

## THE CRYSTAL STRUCTURE OF *p,p'*-DIMETHOXYDIPHENYL DITELLURIDE (*p*-MeOC<sub>6</sub>H<sub>4</sub>)<sub>2</sub>Te<sub>2</sub>

S. LUDLOW and A.E. McCARTHY

Department of Chemistry, University of Aston in Birmingham, Birmingham B4 7ET  
(Great Britain)

(Received April 24th, 1981)

### Summary

The structure of *p,p'*-dimethoxydiphenyl ditelluride differs from that of other ditellurides so far investigated in that it consists of two distinct repeating molecules and there is a slight spiralling effect in the network of tellurium atoms in the *b* direction with intermolecular tellurium distances somewhat less than the sum of the Van der Waals' radii, thus indicating weak bonding.

The crystals are monoclinic with  $a = 29.583(16)$ ,  $b = 6.096(5)$ ,  $c = 33.910(14)$  Å,  $\beta = 93.80(5)^\circ$ ,  $Z = 16$  and the space group is  $C2/c$ . The structure has been determined by three dimensional X-ray analysis at  $20 \pm 2^\circ\text{C}$  and the final  $R$  value calculated from 1802 reflections was 0.06. In one molecule of the structure the two tellurium atoms have a bond length of  $2.715(2)$  Å and a dihedral angle of  $81.2(5)^\circ$  while in the other molecule the bond length between the two tellurium atoms is  $2.705(3)$  Å and the dihedral angle is  $86.8(5)^\circ$ . In both molecules the direction of the Te—Te bond is almost that of the *b* axis. Intermolecular Te—Te distances of  $3.991(3)$  and  $3.983(3)$  Å were found whereas the sum of the Van der Waal's radii are 4.40 Å. The intramolecular distances and angles do not differ significantly from those of other ditellurides.

### Introduction

Although some structures of ditellurides have been published all showing very different packing arrangements i.e. (*p*-ClC<sub>6</sub>H<sub>4</sub>)<sub>2</sub>Te<sub>2</sub> [1], (C<sub>6</sub>H<sub>5</sub>)<sub>2</sub>Te<sub>2</sub> [2], (*p*-CH<sub>3</sub>C<sub>6</sub>H<sub>4</sub>)<sub>2</sub>Te<sub>2</sub> [3], X-ray structural investigations of (*p*-MeOC<sub>6</sub>H<sub>4</sub>)<sub>2</sub>Te<sub>2</sub> have not yet been published. A study of the low frequency vibrational spectra of some diaryl ditellurides [4] including (*p*-MeOC<sub>6</sub>H<sub>4</sub>)<sub>2</sub>Te<sub>2</sub> suggested that all the compounds examined appeared to have C<sub>2</sub> skeletal symmetry which was consistent with the detailed structures found by X-ray methods.

### Experimental

#### Preparation

*p*-Anisyltellurium trichloride was reduced with potassium metabisulphite

[5] and recrystallised from petroleum ether. The crystals grow as small brown needles which show a green metallic lustre and tend to decompose slowly in the presence of air and light.

#### Chemical analysis

Carbon and hydrogen were determined by combustion and the results are as follows: Found: C, 35.6; H, 3.1.  $C_{14}H_{14}O_2Te_2$  calcd.: C, 35.8; H, 3.0%.

Mass spectral analysis showed the parent ion and no species larger than the compound mass.

#### Density

A density column was prepared from tetrabromomethane and carbon tetrachloride and the density was found to be  $2.04 \text{ g cm}^{-3}$  at  $21.5^\circ\text{C}$ .

#### Crystal structure determination

Oscillation, precession and equiinclination Weissenberg photographs of the layers  $h0l-h3l$  were taken using the multiple film technique with  $\text{Cu-K}_\alpha$  radiation. This gave preliminary unit cell dimensions and indicated that the crystals were monoclinic with  $hkl$  present only when  $h + k = 2n$  and  $h0l$  present only when  $l = 2n$ , consistent with the space groups  $Cc$  or  $C2/c$ . The Weissenberg photographs were sent to the S.R.C. microdensitometer service but because the reflections were very close together and frequently very weak, particularly on the layers  $h1l-h3l$ , many could not be measured and finally only those on the zero layer line were assigned intensity values by this method. The remainder were estimated visually with a calibrated intensity strip. Using SHELX 76 (Sheldrick, 1976) [6], 2 177 independent reflections were scaled and corrected for the Lorentz and polarisations factors.  $E$  statistics indicated that the structure was centrosymmetrical, thus reducing the space group to  $C2/c$ . Atomic positions were found and refinement attempted but the error factor remained too high.

Intensities were again measured with a Stoe STADI-2 two-circle diffractometer with graphite-monochromated  $\text{Mo-K}_\alpha$  radiation and a scintillation counter, the crystal dimensions being 0.38 mm in length and 0.078 mm in diameter. The  $\omega$ -scan technique was used with the crystal set up about the  $y$  axis and reflections were scanned in the range  $0.06 < \sin \theta/\lambda < 0.6 \text{ \AA}$ . Data reduction was carried out on 3945 independent reflections and no corrections were made for absorption or extinction. The lattice parameters were again determined and these together with other relevant data are listed in Table 1.

TABLE 1  
CRYSTAL DATA

Molecular formula	$\text{Te}_2\text{C}_{14}\text{H}_{14}\text{O}_2$
Formula weight	469.466
Monoclinic space group	$C2/c$
$a = 29.583(16) \text{ \AA}$	$Z = 16$
$b = 6.096(5) \text{ \AA}$	$D_c = 2.04 \text{ g cm}^{-3}$
$c = 33.910(14) \text{ \AA}$	$\lambda(\text{Mo-K}_\alpha) = 0.71069$
$\beta = 93.80(5)^\circ$	$\mu(\text{Mo-K}_\alpha) = 38.35 \text{ cm}^{-1}$
$V = 6101.82(6) \text{ \AA}^3$	$F(000) = 3486.27$

TABLE 2

FRACTIONAL ATOMIC COORDINATES ( $\times 10^4$ ) AND THERMAL PARAMETERS ( $\times 10^4$ ), WITH ESTIMATED STANDARD DEVIATIONS IN PARENTHESES, FOR NON-HYDROGEN ATOMS (ANISOTROPIC FOR TELLURIUM ATOMS AND ISOTROPIC FOR OXYGEN AND CARBON ATOMS)

Atom	$x/a$	$y/b$	$z/c$	$U$		
Te(1)	218(1)	337(3)	1527(1)			
Te(2)	448(1)	4630(3)	1613(1)			
Te(3)	684(1)	5470(3)	2831(1)			
Te(4)	771(1)	9733(3)	2627(1)			
O(1)	-830(7)	329(38)	-148(6)		675(56)	
O(2)	2208(8)	5075(43)	677(6)		826(66)	
O(3)	1662(7)	5192(39)	4526(6)		682(58)	
O(4)	2607(7)	9478(42)	1799(6)		762(64)	
C(11)	-108(8)	421(42)	945(6)		334(55)	
C(12)	-80(9)	2259(39)	690(8)		349(64)	
C(13)	-306(10)	2182(45)	314(9)		451(73)	
C(14)	576(10)	529(49)	198(8)		499(68)	
C(15)	-594(10)	-1340(44)	449(8)		432(70)	
C(16)	-382(9)	-1346(39)	825(7)		335(60)	
C(17)	-818(13)	2149(60)	-398(10)		783(110)	
C(21)	1053(8)	4708(43)	1299(7)		381(60)	
C(22)	1353(9)	6319(42)	1386(8)		418(67)	
C(23)	1737(10)	6627(47)	1173(8)		509(76)	
C(24)	1836(9)	4997(44)	908(8)		473(71)	
C(25)	1542(14)	3313(66)	824(12)		864(117)	
C(26)	1154(12)	3146(51)	1025(9)		605(89)	
C(27)	2458(14)	6900(68)	681(13)		960(129)	
C(31)	1038(9)	5449(48)	3392(7)		456(64)	
C(32)	987(10)	3799(44)	3637(9)		470(75)	
C(33)	1196(10)	3616(49)	4014(9)		511(77)	
C(34)	1470(10)	5313(57)	4131(9)		622(81)	
C(35)	1547(11)	7184(48)	3888(9)		542(81)	
C(36)	1320(10)	7164(42)	3524(8)		423(70)	
C(37)	1914(13)	6877(65)	4691(11)		852(118)	
C(41)	1409(8)	9564(43)	2364(7)		357(57)	
C(42)	1728(10)	7812(44)	2452(9)		446(73)	
C(43)	2117(10)	7753(43)	2269(8)		436(73)	
C(44)	2226(9)	9391(44)	2000(8)		419(67)	
C(45)	1933(10)	11137(42)	1923(8)		442(74)	
C(46)	1531(10)	11235(41)	2117(8)		402(67)	
C(47)	2887(13)	7708(67)	1839(12)		875(121)	
Atom	$U_{11}$	$U_{22}$	$U_{33}$	$U_{23}$	$U_{13}$	$U_{12}$
Te(1)	477(12)	285(8)	510(12)	78(9)	-17(9)	-14(9)
Te(2)	454(12)	291(8)	505(12)	-11(9)	33(9)	12(9)
Te(3)	564(13)	319(8)	521(12)	-0(10)	37(10)	-46(10)
Te(4)	599(13)	285(8)	530(12)	16(9)	73(10)	65(9)

The atomic parameters for tellurium were found by direct methods using SHELX 76 (Sheldrick, 1976) [6] and confirmed by analysis of the Patterson map. The positions of the oxygen and carbon atoms were found by using a difference map. Anisotropic temperature factors were calculated for the tellurium atoms and isotropic for oxygen and carbon atoms. The positional and temperature factor parameters for tellurium, oxygen and carbon were refined by four cycles of blocked full matrix least squares refinement to a final  $R$  value

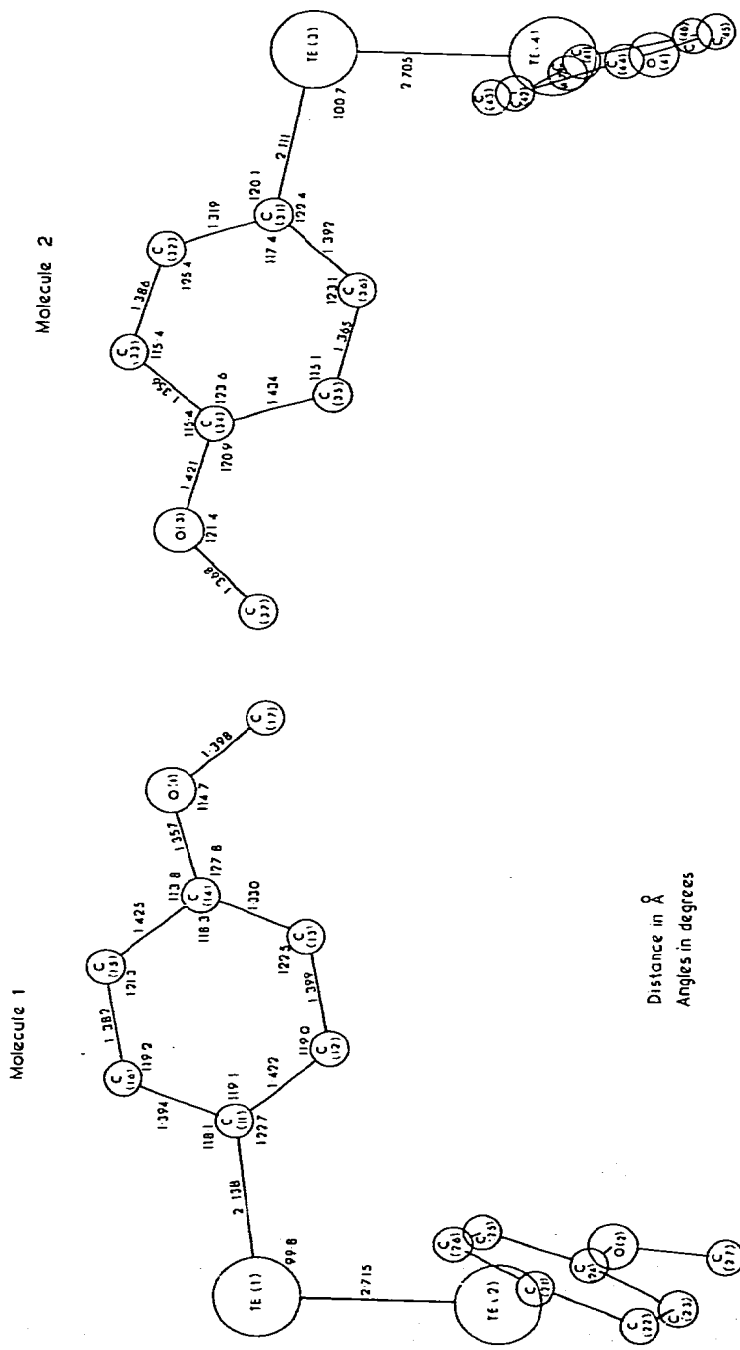
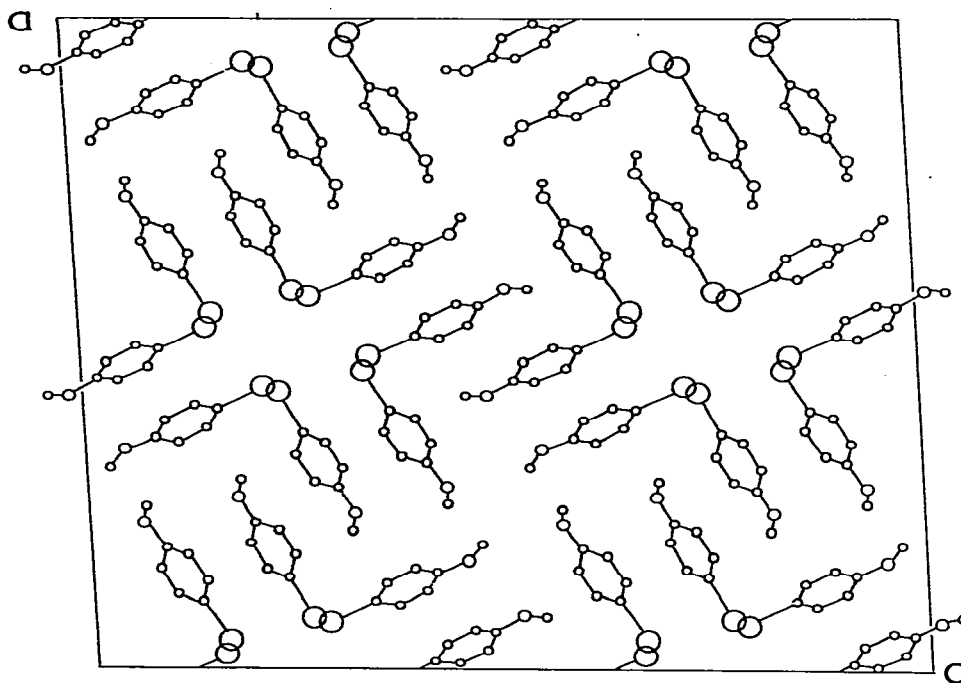


Fig. 1. Configuration of the two distinct molecules in the structure of *p,p'*-dimethoxydiphenyl ditelluride.



010 projection

Fig. 2. *p,p'*-Dimethoxydiphenyl ditelluride,  $(p\text{-MeOC}_6\text{H}_4)_2\text{Te}_2$ .

of 0.0598 for 1 802 independent observed reflections for which  $I > 2\sigma(I)$ .

$$R = \frac{\sum \|F_{\text{obs}} - |F_{\text{calc}}|\|}{\sum |F_{\text{obs}}|}$$

Hydrogen atoms were included in the calculation in theoretical positions. The values of the final atomic coordinates and temperature coefficients are listed in Table 2 and Figs. 1 and 2 show the two distinct molecules and the 010 projection of the structure respectively.

TABLE 3

COMPARISON OF THE UNIT CELL OF *p,p'*-DIMETHOXYDIPHENYL DITELLURIDE WITH THOSE OF RELATED DITELLURIDES

Formula	Symmetry	Space group	<i>a</i> (Å)	<i>b</i> (Å)	<i>c</i> (Å)	$\beta$	<i>V</i> (Å <sup>3</sup> )	<i>Z</i>
$(p\text{-MeOC}_6\text{H}_4)_2\text{Te}_2$ <sup>a</sup>	Mono- clinic	<i>C2/c</i>	29.583	6.096	33.910	93.80	6101.82	16
$(p\text{-ClC}_6\text{H}_4)_2\text{Te}_2$ [1]	Mono- clinic	<i>P2<sub>1</sub>n</i>	14.34	6.47	15.09	101.5	1371.94	4
$(\text{C}_6\text{H}_5)_2\text{Te}_2$ [2]	Ortho- rhombic	<i>P2<sub>1</sub>2<sub>1</sub>2<sub>1</sub></i>	27.028	8.703	5.221		122.8	4
$(p\text{-CH}_3\text{C}_6\text{H}_4)_2\text{Te}_2$ [3]	Ortho- rhombic	<i>Pbc2<sub>1</sub></i>	8.305	26.329	6.439		1407.97	4

<sup>a</sup> This work.

## Discussion

It may be seen from Table 3 that the unit cell dimensions and space groups of  $(p\text{-MeOC}_6\text{H}_4)_2\text{Te}_2$  differ from those of related ditellurides that have been studied. The unit cell is much larger and the structure consists of two distinct repeating molecules. Bond lengths and bond angles are given in Table 4 and these agree favourably with the values found in related ditellurides. In molecule 1 Te(1) and Te(2) are bonded almost vertically along the  $b$  axis direction with bond length 2.715(2) Å and molecule 2 has Te(3) and Te(4) similarly bonded

TABLE 4

INTRAMOLECULAR DISTANCES (Å) AND ANGLES ( $^\circ$ ) WITH STANDARD DEVIATIONS IN PARENTHESES FOR  $p,p'$ -DIMETHOXYDIPHENYL DITELLURIDE

Molecule 1		Molecule 2	
Te(1)—Te(2)	2.715(2)	Te(3)—Te(4)	2.705(3)
Te(1)—C(11)	2.138(22)	Te(3)—C(31)	2.111(25)
C(11)—C(12)	1.422(33)	C(31)—C(32)	1.319(36)
C(12)—C(13)	1.399(34)	C(32)—C(33)	1.386(35)
C(13)—C(14)	1.330(38)	C(33)—C(34)	1.356(41)
C(14)—C(15)	1.425(36)	C(34)—C(35)	1.434(42)
C(15)—C(16)	1.382(32)	C(35)—C(36)	1.365(36)
C(16)—C(11)	1.394(33)	C(36)—C(31)	1.392(37)
O(1)—C(14)	1.357(28)	O(3)—C(34)	1.421(31)
O(1)—C(17)	1.398(38)	O(3)—C(37)	1.368(41)
Te(2)—C(21)	2.144(24)	Te(4)—C(41)	2.143(24)
C(21)—C(22)	1.342(34)	C(41)—C(42)	1.443(36)
C(22)—C(23)	1.400(36)	C(42)—C(43)	1.342(37)
C(23)—C(24)	1.383(37)	C(43)—C(44)	1.404(35)
C(24)—C(25)	1.364(44)	C(44)—C(45)	1.386(35)
C(25)—C(26)	1.376(44)	C(45)—C(46)	1.400(35)
C(26)—C(21)	1.376(37)	C(46)—C(41)	1.380(33)
O(2)—C(24)	1.395(30)	O(4)—C(44)	1.359(30)
O(2)—C(27)	1.336(43)	O(4)—C(47)	1.361(41)
C(11)—Te(1)—Te(2)	99.8(0.7)	C(31)—Te(3)—Te(4)	100.7(0.8)
C(12)—C(11)—Te(1)	122.7(1.8)	C(32)—C(31)—Te(3)	120.1(2.2)
C(16)—C(11)—Te(1)	118.1(1.8)	C(36)—C(31)—Te(3)	122.4(2.1)
C(16)—C(11)—C(12)	119.1(2.2)	C(36)—C(31)—C(32)	117.4(2.5)
C(13)—C(12)—C(11)	119.0(2.3)	C(33)—C(32)—C(31)	125.4(2.8)
C(14)—C(13)—C(12)	122.5(2.7)	C(34)—C(33)—C(32)	115.4(2.8)
C(15)—C(14)—C(13)	118.3(2.7)	C(35)—C(34)—C(33)	123.6(3.0)
C(16)—C(15)—C(14)	121.3(2.5)	C(36)—C(35)—C(34)	115.1(2.8)
C(11)—C(16)—C(15)	119.2(2.3)	C(31)—C(36)—C(35)	123.1(2.6)
O(1)—C(14)—C(13)	127.8(2.8)	O(3)—C(34)—C(33)	115.4(2.8)
O(1)—C(14)—C(15)	113.8(2.5)	O(3)—C(34)—C(35)	120.9(2.8)
C(17)—O(1)—C(14)	114.7(2.5)	C(37)—O(3)—C(34)	121.4(2.6)
C(21)—Te(2)—Te(1)	100.3(0.7)	C(41)—Te(4)—Te(3)	99.3(0.7)
C(22)—C(21)—Te(2)	117.9(2.0)	C(42)—C(41)—Te(4)	122.1(1.9)
C(26)—C(21)—Te(2)	123(2.1)	C(46)—C(41)—Te(4)	119.2(1.9)
C(26)—C(21)—C(22)	119.1(2.6)	C(46)—C(41)—C(42)	118.6(2.4)
C(23)—C(22)—C(21)	112.1(2.6)	C(43)—C(42)—C(41)	119.5(2.6)
C(24)—C(23)—C(22)	116.9(2.7)	C(44)—C(43)—C(42)	121.4(2.6)
C(25)—C(24)—C(23)	121.2(3.1)	C(45)—C(44)—C(43)	120.1(2.6)
C(26)—C(25)—C(24)	119.6(3.6)	C(46)—C(45)—C(44)	118.9(2.5)
C(21)—C(26)—C(25)	120.4(3.2)	C(41)—C(46)—C(45)	121.1(2.4)
O(2)—C(24)—C(23)	123.3(2.5)	O(4)—C(44)—C(43)	126.0(2.6)
O(2)—C(24)—C(25)	115.1(2.8)	O(4)—C(44)—C(45)	113.8(2.5)
C(27)—O(2)—C(24)	118.6(2.8)	C(47)—O(4)—C(44)	116.0(2.7)

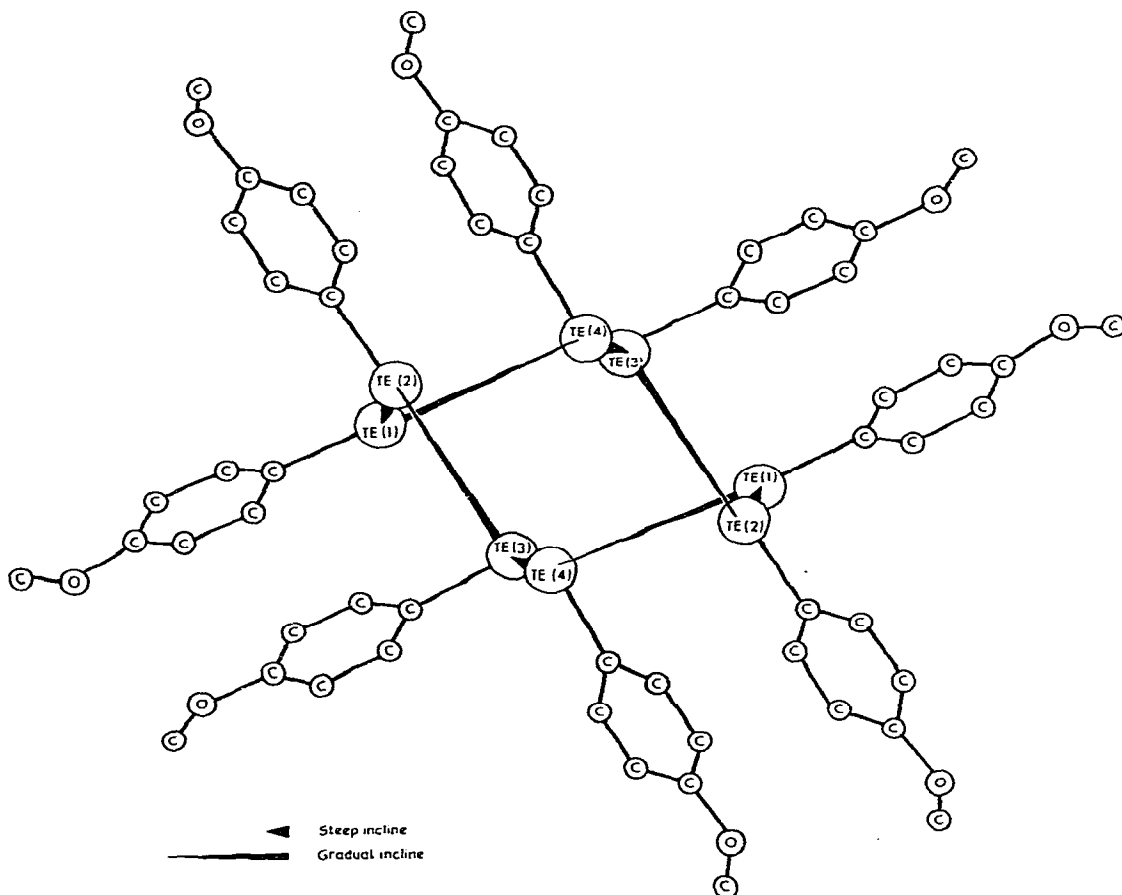


Fig. 3. Spiralling effect in tellurium network in  $p,p'$ -dimethoxydiphenyl ditelluride.

in the  $b$  direction with bond length  $2.705(3) \text{ \AA}$ , both distances being shorter than the single covalent Te—Te bond length ( $2.74 \text{ \AA}$ ) of Pauling [7]. On the other hand Te(1)—C(11), Te(2)—C(21), Te(3)—C(31) and Te(4)—C(41) distances all correspond to single covalent bonds. There is a slight spiralling effect in the repeating network of tellurium atoms in the  $b$  direction (Fig. 3), and examination of the packing distances of the tellurium atoms (Table 5) shows that the shortest distances between Te(1) and Te(4) is  $3.991(3) \text{ \AA}$  and between Te(2) and Te(3) is  $3.983(3) \text{ \AA}$ , while the sum of the Van der Waals' radii is  $4.40 \text{ \AA}$ , thus indicating some weak bonds between molecules. The dihedral angles and the angles of rotation of the benzene rings serve to describe molecular conformations in the ditellurides. These were calculated for  $(p\text{-MeOC}_6\text{H}_4)_2\text{Te}_2$  and

TABLE 5

PACKING DISTANCES IN  $\text{\AA}$ : SHORTEST INTERMOLECULAR Te—Te DISTANCES FOR  $p,p'$ -DIMETHOXYDIPHENYL DITELLURIDE

Te(1)—Te(3)	4.630	5.426	Te(2)—Te(3)	3.983	4.173
Te(1)—Te(4)	3.991	4.247	Te(2)—Te(4)	4.606	5.458

TABLE 6

CHARACTERISTIC ANGLES (°) OF *p,p'*-DIMETHOXYDIPHENYL DITELLURIDE COMPARED WITH THOSE OF RELATED DITELLURIDES [3]

	$(p\text{-MeOC}_6\text{H}_4)_2\text{Te}_2$ <i>C2/c</i>		$(p\text{-CH}_3\text{C}_6\text{H}_4)_2\text{Te}_2$ <i>Pbc2_1</i>	$(p\text{-ClC}_6\text{H}_4)_2\text{Te}_2$ <i>P2_1/n</i>	$(\text{C}_6\text{H}_5)_2\text{Te}_2$ <i>P2_12_12_1</i>
	Molecule 1	Molecule 2			
Dihedral angle (°)	81.2(5)	86.8(5)	85.7(4)	72.0	88.5
Angle of relative rotation of benzene rings (°)	51.2(5)	75.2(5)	73.4(3)	152.6	159.9
Angle of rotation of benzene rings I and II, relative to C(11)—Te(1)—Te(2) plane (°)	15.1(5)				
relative to C(21)—Te(2)—Te(1) plane (°)	21.8(5)				
Angle of rotation of benzene rings I and II, relative to C(31)—Te(3)—Te(4) plane (°)		15.3(5)			
relative to C(41)—Te(4)—Te(3) plane (°)		20.1(5)			
Angle of rotation of benzene ring I relative to C(1)—Te(1)—Te(2) plane (°)			38.0(4)	50.7	87.7
Angle of rotation of benzene ring II relative to C(8)—Te(2)—Te(1) plane (°)			37.0(4)	96.3	101.5

they are compared with those of related compounds in Table 6.

There are considerable differences between the molecular orientations of the four ditellurides that have now been examined in detail which may be attributed to different stacking arrangements.

### Acknowledgements

The authors wish to thank Dr. T.A. Hamor of the University of Birmingham for instruction in the use of the Stoe STADI-2 two circle diffractometer and for some computing facilities, and also our colleagues, Dr. A.W. Downs, Dr. N.W. Grimes and Professor W.R. McWhinnie of the University of Aston in Birmingham for helpful discussions.

### References

- 1 F.H. Kruse, R.E. Marsh and J.D. McCullough, *Acta Crystallogr.* **10** (1957) 201.
- 2 G. Llabres, O. Dideberg and L. Dupont, *Acta Crystallogr. B*, **28** (1972) 2438.
- 3 M.R. Spirlet, G. van den Bossche, O. Dideberg and L. Dupont, *Acta Crystallogr. B*, **35** (1979) 1727.
- 4 W.R. McWhinnie and P. Thavornnyutikarn, *J. Organometal. Chem.*, **35** (1972) 149.
- 5 G.T. Morgan and R.E. Kellet, *J. Chem. Soc.*, (1962) 1080.
- 6 G.M. Sheldrick, SHELX 76, Program for Crystal Structure determination, University of Cambridge, England, 1976.
- 7 L. Pauling, *The Chemical Bond*, Cornell Univ. Press, Ithaca, 1967, pp. 136—137.