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## A $^{125}\text{Te}$ NMR STUDY OF THE EXCHANGE REACTION BETWEEN DIARYLDITELLURIDES \*

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### Summary

$^{125}\text{Te}$  NMR is used to study the chemical exchange between diarylditellurides. It is shown that the exchange is slow, and that is a thermal process. NMR parameters ( $\delta$ ,  $T_1$ ,  $^1J(\text{TeTe})$ ) of  $^{125}\text{Te}$  of ditellurides are given.

### 1. Introduction

The first indirect observation of tellurium NMR was by McFarlane [1,2], but the direct observation of the tellurium-125 resonance allows a better understanding of some chemical properties of this element [3–8]. We report here the use of  $^{125}\text{Te}$  and  $^{123}\text{Te}$  NMR in the study of the chemical exchange reactions between *para*-substituted diarylditellurides. Farrar [9] claimed that these ditellurides are dissociated into radicals, but vibrational [10] and Mössbauer spectroscopy [11] together with cryometric [12,13] measurements offered no proof of this proposition. In a more recent paper one of us [14] demonstrated an exchange reaction between ditellurides  $\text{R}_2\text{Te}_2$  and  $\text{R}_2^1\text{Te}_2$  using mass and proton NMR spectroscopy. The exchange reaction may be written as:



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In this paper we show that tellurium NMR is a powerful tool for the study of such systems and we find that oxygen reacts with these molecules to give new compounds. However, when oxygen and light are absent the exchange process (1) continues. The exchange is a thermal process, which is very slow.

## 2. Experimental

2.1. The diarylditellurides used in this study were synthesised by literature methods:  $(C_6H_5)_2Te_2$  [9],  $(p-CH_3C_6H_4)_2Te_2$  [15],  $(p-EtOC_6H_4)_2Te_2$  [12] and  $(p-ClC_6H_4)_2Te_2$  [16].

2.2. The  $^{125}Te$  NMR spectra were measured on a Bruker WH 90C spectrometer at 28.40 MHz, and  $^{123}Te$  at 23.57 MHz, in the Fourier mode.  $90^\circ$  pulses were used, except when indicated, without waiting time, since  $T_1$  is below 2 sec.  $^{13}C$  NMR spectra were obtained on the same instrument at 22.63 MHz, the sample temperature was  $26^\circ C$ . Special experiments are described in the text.

2.3.  $^{13}C$  chemical shifts are referred to TMS as internal reference. For tellurium, chemical shifts are referred to pure  $(CH_3)_2Te$  with about 5%  $C_6D_6$  for lock purposes. Referencing is achieved by the substitution method, which consists of the interchange of the sample and reference in the probe. This method avoids the bulk magnetic susceptibility correction for the sample. The effect of the difference of chemical shift between deuteriochloroform and perdeutero-benzene used as lock (about 0.1 ppm) is neglected, since there may be many other experimental errors, such as the temperature effect, which is about 0.16 ppm/ $^\circ C$  [17]. The signs of the chemical shifts follow the IUPAC convention [18].

2.4. As the proton—tellurium coupling constants are small and as there is no NOE, as previously shown for tellurium [17], all measurements of spectra were performed without proton decoupling.

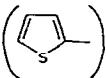
## 3. Results

### 3.1. NMR spectra of pure compounds

Table 1 presents some NMR parameters for pure diarylditellurides in  $CDCl_3$ . The literature reports  $^{13}C$  NMR data only for diphenylditelluride [2,19] and our values agree with those. These results allow the assignment of the carbons using published increments for the phenyl ring [20].

We have also measured the one-bond coupling constant between the two tellurium atoms. This was achieved using the  $^{123}Te$  resonance and observing the  $^{125}Te$  satellites. This is easier than attempting to observe the  $^{123}Te$  satellites in the  $^{125}Te$  NMR spectra. The coupling constant is found to be concentration dependent, and its value ranges from 213 to 223 Hz for the di-*p*-ethoxyphenylditelluride. The other  $^{123}Te$ — $^{125}Te$  coupling constants lie within the range 257—269 Hz. By contrast, the one-bond  $^{13}C$ — $^{125}Te$  coupling constant is independent of concentration and is equal to  $332 \pm 1$  Hz for the *p*-ethoxy derivative and  $304 \pm 1$  Hz for the *p*-methyl derivative.

TABLE 1  
NMR SPECTRAL PARAMETERS OF SOME DIARYLDITELLURIDES IN  $\text{CDCl}_3$ <sup>a</sup>

	$\delta(^{125}\text{Te})$	$T_{1\rho}$ ( $^{125}\text{Te}$ ) (sec.)	$\delta(^{13}\text{C}(1))$	$\delta(^{13}\text{C}(2))$	$\delta(^{13}\text{C}(3))$	$\delta(^{13}\text{C}(4))$	Other $\delta(^{13}\text{C})$
$(\text{C}_6\text{H}_5)_2\text{Te}_2$	420.8		108.0	137.6	129.2	128.0	
$(p\text{-CH}_3\text{C}_6\text{H}_4)_2\text{Te}_2$	432.2	1.4	104.3	138.3	130.2	138.3 <sup>b</sup>	20.7
$(p\text{-ClC}_6\text{H}_4)_2\text{Te}_2$	451.8		105.4	139.4	129.7	135.1	
$(p\text{-EtOC}_6\text{H}_5)_2\text{Te}_2$	456.0	1.7	92.4	140.5	115.6	159.7	63.1, 14.3
 $_2\text{Te}_2$	264.1						

<sup>a</sup>  $\delta(^{125}\text{Te}) \pm 0.2$  in ppm referred to external pure  $(\text{Me})_2\text{Te}$  and  $\delta(^{13}\text{C}) \pm 0.1$  in ppm referred to internal TMS. Temperature 26°C. <sup>b</sup>  $\pm 0.3$  ppm.

### 3.2. $^{13}\text{C}$ NMR spectra of mixtures

To study the exchange reaction in more detail we have examined the  $^{13}\text{C}$  NMR spectra of the following mixtures:

- (i)  $(p\text{-ClC}_6\text{H}_4)_2\text{Te}_2 + (p\text{-EtOC}_6\text{H}_4)_2\text{Te}_2$
- (ii)  $(p\text{-CH}_3\text{C}_6\text{H}_4)_2\text{Te}_2 + (p\text{-EtOC}_6\text{H}_4)_2\text{Te}_2$

The  $^{13}\text{C}$  chemical shifts of these two equimolar mixtures show no differences from the individual pure compounds and the spectra are the sum of the contributions from each component; thus no conclusions may be drawn as to the nature of the exchange, since there is no interaction between the aryl groups.

### 3.3. $^{125}\text{Te}$ NMR spectra of mixtures

We have studied the three following mixtures:

- (i)  $(p\text{-ClC}_6\text{H}_4)_2\text{Te}_2 + (p\text{-EtOC}_6\text{H}_4)_2\text{Te}_2$
- (ii)  $(p\text{-CH}_3\text{C}_6\text{H}_4)_2\text{Te}_2 + (p\text{-EtOC}_6\text{H}_4)_2\text{Te}_2$
- (iii)  $(p\text{-CH}_3\text{C}_6\text{H}_4)_2\text{Te}_2 + (p\text{-ClC}_6\text{H}_4)_2\text{Te}_2$

When equimolar mixtures are prepared in  $\text{CDCl}_3$  without special care (e.g. no removal of dissolved dioxygen) and examined in a conventional 10 mm tube, four lines immediately appear, and their chemical shifts and intensities are presented in Table 2. The labelling of the lines is from low field to high field, and typical spectra are reproduced in Fig. 1.

From these experiments we have positive proof that exchange occurs. The exchange is not fast since individual lines are observed, but the resonance arising from the symmetrical ditelluride species cannot be assigned directly as there are not always resonances corresponding to the pure compounds. The complete assignment is given later. The other interesting feature is that the line intensities are not as we would expect for a slowly exchanging system. Since we start with equimolar mixtures, a pair of lines of equal intensity should arise from the dis-

TABLE 2

$^{125}\text{Te}$  CHEMICAL SHIFTS (in ppm referred to external  $(\text{CH}_3)_2\text{Te}$  at  $26^\circ\text{C}$  and intensity in percent of the total intensity for the three mixtures studied in  $\text{CDCl}_3$ . Letters A, B, C, D refer to the lines as depicted in Fig. 1)

	Mixture i		Mixture ii		Mixture iii	
	$\delta(^{125}\text{Te})$	I (%)	$\delta(^{125}\text{Te})$	I (%)	$\delta(^{125}\text{Te})$	I (%)
A	475.2	24	459.3	24	451.5	26
B	462.7	20	456.3	25	446.9	26
C	455.3	32	433.9	25	436.8	26
D	444.3	24	430.5	26	431.6	22

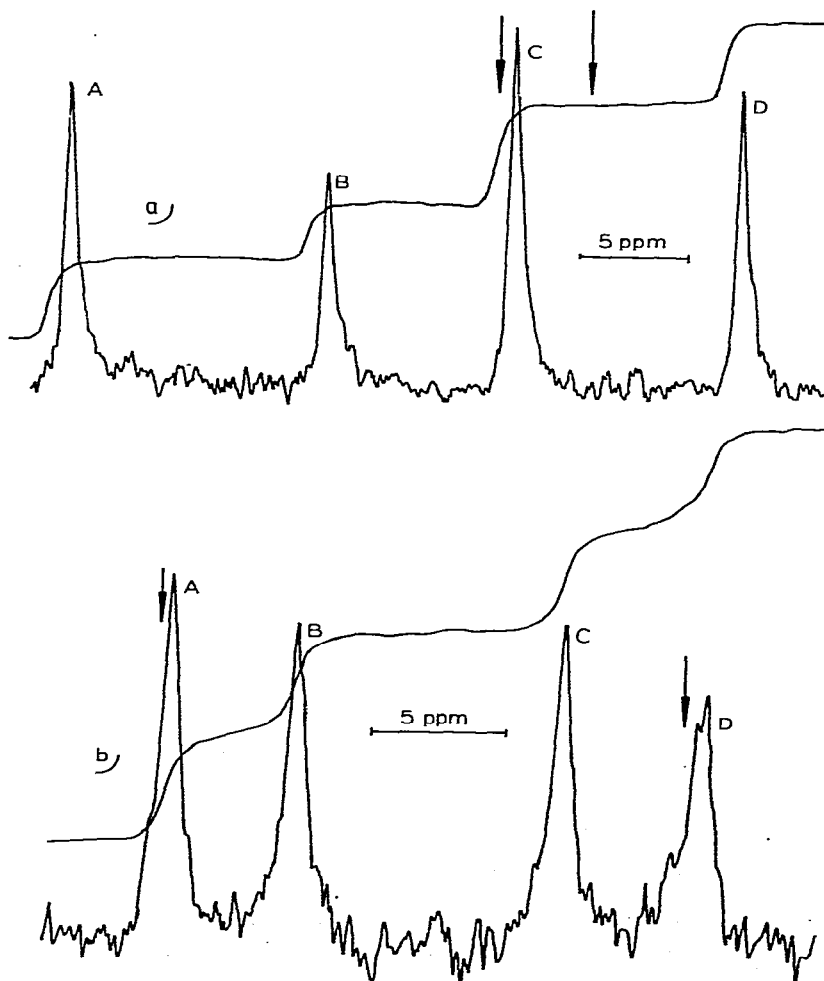


Fig. 1.  $^{125}\text{Te}$  NMR spectra of equimolar mixtures:

a) Mixture i:  $(p\text{-ClC}_6\text{H}_4)_2\text{Te}_2 + (p\text{-EtOC}_6\text{H}_4)_2\text{Te}_2$

b) Mixture iii:  $(p\text{-ClC}_6\text{H}_4)_2\text{Te}_2 + (p\text{-CH}_3\text{C}_6\text{H}_4)_2\text{Te}_2$

Arrows indicate the positions of the resonances of the pure compounds (Table 1).

TABLE 3  
SOLVENT EFFECT ON MIXTURE i<sup>a</sup>

Solvent	$\delta_A$	$\delta_B$	$\delta_C$	$\delta_D$
CDCl <sub>3</sub>	475.2	462.7	455.3	444.3
C <sub>6</sub> D <sub>6</sub>	473.5	460.3	450.6	438.5
	(1.7)	(2.4)	(4.7)	(5.8)
(CD <sub>3</sub> ) <sub>2</sub> CO	456.1	438.6	431.3	414.6
	(19.1)	(24.1)	(24.0)	(29.7)
THF	461.1	448.7	441.7	426.9
	(14.1)	(14.0)	(13.6)	(17.4)

<sup>a</sup> Values in parenthesis are the differences  $\delta(\text{CDCl}_3) - \delta(\text{Solvent})$ .

symmetric species (R<sub>2</sub>TeR<sup>1</sup>) and a further pair of lines with components of equal intensity should arise from the remaining symmetric species (R<sub>2</sub>Te<sub>2</sub> + R<sub>2</sub><sup>1</sup>Te<sub>2</sub>). In fact the predicted intensity relationships are not observed (Table 2), and the effect is most marked with mixture i.

The solvent effect has been studied both by changing the solvent with the same concentration of ditellurides and by investigating the dilution effect with mixtures i and ii. Table 3 presents data in different solvents, and Table 4 illustrates the effect of dilution in two different solvents.

Dilution leads to a deshielding of the same order for all resonances together. In contrast the solvent effect is large and more pronounced for lines C and D.

The assignment of resonances to individual tellurium-containing species has been achieved by measurement of the one-bond coupling constants between the two tellurium atoms. Only the dissymmetrical species will give an AB case giving rise to the <sup>1</sup>J(<sup>125</sup>Te—<sup>125</sup>Te) coupling constant. The observed couplings are gathered into Table 5. The coupling constants are solvent and concentration dependent, and allow the assignment of different lines to the various species in mixtures i and ii:

Mixture i:

line A, (*p*-EtOC<sub>6</sub>H<sub>4</sub>)Te-;      line B, (*p*-EtOC<sub>6</sub>H<sub>4</sub>)<sub>2</sub>Te<sub>2</sub>;  
line C, (*p*-ClC<sub>6</sub>H<sub>4</sub>)<sub>2</sub>Te<sub>2</sub>;      line D, (*p*-ClC<sub>6</sub>H<sub>4</sub>)Te-

TABLE 4  
EFFECT OF 4-FOLD DILUTION ON MIXTURE i IN C<sub>6</sub>D<sub>6</sub> AND A 3-FOLD DILUTION OF MIXTURE ii IN CDCl<sub>3</sub>

		$\delta(\text{Te})$ (ppm)	<i>I</i> (%)	Dilute soln.		$\Delta\delta$ (ppm)
				$\delta(\text{Te})$ (ppm)	<i>I</i> (%)	
Mixture i	A	473.5	23	469.1	26	4.4
	B	460.3	15	456.1	18	4.2
	C	450.6	35	445.5	33	5.1
	D	438.5	27	433.7	23	4.8
Mixture ii	A	459.3	24	457.3	23	2.0
	B	456.3	25	453.3	23	2.5
	C	433.9	25	431.9	24	2.0
	D	430.5	26	428.3	30	2.2

TABLE 5  
ONE-BOND COUPLING CONSTANTS BETWEEN  $^{125}\text{Te}$  AND  $^{125}\text{Te}$  IN DISSYMMETRICAL SPECIES

Species	Split lines	Solvent	$^1J(^{125}\text{Te}-^{125}\text{Te})$ (Hz)
(i) $\text{EtOC}_6\text{H}_4\text{TeTeC}_6\text{H}_4\text{Cl}$	A and D	$\text{CDCl}_3$	170
	A and D	$\text{C}_6\text{D}_6$	175
	A and D	dilute	178
(ii) $p\text{-EtOC}_6\text{H}_4\text{TeTeC}_6\text{H}_4\text{CH}_3$		$\text{C}_6\text{D}_6$	
	B and C	$\text{C}_6\text{D}_6$	207

Mixture ii:

line A,  $(p\text{-EtOC}_6\text{H}_4)_2\text{Te}_2$ ; line B,  $(p\text{-EtOC}_6\text{H}_4)\text{Te}$ ;  
line C,  $(p\text{-CH}_3\text{C}_6\text{H}_4)\text{Te}$ ; line D,  $(p\text{-CH}_3\text{C}_6\text{H}_4)_2\text{Te}_2$ .

In mixture iii, the assignments followed from the data for i and ii:

Mixture iii:

line A,  $(p\text{-ClC}_6\text{H}_4)_2\text{Te}_2$ ; line B,  $(p\text{-ClC}_6\text{H}_4)\text{Te}$ ;  
line C,  $(p\text{-CH}_3\text{C}_6\text{H}_4)\text{Te}$ ; line D,  $(p\text{-CH}_3\text{C}_6\text{H}_4)_2\text{Te}_2$ .

In the latter case the resonances of the symmetrical species are very close to those of the pure compounds in the same solvent (Table 1).

#### 4. Discussion

4.1. The fact that  $^1J(\text{Te}-\text{Te})$  may be measured means that the exchange is very slow, with an upper limit for its rate of about  $(J(\text{Te}-\text{Te}))^{-1}$  or  $4 \times 10^{-3} \text{ sec}^{-1}$ . We have tried to observe the establishment of the equilibrium by measuring spectra just after mixing and at different times later. The results for mixture i in  $\text{CDCl}_3$  are presented in Table 6. The chemical shifts are immediately established, but the intensities observed in the first measurement show that the system has not completely reached equilibrium, and this confirms the slow rate of this exchange. The rates of exchange depend on the mixture and solvent. Mixture ii in  $\text{C}_6\text{D}_6$  has a line width of 4 Hz and allows the measurement of  $^3J(\text{Te}-\text{H})$  (Fig. 2) which is 4.5 Hz for lines A and C and 6 Hz for lines B and D. This leads to a rate of exchange of less than  $0.3 \text{ sec}^{-1}$ . For the other mixtures the measurements of the proton-tellurium coupling constant is impossible and the line widths are greater. Mixture i in  $\text{C}_6\text{D}_6$  has a line width of 20 Hz and in  $\text{CDCl}_3$  of 12 Hz, while mixture ii has a line width of 20 Hz in  $\text{CDCl}_3$ , and thus in these cases the exchange is faster.

TABLE 6  
CHANGE OF SIGNALS FROM MIXTURE i IN  $\text{CDCl}_3$  WITH TIME AFTER MIXING

Time after mixing (min)	$\delta_A$ (ppm)	$I_A$ (%)	$\delta_B$ (ppm)	$I_B$ (%)	$\delta_C$ (ppm)	$I_C$ (%)	$\delta_D$ (ppm)	$I_D$ (%)
0	474.7	20.5	462.1	20.5	454.7	35	443.7	24
20	475.2	24	462.7	18	455.3	32	444.3	26
$\infty$	475.3	23.5	462.7	18	455.3	33	444.4	25.5

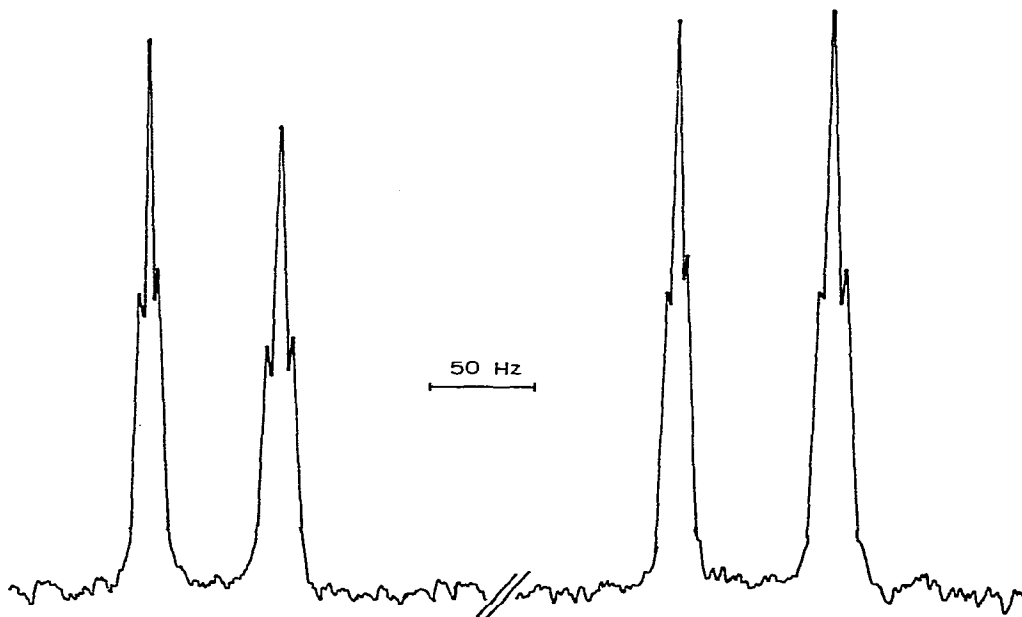


Fig. 2. Undecoupled  $^{125}\text{Te}$  NMR spectra of mixture *i* in  $\text{C}_6\text{D}_6$  showing the three-bond  $^{125}\text{Te}$ - $^1\text{H}$  coupling constant.

4.2. We have observed that solutions stored in the laboratory without special care eventually give a white precipitate which covers the wall of the container. A similar precipitate was noted during attempts to obtain molecular weight data by vapour phase osmometry for solutions of individual ditellurides in benzene; furthermore, the molecular weights determined were scattered over a large range of values and reproducibility was poor. It was noted that when the experimental solutions were put aside the colour became less intense until finally only a pale yellow solution in contact with a white solid remained. Elemental analysis of the solid suggests an empirical formula " $(\text{RTeO})_2\text{O}$ " ( $\text{R} = \text{aryl}$ ). Infra-red analysis shows strong bands centred on  $550\text{ cm}^{-1}$  which are very characteristic of  $\nu(\text{Te}-\text{O})$  [22]. Thus the product certainly contains oxygen. Work by others in

TABLE 7

CHEMICAL SHIFTS AND INTENSITIES OF MIXTURE *i* IN  $\text{CDCl}_3$  UNDER DIFFERENT CONDITIONS. In parenthesis are shown the linewidth in Hz

Conditions	$\delta_A$ (ppm)	$I_A$ (%)	$\delta_B$ (ppm)	$I_B$ (%)	$\delta_C$ (ppm)	$I_C$ (%)	$\delta_D$ (ppm)	$I_D$ (%)
Ordinary	475.2	24	462.7	20	455.3	32	444.3	24
Without $\text{O}_2$	471.2	27	459.3	23	450.3	23	440.0	27
Without $\text{O}_2$ and without light	469.6	25	457.9	25	448.5	25	438.5	25
Saturated with $\text{O}_2^a$	473.0 (14)	25	460.2 (14)	25	451.1 (23)	25	439.0 (23)	25

<sup>a</sup> We observed the same behaviour in  $\text{C}_6\text{D}_6$ .

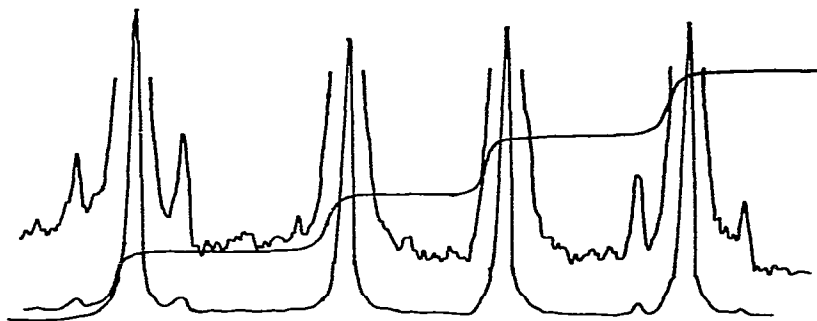


Fig. 3.  $^{125}\text{Te}$  NMR spectra of mixture *i* in  $\text{CDCl}_3$  without dioxygen. Compare line intensities with those in Fig. 1.

our laboratory has independently demonstrated a reaction of ditellurides in solution with dioxygen capable of producing radical intermediates [23] and so we must accept that dioxygen in our solvents may play a role in producing the spectroscopic data described above.

To evaluate this hypothesis we prepared a sample of mixture *i* with degassed  $\text{CDCl}_3$ , and then observed a normal spectrum, as indicated in Table 7 and shown in Fig. 3. The intensities of lines A and D of the dissymmetric species are equal, as are lines B and C corresponding to the symmetric species.

We have also attempted to determine whether or not the exchange may be photochemically initiated (as is the reaction of the diarylditelluride with dioxygen [23]). For this purpose a 10 mm sample tube was painted black and the appropriate quantities (equimolar) of the ditellurides were weighed into the tube. The solids were then covered with degassed  $\text{CDCl}_3$  in the dark and sealed into the tube. The resulting spectral data are given in Table 7. The exchange occurs without photochemical assistance, and line intensities are similar to those for the previous sample in degassed solvent. The small difference that is observed may possibly arise from the influence of light, but it is at the limit of precision of the measurements. The exchange is a thermal process. In order to study the influence of  $\text{O}_2$  in more detail we saturated mixture *i* with this gas. The chemical shifts and intensities remained approximately constant within the experimental error arising from a solvent effect which comes from the evaporation of the solvent. In contrast, the line widths of the signals from the *p*- $\text{EtOC}_6\text{H}_4\text{Te}$  group are slightly increased (14 Hz), and those of the *p*- $\text{ClC}_6\text{H}_4\text{Te}$  signals increase to a greater extent (23 Hz). This indicates that the oxygen preferentially interacts with the tellurium atom bounded to the *p*- $\text{ClC}_6\text{H}_4$  part. In other mixtures this behaviour is not observed.

4.3. Another interesting feature of these spectra are the chemical shifts obtained in mixtures compared with those for the pure compounds. Usually, in a mixture of two compounds undergoing a slow exchange, the chemical shifts of the original molecules, if some remain, are the same for the two solutions at identical concentrations. Tables 1 and 2 and Fig. 1 show that this is not the case in our systems. This becomes understandable if we study a mixture con-



TABLE 8

INFLUENCE OF VARYING THE RATIO X, THE NUMBER OF MOLES OF  $(p\text{-EtOC}_6\text{H}_4\text{Te})_2$ /NUMBER OF MOLES OF  $(p\text{-ClC}_6\text{H}_4\text{Te})_2$ , ON THE CHEMICAL SHIFTS OF THE DIFFERENT COMPOUNDS IN  $\text{CDCl}_3$

X	$\delta_A$ (ppm)	$\delta_B$ (ppm)	$\delta_C$ (ppm)	$\delta_D$ (ppm)
0	—	—	447.3	—
0.25	468.4	—	447.3	437.5
0.50	468.4	457.0	447.3	437.7
0.75	468.4	457.0	447.3	437.7
1	468.7	457.2	447.4	437.9

taining a different quantity of one of the components. Table 8 presents the results in one case. All the chemical shifts remain constant and a small increase appears only for the most concentrated solution. This shows that the chemical shifts of the original symmetrical molecules in fact arise from equimolar mixtures. Thus comparisons of tellurium chemical shifts must be made with care even on very similar molecules. Solvent concentration and temperature effects [17] may have significant effects.

4.4. The anomalous intensities listed in Table 2 are not well understood. We can say that this is not a pulse effect [21] in an exchanging system or a dynamic effect in the acquisition of the decay. The last possibility was easily eliminated by using a waiting time equal to  $10T_1$  between each scan and a careful adjustment of the receiver gain to avoid any saturation of the ADC converter. The pulse length also has no effect, since use of a smaller pulse angle of about  $10^\circ$ , which is below the value proposed by Ernst [21], leads to the same spectra. A CIDNP effects remains possible, or different rates of oxidation for the four species, leading to different concentration after some hours. But further experimental results not described in this paper cannot be interpreted on the basis of either of these two effects, and further experiments are in progress.

## 5. Conclusion

Diarylditellurides undergo exchange in solution at room temperature. This explains why  $^1J(^{125}\text{Te}\text{—}^{125}\text{Te})$  in mixtures changes with the solvent or the dilution. Pure diarylditellurides may also be exchanging species, and this would explain some discrepancies in the measurement of  $^1J(^{125}\text{Te}\text{—}^{123}\text{Te})$  on symmetrical species by other workers [24] and ourselves.

One of the most interesting features is the role of dioxygen in the exchange mechanism. Our results demonstrate that the reaction can be influenced by dioxygen in the solvent, and thus that care must be taken in the studies of chemical mechanisms in tellurium chemistry.

## References

- 1 H.C.E. McFarlane and W. McFarlane, *J. Chem. Soc., Dalton*, (1973) 2416.
- 2 W. McFarlane, F.J. Berry and B.C. Smith, *J. Organometal. Chem.*, 113 (1976) 139.
- 3 T. Drackenberg, F. Fringuelli, S. Gronowitz, A.B. Hörnfeld, I. Johnson and A. Taticchi, *Chem. Script.*, 10 (1976) 139.
- 4 K.U. Buckler, J. Kronenbitter, O. Lutz and A. Nolle, *Z. Naturforsch.*, 32A (1977) 1263.
- 5 W. Koch, O. Lutz and A. Nolle, *Zeitsch. Phys.*, A289 (1979) 17.
- 6 G.J. Schröbilgen, R.C. Burns and P. Granger, *J. Chem. Soc. Chem. Commun.*, (1978) 957.
- 7 C.R. Lassigne and E.J. Wells, *J. Chem. Soc. Chem. Commun.*, (1978) 956.
- 8 G.V. Fazakerley and M. Celotti, *J. Mag. Reson.*, 33 (1979) 219.
- 9 W.V. Farrar, *Research (London)*, 4 (1951) 177.
- 10 W.R. McWhinnie and P. Thavorniyutikarn, *J. Organometal. Chem.*, 35 (1972) 149.
- 11 C.H.W. Jones, R. Schultz, W.R. McWhinnie and N.S. Dance, *Canad. J. Chem.*, 54 (1976) 3234.
- 12 G.T. Morgan and H.D.K. Drew, *J. Chem. Soc.*, (1925) 2307.
- 13 G.T. Morgan and R.E. Kellett, *J. Chem. Soc.*, (1926) 1080.
- 14 N.S. Dance, W.R. McWhinnie and C.H.W. Jones, *J. Organometal. Chem.*, 125 (1977) 291.
- 15 P. Thavorniyutikarn, Ph. D. Thesis, University of Aston in Birmingham, 1972.
- 16 I.D. Sadekov, L.M. Sayapira, A.Ya. Bushkov and V.I. Minkin, *Zh. Obsch. Khim.*, 41 (1971) 2713.
- 17 P. Granger and S. Chapelle, *J. Magn. Reson.*, 39 (1980) 329.
- 18 Recommendation for the Presentation of NMR Data for Publication in Chemical Journals; a) *Pure Appl. Chem.*, 29 (1972) 627; b) *Pure Appl. Chem.*, 45 (1976) 217; c) *Org. Magn. Reson.*, 11 (1978) 267.
- 19 A. Forchioni, V. Galasso, K.J. Irgolic and G.C. Pappalardo, *J. Organometal. Chem.*, 135 (1977) 327.
- 20 D.F. Ewing, *Org. Magn. Reson.*, 12 (1979) 499.
- 21 S. Schaublin, A. Höhener and R.R. Ernst, *J. Magn. Reson.*, 13 (1974) 196.
- 22 P. Thavorniyutikarn and W.R. McWhinnie, *J. Organometal. Chem.*, 50 (1973) 135.
- 23 J.D. Miller and R. Mehdi, personal communication to W.R.M.
- 24 E.J. Wells, private communication to P.G.