Reactions of Some *ortho*-Tellurated Compounds with Intramolecular Co-ordinate Bonds*

Anatoly G. Maslakov,[a] **William R. McWhinnie,**[a] **Michael C. Perry,**[a] **Nirmala Shaikh,**[a] **Sean L. W. McWhinnie**[b] **and Thomas A. Hamor**[c]

[a] *Department of Chemical Engineering & Applied Chemistry, Aston University, Aston Triangle, Birmingham B4 7ET, UK*

[b] *Chemistry Department, Brunel University, Uxbridge, Middlesex UB8 3PH, UK*

[c] *School of Chemistry, University of Birmingham, PO Box 363, Birmingham B15 2TT, UK*

Reaction of 2-$(Br_3Te)C_6H_4CH{=}NC_6H_4Me$-*p* **1** with BH_4^- results in reduction at both the tellurium and double-bond centres to afford 2-$(BrTe)C_6H_4CH_2NH(C_6H_4Me$-*p*) **2**, however substitution of *p*-tolyl by a more sterically demanding group such as 2,4,6-tri-*tert*-butylphenyl precludes reduction of the double bond. The crystal and molecular structure of **2** has been determined: monoclinic, space group $P2_1/n$, with a = 11.010(4), b = 9.231(2), c = 14.862(7) Å, β = 110.80(4)° and Z = 4; R = 0.0533 for 1180 observed reflections. The tellurium atom is three-co-ordinate with Br–Te–N 165.3(3), Br–Te–C(1) 91.5(4) and N–Te–C(1) 74.9(5)° and Te–C(1) 2.125(16), Te–Br 2.663(3) Å and a Te $\cdots$ N interaction of 2.375(13) Å. A survey of available structural data for *ortho*-tellurated compounds suggests this interaction to be stronger when the donor nitrogen atom is sp^2 rather than sp^3 hybridised. A multinuclear (^1H, ^{13}C, ^{123}Te, ^{125}Te) and variable-temperature (^1H) NMR study of compound **2** in chloroform solution is interpreted in terms of an equilibrium between N(sp^3) co-ordinated and non-co-ordinated forms. New multinuclear (^1H, ^{19}F, ^{123}Te) NMR together with Raman data for related compounds containing Te $\cdots$ N(sp^2) interactions *e.g.* 2-$XTeC_6H_4CH{=}NC_6H_4Me$-*p* (X = F, Cl, Br or I) provide further support for the reality of the intramolecular co-ordination and ν(Te–N) is assigned in the region 206–219 cm^{-1}.

Compounds such as organotellurenyl halides, RTeX (X = halogen), are generally reactive but they may be kinetically stabilised if R is a sterically demanding group.[1] Alternatively, such compounds may be stabilised by reduction of the Lewis acidity of the central tellurium atom by intramolecular co-ordination.[2] Compounds in which intramolecular co-ordination has been particularly studied include those containing nitrogen donor atoms, *e.g.* 2-(phenylazophenyl-*C*^{1},*N*)-[3] and 2-(2-pyridyl)phenyl-tellurium[4] derivatives, *i.e.* sp^2 donor nitrogen atoms. Further examples of materials in this class include those containing azomethine groups, *e.g.* *o*-$C_6H_4CH{=}NR(TeX)$ moieties (X = halogen).[5] Far fewer examples of intramolecular co-ordination of tellurium to sp^3 nitrogen atoms are found in the literature, indeed to date only two[6,7] have been structurally characterised.

This paper brings together some new data (multinuclear NMR and Raman) for a range of azomethine derivatives of tellurium and also explores the nature of products arising from the reduction of the azomethine linkage to an amine (CH_2NHR), resulting in intramolecular co-ordination to an sp^3 nitrogen atom.

Experimental and Results

Synthesis of Organotellurium Compounds (*see Scheme* 1).—*2-Bromotelluro-*N*-(*p*-tolyl)benzylamine* **2**. A suspension of [2-(*p*-tolyliminomethyl)phenyl-*C*^{1},*N*]tellurium(IV) tribromide **1** (2.8 g, 5 mmol) in absolute ethanol (60 cm^3) was treated dropwise under argon with a solution of $NaBH_4$ (0.57 g, 15 mmol) in absolute ethanol (40 cm^3). Following an exothermic reaction, the resulting pale orange solution was stirred at room temperature for 1 h, filtered, and taken to dryness on a rotatory evaporator. The solid residue was extracted with hot chloroform (50 cm^3), filtered, and diluted with hexane to the point of 'muddiness'. Following filtration and cooling red crystals were formed. Yield 1.17 g (62%), m.p. 115 °C (from chloroform–hexane) (Found: C, 43.2; H, 3.65; N, 3.40. $C_{14}H_{14}BrNTe$ requires C, 41.6; H, 3.45; N, 3.45%).

A similar experiment starting with the Schiff base **3** formed by condensation of 2-trichlorotellurobenzaldehyde[8] and 2,4,6-tri-*tert*-butylaniline gave, following work-up, [2-(2,4,6-tri-*tert*-butylphenyliminomethyl)phenyl-*C*^{1},*N*]tellurium(II) chloride **4**, m.p. 235 °C (Found: C, 58.0; H, 6.60; N, 2.70. $C_{25}H_{34}ClNTe$ requires C, 58.6; H, 6.65; N, 2.75%).

Further reactions of compound 1 *with tetrahydridoborate.* A suspension of compound **1** (4.22 g, 7.5 mmol) in benzene (40 cm^3) was treated dropwise with a solution of $NaBH_4$ (0.76 g, 20 mmol) in ethanol (20 cm^3). The mixture was heated under reflux for 30 min and water (20 cm^3) was added. The organic layer was separated and dried ($CaCl_2$), then evaporated to two thirds of the original volume. Hexane (5 cm^3) was added and, following filtration and cooling to room temperature, brownish red crystals of compound **5** were formed. The solid was filtered off and washed with hexane. Yield 1.41 g (58%), m.p. 136 °C; ^1H NMR ($CDCl_3$): δ 3.82 (1 H, t, NH) and 4.37 (2 H, d, CH_2). IR: 3414 and 3326 cm^{-1} [ν(NH)] (Found: C, 52.0; H, 4.40; N, 4.15. $C_{28}H_{28}N_2Te_2$ requires C, 51.9; H, 4.35; N, 4.35%).

Compound **5** (0.55 g, 0.84 mmol) in chloroform (10 cm^3) was treated dropwise with a solution of SO_2Cl_2 (0.2 cm^3, 2.52 mmol) in chloroform (5 cm^3). The red solution became pale yellow and a copious deposition of pale yellow plate-like crystals occurred after 3 min. The solid, compound **6**, was filtered off, washed with hexane and dried. Yield 0.6 g, 90%, m.p. 196 °C. ^1H NMR [$(CD_3)_2SO$]: δ 2.29 (CH_3, 3 H, s), 5.08 (CH_2, 2 H, s) and 7.1–8.43 (aromatic, 8 H, m).

Compound **6** (0.5 g, 1.2 mmol) was suspended in refluxing triethylamine during 40 min. The amine was removed on a

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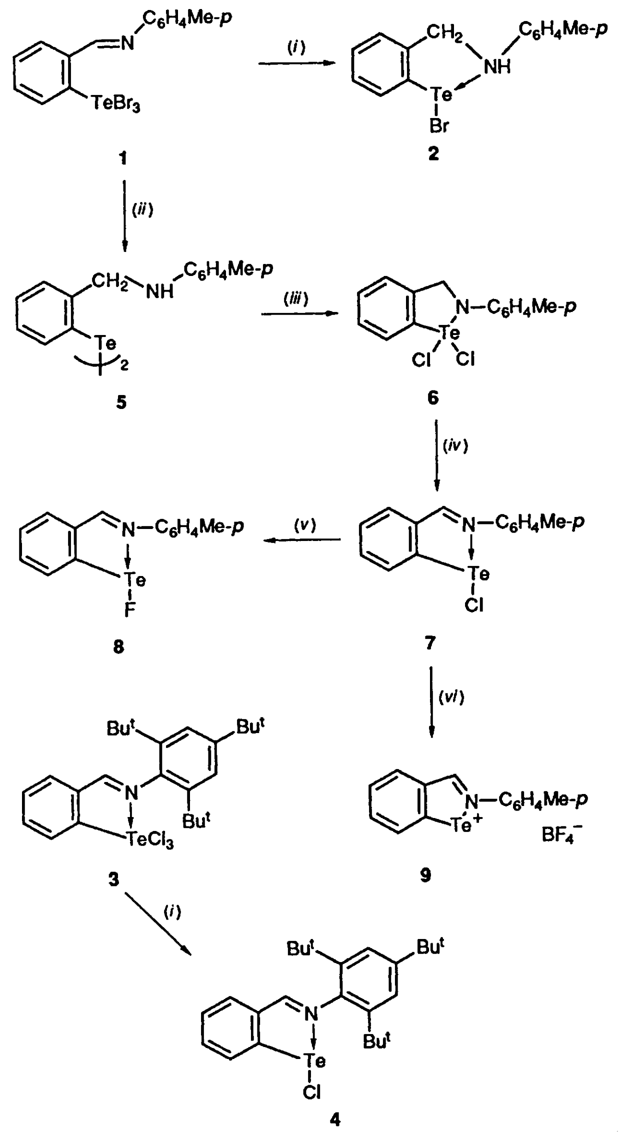
* *Supplementary data available:* see Instructions for Authors, *J. Chem. Soc., Dalton Trans.*, 1993, Issue 1, pp. xxiii–xxviii.



Scheme 1 (i) EtOH, BH_4^-, Ar; (*ii*) C_6H_6, BH_4^-, EtOH–water; (*iii*) SO_2Cl_2; (*iv*) NEt_3; (*v*) AgF; (*vi*) Me_2CO, $AgBF_4$

rotatory evaporator and the solid residue was dissolved in chloroform (10 cm^3) and diluted with hexane (5 cm^3). Yellow crystals were obtained of the previously known [2-*p*-tolyliminomethyl)phenyl-C^1,*N*]tellurium(II) chloride **7**,[9] yield 0.22 g (51%), m.p. 178 °C (lit.,[5b] 180 °C). ^1H NMR ($CDCl_3$): δ 2.39 (CH_3, 3 H, s), 7.19–8.67 (aromatic, 8 H, m) and 9.27 (CH=, 1 H, s).

Reactions of [2-(p-*tolyliminomethyl*)*phenyl*]*tellurium*(II) *chloride or bromide with silver*(I) *salts*. (*a*) Silver(I) fluoride (0.64 g, 5 mmol) in HPLC-grade acetone (40 cm^3) was poured into a solution of compound **2** (2.0 g, 5 mmol). A cloudy solution formed which on stirring at room temperature for 40 min became clear with the settlement of a precipitate of AgBr. The solution was filtered and acetone (*ca.* 50 cm^3) was removed on a rotatory evaporator; the remaining solution was stored overnight in a refrigerator at +5 °C. The precipitate of [2-(p-*tolyliminomethyl*)*phenyl*]*tellurium*(II) *fluoride* **8** which had formed was filtered off, washed with hexane and dried. Yield 78%, m.p. 154 °C (Found: C, 47.5; H, 3.65; N, 4.15. $C_{14}H_{12}FNTe$ requires C, 49.3; H, 3.50; N, 4.10%).

(*b*) A solution of compound **7** (5 g, 14 mmol) in HPLC-grade acetone (150 cm^3) was treated dropwise with a solution of silver(I) tetrafluoroborate (2.73 g, 14 mmol) in dry acetone (40 cm^3). The mixture was stirred at room temperature for 1 h until the initially cloudy solution became clear with the precipitate of AgCl well separated. The mixture was filtered and the filtrate concentrated to 50 cm^3 on a rotatory evaporator. Dilution with diethyl ether (90 cm^3) afforded a yellow-orange oil which crystallised after 10 h at +5 °C. The crystals of N-p-*tolylbenzoisotellurazolium tetrafluoroborate* **9** were filtered off, washed with hexane, and dried. Yield 65%, m.p. 129–130 °C. The product was similar to the known perchlorate salt.[10]

Benzoisotellurazole. This compound was prepared by the method of Weber *et al.*[11] The ^{15}N-enriched species was prepared by the substitution of $^{15}NH_3$ for ammonia in the preparative procedure. The m.p. observed (154–160 °C, not sharp) differed from the literature value[10] (173 °C), however the ^1H NMR spectra for both the ^{14}N and ^{15}N species suggested the compounds were pure (Found C, 36.0; H, 2.25; N, 5.80. C_7H_5NTe requires C, 36.4; H, 2.20; N, 6.05%).

o-*Tellurated benzaldehydes.* *o*-Bromotellurobenzaldehyde was prepared by the method of Piette and Renson[8] (Found: C, 27.1; H, 1.80. C_7H_5BrOTe requires C, 26.9; H, 1.60%). This material was converted into the tribromide *o*-(Br_3Te)-C_6H_4CHO, m.p. 214 °C. *o*-Dibromo(butyl)tellurobenzaldehyde *o*-(Br_2BuTe)C_6H_4CHO, m.p. 116–119 °C, was prepared by bromination of *o*-butyltellurobenzaldehyde.[12]

Physical Measurements.—Proton (300.133), ^{13}C (75.469), ^{15}N (30.423), ^{19}F (282.374), ^{123}Te (78.580) and ^{125}Te (94.735 MHz) NMR spectra were obtained at the indicated frequencies with a Bruker AC300 spectrometer. Chemical shifts are cited with respect to $SiMe_4$ (^1H and ^{13}C), $NaNO_3$ (^{15}N), NaF (^{19}F) and Me_2Te (^{123}Te, ^{125}Te). Infrared spectra were obtained for KBr discs with a Perkin Elmer 1710 FTIR instrument, Raman spectra on a Perkin Elmer FT-Raman 1700X spectrometer using a Nd-YAG laser (1064 nm) and an InGaAs NIR detector cooled to 77 K from solids as powders pressed into a cup sample holder. Mass spectral data were obtained from the SERC Mass Spectrometry Service Centre, Swansea.

Structural and X-Ray Crystallographic Investigations.—An air-stable yellow crystal of compound **2** was mounted on an Enraf-Nonius CAD-4 diffractometer and data were collected at room temperature; cell dimensions and intensities were measured by ω–2θ scans with graphite-monochromated Mo-Kα radiation.

Crystal data. $C_{14}H_{14}BrNTe$, M_r = 403.8, monoclinic, space group $P2_1/n$, a = 11.010(4), b = 9.231(2), c = 14.862(7) Å, β = 110.80(4)°, U = 1412.0 Å^3, Z = 4, D_c = 1.899 g cm^{-3}, $F(000)$ = 768, μ(Mo-Kα) = 5.15 mm^{-1}, λ = 0.710 69 Å.

2491 Reflections were scanned in the range $2 < \theta < 26°$ and of these 1809 were independent (R_{int} 0.047) and 1180 having $I > 2.5\sigma(I)$ were considered observed and used in the analysis. Three standard reflections measured every 2 h showed no significant variation in intensity.

The structure was determined by Patterson and Fourier methods and refined by least squares using anisotropic thermal parameters for non-hydrogen atoms. Hydrogen atoms were placed in calculated positions [d(C–H) 1.08 Å] riding on their respective bonding atoms. Weights, $w = 1/[\sigma^2(F) + 0.0001F^2]$, were used in the least-squares refinement and an empirical absorption correction[13] was applied (maximum and minimum transmission factors 0.71 and 0.49, respectively). The calculations were terminated when all shift/e.s.d. ratios were <0.1 and R = 0.0533, R' = 0.0692 for 1178 observed reflections. The residual electron density in a final difference map was within the range −1.18 to +0.79 e Å^{-3}. Two reflections, 002 and 101 which are affected by extinction, were removed from the final refinement cycles.

Computations were carried out on the University of Birmingham IBM 3090 computer with the SHELXS 86,[14] SHELX 76[15] and DIFABS[13] programs. The molecular diagram (Fig. 1) was drawn using PLUTO.[16] Fractional atomic coordinates are given in Table 1 and bond lengths and angles in Table 2.

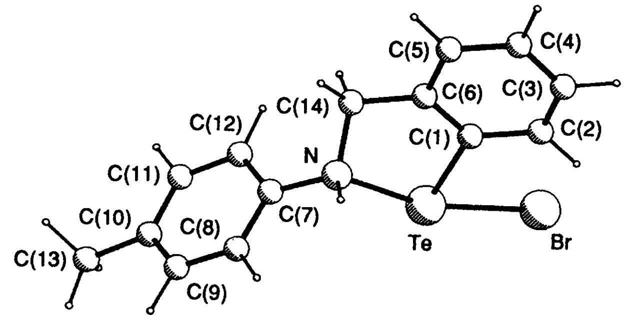


Fig. 1 The molecular structure of 2-bromotelluro-*N*-(*p*-tolyl)benzylamine

Table 1 Fractional atomic coordinates ($\times 10^4$) with estimated standard deviations (e.s.d.s) in parentheses for compound **2**

Atom	*x*	*y*	*z*
Te	2230(1)	441(1)	2269(1)
Br	605(3)	1149(3)	3164(2)
N	3190(11)	−444(15)	1176(9)
C(1)	941(13)	−1189(17)	1458(10)
C(2)	38(15)	−1921(19)	1766(12)
C(3)	−710(16)	−2992(19)	1193(12)
C(4)	−608(16)	−3340(20)	329(12)
C(5)	281(14)	−2610(19)	22(11)
C(6)	1068(13)	−1516(19)	593(10)
C(7)	4165(13)	546(22)	1076(10)
C(8)	5481(15)	229(20)	1557(11)
C(9)	6399(16)	1230(24)	1531(13)
C(10)	6098(14)	2501(23)	1072(11)
C(11)	4837(17)	2741(20)	565(13)
C(12)	3852(17)	1818(23)	549(16)
C(13)	7097(17)	3611(22)	1116(13)
C(14)	2024(14)	−694(20)	290(11)

Table 2 Bond lengths (Å) and bond angles (°) with e.s.d.s in parentheses

Te–Br	2.663(3)	C(5)–C(6)	1.404(21)
Te···N	2.375(13)	C(6)–C(14)	1.491(20)
Te–C(1)	2.125(16)	C(7)–C(8)	1.400(20)
N–C(7)	1.457(20)	C(7)–C(12)	1.386(24)
N–C(14)	1.495(18)	C(8)–C(9)	1.380(23)
C(1)–C(2)	1.406(20)	C(9)–C(10)	1.339(23)
C(1)–C(6)	1.375(19)	C(10)–C(11)	1.342(21)
C(2)–C(3)	1.372(22)	C(10)–C(13)	1.488(23)
C(3)–C(4)	1.368(22)	C(11)–C(12)	1.372(25)
C(4)–C(5)	1.391(23)		

Br–Te–N	165.3(3)	C(1)–C(6)–C(14)	119.2(14)
Br–Te–C(1)	91.5(4)	C(5)–C(6)–C(14)	122.3(14)
N–Te–C(1)	74.9(5)	N–C(7)–C(8)	118.9(16)
Te–N–C(7)	112.2(10)	N–C(7)–C(12)	123.0(14)
Te–N–C(14)	101.8(8)	C(8)–C(7)–C(12)	118.1(16)
C(7)–N–C(14)	116.1(11)	C(7)–C(8)–C(9)	118.8(17)
Te–C(1)–C(2)	124.3(12)	C(8)–C(9)–C(10)	123.4(17)
Te–C(1)–C(6)	114.6(11)	C(9)–C(10)–C(11)	116.8(16)
C(2)–C(1)–C(6)	121.1(15)	C(9)–C(10)–C(13)	122.4(16)
C(1)–C(2)–C(3)	118.9(15)	C(11)–C(10)–C(13)	120.8(18)
C(2)–C(3)–C(4)	121.4(16)	C(10)–C(11)–C(12)	124.1(18)
C(3)–C(4)–C(5)	119.7(16)	C(7)–C(12)–C(11)	118.7(16)
C(4)–C(5)–C(6)	120.4(16)	N–C(14)–C(6)	106.8(12)
C(1)–C(6)–C(5)	118.5(14)		

Additional material available from the Cambridge Crystallographic Data Centre comprises H-atom coordinates and thermal parameters.

Table 3 Variable-temperature ^{1}H and single-temperature ^{125}Te NMR data for compound **2** (see Fig. 2)

$\delta(^1H)^a$				
NH	H_α	CH_2	$\delta(^{125}Te)^b$	*T*/°C
5.17 (br)^c	7.98, 7.95 (d)	4.54, 4.52 (d)	1511, 1407	+25
5.65 (t), 5.55 (t)	$\left.\begin{matrix}7.93\\7.90\end{matrix}\right\}d\ \left.\begin{matrix}7.88\\7.85\end{matrix}\right\}d$	4.51, 4.49 (d)		−10
6.03 (t), 5.91 (t) (*J* = 7 Hz) 1:2.45^e	$\left.\begin{matrix}7.89\\7.87\end{matrix}\right\}d\ \left.\begin{matrix}7.85\\7.83\end{matrix}\right\}d$ *J* = 6.84, 7.80 Hz 1.89:1^e	4.48 (m)^d		−40

[a] In ppm relative to $SiMe_4$. [b] In ppm relative to Me_2Te. [c] Removed in D_2O; δ 4.98 at 50 °C. [d] $\delta(^{13}C)$ 57.49 and 58.86. [e] Ratio of more intense to less intense.

Other physical data are tabulated. Thus Table 3 presents variable-temperature NMR studies of compound **2**, Table 4 summarises multinuclear NMR studies of other compounds and Table 5 lists data selected from Raman studies of a range of organotellurium compounds.

Discussion

Scheme 1 illustrates the new reactions and syntheses which constitute the background to this contribution. It is known that tetrahydroborate can reduce centres of unsaturation in organotellurium compounds concurrently with reduction of the tellurium atom. Thus, for example, treatment of 2-(phenylazophenyl-*C*^{1},*N*)tellurium trichloride with an excess of BH_4^- affords di(*o*-aminophenyl) ditelluride.[3] It is therefore not unexpected that treatment of compound **1** should give **2** or **5** depending upon the conditions. That the azomethine linkage has been reduced was confirmed by IR, NMR spectroscopy, and in the case of **2** by X-ray crystallography (see below). Additional chemical support for the reduction of CH=NR to CH_2NHR is provided by the sequence **5** $\longrightarrow$ **6** $\longrightarrow$ **7** in Scheme 1 where the dehydrochlorination of **6** gives the known **7**.[9,10] It was interesting that the reduction of the azomethine group could be inhibited by substitution of the N atom with a sterically demanding group *e.g.* 2,4,6-tri-*tert*-butylphenyl as in **3** which on reduction with BH_4^- gives **4** an analogue of **7** (IR, NMR spectroscopy). The straightforward conversion of **7** into the fluoro-derivative **8** provides a material suitable for multinuclear NMR studies (see below) and **9** (the perchlorate salt of which is known[10]) provides a candidate for Raman study. In addition, a range of other compounds was prepared for Raman work (see Experimental section and Table 5).

Structural Studies.—A fast atom bombardment mass spectrum of compound **2** revealed a significant number of clusters with *m*/*z* values considerably in excess of that of the parent ion and with isotopic patterns consistent with the presence of two tellurium atoms, *e.g.* $R_2Te_2^+$, $R_2Te_2Br^+$ and $R_2Te_2Br_2^+$ (R = *o*-$C_6H_4CH_2NHC_6H_4Me$-*p*). The observation of 'Te_2' fragments has been successfully correlated in the past[19] with association in the solid state, but this is not always the case. 2-(2-Pyridyl)phenyltellurium(II) bromide gave an extremely complex mass spectrum,[20] but its crystal structure with six monomeric species in the unit cell showed no significant intermolecular contacts.[21] Thus crystallographic studies were undertaken for **2** to provide further data on sp^3 N$\rightarrow$Te intramolecular interactions rather than in any expectation of observing significant intermolecular contacts.

The molecular structure of compound **2** is shown in Fig. 1. The tellurium atom is bonded to a carbon atom and a bromine atom, Te–C(1) 2.125(16) and Te–Br 2.663(3) Å, and shows a Te···N separation of 2.375(13) Å. These distances may be compared with those found[5b] in the related [2-(phenylamino-

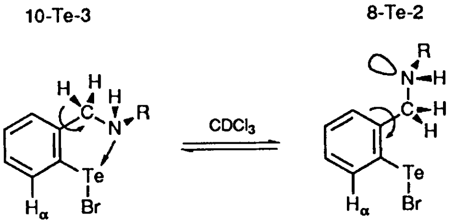


Fig. 2 N-Co-ordinated and non-co-ordinated forms of compound **2** (see Scheme 1 and Table 3); R = C_6H_4Me-*p*

methyl)phenyl]tellurium(II) chloride where the Te $\cdots$ N distance is 0.15 Å shorter than in **2**. Since other data,[2,21] show the *trans* influences of Cl^- and Br^- to be the same in RTeX (X = Cl or Br), the significantly longer Te $\cdots$ N in **2** seems to arise from the hybridisation state of the N atom (sp^3), since typical (sp^2)N $\cdots$ Te distances are around 2.24 Å.[2] Two cases of (sp^3)N $\cdots$ Te interactions in the literature have distances close to the value reported here, *i.e.* 2.472, 2.424 Å in $[Te_2(\mu\text{-}O)_2Cl_2L_2]$[7] (HL = 1,4,7,10-tetraazacyclododecane) and 2.42 Å in [2-(dimethylaminomethyl)phenyl]tellurium(IV) tribromide.[6]

The Te–C(1) bond length compares with the mean value of Te–C (aromatic) of 2.166 Å given by Allen *et al.*[22] and with the 2.111(6) Å observed for Te–C in 2-(2′-pyridyl)phenyltellurium(II) bromide.[21] The Te–Br distance is characteristic of such distances when the Br atom is not involved in any secondary interactions and is intermediate between the 2.63 Å found for [2-(dimethylaminomethyl)phenyl]tellurium(IV) tribromide[6] and the 2.71(1) Å for 2-(2′-pyridyl)phenyltellurium(II) bromide.[21]

The Te $\cdots$ N interaction may be considered significant since the resulting five-membered ring has the characteristic envelope formation. The Te, C(1), C(6) and C(14) atoms are coplanar to within ±0.013 Å and the nitrogen atom is displaced by 0.84 Å from the plane of the other four atoms. The phenyl ring with atoms C(7)–C(12) is orientated at an angle of 97° to the mean plane of the five-membered ring.

The ^{125}Te NMR spectrum of compound **2** in $CDCl_3$ solution shows two resonances separated by 104 ppm. No ^{123}Te–^{125}Te coupling is seen (^{123}Te spectrum), hence the resonances are likely to arise from distinct molecular species. The ^{1}H NMR spectra at 25 °C and at room temperature show a broad peak for the NH resonance which is removed on shaking the solution with D_2O. A doublet is seen for the proton α to tellurium on the aromatic ring (H_α, Table 3) and a further doublet is assigned to the CH_2 protons. On cooling to −10 °C (and ultimately to −40 °C) the NH proton gives two triplets [$J(^1H\text{–}^{14}N) \approx 7$ Hz] and the H_α resonance appears as a pair of well resolved doublets. The behaviour of the methylene proton resonance is more complex with a multiplet structure occurring at −10, −30 and −40 °C. This arises from overlapping triplets of doublets involving coupling to ^{14}N and ^{1}H. The ^{13}C NMR spectrum shows distinct signals for two CH_2 environments. There is little doubt that an equilibrium exists in $CDCl_3$ solution between two forms of **2**, the rate of interchange at room temperature being slow on the ^{125}Te NMR time-scale and fast on the ^{1}H NMR time-scale. The most compelling interpretation is that the two forms have co-ordinated and non-co-ordinated sp^3 N atoms as depicted on Fig. 2. Such phenomena have been observed for sp^2 N–Te interactions but only in strongly donor solvents such as dimethyl sulfoxide (dmso)[23] where the solvent replaces the co-ordinated nitrogen atom resulting in a small ^{125}Te chemical shift difference between the species. In this case, a very much weaker $CDCl_3 \cdots$ Te interaction gives an effective equilibrium (1) where the *N*-X-*L* classification is used[24]

$$\text{10-Te-3 tellurane} \rightleftharpoons \text{8-Te-2 tellurane} \qquad (1)$$

(*N* number electrons around central atom; X = S, Se or Te; *L* = number of ligands bound to central atom). This accounts for the more dramatic ^{125}Te chemical shift difference of 104 ppm with the more dominant species containing co-ordinated nitrogen having the more shielded shift (δ 1407), *i.e.* the 10-Te-3 tellurane. It is of interest that Feikus and Laur[25] have recently reported on the surprising stability of RTeCl (R = alkyl) in solution in non-co-ordinating solvents, *i.e.* further examples of 8-Te-2 telluranes.

Further NMR Studies.—Although a considerable body of structural data is now available for compounds containing intramolecular Te $\cdots$ N interactions,[2] relatively little spectroscopic data has been published for such systems other than as required for characterisation. Some work has been done with ^{15}N-enriched compounds to determine $J(^{15}N\text{–}^{125}Te)$.[10] Since the same intermediate was involved as for other preparations in this work, the opportunity was taken to synthesise ^{15}N-enriched benzoisotellurazole. This allowed measurement of $J(^{15}N\text{–}^{125}Te)$ (Table 4) for a molecule with a covalent Te–N bond and a value of 157 Hz was recorded. This is higher than other values in the literature[10] some of which are cited in Table 4 and that fact may reflect a greater degree of s character in the tellurium bonding orbital of the tellurazole than when co-ordinate bonds are involved. In general Te $\cdots$ N interactions are slightly shorter ($\approx$2.7 Å[2]) in tellurides *e.g.* $RTeBu^n$,[17] R_2Te[18] (R = *o*-C_6H_4-CH=NPh) than for ditellurides (*e.g.* $\approx$2.9 Å[5a]), thus for the co-ordinate bond there seems to be no obvious relationship between bond length (strength?) and the magnitude of $J(^{15}N\text{–}^{125}Te)$.

That intramolecular co-ordination (Te $\cdots$ N) provides an effective pathway for spin–spin coupling is also illustrated by a study of compound **8**. The advantage of fluoro-compounds is that this halogen resonace may be monitored, thus in addition to the major coupling to both magnetic isotopes of tellurium, *e.g.* $J(^{19}F\text{–}^{123}Te)$ = 1346.5 Hz, a remote coupling to the methine proton of 13.33 Hz is seen in both the ^{19}F and ^{1}H NMR spectra. Coupling of the methine proton to tellurium is also observed. The tellurium atom in the fluoro-compound is considerably more deshielded (δ 1634) than those in similar chloro-, bromo-, and iodo-compounds [*e.g.* $ClTeC_6H_4CH$=NPh, δ(^{125}Te) 1355[10]]. The difference may be attributed to the enhanced electronegativity of fluorine which will favour removal of non-bonded electron density to the 'axial' atoms.

Raman Studies.—It was recently suggested[26] that the excellent quality of routine Raman spectra given by organotellurium compounds made it the method of choice for studies of vibrational spectra. The compounds studied in this paper further underline that point. The assignments of Table 5 for ν(TeX) (X = halide) are easy to make and the data for the trihalides are quite comparable to those for similar derivatives of 2-phenylpyridine and azobenzene.[26] For compound **8** ν(TeF) is at 413 cm^{-1}; to our knowledge this is the first assignment of ν(TeF) for such a compound. The corresponding chloride shows ν(TeCl) at 236 cm^{-1}, somewhat higher than the values for the corresponding 2-phenylpyridine and azobenzene derivatives ($\approx$220 cm^{-1}).[26] However, in this case another very strong band is located at 214 cm^{-1} whereas the fluoride, bromide and iodide have but a medium-intensity band in that region (Table 5). It is proposed that this band is ν(TeN) and that the similarity in energy of ν(TeCl) and ν(TeN) results in strong coupling of the vibrations and an enhancement of the intensity of ν(TeN) as well as, probably, shifts from the 'natural' frequencies. This fortuitous circumstance allows more confident assignment of this vibration than has previously been possible. Indeed, a tentative assignment of ν(TeN) has only been made for (2-phenylazophenyl-C^1,*N*)tellurium(II) chloride at 247 cm^{-1}. The higher frequency for the azobenzene derivative may reflect the fact that the average Te–N bond length is $\approx$0.08 Å shorter[2] than for **7**. The observed range for ν(TeN) in Table 5 reflects the conclusions of crystallographic studies that the co-ordinate interaction is real but relatively weak. The above result has also

Table 4 New multinuclear NMR data for compounds with tellurium–nitrogen bonds

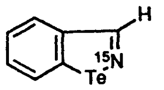
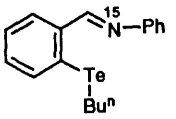
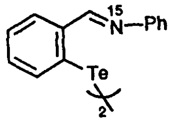
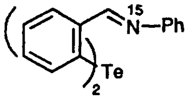
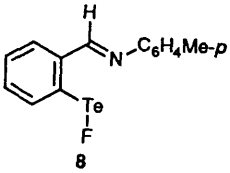
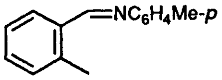
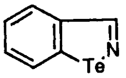
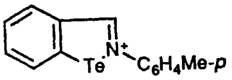
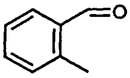
Compound	Coupling constants (Hz)	Chemical shift	Ref.
	$J(^1H-^{15}N) = 13.37$ $J(^{15}N-^{125}Te) = 157$	$\delta(^1H$ *vs.* $SiMe_4)$ 10.30 $\delta(^{15}N$ *vs.* $NaNO_3)$ 0.107 $\delta(^{125}Te$ *vs.* $Me_2Te)$ 1589	This work
	$J(^{15}N-^{125}Te) = 101.4$		10, 17
	$J(^{15}N-^{125}Te) = 135.3$		10, 17
	$J(^{15}N-^{125}Te) = 61$		10, 18
 8	$J(^{123}Te-^{19}F) = 1346.5$ $J(^{125}Te-^{19}F) = 1617.8$ $J(^{19}F-^1H) = 13.33$ $J(^{125}Te-^1H) = 16.5$	$\delta(^{123}Te$ *vs.* $Me_2Te)$ 1634.8 $\delta(^{125}Te$ *vs.* $Me_2Te)$ 1633.5 $\delta(^{19}F$ *vs.* NaF) −68.57 $\delta(^1H$ *vs.* $SiMe_4)$ 9.414	This work

Table 5 Selected Raman data for organotellurium compounds together with some ^1H NMR data

	$\Delta\nu/cm^{-1}$			$\delta(CH=Y)$
Compound	Te–X	Te←N	C=O[ν(C=O), IR]	(Y = NR′ or O)*
R = 				
$RTeCl_3$	291, 274, 270			
$RTeBr_3$	196, 179, 175			
RTeF	413s	219m		9.196
RTeCl	236s	214s		
RTeBr	161s	214m		
RTeI		206m		
		249m		
		206m		
R′ = 				
$R'TeBr_3$	219, 215		1607 (1604)	10.244
R′TeBr	181		1587 (1579)	10.527
$R'(Bu^n)TeBr_2$	166 (br)		1690 (1691) 1673 (1671)	10.11

s = Strong, m = medium. * Relative to $SiMe_4$. In $CDCl_3$.

led to tentative assignments of ν(TeN) for benzoisotellurazole and for compound **9** (Table 5).

Given that 2-tellurated benzaldehydes were required as synthetic intermediates, new data for those materials have been appended to Table 5. Little comment is required beyond the remark that the Lewis acidity of the tellurium(II) bromide appears greater than that of the tellurium(IV) tribromide, a fact reflected both by the position of ν(C=O) and the greater deshielding of the aldehyde proton.

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