Studies of Tellurium Shielding by Heteronuclear Magnetic Double Resonance in a Representative Series of Compounds

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Tellurium-125 chemical shifts determined by heteronuclear double resonance in a range of organotellurium compounds are found to parallel closely the ^{77}Se chemical shifts in analogous compounds. The tellurium shielding decreases as the electronegativity of substituents increases and this is attributed to dominance by the paramagnetic term. Variations in ΔE do not appear to be important.

UNTIL recently, chemical-shift data for many of the heavier nuclei have been sparse because of problems of low natural abundance and sensitivity to n.m.r. detection.[1] However, these difficulties have now been greatly alleviated by double resonance [2] and Fourier transform [3] methods, and measurements of series of related molecules are now possible. Comparative data for ^{13}C, ^{29}Si, and ^{119}Sn indicate [4,5] that there are similarities of trends within the same group of the Periodic Table (the only naturally occurring magnetic isotope of germanium is ^{73}Ge with spin quantum number $\frac{9}{2}$ so that the nuclear quadrupole has seriously limited the number of compounds for which data are available) but the situation here is complicated by the possibility of different degrees of π-bonding. The Group VI elements selenium and tellurium are particularly suitable for comparative purposes because each has an isotope of moderate abundance with spin quantum number $\frac{1}{2}$, and they are in adjacent periods. The literature contains a large number of ^{77}Se chemical shifts [6-8] and a few ^{125}Te ones; [9-10] in this paper we present ^{125}Te chemical shifts and coupling constants in an additional 16 organotellurium compounds with a range of substituents. This procedure is better than simply comparing overall *ranges* of chemical shifts since these may be limited by the compounds available.

EXPERIMENTAL

The organotellurium compounds were prepared by standard methods, correct physical properties and the absence of spurious peaks from their proton n.m.r. spectra being taken as criteria of purity. MeSeTePr^i was made by equilibrating Me_2Se_2 and $Te_2Pr^i_2$. ^{1}H-{^{125}Te} double resonance experiments were performed as described elsewhere [8] by use of a modified 60 MHz JEOL spectrometer and neat samples containing dichloromethane or benzene for field stabilisation and referencing. Solid telluronium salts were examined as concentrated solutions in D_2O. We thank Dr. J. D. Kennedy for samples of $(Me_3Sn)_2Te$ and $(Me_3Sn)_2Se$.

RESULTS AND DISCUSSION

The isotope ^{125}Te ($I = \frac{1}{2}$) has a natural abundance of 7% so the resonances of protons separated by two or three bonds from a tellurium atom are flanked by satellites separated by $^nJ(^{125}\mathrm{Te}\cdots\mathrm{H})$ ($n = 2$ or 3). Observation of these, and irradiation at *ca.* 18·95 MHz, then gave the ^{125}Te resonant frequencies to ± 10 Hz or better which is equivalent to $\pm 0{\cdot}4$ p.p.m. The frequencies quoted in the Table are corrected to a polarising field strength in which Me_4Si would give a proton resonance of exactly 100 MHz.[2] Coupling constants involving ^{125}Te should be larger than those involving ^{77}Se in analogous compounds by a factor of $\gamma(^{125}\mathrm{Te}) \,.\, \psi_{5s}{}^2(\mathrm{O})(\mathrm{Te})/\gamma(^{77}\mathrm{Se}) \,.\, \psi_{4s}{}^2(\mathrm{O})(\mathrm{Se}) =$ *ca.* 2, and comparison of the data of the Table with literature values for $^nJ(^{77}\mathrm{Se}\cdots\mathrm{H})$ confirms that this is generally so. An important consequence of this is that in any particular type of compound tellurium satellites are less likely to be hidden by the central proton peak than are selenium ones. Thus in Ph_2Te it was possible to measure a

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[1] P. R. Wells, 'Determination of Organic Structures by Physical Methods,' ed. F. C. Nachod and J. J. Zuckerman, Academic Press, New York, 1971, vol. 4, p. 233.

[2] W. McFarlane, *Ann. Reports N.M.R. Spectroscopy*, 1968, **1**, 135; 1972, **5**, 353.

[3] D. G. Gillies and D. Shaw, *Ann. Reports N.M.R. Spectroscopy*, 1972, **5**, 557.

[4] A. Pregosin and E. Randall, ref. 1, p. 263.

[5] W. McFarlane and R. J. Wood, *J. Organometallic Chem.*, 1972, **40**, C17.

[6] T. Birchall, R. J. Gillespie, and S. L. Vekris, *Canad. J. Chem.*, 1965, **43**, 1672.

[7] M. Lardon, *J. Amer. Chem. Soc.*, 1970, **92**, 5063.

[8] W. McFarlane and R. J. Wood, *J.C.S. Dalton*, 1972, 1397.

[9] G. Pfisterer and H. Dreeskamp, *Ber. Bunsengesellschaft phys. Chem.*, 1969, **73**, 654.

[10] G. W. Fraser, R. D. Peacock, and W. McFarlane, *Mol. Phys.*, 1969, **17**, 291.

tellurium chemical shift by double resonance, whereas in Ph_2Se the selenium chemical shift could not be obtained in this way.

N.m.r. parameters of organotellurium compounds

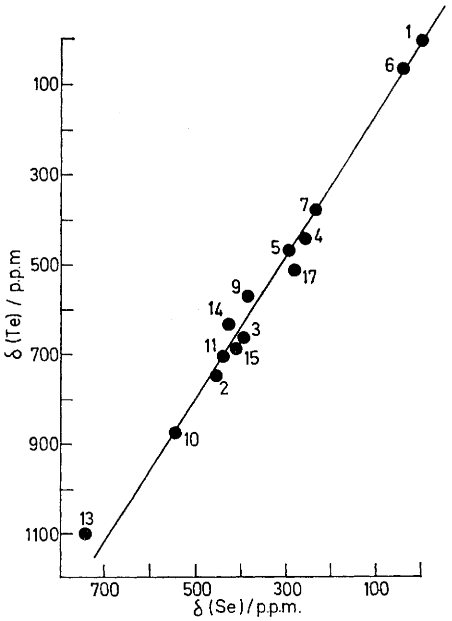
No.	Compound	$\Xi(^{125}Te)$/Hz	$\delta(^{125}Te)$ p.p.m. [i]	$\delta(H_\alpha)$ p.p.m. [j]	$\delta(H_\beta)$ p.p.m. [j]	$^2J(^{125}Te–H)$ Hz	$^3J(^{125}Te–H)$ Hz	Notes
1	Me_2Te	31 549 802 ± 2	0	4·14	—	21·6	—	*a*
2	Me_2TeCl_2	31 573 444 ± 16	749	3·13	—	25·7	—	*b*
3	Me_2TeBr_2	31 570 897 ± 8	669	3·19	—	25·8	—	*b*
4	$Me_3Te^+I^-$	31 563 771 ± 2	443	2·18	—	24·4	—	*e*
5	$EtMe_2Te^+Br^-$	31 564 645 ± 16	470	2·31 (Me)	2·99 (Et)	24·0 (Me)		*c*
6	Me_2Te_2	31 551 796 ± 5	63	2·63	—	23·5	*h*	*b*
7	Et_2Te	31 561 775 ± 16	380	2·57	1·59		22·7	*d*
8	Et_2Te_2	31 555 732 ± 16	188	3·01	1·59		34·5	*b*
9	$Et_3Te^+Br^-$	31 567 868 ± 16	573	3·00	1·51		32·7	*c*
10	Et_2TeBr_2	31 577 535 ± 16	879	3·50	1·70		32·8	*b*
11	Pr^i_2Te	31 572 112 ± 8	707	3·32	1·55		26·4	*b*
12	$Pr^i_2Te_2$	31 559 354 ± 16	303	3·40	1·60		22·2	*b*
13	$Pr^i_2TeBr_2$	31 584 676 ± 3	1105	3·92	1·78		32·8	*b*
14	$MePr^i_2Te^+I^-$	31 569 691 ± 80	630	*g*	*g*	*g*	*g*	*c*
15	Ph_2Te	31 571 516 ± 8	688	7·3—8·1				*b*
16	$(Me_3Sn)_2Te$	31 511 510 ± 8	−1214	—	0·53	—	2·9	*b*
17	MeSeTeMe	31 565 983	512	2·56	2·66	23·9	2·0	*d,f*
18	$MeSeTePr^i$	31 576 940 ± 50	860	3·29	2·60 (Se)		1·7	*b*

[a] Neat liquid. [b] Solution in dichloromethane. [c] Solution in deuterium oxide. [d] Solution in benzene. [e] Solution in $[^2H_6]$-dimethyl sulphoxide. [f] Taken from ref. 9. [g] Protons in the Pr^i groups are magnetically inequivalent: detailed analysis to be published elsewhere. [h] This coupling constant is reported to be zero in ref. 9. We have failed to observe 'inner' ^{125}Te satellites, but this could be due to dissociation. [i] To low field of Me_2Te. [j] To low field of Me_4Si.

In the Figure the tellurium chemical shifts [relative to $\delta(Me_2Te) = 0$] are plotted against the selenium chemical shifts [relative to $\delta(Me_2Se) = 0$] in analogous organoselenium compounds. In most cases the choice of suitable pairs of compounds is obvious, but care is needed with the ditellurides. For example the ^{125}Te chemical shift of Me_2Te_2 should be compared with the ^{77}Se chemical shift of MeSeTeMe, and the ^{125}Te chemical shift of MeSeTeMe compared with the ^{77}Se chemical shift of Me_2Se_2. The data for Et_2Te_2 and $Pr^i_2Te_2$ are not plotted because results for suitable mixed species were not available; however, the tellurium chemical shifts in Me_2Te_2, Et_2Te_2, and $Pr^i_2Te_2$ are linearly related to the selenium chemical shifts in the corresponding diselenides, so it seems likely that the points would lie on the line drawn in the Figure.

The ^{125}Te chemical shift of Me_2Te_2 was found to be concentration dependent. For example, a 2M solution in benzene gave $\delta(Te) = 303$ p.p.m. and on dilution this changed monotonically to 293 p.p.m. at 0·02M concentration. We have found that $\lambda_{max.}$ for Me_2Te_2 decreases from 410 to 385 nm on dilution in hexane and other solvents, and other ditellurides behaved similarly. The selenium chemical shift and $\lambda_{max.}$ for Me_2Se_2 were unaffected by dilution.

A major advantage of the double-resonance technique used is that no diamagnetic bulk susceptibility correction is needed to the observed chemical shifts. Additionally for heavy nuclei, other medium effects which might affect the shifts, *e.g.*, dispersion forces and ring currents of solvent molecules, should be negligible compared with the overall range of shifts observed. Our limited solvent studies confirm that this is so for tellurium (even with the ditellurides which display the greatest effects the maximum change was only 10 p.p.m.). The shielding of the tellurium nucleus can thus be considered to be the sum of the diamagnetic (σ^d) and the paramagnetic (σ^p) contributions.[11] Although σ^d itself is large, it is due mainly to the inner electrons of the atom in question and so for heavy nuclei variations in this



^{125}Te chemical shifts (to low field of Me_2Te) in organotellurium compounds plotted against ^{77}Se chemical shifts (to low field of Me_2Se) in corresponding species. The value for $(Me_3Sn)_2Te$ lies close to the straight line but is not plotted because it is well off-scale to high field. For key to compounds, see the Table

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[11] J. W. Emsley, J. Feeney, and L. H. Sutcliffe, 'High Resolution N.M.R. Spectroscopy, Pergamon, Oxford, 1965.

term arising from changes in substituents which affect the valence electrons will be negligible compared with the *variations in* σ^p. Jameson and Gutowsky have suggested that σ^p is given by [12] equation (1) where Δ is a

$$\sigma^p = -\frac{2e^2h}{3m^2c^2\Delta}\left(\langle r^{-3}\rangle_{5p}P + \langle r^{-3}\rangle_{5d}D\right) \qquad (1)$$

mean electronic excitation energy, $\langle r^{-3}\rangle_{5p}$ and $\langle r^{-3}\rangle_{5d}$ are the average values of the inverse cubes of the valence *p*- and *d*-electron radii, and *P* and *D* depend upon the unbalance of the valence electrons of the tellurium atom. [Note that owing to pressure from ^{13}C n.m.r. spectroscopists opposite sign conventions are used for σ and δ(Te).] Most of the compounds considered here can be discussed in terms of sp^n hybridisation of the tellurium atom, so the *D* term will be unimportant, and the *P* term will dominate. The latter will increase as the electron-withdrawing ability of the substituents attached to tellurium becomes greater. This then accounts for the high-field ^{125}Te chemical shift of $(Me_3Sn)_2Te$ in which the tellurium atom is attached to two atoms of very low electronegativity, and for the low-field shifts in compounds in which tellurium is attached to electronegative groups.

Equation (1) predicts that tellurium chemical shifts should parallel selenium shifts in analogous compounds and the correlation shown in the Figure demonstrates this to be true. Provided that the *P* terms for selenium and tellurium are the same in analogous compounds (and that the *D* terms can be neglected) the plot of $\delta(^{125}Te)$ against $\delta(^{77}Se)$ should have a slope given by expression (2).

$$\langle r^{-3}{}_{5p(\mathrm{Te})}\rangle \,.\, \Delta(\mathrm{Se})/\langle r^{-3}{}_{4p(\mathrm{Se})}\rangle \,.\, \Delta(\mathrm{Te}) \qquad (2)$$

For selenium and tellurium compounds it is difficult to obtain a reasonable estimate of Δ to use in equation (1); however, changes in this should parallel those in the position of the first absorption maximum in the visible–u.v. spectrum. To some extent this view is supported by the observation that dilution of Me_2Te_2 decreased the wavelength of this absorption by *ca.* 6% (*i.e.*, the energy of the transition increased) and this was accompanied by a shift of *ca.* 10 p.p.m. to high field in $\delta(^{125}Te)$. These changes are in the relative directions predicted by equation (1), but the quantitative implication that $\sigma^P = ca.\ 160$ p.p.m. seems much too small since the chemical shift of Me_2Te_2 is near the middle of a range of at least 2200 p.p.m., and the apparent agreement is probably fortuitous. However, since the points for the ditellurides do lie on the straight line shown in the Figure it seems reasonable to take $\Delta(\mathrm{Se})/\Delta(\mathrm{Te}) \sim \lambda(\mathrm{Te})/\lambda(\mathrm{Se}) = ca.\ 1{\cdot}25$ where λ is the wavelength of the electronic absorption.

Estimates of $\langle r^{-3}{}_{np}\rangle$ for tellurium and selenium vary, but their ratio is also *ca.* 1·25, so the plot of the Figure should have a slope of 1·5—1·6. The actual slope is 1·8 so the agreement is reasonable, especially in view of the approximations involved in the preceding treatment. In Group IV a similar treatment led to unexplained factors of 2·1 and 2·5 in passing from carbon to silicon and from silicon to tin respectively.[5]

It is known that ^{31}P chemical shifts in organophosphines, R_3P, and related compounds are in the opposite order to what would be expected on the basis of dominance by the inductive effect. That is, the phosphorus shielding *decreases* in the order Me > Et > Pr^i > Bu^t, and extensive studies [13] have shown that the effect is related to the amount of α-chain branching in R. More recently ^{77}Se chemical shifts have been found to display the same feature,[8] and the limited data available for suitable fluorine compounds show that this is also true of ^{19}F shielding.[14] Our results now show that ^{125}Te shielding is affected similarly and it appears likely that the effect arises when the nucleus in question belongs to an atom with a closed *s*-shell since it is not displayed by ^{13}C, ^{29}Si, or ^{119}Sn shieldings.

Our results show that tellurium magnetic shielding closely parallels that of selenium in analogous compounds, but that the sensitivity to changes in molecular structure is *ca.* 1·8 times greater. This is in broad agreement with Jameson and Gutowsky's prediction,[12] and ^{125}Te chemical shifts can be predicted with fair accuracy from the Figure if the corresponding ^{77}Se data are available.

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[12] C. J. Jameson and H. S. Gutowsky, *J. Chem. Phys.*, 1964, **40**, 1714.

[13] S. O. Grim, W. McFarlane, and E. F. Davidoff, *J. Org. Chem.*, 1967, **32**, 781.

[14] J. W. Emsley and L. Phillips, *Progr. N.M.R. Spectroscopy*, 1971, **7**, 1.