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THE SYNTHESIS AND SPECTROSCOPIC EXAMINATION OF TELLURONIUM SALTS BASED ON THE 1-ORGANO-3,4-BENZO-1-TELLURACYCLOPENTANE CATION

ALI Z. AL-RUBAIE, WILLIAM R. MCWHINNIE,
Department of Chemistry, University of Aston in Birmingham, Birmingham B4 7ET (Great Britain)

PIERRE GRANGER,
I.U.T. de Rouen (Universite de Rouen), BP 47 76130 Mont Saint Aignan (France)

and STELLA CHAPELLE
Service Commun. de RMN de Rouen (France)

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Summary

The syntheses of a new range of telluronium salts based on the 1-organo-3,4-benzo-1-telluracyclopentane cation are reported (C_8H_8TeRX: R = CH_3, CH_2CH_3, X = I; R = CH_3, X = PhCOO; R = CH_3, X = ClO_4; R = CH_3, X = BPh_4; R = Ph, X = BPh_4; R = CH_2Ph, $CH_2CH{=}CH_2$, CH_2COPh, X = Br.) Solution studies using ^1H, ^{13}C and ^{125}Te NMR spectroscopy in conjunction with conductivity and molecular weight measurements show the salts to be associated via weak "ionic" bonds in solvents of lower polarity such as chloroform but to be more ionic and strongly solvated in DMSO. Solvents such as DMF provide an intermediate and more complex situation.

Mass spectra indicate that association can extend to the gas phase and some novel features in the spectra are discussed. Infrared studies indicate polymorphism for 1-methyl-3,4-benzo-1-telluracyclopentane perchlorate with one form containing perchlorate ions interacting with tellurium.

Introduction

We recently published two papers [1,2] describing a series of methyldiphenyltelluronium salts. It was observed that these materials, $(CH_3)Ph_2TeX$, reductively eliminated CH_3X in solvents such as chloroform with a rate which was dependent on the anionic group, X. Some evidence for the involvement of

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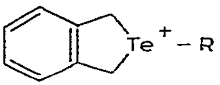
free radicals was obtained from spin trapping experiments applied to both the reductive elimination and also to the reverse reaction, oxidative addition of CH_3X to Ph_2Te [2]. Accurate solution molecular weight data were difficult to obtain due to decomposition of the salts, however in the case of $(CH_3)Ph_2Te(OOCPh)$ [2,3], which undergoes reductive elimination of methyl benzoate only very slowly, it was shown that the molecular weight approached that of a dimer. Thus, for weakly polar solvents, the dominant solution species is unlikely to be a monomeric "covalent" form of the "salt", although the reductive elimination may occur from the monomer produced by dissociation of an oligomer.

It is now well established from crystallographic studies that association of telluronium salts is common. It may be to dimers [4], to tetramers [5], to dimers and tetramers [6] and to more extensive arrays [7]. The association is usually via long secondary bonds showing a high degree of ionic character. Only in one instance to date, $(CH_3)_3TeBPh_4$, can the structure be said to be based on a true triorganotelluronium cation [8]. That this tendency to association should extend to solutions in solvents of lowish polarity is not surprising, however the contention that such solution association occurs is based on the somewhat slender evidence referenced above. Ziolo and Titus [9] have however referred to data for a range of triphenyltelluronium salts which suggest these to be associated in weakly polar or non-polar solvents.

In this paper we report the synthesis, solution properties and some solid state data for a range of telluronium salts which are stable to decomposition via reductive elimination. A suitable series proved to be that based on the 1-organo-3,4-benzo-1-telluracyclopentane cation (I).



(I)

Experimental and results

(a) Synthesis

1,1′-Diiodo-3,4-benzo-1-telluracyclopentane. This compound was prepared following the literature [10]. The product was recrystallised from dimethylformamide (DMF) to m.p. 226—228°C (α) and 223—224°C (β) (lit. [10] 225°C (α), 222°C (β)). Found: C, 19.7; H, 1.70. $C_8H_8TeI_2$ calcd.: C, 19.8; H, 1.66%.

3,4-Benzo-1-telluracyclopentane. A boiling methanolic solution of 1,1′-diiodo-3,4-benzo-1-telluracyclopentane was treated with sodium borohydride until the orange colour just disappeared. The solution was filtered, poured into water (1000 cm^3) and extracted several times with diethyl ether. The combined ether extracts were dried over $CaCl_2$ and taken to dryness on a rotatory film evaporator. The residue was recrystallised from petroleum ether (60/80) to afford yellow plates m.p. 43—44°C (lit. [11] 44—46°C) Found: C, 41.4; H, 3.50. C_8H_8Te calcd.: C, 41.4; H, 3.48%. During the course of this work Zumbulyadis and Gysling prepared this compound by hydrazine reduction of the diiodide [12].

1-Methyl-1-iodo-3,4-benzo-1-telluracyclopentane. Excess (6 cm^3) freshly distilled iodomethane together with 3,4-benzo-1-telluracyclopentane (2.32 g, 0.01 mol) were placed in a flask flushed with dry dinitrogen. An exothermic reaction took place giving pale yellow crystals which, on recrystallisation from a mixture of ethanol and water gave bright white crystals which decomposed at 190—192°C. Found: C, 28.9; H, 2.90. $C_9H_{11}TeI$ calcd.: C, 28.9; H, 2.79%.

The following salts were then prepared by oxidative addition of the appropriate halide under the above conditions.

1-Ethyl-1-iodo-3,4-benzo-1-telluracyclopentane. The white precipitate formed after 2 h, m.p. 185—186°C (dec.). Found: C, 31.2; H, 3.60. $C_{10}H_{13}TeI$ calcd.: C, 31.0; H, 3.40%.

1-Allyl-1-bromo-3,4-benzo-1-telluracyclopentane. The white crystals melted with decomposition 166—168°C. Found: C, 37.2; H, 3.90. $C_{11}H_{13}TeBr$ calcd.: C, 37.5; H, 3.70%.

1-Benzyl-1-bromo-3,4-benzo-1-telluracyclopentane. White crystals m.p. 170—172°C (dec.). Found: C, 44.6; H, 3.90; Br, 20.4. $C_{15}H_{15}TeBr$ calcd.: C, 44.7; H, 3.80; Br, 19.8%.

1-Phenacyl-1-bromo-3,4-benzo-1-telluracyclopentane. 3,4-Benzo-1-telluracyclopentane (2.32 g; 0.01 mol) and phenacylbromide (2.0 g; 0.01 mol) were mixed and sufficient diethyl ether was added to dissolve the reactants. The flask was stoppered and left overnight. The deposited white solid was separated, washed with ether and dried over P_4O_{10}. Recrystallisation from ethanol/water (3/1) gave white crystals m.p. 166—168°C (dec.). Found: C, 44.7; H, 3.70; Br, 20.9. $C_{16}H_{15}BrOTe$ calcd.: C, 44.6; H, 3.49; Br, 18.7%.

1-Methyl-3,4-benzo-1-telluracyclopentane perchlorate. 1-Methyl-1-iodo-3,4-benzo-1-telluracyclopentane (0.37 g, 0.001 mol) dissolved in hot ethanol (20 cm^3) was added to an aqueous solution of silver perchlorate (0.21 g, 0.001 mol). The solution was stirred for 2 h, then heated for 15 min and filtered hot to remove silver iodide. The filtrate was allowed to evaporate at room temperature and the white material deposited was recrystallised from ethanol/water (4/1) to give white needles m.p. 179—182°C (dec.). Found: C, 29.9; H, 2.90. $C_9H_{11}ClO_4Te$ calcd.: C, 31.1; H, 3.20%.

1-Methyl-3,4-benzo-1-telluracyclopentane benzoate. This compound was initially prepared by Mallaki [13]. 1-Methyl-1-iodo-3,4-benzo-1-telluracyclopentane (1 g, 0.0025 mol) was treated with silver benzoate (0.57 g, 0.0025 mol) in distilled water (50 cm^3). The mixture was initially stirred at room temperature for 30 min, then heated under reflux for 2 h. The solution was filtered hot to remove silver iodide and the filtrate was allowed to evaporate slowly. The white product was collected, m.p. 155°C. Found: C, 51.6; H, 4.60. $C_{16}H_{16}O_2Te$ calcd.: C, 52.3; 4,36%.

1-Methyl-3,4-benzo-1-telluracyclopentane tetraphenylborate. A hot ethanolic solution of 1-methyl-1-iodo-3,4-benzo-1-telluracyclopentane (0.37 g, 0.001 mol) was treated with ethanolic sodium tetraphenylborate (0.34 g, 0.001 mol) to give a voluminous white precipitate. The mixture was stirred for 2 h and then boiled with stirring for 15 min. On cooling to room temperature, the settled solid was separated and washed with water and ethanol and dried in vacuo over P_4O_{10}. Recrystallisation from DMF/H_2O gave white crystals of m.p. 208°C (dec.). Found: C, 69.6; H, 5.20. $C_{33}H_{31}BTe$ calcd.: C, 70.0; H, 5.48%.

1-Phenyl-3,4-benzo-1-telluracyclopentane tetraphenylborate. A variation of the method recently reported by Ziolo et al. was used [14]. A mixture of 1,1'-diiodo-3,4-benzo-1-telluracyclopentane (2.42 g, 0.002 mol) with $NaBPh_4$ (3.42 g, 0.01 mol) in dry ethanol (100 cm^3) was placed in a round bottomed flask (250 cm^3) and heated to reflux with stirring for 3—4 h. The solution was filtered hot and crystals of $C_{32}H_{33}BTe$ collected in quantitative yield. The product was washed with water and methanol and recrystallised from water/DMF to m.p. 184°C (dec.). Found: C, 72.0; H, 5.20. $C_{38}H_{33}BTe$ calcd.: C, 72.6; H, 5.30%.

An attempt to prepare 1-methyl-1-fluoro-3,4-benzo-1-telluracyclopentane by treating the 1-iodo derivative with silver oxide, to remove the iodide as silver iodide, and subsequent treatment of the telluronium hydroxide with HF failed.

(b) Physical measurements

Infrared spectra were obtained as Nujol mulls or KBr discs in the range 4000—200 cm^{-1} using a Perkin—Elmer 457 spectrophotometer. ^1H NMR data were obtained with a Perkin—Elmer R14 instrument at 60 MHz using TMS as internal reference. ^{125}Te spectra were measured on a Bruker WH 90C spectrometer at 28.40 MHz in the Fourier mode. 90° pulses were used without waiting time since T_1 is below 2 sec. ^{13}C data were obtained on the same instrument at 22.63 MHz. The sample temperature was 26°C.

Conductivity data were measured with a standard bridge and a Mullard type E7591/B cell of cell constant 1.46. Molecular weight data were obtained using a Knauer Vapour Pressure Osmometer. Mass spectra were measured at 70 eV with an AEI MS9 instrument.

(c) Results

Some representative ^1H NMR data are gathered into Table 1. Generally the data are gathered for dimethyl sulphoxide (DMSO) solutions, but 1-methyl-1-iodo-3,4-benzo-1-telluracyclopentane was examined also in DMF and $CDCl_3$. All three solutions of the compound gave ^1H NMR spectra which were invariant over 30 h. No salt studied showed reductive elimination of alkyl or aryl halide. Table 2 contains some ^{13}C NMR data and ^{125}Te NMR data are presented in Table 3.

Molecular weight measurements (chloroform, 25°C) were made on 1-methyl-1-iodo- (and -1-benzoato)-3,4-benzo-1-telluracyclopentane: $C_8H_8Te(CH_3)I$ found: 742; calcd.: 373 (monomer), 746 (dimer). $C_8H_8Te(CH_3)(OOCPh)$: found: 731; calcd.: 367 (monomer), 734 (dimer).

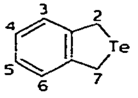
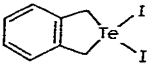
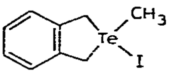
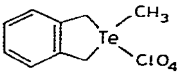
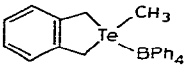
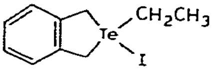
Conductivity data (DMSO and DMF) are given in Table 4. The measurements given relate to concentrations of 10^{-3} *M*, however, each compound in each solvent was studied as a function of concentration. Marked curvature was found for plots of Λ_M vs. $(\text{concentration})^{1/2}$ for DMF solutions, graphical data may be obtained in reference 15.

Table 5 contains infrared assignments for ν(Te—alkyl) for appropriate compounds. The most interesting feature observed in the infrared study was for 1-methyl-3,4-benzo-1-telluracyclopentane perchlorate. In a Nujol mull features typical of ionic perchlorate were observed at 1075 (s, br) ($\nu_{as}(ClO)$) and 628 cm^{-1} ($\delta(ClO)$). However, if the material is pressed into a KBr disc well resolved

TABLE 1

SOME ^{1}H NMR DATA FOR 3,4-BENZO-1-TELLURACYCLOPENTANE DERIVATIVES

(Data for all compounds prepared are in ref. 15)

Compound	Solvent	Chemical shifts (ppm); TMS = 0 ppm	$J(^1H—^{125}Te)$ (Hz)
	$CDCl_3$	H(2,7): 4.65(s); H(3,4,5,6): 7.15—7.3(m)	22.26 (CH_2)
	DMSO-d_6	H(2,7): 4.46(s); H(3,4,5,6) 7.05—7.2(m)	22.3 (CH_2)
	DMSO-d_6	H(2,7): 4.75(s); H(3,4,5,6) 7.2—7.4(m)	24.0
	$CDCl_3$	CH_3: 2.42(s); H(2,7): 4,28, 5.00 (J(HH) 15 Hz); H(3,4,5,6): 6.9—7.3(m)	24.6 (CH_3)
	DMSO-d_6	CH_3: 1.98(s); H(2,7): 3.96, 4.26, (J(HH) 15 Hz); H(3,4,5,6): 6.8—7.3(m)	24.0 (CH_3)
	DMF	CH_3: 2.25(s); H(2,7): 4.20, 4.60 (J(HH) 15 Hz); H(3,4,5,6): 7.2—7.45(m)	23.8 (CH_3)
	DMSO-d_6	CH_3: 1.98(s); H(2,7): 3.99, 4.29 (J(HH) 15 Hz); H(3,4,5,6): 7.0—7.5(m)	22.4 (CH_3)
	DMSO-d_6	CH_3: 2.05(s); H(2,7): 4.05, 4.28 (J(HH) 14.7 Hz); H(3,4,5,6): 6.8—7.2(m)	18.6 (CH_3)
	DMSO-d_6	CH_3: 1.26(t); CH_2: 2.72 (q); H(2,7): 4.07, 4.37 (J(HH) 15 Hz); H(3,4,5,6): 7.2—7.45(m)	18.0 (CH_2)

splitting of these features is observed: 1145, 1120, 1085 cm^{-1} (ν_{as}) and 630, 640 cm^{-1} (δ).

Mass spectroscopic data are condensed into Table 6. A more complete tabulation is located in reference 15. The information for $C_8H_8TeCH_2PhBr$ was obtained at 24 eV.

(continued on p. 294)

TABLE 2

^{13}C NMR DATA FOR 1-ALKYL-1-IODO-3,4-BENZO-1-TELLURACYCLOPENTANE

($\delta(^{13}C) \pm 0.1$ ppm internally referenced to TMS).

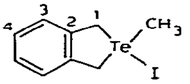
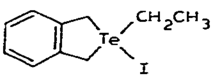
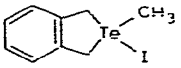
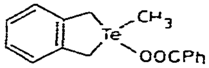
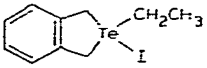
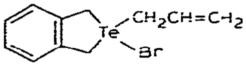
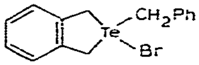
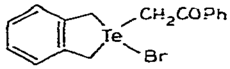
Compounds	Solvent	$\delta(^{13}C(1))$	$\delta(^{13}C(2))$	$\delta(^{13}C(3))$	$\delta(^{13}C(4))$	Other $\delta(^{13}C)$
	$CDCl_3$	36.7	138.4	127.9	130.1	7.1
	DMSO	34.4	138.7	126.6	129.1	5.6
	DMF	35.4	139.2	127.1	129.5	7.4
	$CDCl_3$	36.0	138.9	127.7	129.4	10.9, 21.9
	DMF	33.7	139.5	126.9	129.0	10.0, 19.8

TABLE 3

^{125}Te NMR DATA FOR 3,4-BENZO-1-TELLURACYCLOPENTANE DERIVATIVES (reference $(CH_3)_2Te$) [a]

Compound	Solvent	δ (^{125}Te) (ppm)
	$CDCl_3$	652.0
	DMSO	651.4
	DMF	657.2
	$CDCl_3$	687.0
		($\Delta\nu_{1/2}$ 36 Hz)
	$CDCl_3$	706.4
	DMSO	708.9
	DMSO	688.3
	DMSO	722.3
	DMSO	693.5
	DMF	680.1

[a] Spectra referenced to neat $(CH_3)_2Te$ using the substitution method: C. Brevarol and P. Granger, Handbook of High Resolution Multinuclear NMR, Wiley, N.Y., 1981. [b] C_8H_8Te, δ +268 ppm ($CDCl_3$); $C_8H_8TeI_2$, δ +829 ppm (DMF), both vs. $(CH_3)_2Te$ [12].

TABLE 4

CONDUCTIVITY DATA (10^{-3} *M* SOLUTIONS) FOR A SERIES OF 1-ORGANO-3,4-BENZO-1-TELLURACYCLOPENTANE TELLURONIUM SALTS: C_8H_8TeRX

R	X	Λ_M (DMSO) [a] (ohm^{-1} cm^2 mol^{-1})	Λ_M (DMF) [a] (ohm^{-1} cm^2 mol^{-1})
CH_3	I	32.6	64.0
CH_2CH_3	I	30.8	61.8
$CH_2CH=CH_2$	Br	33.6	61.2
CH_2Ph	Br	31.0	45.3
CH_2COPh	Br	—	32.1
CH_3	BPh_4	21.9	43.8
Ph	BPh_4	—	46.1

[a] $[(C_2H_5)_4N]Cl$: Λ_M 30 (DMSO); 80 (DMF) ohm^{-1} cm^2 mol^{-1}.

TABLE 5

ν(Te—R) (R = alkyl) FOR A RANGE OF 1-ALKYL-3,4-BENZO-1-TELLURACYCLOPENTANE-TELLURONIUM SALTS: C_8H_8TeRX

R	X	ν(Te—alkyl (cm^{-1})
CH_3	I	538
CH_3	ClO_4	540
CH_3	BPh_4	535
CD_3	I	500
CH_2CH_3	I	538
$CH_2CH{=}CH_2$	Br	535
CH_2Ph	Br	538

TABLE 6

MASS SPECTRA OF TELLURONIUM SALTS BASED ON 3,4-BENZO-1-TELLURACYCLOPENTANE (relative to ^{12}C, ^{1}H, ^{16}O, ^{81}Br, ^{127}I, ^{130}Te)

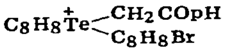
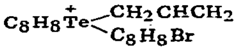
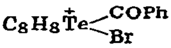
m/e	Possible ion	Relative intensity					
		R = CH_3 X = I	R = benzyl X = Br	R = CH_2CH_3 X = I	R = allyl X = Br	R = CH_2COPh X = Br	R = Ph X = BPh_4
630	$C_8H_8\overset{+}{Te}(Ph)$ BPh_4						4
538	 $C_8H_8\overset{+}{Te}{<}^{CH_2COpH}_{C_8H_8Br}$					4	
460	 $C_8H_8\overset{+}{Te}{<}^{CH_2CHCH_2}_{C_8H_8Br}$				3		
434	 $C_8H_8\overset{+}{Te}{<}^{CH_2COPh}_{Br}$					40	
420	 $C_8H_8\overset{+}{Te}{<}^{COPh}_{Br}$					7	
390	$C_8H_8Te(C_2H_5)I^+$			4			
388	$C_8H_8Te(Ph)_2{}^+$						4
376	$C_8H_8Te(CH_3)I^+$	4					
356	$C_8H_8Te(CH_2CHCH_2)^+Br$				25		
339	$C_8H_8TeCOPh^+$					20	
111	$C_8H_8TePh^+$		3			5	9
84	Ph_2Te^+						100
75	$C_8H_8Te(CH_2CHCH_2)^+$				8		
63	$C_8H_8TeCH_2CH_3{}^+$			15			
60	$C_6H_4(CH_2Br)(CH_2Ph)^+$		9				

TABLE 6 (continued)

m/e	Possible ion	Relative intensity					
		$R = CH_3$ $X = I$	R = benzyl X = Br	$R = CH_2CH_3$ $X = I$	R = allyl X = Br	$R = CH_2COPh$ $X = Br$	R = Ph $X = BPh_4$
249	$C_8H_8Te(CH_3)^+$	6					
234	$C_8H_8Te^+$	100	100	100	100	100	
207	$PhTe^+$	100		11	49	69	100
200	$PhCOCH_2Br^+$					100	
186	$C_6H_5COBr^+$					100	
172	$PhCH_2Br^+$		100				
156	$CH_3CH_2I^+$			100			
142	CH_3I^+	100					
121	$CH_2CHCH_2Br^+$				100		
106	$PhCO^+$					100	
104	$C_8H_8^+$	100	100	100	100	100	
91	$C_7H_7^+$		95			100	
77	Ph^+		100	100	100	100	100

Discussion

Solution data

The main thrust of this work was to gain more information on the nature of telluronium salts in solution. The series based on the 1-organo-3,4-benzo-1-telluracyclopentane cation was selected because the materials were stable to reductive elimination as shown by the constancy of NMR spectra over periods in excess of 30 h.

The conductivity data (Table 4) show, in DMSO at least, that the materials dissociate as 1/1 electrolytes. Plots of Λ_M against $(\text{concentration})^{1/2}$ are linear over the range 10^{-3}—10^{-4} *M*; the tetraphenylborate salts are an exception. By contrast, in DMF, values of Λ_M considerably lower than those expected for 1/1 electrolytes (about 80 $\text{ohm}^{-1}\ \text{cm}^2\ \text{mol}^{-1}$) are observed indicating that the compounds are much more associated in this solvent. The data for those salts, particularly in DMSO, show that they are much more "ionic" than the series $Ph_2(CH_3)TeX$ (X = Cl, Br, I, OOCPh) [2].

The methylene protons (2 and 7, Table 1) give a singlet for 3,4-benzo-1-telluracyclopentane and for the 1,1′-diiodo derivative. However, formation of the telluronium salts changes the methylene spectrum to a simple AB pattern as would be expected for a pyramidal distribution of tellurium—carbon bonds. The coupling constant, $^2J_{2a2b}$ ($=^2J_{7a7b}$), is around 15 Hz a value consistent with sp^3 hybridised carbon.

The ^{1}H NMR data (Table 1) for 1-methyl-1-iodo-3,4-benzo-1-telluracyclopentane show the deshielding of the methyl protons to follow the order $CDCl_3$ > DMF > DMSO. This is the inverse of solvating power of the solvents and, together with the conductivity data, can be used to support the concept of strongly solvated ions in DMSO solution. It is also observed that the non-equivalence of the protons on carbon 2 (or 7) is increasing from DMSO (0.3 ppm) to DMF (0.4 ppm) and $CDCl_3$ (0.72 ppm). This also supports the view of a different environment in DMSO and $CDCl_3$ solutions and would be consistent with the model of anion—cation interaction in $CDCl_3$, perhaps via bonds of non-negligible covalent character. Certainly this interaction is sufficiently strong for dimers to exist at 25°C, the temperature of molecular weight measurements.

The change of counter ion (I^-, ClO_4^-, BPh_4^-) does not lead to an evolution of non-equivalence of the carbon 2 (or 7) protons. This remains around 0.3 ppm in DMSO and, simultaneously, the value of $\delta(CH_3)$ is always around 2 ppm. We observe the same behaviour for replacement of CH_3 by C_2H_5. This implies the same associated form or, in our view more probably, the same solvated ionic form of the telluronium cation in DMSO.

^{13}C NMR data for 1-methyl-1-iodo-3,4-benzo-1-telluracyclopentane (Table 2) show similar trends. It has been argued that the chemical shifts of carbon atoms bound to tellurium will be sensitive to the polarity of the Te—C bond [16], thus the δ(C(1)) and $\delta(CH_3)$ values in $CDCl_3$ and DMSO both point to a more positive tellurium atom in $CDCl_3$ solution than in DMSO solution.

The ^{125}Te NMR data (Table 3) give useful information. The first point to note is the relative invariance of $\delta(^{125}Te)$ for 1-methyl-1-iodo-3,4-benzo-1-telluracyclopentane with solvent, in contrast to the ^{1}H and ^{13}C results; however, when exchange processes may be eliminated, it seems generally true that $\delta(^{125}Te)$ does not show marked solvent dependence [17]. This fact shows the surroundings of the tellurium atom to be similar in these solvents and that little electronic change occurs at the tellurium nucleus. As is well known [12] the tellurium chemical shift is clearly sensitive to change of groups covalently bound to tellurium e.g. R = $CH_2CH{=}CH_2$, CH_2Ph, CH_2COPh (in I) with anion bromide in DMSO as solvent (Table 3). Perhaps of more significance is the fact that $\delta(^{125}Te)$ changes by some 25 ppm between 1-methyl-1-iodo- and 1-methyl-1-benzoato-3,4-benzo-1-telluracyclopentane in $CDCl_3$ solution. These are the two compounds shown to be dimers in chloroform, hence it would be anticipated that δ(Te) should be sensitive to change of anionic group. This is then consistent with the ^{1}H NMR data discussed above. No $^1J(^{125}Te—^{123}Te)$ is seen, also the (proton decoupled) resonance is a clear singlet, the model of association via relatively long "ionic" type bonds (anion bridge) remains valid. Zumbulyadis and Gysling [12] have observed a correlation between halogen electronegativities and $\delta(^{125}Te)$ for the 1,1-dihalo-3,4-benzo-1-telluracyclopentane compounds. In our case benzoate produces a larger downfield shift than iodide in the 1-methyl series in agreement with our previously expressed view that the effective electronegativity of benzoate is greater than those of the heavier halogens [2,3].

The combined NMR and conductivity study leads us to believe that in strongly solvating solvents such as DMSO, an ionic model is most appropriate with relatively strong solvation of the telluronium cation providing the driving force for dissociation. In solvents of lower polarity, association of the telluronium cation with the anion via weak ionic bonds is preferred giving, in at least two cases studied, symmetric dimers.

Solid-state data and mass spectra

The IR spectra of the salts gave little structural information. We list in Table 5 the position of ν(Te—alkyl), the assignment being aided by the replacement of the 1-CH_3 group by a 1-CD_3 group in $C_8H_8Te(CH_3)I$. The shift of $\nu(Te—CH_3)$ from 538 to 500 cm^{-1} on deuteriation revealed a previously hidden band at 520 cm^{-1} which is paired with another at 540 cm^{-1} (560 cm^{-1}) in the undeuteriated compound. A convenient, though doubtless oversimple description of these modes is ν_s- and $\nu_{as}(Te—CH_2)$. The sensitivity to deuteration of the methyl group indicates coupling with $\nu(Te—CH_3)$.

The most interesting IR result concerned 1-methyl-3,4-benzo-1-telluracyclopentane perchlorate. As a Nujol mull the bands characteristic of ionic perchlorate are seen. However if the compound is pressed into a KBr disc, clean splitting of both ν_3 and ν_4 of the perchlorate counter ion is seen (experimental section). This implies that the effective symmetry of the ion has been lowered to C_{2v}, possibly by weak interaction with tellurium. A change in polymorphic form on pressing a KBr disc is by no means unknown [18]. Others have provided examples involving perchlorate from organometallic chemistry [19] and from coordination chemistry [20]. We have observed the phenomenon with an organic perchlorate [21].

The mass spectra of a number of the new compounds reported here were recorded and data is presented in Table 6. The spectra were in general complex, but certain features were common to most spectra studied. Thus the ion $C_8H_8Te(R)X^+$ (parent) was usually observed at low relative intensity (rel. int.) by contrast the telluride ion $C_8H_8Te^+$ and also RX^+ are seen at rel. int. 100%. It seems probable that we are observing a mass spectrum derived both from the salt and from thermolysis products and the scheme in Fig. 1 isolates features which are common to virtually all spectra.

The loss of tellurium from the telluride ion to give benzocyclobutane cation is supported by a metastable transition at $m/e = 42.6$. The thermal elimination of tellurium from the telluride at 500°C and 0.4—0.5 mmHg of helium gas has been used as a synthetic method for the cyclobutane [11].

In two cases, the 1-allyl- and 1-phenacyl-3,4-benzo-1-telluracyclopentane bromides, ions of low rel. int. were seen with m/e in excess of P^+. This would indicate that the association implied from some solution measurements is carried through to the gas phase. In Fig. 2 we present our speculation concerning the fragmentation of a telluronium salt $\{C_8H_8Te(R)X\}_n$ (g) where n may be at least 2. Included in the scheme are suggestions as to how other unexpected (but carefully checked) features of the spectra arose e.g. the ions at m/e corresponding to $PhTe^+$ and Ph^+.

The mass spectra certainly help to provide further support for the view that telluronium salts are associated in various phases. One compound which merits

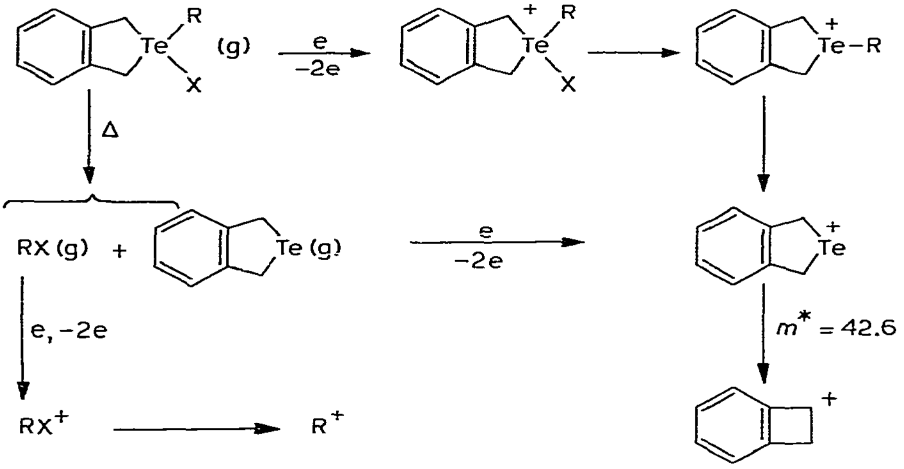


Fig. 1. Features common to mass spectra of 1-organo-3,4-benzo-1-telluracyclopentanetelluronium salts.

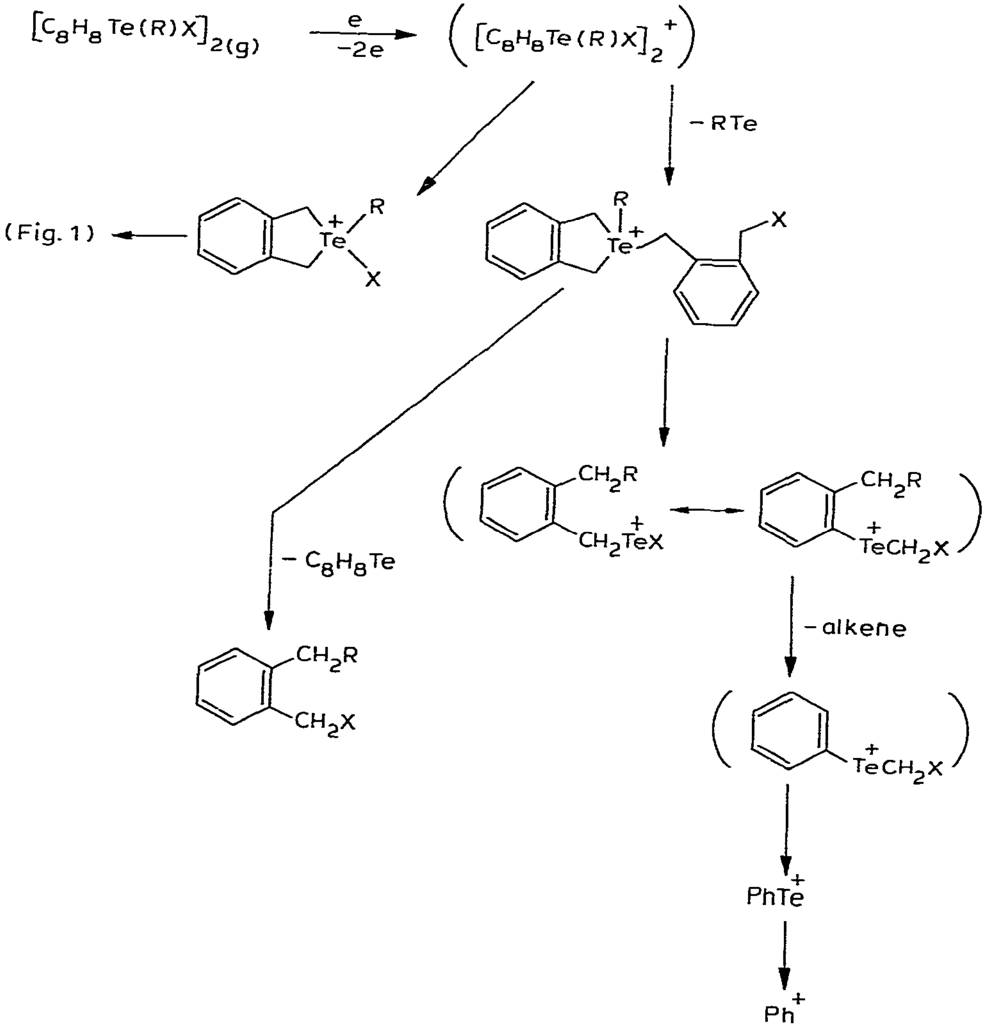


Fig. 2. Suggested origin of some ions observed in the mass spectra of telluronium salts. No ions corresponding to those in round brackets were actually observed.

special mention is 1-phenyl-3,4-benzo-1-telluracyclopentane tetraphenylborate. The mass spectrum clearly indicates the ion $C_8H_8Te(Ph)_2^+$ to be present. We have since synthesised $C_8H_8Te(Ph)_2$ from the tetraphenylborate salt and will report on this, and the use of related compounds in organic synthesis in due course [22]. The X-ray crystal and molecular structure of $C_8H_8Te(Me)BPh_4$ has been determined [23] and shows the interesting feature of a close contact between tellurium and one phenyl ring of the BPh_4^- ion. This compound also gave a surprisingly low conductivity in DMSO (Table 4).

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