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^1H—{^{125}Te} HETERONUCLEAR MAGNETIC DOUBLE RESONANCE IN SOME ORGANOTELLURIUM COMPOUNDS

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Summary

^1H—{^{125}Te} Heteronuclear magnetic double resonance experiments have been used to determine tellurium chemical shifts for fifteen organotellurium compounds containing ^{125}Te in natural abundance.

Introduction

The three naturally most abundant isotopes of tellurium have nuclear spin quantum numbers of zero, and are therefore unsuitable for investigation by

TABLE 1

^{125}Te NMR PARAMETERS FOR ORGANOTELLURIUM COMPOUNDS

Compound	Solvent	$\Xi(^{125}Te)$ (Hz)	$\delta(^{125}Te)$ (ppm [a])	$\delta(H)$ (ppm)	$^2J(^{125}Te-H)$ (Hz)
Ph_2Te	CH_2Cl_2	31571515	688	8.41—7.44	
Ph_2Te	$(CH_3)_2SO$	31571415	685	7.96—7.18	
$(p\text{-}MeC_6H_4)_2Te$	CH_2Cl_2	31570719	663	7.77	
Ph_2TeCl_2	CH_2Cl_2	31580764	981	8.22—7.54	
$PhMeTeI_2$	CH_2Cl_2	31571817	698	2.57	25.5
$(p\text{-}MeC_6H_4)(Me)TeI_2$	CH_2Cl_2	31570728	663	3.60	26.2
$(p\text{-}MeOC_6H_4)(Me)TeI_2$	CH_2Cl_2	31570752	664	3.45	24.0
$(p\text{-}EtOC_6H_4)(Me)TeI_2$	CH_2Cl_2	31570939	670	3.53	26.2
$(Ph)_2(Me)TeI$	$(CH_3)_2SO$	31568588	595	3.32	25.0
$(o\text{-}MeC_6H_4)_2(Me)TeI$	$(CH_3)_2SO$	31568110	580	2.55	23.2
$(Ph)(Me)_2TeI$	$(CH_3)_2SO$	31567166	550	2.43	25.0
$(p\text{-}MeOC_6H_4)(Me)_2TeI$	$(CH_3)_2SO$	31567156	550	2.41	24.0
$(p\text{-}EtOC_6H_4)(Me)_2TeI$	$(CH_3)_2SO$	31566915	542	2.27	25.0
$Te_2(CH_2CO_2H)_2$	$(CH_3)_2SO$	31566765	538	3.74	33.0
$(Cl_3TeCH_2CO)_2O$	$(CH_3)_2SO$	31577070	864	4.23	27.7
$CH_2(TeCl_3)_2$	$(CH_3)_2SO$	31587601	1198	4.08	36.0

[a] To low field of Me_2Te.

NMR spectroscopy. Tellurium-125 has spin $\frac{1}{2}$, and difficulties associated with its low natural abundance (7%) and low sensitivity to NMR detection (3.16% of that of the proton at the same field strength) can be partially avoided by using heteronuclear double resonance techniques [1—4].

Tellurium-125 NMR data are recorded in Table 1 for twelve aryl-tellurium compounds, which might be expected to display similar trends to those found in alkyltellurium compounds [4], and for three derivatives of acetic anhydride [5].

Results and discussion

The only aryltellurium compound which has been investigated previously by heteronuclear magnetic double resonance is diphenyl telluride. The chemical shift for diphenyl telluride in methylene chloride reported here, $\delta(^{125}Te)$ 688 ppm agrees with the earlier value [4]. The similar chemical shift in dimethyl sulphoxide, $\delta(^{125}Te)$ 685 ppm, supports the prediction that solvent effects on ^{125}Te chemical shifts are slight [4]. The smaller chemical shift for di-*p*-tolyl telluride, $\delta(^{125}Te)$ 663 ppm, suggests that the tellurium nucleus is more shielded by the supply of electrons from the *para*-methyl group. The coupling constants, $^{3}J(^{125}Te—H)$, could not be measured for diaryl tellurides because the spectra were strongly second order, and only a small part of the satellite lines could be observed.

The addition of chlorine to diphenyl telluride gives diphenyltellurium(IV) dichloride. Tellurium satellites were not observed in the proton spectrum, and the ^{125}Te resonance frequency was recorded when maximum perturbation of the proton signals occurred. The large chemical shift of diphenyltellurium(IV) dichloride, $\delta(^{125}Te)$ 981 ppm, indicates deshielding of the tellurium nucleus by electronegative chlorine. Comparisons with dimethyl telluride [4], $\delta(^{125}Te)$ 0 ppm, and dimethyltellurium(IV) dichloride [4], $\delta(^{125}Te)$ 749 ppm, show that chlorine has a relatively greater effect on the chemical shifts of the methyl than the phenyl derivatives and that the tellurium nucleus is more shielded by methyl than by phenyl.

The proton signals of the methyl groups in aryl(methyl)tellurium(IV) iodides occur as sharp singlets flanked by well defined satellites with coupling constants in the region $^{2}J(^{125}Te—H)$ 23—27 Hz. The four diiodides have chemical shifts in the region $\delta(^{125}Te)$ 663—698 ppm. As expected, the tellurium nucleus is the least shielded in phenylmethyltellurium(IV) diiodide. The chemical shifts of the two diarylmethyltellurium(IV) iodides are smaller, $\delta(^{125}Te)$ 580—595 ppm, indicating that the tellurium nucleus becomes more shielded when iodine is replaced by methyl. The replacement of aryl by methyl causes further shielding. The chemical shifts of the three aryldimethyltellurium(IV) iodides are in the region $\delta(^{125}Te)$ 542—550 ppm whereas the value for trimethyltellurium(IV) iodide is $\delta(^{125}Te)$ 443 ppm [4].

The proton signals of the three methylene derivatives occur as sharp singlets flanked by satellites with somewhat greater coupling constants, $^{2}J(^{125}Te—H)$ 27—36 Hz. The chemical shift of ditellurodiacetic acid, $Te_2(CH_2CO_2H)_2$, $\delta(^{125}Te)$ 538 ppm is smaller then that of its precursor, the anhydride $(Cl_3TeCH_2CO)_2O$, $\delta(^{125}Te)$ 864 ppm, which contains electronegative chlorines. The large chemical shift of the hexachloride, $CH_2(TeCl_3)_2$, $\delta(^{125}Te)$ 1198 ppm, reflects the powerful withdrawal of electrons by chlorine in a small molecule, and shows the greatest deshielding of the tellurium nucleus of all the compounds investigated.

Experimental

The proton NMR spectra of concentrated solutions of organotellurium compounds containing tetramethylsilane as an internal standard were recorded on a modified JEOL 60MH spectrometer operating at 59.996 MHz. A frequency of ca. 18.94 MHz was varied until a change in the appearance of the spectrum arising from loss of ^{125}Te—^1H coupling occurred. The decoupling amplitude was then reduced until an accurate value (±100 Hz) of the ^{125}Te resonance frequency, ν(Hz), was obtained. This was corrected to a resonance frequency, $\Xi(^{125}Te)$(Hz) which refers to a polarising field strength in which the proton resonance for tetramethylsilane would be at 100 MHz exactly, using the relationship:

$$\Xi(^{125}\mathrm{Te}) = 10^8\nu/59.996(10^6 - \delta)$$

where δ(ppm) is the apparent chemical shift of the satellite. Tellurium chemical shifts, $\delta(^{125}Te)$(ppm), relative to dimethyl telluride [4] for which $\Xi(^{125}Te)$ is 31549802 Hz, are calculated from the relationship:

$$[\delta(^{125}\mathrm{Te}) = \Xi(^{125}\mathrm{Te})(\mathrm{compound}) - \Xi(^{125}\mathrm{Te})(\mathrm{Me_2Te})]/\ 31.55$$

Hence positive values $\delta(^{125}Te)$ are to low field of dimethyl telluride.

The organotellurium compounds were prepared by conventional methods [5,6]. Satisfactory melting points and analyses and the absence of spurious peaks from the proton NMR spectra were taken as criteria of purity.

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References

1 G. Pfisterer and H. Dreeskamp, Ber. Bunsengesell. Phys. Chem., 73 (1969) 654.
2 W. McFarlane, Ann. Reports NMR Spectroscopy, 1 (1968) 135, 5 (1972) 353.
3 G.W. Fraser, R.D. Peacock, and W. McFarlane, Mol. Phys. 17 (1969) 291.
4 H.C.E. McFarlane and W. McFarlane, J. Chem. Soc. Dalton Trans., (1973) 2416.
5 G.T. Morgan and H.D.K. Drew, J. Chem. Soc., (1925) 531.
6 F.J. Berry, E.H. Kustan, M. Roshani, and B.C. Smith, J. Organometall. Chem., 99 (1975) 115.