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AMINOARYLTELLURIUM(IV) TRIHALIDES

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SUMMARY

The preparation and properties of some aminoaryltellurium(IV) trihalides are reported. Conductivity measurements show the compounds to behave as 1:1 electrolytes when in dilute solution. Cryoscopic measurements reflect the molecular, and sometimes polymeric, nature of the materials in more concentrated solutions. The ^1H nmr and infrared spectra are discussed.

INTRODUCTION

Although the preparation and properties of aryltellurium compounds are now well established, the only amino substituted aryltellurium(IV) derivatives which have been reported are the

1-N,N dimethylaniline-4-tellurium(IV)-dichloride [1] and -trihalides [2]. This work reports the formation of the aniline-; o-toluidine-; p-toluidine-; 2,4-dimethylaniline-; 2,6-dimethylaniline-; and monomethylaniline-tellurium(IV) trihalides and describes some physical and spectroscopic studies of their properties.

EXPERIMENTAL

The aminoaryl tellurium(IV) trihalides were prepared from either the aminehydrogenhexahalotellurates, $(\text{AmH})_2\text{TeX}_6$, ($\text{Am}=\text{amine}$, $\text{X}=\text{halogen}$) or the amine tellurium tetrahalide adduct $2\text{Am} \cdot \text{TeX}_4$, in methanolic solution [2]. Analytical data are summarised in Table 1.

Conductance measurements were performed under dry conditions at $30 \pm 1^\circ\text{C}$ using a conductance bridge and dip type cell with a smooth platinum electrode.

Molecular weights were determined cryoscopically in nitrobenzene.

^1H nmr spectra were recorded in d-acetone or d-acetonitrile using tetramethylsilane as an internal reference.

RESULTS AND DISCUSSION

The formation of aminoaryl tellurium(IV) trihalides from the $2\text{Am} \cdot \text{TeX}_4$ adducts involves electrophilic substitution of the aromatic ring by tellurium(IV). Substitution occurs at the para position unless it is otherwise occupied. The formation from hexahalotellurates suggests that these species dissociate into the amine and tellurium tetrahalide in methanolic solution.

The aminoaryl tellurium(IV) trihalides, RTeX_3 are crystalline solids which are fairly stable in dry air, but are hydrolysed

in the order Cl>Br>I to tellurium dioxide, aminohydrogen halide and halogen acid. No intermediate products of the type $\text{RTe}(\text{OH})\text{X}_2$, $\text{RTe}(\text{OH})_2\text{X}$ or $\text{RTe}(\text{O})\text{X}$ were isolated as is observed during the hydrolyses of unsubstituted aryltellurium(IV) trihalides [3]. The breakdown of the tellurium-carbon bond in the aminoaryl-tellurium(IV) trihalides is presumably a result of the initial facile formation of the aminohydrogen halide and halogen acid.

The compounds are soluble in solvents of high dielectric constant but are insoluble in non polar solvents.

The molar conductances of some of the aminoaryltellurium(IV) trihalides in acetone, acetonitrile and nitrobenzene solution are recorded in Table 2.

The values increase with dilution but lie within or close to the expected [4] ranges for 1:1 electrolytes containing ca. 10^{-3}M of solute and reflect the likely formation in dilute solution of RTeX_2^+ and X^- ions. Such behaviour is different from that of the unsubstituted aryltellurium(IV) trichlorides which do not dissociate in solution [5] and is due to the more polar character of the material containing an amine group. It has been noted [4] that the concentration ranges selected for such measurements are often arbitrarily chosen and that the method of determination requires the assumption of a molecular weight which may be erroneous. Those aminoaryltellurium(IV) tribromides and triiodides which were sufficiently soluble ($>10^{-3}\text{g eq l}^{-1}$) in acetonitrile were therefore investigated over a wider concentration range and the results subjected to the Onsager Law. Values of the equivalent conductance at infinite dilution, Λ_e , and $(A + \omega B\Lambda_e)$ are recorded in Table 3. A comparison of calculated and experimental values of $(A + \omega B\Lambda_e)$ show the compounds to behave as 1:1 electrolytes. The experimental

TABLE I

ANALYTICAL DATA FOR NEW COMPOUNDS

Compound	C II	N II	Hal	Te	Molecular formula	C II	Calcd (%) II	N II	Hal	Te
anilinetellurium										
-trichloride	22.00	1.78	4.27	32.44	C ₆ H ₆ NC ₁ ₃ Te	22.15	1.84	4.31	32.76	39.07
-tribromide	16.12	1.56	2.96	52.06	C ₆ H ₆ NBr ₃ Te	15.66	1.30	3.04	52.22	27.76
-triiodide					C ₆ H ₆ NI ₃ Te	11.98	1.00	1.33	63.44	21.24
<u><i>p</i></u> -toluidinetellurium										
-trichloride	4.38	29.62	36.60	C ₇ H ₈ NC ₁ ₃ Te	24.70	2.35	4.13	31.34	37.46	
-tribromide	18.09	1.86	50.30	26.41	C ₇ H ₈ NBr ₃ Te	17.73	1.69	2.95	50.67	26.94
-triiodide	2.26	61.23	20.50	C ₇ H ₈ NI ₃ Te	13.67	1.30	2.28	62.00	20.76	
<u><i>p</i></u> -toluidinetellurium										
-trichloride	4.46	29.77	37.92	C ₇ H ₈ NC ₁ ₃ Te	24.70	2.35	4.13	31.34	37.46	
-tribromide	2.88	51.80	26.36	C ₇ H ₈ NBr ₃ Te	17.73	1.69	2.95	50.67	26.94	
-triiodide	13.98	1.72	61.56	20.62	C ₇ H ₈ NI ₃ Te	13.67	1.30	2.28	62.00	20.76
<u><i>2,4-dimethylaniline</i></u> -tellurium										
-trichloride	3.52	30.60	36.08	C ₈ H ₁₀ NC ₁ ₃ Te	27.20	2.83	3.96	30.17	35.97	
-tribromide	2.89	48.49	25.92	C ₈ H ₁₀ NBr ₃ Te	19.69	2.05	2.87	49.22	26.17	
-triiodide	14.87	1.15	60.55	20.23	C ₈ H ₁₀ NI ₃ Te	15.27	1.59	2.23	60.61	20.30

2,6-dimethylaniline-

-tellurium									
-trichloride	27.10	2.80	3.71	30.20	36.00	$C_8H_{10}NCl_3Te$	27.20	2.83	3.96
-tribromide	19.15	2.79		48.86	25.82	$C_8H_{10}NBr_3Te$	19.69	2.05	2.87
-triiodide				60.58	20.14	$C_8H_{10}NI_3Te$	15.27	1.59	2.23
methylaniline-									
-tellurium									
-trichloride	4.12	30.87	36.98			$C_7H_8NCl_3Te$	24.70	2.35	4.13
-tribromide	17.46	1.55	3.07	50.26	26.30	$C_7H_8NBr_3Te$	17.73	1.69	2.95
-triiodide	13.69	1.71	2.23	62.06	20.40	$C_7H_8NI_3Te$	13.67	1.30	2.28

TABLE 2

MOLAR CONDUCTANCE DATA FOR AMINOARYLTELLURIUM(IV) TRIHALIDES

Aminoaryl Group	ACETONITRILE			NITROBENZENE			ACETONE		
	Molar Concentration $\text{cx}10^3$ mol l^{-1}	Molar Conductance Λ_m $\text{ohm}^{-1} \text{cm}^2 \text{ mol l}^{-1}$	Concentration $\text{cx}10^3$ mol l^{-1}	Molar Conductance Λ_m $\text{ohm}^{-1} \text{cm}^2 \text{ mol l}^{-1}$	Concentration $\text{cx}10^3$ mol l^{-1}	Molar Conductance Λ_m $\text{ohm}^{-1} \text{cm}^2 \text{ mol l}^{-1}$	Conductance κ $\text{ohm}^{-1} \text{cm}^2 \text{ mol l}^{-1}$	Conductance κ $\text{ohm}^{-1} \text{cm}^2 \text{ mol l}^{-1}$	Conductance κ $\text{ohm}^{-1} \text{cm}^2 \text{ mol l}^{-1}$
TRICHLORIDES									
aniline	2.0	114.1				1.0		100.2	
	1.6	116.1				0.5		106.7	
	1.0	124.1				0.25		128.5	
	0.5	137.3							
<i>o</i> -toluidine	1.0	84.8				1.0		102.8	
	0.5	99.1				0.5		114.4	
	0.25	119.8				0.25		120.5	
<i>p</i> -toluidine	1.0	79.7				1.0		106.0	
	0.5	98.5				0.5		110.6	
	0.25	108.0				0.25		116.5	
2,4-dimethylaniline	1.0	87.7							
	0.25	106.4							

2,6-dimethylaniline	1.0 0.25	90.5 111.2						
methylaniline	1.0 0.25	115.2 135.1						
1-N,N-dimethylaniline	1.0 0.25 0.10	86.8 97.9 117.3	1.0 1.0 0.5	16.5 18.0 19.5	1.6 1.0 0.25	106.8 100.2 106.7 128.5	121.3	
TRIFLOROMIDES								
aniline	2.0 1.0	146.3 163.0	3.0 2.4 1.2	25.2 26.1 27.5	2.1 1.6 1.1	128.8 131.8 136.6		
<u>O</u> -toluidine	2.6 1.0	142.4 149.0	1.0 0.8 0.5	21.8 24.3 29.9	2.0 1.5 1.0	125.9 128.4 130.6		
p-toluidine	2.0 1.0	140.3 143.8	1.0 0.8 0.5	27.5 26.7 31.1	3.0 2.0 1.0	123.6 126.4 129.7		
2,4-dimethylaniline	2.0 1.0	139.7 148.6	1.0 0.6 0.2	19.2 24.0 27.0	0.5 0.3 0.1	130.6 135.2 142.8		

Table 2 continued

<u>2,6-dimethylaniline</u>	2.8	137.1	1.0	18.6	0.5	132.1
	1.8	141.7	0.6	23.0	0.3	136.6
			0.2	27.0	0.1	142.8
 methylaniline	 2.0	 145.5	 2.3	 27.6	 3.0	 118.4
	1.0	166.3	1.8	28.3	2.0	121.6
			1.0	29.5	1.0	125.0
 <u>1-N,N-dimethylaniline</u>	 2.0	 127.0	 1.5	 18.3	 1.5	 102.0
	1.0	140.9	1.0	24.3	1.0	114.0
			0.5	28.3	0.5	120.4
 TRIICIDIDES						
<u>aniline</u>	1.0	126.0	1.0	22.2	0.5	120.0
	0.8	130.0	0.6	26.0	0.3	148.0
	0.6	140.0	0.2	30.6	0.1	160.0
 <u>α-toluidine</u>	 5.0	 116.0	 1.0	 21.0	 1.0	 120.0
	1.0	132.0	0.6	25.0	0.5	138.0
	0.5	144.0	0.2	28.2	0.1	168.0
 <u>p-toluidine</u>	 1.0	 132.0	 1.0	 19.8	 1.0	 114.0
	0.6	150.0	0.6	23.8	0.6	140.0
	0.2	162.0	0.2	27.0	0.2	153.0

Table 2 continued

2,4-dimethylaniline	0.5	140.0	0.5	26.4	0.1	132.0
	0.3	152.0	0.3	30.0	0.08	157.5
	0.1	168.0	0.1	36.0	0.06	180.0
2,6-dimethylaniline	0.5	134.0	0.4	25.2	0.1	126.0
	0.3	138.0	0.3	30.0	0.08	142.5
	0.1	144.0	0.1	35.4	0.06	170.0
methylaniline	2.0	133.9	1.5	22.3	1.0	114.5
	1.0	143.2	1.0	25.8	0.8	120.3
			0.5	28.2	0.5	130.6
1-N,N-dimethylaniline	1.5	120.5	1.5	21.1	1.0	109.0
	1.0	130.2	1.0	24.5	0.8	112.7
	0.5	138.1	0.5	27.1	0.5	118.2

TABLE 2

VALUES OF $(\frac{A + \beta}{2} \Delta_{1,2})$ FOR AMINOARYLTELLURUM(IV)-TRIBROMIDES AND
TRIIODIDES IN ACETONITRILE

Compound	$\frac{\Delta_{1,2}}{(\text{ohm}^{-1})}$	$(\frac{A + \beta}{2} \Delta_{1,2})$ Calcd.	$(\frac{A + \beta}{2} \Delta_{1,2})$ Found	Ratio (Found/Calcd.)
TRIBROMIDES				
aniline	150	342.8	468.0	1.36
<u>o</u> -toluidine	161	350.8	418.0	1.19
<u>p</u> -toluidine	159	349.4	529.4	1.43
2,4-dimethylaniline	155	346.5	382.3	1.10
2,6-dimethylaniline	163	352.3	500.0	1.42
methylaniline	153	345.0	479.2	1.39
1-N,N dimethylaniline	153	345.0	578.0	1.67
TRIIODIDES				
methylaniline	152	344.2	400.0	1.16
1-N,N dimethylaniline	167	355.2	459.0	1.29

values of $(A + \omega B \lambda)$ do not approach those calculated for 1:2 electrolytes. The ratios which were found to be higher than expected may reflect incomplete dissociation or ion pair formation as observed during similar studies of the tetra-alkylammonium halide [6].

The molecular weights of aminoaryl tellurium(IV) trihalides in nitrobenzene are given in Table 4.

The low molecular weights of the compounds in concentrations below 10 mmol l^{-1} are consistent with the dissociation of the compounds as described by the conductance data at even lower concentrations. At higher concentrations the molecular weights resemble the formula weights and suggest that the materials exist in the molecular form. The solubility of compounds of the type RTeX_3 (where $\text{R} = \text{C}_6\text{H}_4\text{N}(\text{H})\text{CH}_3, \text{C}_6\text{H}_4\text{N}(\text{CH}_3)_2, \text{X} = \text{Cl}, \text{Br}, \text{I}$) is appreciable and the measurements indicate the formation of polymeric species in solution as has been observed in the methyltellurium(IV) trihalides [7,8]. It seems that the electron donating effect of methyl groups in aminoaryl tellurium(IV) trihalides produces maximum solubility when the methyl groups are attached to the nitrogen atom by optimising the polar nature of the materials. Compounds in which the methyl group on the aromatic ring are in positions which are not para to the tellurium trihalide are markedly less soluble to the extent that for some compounds the molecular weights could not be determined.

The order of solubility of 1-N,N dimethylaniline-4-tellurium trihalides in nitrobenzene is $\text{Cl} > \text{I} > \text{Br}$ and follows the trend in solubility of the phenyltellurium trihalides in benzene [9]. The solubility of the other aminoaryl tellurium(IV) trihalides is in the order $\text{Cl} > \text{Br} > \text{I}$ which corresponds with the trend observed for methyl-tellurium(IV) trihalides [7].

TABLE 4
 CRYOSCOPIC MEASUREMENTS OF AMINOARYTELLURIUM(IV) TRIHALIDES
 IN NITROBENZENE

Compound	Formula Weight	Concentration mmol l ⁻¹	Molecular Weight
TRICHLORIDES			
aniline	325.5	4.93 7.12 9.11 10.93 14.94 18.20	275 309 323 356 365 374
<u>o</u> -toluidine	339.5	2.19 4.03 5.98 7.63 10.03	223 274 304 311 340
2,4-dimethylaniline	353.5	2.10 2.84 3.93 4.98 6.16	223 241 278 302 327
2,6-dimethylaniline	353.5	2.06 2.63 3.01 4.23 5.06	219 223 256 299 307
methylaniline	339.5	5.12 11.70 15.74 21.08 23.97 25.96	298 341 356 373 391 407
1-N,N-dimethylaniline	353.5	24.38 25.56 28.73 39.79 49.80 51.05 55.36 59.69	350 345 347 355 355 413 587 703

Table 4 continued

TRIBROMIDES

aniline	459	4.69 7.44 9.30 10.49 11.82	323 410 427 444 465
<u><i>o</i>-toluidine</u>	473	4.36 6.39 8.32 10.05	307 363 393 407
<u><i>p</i>-toluidine</u>	473	2.44 4.11 5.45 6.53	244 308 327 356
methylaniline	473	4.94 11.26 15.41 20.07	351 456 486 518
1-N,N-dimethylaniline	487	20.63 21.60 22.53 34.67 40.16 43.15 45.80	480 485 468 482 521 712 942

TRIIODIDES

methylaniline	614	3.95 5.04 6.81 8.62 10.65 13.42	485 530 558 577 617 659
1-N,N-dimethylaniline	628	37.85 38.15 39.96 50.21 50.92 51.83 53.40	620 585 621 626 868 1109 1242

TABLE 5

'H NMR CHEMICAL SHIFTS FOR ARYL PROTONS

Compound	Solvent	δ_{ppm}	δ_{ppm}
anilinettellurium-trichloride	d-acetone	7.57	
-tribromide	"	7.65	
-triiodide	"		8.34
1-N,N-dimethylamino tellurium-trichloride	d-acetonitrile	7.63	7.54
-tribromide	"	7.61	7.50
-triiodide	"	7.24	6.96
di-p-tolyltellurium(IV)-dichloride	carbon tetrachloride	8.17	7.47
-dibromide	"	8.17	7.41
-diiodide	"	8.06	7.26

¹H nmr spectra of aminoaryl tellurium(IV) trihalides showed the aryl proton signals to resonate at lower field than in the parent amines and reflect the deshielding effect of the electron withdrawing tellurium trihalide group. The 1-N,N dimethylaniline tellurium(IV) trihalides gave AA'BB' spectra characteristic of 1,4-disubstituted rings whilst the other compounds gave either broad lines or complex multiplets. The 1-N,N dimethylaniline-4-tellurium(IV) trihalides which were found to be largely associated in solution showed the deshielding of the aryl proton signals (Table 5) to follow the order Cl>Br>I which reflects the electron withdrawing effect of the more electronegative ligands and corresponds with the trend observed for the soluble diphenyltellurium(IV) dihalides. The aryl proton signals in the less soluble aminoaryl tellurium(IV) trihalides showed the order of deshielding to be I>Br>Cl. Presumably the greater deshielding in the less soluble triiodide results from the retention of a higher degree of positive charge by the RTeI₂⁺ cation.

The far infrared data for some of the aminoaryl tellurium trihalides are given in Table 6 and show good agreement with those reported for the phenyl tellurium(IV) trihalides [9]. The absence of lattice absorption indicates the unlikely ionic formulation ArTeX₂⁺ X⁻ in the solid state. The spectra are consistent with the assignation attributed to the phenyl tellurium(IV) trihalides as polymeric species involving halide bridges between the tellurium atoms [9]. The bands have been ascribed to Te-C, Te-halogen (terminal) and Te-halogen (bridge) stretching frequencies and Te-halogen deformation vibrations. The N-H stretching frequency remains unchanged on forming the aminoaryl tellurium(IV) trihalide from the parent compound and confirms that linkage of the tellurium is to a carbon atom in the aromatic ring rather than the nitrogen atom of the amine group.

TABLE 6

FAR INFRARED DATA FOR AMINOARYLTELLURIUM(IV) TRIHALIDES

	<u>aniline</u> <u>cm⁻¹</u>	<u>o-toluidine</u> <u>cm⁻¹</u>	<u>p-toluidine</u> <u>cm⁻¹</u>	<u>2,4-dimethylaniline</u> <u>cm⁻¹</u>
TRICHLORIDES	375(sb) 232(s) 200(sh) 168(mb) 145(m)	320(mb)		340(sb)
TRIBROMIDES	365(wb) 185(vs) 147(m) 109(sh)	357(wb) 187(vs) 150(sh) 104(m)	278(wb) 192(vs) 145(sh) 112(sh)	263(w) 255(m) 188(vs) 152(sh) 118(sh)
TRIIODIDES	280(wb) 151(sh) 140(sb) 130(sb) 105(wb)	280(vw) 152(mb) 141(sb) 116(w)	276(vw) 140(mb) 115(w)	273(vw) 138(sb) 115(w)

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<u>2,6-dimethylaniline</u> <u>cm⁻¹</u>	<u>methylaniline</u> <u>cm⁻¹</u>	<u>1-λ,N-dimethylaniline</u> <u>cm⁻¹</u>	<u>Assignment</u>
328(sh) 326(s)	321(wb)	336(sb) 330(sh) 325(sh)	ν Te-Cl terminal
	242(s) 200(s)	227(sb)	ν Te-C
	177(sh) 150(sh)	150(sh)	ν Te-Cl bridge
269(sh) 245(wb)	221(sh)	238(wb)	ν Te-C
187(1s)	180(1s)	189(s)	ν Te-Br terminal
150(sh) 115(sh)	145(sh) 120(w)	145(sh) 110(w)	ν Te-Br bridge
286(vw)	280(wb)	273(vw)	ν Te-C
151(sh)	145(vs)	157(1s)	ν Te-I terminal
140(sb)	100(m)	108(m)	ν Te-I bridge
112(vw)			

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