) and treated with aqueous NH_4Cl and saturated aqueous NaCl. The organic layer was dried either with anhydrous $MgSO_4$ or $CaCl_2$, and the solvent was evaporated.

2.1.2. Bis(phenyltelluro)ethyne (**1**)

From diphenylditelluride [24–26] (1.23 g, 3.0 mmol) and Br_2. A solid material with a characteristic odor was obtained and washed with petroleum ether until it remained a pale yellow solid (1.00 g, 2.3 mmol, 77%). The product was recrystallized in petroleum ether–CH_2Cl_2, m.p. 83–84 °C (84–86 °C [14]). Crystals suitable for X-ray diffraction were obtained from slow evaporation of a solution in ethyl acetate. Anal. Calc. for $C_{14}H_{10}Te_2$: C, 38.80; H, 2.33; Te, 58.88. Found: C, 39.14; H, 2.34; Te, 59.05%.^{13}C-NMR ($CDCl_3$): 134.9 (*C*–C–Te), 129.7 (*C*–C–C–Te), 127.9 (*C*–C–C–C–Te), 114.5 (C_{ar}–Te), 73.3 (*C*≡*C*). ^{1}H-NMR and IR data are given in [14].

2.1.3. Bis(p-methylphenyltelluro)ethyne (**2**)

From di-p-methylphenylditelluride [25,27] (2.19 g, 5.0 mmol) in benzene (80 ml) and I_2. The crude product was purified by column chromatography on silica gel G (120 g). Petroleum ether elution afforded the pure compound as a pale brown crystalline solid (1.59 g, 3.4 mmol, 69%), m.p. 106–108 °C. Crystals suitable for X-ray diffraction were obtained from vapor diffusion of chloroform into a solution in petroleum ether. Anal. Calc. for $C_{16}H_{14}Te_2$: C, 41.64; H, 3.06; Te, 55.30. Found: C, 41.55; H, 3.19; Te, 55.45%. ^{1}H-NMR ($CDCl_3$): 7.58 and 7.08 (AA′BB′ system, 8H, 2C_6H_4), 2.33 (s, 6H, 2CH_3). ^{13}C-NMR ($CDCl_3$): 138.1 (*C*–Me), 135.5 (*C*–C–Te), 130.6 (*C*–C–C–Te), 110.1 (C_{ar}–Te), 72.1 (*C*≡*C*), 21.1 (*C*H_3). IR (KBr, cm^{-1}): 1482, 1008, 797, 659.

2.1.4. Bis(p-dimethylaminophenytelluro)ethyne (**3**)

From di-p-dimethylaminophenylditelluride [25] (2.20 g, 5.0 mmol) and I_2. The crude product was extracted with petroleum ether; the residue was a light brown crystalline solid (2.17 g, 4.2 mmol, 84%), m.p. 104–107 °C. Crystals suitable for X-ray diffraction were obtained from slow evaporation of a solution in chloroform. Anal. Calc. for $C_{18}H_{20}N_2Te_2$: C, 41.61; H, 3.88; N, 5.39; Te, 49.12. Found: C, 41.59; H, 3.71; N, 5.15; Te, 49.19%. ^{1}H-NMR ($CDCl_3$): 7.60 and 6.53 (AA′BB′ system, 8H, 2C_6H_4), 2.89 (s, 12H, 4CH_3). ^{13}C-NMR ($CDCl_3$): 150.0 (*C*–N–Me_2), 139.4 (*C*–C–Te), 113.6 (*C*–C–C–Te), 99.3 (C_{ar}–Te), 67.9 (*C*≡*C*, 40.3 (*C*H_3). IR (KBr, cm^{-1}): 1583, 1496, 1340, 811, 647.

2.1.5. Bis(p-fluorophenyltelluro)ethyne (**4**)

From di-p-fluorophenylditelluride [24,25] (1.34 g, 3.0 mmol) and Br_2. The crude product was column-chromatographed on silica gel G (80 g). Elution with petroleum ether–CH_2Cl_2 (8/2) gave a white crystalline solid (1.05 g, 2.2 mmol, 75%), m.p. 105–106 °C. Anal. Calc. for $C_{14}H_8F_2Te_2$: C, 35.82; H, 1.72; Te, 54.37. Found: C, 35.90; H, 1.45; Te, 54.28%. ^{1}H-NMR ($CDCl_3$): 7.67 and 7.00 (AA′BB′ system, 8H, 2C_6H_4). ^{13}C-NMR ($CDCl_3$): 165.1 (*C*–F), 137.5 (*C*–C–Te), 117.4 (*C*–C–C–Te), 107.7 (C_{ar}–Te), 73.3 (*C*≡*C*). IR (KBr, cm^{-1}): 1575, 1482, 1223, 1158, 823, 658.

2.1.6. Bis(p-chlorophenyltelluro)ethyne (**5**)

From di-p-chlorophenylditelluride [24,25] (1.23 g, 2.6 mmol) and Br_2, at −5 °C. The crude product was extracted with petroleum ether until remained a crystalline white solid (0.74 g, 1.5 mmol, 57%), m.p. 154–156 °C. Anal. Calc. for $C_{14}H_8Cl_2Te_2$: C, 33.48; H, 1.61; Te, 50.80. Found: C, 33.17; H, 1.66; Te, 51.13%. ^{1}H-NMR ($CDCl_3$): 7.60 and 7.26 (AA′BB′ system, 8H, 2C_6H_4). ^{13}C-NMR ($CDCl_3$): 135.9 (*C*–C–Te), 134.2 (*C*–Cl), 126.9 (*C*–C–C–Te), 111.5 (C_{ar}–Te), 73.2 (*C*≡*C*). IR (KBr, cm^{-1}): 1467, 1085, 1005, 811, 660.

2.1.7. Bis(p-bromophenyltelluro)ethyne (**6**)

From di-p-bromophenylditelluride [24,25] (1.70 g, 3.0 mmol) and Br_2. The crude product obtained was extracted with petroleum ether until remained a crystalline light brown solid (0.74 g, 1.3 mmol, 42%), m.p. 162–164 °C. Anal. Calc. for $C_{14}H_8Br_2Te_2$: C, 28.44; H, 1.36; Te, 43.16. Found: C, 28.72; H, 1.28; Te, 43.00%. ^{1}H-NMR (Me_2SO-d_6): 6.94 and 6.74 (AA′BB′ system, 8H, $2C_6H_4$). ^{13}C-NMR ($CDCl_3$): 137.5 (*C*–Br), 135.0 (*C*–C–Te), 130.7 (*C*–C–C–Te), 113.2 (C_{ar}–Te), 77.2 ($C{\equiv}C$). IR (KBr, cm^{-1}): 1467, 1373, 1000, 806, 661.

2.1.8. Bis(p-iodophenyltelluro)ethyne (7)

From di-*p*-iodophenylditelluride [28] (1.98 g, 3.0 mmol) and Br_2. After addition of BrMgC≡CMgBr, the solution was stirred for 2 h. The crude product was extracted with petroleum ether until it remained a crystalline pale yellow solid (1.08 g, 1.6 mmol, 53%), m.p. 193–195 °C. Crystals suitable for X-ray diffraction were obtained from slow evaporation of a solution in acetone. Anal. Calc. for $C_{14}H_8I_2Te_2$: C, 24.54; H, 1.18; Te, 37.24. Found: C, 25.02; H, 1.10; Te, 37.16%. ^{1}H-NMR (Me_2SO-d_6): 8.11 and 7.55 (AA′BB′ system, 8H, $2C_6H_4$). ^{13}C-NMR ($CDCl_3$): 136.4 (*C*–C–Te), 136.3 (*C*–I), 123.2 (*C*–C–C–Te), 114.9 (C_{ar}–Te), 71.9 ($C{\equiv}C$). IR (KBr, cm^{-1}): 1462, 1369, 994, 800, 663.

2.1.9. Bis(p-biphenyltelluro)ethyne (**8**)

From di-*p*-biphenylditelluride [25,27] (1.69 g, 3.0 mmol) in THF (50 ml)–benzene (25 ml) and Br_2, at 50 °C. After 30 min the mixture turned to a transparent dark violet solution. The stirring was maintained for 30 min more and then was added BrMgC≡CMgBr, at 0 °C. The crude product was dissolved in CH_2Cl_2 and treated with petroleum ether. A pale yellow powder precipitated from the solution, was filtered off and dried (0.88 g, 1.5 mmol, 50%), m.p. 176–180 °C. Anal. Calc. for $C_{26}H_{18}Te_2$: C, 53.32; H, 3.10; Te, 43.58. Found: C, 52.89; H, 3.37; Te, 43.91%. ^{1}H-NMR ($CDCl_3$): 7.75–7.33 (m, 18H, H_{ar}). ^{13}C-NMR ($CDCl_3$): 141.8 and 140.2 (C_{ar}), 135.4, 128.8, 128.5, 127.6 and 127.0 (*C*–H), 113.2 (C_{ar}–Te), 73.2 ($C{\equiv}C$). IR (KBr, cm^{-1}) 1477, 1003, 825, 756, 695.

2.1.10. Bis(p-phenoxyphenyltelluro)ethyne (**9**)

From di-*p*-phenoxyphenylditelluride [27] (2.97 g, 5.0 mmol) and I_2. The crude product was dissolved in CH_2Cl_2 and treated with pentane. Pale yellow crystals precipitated from the solution and were filtered off and dried (2.20 g, 3.6 mmol, 71%), m.p. 176–179 °C. Crystals suitable for X-ray diffraction were obtained from slow evaporation of a solution in chloroform. Anal. Calc. for $C_{26}H_{18}O_2Te_2$: C, 50.56; H, 2.94; Te, 41.32. Found: C, 50.39; H, 3.09; Te, 41.20%. ^{1}H-NMR ($CDCl_3$): 7.64 and 6.89 (AA′BB′ system, 8H, $2C_6H_4$), 7.33–7.00 (m, 10H, $2C_6H_5$). ^{13}C-NMR ($CDCl_3$): 158.0 and 156.5 (C_{ar}–O), 137.4, 129.8, 127.7, 120.0 and 119.2 (*C*–H), 106.3 (C_{ar}–Te), 73.0 ($C{\equiv}C$). IR (KBr, cm^{-1}): 1573, 1481, 1240, 1168, 865, 838, 812, 798, 750, 691, 673.

2.1.11. Bis(α-naphthyltelluro)ethyne (**10**)

From di-α-naphthylditelluride [25,29] (0.54 g, 1.1 mmol) and Br_2. The crude product was extracted with petroleum ether and produced a light brown fine powder (0.57 g, 1.1 mmol, 97%), m.p. 128–130 °C. Anal. Calc. for $C_{22}H_{14}Te_2$: C, 49.53; H, 2.64; Te, 47.83. Found: C, 49.60; H, 2.71; Te, 47.78%. ^{1}H-NMR ($CDCl_3$): 7.22–6.50 (m, 14H, H_{ar}). ^{13}C-NMR ($CDCl_3$): 137.3, 134.8, 133.7, 130.9, 129.7, 129.1, 127.3, 127.0 and 126.7 (C_{ar}), 118.3 (C_{ar}–Te), 74.8 ($C{\equiv}C$). IR (KBr, cm^{-1}): 1497, 1251, 789, 767, 660.

2.1.12. Bis(β-naphthyltelluro)ethyne (**11**)

From di-*p*-naphthylditelluride [29] (1.53 g, 3.0 mmol) and Br_2. The crude product was extracted with petroleum ether giving a yellow powder (1.17 g, 2.2 mmol, 73%), m.p. 130–131 °C. Anal. Calc. for $C_{22}H_{14}Te_2$: C, 49.53; H, 2.64; Te, 47.83. Found: C, 49.18; H, 2.71; Te, 47.76%. ^{1}H-NMR (Me_2SO-d_6): 8.28 (s, 2H, *H*C1), 7.84–7.40 (m, 12H, H_{ar}). ^{13}C-NMR (Me_2SO-d_6): 134.4, 133.8, 132.1, 132.0, 128.5, 127.7, 127.0, 126.5 and 126.4 (C_{ar}), 114.1 (C_{ar}–Te), 74.2 ($C{\equiv}C$), IR (KBr, cm^{-1}): 1579, 1496, 857, 819, 751, 656.

2.2. Physical measurements

Melting points were determined on an electrically heated hot stage (Koffler type, Reichert Thermovar) and were not corrected. ^{1}H- and ^{13}C-NMR spectra were recorded using a Bruker AC-F200 instrument, except for **11**, which was measured with a Bruker AM-400 spectrometer. All NMR spectra were recorded for ca. 10% solutions in $CDCl_3$ containing 0.01% Me_4Si as an internal standard, except for ^{1}H of **6**, **7** and **11**, and for ^{13}C of **11**, which were recorded in Me_2SO plus Me_4Si. IR spectra were recorded using a Nicolet Magna IR 560 spectrometer in KBr disks.

2.3. X-ray structure determinations

Unit cell and intensity measurements were carried out on an Enraf–Nonius CAD-4 diffractometer, using graphite-monochromated Mo–K_{α} radiation ($\lambda = 0.71069$ Å). Crystal data, intensity data collection parameters (only those which vary from compound to compound) and final refinement results are summarized in Table 1.

Unit-cell parameters were obtained from least-squares fit of the setting angles of automatically centered reflections. Intensity data were recorded using an $\omega-2\theta$ scan mode with ω scan width $0.80+0.35\tan\theta$ and variable ω speed (1.3–5.5° min^{-1}). The check reflections were monitored either every 1 h (**2**, **9**) or 2 h (**1**, **3**, **7**) of exposure. The data were scaled using the check reflections and corrected by Lp effects. Empirical absorption corrections were applied, based on 36 psi

Table 1
Crystal data, intensity data collection parameters and final refinement results

	1	**2**	**3**	**7**	**9**
(a) *Crystal data*					
Formula	$C_{14}H_{10}Te_2$	$C_{16}H_{14}Te_2$	$C_{18}H_{20}N_2Te_2$	$C_{14}H_8I_2Te_2$	$C_{26}H_{18}O_2Te_2$
Molecular weight	433.42	461.48	519.56	685.20	617.60
Color	Pale yellow	Pale brown	Pale brown	Pale yellow	Pale yellow
Morphology	Plate	Elong. prism	Plate	Prism	Prism
Specimen size (mm)	0.38 × 0.22 × 0.07	0.52 × 0.11 × 0.05	0.47 × 0.33 × 0.08	0.52 × 0.18 × 0.07	0.41 × 0.17 × 0.12
T (K)	295(2)	295(2)	295(2)	295(2)	295(2)
a (Å)	8.224(1)	6.067(6)	21.534(3)	6.151(1)	5.767(2)
b (Å)	7.699(1)	15.532(3)	7.9128(7)	15.520(1)	12.192(1)
c (Å)	21.423(3)	16.087(7)	16.297(1)	16.976(1)	15.949(1)
β (°)	99.86(1)		137.76(1)		91.85(2)
V (Å^3)	1336.4(6)	1515.9(17)	1866.7(3)	1620.6(3)	1120.8(4)
Crystal system	Monoclinic	Orthorhombic	Monoclinic	Orthorhombic	Monoclinic
Space group (No.)	$P2_1/c$ (14)	$Pbaa$ (54)	$C2/c$ (15)	$Pbaa$ (54)	Pc (7)
Z	4	4	4	4	2
D_{calc} (g cm^{-3})	2.154	2.022	1.849	2.808	1.830
F(000)	792	856	984	1208	588
μ(Mo–K$_\alpha$) (cm^{-1})	4.336	3.829	3.124	7.391	2.622
2θ Range (°) for cell	9.9–14.0	11.5–14.1	10.1–14.0	9.8–13.8	11.8–14.0
Number of reflections for cell	25	23	25	25	25
(b) *Data collection*					
2θ Range (°)	1.9–25.0	2.53–24.95	2.5–25.0	1.2–25.0	1.7–25.0
h range	−9, 9	−7, 7	−25, 17	0, 7	−6, 6
k range	0, 9	0, 18	0, 9	0, 18	0, 14
l range	0, 25	0, 19	0, 19	0, 20	0, 18
Mean ΔI for checks (%)	< 1	< 1	< 1	2.7	< 1
Number of reflections measured	2348	2465	1701	1431	1961
Number of reflections unique	2348	1335	1644	1431	1961
R_{int}		0.0516	0.0089		
(c) *Refinement (last cycle)*					
Weighting scheme (a, b)	0.0514, 0.0	0.1112, 0.0	0.0600, 0.0	0.0393, 2.9382	0.0293, 0.0118
Transmission coefficient (T_{max}, T_{min})	0.738, 0.330	0.826, 0.483	0.779, 0.302	0.596, 0.315	0.730, 0.615
Number of reflections observed [$I > 2\sigma(I)$]	1436	954	1235	1061	1876
Number of parameters refined	145	83	102	82	271
$R[I > 2\sigma(I)]$	0.0321	0.0638	0.0367	0.0288	0.0171
$R_w[I > 2\sigma(I)]$	0.0797	0.1467	0.1009	0.0765	0.0441
S (goodness-of-fit)	1.143	1.153	1.250	1.176	1.069
Δ/σ max.	0.002	0.005	0.001	0.001	0.001
Δ/σ mean	0.0001	0.0005	0.0001	0.0001	0.0001
$\Delta\rho_r$ (min., max.) (e Å^{-3})	−0.94, 0.80	−1.75, 2.90	−0.46, 1.13	−0.67, 0.58	−0.29, 0.28

scan measurements [30] for each of nine representative strong reflections.

The space groups of **1**, **2** and **7** were uniquely determined by the systematic absences. For **3**, the systematic absences were consistent with space groups Cc (No. 9) and $C2/c$ (No. 15); the latter space group was initially assumed, and this selection was confirmed by refinement. For **9**, the systematic absences were consistent with Pc (No. 7) and $P2/c$ (No. 13); the former was chosen on the basis of intensity statistics and the value of Z, and confirmed by refinement. The structures were solved by direct methods [31] and refined on F^2 by full-matrix least-squares [32] using all reflections with $I > 0$, anisotropic displacement parameters and weights $w = [\sigma^2(F_0^2) + (aP)^2 + bP]^{-1}$, with $P = (F_0^2 + 2F_c^2)/3$. The hydrogen atoms were placed in calculated positions using a riding atom model with fixed C–H distances [0.93 Å for C(sp^2), 0.96 Å for C(sp^3)] and $U_{iso} = pU_{eq}$(parent atom) [$p = 1.2$ for C(sp^2), 1.5 for C(sp^3)]. A single orientation parameter was refined for each methyl group. The final difference Fourier syntheses were featureless. The large residual electronic density observed in **2** can be attributed to a poor absorption correction, due to the unfavorable specimen morphology; the four largest peaks (2.90–1.49 e Å^{-3}) were within 1.0 Å of the Te atom; the fifth largest peak was 0.58 e Å^{-3} high.

The CAD-4 software [33] was used for cell refinement and data collection, while the CRYSTAN program [34] was used for data reduction. Geometrical calculations were carried out with the PARST-95 program [35], and the drawings were made using the ZORTEP program [36]. Complex neutral-atom scattering factors and mass absorption coefficients were taken from reference [37].

3. Results and discussion

In this work a general route to bis(aryltelluro)ethynes, employing electrophilic tellurium species, was used. In spite of the instability of aryltellurenyl halides, ArTeX, in the solid state [38] (though a tetramer, $Ph_4Te_4I_4$ has been recently structurally characterized, [39]), they are stable in solution and react in this form with Grignard reagents, giving mixed tellurides [23]. In the present study we exploited this reaction as a general method for preparing the title compounds, starting from ethynyliden dimagnesium bromide, BrMgC≡CMgBr. This synthetic pathway was previously used by us to prepare the *p*-methoxyphenyl derivative [13].

The bis(aryltelluro)ethynes were synthesized in good yields (42–97%) by the reaction of two equivalents of the corresponding aryltellurenyl halides with the Grignard reagent, in THF solution, under N_2. The aryltellurenyl halides were formed in situ by the addition of Br_2 to a solution of the bisarylditellurides, ArTeTeAr [13,23,40].

$$\mathrm{ArTeTeAr}\xrightarrow[\mathrm{THF,\ N_2\ atm.,\ 0\ ^\circ C}]{X_2} 2\,[\mathrm{ArTeX}]$$

$$\xrightarrow[\mathrm{THF,\ N_2\ atm.,\ 0\ ^\circ C}]{\mathrm{BrMgC{\equiv}CMgBr}} \mathrm{ArTeC{\equiv}CTeAr} + 2\,\mathrm{MgX_2}$$

Ar = C_6H_5 (**1**), p-MeC_6H_4 (**2**), p-$Me_2NC_6H_4$ (**3**), p-FC_6H_4 (**4**), p-ClC_6H_4 (**5**), p-BrC_6H_4 (**6**), p-IC_6H_4 (**7**), p-PhC_6H_4 (**8**), p-$PhOC_6H_4$ (**9**), α-$C_{10}H_7$ (**10**), β-$C_{10}H_7$ (**11**); X = Br or I.

In addition to the title compounds, aryl ethyl tellurides (**A**), aryl ethynyl tellurides (**B**), diaryl tellurides (**C**), diethyl tellurides (**D**) and aryl ethyl tellurium dihalides (**E**) were isolated as major by-products [23].

$$[\mathrm{ArTeBr}] + \mathrm{EtMgBr} \rightarrow \underset{\mathbf{A}}{\mathrm{ArTeEt}} + \mathrm{MgBr_2}$$

$$[\mathrm{ArTeBr}] + \mathrm{BrMgC{\equiv}CH} \rightarrow \underset{\mathbf{B}}{\mathrm{ArTeC{\equiv}CH}} + \mathrm{MgBr_2}$$

$$2\mathrm{ArTeEt} \rightarrow \underset{\mathbf{C}}{\mathrm{ArTeAr}} + \underset{\mathbf{D}}{\mathrm{EtTeEt}}$$

$$\mathrm{ArTeEt} + \mathrm{Br_2} \rightarrow \underset{\mathbf{E}}{\mathrm{ArTe(Br)_2Et}}$$

The structure analyses of **1**, **2**, **3**, **7** and **9** showed that all five crystals consist of discrete molecules of the respective bis(aryltelluro)ethynes. Compounds **2** and **7** are isostructural. In these two crystal structures the middle points of the triple bonds lay on two-fold axes (Wyckoff site c) and, therefore, the molecules have crystallographic C_2 point symmetry and only half of each molecule is crystallographically independent. The same arrangement exists in **3** (in this case the triple bond's center is on a Wyckoff site e).

All the compounds display the same basic geometry (Figs. 1–5), in which the Te–C≡C–Te moieties have an approximate linear arrangement, while the coordination at the Te atoms is angular, as predicted by the valence-shell electron-pair repulsion (VSEPR) model for an AX_2E_2 molecule [41]. The deviations of the Te and C(sp) atoms from the corresponding least-squares lines are small [range: 0.0093(6)–0.067(7) Å]. The C–Te–C angles [range: 94.2(3)–97.2(2)°] are substantially smaller than the tetrahedral value (109.5°), due to the repulsion of the lone pairs of electrons on the bonded ones. Their values are comparable to 93.4(2)°, observed in $[(p\text{-}MeOC_6H_4)Te]_2C_2$ [13], and with those observed in diaryltellurides, e.g. 94.8(2)° in $(p\text{-}EtOC_6H4)Te(o\text{-}C_6H_4(o\text{-}C_5NH_4))$ [42], 96.3(2)° in $[o\text{-}(p\text{-}MeOC_6H_4N{:}C)C_6H_4]_2Te$ [43], 96.2(2)° in $(o\text{-}PhC_6H_4)_2Te$ [44] and 99.5(1)° in $(p\text{-}MeOC_6H_4)_2Te$ [45].

As expected, the Te–C(sp^2) distances [range: 2.103(5)–2.142(6) Å] are significantly longer than the Te–C(sp) bond lengths [range: 2.021(6)–2.058(6) Å]. These values can be compared with 2.109(6) and 2.037(5) Å, respectively, found in $[(p\text{-}MeOC_6H_4)Te]_2C_2$ [13]. The Te–C(sp^2) distances are similar to 2.116(20) Å, tabulated by Allen et al. [46], and to those found in diaryltellurides, e.g. 2.105(5) and 2.125(5) Å in $(o\text{-}PhC_6H_4)_2Te$ [44], 2.110(3) and 2.112(3) Å in $(p\text{-}MeOC_6H_4)_2Te$ [45], 2.128(4) and 2.162(4) Å in $[o\text{-}(p\text{-}MeOC_6H_4N{:}C)C_6H_4]Te$ [43], 2.138(6) and 2.144(6) Å in $(p\text{-}EtOC_6H_4)Te(o\text{-}C_6H_4(o\text{-}C_5NH_4))$ [42]. The Te–C(sp) distances are analogous to those observed in various transition-metal η^2-bonded alkyl- and aryltelluroethynes [range: 2.01(1)–2.075(8) Å] [15,47].

The C≡C bond lengths [range: 1.166(12)–1.203(11) Å] can be compared with 1.183(14) Å, given by Allen et al. [46] for a general carbon–carbon triple bond, and with 1.196(4) Å in $(C_4H_9)TeCl_2(C_8H_5)$ [48], and are slightly shorter than 1.210(11) Å observed in $[(p\text{-}MeOC_6H_4)Te]_2C_2$ [13].

In all five compounds the Te atoms are ca. coplanar with the bonded phenyl rings [maximum deviation from the mean plane: 0.1503(4) Å].

The C(sp^2)–Te···Te–C(sp^2) torsion angles vary widely, and represent the only important difference between the solid-state molecular geometries of these compounds. This variability is associated with the unhindered rotation about the Te–C(sp) bonds, so that the molecular conformations about the Te–C≡C–Te axis are dictated by the packing forces.

Although Te(IV) compounds, especially Te(IV) halides, are well known for their tendency to form secondary bonds [16,49], this phenomenon is not as

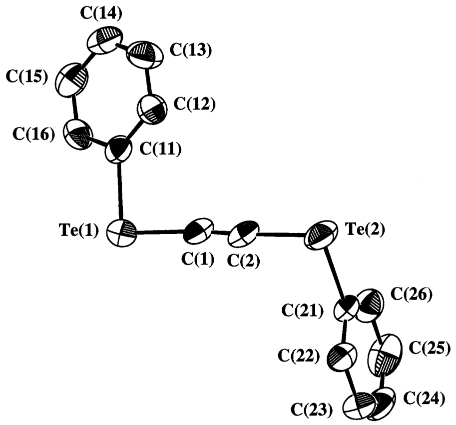

Fig. 1. Molecular structure of **1** showing the atomic labeling scheme. The displacement ellipsoids are drawn at 50% level.

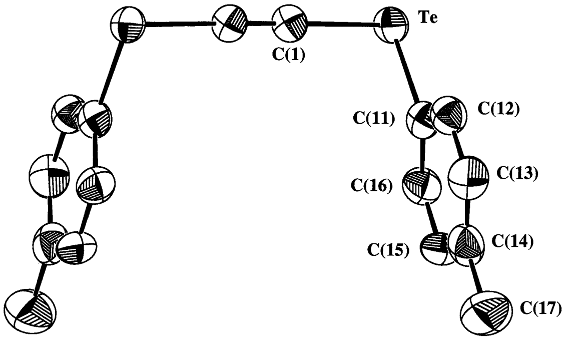

Fig. 2. Molecular structure of **2** showing the atomic labeling scheme. The displacement ellipsoids are drawn at 50% level.

near as frequent in Te(II) compounds. Accordingly, in the crystal structures of **1**, **2**, **3**, **7** and **9** the packing is mainly due to van der Waals interactions, and those non-bonded contacts shorter than the sum of the van der Waals radii (Te: 2.06 Å, N: 1.55 Å) [50] (see Table 2) are only marginally so. In **2** and **7** (which are isostructural) the shortest Te···Te contacts lay on lines bisecting the C(1)–Te(1)–C(11) angles, but there is not a definite coordination pattern. The structure of **9** displays a Te(1)···Te(2) contact in which Te(1) is coplanar with the C(2)–Te(2)–C(21) group [*trans* to C(21)], so that Te(2) displays a T-shaped coordination [51]. This secondary bond is perpendicular to the C(1)–Te(1)–C(11) plane. In the structure of **3** the Te atom is also T-coordinated, because of a Te(1)···N(1) interaction in which N(1) is coplanar with the C(1)–Te(1)–C(11) moiety [*trans* to C(1)]. This non-bonded interaction is perpendicular to the C(14)N(1)C(17)C(18) group, and the nitrogen atom exhibits some degree of pyramidalization [N(1) is 0.199(5) Å out of the plane of the C atoms, towards the Te(1) atom].

Table 2
Selected geometric parameters (Å, °)

	1	**2** ^{a}	**3** ^{b}	**7** ^{a}	**9**
(a) *Bond distances*					
Te(1)–C(1)	2.025(6)	2.031(8)	2.058(6)	2.021(6)	2.022(6)
Te(2)–C(2)	2.043(6)				2.035(6)
Te(1)–C(11)	2.110(5)	2.116(9)	2.103(5)	2.142(6)	2.110(5)
Te(2)–C(21)	2.128(5)				2.136(5)
C(1)≡C(2)	1.188(7)	1.19(2)	1.166(12)	1.203(11)	1.192(7)
(b) *Bond angles*					
C(1)–Te(1)–C(11)	97.2(2)	94.2(3)	96.5(2)	94.6(2)	95.5(2)
C(2)–Te(2)–C(21)	95.3(2)				94.3(2)
Te(1)–C(1)≡C(2)	175.1(5)	179.1(6)	175.1(8)	178.0(8)	175.1(4)
Te(2)–C(2)≡C(1)	177.2(5)				178.6(5)
(c) *Torsion angles*					
C(11)–Te(1)···Te(2)–C(21)	−132.8(2)	−68.5(3)	93.7(3)	−67.0(2)	96.7(2)
(d) *Non-bonded contacts*					
Te(1)···Te(1)^{iii}	3.916(1)				3.9162(5)
Te(1)···Te(1)^{iv}	4.062(3)				4.0877(7)
Te(2)···Te(1)^{v}		3.8360(7)			
C(2)–Te(2)···Te(1)^{v}		77.02(12)			
C(21)–Te(2)···Te(1)^{v}		171.29(9)			
Te(1)···N(1)^{vi}					3.301(8)
C(1)–Te(1)···N(1)^{vi}					173.8(2)
C(11)–Te(1)···N(1)^{vi}					78.4(2)

Symmetry codes: (i) $-x+2, -y+1, z$; (ii) $-x+1, y, -z+2$; (iii) $x, -y+2, -z+1$; (iv) $x-2, y, -z+1$; (v) $x-1, y, z$; (vi) $-x+2, y+2, -z+2$.

[a] In compounds **2** and **7** is: Te(2) = Te(1)^{i}, C(2) = C(1)^{vi}, C(21) = C(11)^{ii}.

[b] In compound **3** is: Te(2) = Te(1)^{ii}, C(2) = C(1)^{ii}, C(21) = C(11)^{ii}.

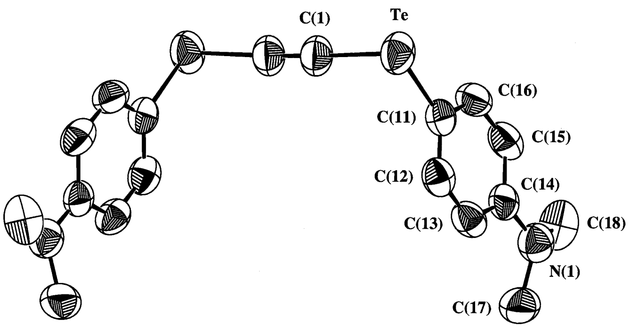

Fig. 3. Molecular structure of **3** showing the atomic labeling scheme. The displacement ellipsoids are drawn at 50% level.

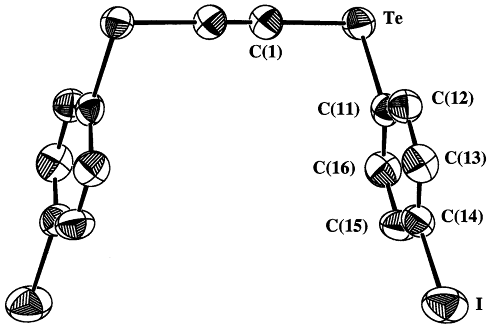

Fig. 4. Molecular structure of **7** showing the atomic labeling scheme. The displacement ellipsoids are drawn at 50% level. The displacement ellipsoids are drawn at 50% level.

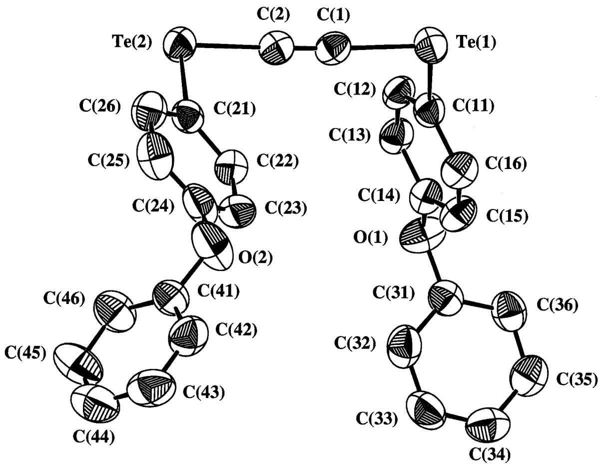

Fig. 5. Molecular structure of **9** showing the atomic labeling scheme. The displacement ellipsoids are drawn at 50% level.

4. Supplementary material

Crystallographic data for the structural analyses have been deposited with the Cambridge Crystallographic Data Centre; CCDC No. 178884 for **1**, CCDC No. 178885 for **2**, CCDC No. 178886 for **3**, CCDC No. 178887 for **7** and CCDC No. 178888 for **9**. The relevant geometric parameters of the molecules are given in Table 2, and the structures are shown in Figs. 1–5.

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