Carbon-13 Nuclear Magnetic Resonance Studies of Organotellurium Compounds

By **Raj K. Chadha** and **Jack M. Miller,*** Department of Chemistry, Brock University, St. Catharines, Ontario L2S 3A1, Canada

Carbon-13 n.m.r. data for a number of phenyl- and *p*-methoxyphenyl-tellurium compounds are reported. Variations in the chemical shifts and one-bond tellurium–carbon coupling constants are discussed in terms of the polarity of the tellurium–carbon bond. *p*-Methoxyphenyltellurium compounds show deviations from additive principles.

ALTHOUGH there have been numerous publications in recent times on the ^{13}C n.m.r. spectra of organometallic compounds,[1-5] only limited data on organotellurium compounds are available [6-10] and the literature lacks a systematic investigation of these compounds. This is perhaps due to the low solubility of these compounds and the long relaxation times (*ca.* 50 s) for carbon atoms bound to tellurium,[8] which renders one-bond coupling-constant measurements extremely difficult.

In continuation of our studies on organotellurium compounds,[11] we report here ^{13}C n.m.r. chemical shifts and coupling constants for representative organotellurium compounds and discuss their implications.

RESULTS AND DISCUSSION

Chemical-shift Data.—The chemical-shift data are presented in Table 1. The assignment of the signals of the ring carbon atoms was made by the use of closely related aromatic compounds,[8,12,13] and by the fact that C^1 and C^2 signals in contrast to C^3 and C^4 signals contain satellites due to spin–spin coupling with ^{125}Te.

It is apparent from Table 1 that there is a large vari-

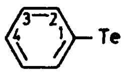
TABLE 1

Carbon-13 n.m.r. data [a] and substituent shifts [b] of aryltellurium compounds

Compound	Solvent	δ(C^1)	δ(C^2)	δ(C^3)	δ(C^4)	^1J(C–Te)	^2J(C–Te)	δ(C^5) [c]	δ(C^α) [d]	δ(C^β) [d]
(1) Te_2Ph_2 [e]	$CDCl_3$	108.0	137.6	129.2	128.0	55.0	21.1			
		(−20.7)	(+8.9)	(+0.5)	(−0.7)					
(2) $TePh_2$	$CDCl_3$	114.7	137.9	129.4	127.7	112.0	22.9 [f]			
		(−14.0)	(+9.2)	(+0.7)	(−1.0)					
(3) $TePh_2Cl_2$	[$^2H_6$]dmso	138.0	134.3	129.2	130.9	356.0	26.5			
		(+9.3)	(+5.6)	(+0.5)	(+2.2)					
(4) $TePh_2Br_2$	[$^2H_6$]dmso	134.9	135.6	129.1	130.7	308.4	22.0			
		(+6.2)	(+6.9)	(+0.4)	(+2.0)					
(5) $TePh_2I_2$	[$^2H_6$]dmso	129.8	137.7	129.3	130.1					
		(+1.1)	(+9.0)	(+0.6)	(+1.4)					
(6) $TePhCl_3$ [g]	CD_3CN		134.1	130.6	133.1					
	[$^2H_6$]dmso	152.5	133.0	128.5	130.0					
		(+23.8)	(+4.3)	(−0.2)	(+1.3)					
(7) $TePhBr_3$	[$^2H_6$]dmso	143.8	135.4	128.2	130.0					
		(+15.1)	(+6.7)	(−0.5)	(+1.3)					
(8) $TePhI_3$	[$^2H_6$]dmso	150.5	131.2	129.3	132.0					
		(+21.8)	(+2.5)	(+0.6)	(+3.3)					
(9) [NEt_2H_2][$TePhCl_4$]	[$^2H_6$]dmso	153.4	133.2	127.8	129.8	491.9	11.0		41.6	11.0
		(+24.7)	(+4.5)	(−0.9)	(+1.1)					
(10) $Te_2(C_6H_4OMe\text{-}p)_2$	$CDCl_3$	97.6	140.3	115.2	160.0	160.2	19.3	55.2		
		(−23.2)	(+10.7)	(+1.1)	(0.0)					
(11) $Te(C_6H_4OMe\text{-}p)_2$	$CDCl_3$	104.4	139.7	115.3	159.6	190.8	23.9	55.0		
		(−16.4)	(+10.1)	(+1.2)	(−0.4)					
(12) $Te(C_6H_4OMe\text{-}p)_2Cl_2$	$CDCl_3$	125.4	135.5	115.7	162.4	285.4	35.8	55.6		
		(+4.6)	(+5.9)	(+1.6)	(+2.4)					
(13) $Te(C_6H_4OMe\text{-}p)_2Br_2$	$CDCl_3$	121.5	136.8	115.9	162.3	259.9	30.3	55.6		
		(+0.7)	(+7.2)	(+1.8)	(+2.3)					
(14) $Te(C_6H_4OMe\text{-}p)_2I_2$	$CDCl_3$	115.5	138.7	116.1	162.0		24.8	55.6		
		(−5.7)	(+9.1)	(+2.0)	(+2.0)					
(15) $Te(C_6H_4OMe\text{-}p)Cl_3$ [g]	CD_3CN	146.3	136.6	116.3	164.0			56.7		
	[$^2H_6$]dmso	142.4	134.9	113.9	160.7	359.8	14.7	55.4		
		(+21.6)	(5.3)	(−0.2)	(+0.7)					
	C_2D_6CO	143.9	134.1	115.1	160.0			55.9		
(16) $Te(C_6H_4OMe\text{-}p)Br_3$	[$^2H_6$]dmso	134.4	137.6	113.6	160.4					
		(+13.6)	(+8.0)	(−0.5)	(+0.4)					
(17) $Te(C_6H_4OMe\text{-}p)I_3$	[$^2H_6$]dmso–$CDCl_3$	140.7	133.2	114.5	161.9			55.9		
		(+19.8)	(+3.6)	(+0.4)	(+1.9)					
(18) $Te(C_6H_4OMe\text{-}p)Cl_2$	$CDCl_3$	127.6	135.8	115.5	162.9			55.7	45.7	15.6
		(+6.8)	(+6.2)	(+1.1)	(+2.9)					
(19) $Te(C_6H_4OMe\text{-}p)Cl_2(NC_4H_8)$	$CDCl_3$	128.4	135.6	115.3	161.4			55.6	51.3	25.7
		(+7.6)	(+6.0)	(+1.2)	(+1.4)					
(20) [NEt_2H_2]-[$Te(C_6H_4OMe\text{-}p)Cl_4$]	$CDCl_3$	142.2	135.7	114.4	161.6			55.7	43.3	11.3
		(+21.4)	(+6.1)	(−0.3)	(+1.6)					

[a] Chemical-shift values in p.p.m., coupling constants in Hz; dmso = dimethyl sulphoxide. [b] Given in parentheses. [c] OC^5H_3. [d] $NC^\alpha H_2C^\beta H_3$. [e] Chemical-shift data agree with ref. 8. [f] ^3J(Te–C) 14.7 Hz. [g] Δδ(^{13}C) values calculated only for [$^2H_6$]dmso solutions.

ation among the chemical shifts of carbon atoms, C^1, bound to tellurium. The factors which could be invoked to explain this variation are differences in anisotropy, and the length and polarity of the Te–C bond. Magnetic anisotropy effects originating in the tellurium substituents are difficult to evaluate and are expected to be small.[8] The Te–C bond length in different aryltellurium compounds varies in the range 2.12 ± 0.02 Å [14,15] and therefore can be assumed as approximately constant. It appears, therefore, that the polarity of the Te–C bond has the larger effect on C^1 chemical shifts. On going from iodides to chlorides or dichlorides to aryltetrachlorotellurates *etc.*, there is an increasing positive charge on tellurium which corresponds to an increase in the polarity of the Te–C bond. This in turn is associated with a change in the paramagnetic term due to changes in average excitation energy, ΔE, and the dimensions of the bonding orbitals. Large downfield shifts for C^1 in tellurides and ditellurides result from shielding effects of the electropositive tellurium atom.



The C^1 signal in aryltellurium trihalides $TeRX_3$ is quite broad and the chemical-shift values show a pronounced solvent dependence. Contrary to the expectations based on Te–C polarity, the C^1 chemical shift of $TeRI_3$ is observed at lower field than $TeRBr_3$ and only 2—3 p.p.m. higher field than $TeRCl_3$. All these results can be explained by the fact that the $TeRX_3$ compounds are associated in the solid state [15] and in solution [16,17] to different extents. Therefore, the chemical shifts are determined not only by inductive effects but also by the solvent and the state of aggregation. The ^{13}C n.m.r. spectra of the $TeRX_3$ compounds could not be studied at lower temperatures because of solubility problems.

Substituent shifts, $\Delta\delta(^{13}C)$ values (*i.e.* the contributions from various tellurium substituents to the shielding of ^{13}C nuclei of the ring), are calculated taking $\delta(^{13}C)$ values for benzene as 128.7 p.p.m. and for anisole as 120.8 (C^1), 129.6 (C^2), 114.1 (C^3), and 160.0 p.p.m. (C^4) and are recorded in Table 1 in parentheses. Chemical-shift values for *p*-methoxyphenyltellurium compounds when calculated theoretically according to the addivity scheme [12] show deviations from the experimentally obtained values. These deviations [$\Delta\Delta\delta(^{13}C)$ values] are calculated by subtracting $\Delta\delta(^{13}C)$ values for phenyl compounds from $\Delta\delta(^{13}C)$ values for *p*-methoxyphenyl compounds and are collected in Table 2. Examination of this Table shows that these parameters vary appreciably for C^1 to C^4 atoms, and the largest variation occurs for C^1. Such a deviation for *p*-disubstituted phenyl compounds has been found to be significant for compounds in which the electronegativity of the key atoms, Y, is reduced compared with carbon, *e.g.* for Si, Ge, Sn,[18,19,*] S, and Se,[20,21] so that it was not surprising to find similar behaviour with the tellurium compounds.

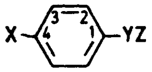


TABLE 2

Deviations of the chemical-shift values from the calculated values, $\Delta\Delta\delta(^{13}C)$

Compound	C^1	C^2	C^3	C^4
(10)	−2.5	+1.8	+0.6	+0.7
(11)	−2.4	+0.9	+0.5	+0.6
(12)	−4.7	+0.3	+1.1	+0.2
(13)	−5.5	+0.2	+1.4	+0.3
(14)	−6.8	+0.1	+1.4	+0.6
(15)	−2.2	+1.0	0.0	−0.6
(16)	−1.5	+1.3	0.0	−0.9
(17)	−2.0	+1.1	−0.2	−1.4
(20)	−3.3	+1.6	+0.6	+0.5

The negative values of $\Delta\delta(^{13}C)$ for C^4 suggest that the tellurium atom in tellurides and ditellurides possesses π-donor properties,† and the positive values of $\Delta\delta(^{13}C)$ for C^4 for organotellurium halides suggest that the tellurium substituents are π acceptors in nature. Therefore, the model of Taft and co-workers,[22] which supposes that the σ charge density at C^1 regulates the ease of π polarisation at this atomic position by the distant *para* substituent, X, cannot be employed as an explanation for the failure of the additivity principle. Lynch's [18] model of modifying ΔE of the C^1 atom under the influence of Y works on the supposition that the deviations for C^2, C^3, and C^4 atoms are insignificant, and this is contradictory to our data. A recent model of Kalabin *et al.*,[21] based on dipole moments and Kerr constants, suggests that the reason for non-additivity in the aromatic compounds of Group 6 is due to the change in the effective conformation under the influence of substituent X, realised by the rotation of the YZ group about the C–Y(Se) bond. Although only limited data are available for dipole moments of aryltellurium compounds,[23-26] they appear to indicate conformational changes with the substituents in the aromatic ring. Therefore, our results are best explained by this model. As a result of conformational changes in going from phenyl to *p*-methoxyphenyl derivatives, there is a possibility of the weakening of 5*p*–2*p* conjugation between tellurium and the ring. This may be responsible for generally more positive values of $\Delta\delta(^{13}C^4)$ (except for $TeRX_3$). In addition, the change in the C^1 and C^2 shielding resulting from the decrease in the direct steric interaction between halogen atoms and the ring gives rise to the positive values of $\Delta\Delta\delta(^{13}C^2)$; a decrease in the π polarisability of the tellurium substituents may explain the considerable deviations observed for C^1 although it is significant for the other positions of the ring also.

Te–C *Coupling Constants*.—Tellurium-125 satellite signals were detected for some of the compounds where solubilities were sufficient, and are recorded in Table 1.

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[*] Although the authors of ref. 19 did not calculate $\Delta\Delta\delta(^{13}C)$ values, the observed ρ_I and ρ_R values for *para*-substituted phenyltrimethyl-silanes and -germanes indicate even greater non-additivity.

[†] There is a good linear relationship between $\delta(^{13}C^{para})$ values and Δq_π, π-electron charge densities,[13] so that it is possible to use these values to determine the π-inductive effects of the tellurium substituents.

If it is assumed that the Te–C coupling mechanism is dominated by the Fermi-contact term, the magnitude of ${}^1J$(Te–C) can be represented as[27] $(C/\Delta E) \cdot \alpha_{(\mathrm{Te})}{}^2 \cdot \alpha_{(\mathrm{C})}{}^2 \cdot \psi_{5s(\mathrm{Te})}{}^2(0) \cdot \psi_{2s(\mathrm{C})}{}^2(0)$ (C = a constant). Within a closely related series of compounds, ΔE may be considered to have a constant value and differences in the coupling constants can be explained in terms of variation of α^2, the percentage *s* character of the hybrid orbitals used to form the Te–C bond, and $\psi^2(0)$, the valence *s*-electron density at the nucleus related to the effective nuclear charge. Since $\Delta\delta(^{13}C^1)$ values are a measure of the polarity of Te–C bonds or the nuclear charge on tellurium, a plot of $\Delta\delta(^{13}C^1)$ against ${}^1J$(Te–C) can be helpful in determining the dependence of ${}^1J$(Te–C) on α^2 or $\psi^2(0)$. Figure 1 shows a linear relationship between them, and that there are different straight lines for phenyl- and *p*-methoxyphenyl-tellurium compounds. Since ${}^1J$(Te–C) values of bi- and quadri-valent tellurium compounds, which involve different Te–C hybrid orbitals,[28] fall on the same straight line the dependence of ${}^1J$(Te–C) on α^2 can be ruled out. Thus the main factor involved in determining one-bond coupling constants is $\psi^2(0)$. Tellurium-125 Mössbauer isomer-shift values also give an estimate of the variations of $\psi^2(0)$. An approximately linear relationship between ${}^1J$(Te–C) and ^{125}Te Mössbauer δ values[28,29] is further evidence for the dependence of ${}^1J$(Te–C) mainly upon the *s*-electron density at the tellurium nucleus (see Figure 2). The broad natural width of the ^{125}Te transition causes large errors in δ, which makes it a rather insensitive probe to small changes in the 5*s* or 5*p* tellurium-orbital populations compared to n.m.r. coupling constants.

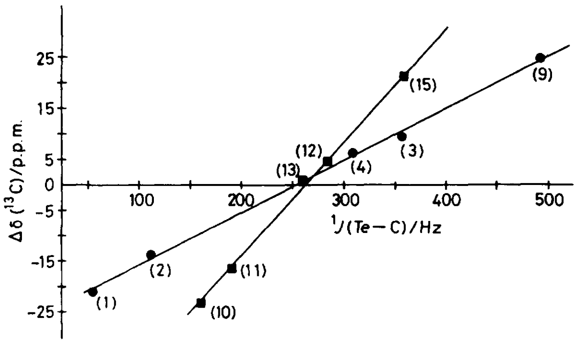

FIGURE 1 Plot of $\Delta\delta(^{13}C)$ against ${}^1J$(Te–C) for phenyl- (●) and *p*-methoxyphenyl-tellurium (■) compounds

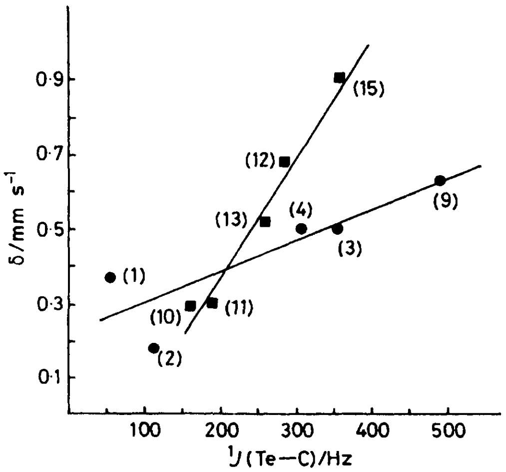

FIGURE 2 Plot of ${}^1J$(Te–C) against ^{125}Te Mössbauer isomer shift taken from refs. 28 and 29 for phenyl- (●) and *p*-methoxyphenyl-tellurium (■) compounds

Since there is no correlation between ${}^1J$(Te–C) and ${}^2J$(Te–C), we can conclude that the two-bond coupling shows a complex dependence on steric and electronic factors.

EXPERIMENTAL

Carbon-13 chemical shifts and coupling constants were measured on a Bruker WP-60 Fourier-transform multinuclear magnetic resonance spectrometer operating at 15.08 MHz with an internal deuterium lock. Field/frequency stabilisation was established by the deuterium signal of the solvent. The spectra were taken under conditions of proton-noise decoupling as well as off-resonance proton decoupling using a 0.1—0.05 mol dm^{-3} solution in the appropriate solvent and $SiMe_4$ as an internal standard. The normal operating temperature was *ca.* 300 K and pulse widths of 3.1 μs (30°) and repetition rate of 1.1 s were used. 30 000—50 000 Scans were required to get a useful spectrum using quadrature detection. Chemical shifts are accurate to 0.1 p.p.m. and coupling constants to 1.0 Hz.

Organotellurium compounds were prepared by the methods already described.[11,14,30]

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