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THE PREPARATION OF DI-t-BUTYL DITELLURIDE AND DI-t-BUTYL TELLURIDE AND THE ^{125}Te NMR AND MÖSSBAUER SPECTRA OF SOME DIALKYL TELLURIDES AND DITELLURIDES

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Summary

The synthesis of di-t-butyl ditelluride, t-Bu_2Te_2, and di-t-butyl telluride, t-Bu_2Te, are reported together with that of di-(neo-hexyl) ditelluride. New syntheses of Me_2Te_2 and i-Pr_2Te_2 are presented. The high resolution ^{125}Te NMR data and the Mössbauer data for these compounds are discussed. The use of tellurium-proton couplings in high resolution ^{125}Te NMR spectra in assigning the resonances in mixed dialkyl ditellurides is also illustrated.

Introduction

As part of a detailed comparative NMR and ^{125}Te Mössbauer study of the tellurides $(Me_3X)_2Te$ and related compounds, where X = C, Si, Ge, Sn and Pb, it was of interest to synthesize the compounds t-Bu_2Te and t-Bu_2Te_2, which at the outset of this work had not previously been reported. During the course of our experiments Engman and Cava [1] reported the synthesis of t-Bu_2Te_2, while O'Brien et al. [2] published the results of a ^{125}Te NMR study of symmetrical and unsymmetrical dialkyl ditellurides, including t-Bu_2Te_2. The latter authors did not describe their synthesis of t-Bu_2Te_2 but referred to a paper in press.

We report here an attempted synthesis of t-Bu_2Te_2 which unexpectedly resulted in the formation of (neo-Hex)$_2$Te$_2$, $[(CH_3)_3CCH_2CH_2]_2Te_2$. A successful synthesis of t-Bu_2Te_2 is described together with the first reported synthesis of t-Bu_2Te. The compounds were characterized by high resolution ^{125}Te NMR spectroscopy and in the case of (neo-Hex)$_2$Te$_2$ by high resolution ^{13}C NMR spectroscopy. The ^{125}Te Mössbauer spectra of these compounds are also reported.

We also report the high resolution ^{125}Te NMR spectra of some mixed dialkyl ditellurides and show that the tellurium-proton couplings can be used to unequivocally assign the resonances for the mixed ditellurides.

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Experimental

Engman and Cava [1] have described the synthesis of the first di-t-alkyl ditelluride, t-Bu_2Te_2, which is an oil, by the reaction of t-BuLi with tellurium in dry THF followed by air oxidation. We had, prior to their publication, attempted a similar synthesis in which t-BuLi was added to dry THF at room temperature and the solution then cooled to $-78°C$. Elemental tellurium was added and on warming to $-10°C$ the tellurium dissolved smoothly to yield a dark red-brown solution which was air oxidized and the reaction mixture worked up to produce a red solid with a melting point of 35°C. This solid gave the chemical analysis C, 33.95 (33.80)%; H, 6.20 (6.10)%, consistent with the formulation $[(CH_3)_3CCH_2CH_2]_2Te_2$. The NMR spectra were also consistent with this formula as will be described below. It is apparent that the t-BuLi had reacted with the THF at room temperature to produce $(CH_3)_3CCH_2CH_2Li$ which on reaction with the tellurium yielded the observed ditelluride. It is now clear that had the addition of t-BuLi to THF been made at $-78°C$ this latter reaction would have been suppressed and t-Bu_2Te_2 obtained as described in ref. 1.

The ditelluride t-Bu_2Te_2 was subsequently prepared in our laboratory by the reaction of t-BuMgCl with $TeCl_4$ in THF.

$$\text{t-BuMgCl} + TeCl_4 \xrightarrow{THF} \text{t-}Bu_2Te_2 + \text{t-}Bu_2Te$$

This reaction produced a mixture of t-Bu_2Te_2 and t-Bu_2Te together with a third unidentified tellurium compound which may be t-BuTeCl. All three compounds are liquid at room temperature and pressure. The ditelluride is a red liquid with a boiling point of 81°C at 1 mmHg, while the telluride is a pale yellow liquid of boiling point 50–60°C at 1 mmHg. The third compound was present in the latter fraction in very small amounts and was difficult to separate by fractional distillation.

The ditelluride, t-Bu_2Te_2, was also subsequently prepared in 82% yield by reaction of t-BuMgCl with elemental tellurium in dry THF and in the presence of HMPTA (hexamethylphosphorustriamide). In the absence of HMPTA the tellurium does not dissolve and no reaction is observed.

While the ditelluride slowly decomposes in the light to precipitate elemental tellurium, solutions of ditelluride were found to be stable over many months at 0°C in the dark. The unidentified third compound was found to decompose at room temperature to form the ditelluride, as evidenced by the ^{125}Te NMR spectra.

In addition to t-Bu_2Te and t-Bu_2Te_2, it was also of interest to study the NMR spectra of Me_2Te_2 and i-Pr_2Te_2 and a new synthesis for these compounds was developed. This synthesis was based on the recent observation that elemental tellurium is reduced to telluride by an excess of Super-Hydride® ($LiBEt_3H$) [3–5]. In the present case the reduction was carried out in THF under dry nitrogen using $LiBEt_3H$ in slightly more than a 1/1 molar ratio with tellurium and the resulting purple solution of Li_2Te_2 was then reacted with methyl iodide or isopropyl iodide. A red solution of the corresponding dialkyl ditelluride was formed and, following removal of the volatile components in vacuum, the dialkyl ditelluride was obtained on distillation under reduced pressure in 80% yield. This present method is a very convenient and direct one-pot synthesis of the dialkyl ditellurides.

^{125}Te NMR spectra were obtained on a Bruker WM400 spectrometer at 126 MHz operating at ambient temperature. Resonances were found by utilizing 166 KHz sweep widths, 10 μsec (25°) pulse width and a 0.01 sec delay between acquisitions. Final spectra were obtained at the appropriate frequency generally using a 5 KHz sweep width and 90° pulse widths with no delay. No broadband decoupling was employed. Data acquisition consisted of 16 K data points which were zero filled to 32 K data points for the Fourier transform. Linewidths were in the range of 6 to 12 Hz. Samples were prepared in $CDCl_3$ for field shimming. In cases where the deuterium lock was insensitive to the shim coils the homogeneity was adjusted by monitoring the FID.

Mössbauer spectra were recorded using a conventional constant acceleration drive with the source and absorbers immersed in liquid helium. The source was a 2.5 mCi ^{125}Sb/Cu source (New England Nuclear) and 35.5 keV Mössbauer γ-ray was monitored through the keV escape peak using a Xe/CO_2 proportional counter. Absorbers were ca. 200 mg cm^{-2} of natural abundance compound. The spectra were computer fitted to Lorentzians.

Characterization of the compounds by NMR spectroscopy

The proton-coupled ^{125}Te high resolution NMR spectra of t-Bu_2Te_2 and t-Bu_2Te are shown in Fig. 1. The spectra clearly show the coupling of tellurium to an odd and to an even number of protons in t-Bu_2Te_2 and t-Bu_2Te respectively. The ^{125}Te chemical shifts with respect to neat Me_2Te are shown in Table 1. The ^{125}Te NMR spectrum of the third compound formed in the reaction of $TeCl_4$ with t-BuMgCl is also given in Fig. 1 and clearly shows the presence of a coupling to an odd number of protons, consistent with this being a tellurenyl compound.

In Fig. 2 is shown a ^{125}Te NMR spectrum illustrating the relative tellurium chemical shifts of all three tellurium species as observed in the t-Bu_2Te fraction separated from the products formed in the reaction of the $TeCl_4$ with t-BuMgCl. The resonance at 694 ppm decreased in intensity on standing and that due to t-Bu_2Te_2 at 499 ppm increased in intensity. This again points to the possible identification of the unknown species at 694 ppm as t-BuTeCl. However, due to the instability of this latter compound a more definitive characterization was not possible. In a further experiment it was shown that the tellurium species with a resonance at 694 ppm was also formed in small yield in the direct controlled chlorination of t-Bu_2Te_2.

The ^{125}Te solution NMR of $(neo\text{-}Hex)_2Te_2$ is also shown in Fig. 1. Here the tellurium coupling to the adjacent methylene groups yields a triplet which is split further by the next-nearest methylene protons. The proton-decoupled ^{13}C spectrum of $(neo\text{-}Hex)_2Te_2$ is shown in Fig. 3a and the methylene carbons, the quaternary carbon and the methyl carbons are identified. The assignment is supported by the splittings observed in the proton-coupled ^{13}C spectrum (Fig. 3b). The latter may be compared with the proton-coupled ^{13}C spectrum of t-Bu_2Te_2 in Fig. 3c, where only a quaternary carbon and the methyl carbons are observed.

The ^{125}Te chemical shifts reported here, relative to Me_2Te (neat) as reference standard, are generally somewhat larger than those reported in the literature. It may be noted that the chemical shifts exhibit a small temperature dependence ($\delta(Me_2Te)$ -1.58 ppm at 288 K and 0 ppm at 298 K) and a solvent dependence.

The ^{125}Te chemical shifts are of interest from a number of stand-points. Thus the

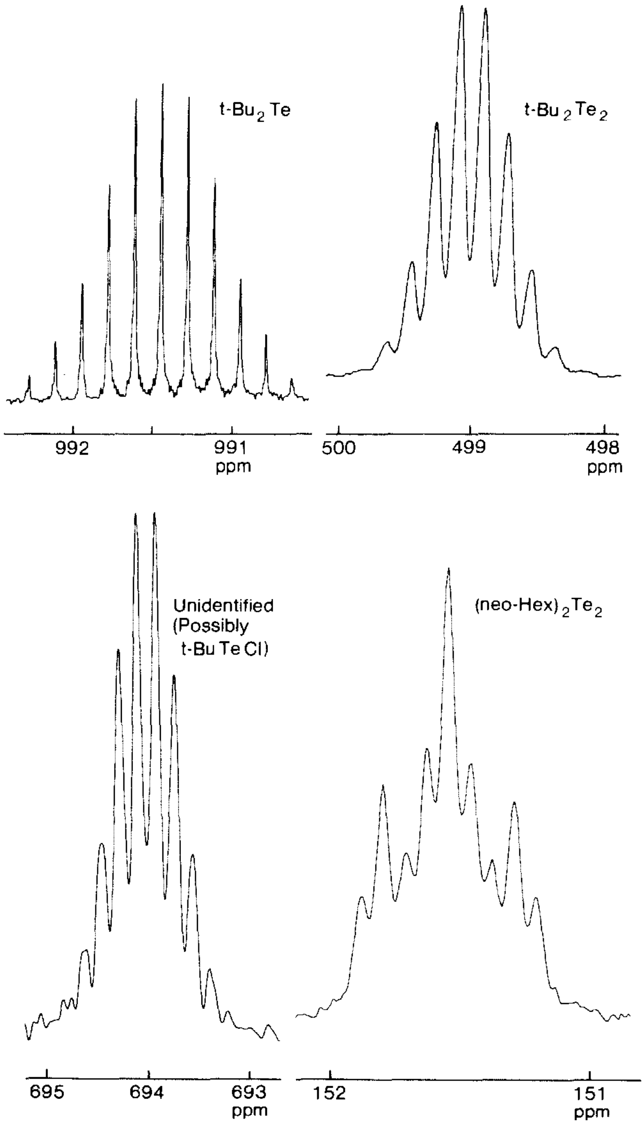

Fig. 1. ^{125}Te NMR spectra of t-Bu$_2$Te, t-Bu$_2$Te$_2$, the third tellurium species, possibly t-BuTeCl, and (neo-Hex)$_2$Te$_2$.

effect of α-methyl substitution on the chemical shifts observed for the symmetrical dialkyl ditellurides [2,6] and for the diselenides, selenides and selenols [7,8] have been commented on previously. It has been found that as the number of methyl groups on the α-carbon increases the chemical shifts of the symmetrical dialkyldiselenides [8] and ditellurides [2] become more positive corresponding to a decreased shielding at the selenium or tellurium. This is somewhat at odds with the result that would be expected simply on the basis of the inductive effect of the alkyl groups [8]. Thus it is generally assumed that the magnetic shielding of the heavier nuclei is

TABLE 1

^{125}Te NMR CHEMICAL SHIFT WITH RESPECT TO NEAT Me_2Te; POSITIVE SHIFTS ARE DOWNFIELD FROM Me_2Te

	Symmetrical tellurides			Symmetrical ditellurides		
	δ	solvent	ref.	δ	solvent	ref.
Me	0	neat		69	$CDCl_3$	2
				63	CH_2Cl_2	7
				73.4	$CDCl_3$	This work
Et	380	C_6H_6	7	186	$CDCl_3$	2
	376	$CDCl_3$	6	188	CH_2Cl_2	7
i-Pr	707	CH_2Cl_2	7	313	$CDCl_3$	2
	696	$CDCl_3$	6	303	CH_2Cl_2	7
				318.6	$CDCl_3$	This work
t-Bu	991.7	$CDCl_3$	This work	497	$CDCl_3$	2
	999		6	499	$CDCl_3$	This work
neo-Hex				151.5	$CDCl_3$	This work

dominated by the Ramsey paramagnetic term [7,9]:

$$\sigma_p \propto -\frac{1}{\Delta E}\left(\langle r^{-3}\rangle_{5p}P + \langle r^{-3}\rangle_{5d}D\right)$$

where ΔE is the 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 on the unbalance of the valence electrons of the tellurium atom. If ΔE can be considered to be constant within a series of compounds and if the tellurium *p*-orbitals are dominant in bonding, ignoring the *d*-orbitals, it would then be expected that as the electron withdrawing ability of the alkyl ligand decreases in going from Me to t-Bu that the shielding at the tellurium or selenium nucleus would

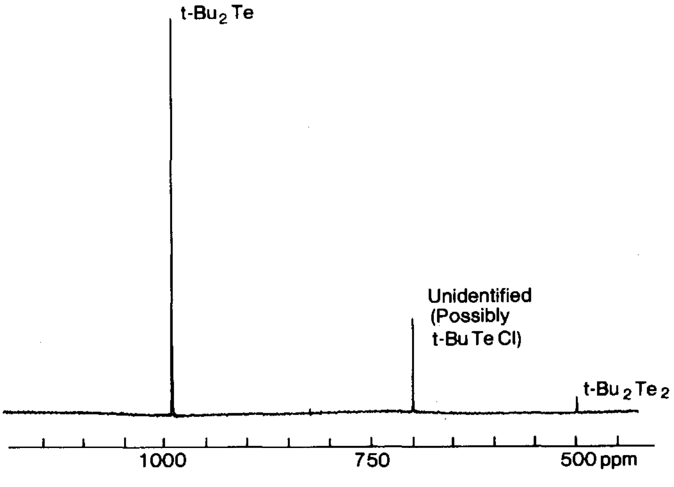

Fig. 2. The ^{125}Te NMR spectrum of the t-Bu_2Te fraction from the reaction of $TeCl_4$ with t-BuMgCl.

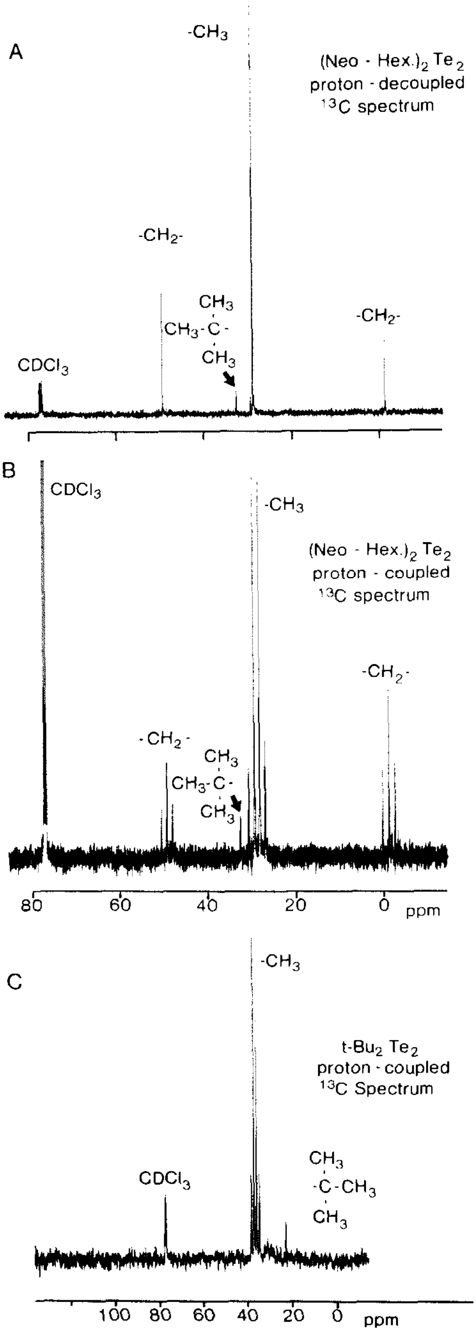

Fig. 3. (a) The proton-decoupled ^{13}C NMR spectrum of (neo-Hex)$_2$Te$_2$, (b) the ^{13}C proton-coupled spectrum of (neo-Hex)$_2$Te$_2$ and (c) the proton-coupled spectrum of t-Bu$_2$Te$_2$.

increase and that the chemical shift would become more negative. In fact the inverse is observed, and a systematic increase in chemical shift is observed as the number of α-methyl groups increases (see Table 1 for the ditellurides).

TABLE 2

^{125}Te NMR CHEMICAL SHIFTS WITH RESPECT TO NEAT Me_2Te FOR THE SYMMETRICAL DIALKYL DITELLURIDES

Symmetrical ditellurides	δ^a(ppm)
n-Pr	124
n-Bu	133
i-Pent	140
neo-Hex	151.5 (This work)

[a] Data for the first three compounds are taken from ref. 2.

The present results add to the data for the tellurides. It can be seen from Table 1 that the trend of increasing chemical shift with α-carbon substitution continues through to t-Bu_2Te. This is consistent with the very recent findings of O'Brien et al. [6].

With regard to the chemical shift of $(neo\text{-}Hex)_2Te_2$, it is apparent that the effect of γ-carbon substitution in the dialkyl ditellurides commented on by O'Brien et al. [2] also holds for this compound (Table 2). Thus as the number of γ-methyl groups increases from zero in $CH_3CH_2CH_2$ to three in $(CH_3)_3CCH_2CH_2$ the ^{125}Te NMR chemical shift again shows a systematic increase, although the increase is only ca. 9 ppm for each γ-methyl group added in comparison with ca. 140 ppm for each α-methyl group. This increase in δ with methyl substitution again runs counter to the

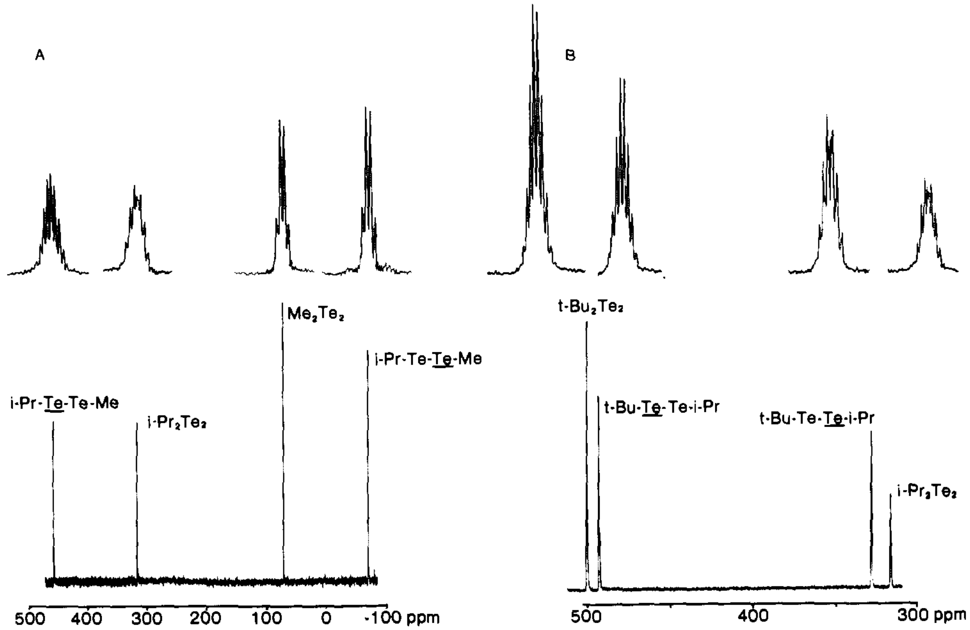

Fig. 4. ^{125}Te NMR spectra of (a) Me_2Te_2 and i-Pr_2Te_2 and their mixed ditellurides and (b) t-Bu_2Te_2 and i-Pr_2Te_2 and their mixed ditellurides.

trend that might have been expected if the inductive effect of the alkyl group was dominant in influencing the shielding at the tellurium.

While the chemical shifts of the symmetrical tellurides and ditellurides appear to be somewhat anomalous, the chemical shifts of the unsymmetrical dialkyl ditellurides are even more difficult to understand. O'Brien et al. [2] observed that for Me_2Te_2 (δ 69 ppm) and $i\text{-}Pr_2Te_2$ (δ 313 ppm) on mixing the unsymmetrical ditelluride yielded chemical shifts of δ(Me-*Te*-Te-i-Pr) – 74 ppm and δ(Me-Te-*Te*-i-Pr) 455 ppm, i.e., the methyl tellurium which initially was at lower frequency showed a negative shift and the i-Pr tellurium, initially at higher frequency, a positive shift. In sharp contrast, for $i\text{-}Pr_2Te_2$ (δ 313 ppm) and $t\text{-}Bu_2Te_2$ (δ 497 ppm) the unsymmetrical ditelluride gave shifts of δ(i-Pr-*Te*-Te-t-Bu) 325 ppm and δ(i-Pr-Te-*Te*-t-Bu) 490 ppm, i.e., the lower resonance frequency showing a positive shift and the higher resonance frequency a negative shift.

In assigning the resonances of the unsymmetrical ditellurides, O'Brien et al. relied on the principle that the effect of a structural change on the chemical shift of an atom decreases as the site of the change is moved away from the atom. Given the rather unusual behaviour of the chemical shifts of the symmetrical and unsymmetrical dialkyl ditellurides, it was of interest to confirm the assignment of the resonances and this was done employing the high resolution proton-coupled ^{125}Te NMR spectra (Fig. 4). The mixtures $Me_2Te_2/t\text{-}Bu_2Te_2$ and $i\text{-}Pr_2Te_2/t\text{-}Bu_2Te_2$ were studied and in each case each tellurium in the unsymmetrical ditelluride could be unequivocally identified through its tellurium-proton coupling pattern. The results of these experiments confirm the assignments made by O'Brien et al. as illustrated in Fig. 4.

Mössbauer spectroscopy

The ^{125}Te Mössbauer data are summarized in Table 3 and a sample spectrum is shown in Fig. 5. The Mössbauer isomer shift is a relative measure of the *s*-electron density at the nucleus and reflects the occupancy of the tellurium 5*s* orbital and the 5*p* orbitals on tellurium. Removal of 5*s* electron density decreases the ^{125}Te isomer shift while removal of 5*p* electron density increases the isomer shift through deshielding of the 5*s* electrons. The quadrupole splittings reflect the electric field gradient generated at the tellurium nucleus by the imbalance in the 5*p* orbital populations. In the dialkyl tellurides and ditellurides the large quadrupole splittings

TABLE 3

MÖSSBAUER DATA

	δ [a] (±0.08) (mm s^{-1})	Δ (±0.2) (mm s^{-1})
Me_2Te	0.06	10.5
$t\text{-}Bu_2Te$ [b]	0.19	10.5
Me_2Te_2	0.26	12.3
$i\text{-}Pr_2Te_2$	0.37	11.0
$t\text{-}Bu_2Te_2$	0.32	11.0
$(neo\text{-}Hex)_2Te_2$	0.38	10.5

[a] δ Mössbauer isomer shift relative to ^{125}I (Cu), source and absorber at 4.2 K. [b] $t\text{-}Bu_2Te$ contained traces of the unidentified tellurium impurity.

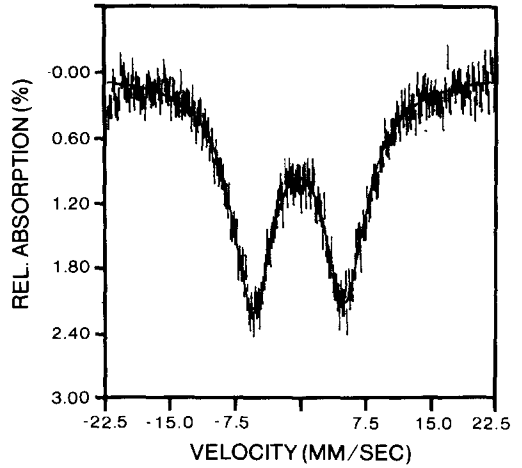

Fig. 5. ^{125}Te Mössbauer spectrum of i-Pr_2Te_2 measured at 4.2 K.

arise from the *p*-orbital imbalance between the Te–C bonds and the lone pairs on tellurium. As 5*p* electron density is removed from tellurium through bonds to the alkyl groups the quadrupole splitting would be expected to increase with increasing electronegativity of the alkyl group. Depending on the relative *s*–*p* character of the Te–C bond the Mössbauer isomer shift may be influenced as well.

As can be seen from Table 3 the Mössbauer isomer shifts and quadrupole splittings are similar for t-Bu_2Te and Me_2Te and the values for the ditellurides are also similar, although Me_2Te_2 does exhibit a significantly larger quadrupole splitting. The latter observation is consistent with the greater electronegativity of the Me group and an increased removal of 5*p* electron density from the tellurium. This molecule will also presumably have a larger asymmetry parameter which will further enhance the magnitude of the quadrupole splitting. The ditellurides generally have a larger quadrupole splitting than the tellurides reflecting the difference in the Te–Te and Te–C bonds.

There does not appear to be any simple relationship for dialkyl tellurides and ditellurides between the ^{125}Te NMR data obtained in solution and the Mössbauer data obtained in the solid state on pure solids or frozen neat liquids. Thus the NMR chemical shifts span a wide range and show the inverse trend in terms of shielding about the tellurium nucleus to that expected on the basis of simple electronegativity arguments. The Mössbauer isomer shifts and quadrupole splittings on the other hand are each very similar for the dialkyl tellurides and ditellurides while in Me_2Te_2 there is clear evidence from the quadrupole splitting for increased removal of 5*p* electron density from tellurium by the more electronegative Me group.

One possible explanation for the absence of any correlation between the ^{125}Te Mössbauer and NMR data could lie in the fact that the environment about tellurium is significantly different in the solid state to that in solution. However there is no evidence from crystal structure data for any intermolecular interactions in the solid state in the tellurides or ditellurides that could lead to such a difference.

An alternative explanation may lie in variations in the ΔE^{-1} term for the NMR chemical shift in the tellurides and ditellurides. In analogy with the diselenides [7], the ΔE^{-1} term in the expression for the paramagnetic contribution to the shielding for the tellurium compounds may be large. Since this would imply a corresponding sensitivity to changes in the population of excited states, this could explain the significant temperature dependence of the ^{125}Te NMR chemical shifts. Moreover, variations in ΔE^{-1} from one compound to another may also be the dominant factor in determining the chemical shifts for the dialkyl tellurides and ditellurides rather than changes in the *p*-orbital imbalance. One would then not expect any correlation between the NMR and Mössbauer data.

Acknowledgement

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