

The crystal and molecular structures of 2-(2-pyridyl)phenyltellurium(II) chloride and of two modifications of 2-(2-pyridyl)phenyltellurium(II) iodide; chemical investigations of organotellurium iodides

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Abstract

The structures of the title compounds were determined. The structure of 2-(2-pyridyl)phenyltellurium(II) chloride (**1**) is triclinic and consists of discrete molecules with average bonding distances over six independent molecules Te–Cl 2.606(11), Te–C 2.077(7) Å and a short Te···N interaction distance of 2.205(11) Å. The structure of the molecule in the 'pure' compound is compared with that previously reported in which it forms a 2:1 inclusion compound with *p*-ethoxyphenylmercury(II) chloride. One form of the related iodide (**2**) is triclinic and isomorphous with the above chloride; selected bond distances are Te–I 2.937(1), Te–C 2.095(18) and Te–N 2.260(10) Å. A second form of the iodide (**3**) is monoclinic (*Z* = 4) and yields more accurate parameters: Te–I 2.917(11), Te–C 2.112(6), Te–N 2.268(5) Å. The syntheses of the new organytellurium(II) iodides are given together with those of 'RTeI₃', where R = 2-(2-pyridyl)phenyl- or 2-phenylazophenyl-; it is suggested on the basis of spectroscopic examination (NMR and Raman) that the oxidation state of tellurium in these 'triiodide' species is (II).

Keywords: Tellurium; Halide; X-ray diffraction

1. Introduction

In an earlier paper [1] we described the migration of an organic group from tellurium to mercury via the formation of an intermediate co-ordination compound between an organotellurium compound and HgCl₂. The overall stoichiometry of the process was



where R = 2-(2-pyridyl)phenyl- and R' = *p*-ethoxyphenyl-. The crystal and molecular structure of the 'inclusion' compound (RTeCl)₂R'HgCl was determined [2]; the unit cell was shown to contain molecules of the organomercury sandwiched between two molecules of the organotellurium compound. However, no intermolecular contacts were observed, all intermolecular atomic distances being close to, or greater than, the van

der Waals distances. The structure of 2-(2-pyridyl)phenyltellurium(II) bromide was also determined [2] and, again, no significant intermolecular contacts were observed between the six independent molecules in the unit cell.

Previously, there had been a preference to work with the bromides of the 2-(2-pyridyl)phenyl- series, largely due to a greater ease of initial synthesis, but recently a need to prepare 2-(2-pyridyl)phenyltellurium(II) chloride as a synthetic intermediate for the synthesis of the monoiodides arose, and the opportunity to determine the crystal and molecular structure was taken. There are two points of interest: first, to determine if any intramolecular dimensions might differ between the pure compound and the molecule in the inclusion compound above; secondly, to investigate the presence or absence of any intermolecular contacts in the solid state. The paper also includes a comparative crystallographic study of the monoiodides, RTeI, as well as an investigation of the nature of the related triiodides, RTeI₃.

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2. Experimental and results

2-(2-pyridyl)phenyltellurium(II) chloride (**1**) was prepared using standard methods [3], thus 2-(pyridyl)phenylmercury(II) chloride, RHgCl , underwent trans-metalation with tellurium(IV) chloride to give impure RTeCl_3 which was reduced with hydrazine hydrate to give RTeCl . The monochloride was crystallised from ethanol, m.p. 128–130°C. Anal. Found: C, 40.8; H, 2.60; N, 4.35. $\text{C}_{11}\text{H}_8\text{ClNTe}$ requires C, 41.7; H, 2.55; N, 4.42%. A single crystal was selected for X-ray crystallographic studies.

2.1. 2-(2-Pyridyl)phenyltellurium(II) iodide

Sodium iodide (1.5 g, 10 mmol) in acetone (40 cm^3) was poured into a solution of 2-(2-pyridyl)phenyltellurium(II) chloride (1.64 g, 5 mmol) in acetone (100 cm^3). The solution was stirred at room temperature for 40 min over which period the colour changed from yellow to a cloudy orange. On setting aside for 40 min the cloudy solution cleared with the precipitation of NaCl. The solution was filtered, acetone was removed (rotatory evaporator), and the orange residue taken up in dichloromethane. Removal of dichloromethane and subsequent recrystallisation from acetonitrile–methanol (1:1) gave the triclinic form (**2**), m.p. 162–164°C. An exactly similar method starting with 2-phenylazophenyl(*C',N*)tellurium(II) chloride [4] was used to prepare the corresponding monoiodide which was recrystallised from dichloromethane in 87% overall yield to m.p. 150–152°C.

2.2. 2-(2-Pyridyl)phenyltellurium(II) triiodide and 2-phenylazophenyl(*C',N*)tellurium(II) triiodide

Excess sodium iodide (e.g. 4.5 g, 30 mmol) in acetone (40 cm^3) was poured into a solution of 2-(2-pyridyl)phenyltellurium(IV) tribromide (or 2-phenylazophenyl(*C',N*)tellurium(IV) trichloride) (5 mmol) in acetone (100 cm^3). The solution was treated as above for the monoiodide preparation when, following removal of NaCl and of acetone a purple solid remained (red for the 2-phenylazophenyl-compound). In both cases the materials were purified by reprecipitation from

dichloromethane: $\text{C}_{11}\text{H}_8\text{I}_3\text{NTe}$, m.p. greater than 230°C (87% yield), $\text{C}_{12}\text{H}_9\text{I}_3\text{N}_2\text{Te}$, m.p. 102–105°C (yield 88%). Attempts to grow crystals for crystallography always gave the monoiodide; in the case of the 2-(2-pyridyl)phenyl-compound, recrystallisation of the material from acetonitrile–methanol (1:1) gave the monoclinic form of the monoiodide (**3**), m.p. 192–194°C. Analytical data for the new compounds are in Table 1.

2.3. Physical measurements

Infrared spectra were obtained for KBr discs with a BIO-Rad, FTS-40A FTIR spectrometer. Raman data were obtained on a Perkin–Elmer FT-Raman 1700X spectrometer using a Nd–YAG laser (1064 nm) and an InGaAs NIR detector cooled to 77 K. Spectra were obtained from solids as powders pressed into a cup sample holder. Proton (3000.133), ^{13}C (75.469), ^{125}Te (78.580) MHz NMR spectra were obtained with a Bruker AC 300 spectrometer at the indicated frequencies; references used were TMS (^1H , ^{13}C) and Me_2Te (^{125}Te). Proton and ^{13}C NMR data were used for characterisation purposes; the data were unremarkable and are not presented in this paper. Mass spectra of R'TeI_3 and of R'TeI (electron impact) were provided by Dr. Peter Ashton (University of Birmingham) (n.b. $\text{R}' = \text{C}_{12}\text{H}_9\text{N}_2-$).

2.4. Crystallographic analysis

Cell dimensions and intensity data were measured from crystals mounted on a Rigaku R-Axis II area detector diffractometer using $\text{Mo K}\alpha$ radiation.

$\text{C}_{11}\text{H}_8\text{ClNTe}$ (**1**), crystal size $0.4 \times 0.3 \times 0.2 \text{ mm}^3$, θ_{max} 27.5°; 5825 unique reflections with $I > \sigma(I)$ were measured of which 3540 were considered observed ($I > 3.5\sigma(I)$).

$\text{C}_{11}\text{H}_8\text{INTe}$ (**2**) (triclinic), crystal size $0.2 \times 0.2 \times 0.15 \text{ mm}^3$, θ_{max} 25°; 8662 unique reflections with $I > \sigma(I)$ were measured, of which 7064 were considered observed ($I > 3.5\sigma(I)$).

$\text{C}_{11}\text{H}_8\text{INTe}$ (**3**) (monoclinic), crystal size $0.15 \times 0.08 \times 0.05 \text{ mm}^3$, θ_{max} 25°; 1977 unique reflections were measured ($I > \sigma(I)$) and were used in the analysis.

Table 1
Analytical data for compounds considered

Compound	Colour	Found (%)			Calculated (%)		
RTeI (triclinic)	Orange	30.7	2.10	3.25	32.3	1.95	3.40
RTeI (monoclinic)	Orange	31.9	2.00	3.31	32.3	1.95	3.40
RTeI_3	Dark-purple	24.5	1.80	2.20	19.9	1.20	2.10
R'TeI	Dark-red	33.4	2.25	6.25	33.1	2.10	6.45
R'TeI_3	Dark-purple	22.3	1.55	4.15	20.9	1.30	4.10

$\text{R} = \text{C}_{11}\text{H}_8\text{N}-$; $\text{R}' = \text{C}_{12}\text{H}_9\text{N}_2-$.

Table 2
Atomic coordinates ($\times 10^4$) and isotropic displacement parameters ($\text{\AA}^2 \times 10^3$) for $\text{C}_{11}\text{H}_8\text{ClNTe}$

	x	y	z	U/U_{eq}^a
Te(A)	-2(2)	29(2)	-50(2)	77(1)
Te(B)	-2307(2)	-2215(1)	-2458(2)	72(1)
Te(C)	1132(2)	-3519(2)	-1169(2)	79(1)
Te(D)	-1312(2)	-5633(1)	-3760(2)	75(1)
Te(E)	-4389(2)	-4327(2)	-5397(2)	79(1) ^b
Te(E')	-6811(36)	-1357(27)	-8403(38)	60(9) ^c
Te(F)	3030(2)	859(2)	1514(2)	78(1) ^b
Te(F')	5829(42)	3550(32)	4859(44)	73(9) ^c
Cl(A)	127(8)	562(8)	2391(8)	88(2)
Cl(B)	-2454(10)	-2038(7)	-158(8)	95(3)
Cl(C)	1378(12)	-3773(8)	-3445(9)	107(4)
Cl(D)	-1377(8)	-5890(6)	-6215(7)	78(2)
Cl(E)	-4376(9)	-4512(7)	-3085(8)	91(3)
Cl(F)	3330(8)	-538(6)	-435(8)	81(2)
N(1A)	-294(25)	-87(20)	-2138(27)	74(7)
C(1A)	-1296(35)	1279(27)	-631(37)	88(10)
C(2A)	-1861(30)	1977(23)	222(33)	75(8)
C(3A)	-2742(37)	2796(30)	-223(40)	98(11)
C(4A)	-3069(42)	2871(34)	-1565(44)	108(12)
C(5A)	-2573(35)	2161(26)	-2358(38)	88(10)
C(6A)	-1658(28)	1346(22)	-1901(30)	67(7)
C(7A)	-1149(31)	590(23)	-2764(32)	75(8)
C(8A)	-1305(37)	598(30)	-4051(38)	94(10)
C(9A)	-716(32)	-212(25)	-4779(35)	80(9)
C(10A)	105(38)	-208(30)	-4136(40)	99(11)
C(11A)	345(35)	-866(28)	-2786(37)	89(10)
N(1B)	-2429(26)	-2129(21)	-4460(28)	76(7)
C(1B)	-3535(28)	-873(22)	-2861(29)	64(7)
C(2B)	-4023(33)	-229(26)	-1961(36)	84(9)
C(3B)	-4875(33)	665(26)	-2310(36)	85(9)
C(4B)	-5183(40)	892(32)	-3549(42)	101(11)
C(5B)	-4638(39)	251(30)	-4474(42)	99(11)
C(6B)	-3801(31)	-678(23)	-4122(31)	73(8)
C(7B)	-3258(26)	-1356(20)	-5063(27)	59(6)
C(8B)	-3443(35)	-1258(28)	-6311(35)	87(10)
C(9B)	-2880(46)	-1994(36)	-7003(52)	119(14)
C(10B)	-2028(39)	-2783(32)	-6543(35)	103(12)
C(11B)	-1794(36)	-2833(27)	-5284(32)	87(10)
N(1C)	1239(29)	-353(22)	826(31)	86(8)
C(1C)	2322(30)	-4831(23)	-724(31)	72(8)
C(2C)	2918(31)	-5548(25)	-1551(36)	82(9)
C(3C)	3681(38)	-6427(30)	-1123(42)	98(11)
C(4C)	3957(39)	-6633(31)	143(40)	106(12)
C(5C)	3413(35)	-5973(28)	936(38)	93(11)
C(6C)	2602(32)	-5073(25)	549(34)	78(9)
C(7C)	2013(34)	-4360(26)	1407(32)	81(9)
C(8C)	2194(45)	-4520(35)	2712(37)	112(13)
C(9C)	1532(45)	-3671(36)	3338(53)	128(16)
C(10C)	723(46)	-2903(37)	2831(52)	133(16)
C(11C)	630(34)	-2798(26)	1526(34)	82(9)
N(1D)	-864(32)	-5645(25)	-1677(33)	93(9)
C(1D)	-15(28)	-6941(22)	-3414(30)	67(7)
C(2D)	457(31)	-7610(23)	-4356(33)	75(8)
C(3D)	1310(30)	-8409(24)	-3933(33)	77(8)
C(4D)	1734(34)	-8628(27)	-2744(36)	88(9)
C(5D)	1330(32)	-7990(25)	-1803(35)	79(8)
C(6D)	416(29)	-7128(22)	-2119(30)	69(8)
C(7D)	-84(28)	-6444(22)	-1170(30)	66(7)
C(8D)	286(31)	-6536(24)	145(31)	75(8)
C(9D)	-249(36)	-5765(28)	950(40)	91(10)
C(10D)	-1063(34)	-5009(27)	435(32)	85(9)
C(11D)	-1400(35)	-4918(28)	-832(32)	89(10)

2.5. Crystal data

(1), $M_r = 317.2$, triclinic, space group $P1$, $a = 12.024(5)$, $b = 13.366(5)$, $c = 11.111(5)$ Å, $\alpha = 102.87(3)$, $\beta = 109.83(3)$, $\gamma = 77.46(3)^\circ$, $U = 1618$ Å³, $Z = 6$, $D_c = 1.953$ g cm⁻³, $\mu(\text{Mo K}\alpha) = 2.96$ mm⁻¹.

(2), $M_r = 408.7$, triclinic, space group $P1$, $a = 12.227(2)$, $b = 13.395(2)$, $c = 11.628(2)$ Å, $\alpha = 103.34(1)$, $\beta = 108.13(2)$, $\gamma = 78.42(1)^\circ$, $U = 1744$ Å³, $Z = 6$, $D_c = 2.335$ g cm⁻³, $\mu(\text{Mo K}\alpha) = 5.17$ mm⁻¹.

(3), $M_r = 408.7$, monoclinic, space group $P2_1/c$, $a = 8.319(2)$, $b = 19.644(4)$, $c = 7.822(2)$ Å, $\beta = 114.79(2)^\circ$, $U = 1160(5)$ Å³, $Z = 4$, $D_c = 2.339$ g cm⁻³, $\mu(\text{Mo K}\alpha) = 5.18$ mm⁻¹.

The two triclinic crystal structures which are isomorphous were determined [5] by Patterson and Fourier methods and refined [6] by least squares with anisotropic thermal parameters for tellurium and halogen, and isotropic parameters for carbon and nitrogen atoms. The monoclinic form of the iodide was determined by direct methods [5] and refined by least squares with anisotropic parameters for all non-hydrogen atoms. Hydrogen atoms were placed in calculated positions, riding on their respective bonded atoms. Function minimised: $\sum w(F_o^2 - F_c^2)^2$, $w = 1/[\sigma^2(F_o^2) + (aP)^2 + bP]$, where $P = (F_o^2 + 2F_c^2)/3$, and $a = 0.124$, $b = 7.30$ (chloride), $a = 0.059$, $b = 21.88$ (triclinic iodide), $a = 0.018$, $b = 3.95$ (monoclinic iodide). The calculations were terminated when all shift/e.s.d. ratios were less than 0.1 and,

R , $wR_2 = 0.0726$, 0.2000 (3540 reflections) 0.0569 , 0.1446 (7064 reflections) and 0.0408 , 0.0762 (1977 reflections) with data/parameter ratios of 8.7, 17.4 and 15.6 for the chloride and the two iodide structures respectively. The residual electron densities were, respectively, within the ranges 1.1 to -1.2 e Å⁻³, 0.63 to -0.98 e Å⁻³ and 0.56 to -0.87 e Å⁻³.

Atomic coordinates are given in Tables 2–4. Selected geometrical parameters are listed in Table 5. Hydrogen atom co-ordinates, anisotropic thermal parameters and full lists of bond lengths and angles have been deposited with the Cambridge Crystallographic Data Centre. Fig. 1 gives a PLUTO [7] plot of one molecule of 2-(2-pyridyl)phenyltellurium(II) chloride, showing the atom numbering. Fig. 1 also represents the iodide molecule, the only visible difference being an approximately 0.3 Å longer tellurium–halogen bond in that molecule.

3. Discussion

2-(2-pyridyl)phenyltellurium(II) chloride was first recognised as a component of an inclusion compound [2] which arose as indicated in the Introduction [1]. Interestingly, the substitution of $\text{RR}'\text{Te}$ for $\text{RR}'\text{Te}$ in Eq. (1), where $\text{R}' = p$ -methoxyphenyl-, causes the reaction to terminate at the acid–base complex stage and no migration of organic groups occurs. The reason for the difference is not immediately apparent.

Table 2 (continued)

	x	y	z	U/U_{eq}^a
N(1E)	-4692(25)	-3924(20)	-7300(26)	74(7)
C(1E)	-5562(40)	-2935(33)	-5391(44)	103(12)
C(2E)	-5946(34)	-2436(26)	-4317(36)	85(9)
C(3E)	-6786(40)	-1484(32)	-4456(46)	109(13)
C(4E)	-7137(46)	-1088(38)	-5615(48)	119(14)
C(5E)	-6737(39)	-1628(31)	-6701(43)	101(12)
C(6E)	-5964(32)	-2513(25)	-6542(34)	78(8)
C(7E)	-5469(33)	-3061(26)	-7559(35)	83(9)
C(8E)	-5749(38)	-2731(30)	-8806(38)	98(11)
C(9E)	-5257(46)	-3326(37)	-9732(48)	132(16)
C(10E)	-4469(38)	-4172(29)	-9448(40)	96(11)
C(11E)	-4222(35)	-4475(27)	-8260(35)	85(9)
N(1F)	3165(26)	2176(20)	3208(27)	80(7)
C(1F)	4787(27)	1162(20)	2059(28)	66(7)
C(2F)	5649(29)	585(23)	1500(31)	71(7)
C(3F)	6820(35)	849(25)	1954(33)	88(9)
C(4F)	7126(34)	1696(25)	2985(34)	94(10)
C(5F)	6256(29)	2244(23)	3470(32)	75(8)
C(6F)	5137(29)	1975(22)	3100(31)	72(7)
C(7F)	4230(27)	2496(21)	3711(28)	66(7)
C(8F)	4417(33)	3298(26)	4753(35)	86(9)
C(9F)	3475(32)	3820(25)	5235(35)	83(9)
C(10F)	2331(38)	3473(28)	4566(38)	93(10)
C(11F)	2247(33)	2627(25)	3644(33)	82(9)

^a For the Te and Cl atoms U_{eq} is defined as one-third of the trace of the orthogonalised U_{ij} tensor.

^b Site occupancy 0.95.

^c Site occupancy 0.05; refined isotropically.

Table 3

Atomic coordinates ($\times 10^4$) and isotropic displacement parameters ($\text{\AA}^2 \times 10^3$) for $\text{C}_{11}\text{H}_8\text{INTe}$ (triclinic)

	x	y	z	U/U_{eq}^a
Te(A)	-76(2)	-38(1)	-292(2)	62(1)
Te(B)	-2349(2)	-2236(1)	-2676(1)	58(1)
Te(C)	1196(2)	-3570(1)	-906(2)	65(1)
Te(D)	-1170(2)	-5754(1)	-3518(2)	63(1)
Te(E)	-4395(2)	-4414(2)	-5308(2)	56(1) ^b
Te(E')	-6779(9)	-1376(8)	-8383(9)	57(3) ^c
Te(F)	2977(2)	729(2)	1418(2)	59(1) ^b
Te(F')	5836(10)	3492(9)	4921(10)	65(3) ^c
I(A)	153(2)	239(2)	2365(2)	76(1)
I(B)	-2384(2)	-2133(2)	-154(2)	89(1)
I(C)	1309(2)	-3663(2)	-3387(2)	103(1)
I(D)	-1313(2)	-5933(2)	-6162(2)	78(1)
I(E)	-4389(2)	-4671(2)	-2868(2)	81(1)
I(F)	3261(2)	-888(2)	-688(2)	79(1)
N(1A)	-454(19)	-30(17)	-2302(20)	65(6)
C(1A)	-1378(19)	1185(18)	-593(20)	49(5)
C(2A)	-1916(24)	1829(23)	257(27)	81(8)
C(3A)	-2760(28)	2656(26)	-8(31)	94(10)
C(4A)	-3067(28)	2836(26)	-1190(28)	87(9)
C(5A)	-2672(24)	2249(22)	-2047(27)	73(8)
C(6A)	-1802(22)	1380(19)	-1821(23)	60(6)
C(7A)	-1256(20)	739(18)	-2732(20)	53(6)
C(8A)	-1535(25)	751(23)	-3988(26)	77(8)
C(9A)	-963(27)	53(24)	-4704(29)	85(9)
C(10A)	-98(27)	-731(25)	-4204(29)	86(9)
C(11A)	154(29)	-742(25)	-3025(29)	86(9)
N(1B)	-2531(19)	-2060(17)	-4633(19)	63(6)
C(1B)	-3487(20)	-911(18)	-2906(20)	50(6)
C(2B)	-4064(23)	-233(21)	-2055(24)	62(7)
C(3B)	-4856(27)	600(25)	-2297(29)	84(9)
C(4B)	-5143(28)	882(26)	-3456(28)	86(9)
C(5B)	-4679(25)	288(24)	-4358(29)	79(9)
C(6B)	-3898(20)	-657(19)	-4142(21)	53(6)
C(7B)	-3356(20)	-1311(19)	-5029(21)	54(6)
C(8B)	-3579(32)	-1198(29)	-6286(33)	105(11)
C(9B)	-2936(25)	-1896(23)	-7029(29)	82(9)
C(10B)	-2209(26)	-2724(24)	-6587(28)	85(8)
C(11B)	-1976(24)	-2810(22)	-5364(24)	68(7)
N(1C)	1437(19)	-3702(17)	1056(20)	64(6)
C(1C)	2400(19)	-4953(18)	-584(20)	49(5)
C(2C)	2855(29)	-5550(27)	-1521(32)	90(10)
C(3C)	3670(32)	-6479(29)	-1261(35)	102(11)
C(4C)	3922(36)	-6662(32)	-102(35)	112(12)
C(5C)	3423(25)	-6089(23)	728(28)	75(8)
C(6C)	2647(21)	-5204(19)	561(22)	58(6)
C(7C)	2061(24)	-4506(22)	1461(25)	68(7)
C(8C)	2326(23)	-4754(21)	2583(23)	65(7)
C(9C)	1826(32)	-4078(29)	3385(36)	108(11)
C(10C)	1047(25)	-3301(23)	3040(27)	78(8)
C(11C)	800(30)	-3003(28)	1837(29)	91(10)
N(1D)	-767(18)	-5791(17)	-1516(19)	60(5)
C(1D)	137(22)	-7061(20)	-3242(23)	60(7)
C(2D)	546(18)	-7688(17)	-4234(21)	52(6)
C(3D)	1424(24)	-8504(23)	-3917(27)	77(8)
C(4D)	1842(26)	-8658(23)	-2759(27)	79(8)
C(5D)	1362(24)	-8103(22)	-1799(27)	73(8)
C(6D)	528(21)	-7258(19)	-2102(22)	57(6)
C(7D)	67(25)	-6565(23)	-1120(27)	75(8)
C(8D)	379(24)	-6730(22)	92(25)	73(8)
C(9D)	-148(25)	-6017(22)	898(27)	76(8)
C(10D)	-917(23)	-5215(22)	553(25)	71(7)
C(11D)	-1205(29)	-5078(27)	-668(29)	89(10)

Table 3 (continued)

	x	y	z	U/U_{eq}^a
N(1E)	-4628(17)	-4045(16)	-7207(18)	54(5)
C(1E)	-5510(21)	-3008(18)	-5281(21)	52(6)
C(2E)	-5972(22)	-2489(20)	-4296(23)	62(7)
C(3E)	-6732(27)	-1536(25)	-4387(29)	85(9)
C(4E)	-7158(27)	-1172(25)	-5535(28)	87(9)
C(5E)	-6587(25)	-1687(23)	-6464(28)	74(8)
C(6E)	-5863(22)	-2615(20)	-6364(23)	62(7)
C(7E)	-5441(21)	-3164(19)	-7402(22)	55(6)
C(8E)	-5655(28)	-2871(25)	-8527(28)	83(9)
C(9E)	-5220(26)	-3450(24)	-9457(28)	81(8)
C(10E)	-4423(25)	-4320(22)	-9245(26)	72(8)
C(11E)	-4243(21)	-4636(21)	-8120(22)	62(7)
N(1F)	3038(18)	2037(16)	3063(18)	67(6)
C(1F)	4694(20)	1081(18)	1986(21)	59(6)
C(2F)	5532(25)	534(23)	1424(27)	78(8)
C(3F)	6667(26)	821(23)	1891(26)	75(8)
C(4F)	6932(26)	1588(22)	2824(26)	75(8)
C(5F)	6104(22)	2097(21)	3430(24)	71(7)
C(6F)	5002(20)	1838(18)	2998(20)	56(6)
C(7F)	4086(20)	2392(18)	3602(21)	59(6)
C(8F)	4271(22)	3185(19)	4632(22)	64(6)
C(9F)	3252(21)	3649(20)	5034(23)	62(7)
C(10F)	2236(29)	3346(25)	4483(28)	88(9)
C(11F)	2109(27)	2546(23)	3466(27)	80(8)

^a For the Te and I atoms U_{eq} is defined as one-third of the trace of the orthogonalized U_{ij} tensor.

^b Site occupancy 0.83.

^c Site occupancy 0.17; refined isotropically.

Considering first the chloride and the triclinic form of the iodide, each structure has six independent molecules in the unit cell which are virtually identical. Bond lengths and selected angles, averaged over the six molecules, are listed in Table 5. Apart from the tellurium-halogen bond length, there is a close correspondence between the two structures. The 2-(2-pyridyl)phenyl- residues are essentially planar, r.m.s. atomic deviations ranging from 0.022 to 0.045 Å in the

chloride and from 0.025 to 0.040 Å in the iodide. The dihedral angles between the pyridyl and the phenyl rings are all less than 3.6°. The estimated standard deviations in these angles are, however, relatively large,

Table 4
Atomic coordinates ($\times 10^4$) and equivalent isotropic displacement parameters ($\text{Å}^2 \times 10^3$) for $C_{11}H_8INTe$ (monoclinic)

	x	y	z	U_{eq}^a
Te(1)	2554(1)	2036(1)	705(1)	43(1)
I(1)	3570(1)	605(1)	1001(1)	68(1)
N(1)	1457(7)	3107(3)	-15(7)	44(1)
C(1)	-39(8)	1894(3)	-1397(8)	40(1)
C(2)	-831(9)	1259(4)	-1963(9)	52(2)
C(3)	-2522(10)	1222(4)	-3394(10)	64(2)
C(4)	-3423(10)	1815(5)	-4236(10)	66(2)
C(5)	-2656(10)	2435(4)	-3646(10)	58(2)
C(6)	-962(8)	2492(3)	-2205(9)	46(2)
C(7)	-115(9)	3152(3)	-1507(9)	46(2)
C(8)	-768(11)	3795(4)	-2230(12)	66(2)
C(9)	206(13)	4361(4)	-1454(14)	75(2)
C(10)	1819(13)	4302(4)	102(13)	72(2)
C(11)	2408(11)	3671(4)	790(11)	57(2)

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

Table 5
Bond lengths (Å) and selected angles (deg) with e.s.d.s in parentheses

	X = Cl ^a	X = I ^a (triclinic)	X = I (monoclinic)
Te-X	2.606(11)	2.937(11)	2.917(1)
Te...N(1)	2.205(11)	2.260(10)	2.268(5)
Te-C(1)	2.077(7)	2.095(18)	2.112(6)
C(1)-C(2)	1.402(8)	1.405(9)	1.392(9)
C(2)-C(3)	1.405(13)	1.402(17)	1.384(10)
C(3)-C(4)	1.394(17)	1.367(17)	1.391(11)
C(4)-C(5)	1.370(20)	1.365(25)	1.363(11)
C(5)-C(6)	1.404(17)	1.397(13)	1.392(9)
C(6)-C(1)	1.401(12)	1.393(19)	1.401(9)
C(6)-C(7)	1.440(5)	1.465(10)	1.467(9)
C(7)-C(8)	1.405(16)	1.395(12)	1.397(9)
C(8)-C(9)	1.389(16)	1.380(17)	1.361(11)
C(9)-C(10)	1.352(19)	1.352(19)	1.388(13)
C(10)-C(11)	1.382(18)	1.397(21)	1.359(10)
C(11)-N(1)	1.379(16)	1.372(16)	1.353(8)
N(1)-C(7)	1.354(13)	1.342(16)	1.342(8)
N(1)...Te-X	168.2(5)	170.5(4)	170.7(1)
N(1)...Te-C(1)	75.7(4)	75.7(5)	75.9(2)
C(1)-Te-X	92.9(4)	95.2(3)	95.6(2)

^a Averaged values; e.s.d.s in mean values calculated from $\{\sum(x-x_i)^2/[n(n-1)]\}^{1/2}$.

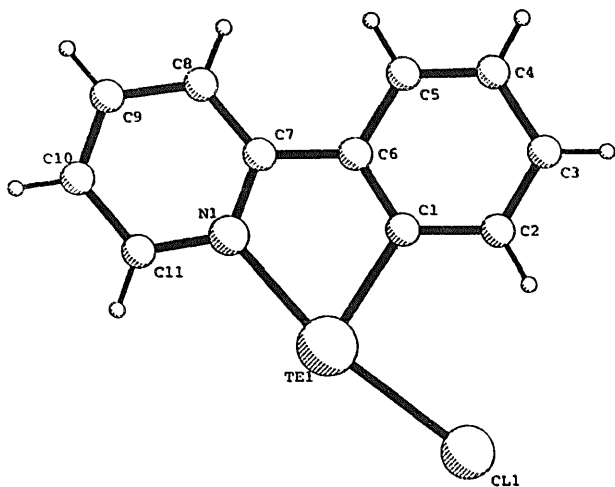


Fig. 1. PLUTO plot of one molecule of 2-(2-pyridyl)phenyltellurium(II) chloride.

of the order of 2° . E.s.d.s in bond lengths and angles are also relatively large, averaging in the chloride structure 0.05 \AA for C–C and C–N, 0.03 \AA for Te–N and Te–C, 0.01 \AA for Te–Cl and $1\text{--}5^\circ$ for bond angles. The corresponding values in the iodide structure are somewhat smaller, $0.04\text{--}0.03 \text{ \AA}$ for C–C and C–N, 0.02 for Te–N and Te–C, 0.003 \AA for Te–I, and $1\text{--}4^\circ$ for bond angles.

The monoclinic form of the iodide yields more accurate parameters (Table 5). The organic residue is again near-planar, r.m.s. atomic deviation 0.046 \AA , and phenyl–pyridyl interplanar angle $5.2(4)^\circ$.

The tellurium atom is bonded to a halogen atom and to an aromatic carbon atom. The Te–Cl distance is at the upper end of the range $2.34\text{--}2.60 \text{ \AA}$ given by Allen et al. [8] for this bond, and compares with 2.568 \AA in 1-chloro-1-hydro-*N-p*-tolyl-1-telluraisoindole [9], while the Te–I distance is in good agreement with the value given by Allen et al. of 2.926 \AA and is close to the Te–I bond length in 1-iodo-1-hydro-*N-p*-tolyl-1-telluraisoindole of 2.936 \AA [10]. The Te–C bonds are slightly shorter than the 2.116 \AA given by Allen et al. but are close to those reported in Refs. [9] and [10] of 2.098 and 2.102 \AA . The Te–N distances of $2.205(11) \text{ \AA}$ (chloride) and $2.260(10)$, $2.268(5) \text{ \AA}$ (iodide) are typical [2,9,10] of this type of interaction when the bonded atom trans to the nitrogen is chlorine, bromine or iodine. This interaction has the effect of holding the organic ligand in a planar configuration.

Closer inspection of the Te–N distances, however, appears to indicate a slight trend for these distances to increase as the atomic number of the trans halogen increases. Thus Te–N = 2.205 \AA (chloride), 2.236 \AA (bromide) [2], and 2.260 , 2.268 \AA (iodide). Not entirely consistent with this trend is the Te–N distance of 2.236 \AA in the chloride in the 2:1 inclusion complex with *p*-ethoxyphenylmercury(II) chloride [2].

In both the chloride and the triclinic form of the iodide, two molecules, E and F, are affected by disorder, so that 5% of the molecules (chloride) and 17% (iodide) are rotated by 180° about a line perpendicular to the plane of the molecule, and passing through the mid-point of the C6–C7 inter-ring bond. The disordered tellurium atoms [Te(E') and Te(F')] show up clearly in difference maps. The corresponding halogen atoms do not appear to be affected by this disorder. However, disorder of the halogens may be concealed, since the probable positions of halogen (E') and (F') coincide closely with the major halogen sites (F) and (E) respectively. Thus the distances Te(E')–Cl(F) and Te(F')–Cl(E) are $2.78(4)$ and $3.08(4) \text{ \AA}$, while Te(E')–I(F) and Te(F')–I(E) are $2.919(10)$ and $3.161(11) \text{ \AA}$. The relevant angles, halogen–Te'–N', where N' coincides with C5 are all close to 180° . The crystal structure of the bromide [2], RTeBr¹, is isomorphous and exhibits a similar disorder, 6% of the molecules being affected, intermediate in extent between that shown by the chloride and the iodide. It is noteworthy that the minor component Te–halogen distances (mean 2.93 \AA (chloride), 3.04 \AA (iodide)) are closer to the values measured for the major component (2.606 \AA (chloride), 2.937 \AA (iodide)) in the iodide than in the chloride structure. The situation in the bromide structure [2] is again intermediate. This feature may account for the differing degrees of disorder in the three structures. An alternative, but crystallographically equivalent, interpretation of the disorder is that only the RTe residues are affected by disorder, while the halogen atoms are in fixed positions.

The data for 2-(2-pyridyl)phenyltellurium(II) chloride in the 2:1 inclusion complex [2] are in good agreement with those reported here. Thus the distances for Te–Cl, Te–C and Te–N are $2.558(1)$, $2.080(25)$ and $2.236(6) \text{ \AA}$. In the corresponding bromide [2], Te–C and Te–N are $2.111(6)$ and $2.236(11) \text{ \AA}$, similar to the values found in the chloride and iodide; the Te–Br bond is, as expected [8], intermediate in length at $2.707(11) \text{ \AA}$.

The closest Te...halogen intermolecular separations are $3.92(1) \text{ \AA}$ and $4.145(3) \text{ \AA}$ in the chloride and iodide respectively, which correspond closely to normal van der Waals interactions.

Synthesis of 2-(2-pyridyl)phenyltellurium(II) iodide (RTeI) and of phenylazophenyl(*C,N'*)tellurium(II) iodide (R'TeI) by metathesis involving sodium iodide and the corresponding chlorides works well. Products 'RTeI₃' and 'R'TeI₃' are also obtained from the reaction of an organytellurium(IV) trichloride/tribromide

¹ A different choice of unit cell axes was made for the bromide. Application of the matrix /00–1/100/010/ transforms the cells quoted above for the title compounds to that of the bromide given in Ref. [2].

Table 6
X-ray photoelectron spectra — tellurium and iodine binding energies (BEs)

Compound	Tellurium BE	Iodine BE
	(± 0.2 eV)	(± 0.2 eV)
R'TeI	573.3, 574.5, 576.6	618.1, 619.2
RTeI	573.2, 574.3	618.1, 619.2
R'TeI ₃	573.2, 574.5, 576.6	618.1, 619.2

R = C₁₁H₈N⁻; R' = C₁₂H₉N₂⁻.

with an excess of sodium iodide. However, when these materials are recrystallised the monoiodide is obtained; interestingly, in the case of RTeI it is the monoclinic form that is obtained, rather than the more usual triclinic form.

The monoiodides, RTeI ($\delta = 1135$ ppm vs. Me₂Te) and R'TeI ($\delta = 1313$ ppm vs. Me₂Te), give ¹²⁵Te NMR spectra consistent with expectation for Te(II) compounds; however, the materials which analyse as 'R'TeI₃' and 'R'TeI₃' fail to give ¹²⁵Te resonances. Furthermore, if a mole equivalent of diiodine is added to a solution of the monoiodides the NMR signal is lost. A possible explanation is that the solutions containing diiodine, and those of the triiodides, contain a charge transfer complex, with which a degree of paramagnetism is associated, of the monoiodide and diiodine:



An alternative is that the triiodides contain the [I₃]⁻ ion, although, if so, the NMR observations are puzzling. An X-ray photoelectron (XPS) study was initiated and data (binding energies) are in Table 6. Two peaks may be resolved for iodine in R'TeI₃ with binding energies of 618.1 and 619.2 eV; superficially this is consistent with two distinct forms of iodine. However, caution is clearly needed since the monoiodides also give identical peaks. The explanation is in the Te region of the XPS spectrum where the data (Table 6) indicate that there are two minor components at 573.3 and 576.6 eV which correspond to Te(IV) and Te(0) respectively [11,12]. The latter has arisen from radiation damage of the sample [13], and can explain the appearance of extra iodine peaks even in the monoiodides. Thus the XPS is rather inconclusive and the main conclusion that can be drawn is that the major Te peak from both triiodides and monoiodides corresponds to tellurium in oxidation state (II). To that extent, the balance of evidence is that a formulation based on tellurium(IV) may be excluded. Mass spectroscopic data were similar for the two compounds R'TeI₃ and R'TeI. A weak parent ion was seen for the latter compound at $m/e = 438$ (¹³⁰Te); other major tellurium containing peaks in both spectra corresponded to R'₂Te⁺, R'Te⁺, (dibenzotellurophene)⁺, and C₆H₄Te⁺. In addition, a significant feature at $m/e = 257$ corresponded to C₁₈H₁₃N₂⁺, a fragment derived from R'₃Te⁺, the observation of which suggests that

considerable thermolysis of the materials had occurred prior to passage to the vapour phase. One significant difference between the two spectra was the observation of a significant (60% of base peak, $m/e = 311$, R'Te⁺) feature at $m/e = 127$ which is attributed to I⁺ arising from loosely bound I₂.

Raman data were obtained for R'TeI and R'TeI₃ (R' = phenylazophenyl-) and also for RTeI (R = 2-(2-pyridyl)phenyl-). The azobenzene derivatives fluoresced but gave spectra which were dominated by an intense shift at $\Delta\nu = 1355$ cm⁻¹ $\nu(\text{N}=\text{N})$, as previously observed for related compounds [14]; the identity of the spectra in the region above 200 cm⁻¹ strongly suggested that the same molecular component containing a phenylazophenyl-group was present in both materials, thereby providing further support to the view that the 'triiodide' is a weak charge transfer complex of the monoiodide and diiodine. Unfortunately, no data could be obtained below 200 cm⁻¹ and hence no confident assignment of $\nu(\text{Te}-\text{I})$ can be offered for RTeI. The proposed formulation is comparable with that suggested for tris-dialkyldithiocarbamate-derivatives of phenylazophenyl(C,N')tellurium compounds [15]. This behaviour is in contrast to that of 'simple' organotellurium compounds, *p*-ROC₆H₄TeX₃ (R = Et or Me; X = I or dithiocarbamate) where authentic triiodides [16] and tris-dithiocarbamate [17] derivatives are well characterised. The difference in behaviour may reflect the greater stabilisation of Te(II) than Te(IV) by intramolecular co-ordination [18].

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