# Substituent Effects and Stereochemistry in <sup>125</sup>Te NMR Spectroscopy. Diorganyltellurium Dihalides and Some Tellurides and Ditellurides<sup>†</sup>

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<sup>125</sup>Te, <sup>19</sup>F and <sup>13</sup>C NMR data for 33 compounds containing tellurium substituents are presented. The <sup>125</sup>Te chemical shifts in (PhTeCl<sub>2</sub>)R compounds are between  $\delta = 878$  and 1023; in corresponding (PhTeF<sub>2</sub>)R compounds they are 220 to 360 ppm larger. Effects of substituents and conformational interconversions (dynamic <sup>125</sup>Te NMR) are discussed. Several diastereomers were identified in (PhTeCl<sub>2</sub>)R derivatives which are stable at room temperature and differ in the configuration at the tellurium atom (restricted pseudo-rotation). It is shown that <sup>125</sup>Te is a well suited nucleus for chiral recognition.

KEY WORDS <sup>125</sup>Te NMR <sup>19</sup>F NMR <sup>13</sup>C NMR Substituent effects Dynamic <sup>125</sup>Te NMR Phenyltellurenylalkanes Diorganotellurium halides Chiral recognition

## INTRODUCTION

The element tellurium provides two NMR-active isotopes, <sup>123</sup>Te and <sup>125</sup>Te, both of which are spin- $\frac{1}{2}$  nuclei. However, <sup>125</sup>Te is preferred owing to its much higher natural abundance (ca. 7%) and receptivity, which is about 12.5 times that of <sup>13</sup>C. These properties make <sup>125</sup>Te a readily detectable nucleus and <sup>125</sup>Te NMR spectroscopy an important tool in organotellurium chemistry. Consequently, several reviews have appeared during the last 15 years.<sup>1-4</sup> Interestingly, however, there seem to be only very few stereochemical applications of <sup>125</sup>Te NMR. For example, it has been reported that the <sup>125</sup>Te chemical shifts in the two 3-endo- and 3-exophenyltellurenyl camphor diastereomers differ by as much as 177 ppm.<sup>5</sup> Positive results in investigating stereochemical effects on <sup>77</sup>Se NMR parameters<sup>6-8</sup> prompted us to extend our interest to the <sup>125</sup>Te nucleus, and in this paper we report our first results.

## EXPERIMENTAL

### NMR measurements

<sup>125</sup>Te NMR spectra were recorded at 126.3 MHz (Bruker AM-400 spectrometer) in 0.2-1 M CDCl<sub>3</sub> solution in 5 or 10 mm probes without decoupling. Pulse

CCC 0749-1581/94/050303-09 © 1994 by John Wiley & Sons, Ltd. widths were calibrated to flip angles of *ca.* 30°. Repetition rates were 0.6 s. Spectral widths were 166 kHz and the digital resolution 10.2 Hz. If necessary, the digital resolution was reduced to 0.6 Hz and repetition rates were 2.2 s. <sup>125</sup>Te chemical shifts are referred to that of external 1 M PhTeTePh in CDCl<sub>3</sub> ( $\delta = 420$ ) corresponding to  $\delta = 0$  for (CH<sub>3</sub>)<sub>2</sub>Te.<sup>4</sup>

<sup>19</sup>F NMR spectra were recorded under standard conditions at 75.4 MHz (Bruker WP-80 spectrometer) or 94.2 MHz (Bruker WP-100 spectrometer) in 0.2–1 M CDCl<sub>3</sub> solution in 5 mm probes. The <sup>19</sup>F chemical shifts are referred to internal (5%) CFCl<sub>3</sub> ( $\delta = 0$ ).

For all <sup>1</sup>H and <sup>13</sup>C NMR spectra including DEPT and COSY techniques, standard Bruker software and parameters were used. <sup>1</sup>H and <sup>13</sup>C chemical shifts are referenced to tetramethylsilane ( $\delta = 0$ ).

IR spectra in the range 4000–600 cm<sup>-1</sup> were recorded from CHCl<sub>3</sub> solutions on a Perkin-Elmer Model 1310 spectrophotometer; for the range of 500–100 cm<sup>-1</sup> a Perkin-Elmer 1700 X Fourier transform IR spectrophotometer was used. Electron impact (70 eV) mass spectra were obtained on a Varian MAT CH-7 spectrometer; m/z values refer to fragments containing the <sup>130</sup>Te and <sup>35</sup>Cl isotope (if present).

## Syntheses

The following compounds were prepared by the methods cited:  $Ph_2Te_2$ , <sup>9</sup> 15,<sup>10</sup> 17 and 18,<sup>11</sup> 21 and 22.<sup>12</sup>

Compound  $16^{13}$  was obtained from the reaction of TeCl<sub>4</sub> with diphenyl ether,<sup>14</sup> column chromatography (silica gel) of the crude reaction product with toluene–

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ethanol-acetic acid-water (200:33:3.5:1) as eluent and recrystallization of pure 16 from benzene.

In general, all experiments involving  $Te^{II}$  species were carried out under strict light protection (dark-room conditions with a red safety light). All solvents were dried prior to use, and all reactions were performed under exclusion of moisture and oxygen. Reaction progress and/or liquid chromatography (LC, silica gel and the specified eluent) were monitored by TLC.

All unsubstituted phenyltellurenylalkanes were synthesized by the general procedure A, the  $\alpha$ phenyltellurenyl-substituted carboxylic esters by procedure B, mainly following a short notice in Ref. 15. All diorganotellurium dichlorides were obtained by the reaction of the corresponding crude product from procedure A or B with SO<sub>2</sub>Cl<sub>2</sub> (procedure C or C'). Diorganotellurium difluorides were prepared following procedure D.

General procedure A: syntheses of phenyltellurenylalkanes. A 1.00 g (2.44 mmol) amount of Ph<sub>2</sub>Te<sub>2</sub> was dissolved in 30 ml of ethanol and NaBH<sub>4</sub> (ca. 5.4 mmol) was added until the red colour changed to slight yellow. The suspension was refluxed for 45 min and cooled to room temperature under an inert atmosphere and 5.0 mmol of alkyl bromide or iodide were added dropwise. The mixture was stirred for 30 min at room temperature and refluxed for 90 min. After cooling, the suspension was poured into 500 ml of CCl<sub>4</sub>-brine (1:1). The organic layer was separated, the water layer extracted three times with 20 ml of CCl<sub>4</sub> and the combined organic solutions were dried over MgSO<sub>4</sub>. After concentration and evaporation in vacuo, a yellow oil was obtained in all cases which was used for chlorination (procedure C) without further purification. If necessary, the product was purified by LC (light petroleum-ethyl acetate, 20:1). The yields of the isolated products were ca. 80%.

General procedure B: syntheses of *a*-phenyltellurenylsubstituted carboxylic esters. The reaction was started in two separate flasks which were connected by a small glass bridge. The lithium enolate of the corresponding carboxylic acid ester was prepared in the first flask by the reaction of lithium diisopropylamide (5.0 mmol) and the unsubstituted ester (5.0 mmol) in 70 ml of tetrahydrofuran (THF) at  $-78^{\circ}$ C. Phenyltellurenyl iodide was generated in situ in the second flask by combining Ph<sub>2</sub>Te<sub>2</sub> (2.44 mmol) and iodine (2.44 mmol) in 70 ml of THF. At  $-78^{\circ}$ C the lithium enolate solution was poured through the glass bridge into the cooled phenyltellurenyl iodide solution. The suspension was stirred for 30 min and then for a further 90 min without cooling. The reaction mixture was filtered over silica gel at room temperature to remove the salts formed. Further purification was also done by LC (light petroleum-diethyl ether, 15:1). The yields of the isolated products were ca. 70-80%.

General procedure C: chlorination of diorganotellurium(II) compounds with  $SO_2Cl_2$  to diorgano tellurium(IV) dichlorides. A 1.0 mmol amount of the respective phenyltellurenyl-substituted precursor was dissolved in 20 ml of  $CCl_4$  and 1.0 mmol of  $SO_2Cl_2$  was added within 20 s at room temperature under vigorous stirring. After 10 h the solution was filtered and the residue washed with  $CCl_4$ . Compounds 1 and 2 were the only solid pure products available by this procedure; 1 could be recrystallized from methanol for an x-ray investigation (supplementary material available from the authors). In all other cases slightly coloured oils of high viscosity were obtained after concentration and evaporation *in vacuo*. Especially for secondary alkanes it was sometimes necessary to purify by LC (silica gel, toluene-ethanol-acetic acid, 500:25:1) to obtain pure products. The yield of the isolated products were *ca.* 90%.

Variant of the general procedure C (C'). The procedure leading to three-isomer mixtures is identical with procedure C with the following exception: in the starting chlorination step, 1.4-2.0 eq. of SO<sub>2</sub>Cl<sub>2</sub> were used and added dropwise over a period of 3 h. LC was always done to separate the isomeric products from some decomposition products (e.g. PhTeCl<sub>3</sub>). The yields of the isolated products were *ca*. 50%.

General procedure D: halogen exchange from diorganotellurium dichlorides with potassium fluoride. A 1.0 mmol amount of diorganotellurium dichloride was dissolved in 20 ml of dry acetonitrile, mixed with 20 eq. of KF (anhydrous) and stirred vigorously for 5 days at room temperature. The resulting suspension was filtered and the residue washed with 30 ml of dichloromethane. The solution was evaporated *in vacuo* and the residue was dissolved in chloroform and filtered. Finally, evaporation *in vacuo* yielded 90–95% of product in all cases.

The following bond lengths and angles were determined by x-ray analysis of 1: Te—Cl, 2.535(1) and 2.477(2) Å; Te—C<sup>Me</sup>, 2.113(7) Å; Te—C<sup>Ph</sup>, 2.114(4) Å; Cl—Te—Cl, 174.6(1)°; C—Te—C, 99.5(2)°; C—Te—Cl, 87.6–89.1°.

All IR and MS data support the structures given in Scheme 1. A compilation including a comprehensive list of the x-ray analysis results is available as supplementary material from the correspondence author on request. NMR data are collected in Table 1.

## RESULTS

All NMR data are collected in Table 1; those of **19** have already been published previously.<sup>7</sup> <sup>19</sup>F NMR data are listed in the footnotes to Table 1.

In a number of representative cases we observed the change of <sup>125</sup>Te chemical shifts with temperature. We found considerable linear dependences for tellurides (20), 25.9 ppm in 95 K, i.e. ca. 0.28 ppm K<sup>-1</sup> or ca. 35 Hz K<sup>-1</sup>) and for ditellurides (22, 33.4 ppm in 88 K, i.e. ca. 0.38 ppm K<sup>-1</sup> or ca. 48 Hz K<sup>-1</sup>), and in both cases smaller  $\delta$ -values at lower temperature. In contrast, the temperature dependence is smaller and of opposite sign for alkyl phenyltellurium dichlorides (e.g. 7, -0.02 ppm K<sup>-1</sup> or ca. -2.5 Hz K<sup>-1</sup>) and the corresponding tellurium difluorides (e.g. 9, -0.15 ppm K<sup>-1</sup> or ca. -19 Hz K<sup>-1</sup>). No obvious explanation for this divergent behaviours can be given.

Table 1.	125Te.	<sup>13</sup> C and	۱H	chemical	shifts o	of	compounds	1	-18 a	and 20-	-33°-c
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Compound	<sup>125</sup> Te	<sup>13</sup> C	'n
1	804	1: 30.6	1 : 3.28 s
2	905	1: 45.3 (162); 2: 10.4	1: 3.69 g; 2: 1.82 t (45)
3	878	1:54.2 (160); 2: 19.1; 3: 15.7	1: 3.70 t; 2: 2.25 m; 3: 1.17 t
4	1023	1/3: 19.9; 2: 57.5 (155)	1/3: 1.76 d; 2: 4.17 septet
5	883	1: 51.9; 2: 27.3; 3: 24.3; 4: 13.5	1: 3.71 t; 2: 2.17 m; 3: 1.52 m; 4: 0.99 t
6	1007	1 : 17.0; 2: 65.8; 3: 27.3; 4: 13.4	1: 1.68 d; 2: 4.03–4.12 m;
			3: 2.05–2.25 2 m; 4: 1.13 t
<b>7</b> <sup>d</sup>	880	1: 51.6 (167); 2: 25.0; 3: 30.4, 4: 30.8;	1: 3.72 t; 2: 2.21 m; 3: 1.51 m;
		5: 22.1; 6: 13.8	4/5: 1.28–1.40 m; 6: 0.89 t
<b>8</b> <sup>d</sup>	1000	1:65.8;2/6:29.3;3/5:28.2;4:25.0	1; 4.09 tt; 2/6: 2.01–2.20 m;
			3/5: 1.22–1.44 m, 1.83–1.94 m;
			4ax: 1.22-1.44 m; 4eg; 1.69 m
9 <sup>e</sup>	1168	1 : 26.4	1 : 2.56 t
10 <sup>f</sup>	1204	1: 38.1; 2: 8.7	1 : 2.98 m; 1.48 tt
11 <sup>g</sup>	1193	1: 47.4; 2: 17.8; 3: 15.6	1: 2.96 m; 2: 1.92 m; 3: 1.05 t
12 <sup>h</sup>	1242	1/3: 18.9; 2: 50.0	1/3: 1.51 dt: 2: 3.15 m
13	1236	1: 15.6; 2: 58.3; 3: 26.3; 4: 13.0	1: 1.38 dt; 2: 3.00 m; 3: 1.86 m, 2.03 m; 4: 1.08 t
14 <sup>i</sup>	1228	1: 58.9; 2/6: 28.6; 3/5: 27.5; 4: 25.3	1: 3.10 m; 2/6: 1.73 m, 2.05 m;
		· , · · , ·	3/5: 1.20-1.45 m, 1.73 m;
			4ax: 1.20–1.45 m; 4eg: 1.60 m
15	1127 <sup>ĸ</sup>	1 : 42.4 (150) ; 2 : 32.1 ; Ac : 177.4, 21.8	1: 3.08 m (44, 13); 2: 2.46 m; Ac: 1.90 s
16	693	1/9: 124.5; 1a/9a: 115.4; 2/8: 134.0; 3/7: 133.6;	1/9: 7.25 m (25); 2/8: 8.02 m;
		4/6: 119.7; 4a/6a: 151.1; Ac: 178.3, 21.6	3/4/6/7: 7.52–7.57 m; Ac: 1.82 s
17	957	Ac: 177.4, 22.2	Ac: 1.76 s
18	991	1/6: 133.7; 2/5: 128.4*; 3/4: 131.2*	2/3/4/5: 7.31–7.53 m (overlapped by Ph signals)
20	460	1: 8.7; 2: 31.7; 3: 31.5; 4: 31.0; 5: 22.4; 6: 14.0	1: 2.91 t; 2: 1.82 m; 3: 1.39 m;
			4/5:1.26-1.32 m; 6: 0.89 t
21'	ca. 229	1 : 22.3; 2/6 : 37.9; 3/5 : 28.2; 4 : 25.7	1: 3.37 tt; 2/6: 1.24–1.65 m, 2.08 m;
			3/4/5: 1.24–1.65 m
22	284	1 : 24.9; 2/7 : 39.1; 3/4/5/6 : 27.8, 28.1	1: 3.56 tt; 2/7: 1.77 dtd, 2.20 dm;
			3/4/5/6: 1.37-1.48 m, 1.49-1.62 m
23	623	1: 173.5; 2: 6.2; Et: 61.2 (CH <sub>2</sub> ), 14.3 (CH <sub>3</sub> )	2: 3.51 s; Et: 4.06 q (CH <sub>2</sub> ), 1.15 t (CH <sub>3</sub> )
24	831	1: 175.8; 2: 17.4; 3: 19.2; OMe: 51.9	2: 3.94 q; 3: 1.66 d; OMe: 3.58 s
<b>25</b> <sup>m</sup>	803/810	1 : 175.2/175.1 ; 2 : 18.3/18.2 ; 3 : 19.4/19.1	2: 3.82/3.89 2q; 3: 1.64/1.67 2d
26	848	1: 165.6; 53.3; Et: 63.4 (CH <sub>2</sub> ), 14.0 (CH <sub>3</sub> )	2: 4.46 s; Et: 4.31 q (CH <sub>2</sub> ), 1.32 t (CH <sub>3</sub> )
27	990	n	n
28	997	1 : 167.6; 2 : 62.8; 3 : 12.7;	2: 4.63 q; 3: 1.75 d; <i>t</i> -Bu: 1.51 s (CH <sub>3</sub> )
		<i>t</i> -Bu: 85.0 (C), 27.9 (CH <sub>3</sub> )	
29	938	1: 165.4; 2: 75.4; 3: 36.1;	2: 4.68 s; 4/5/6: 1.34 s; OMe: 3.18 s
		4/5/6: 30.3; OMe: 51.1	
<b>30</b> <sup>d, m</sup>	983/989	1: 168.2/168.6; 2: 62.0/62.4; 3: 12.7/13.1	2: 4.65–4.85 m; 3: 1.65–1.73 m
31 <sup>m, o</sup>	1219/1224	1: 169.0/169.2; 2: 56.3/57.0; 3: 11.3/11.4	p
32	899	1:51.4; 2: 20.5; 3: 34.1; C=O: 172.7;	1: 3.69 t; 2/3: 2.50-2.55 m;
		OEt: 61.1 (CH <sub>2</sub> ), 14.1 (CH <sub>3</sub> )	OEt: 4.14 q (CH <sub>2</sub> ), 1.24 t (CH <sub>3</sub> )
33ª	1192	1: 43.7; 2: 19.3; 3: 34.4; C=O: 172.0;	1: 2.94 (25) m; 2: 2.10 m; 3: 2.31 t;
		OEt: 60.3 (CH <sub>2</sub> ), 13.9 (CH <sub>3</sub> )	OEt: 4.00 q (CH <sub>2</sub> ), 1.12 t (CH <sub>3</sub> )

<sup>a</sup> Data in parentheses are absolute values of <sup>13</sup>C,<sup>125</sup>Te (±1 Hz) and <sup>1</sup>H,<sup>125</sup>Te coupling constants (±1 Hz), respectively. Solvent, CDCl<sub>3</sub>; chemical shifts are referenced to  $(CH_3)_2$ Te  $(^{125}$ Te) ( $\delta = 420$ ) and tetramethylsilane  $(^{13}C, ^{11}H)$  ( $\delta = 0$ ), and are reported in ppm. For further experimental details, see text. Atom numbering refers to IUPAC rules; in the case of **16** and **32/33** the numbering is indicated in Scheme 1. Data with asterisks may be interchanged.

<sup>b</sup> <sup>13</sup>C assignments are based on DEPT and COSY spectra. <sup>1</sup>H multiplicities are indicated by s = singlet, d = doublet, t = triplet, q = quartet, m = multiplet. <sup>1</sup>H signal intensities are as expected in all cases. <sup>125</sup>Te signal multiplicities are as expected.

<sup>c</sup> Phenyl rng signals are not included. They are as follows: *ortho*-protons  $\delta({}^{1}H) = 8.10-8.20$  for PhTe(Cl<sub>2</sub>)R and  $\delta({}^{1}H) = 7.90-7.95$  for PhTe(F<sub>2</sub>)R; for *meta*- and *para*-protons  $\delta({}^{1}H) = 7.48-7.54$ ; for *ipso*-carbons  $\delta({}^{13}C) = 128.0-131.7$  for PhTe(Cl<sub>2</sub>)R and  $\delta({}^{13}C) = 132.5-134.5$  for PhTe(F<sub>2</sub>)R; for *ortho*-carbons  $\delta({}^{13}C) = 131.8-133.9$ ; for *meta*-carbons  $\delta({}^{13}C) = 129.7-130.0$ ; for *para*-carbons  $\delta({}^{13}C) = 131.2-131.7$ 131.8.

<sup>a</sup> Data refer to isomer A only taken from the equimolar SO<sub>2</sub>Cl<sub>2</sub> experiment. For the other isomers see text; <sup>13</sup>C NMR data in supplementary material. \*  $\delta$ (<sup>19</sup>F) = -126.2; <sup>1</sup>J(<sup>125</sup>Te, <sup>19</sup>F) = 700; <sup>2</sup>J(<sup>19</sup>F, <sup>13</sup>C) = 9; <sup>3</sup>J(<sup>19</sup>F, <sup>1</sup>H) = 7.6. \*  $\delta$ (<sup>19</sup>F) = -135.8; <sup>1</sup>J(<sup>125</sup>Te, <sup>19</sup>F) = 700; <sup>2</sup>J(<sup>19</sup>F, <sup>13</sup>C) = 8; <sup>3</sup>J(<sup>19</sup>F, <sup>1</sup>H) = 6; <sup>4</sup>J(<sup>19</sup>F, <sup>1</sup>H) = 1. \*  $\delta$ (<sup>19</sup>F) = -134.7; <sup>1</sup>J(<sup>125</sup>Te, <sup>19</sup>F) = 715; <sup>2</sup>J(<sup>19</sup>F, <sup>13</sup>C) = 7; <sup>3</sup>J(<sup>19</sup>F, <sup>13</sup>C) = 3; <sup>4</sup>J(<sup>19</sup>F, <sup>1</sup>H) = 1. \*  $\delta$ (<sup>19</sup>F) = -143.0; <sup>1</sup>J(<sup>125</sup>Te, <sup>19</sup>F) = 710; <sup>2</sup>J(<sup>19</sup>F, <sup>13</sup>C) = 3; <sup>3</sup>J(<sup>19</sup>F, <sup>13</sup>C) = 3; <sup>4</sup>J(<sup>19</sup>F, <sup>1</sup>H) = 1.3. \*  $\delta$ (<sup>19</sup>F) = -137.6/-148.1; <sup>1</sup>J(<sup>125</sup>Te, <sup>19</sup>F) = 735/697; <sup>2</sup>J(<sup>19</sup>F, <sup>19</sup>F) = 180; <sup>2</sup>J(<sup>19</sup>F, <sup>13</sup>C) = 7; <sup>3</sup>J(<sup>19</sup>F, <sup>1</sup>H) = 5; <sup>4</sup>J(<sup>19</sup>F, <sup>1</sup>H) = 1.2. \*  $\delta$ (<sup>19</sup>F) = -142.2; <sup>1</sup>J(<sup>125</sup>Te, <sup>19</sup>F) = 705; <sup>2</sup>J(<sup>19</sup>F, <sup>13</sup>C) = 6; <sup>3</sup>J(<sup>19</sup>F, <sup>1</sup>H) = 5. material.

<sup>k</sup> Multiplicity: triplet of triplets (tt).
<sup>l</sup> Coalescence of the <sup>125</sup>Te resonances at room temperature; for details see text.

<sup>m</sup> Mixture of diastereomers. Only resonances of the propanoyloxy part.

<sup>a</sup> Only one <sup>125</sup>Te resonance. <sup>13</sup>C and <sup>1</sup>H NMR spectra not interpretable owing to rapid decomposition. <sup>o</sup> Four <sup>19</sup>F resonances, see Table 3;  ${}^{3}J({}^{19}F,{}^{13}C) = 9$ .

<sup>P</sup> Severe signal overlap. <sup>q</sup>  $\delta({}^{19}F) = -133.3; {}^{1}J({}^{125}Te, {}^{19}F) = 695; {}^{2}J({}^{19}F, {}^{13}C) = 8; {}^{3}J({}^{19}F, {}^{1}H) = 7.$ 



Scheme 1. Structures of tellurium-containing compounds 1-33.

<sup>125</sup>Te signal half-height widths were ca. 40–50 Hz for the tellurides (PhTeR) and ditellurides, a line broadening which can be attributed to slight temperature gradients within the 10 mm probes. Even larger line widths were observed for the tellurium dichlorides (50–70 Hz), although the  $\delta$ (<sup>125</sup>Te) temperature dependence is marginal. The reason could be an interaction with the quadrupolar chlorine nuclei. Consequently, this effect does not exist in the tellurium difluorides where, indeed, we found linewidths of ca. 5 Hz only.

Within the range of concentrations used in this study there is no remarkable concentration effect on  $^{125}$ Te chemical shifts.

Coupling constants involving <sup>125</sup>Te nuclei can be determined fairly easily either directly or by observing the <sup>125</sup>Te satellites in the spectrum of the coupling partner. Owing to the negative magnetogyric ratio of <sup>125</sup>Te, one-bond <sup>13</sup>C,<sup>125</sup>Te coupling constants are expected to be positive.<sup>2,4</sup> The values should be approximately twice as large as those in corresponding <sup>77</sup>Se analogues.<sup>2,4</sup> We found values of 160-170 Hz for the tellurium dichlorides. This is the range expected for diorganyl tellurides with sp<sup>3</sup>-hybridized carbon atoms including alkyl phenyltellurides.<sup>16,17</sup> Hence we have to conclude that oxidation of the tellurium atom by chlorination does not affect significantly the magnitudes of one-bond  ${}^{13}C$ ,  ${}^{125}Te$  coupling constants.  ${}^{2}J({}^{1}H, {}^{125}Te)$ and  ${}^{3}J({}^{1}H, {}^{125}Te)$  are apparently negative and can be of considerable and similar magnitude.<sup>2,17</sup> Large (probably positive)  ${}^{1}J({}^{19}F, {}^{125}Te)$  coupling constants have been reported which are in the range 2700-3800 Hz for  $Te^{VI}$  derivatives.<sup>2</sup> The coupling constants in our alkylaryltellurium difluorides (Te<sup>IV</sup>) are much smaller (695-715 Hz); those of other diorganyltellurium difluorides reported in the literature are in a similar range, e.g. Ph<sub>2</sub>TeF<sub>2</sub> 540 Hz.<sup>18</sup>

## DISCUSSION

### <sup>125</sup>Te chemical shifts and substituent effects

<sup>125</sup>Te NMR data for a number of diorganyl tellurides and ditellurides have been reported previously.<sup>1-4,12,19-22</sup> <sup>125</sup>Te chemical shifts depend strongly on the structure of the organyl group and the oxidation state of the tellurium atom. Those of tellurides (RTeR') have a very wide resonance range and appear between  $\delta = 0$  (Me<sub>2</sub>Te) and *ca.* 1000. Oxidation of the tellurium atom generally leads to a distinct deshielding  $^{1-4,20}$  In the case of the carboxylic acid derivatives 23-33 in Table 1, chlorination leads to an increase in the  $\delta$ -values in the range  $160 \pm 20$  ppm. Exchange of the chlorine atoms by the much more electronegative fluorine leads to a further deshielding by 300 ppm and more. These effects, however, are dependent of the character of the organyl residues as well, as shown in Fig. 1.

For various dialkyl tellurides it has been found that the substituent effects of carbon fragments in the alkyl residues (SCS) on the <sup>125</sup>Te chemical shifts correspond well with SCS effects on <sup>77</sup>Se chemical shifts of analogous selenides, the slope of the correlation being  $1.71^{12,19,20}$  (Fig. 1). However, the SCS in the tellurium dichlorides [(PhTeCl<sub>2</sub>)R] are much smaller (Fig. 1). Here the slope is only 0.97, i.e. the <sup>125</sup>Te nuclei have approximately the same sensitivity as <sup>77</sup>Se. The slope is further decreased to 0.33 when the chlorine atoms are replaced with the much more electronegative fluorine atoms (Fig. 1). The good correlations show that the SCS trends are the same in all three types of molecules.

Such loss of sensitivity has also been observed for  $^{77}$ Se. A reduction by a factor of *ca*. 4 in the SCS sensi-



**Figure 1.** <sup>125</sup>Te chemical shifts of some alkanes substituted with three different kinds of tellurium functionalities [PhTeR<sup>12</sup>, (PhTeCl<sub>2</sub>)R, and (PhTeF<sub>2</sub>)R, respectively] plotted against <sup>77</sup>Se chemical shifts of corresponding selenium analogues (PhSeR<sup>8,12</sup>). For a better comparability the <sup>125</sup>Te chemical shifts are referred to the methyl derivative [(PhTeX<sub>2</sub>)-Me; X = electron pair, Cl, F:  $\Delta = 0$ ] in each series; in order not to confuse these values with the <sup>125</sup>Te chemical shifts in Table 1, the symbol  $\Delta$ (<sup>125</sup>Te) is used here.

tivity is found when phenylalkyl selenides are compared with the corresponding selenium oxides.<sup>7,8</sup> In fact, this seems to be a general trend. For example, we found similar <sup>33</sup>S chemical shifts for phenylsulphone groups (PhSO<sub>2</sub>) in axial and equatorial positions at a cyclohexane ring.<sup>23</sup> Apparently, the <sup>33</sup>S nuclei are not capable of a clear differentiation between  $\gamma$ -carbons in gauche and antiperiplanar orientations, respectively.<sup>23</sup> Unfortunately, it was not possible to record the <sup>33</sup>S chemical shifts of the corresponding sulphides owing to extremely line broadening in this class of compounds,<sup>24</sup> but the above-mentioned insensitivity of the sulphone <sup>33</sup>S chemical shifts seems to confirm the trend.

<sup>125</sup>Te chemical shifts of tellurium dicarboxylates seem to be unknown in the literature. Our data for **15–18** show that their range is somewhere between those for the dichlorides and the diffuorides, and this meets the expectation based on the assumption of a more or less linear correlation with the electronegativity of the attached heteroatoms.<sup>20</sup> However, there is again a strong dependence of the <sup>125</sup>Te chemical shifts on the structure of the organyl groups attached to Te and O. Two alkyl groups at Te (**15**) cause a strong deshielding ( $\delta = 1127$ ) whereas conjugation with aryl substituents shifts the <sup>125</sup>Te signal to lower frequencies. If the Te atom is fixed in a planar  $\pi$ -system, the shielding can be very strong (**16**:  $\delta = 693$ ), whereas with two phenyl rings it is much less pronounced (**17**:  $\delta = 957$ ), probably owing to a distortion of the phenyl rings away from coplanarity.

# Conformational behaviour of tellurium-substituted cyclohexanes

The variable-temperature <sup>125</sup>Te NMR spectra of the monosubstituted cyclohexane derivative **19** have been published previously and a ratio of axial vs. equatorial conformers of 1:6.4 (A-value = 0.9) has been found.<sup>7</sup> In contrast, no coalescence effects could be detected for the tellurium dihalides **8** and **14**, even on cooling to 210–



Figure 2. Position of  $\gamma$ - and  $\delta$ -carbons in 8 as compared with 4.

220 K. This is due to the high A-values of the voluminous  $PhTeX_2$  substituents, which act like steric anchors being fixed in the equatorial position.

The <sup>125</sup>Te chemical shift of **8** is  $\delta = 1000$ , a value which is only slightly smaller than that of the isopropyl analogue 4 ( $\delta = 1023$ ) so that a double y-effect of ca. -30 ppm results from the  $\gamma$ -carbons in 8 (a few ppm have to be added for a positive  $\delta$ -effect; cf. Fig. 2). A corresponding estimation for the PhTe substituent yields -60 ppm for the equatorial and -190 ppm for the axial conformer of 19. (The <sup>125</sup>Te chemical shifts of 19 were recorded at 243 K and were extrapolated to room temperature for the comparison with PhTe-i- $Pr.^{12}$ ) Thus, the above -30 ppm effect corresponds well to a double y-anti effect and is in clear contradiction to a double  $\gamma$ -gauche effect, especially if one takes into account a 40-50% reduction as compared with the telluride analogue 19 (see previous section). This argument is further confirmation of a fixed equatorial position of the PhTeX<sub>2</sub> substituents.

Qualitatively analogous arguments are valid for the difluoride 14. Here the  $^{125}$ Te chemical shift difference between 14 and 12 is only 14 ppm.

The conformational behaviour of the ditelluride 21 is more complex than that of 19 because, in principle, three different conformers, 21ee, 21ae and 21aa, may occur (Fig. 3). Figure 4 shows schematically the signal positions observed in a variable-temperature experiment with 21.



Figure 3. Conformational behaviour of 21.



Figure 4. <sup>125</sup>Te signal positions of **21** at different temperatures (in K).

At high temperatures (>300 K) only one average signal for all possible conformers [21(av)] is visible. However, three different signals can be identified below 230 K. In the centre appears the most intensive one belonging to 21ee, whereas the other two correspond to 21ae; the signal with the highest <sup>125</sup>Te chemical shift  $(\delta = 290-300)$  is that of Te in an equatorial and that with the lowest ( $\delta = 70-80$ ) is that of Te in an axial position. The signal intensity ratio of 21ee: 21ae is ca 9:1, i.e. it is higher than that of 19, indicating a slightly higher A-value of the cyclo-HexTeTe substituent (ca. 1.0). Hence it is not surprising that the third conceivable conformer (21aa) could not be identified owing to its very low abundance. It is interesting that the <sup>125</sup>Te chemical shift difference in 21ae is ca. 220 ppm, much larger than that found in 19 (ca. 130 ppm). This can be attributed to additive substituent effects from the two cyclohexyl groups as described previously for other unsymmetrical ditellurides.19

As expected, no coalescence effects could be observed in 22 owing to the low ring inversion barrier of the cycloheptyl ring.

# Diastereomers with different tellurium atom configurations

During the syntheses of the phenylalkyltellurium dichlorides we found a very interesting stereochemical aspect in this class of molecules which apparently has never been noticed before. It is well accepted that the substituents and the lone electron pair form a trigonal bipyramid around the Te<sup>IV</sup> atom in these compounds.<sup>4,25,26</sup> Moreover, all experimental facts suggest that the halogen atoms strongly prefer the axial positions in these biyramids,<sup>25,26</sup> and this has been confirmed by x-ray analyses, e.g. of 1 (Fig. 5)<sup>27</sup> and (C<sub>6</sub>F<sub>5</sub>)<sub>2</sub>TeF<sub>2</sub>.<sup>28</sup>

If in the reaction of PhTeR with  $SO_2Cl_2$  an equimolar amount of  $SO_2Cl_2$  is used, only a single isomer is isolated which, in the following, is characterized by adding the letter A to its compound number (cf. Fig. 6; the experimental evidence for this structural assignment is given below). If, however, an excess (1.5-2 molar) is used, more than one individual compound can be iden-



Figure 5. Graphical representation (ORTEP plot) of 1 (for details see supplementary material).



Figure 6. Conceivable stereoisomers (trigonal bipyramids) of a phenylakyltellurium dichloride (for details see supplementary material).

tified in a mixture which are apparently isomers with respect to the Te configuration. They differ only in their NMR parameters, whereas the mass and IR spectra (even below 600 cm<sup>-1</sup>) of these mixtures and those of the respective single A isomer are not distinguishable. The reason for the appearance of stereoisomers in the  $SO_2Cl_2$ -excess experiments may be an oxidation of the intermediately formed (PhTeCl\_2)R to the Te<sup>VI</sup> species (PhTeCl\_4)R, which, however, is unstable and reduced by an extrusion of Cl<sub>2</sub> which may take place from various Cl positions. Some diorganotellurium-fluorine compounds of Te<sup>VI</sup> species have been described.<sup>29</sup>

For a better insight we investigated this phenomenon in more detail with three representative examples, 7, 8 and 30 (cf. Fig. 6 and Table 2).

Altogether ten isomers are conceivable, including three pairs of enantiomers. For of 7 and 8 we found only three of the above seven diastereomers, one being A with the two axial Cl atoms. As mentioned above, the halogen atom has a strong tendency to adopt axial positions. Hence we can rule out D, F and G with both Cl atoms in equatorial positions. Diastereomers E, F and G are also not likely because of the unfavourable axial position of the free electron pair.<sup>25,26</sup>

It is striking that the A-B-C mixtures of 7 and 8 are similar in their signal sequences and relative intensities. It was not possible to assign B and C, but we found experimental evidence which confirmed the structure of A. Since Te is a chirality centre in B and C but not in A, it should be possible to differentiate between A and B/C by identifying diastereotopic, i.e. anisochronous, <sup>13</sup>C and/or <sup>1</sup>H nuclei in B/C. Unfortunately, in 8 the respective carbon atoms in the cyclohexyl substituent (C-2/6

Table 2.	e diastereomers of 7,			
Compound	R	А	B and/or C	
7	<i>n</i> -Hex	879 (7)	857 (10)/827 (5)	
8	cyclo-Hex	996 (4)	990 (9)/976 (5)	
30	2-Propionic acid	983 (11)	1026 (2)/1003 (1)	
	menthyl ester	989 (11)	1032 (2)/1010 (1)	

<sup>a</sup> Values in parentheses are relative abundances in the SO<sub>2</sub>Cl<sub>2</sub>excess experiments.

<sup>b</sup> Note that always a mixture of **A**, **B** and/or **C** was observed, among which **A** could be identified by comparison with the equimolar  $SO_2CI_2$  experiment.

and C-3/5) are apparently not sensitive enough to give anisochrony effects. The <sup>1</sup>H signals, however, allow an interpretation: whereas in the achiral isomer 7A the H-1 signal is the expected triplet  $[{}^{3}J({}^{1}H,{}^{1}H) = 7.5 \text{ Hz}]$ , the corresponding peaks in 7B and 7C are multi-line signals indicating different chemical shifts for the diastereotopic geminal H-1 protons (AB part of an ABXY spectrum). Similarly, the H-1 signal of 8A is a triplet of triplets (note that the cyclohexane ring is rigid; see previous section) whereas multi-line signals are observed for 8B and 8C again.

The question arises of why the stereoisomers are configurationally stable and do not undergo pseudorotation. Heating them to 333 K, a temperature at which decomposition began, did not produce any coalescence effects in the <sup>125</sup>Te NMR spectrum and no change in the relative abundances of the three isomers occurred. The same stability was found after keeping them at room temperature for more than 1 year. Hence we have to conclude that the process of pseudo-rotation has to overcome an unexpectedly high barrier (estimated as >115 kJ mol<sup>-1</sup>). We could not find any pertinent information in the literature. It is well known that phosphanes, sulphoxides and selenoxides have high inversion barriers and that their configuration is generally stable at room temperature.<sup>30</sup> However, these molecules are tetrahedral and a comparison with the trigonal bipyramids of the tellurium dichlories is questionable.

The situation concerning the stereoisomers observed is different for 30, where a diastereomeric alkyl substituent (propionyl menthyl ester) is present. Both absolute configurations at C-2 of the propanoic acid are present but enantiomerically pure menthol was used, i.e. only two different diastereomeric side-chains exist. In the spectrum of 30A there are only two <sup>125</sup>Te signals and this is consistent with expectation. In that of the mixture of stereoisomers, however, we identified only four further signals, although there should be four for each isomer **B** and **C** with the Te being a chirality centre. Three explanations can be offered: (a) only one diastereomer out of the two possible has been formed for each Te configuration, 30B and 30C; (b) four diastereomers of 30B and four of 30C do exist, but the <sup>125</sup>Te nuclei are not capable of reflecting diastereomeric interactions between the C-2 and the tellurium atoms; (c) all four lines belong to only one Te configuration, i.e. only isomer 30B or 30C has been produced along with 30A.

Argument (a) is very weak because it implies a nearly 100% asymmetric induction during the reaction, and

this is by no means reasonable. Argument (b) is also not good because in the case of **31**, the analogous difluoride with configuration **A**, we found two <sup>125</sup>Te signals with a 5 ppm chemical shift difference, a value very close to the difference observed for **30B/30C** (6 ppm). Hence we are left with explanation (c), i.e. only two different Te configurations, **30A** and **30B** or **30A** and **30C**, are produced during the chlorination with an excess of  $SO_2Cl_2$ .

It should be noted that in the stereoisomers of 30 and 31 the chiral discrimination of the configuration at the attached C-2 atom presented by the  $^{125}$ Te nucleus makes it in principle a very suitable candidate for stereochemical investigations.

## <sup>19</sup>F NMR

The achiral tellurium difluorides 9-12 and 14 give only one <sup>125</sup>Te signal as a triplet due to <sup>19</sup>F couplings. There is only one <sup>19</sup>F signal as a singlet (apart from the <sup>125</sup>Te satellite doublet) in these compounds, proving that both fluorine atoms are in homo- or enantiotopic positions. This is possible only for the configurations A, D, F and G (see Fig. 5). In the preceding section it was argued that A should be by far be the most probable, so that we conclude that in all tellurium difluorides configuration A exists. This argument is confirmed by the observation that in 13 with both enantiomeric sec-butyl groups only two well separated <sup>19</sup>F signals ( $\delta = -148.1$ and -137.6) for the two expected diastereotopic fluorine atoms appear whereas there should be four in 13D, 13F and 13G (two chirality centres: Te and C-2 of the sec-butyl group). In addition, the diastereotopism of the <sup>19</sup>F atoms is reflected by a large difference in the onebond <sup>19</sup>F,<sup>125</sup>Te couplings (697 and 735 Hz). It is conceivable that such tellurium fluorides may be developed into a valuable tool for stereochemical discrimination of chiral chlorides (by converting them into the tellurium fluorides) which otherwise might be difficult to monitor.

Accordingly, four <sup>19</sup>F signals were detected in the spectrum of **31** (Table 3) with the diastereomeric alkyl substituents, another argument for the A configuration of the tellurium atom.

## <sup>13</sup>C NMR

**PhTe substituents.** <sup>13</sup>C NMR data for tellurium compounds are rare in the literature, hence it is of interest to calculate and compare the substituents effects (SCS) of the tellurium-containing groups which are defined as

δ( <sup>19</sup> F) (ppm)	¹J(¹²⁵Te,¹9F) (Hz)	<sup>2</sup> J( <sup>19</sup> F, <sup>19</sup> F) (Hz)	³J{¹⁰F,¹H} (Hz)	δ( <sup>125</sup> Te) <sup>a</sup> (Hz)
-141.9	590.5	169.6	9	
-125.7	644.0	169.6	5	
				1291/1224
-141.5	593.0	168.7	9	,
-126.9	641.0	168.7	5	

signals was not possible owing to insufficient resolution in the <sup>125</sup>Te NMR spectrum.

R	P	'hTeCl <sub>2</sub>	PhTeF <sub>2</sub>			
	α	β	α	β		
Me	32.9 (CH <sub>3</sub> )		28.7 (CH <sub>3</sub> )			
Et	38.8 (CH <sub>2</sub> )	3.9 (CH <sub>3</sub> )	31.6 (CH <sub>2</sub> )	2.2 (CH <sub>3</sub> )		
<i>n</i> -Pr	38.1 (CH <sub>2</sub> )	2.8 (CH <sub>2</sub> )	31.3 (CH <sub>2</sub> )	1.5 (CH <sub>2</sub> )		
<i>i</i> -Pr	41.2 (CH)	3.8 (CH <sub>3</sub> )	33.7 (CH)	2.8 (CH <sub>3</sub> )		
<i>sec-</i> Bu	40.9 (CH)	(1): 3.9 (CH <sub>3</sub> )	33.4 (CH)	1.5 (CH <sub>3</sub> )		
		(3): 2.4 (CH <sub>2</sub> )		(3): 1.4 (CH <sub>2</sub> )		
<i>n</i> -Hex	37.9 (CH <sub>2</sub> )	2.3 (CH <sub>2</sub> )		•		
cyclo-Hex	38.8 (CH)	2.3 (CH <sub>2</sub> )	31.9 (CH)	1.6 (CH <sub>2</sub> )		

Table 4.  $\alpha$ - and  $\beta$ -SCS (ppm) of PhTeCl<sub>2</sub> and PhTeF<sub>2</sub> substituents on aliphatic <sup>13</sup>C nuclei

the difference in the <sup>13</sup>C chemical shifts in the tellurium compounds and the corresponding parent compounds where the tellurium-containing group is replaced with H.  $\alpha$ -SCS denote effects at directly attached carbons,  $\beta$ -SCS those over two bonds and so forth.

 $\alpha$ -SCS of MeTe substituents on aliphatic carbon nuclei are strongly shielding (-15 to -24 ppm).<sup>17</sup> That of the PhTe substituent in PhTeEt is much smaller (-6.4 ppm),<sup>22</sup> and similar values were found for **20-22** (-5.0, -4.7 and -3.8 ppm, respectively). The  $\beta$ -SCS, however, are clearly deshielding; +10.5 ppm has been reported for the methyl carbon in PhTeEt.<sup>22</sup> Again, our values correspond well: **20**, +9.0; **21**, +9.2; and **22**, +10.4 ppm. All SCS values are typical for heavy-atom substituents and resemble those of iodine. Effects beyond the  $\beta$ -carbons are generally negligible.

**PhTeCl<sub>2</sub> and PhTeF<sub>2</sub> substituents.** The  $\alpha$ - and  $\beta$ -SCS (Table 4) of the Te<sup>IV</sup> substituents are in sharp contrast to those of PhTe. A comparison of the methyl derivatives 1 and 9 with other monosubstituted methanes<sup>31</sup> reveals that the  $\alpha$ -SCS of (PhTeF<sub>2</sub>) is close to those of NH<sub>2</sub> and Cl whereas that of PhTeCl<sub>2</sub> is even larger, i.e. between those of NH<sub>2</sub> and OH. Although electronegativity is assumed not to be the exclusive source of  $\alpha$ -carbon deshieldings,<sup>31,32</sup> the two Te<sup>IV</sup> functionalities clearly have strong group electronegativities. The magnitudes of  $\alpha$ -SCS increase with increasing number of

alkyl groups attached to the  $\alpha$ -carbon involved. The  $\beta$ -SCS are small, and at least for PhTeCl<sub>2</sub> a slight dependence on the substitution at the  $\beta$ -carbon can be identified. Substituent effects beyond the  $\beta$ -carbon are small, mostly even negligible.

## <sup>1</sup>H NMR

SCS effects on <sup>1</sup>H chemical shifts are noticeable but this parameter is not a significant tool for the structural determination of such compounds. The  $\beta$ -SCS of (PhTeCl<sub>2</sub>) and (PhTeF<sub>2</sub>) on hydrogen atoms attached to aliphatic carbons are +2.79 to +3.05 and +1.78 to +2.33 ppm, respectively, protons in methyl groups giving higher values than those in methylene or methine fragments. The  $\gamma$ -SCS which could be derived are positive (+0.78 to +0.97 and +0.48 to +0.81 ppm, respectively). Effects beyond the  $\gamma$ -carbon are negligible.

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