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Tellurium-125 Mössbauer and NMR data for tetraphenyltellurium and bis(2,2′-biphenylylene)tellurium

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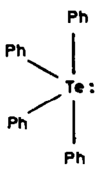
Abstract

The ^{125}Te solution NMR chemical shifts of Ph_4Te (508.9 ppm) and $(C_{12}H_8)_2Te$ (486.3 ppm) have been measured at ambient temperature, together with the ^{125}Te Mössbauer parameters for the neat solids: Ph_4Te (δ 0.09, Δ 5.60 mm s^{-1}), $(C_{12}H_8)_2Te$ (δ 0.42, Δ 6.40 mm s^{-1}) at 4.2 K. These results are compared with those for other organotellurium compounds. The mass spectra of these compounds are also reported.

Introduction

While the ^{125}Te NMR and Mössbauer parameters for a wide range of organotellurium compounds have been reported, one important class of compounds which has not previously been investigated is that of the tetraorganotelluriums.

The synthesis of tetraphenyltellurium was first reported by Wittig and Fritz [1]. The compound is a relatively stable solid which decomposes through an intramolecular process just above 100 °C to yield diphenyl telluride and biphenyl [2]. The X-ray crystal structure [3] of Ph_4Te shows the tellurium to be in a distorted trigonal



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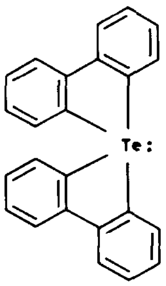

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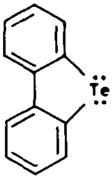

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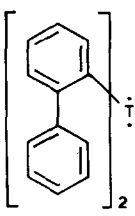

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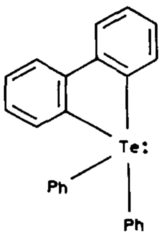

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bipyramidal geometry, with Te–C_{eq} and Te–C_{ax} bond lengths of 213 and 227 to 231 pm respectively. A lone-pair occupies the fifth coordinate position in the equatorial plane and the axial phenyls are bent towards the equatorial groups.

A closely related compound is bis(2,2′-biphenylylene)tellurium, $(C_{12}H_8)_2Te$ (II), which was first synthesised by Hellwinkel and Fahrbach [4]. This compound decomposes above 200 °C to 2,2′-biphenylylenetellurium, (III) and a mixture of biphenylene and tetraphenylene. An X-ray crystal structure of $(C_{12}H_8)_2Te$ has not been reported but the structure of 2,2′-biphenylylene telluride, $C_{12}H_8Te$ (III) [5], shows a C–Te–C bond angle of 81.7° and a Te–C bond length of 208 pm. In $(C_{12}H_8)_2Te$ one can envisage the $C_{12}H_8$ ligands spanning the equatorial–axial positions in a ψ-tbp geometry similar to that in Ph_4Te. This would again imply relatively long Te–C bonds *trans* to one another and shorter Te–C_{eq} bonds.

These two compounds present interesting examples for Mössbauer and NMR study because of the coordination about tellurium. Thus these are only Te–C bonds present and in Ph_4Te these are disposed in a trigonal bypiramidal (tbp) environment in which the Te–C_{eq} and Te–C_{ax} bonds are inequivalent.

Results and discussion

NMR spectra

Tetraphenyltellurium and bis(2,2′-biphenylylene)tellurium have very similar ^{125}Te NMR chemical shifts (Table 1). To provide a basis for comparison, the ^{125}Te NMR spectra of $Ph_3Te^+ X^-$ (X = Cl, Br, I), were also measured. As can be seen from Table 1, while Ph_3Te^+ has a more positive chemical shift than that of Ph_2Te, Ph_4Te has a significantly less positive shift.

The more positive shift of Ph_3Te^+ relative to Ph_2Te indicates that on oxidation from Te^{II} to Te^{IV} and on replacing one lone pair on tellurium with a phenyl ligand, there is a net deshielding of the nucleus. However, the coordination of a fourth phenyl ligand to the Ph_3Te^+ moiety to give Ph_4Te leads to a greater shielding at tellurium and the less positive chemical shift of Ph_4Te. It is interesting that the range of shifts for these compounds is relatively small, only 290 ppm, compared with a total chemical shift range for ^{125}Te of ca. 3000 ppm. Thus the shielding at tellurium is comparable, regardless of whether there are two, three or four phenyl ligands bonded to tellurium in these Te^{II} and Te^{IV} compounds.

Table 1

^{125}Te NMR data

	δ [a] (ppm)	Solvent
Ph_4Te	508.9	benzene
$(C_{12}H_8)_2Te$	486.3	benzene
Ph_2Te	688	benzene
$Ph_3Te^+ Cl^-$	772.7	DMSO
$Ph_3Te^+ Br^-$	779.7	DMSO
$Ph_3Te^+ I^-$	788.4	DMSO

[a] NMR chemical shifts with respect to neat Me_2Te at ambient temperature. Positive shifts are downfield from Me_2Te.

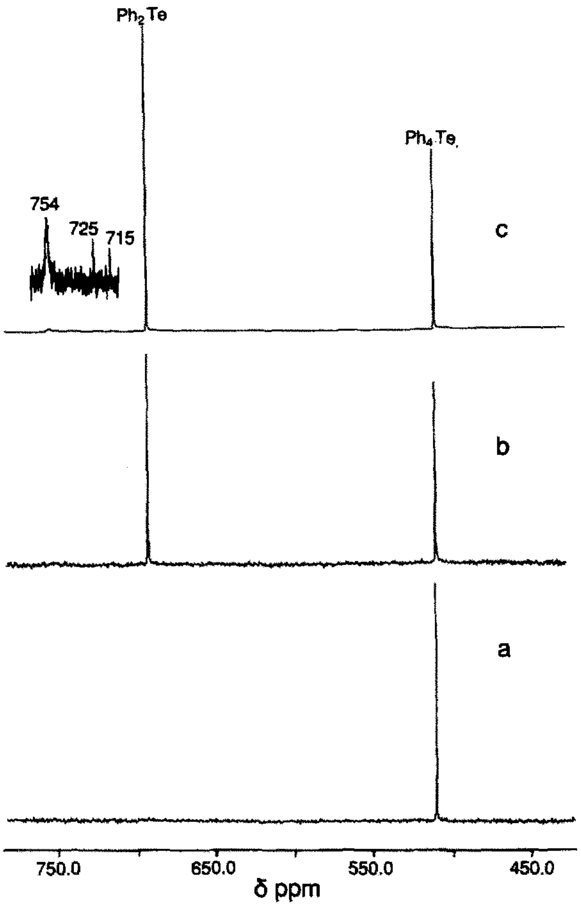


Fig. 1. The ^{125}Te NMR spectra of Ph_4Te in perdeuterated toluene (a) at 25 ° C, (b) heated at 80 ° C for 1 h and (c) heated at 100 ° C for 1 h.

A comparison of the shift for Ph_4Te with other ψ-tbp molecules is of interest. The diaryltellurium dihalides generally have shifts ranging from 800 to 1000 ppm [6]. Thus, Ph_4Te has a smaller shift, presumably reflecting the greater covalency in the trans axial Ph–Te–Ph linkage compared with the X–Te–X linkage.

Because of the similarity in the chemical shift of Ph_4Te and Ph_2Te it was important to ensure that the compound was not decomposing in solution. The ^{125}Te Mössbauer spectra, the mass spectra and the chemical analysis of samples recrystallised from benzene confirmed that this had not happened.

In anticipation of the mass spectral data to be discussed below, it was of interest to determine whether ^{125}Te NMR spectroscopy could be used to follow the thermal decompsotion of Ph_4Te in solution (Fig. 1). On heating a solution of Ph_4Te in perdeuterated toluene at 80 ° C for 1 h, the only decomposition product observed in the ^{125}Te NMR spectrum was Ph_2Te. At 100 ° C some evidence was observed for small traces of compounds with chemical shifts of 754, 725 and 715 ppm. The anticipated intermediate in the thermal decomposition of Ph_4Te would be the

Table 2

^{125}Te Mössbauer data

	δ [a] (mm s^{-1} ($\pm$0.08))	Δ (mm s^{-1} ($\pm$0.10))	Γ (mm s^{-1})	Ref.
Ph_4Te	0.09	5.60	5.2	
$(C_{12}H_8)_2Te$	0.42	6.40	5.8	
Ph_2Te	0.18	10.5		8
$C_{12}H_8Te$	0.14	9.3		8
$(C_{12}H_9)_2Te$	0.22	10.8		8
$Ph_3Te^+\ Cl^-$	0.35	5.8		8

[a] Mössbauer isomer shift with respect to I/Cu, source and absorbers at 4.2 K.

compound $Ph_2TeC_{12}H_8$ (V), and this would be expected to have a chemical shift similar to that of Ph_4Te or $(C_{12}H_8)_2Te$, i.e., around 500 ppm. The identity of the products at 715 to 754 ppm remains unclear. Heating for longer times or at higher temperatures or photolysing the solution did not increase the yield of these minor products.

Mössbauer data

The Mössbauer parameters for Ph_4Te and $(C_{12}H_8)_2Te$ measured at 4.2 K are shown in Table 2 together with those of Ph_2Te, Ph_3Te^+, $C_{12}H_8Te$, $(C_{12}H_9)_2Te$ taken from earlier work [8]. The parameters for Ph_4Te and $(C_{12}H_8)_2Te$ are again similar and are consistent with a similar coordination about the tellurium in these two compounds.

The Mössbauer quadrupole splittings are determined by the *p*-orbital imbalance on tellurium. This in turn will be dependent on the *p*-character of the bonds to tellurium and the stereochemical activity of the lone pairs present. It would be anticipated that the *p*-orbital imlabance will decrease as the number of lone pairs on tellurium decreases and as the coordination number increases. Certainly the quadrupole splittings in Ph_4Te and $(C_{12}H_8)_2Te$ are significantly smaller than those in the tellurides Ph_2Te, $(C_{12}H_9)_2Te$ and $C_{12}H_8Te$ (Table 2). In the latter Te^{II} compounds the very large electric field gradients arise from the imbalance between the two Te–C bonds and the two lone pairs on tellurium. In Ph_4Te and $(C_{12}H_8)_2Te$ which are Te^{IV} there is an increased coordination about tellurium and the presence of only one lone pair and this is reflected in a smaller Δ.

The quadrupole splitting of Ph_4Te can be compared with that of other ψ-tbp molecules such as Ph_2TeCl_2 (Δ 9.6 mm s^{-1}) and Ph_2TeI_2 (Δ 6.3 mm s^{-1}) [9] all of which have just one lone pair. Not surprisingly the splitting in Ph_4Te is smaller, reflecting a greater symmetry about tellurium and a smaller *p*-orbital imbalance. In Ph_4Te the *p*-orbital imbalance between the *trans*-axial Ph–Te–Ph linkage and the lone pair and Te–Ph bonds in the equatorial plane must be smaller than that in Ph_2TeCl_2, for example, where the more electronegative chlorine ligands occupy the *trans*-axial positions.

It is interesting that Ph_4Te and Ph_3Te^+ have similar splittings. In Ph_3Te^+ there are three short Te–Ph bonds in a roughly pyramidal arrangement with a lone-pair occupying the fourth coordinate position. The similarity in the quadrupole splittings

Table 3

Mass spectral data (intensity (%) in parentheses)

Ph_4Te		$(C_{12}H_8)_2Te$	
Ion	m/e [a]	Ion	m/e [a]
$C_{24}H_{18}Te$	436 (1)	$C_{24}H_{18}Te$	436 (2)
$C_{18}H_{15}Te^+$	361 (20)		
$C_{18}H_{13}Te^+$	359		
$C_{24}H_{18}{}^+$	306 (3)	$C_{24}H_{18}{}^+$	306 (1)
$C_{12}H_{10}Te^+$	284 (18)		
$C_{12}H_8Te^+$	282	$C_{12}H_8Te^+$	282 (53)
$C_5H_5Te^+$	207 (5)		
$C_{12}H_{10}{}^+$	154 (100)	$C_{12}H_{10}{}^+$	154 (100)
$C_6H_6{}^+$	78 (20)		
$C_5H_5{}^+$	77 (5)	$C_6H_5{}^+$	77 (20)
		$C_6H_4{}^+$	76

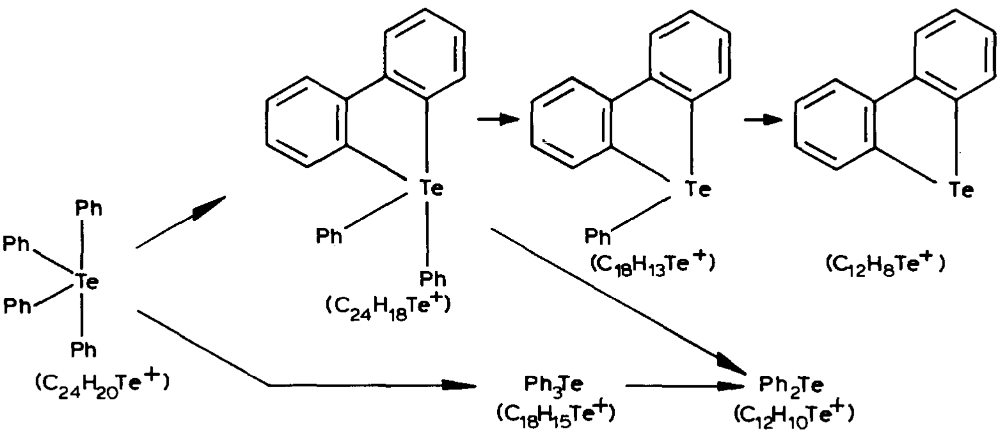
[a] For tellurium containing species m/e is quoted for ^{130}Te.

of Ph_3Te^+ and Ph_4Te again suggests that the Ph–Te–Ph *trans*-axial linkage and the Te–Ph_{eq} bonds have similar *p*-orbital populations.

The Mössbauer isomer shifts which reflect the nuclear *s*-electron densities at the tellurium appear to show a somewhat greater 5*s* character in the lone pair on $(C_{12}H_8)_2Te$ than on Ph_4Te. The relatively small isomer shifts are comparable to those of the organotellurides.

Mass spectra

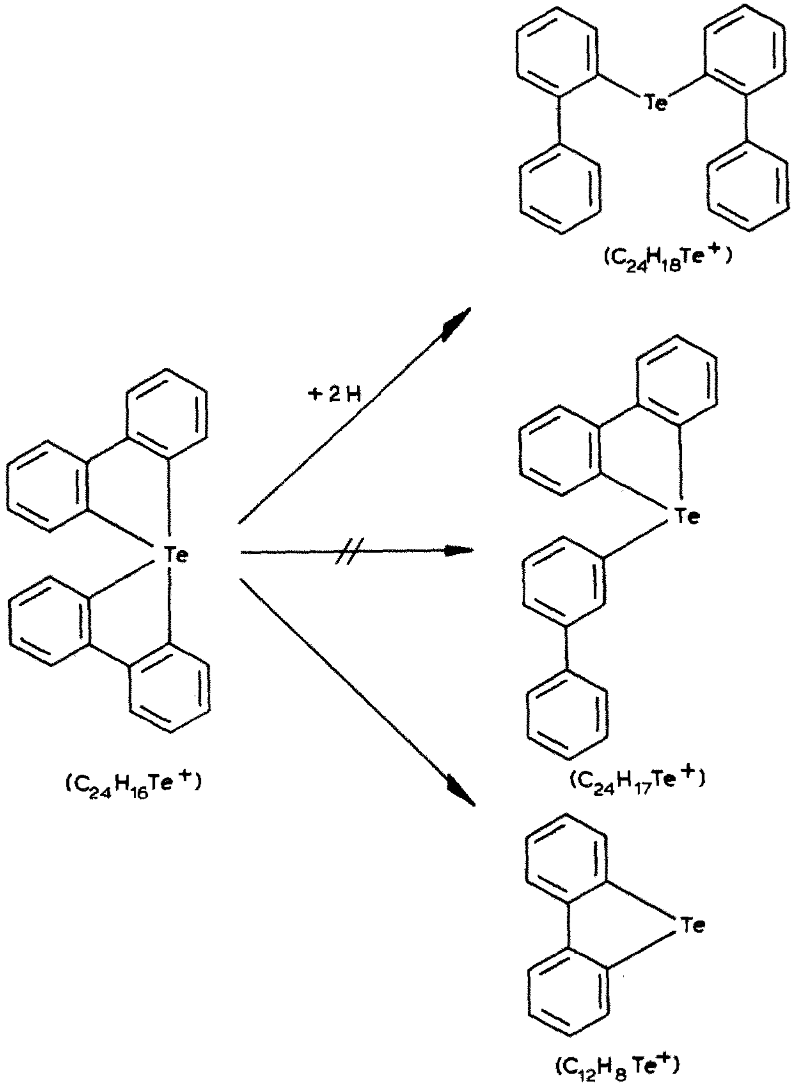
The mass spectra for Ph_4Te and $(C_{12}H_8)_2Te$ are given in Table 3. The parent ion was not observed for Ph_4Te and the heaviest ion observed, $m/e = 436$, corre-



Scheme 1

sponded to the loss of two hydrogen atoms from Ph_4Te, to give $C_{24}H_{18}Te^+$. This is consistent with an intramolecular rearrangement on thermal decomposition of Ph_4Te to give the compound $(Ph_2(C_{12}H_8)Te)$ (V), as suggested by Barton et al. [2] (Scheme 1). The multiplet of peaks which overlap at 361 and 359 (^{130}Te) would then correspond to Ph_3Te^+, $(C_{18}H_{15}Te^+)$, and to the loss of a phenyl group from compound V to give $Ph(C_{12}H_8)Te^+$. Other ions observed in the spectrum included Ph_2Te^+ and $PhTe^+$.

The mass spectrum of $(C_{12}H_8)_2Te$ was simpler but even more intriguing. The heaviest ion peak was again observed at $m/e = 436$, i.e., $C_{24}H_{18}Te^+$. This would appear to correspond to a thermal decomposition product, probably compound IV,



Scheme 2

$(C_{12}H_9)_2Te$ where two hydrogen atoms have been abstracted from other molecules, Scheme 2. The only other tellurium containing species in the spectrum is $C_{12}H_8Te^+$ and in particular no phenyltellurium ions are seen, indicating the absence of ions derived from compound V, for example. The presence of $C_{24}H_{17}Te^+$, which would correspond to the breaking of just one Te–C bond (Scheme 2) would tend to be masked by $C_{24}H_{18}Te^+$ and no evidence for $C_{24}H_{17}Te^+$ was observed.

The mass spectral data are consistent with the known propensity of tetraorganotellurium compounds to thermal decomposition [2]. The apparent pathway for decomposition of $(C_{12}H_8)_2Te$ to give $(C_{12}H_9)_2Te$ parallels that of Ph_4Te to give Ph_2Te. In both cases the decomposition appears to reflect the instability of the $Te–C_{ax}$ bonds in these ψ-tbp molecules.

Experimental

Ph_4Te was prepared [1] by treating Ph_3TeCl, 6.7 g (17 mmol) with PhLi, 1.85 g (22 mmol) at −78 °C in 50 ml of ether under scrupulously anhydrous conditions. The solution was stirred for 24 h at −78 °C, filtered and left to stand. Long yellow needles of Ph_4Te 1.3 g (18%) crystallised out. (Analysis. Found: C, 65.59; H, 4.74. $C_{24}H_{20}Te$ calcd.: C, 66.09; H, 4.63%.) The compound melted with decomposition above 100 °C.

Bis(2,2′-biphenylylene)tellurium was synthesised by reacting 2.2′-dilithium biphenyl, 3.3 g (20 mmol) with tellurium tetrachloride, 2.5 g (9.2 mmol) in 300 ml of ether at −78 °C. On warming to room temperature and stirring for 60 h a light yellow crystalline solid was obtained. The crude product was recrystallised from benzene, yield 0.7 g (16%). Analysis; found: C, 65.70, H, 3.41. $C_{24}H_{16}Te$ calcd.: C, 66.73; H, 3.73%. The compound melted with decomposition above 200 °C.

The NMR spectra were recorded on a Bruker WM 400 NMR spectrometer at a frequency of 126.24 MHz and at ambient temperature. The Mössbauer spectra were recorded using a constant acceleration drive and with the $^{125}Sb/Cu$ source and the absorbers at 4.2 K. The details of the experimental methods used have been given in ref. 10.

Mass spectra were recorded using a Hewlett–Packard 5985 spectrometer.

Acknowledgement

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