Synthesis and properties of novel components for organic metals: dihydrotellurophene derivatives

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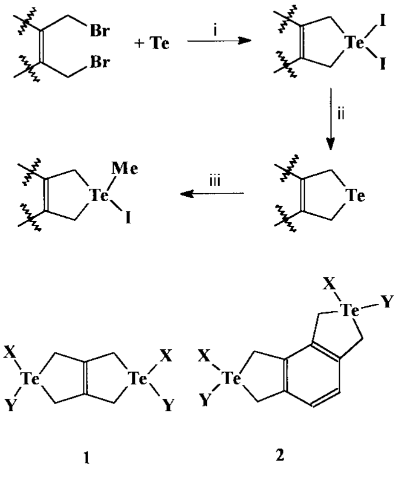
Two series of dihydrotellurophenes have been synthesized: derivatives of 4,6-dihydro-1*H*,3,*H*-telluropheno[3,4-*c*]tellurophene (**1**) and derivatives of 1,3,6,8-tetrahydrobenzo[1,2-*c*;3,4-c′]ditellurophene (**2**). X-Ray structure determinations confirm the tetraiodo structures of **1a** and **2a**. The tetraiodo derivatives are reduced by sodium borohydride to the corresponding dihydrotellurophenes, **1b** and **2b**, which undergo the characteristic divalent tellurium reaction with iodomethane to form telluronium methiodides. Both dihydrotellurophenes **1b** and **2b** are moderate electron donors and react with 7,7,8,8-tetracyanoqiunodimethane TCNQ affording blue semiconductive solids.

The present study was initiated with the purpose of exploring various aspects of dihydrotellurophene chemistry, and in particular the potential of dihydrotellurophenes to form conducting charge-transfer (CT) complexes with electron acceptors. A comprehensive survey of tellurium heterocycles has appeared recently,[1] and some derivatives of dihydrotellurophene have been reported to form CT complexes with electron acceptors.[2,3] Methyl, benzo and quinoxalino derivatives of 2,5-dihydrotellurophene form low conducting CT complexes with 7,7,8,8-tetracyanoquinodimethane (TCNQ) or chloranil, but the electronic structures of these complexes are not well understood.

Results and Discussion

The procedure reported by Ziolo and Günther[4] was used to prepare 4,6-dihydro-1*H*,3,*H*-telluropheno[3,4-*c*]tellurophene **1a**, and 2,2,7,7-tetraiodo-1,3,6,8-tetrahydrobenzo[1,2-*c*; 3,4-c′]ditellurophene **2a** as outlined in Scheme 1. By this method a vicinal bis(bromomethyl) compound reacts with tellurium and a large excess of sodium iodide in 2-methoxyethanol, to give a derivative of 2,2-diiodo-1,3-dihydrotellurophene. Compounds **1a** and **2a** were separated from unreacted tellurium with cold dimethyl sulfoxide (DMSO). Undissolved tellurium was filtered off, and water was added to the DMSO filtrates to precipitate pure **1a** and **2a**, which were obtained as stable, yellow or orange amorphous solids in fair to good yields (60–80%). The identity of compound **1a** was verified by ^{1}H and ^{13}C NMR, mass and IR spectroscopy and microanalysis. Compound **2a** was identified by spectroscopic means only.



1 **2**

a X = I, Y = I
b X = **:**, Y = **:**
c X = Me, Y = I

Scheme 1 *Reagents*: i, NaI, $MeOCH_2CH_2OH$; ii, $NaBH_4$, EtOH; iii, MeI, $MeNO_2$

A reported synthesis[5] of an [1,2-*c*;4,5-c′] isomer of **2a**, where the isomer was obtained as a yellow solid in comparable yields to **2a**, has been reinvestigated recently.[6] The crude [1,2-*c*;4,5-c′] isomer precipitated as a yellow–orange solid, and recrystallization from dimethylformamide (DMF) afforded pure isomer as orange–red crystals in low yield (10–14%). However, most of the crude product (80–90%) was recovered as a yellow amorphous precipitate, which was not further identified.

Having this contradiction in mind, we attempted to grow single crystals for X-ray crystal structure determinations of both **1a** and **2a**. Both compounds form shiny orange crystals from DMSO. Compound **2a** forms a powdery precipitate at first, but after several days, the powder is replaced with crystals. The crystals of **1a** are hygroscopic, and convert into an amporphous solid in a few weeks.

The X-ray diffraction study of **2a** shows that all three rings are almost planar within 0.0119 Å (Fig. 1). The iodine atoms

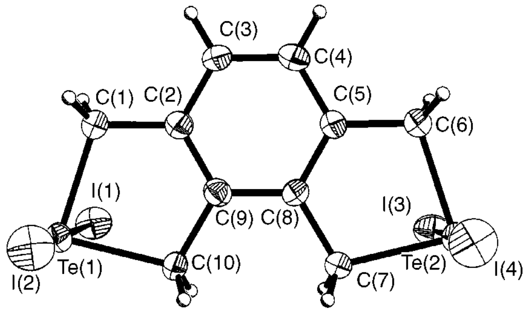


Fig. 1 Molecular structure of **2a** showing 50% probability ellipsoids

are found on either side of, and in a plane almost perpendicular to, this ring system. The I—Te—I angles are 174–176°, and the Te—I bond lengths are in the range of 2.889(1)–2.940(1) Å. In the five-membered rings, the lengths of the saturated Te—C bonds are 2.120(4)–2.149(4) Å, and the C—Te—C angles are 85.7(2)°. The most interesting feature of the **2a** structure is the molecular packing. Firstly, there is a distinct intermolecular interaction between an iodine atom of one molecule, and the Te atom of the next molecule. The Te···I intermolecular contacts are 3.79–3.93 Å, which is significantly shorter than the sum of the van der Waals radii of the corresponding atoms (Te = 2.06, I = 2.06 Å). Secondly, there is an interaction between the Te atoms and the solvent: the polar molecules of DMSO are orientated in a crystal to form a Te···O contact of 2.82–2.91 Å (the van der Waals radius of oxygen is equal to 1.52 Å). Both kinds of intermolecular interaction complete the coordination of the Te atom to form a distorted octahedral coordination (Fig. 2).

The geometrical parameters of **1a** are very similar to those of **2a** (Fig. 3). The iodine atoms are situated on either side of the planar (within 0.009 Å), bicyclic ring system, the I—Te—I angle is 176.92(5)°, the Te—I bond lengths are 2.735(2)–2.786(2) Å, and the C—Te—C angle is 86.2(4)°. The packing diagram of **1a** exhibits the same type of intermolecular interactions as for **2a**, *i.e.* the coordination number of Te is 6 in a distorted octahedron. However, the arrangement of molecules in the crystal is quite different. Whereas the 'herringbone' type structure is observed for **2a**, the layers of molecules in **1a** are separated by layers of solvent molecues, and the Te···I shortened contacts (3.54 Å) are intralayer ones (Fig. 4).

Diiododihydrotellurophenes **1a** and **2a** were reduced with sodium borohydride in ethanol to give the dihydrotellurophenes **1b** and **2b**. Compound **2b** is fairly stable when kept in the dark, but somewhat unstable to light, in good agreement with observations on dihydrobenzo[*c*]tellurophene.[7] The structure of **2b** was verified by ^{1}H and ^{13}C NMR spectroscopy and microanalysis. Compound **1b** decomposes visibly in air and light in less than 1 h. A high resolution mass spectrum was not obtained for this compound. However, the ^{1}H and ^{13}C NMR spectra are in good agreement with the spectra reported for other dihydrotellurophene derivatives.[8]

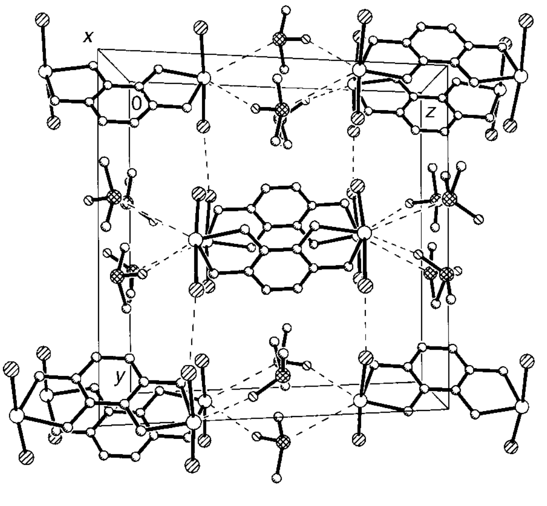


Fig. 2 Projection of the crystal structure of **2a** in the *bc* plane

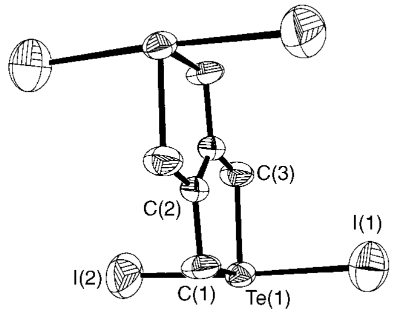


Fig. 3 Molecular structure of **1a** showing 50% probability ellipsoids

Reactions of dihydrotellurophenes with methyl iodide are generally found to give the corresponding methyltelluronium iodides.[1] The precipitate from a reaction of **1b** with methyl iodide is slightly soluble in DMSO, but the solution deposited some dark-grey solid, apparently due to decomposition of the product. The ^{1}H NMR spectrum of this product also supports this observation, since the strong singlet at δ 2.15 (CH_3) is mixed with several others of low intensity. In addition, several doublets at δ 3.2–3.3 (CH_2) are partly covered by the signal from the residual H_2O in the DMSO. Microanalysis shows a somewhat higher content of tellurium and a correspondingly lower content of iodine than would be in good agreement with structure **1c**. The analysis is consistent with loss of hydrogen iodide from one quarter of the tellurium moieties of **1c**; in other words, one quarter of the methyldihydrotelluronium iodide rings have apparently been oxidized to *Te*–methylhydrotellurophene rings.

The cyclic voltammetry measurements of **1b** and **2b** showed only poorly resolved irreversible oxidation peaks at *ca.* 1.3–1.5 V (*vs.* standard calomel electrode, SCE, on a glassy carbon electrode). Reactions of **1b** and **2b** with TCNQ afforded dark-blue microcrystalline powders. Conductivity of the **1b**–TCNQ complex is $1.3–2.5 \times 10^{-5}$, and the conductivity of **2b**–TCNQ is *ca.* 5×10^{-7} S cm^{-1} (measured on pressed pellets, four probe measurements). Microanalysis of **2b**–TCNQ indicates a 1 : 1 adduct. The IR spectra of the present TCNQ complexes confirm the presence of TCNQ radical anions. Li–TCNQ, a known radical anion salt of TCNQ, has CN absorptions at 2202 and 2186 cm^{-1}; the corresponding absorptions of the complexes are at 2218, 2186, 2211 and 2186 cm^{-1} (neutral TCNQ absorbs at 2224 cm^{-1}). Other characteristic absorptions of Li–TCNQ, at 1575, 1508, 1361, 1349 and 1182 cm^{-1}, are found at approximately the same wavenumbers for the **2b**–TCNQ complex also.

Conclusions

The facile formation of the stable tetraiodo tellurophenotellurophene derivative **1a** is demonstrated, and its structure proved by X-ray diffraction measurements.

A reductive elimination of the four iodines on **1a** gives compound **1b**, which is unstable to air and light, and was therefore characterised by spectroscopic means only. Microanalysis of the adduct from **1b** and methyl iodide indicates a 1 : 1 mixture of **1c** and (**1c–HI**). Compound **2a** was prepared in good yields, and its structure has been proved by X-ray structure determination. Compound **2a** was reduced to the dihydrobenzotellurophene derivative **2b**, characterised by ^{1}H and ^{13}C NMR spectroscopy and C, H, microanalysis. Cyclic voltammetry indicates that both **1b** and **2b** are electron donors of moderate strength, and they undergo irreversible oxidation. Both compounds react with TCNQ with the formation of semiconducting complexes. The IR spectra of both confirm the presence of TCNQ anion radicals.

Compounds **1** and **2** merit further investigation, and the continuation of our studies will be reported in due course.

Experimental

General

Mass spectra were obtained on an AEI MS-902 spectrometer at 70 eV electron energy. IR spectra were obtained on a Nicolet

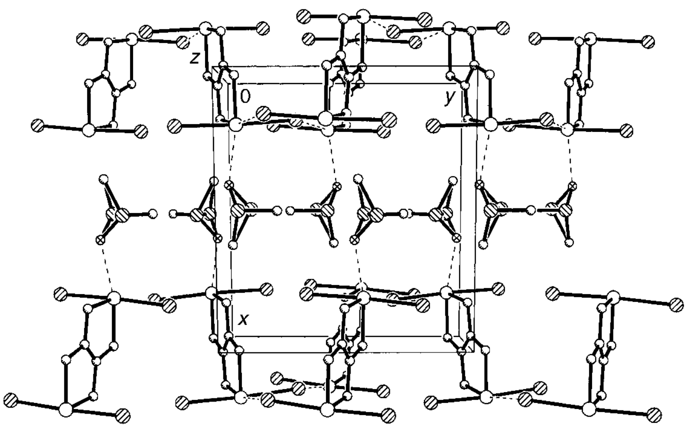


Fig. 4 Projection of the crystal structure of **1a** in the *bc* plane

20-SXC FTIR spectrometer. ^1H and ^{13}C NMR spectra were recorded on a JEOL EX400 NMR spectrometer at 399.65 and 100.40 MHz, respectively, and with tetramethylsilane (TMS) as internal standard. UV–VIS spectra were obtained on a Perkin-Elmer 500 UV–VIS spectrophotometer. Melting points were obtained on a Büchi 530 apparatus and are uncorrected. Merck Kieselgel 60F 254 was used for TLC and Merck silica 63–200 µm was used for column chromatography. Microanalyses were performed by the Analytische Laboratorien, Lindlar, Germany.

The X-ray diffraction measurements of **2a** were carried out using a Syntex P-1 diffractometer (Mo-K$_\alpha$ radiation, graphite monochromator, $\theta/2\theta$ scan $2\theta \leqslant 52°$). *Crystal data*: monoclinic, $C_{10}H_{10}I_4Te_2 \cdot 2DMSO$, 20 °C, $a = 12.786(3)$, $b = 14.116(3)$, $c = 15.266(3)$ Å; $\beta = 112.72(3)°$, $V = 2601.0(9)$ Å^3, $Z = 4$, space group $P2_1/c$, 5661 independent reflections. The structure was interpreted by direct methods and refined anisotropically using SHELX93 to $WR2 = 0.0689$, GOF = 1.05. The H-atoms were placed in calculated positions and included in the calculations with fixed positional and isotropic thermal parameters.

The X-ray diffraction measurements of **1a** were carried out using a Syntex P-1 diffractometer (Mo-K$_\alpha$ radiation, graphite monochromator, $\theta/2\theta$ scan $2\theta \leqslant 60°$). Because of the very weak diffracting capacity of **1a**, the crystals were tested for the possibility of low temperature measurements. However, all attempts to reach low temperature resulted in the destruction of the samples due to transformation into a microcrystalline state. Measurements were, therefore, carried out at ambient temperature. *Crystal data*: monoclinic, $C_6H_8I_4Te_2 \cdot 2DMSO$, 20 °C, $a = 12.336(3)$, $b = 11.008(3)$, $c = 8.660(2)$ Å; $\beta = 102.22(2)°$, $V = 1149.3(5)$ Å^3, $Z = 4$, space group $P2_1/c$; 3493 independent reflections. The semiempirical ψ-scan absorption correction was used. The structure was interpreted by direct methods and refined anisotropically using SHELX93 to $WR2 = 0.1973$ [$(R1 = 0.087$ for 1838 reflections with $F > 4\sigma(F)$], 100 refined parameters; GOF = 1.05. The H-atoms were placed in calculated positions and included in the calculations with fixed positional and isotropic thermal parameters. The poorly diffracting sample and the disorder of the solvent moecules lead to a comparatively high R-factor.

1,4-Dibromo-2,3-bis(bromomethyl)but-2-ene, mp 159–160 °C (recrystallized twice from ethyl acetate) was prepared[9] from 2,3-dimethylbutane; lit.[9] mp 158–159 °C. 1,2,3,4-Tetrakis(bromomethyl)benzene, mp 116–118 °C (ethanol) was prepared[10] from 1,2,3,4-tetramethylbenzene; lit.[10] mp 124–126 °C.

Preparation of 2,2,5,5-tetraiodo-4,6-dihydro-1*H*,3*H*-telluropheno[3,4-*c*]tellurophene 1a and 2,2,7,7-tetraiodo-1,3,6,8-tetrahydrobenzo[1,2-*c*;3,4-*c*′]ditellurophene 2a

General procedure. To a solution of the bromomethyl compound (3 mmol) in 2-methoxyethanol (8 ml for **1a**, 25 ml for **2a**) was added tellurium (6 mmol) and sodium iodide (36 mmol). The suspension was stirred vigorously under reflux for 1 h. The bright orange precipitate was filtered off together with unreacted tellurium and washed with acetone to remove iodine and sodium iodide. Water was added to the methoxyethanol filtrate, and some additional orange precipitate was filtered off. The combined precipitate was dissolved in a minimal amount of DMSO at ambient temperature, tellurium was removed by filtration, and water was added to the filtrate, whereupon compound **1a** or **2a** precipitated, and was filtered off and dried at ambient temperature at 1 Torr for 15 h.

Compound **1a**, 1.51 g (59%), was a yellow amorphous solid, mp 200–210 °C (charring, I_2 evolved); MS [*m*/*z* (% rel. int.)]: 384 (2.1), 382 (1.5), 338 (5.4), 336 (6.9), 332 (6), 128 (59.5), 127 (32.2) 79 (100); υ/cm^{-1} (KBr): 1618 (C=C), 1376, 1133, 1039, 817, 706, 590; δ_H[$(CD_3)_2SO$] 3.95 (CH_2, s); δ_c[$(CD_3)_2SO$] 45.85, 126.29 (Found: C 9.03; H 1.17; I 56.95; Te 32.30. Calc. for $C_6H_8I_4Te_2$ C 8.55; H 0.96; I 60.22; Te 30.27%).

Compound **2a**, 1.3 g (51%), was a yellow–orange powder, mp 240 °C (charring, iodine evolved); MS [*m*/*z* (% rel. int.)]: 389 (2.3), 388 (1.6), 386 (2.1), 384 (7.2), 260 (13), 258 (26.4), 256 (21.6), 254 (67.8), 128 (70) 127 (57.4), 45 (100); δ_H [$(CD_3)_2SO$] 4.68 (4H, s), 4.82 (4H, s), 7.28 (2H, s); υ/cm^{-1} (KBr): 2923, 2874, 1688, 1453, 1354, 1092, 832.

Preparation of a crystalline sample of 1a. Compound **1a** (100 mg) was mixed with DMSO (1 ml), and the mixture was filtered through glass wool. The yellow solution was left in a stoppered vial for *ca.* four weeks. Crystals separated slowly from the solution.

Crop 1. Some of the crystals were collected with a spatula and washed with diethyl ether. These crystals had decomposed in air after *ca.* two weeks.

Crop 2. This was used for X-ray analysis.

Preparation of a crystalline sample of 2a. Compound **2a** (60 mg) was mixed with DMSO (1 ml), and the lemon coloured suspension was filtered (gravity) through glass wool. The yellow–orange filtrate became cloudy, and after 12 h a pale yellow, fluffy precipitate appeared. After one week, some orange crystals had formed, but some of the yellow powdery precipitate was present as well. After 10 d all of the yellow precipitate had been replaced with shiny orange crystals. Some of the crystals were collected with a spatula, washed with diethyl ether and subjected to X-ray analysis.

Preparation of 4,6-dihydro-1*H*,3*H*-telluropheno[3,4-*c*]tellurophene 1b, and 1,3,6,8-tetrahydrobenzo[1,2-*c*;3,4-*c*′]ditellurophene, 2b.

General procedure. A suspension of sodium borohydride (0.64 g, 16 mmol) in ethanol (35 ml) was added dropwise during 10 min to a stirred suspension of **1a** or **2a** (2 mmol) in ethanol (25 ml), kept at 0 °C. A grey precipitate formed upon addition of the reducing agent. The reaction mixture was protected from light and stirred at 0 °C for 1 h after complete addition. Water (60 ml) was added, and the suspension was extracted with benzene (3×40 ml) and dichloromethane (3×40 ml) for **1b**, or chloroform (3×15 ml) for **2b**. The organic extracts were filtered and evaporated to dryness at ambient temperature.

Compound **1b**, 0.36 g (54%), mp 155–160 °C (black, sintering), 180 °C (gas evol.) MS [*m/z* (% rel. int.)]: 340 (26, *M*, ^{130}Te,^{130}Te), 338 (50.5, *M*, ^{130}Te,^{128}Te), 336 (50.7, *M*,^{128}Te,^{128}Te), 335 (13.6), 334 (35.6, *M*, ^{128}Te,^{126}Te), 332 (20, *M*, ^{126}Te,^{126}Te), 254 (22.3), 130 (12.0), 128 (10.5), 126 (6.6), 79 (100); υ/cm^{-1} (KBr) 1437, 1270, 1120, 1070 (s), 777 (s), 629 (s), 587; δ_H[$(CD_3)_2SO$] 3.74 (CH_2, s); δ_c[$(CD_3)_2SO$] 3.33, 125.99.

Compound **2b**, 1.79 g, was a yellow–grey powder, mp > 300 °C (discoloured 170 °C). The work-up procedure for this compound was modified, since a substantial part of **2b** was undissolved after the first chloroform extraction, and settled as a yellow powder at the bottom of the separation funnel. This solid was taken out through the bottom of the funnel and dried, and was found to be spectroscopically identical to the rest of **2b**, obtained from the chloroform extracts; MS [*m/z* (% rel. int.)]: 390 (9.0, *M*, ^{130}Te,^{130}Te), 388 (16.8, *M*, ^{128}Te,^{130}Te), 386 (19.4, *M*, ^{128}Te,^{128}Te), 384 (11.9, *M*, ^{128}Te,^{126}Te), 382 (6.7, *M*, ^{126}Te,^{126}Te), 258 (4.9), 256 (2.5), 130 (100), 129 (17.1), 128 (14.7), 115 (17.3); υ/cm^{-1} (KBr) 2919, 2873, 1468, 1353, 1090, 1028, 838; δ_H[$(CD_3)_2SO$] 4.47 (8H, s), 6.98 (2H, s); δ_H($CDCl_3$) 4.53 (4H, s), 4.59 (4H, s), 6.95 (2H, s); δ_c [$(CD_3)_2SO$] 8.10, 125.94 (Found: C 28.02; H 2.37. Calc. for $C_{10}H_{10}Te_2$ C 31.17; H 2.62; Te 66.21%).

Reactions of 1b and 2b with TCNQ

General procedure. The dihydrotellurophenes **1b** or **2b** (0.05 mmol) and TCNQ (0.05 mmol) were dissolved separately in minimum amounts of warm acetonitrile. The two solutions were mixed, heated under reflux for 1 h, and then filtered to remove small amounts of undissolved material. The reaction mixture from **1b** darkened almost immediately, whereas the one from **2b** became gradually darker over several hours. The solutions were transferred to open beakers and were left for slow evaporation at ambient temperature, and finally at *ca.* 50 °C. Some red–brown material settled on the upper part of the walls of the beakers, whereas dark-blue–black crystals that eventually formed at the bottom of the beakers, were collected.

Compound **1b** + TCNQ; dark-blue powder/microcrystals. υ/cm^{-1} (KBr) 2218 (w), 2186, 1657, 1592(s), 1377 (s), 1262 (s), 1106, 1014, 637.

Compound **2b** + TCNQ; dark blue powder/microcrystals. υ/cm^{-1} (KBr): 2950 (w), 2211 (sh), 2185 (s), 2120 (sh), 1658 (sh), 1595, 1566 (sh), 1502, 1475, 1443, 1366, 1344, 1244, 1189 (Found: C 47.08; H 3.44; N 7.67. Calc. for $C_{22}H_{14}N_4Te_2$: C 44.82; H 2.39; N 9.50; Te 43.28%).

Li–TCNQ (reference). υ/cm^{-1} (KBr): 2202, 2186, 1575, 1508, 1361, 1349, 1182.

Preparation of 2,5-diiodo-2,5-dimethyl-4,6-dihydro-1*H*,3*H*-telluropheno[3,4-*c*]tellurophene 1c

Iodomethane (0.34 g, 2.4 mmol) was added to a solution of **1b** (0.034g, 0.1 mmol) in benzene (10 ml) at ambient temperature. The precipitate was filtered off, washed with diethyl ether and air dried; **1c**, 0.06 g (70%), grey amorphous solid, mp 160 °C (sintering, black). υ/cm^{-1} (KBr) 3411, 2902, 1391(v.s), 1130, 1069, 871, 631; δ_H[$(CD_3)_2SO$] 2.15 (CH_3, s), 3.2–3.3 (CH_2, H_2O, m) [Found: C 16.65; H 2.18; I 33.35; Te 47.10. Calc. for 0.5 ($C_8H_{14}I_2Te_2 + C_8H_{13}ITe_2$): C 17.54; H 2.48; I 33.41; Te 46.58%].

E.H.M. thanks the Norwegian University of Science and Technology, Trondheim, Norway for support and a sabbatical leave of absence. G.F. and D.M. thank the ERASMUS Interuniversity Cooperation Programme for the award of student exchange grants.

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Paper 7/00975E; *Received* 11*th February*, 1997