Carbon-13 nuclear magnetic resonance studies of organotellurium compounds. II. Chemical shift trends

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^{13}C nmr chemical shifts are reported for some aromatic and aliphatic tellurium compounds. For a given organic group, the shift of the C^1 atom varies in the order $RTeCl_4^- \gtrsim RTeCl_3 > R_2TeCl_2 > R_2Te > R_2Te_2$, as expected from electronegative considerations. The C^2 atom experiences an opposite trend while the C^3 and C^4 atoms of the ring experience smaller changes. The chemical shifts of *para*-substituted aromatic tellurium compounds do not show additivity of contributions from the substituents.

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On rapporte les déplacements chimiques en rmn du ^{13}C de quelques composés aromatiques et aliphatiques du tellure. Pour un groupe organique donné, le déplacement de l'atome C^1 varie dans l'ordre $RTeCl_4^- > RTeCl_3 \gtrsim R_2TeCl_2 > R_2Te > R_2Te_2$ que l'on peut prévoir sur la base de considérations d'électronégativité. L'atome C^2 subit une tendance inverse alors que les atomes C^3 et C^4 ne subissent que de faibles changements. Les déplacements chimiques des composés aromatiques du tellure substitués en para ne présentent pas de contributions d'additivité de la part de ces substituants.

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Introduction

^{13}C chemical shift measurements have been found to reflect total carbon atom electron density and, therefore, they have been particularly useful as probes for the study of organometallic compounds. In recent years there have been many publications on ^{13}C nmr studies of organometallic compounds (1–4). However, the available data on tellurium compounds are limited compared with those for sulphur and selenium compounds (5–14). We have recently reported our studies on ^{13}C nmr spectra of phenyl and *p*-methoxyphenyl tellurium compounds (15). We now report here ^{13}C chemical shift data for *p*-phenoxy, *p*-methyl, *p*-chloro, and *p*-bromo phenyl tellurium compounds and some aliphatic tellurium compounds.

Results and discussion

^{13}C chemical shifts are recorded in Table 1. Assignments of the aromatic signals were based on previous studies (8, 15). The assignments in compounds of the type RR'Te and RR'TeCl$_2$ were made by comparison with assignments in R$_2$Te, R'$_2$Te, and their dichlorides. Where the C signals from R and R' are close together, the assignment should be considered tentative. Assignments of aliphatic signals were made by comparison with assignments in closely related compounds (16).

Examination of Table 1 reveals that the effect of change in tellurium substituent is most strongly observed at C^1, to which the tellurium is directly attached, less so at C^2 (*ortho*) and C^4 (*para*), and least at C^3 (*meta*). Plots of the shifts of C^1 (tellurium compound) versus C^1 (carbon *para* to X in C_6H_5X) (Fig. 1) for these compounds show a general linear correlation (r = 0.99) with a slope of 1.4. For a given organic substituent, C^1 chemical shifts vary according to the number of chlorine atoms attached to tellurium, $RTeCl_4^- \gtrsim RTeCl_3 > R_2Te > R_2Te_2$. On going from tetrachloroaryltellurates to ditellurides, there is a decreasing positive charge on tellurium which corresponds to a decrease in the polarity of the Te—C bond. Magnetic anisotropic effects originating in the tellurium substituents are not expected to vary much in this closely related series; moreover, they are expected to be small (8). Thus the polarity of the C—Te bond appears to have the largest effect on the C^1 resonance. C^1 chemical shifts of compounds **1**, **2**, **6**, **7**, and **20** are also dependant upon the inductive effect of —NEt$_2$ and —CH$_2$COCH$_3$.

Figure 1 also shows that there is a linear relationship between δC^2 (aromatic tellurium compounds) and δC^2(C_6H_5X) with a slope of 1.9. For a particular R, δC^2 changes in the opposite direction, i.e., $RTeCl_4^- \simeq RTeCl_3 < R_2TeCl_2 < R_2Te \simeq R_2Te_2$. A similar curve for C^4 signal gives a slope of 1.0.

The substituent shifts (Δδ^{13}C values) are calculated by using δ^{13}C values for aromatic hydrocarbons obtained on the same instrument under similar experimental conditions and are recorded in parentheses in Table 1. The use of Δδ^{13}C *para* values as a probe for understanding the π inductive effects of the substituents in aromatic rings has been very well established (4, 17). The generally upfield shift of Δδ^{13}C^4 in the case of diaryl tellurides and ditellurides suggests that C^4 in the Te derivative is shielded compared to the aromatic

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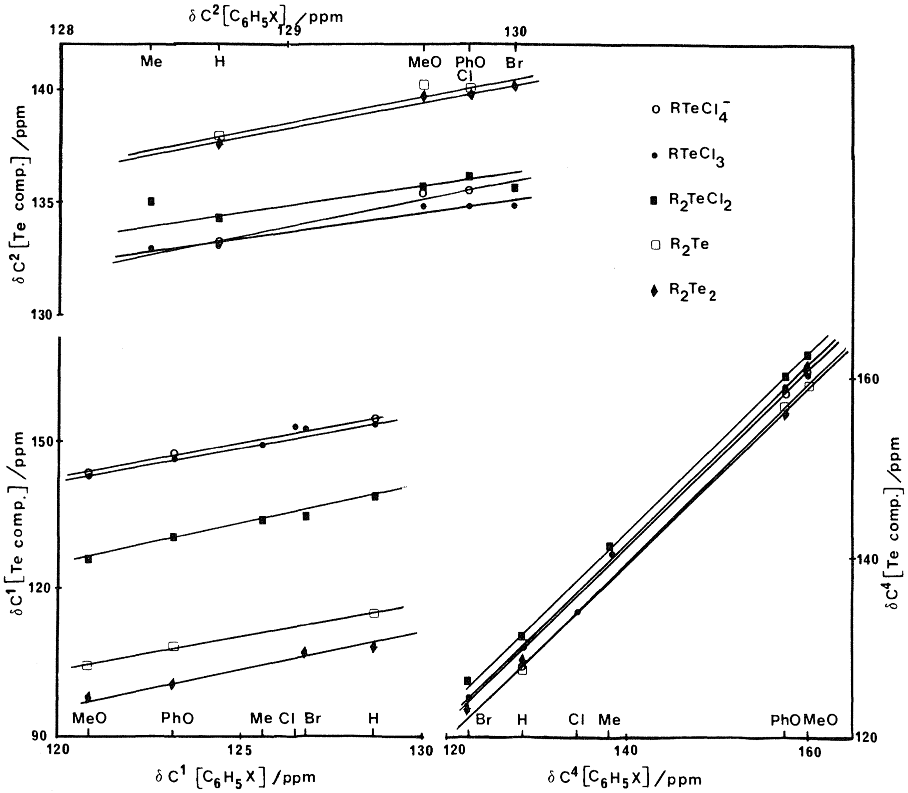

FIG. 1. Plots of δC^n ($n = 1, 2, 4$) for C_6H_5X vs. δC^n for organotellurium compounds. Data for X = H and MeO are taken from ref. 18.

hydrocarbon. The downfield shift for $\Delta\delta^{13}C^4$ for organotellurium halides suggests that the tellurium substituents are π acceptors in nature.

The deviations of chemical shift values ($\Delta\Delta\delta^{13}C$) from the values calculated according to additivity principles (16) are presented in Table 2. The failure of additivity is clearly evident for C^1 and C^2, in particular, from this table. Kalabin *et al.* (6) suggested on the basis of the dipole moments and Kerr's constants that the failure of additivity in *p*-substituted aromatic selenium compounds is due to the deviation of the conformation of the molecule from coplanarity, which occurs with a decrease in the strength of the *para*-substituent X. The signs of $\Delta\Delta\delta^{13}C^1$ for different *para*-substituents on the aromatic ring in tellurium compounds (Table 2) are similar to the corresponding substituents in selenium compounds studied by Kalabin *et al.* (6). This similarity between selenium and tellurium compounds suggests that the factor affecting non-additivity in tellurium compounds may also be conformational, though there is not much information available from the dipole moment data (18–21).

For the aliphatic compounds it can be seen that the C^1 resonances in the tellurides and ditelluride show an upfield shift whereas in the tellurium halides, it shows a downfield shift, dependant upon the halogens attached to the tellurium atom.

Coupling constants

In some of the aliphatic compounds ^{125}Te satellites are observed. The values lie in the range 127–168 Hz and are of the same order of magnitude as the reported ^1J (Te—C) value of 158.5 ± 0.5 Hz in Me_2Te (22) and 118–146 Hz in pentane-2,4-dione tellurium(II) compounds (9). Two bond coupling constants have been observed in some cases and it appears that ^2J depends upon steric as well as electronic factors.

Experimental

^{13}C nmr spectra were obtained on a Bruker WP-60FT NMR according to the method described previously (15).

A majority of the compounds studied are described in the literature (23–25). *p*BrPh(Ph)$TeCl_2$ was prepared by refluxing an equimolar mixture of *p*BrPh$TeCl_3$ and Ph_3SnCl in toluene for 2 h. After removing any suspended impurity by filtration, ligroin

TABLE 1. Carbon-13 nmr data[a] and substituent shifts[b,c] of organotellurium compounds

No.	Compound	Solvent	δC^1	δC^2	δC^3	δC^4	^1J (C—Te)	^2J (C—Te)	δC$^{\mathrm{others}}$			
1	Ph(Et$_2$N)TeCl$_2$	CDCl$_3$	138.1 (+ 9.4)	133.8 (+ 5.1)	129.8 (+ 1.1)	132.3 (+ 3.6)	306.5	29.4	45.7	15.6		
2	*p*MeOPh(Et$_2$N)TeCl$_2$	CDCl$_3$	127.6 (+ 6.8)	135.8 (+ 6.2)	115.5 (+ 1.4)	162.9 (+ 2.9)	260.0	30.3	55.7	45.7	15.6	
3	(*p*PhOPh)$_2$Te	CDCl$_3$	107.8 (− 16.0)	140.1 (+ 10.3)	119.9 (+ 1.0)	157.1 (− 0.3)			158.0	119.5	132.6	122.1
4	(*p*PhOPh)$_2$Te$_2$	CDCl$_3$	100.3 (− 22.9)	139.8 (+ 10.0)	119.2 (+ 0.3)	156.3 (− 1.1)		21.1	158.0	119.2	129.7	121.2
5	(*p*PhOPh)$_2$TeCl$_2$	DMSO-d_6: CDCl$_3$ (1:4)	130.1 (+ 6.9)	136.2 (+ 6.4)	119.1 (+ 0.2)	160.1 (+ 2.7)			158.2	119.4	133.4	124.8
6	*p*PhOPh(Et$_2$N)TeCl$_2$	CDCl$_3$	129.7 (+ 6.5)	136.0 (+ 6.2)	118.5 (− 0.4)	161.6 (+ 4.2)			154.9 45.5	120.3 15.6	130.0	124.9
7	(*p*PhOPh) (C$_4$H$_8$N)TeCl$_2$	DMSO-d_6	129.0 (+ 5.8)	136.2 (+ 6.4)	117.6 (− 1.3)	160.0 (+ 2.6)			155.6 45.5	120.4 24.2	131.0	125.2
8	(*p*PhOPh)TeCl$_3$	DMSO-d_6	145.5 (+ 22.3)	134.9 (+ 5.1)	117.0 (− 1.9)	158.6 (+ 1.2)		22.0	155.1	119.5	130.1	124.4
9	[Et$_2$NH$_2$]$^+$[*p*PhOPhTeCl$_4$]$^-$	DMSO-d_6	146.7 (+ 23.5)	135.6 (+ 5.8)	117.0 (− 1.9)	158.3 (+ 0.9)			155.4 41.3	119.6 10.9	130.2	124.5
10	Ph$_2$(C$_4$H$_4$O$_2$N)TeBr	CDCl$_3$	137.3 (+ 8.6)	132.0 (+ 3.3)	129.6 (+ 0.9)	131.1 (+ 2.4)			178.5	29.7		
11	*p*MePhTeCl$_3$	DMSO-d_6 CDCl$_3$(1:2)	148.4 (+ 22.8)	132.9 (+ 4.5)	129.2 (0.0)	141.4 (+ 3.6)	340.0	20.2	21.2			
12	(*p*MePh)$_2$TeCl$_2$	DMSO-d_6 CDCl$_3$ (1:3)	133.0 (+ 7.4)	135.0 (+ 6.6)	129.5 (+ 0.3)	141.5 (+ 3.7)						
13	(*p*BrPh)$_2$Te$_2$	DMSO-d_6: CDCl$_3$ (1:3)	106.8 (− 20.0)	140.2 (+ 10.2)	132.4 (+ 0.9)	123.0 (+ 0.5)						
14	*p*BrPhTeCl$_3$	DMSO-d_6	151.7 (+ 24.9)	134.9 (+ 4.9)	131.2 (− 0.3)	124.5 (+ 2.0)		18.0				
15	*p*ClPhTeCl$_3$	DMSO-d_6: CDCl$_3$ (1:1)	152.3 (+ 25.8)	135.0 (+ 5.2)	128.0 (− 0.7)	134.0 (− 0.5)						
16	*p*BrPh Te[d] Ph	CDCl$_3$	113.2 (− 13.6) 114.3 (− 14.4)	139.4 (+ 9.4) 138.3 (+ 9.6)	132.6 (+ 1.1) 129.6 (+ 0.9)	122.5 (0.0) 128.2 (− 0.5)						
17	*p*BrPh TeCl$_2$[d] Ph	CDCl$_3$	134.2 (+ 7.4) 135.3 (+ 6.6)	135.3 (+ 5.3) 133.8 (+ 5.1)	133.2 (+ 1.7) 130.2 (+ 1.5)	127.1 (+ 4.6) 132.0 (+ 3.3)						

TABLE 1. (*Concluded*)

No.	Compound	Solvent	δC^1	δC^2	δC^3	δC^4	^1J (C—Te)	^2J (C—Te)	δC^{others}			
18	pMeOPh Te^d Ph	$CDCl_3$	103.3 (− 17.5) 116.0 (− 12.7)	141.1 (+ 11.5) 136.4 (+ 7.7)	115.5 (+ 1.4) 129.3 (+ 0.6)	160.0 (0.0) 127.2 (− 1.5)		22.9 22.9	55.0			
19	*p*MeOPh $TeCl_2$^{d} Ph	DMSO-d_6: $CDCl_3$ (1:1)	127.0 (+ 6.2) 138.2 (+ 9.5)	136.1 (+ 6.5) 134.0 (+ 5.3)	115.0 (+ 0.9) 129.4 (+ 0.7)	161.2 (+ 1.2) 131.0 (+ 2.3)			55.9			
20	*p*MeOPh $TeCl_2$^{d} CH_3COCH_2	$CDCl_3$	118.3 (− 2.5) 67.4 (+ 38.2)	135.6 (+ 6.0) 200.1 (− 4.5)	115.8 (+ 1.7) 29.8 (+ 0.6)	162.4 (+ 2.4)	301.0 165.2		55.6			
21	Ph Te^e Me	CCl_4	112.5 (− 16.6) −16.8 (− 14.7)	136.7 (+ 8.0)	129.0 (+ 0.3)	127.1 (− 1.6)						
22	Me_2Te	$CDCl_3$	−20.2 (− 18.1)				158.8^f					
23	*n*Bu_2Te	$CDCl_3$	4.1 (− 20.9)	35.7 (+ 15.7)	29.5 (− 0.5)	13.2 (0.0)						
24	$(PhCH_2)_2Te_2$^{g}	$CDCl_3$	6.6 (− 14.8)						141.5	128.2	127.9	126.0
25	Me_2TeI_2	DMSO-d_6	19.1 (+ 21.2)				149.6					
26	Me_2TeI_4	$CDCl_3$	20.5 (+ 22.6)									
27	Et_2TeBr_2	$CDCl_3$	39.1 (+ 33.2)	10.3 (+ 4.4)			167.9					
28	Et_2TeI_2	$CDCl_3$	34.9 (+ 29.0)	11.3 (+ 5.4)			127.6					
29	Et_2TeI_4	$CDCl_3$	34.9 (+ 29.0)	11.8 (+ 5.9)								
30	$Et_3Te^+Br^-$	$CDCl_3$	19.3 (+ 13.4)	11.0 (+ 5.1)			145.9	18.4				

[a] Chemical shift values in ppm, coupling constants in Hz.
[b] In parentheses.
[c] A negative value indicates a upfield shift.
[d] Data from R and R′ given in respective lines.
[e] Taken from ref. 7.
[f] Literature (22) value is 158.5 ± 0.5 Hz.
[g] Taken from ref. 27.

TABLE 2. Deviations of the chemical shift values from the calculated values[a], $\Delta\Delta\delta^{13}C$

Compound	$\Delta\Delta\delta^{13}C$			
	C^1	C^2	C^3	C^4
2	− 2.6	+ 1.1	+ 0.3	− 0.7
3	− 2.0	+ 1.1	+ 0.3	+ 0.7
4	− 2.2	+ 1.1	− 0.2	− 0.4
5	− 2.4	+ 0.8	− 0.3	+ 0.5
6	− 3.0	+ 1.1	− 1.5	+ 0.6
8	− 1.5	+ 0.8	− 1.7	− 0.1
9	− 1.2	+ 1.3	− 1.0	− 0.2
11	− 1.0	+ 0.2	+ 0.2	+ 2.2
12	− 1.9	+ 1.0	− 0.2	+ 1.5
13	+ 0.7	+ 1.3	+ 0.4	+ 1.2
14	+ 1.1	+ 0.6	− 0.1	+ 0.7
15	+ 2.0	+ 0.9	− 0.5	− 1.8
16	+ 0.4	+ 0.2	+ 0.4	+ 1.0
	− 0.4	+ 0.4	+ 0.2	+ 0.5
17	− 1.9	− 0.3	+ 1.2	+ 2.4
	− 2.7	− 0.5	+ 1.0	+ 1.1
18	− 3.5	+ 2.3	+ 0.7	+ 1.0
	+ 1.3	− 1.5	− 0.1	− 0.5
19	− 3.1	+ 0.9	+ 0.4	− 1.0
	+ 0.2	− 0.3	+ 0.2	+ 0.1
21	− 2.8	− 1.2	− 0.4	− 0.6

[a] Calculated by subtracting $\Delta\delta^{13}C$ values for phenyl compound (**15**) from $\Delta\delta^{13}C$ values for compounds **2** to **21**.

(30–60°C) was added, and white needles precipitated. The product was filtered, dried, and recrystallised from CH_2Cl_2 to give *p*BrPh(Ph)$TeCl_2$, mp 142–143°C (20), yield 85%. *p*MeOPh-(Ph)$TeCl_2$ was obtained in a similar manner from *p*MeOPhTeCl_3 and Ph_3SnCl, mp 113–144°C, lit. 114–115°C (26). These unsymmetric RR′$TeCl_2$ compounds were reduced with N_2H_4/Et-OH (25) and recrystallised from CH_3OH. *p*BrPh(Ph)Te, mp 67–68°C, lit. 68°C (19), *p*MeOPh(Ph)Te, mp 60–61°C, lit. 61°C (26).

Hydrazine reduction of aryl(dialkylamino)tellurium dichlorides gave diaryl ditellurides instead of aryl(dialkylamino) tellurides.

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