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THE CRYSTAL STRUCTURES OF THE 1-METHYL-3,4-BENZO-1-TELLURACYCLOPENTANE AND 1-PHENYL-1-TELLURACYCLOPENTANE CATIONS IN THEIR TETRAPHENYLBORATE SALTS, $C_8H_8TeMe^+$ BPh_4^- AND $C_4H_8TePh^+$ BPh_4^- *

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Summary

The crystal structures of $C_8H_8TeMe^+$ BPh_4^- (I) and $C_4H_8TePh^+$ BPh_4^- (II) have been determined from three-dimensional X-ray counter data.

I is monoclinic, space group $P2_1/n$ with a 9.175(1), b 17.402(3), c 16.998(3) Å, β 98.92(6)°, $Z = 4$, $R = 5.1\%$ for 1641 observed reflections.

II is triclinic, space group $P\bar{1}$ with a 9.635(3), b 17.721(3), c 16.858(8) Å, α 89.77(2), β 104.36(4), γ 90.16(2)°, $Z = 4$, $R = 9.0\%$ for 6466 observed reflections.

In both I and II tellurium is three-coordinate in a pyramidal geometry, with Te–C distances in the range 2.07(1)–2.14(1) Å (I) and 2.10(1)–2.17(1) Å (II). In both structures short contacts of 3.4–3.5 Å occur between tellurium and carbon atoms of the tetraphenylborate anion.

Introduction

Following earlier structural studies [1,2] of organotellurium(IV) bromides and iodides in which secondary [3] Te ··· halogen interactions occur, we now report the crystal structures of the two tetraphenylborate salts, $C_8H_8TeMe^+$ BPh_4^- (I) and $C_4H_8TePh^+$ BPh_4^- (II). Here secondary bonding would not be expected; nevertheless there is some evidence for cation–anion interaction. Compound I shows a surprisingly low conductivity in dimethylsulphoxide [4] and on pyrolysis produces C_8H_8Te and toluene [5]. An intermediate $C_8H_8Te(Me)Ph$ is probably involved since in the preparation of $C_8H_8TePh^+$ BPh_4^-, $C_8H_8TePh_2$ was isolated [4], which on pyrolysis gives C_8H_8Te and biphenyl [5]. The crystal structure of only one organotellurium(IV) tetraphenylborate has been described to date, that of Me_3Te^+ BPh_4^- [6] in which no cation–anion interaction is apparent, and tellurium is three-coordinate.

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Experimental

Samples of compounds I and II were kindly supplied by Prof. W.R. McWhinnie [4,5].

After preliminary examination by photographic methods, the final cell dimensions and intensity data were measured with graphite-monochromated Mo-K_α radiation on an Enraf-Nonius CAD-4 diffractometer. Two standard reflections were monitored every 2 h. In both I and II crystal decomposition occurred and appropriate scale factors (maximum 1.61 (I) and 1.75 (II)) were applied to compensate for the drop in intensity. Absorption corrections were not carried out. Details of crystal and experimental parameters are given in Table 1.

The tellurium atom of I was located from a Patterson synthesis and those of II by direct methods. Carbon and boron atoms were located by Fourier syntheses. Hydrogen atoms were placed in calculated positions (C–H 1.08 Å) and were allowed to "ride" on their respective carbon atoms in the subsequent least-squares refinements. Final atomic coordinates for I and II are in Tables 2 and 3 *.

TABLE 1

CRYSTAL AND EXPERIMENTAL PARAMETERS

	I	II
Molecular formula	$C_{33}H_{31}BTe$	$C_{34}H_{33}BTe$
Molecular weight	566.0	580.0
Crystallisation liquid	dichloromethane	acetonitrile
Crystal size (mm)	0.4×0.25×0.1	0.4×0.2×0.1
Cell constants (Å)	a 9.175(1) b 17.402(3) c 16.998(3) β 98.92(6)°	a 9.635(3) b 17.721(3) c 16.858(8) α 89.77(2)° β 104.36(4)° γ 90 16(2)°
Cell volume (Å)	2681	2788
Space group	$P2_1/n$	$P\bar{1}$
Z	4	4
Density (g cm^{-3})	1.402	1.382
Absorption coefficient (mm^{-1})	1.0	1.0
Data collection range (λ 0.71069 Å) 2θ	4–50 °	4–50 °
Scan mode	$\omega/2\theta$	$\omega/2\theta$
Scan range (ω°)	1.10 + 0.35 tan θ	1.00 + 0.35 tan θ
Scan speed range (° min^{-1})	1.0–3.3	0.3–3.3
Total data measured	4680	10340
Significant data $[F > n\sigma(F)]$	1641 (n = 5)	6466 (n = 8)
Least-squares weights $w = [\sigma^2(F) + kF^2]^{-1}$	k = 0.0004	k = 0.0015
Maximum shift/error in final least-squares cycle	0.06	0.2
Final R (%)	5.11	9.00

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* Lists of structure factors, thermal parameters, hydrogen atom coordinates and bond angles pertaining to the tetraphenylborate ions are available from the authors.

In the refinement of I all non-hydrogen atoms were allowed to vibrate anisotropically.

The refinement of II was complicated by the occurrence of disorder involving one of the two independent $C_4H_8TePh^+$ cations. Two positions of the cation, with occupancies constrained to add up to 1, were refined. Bond lengths and angles were constrained to be close to expected values. For the lower-occupancy position, atoms C(17), C(18) and C(19) were fixed in position and were not refined and it was not possible to locate C(15), C(16) and C(20) as these lay very close to the corresponding atoms of the higher-occupancy position. The occupancy factors converged to values of 0.723(2) and 0.277(2) for the two positions. In this structure only the Te atoms and the C atoms (C(1)–C(10)) of the ordered cation were assigned anisotropic thermal parameters. Hydrogen atoms were not included for the disordered cation.

TABLE 2

FRACTIONAL ATOMIC COORDINATES ($\times10^4$) FOR $C_8H_8TeMe^+$ BPh_4^- (I) WITH ESTIMATED STANDARD DEVIATIONS IN PARENTHESES

Atom	*x*	*y*	*z*
Te	540(1)	1919(1)	2048(1)
C(1)	1833(15)	1688(7)	3180(7)
C(2)	2112(14)	832(7)	3209(7)
C(3)	2805(16)	479(9)	3918(8)
C(4)	3041(19)	−302(11)	3937(11)
C(5)	2603(20)	−729(9)	3272(11)
C(6)	1979(16)	−392(9)	2588(9)
C(7)	1719(15)	386(8)	2540(8)
C(8)	974(15)	787(8)	1750(7)
C(9)	−1473(14)	1654(8)	2392(8)
B	7195(16)	2892(7)	4568(8)
C(11)	5496(13)	3024(8)	4729(6)
C(12)	4852(18)	3772(8)	4623(7)
C(13)	3471(20)	3906(11)	4839(9)
C(14)	2678(18)	3347(12)	5157(9)
C(15)	3310(18)	2630(11)	5271(8)
C(16)	4696(15)	2491(8)	5055(7)
C(21)	8229(12)	3302(6)	5333(6)
C(22)	8635(13)	4072(7)	5319(7)
C(23)	9407(14)	4461(8)	5980(8)
C(24)	9847(16)	4070(10)	6679(8)
C(25)	9505(15)	3297(9)	6731(8)
C(26)	8694(13)	2917(7)	6053(6)
C(31)	7594(13)	1984(7)	4477(6)
C(32)	8992(14)	1670(7)	4712(7)
C(33)	9332(18)	910(8)	4542(7)
C(34)	8258(19)	441(8)	4121(8)
C(35)	6899(18)	724(8)	3867(7)
C(36)	6567(15)	1466(7)	4030(6)
C(41)	7508(14)	3270(5)	3703(6)
C(42)	6410(16)	3374(7)	3051(7)
C(43)	6778(20)	3624(8)	2314(8)
C(44)	8189(22)	3753(8)	2238(9)
C(45)	9330(19)	3679(7)	2873(8)
C(46)	8988(16)	3420(7)	3610(8)

TABLE 3

FRACTIONAL ATOMIC COORDINATES ($\times 10^4$) AND ISOTROPIC TEMPERATURE FACTORS ($Å^2 \times 10^4$) FOR $C_4H_8TePh^+$ BPh_4^- (II)

Atom	*x*	*y*	*z*	*U*
Te(1)	834(1)	5832(1)	6639(1)	[a]
Te(2′)[b]	4964(1)	8363(1)	1930(1)	[a]
Te(2″)[c]	4118(4)	8422(2)	2648(2)	[a]
C(1)	−1257(10)	5662(6)	6882(7)	[a]
C(2)	−1745(11)	6437(7)	7080(7)	[a]
C(3)	−466(11)	6881(6)	7568(7)	[a]
C(4)	716(10)	6922(5)	7121(6)	[a]
C(5)	1999(6)	5277(5)	7705(5)	[a]
C(6)	2253(12)	4514(6)	7651(7)	[a]
C(7)	2942(14)	4111(7)	8319(8)	[a]
C(8)	3356(13)	4470(7)	9050(8)	[a]
C(9)	3110(14)	5227(7)	9103(7)	[a]
C(10)	2466(11)	5638(6)	8452(6)	[a]
C(11′)[b]	4018(14)	9095(8)	953(8)	708(40)
C(11″)[c]	2418(28)	9163(17)	2066(12)	800
C(12′)[b]	2445(16)	9156(9)	942(8)	807(45)
C(12″)[c]	2023(26)	8857(19)	1131(11)	800
C(13′)[b]	2103(11)	8989(8)	1771(8)	800
C(13″)[c]	3535(35)	8810(20)	892(8)	800
C(14′)[b]	2953(13)	8300(7)	2197(9)	724(39)
C(14″)[c]	4458(32)	8199(21)	1459(9)	800
C(15)	5917(13)	9194(6)	2848(8)	945(37)
C(16)	7057(13)	8954(7)	3483(8)	1003(40)
C(17′)[b]	7925(16)	9497(7)	3997(10)	836(44)
C(17″)[c]	7673	9164	3951	900
C(18′)[b]	7588(16)	10265(8)	3877(10)	910(49)
C(18″)[c]	7401	9936	3974	900
C(19′)[b]	6423(14)	10510(7)	3263(9)	766(41)
C(19″)[c]	6216	10217	3387	900
C(20)	5554(12)	9952(6)	2775(7)	812(31)
B(1)	3174(9)	2139(5)	622(6)	437(21)
B(2)	2071(10)	7050(5)	4445(6)	446(21)
C(21)	2531(8)	2994(4)	628(5)	446(18)
C(22)	1065(9)	3159(5)	300(6)	555(22)
C(23)	493(10)	3862(5)	358(6)	612(24)
C(24)	1311(10)	4436(6)	772(6)	648(25)
C(25)	2767(10)	4303(5)	1107(6)	613(24)
C(26)	3343(9)	3594(5)	1029(6)	553(22)
C(31)	4919(8)	2155(4)	744(5)	439(18)
C(32)	5506(10)	2626(5)	253(6)	612(24)
C(33)	6977(10)	2651(6)	287(7)	668(25)
C(34)	7867(11)	2180(6)	791(7)	709(27)
C(35)	7338(11)	1701(6)	1295(7)	677(26)
C(36)	5876(9)	1677(5)	1249(6)	547(22)
C(41)	2561(9)	1693(5)	−242(6)	503(20)
C(42)	1919(10)	2039(6)	−978(6)	626(24)
C(43)	1508(12)	1633(6)	−1692(8)	779(30)
C(44)	1692(13)	868(7)	−1683(9)	870(34)
C(45)	2272(12)	516(7)	−1013(8)	800(31)
C(46)	2753(11)	934(6)	−278(7)	705(27)
C(51)	2718(9)	1713(4)	1394(5)	438(18)
C(52)	1548(10)	1225(5)	1292(6)	602(23)

TABLE 3 (continued)

Atom	x	y	z	U
C(53)	1117(13)	926(7)	1985(8)	812(31)
C(54)	1791(12)	1104(6)	2728(8)	772(30)
C(55)	2993(11)	1589(6)	2892(7)	736(28)
C(56)	3399(10)	1861(5)	2204(6)	578(23)
C(61)	3092(8)	6611(4)	5242(5)	431(18)
C(62)	3543(9)	5864(5)	5200(6)	531(21)
C(63)	4300(10)	5467(6)	5900(6)	618(24)
C(64)	4614(10)	5793(6)	6635(7)	660(25)
C(65)	4188(10)	6526(6)	6689(7)	662(25)
C(66)	3433(10)	6927(5)	6021(6)	599(23)
C(71)	2464(9)	7945(5)	4403(5)	486(20)
C(72)	3875(10)	8222(5)	4731(6)	636(24)
C(73)	4221(12)	8967(6)	4604(7)	707(27)
C(74)	3223(11)	9453(7)	4192(7)	766(30)
C(75)	1888(11)	9214(6)	3863(7)	728(28)
C(76)	1520(10)	8457(5)	3984(6)	596(23)
C(81)	2246(8)	6723(5)	3584(5)	480(19)
C(82)	3584(10)	6541(5)	3448(6)	597(23)
C(83)	3779(12)	6320(6)	2686(7)	730(28)
C(84)	2608(13)	6261(7)	2046(8)	842(32)
C(85)	1285(13)	6411(6)	2129(8)	840(32)
C(86)	1083(11)	6655(5)	2893(6)	646(25)
C(91)	453(8)	6930(4)	4573(5)	455(19)
C(92)	−220(10)	6213(5)	4453(6)	612(24)
C(93)	−1531(11)	6063(6)	4596(7)	743(29)
C(94)	−2250(13)	6602(6)	4891(7)	817(32)
C(95)	−1673(12)	7315(7)	5044(8)	829(32)
C(96)	−306(10)	7466(6)	4898(6)	623(24)

[a] Anisotropic temperature factors refined. [b] Occupancy 0.723(2). [c] Occupancy 0.277(2).

Computations were carried out largely on the CDC 7600 computer at the University of Manchester Regional Computer Centre with SHELX [7].

Results and discussion

Selected distances and angles are in Table 4. The cation geometries are illustrated in Fig. 1 and those of the tetraphenylborate anions in Fig. 2. The contents of the unit cells of the two structures are shown in Fig. 3. In the following discussion only the ordered cation of structure II is considered, as the dimensions of the disordered cation, although similar, are of relatively low accuracy.

In both I and II tellurium is three-coordinated in a pyramidal geometry with C–Te–C bond angles in the ranges 86.6–95.7 ° (I) and 84.9–99.5 ° (II). In each case the endocyclic angle is less than 90 ° (86.6 and 84.9 °) and the other two angles are also within a fairly small range (94.0–99.5 °). Presumably the endocyclic angle is constrained by the geometry of the five-membered ring and the Te–C bond length. Similar intra-ring angles of 83.5–86.6 ° occur in a number of 1-organo-1-halo-3,4-benzo-1-telluracyclopentanes [1]. The coordination geometry may be considered as basically tetrahedral with a lone pair of electrons occupying the fourth site. In accord with VSEPR theory [8] all the bond angles at tellurium are less than the ideal

TABLE 4

DISTANCES (Å) AND ANGLES (°) IN I AND II

(a) Distances in I			
Te–C(1)	2.136(11)	C(4)–C(5)	1.36(2)
Te–C(8)	2.088(13)	C(5)–C(6)	1.35(2)
Te–C(9)	2.074(13)	C(6)–C(7)	1.38(2)
C(1)–C(2)	1.51(2)	C(2)–C(7)	1.38(2)
C(2)–C(3)	1.41(2)	C(7)–C(8)	1.57(2)
C(3)–C(4)	1.38(2)		
B–C(11)	1.64(2)	C(25)–C(26)	1.43(2)
B–C(21)	1.65(2)	C(26)–C(21)	1.40(1)
B–C(31)	1.64(2)	C(31)–C(32)	1.39(2)
B–C(41)	1.68(2)	C(32)–C(33)	1.40(2)
C(11)–C(12)	1.43(2)	C(33)–C(34)	1.39(2)
C(12)–C(13)	1.39(2)	C(34)–C(35)	1.35(2)
C(13)–C(14)	1.38(2)	C(35)–C(36)	1.36(2)
C(14)–C(15)	1.38(2)	C(36)–C(31)	1.43(2)
C(15)–C(16)	1.40(2)	C(41)–C(42)	1.39(2)
C(16)–C(11)	1.35(2)	C(42)–C(43)	1.42(2)
C(21)–C(22)	1.39(1)	C(43)–C(44)	1.34(2)
C(22)–C(23)	1.41(2)	C(44)–C(45)	1.39(2)
C(23)–C(24)	1.37(2)	C(45)–C(46)	1.41(2)
C(24)–C(25)	1.39(2)	C(46)–C(41)	1.42(2)
(b) Angles in cation of I			
C(1)–Te–C(8)	86.6(5)	C(2)–C(3)–C(4)	120(1)
C(1)–Te–C(9)	95.7(5)	C(3)–C(4)–C(5)	120(2)
C(8)–Te–C(9)	94.0(5)	C(4)–C(5)–C(6)	121(2)
Te–C(1)–C(2)	107(1)	C(5)–C(6)–C(7)	122(2)
Te–C(8)–C(7)	107(1)	C(6)–C(7)–C(2)	119(1)
C(1)–C(2)–C(3)	121(1)	C(6)–C(7)–C(8)	123(1)
C(1)–C(2)–C(7)	120(1)	C(2)–C(7)–C(8)	119(1)
C(3)–C(2)–C(7)	119(1)		
(c) Distances in II			
Te(1)–C(1)	2.172(10)	Te(2′)–C(11′)	2.114
C(1)–C(2)	1.517(14)	C(11′)–C(12′)	1.515
C(2)–C(3)	1.521(15)	C(12′)–C(13′)	1.542
C(3)–C(4)	1.514(13)	C(13′)–C(14′)	1.543
Te(1)–C(4)	2.113(9)	Te(2′)–C(14′)	2.098
Te(1)–C(5)	2.109(9)	Te(2′)–C(15)	2.170
C(5)–C(6)	1.382(13)	C(15)–C(16)	1.396
C(6)–C(7)	1.356(16)	C(16)–C(17′)	1.421
C(7)–C(8)	1.358(16)	C(17′)–C(18′)	1.402
C(8)–C(9)	1.370(16)	C(18′)–C(19′)	1.393
C(9)–C(10)	1.333(15)	C(19′)–C(20)	1.420
C(10)–C(5)	1.386(15)	C(15)–C(20)	1.387
B(1)–C(21)	1.640(11)	B(2)–C(61)	1.649(13)
B(1)–C(31)	1.643(11)	B(2)–C(71)	1.635(12)
B(1)–C(41)	1.634(12)	B(2)–C(81)	1.613(12)
B(1)–C(51)	1.652(13)	B(2)–C(91)	1.639(12)
C(21)–C(22)	1.414(11)	C(61)–C(62)	1.402(11)
C(22)–C(23)	1.376(12)	C(62)–C(63)	1.410(13)
C(23)–C(24)	1.369(13)	C(63)–C(64)	1.335(13)
C(24)–C(25)	1.397(13)	C(64)–C(65)	1.372(13)
C(25)–C(26)	1.395(12)	C(65)–C(66)	1.376(14)
C(21)–C(26)	1.392(11)	C(61)–C(66)	1.392(12)

TABLE 4 (continued)

C(31)–C(32)	1.388(13)	C(71)–C(72)	1.421(12)
C(32)–C(33)	1.404(13)	C(72)–C(73)	1.389(14)
C(33)–C(34)	1.339(14)	C(73)–C(74)	1.348(15)
C(34)–C(35)	1.382(15)	C(74)–C(75)	1.336(14)
C(35)–C(36)	1.392(13)	C(75)–C(76)	1.415(14)
C(31)–C(36)	1.378(12)	C(71)–C(76)	1.352(12)
C(41)–C(42)	1.384(13)	C(81)–C(82)	1.402(12)
C(42)–C(43)	1.376(14)	C(82)–C(83)	1.402(14)
C(43)–C(44)	1.366(16)	C(83)–C(84)	1.358(15)
C(44)–C(45)	1.290(17)	C(84)–C(85)	1.345(16)
C(45)–C(46)	1.421(15)	C(85)–C(86)	1.419(15)
C(41)–C(46)	1.362(12)	C(81)–C(86)	1.406(13)
C(51)–C(52)	1.395(12)	C(91)–C(92)	1.416(12)
C(52)–C(53)	1.432(15)	C(92)–C(93)	1.369(14)
C(53)–C(54)	1.301(15)	C(93)–C(94)	1.348(14)
C(54)–C(55)	1.412(15)	C(94)–C(95)	1.379(15)
C(55)–C(56)	1.398(14)	C(95)–C(96)	1.423(15)
C(51)–C(56)	1.386(12)	C(91)–C(96)	1.395(12)
(d) Angles in cation of II			
C(1)–Te(1)–C(4)	84.9(4)	C(11′)–Te(2′)–C(14′)	87.4
C(1)–Te(1)–C(5)	95.7(4)	C(11′)–Te(2′)–C(15)	99.4
C(4)–Te(1)–C(5)	99.5(4)	C(14′)–Te(2′)–C(15)	97.5
Te(1)–C(1)–C(2)	105.7(6)	Te(2′)–C(11′)–C(12′)	107.0
C(1)–C(2)–C(3)	109.6(8)	C(11′)–C(12′)–C(13′)	114.4
C(2)–C(3)–C(4)	111.2(9)	C(12′)–C(13′)–C(14′)	111.2
C(3)–C(4)–Te(1)	105.7(6)	C(13′)–C(14′)–Te(2′)	105.8
Te(1)–C(5)–C(6)	117.7(7)	Te(2′)–C(15)–C(16)	117.0
Te(1)–C(5)–C(10)	122.9(7)	Te(2′)–C(15)–C(20)	122.9
C(6)–C(5)–C(10)	119.4(9)	C(16)–C(15)–C(20)	119.7
C(5)–C(6)–C(7)	121.1(10)	C(15)–C(16)–C(17′)	119.6
C(6)–C(7)–C(8)	118.6(11)	C(16)–C(17′)–C(18′)	119.3
C(7)–C(8)–C(9)	120.3(12)	C(17′)–C(18′)–C(19′)	121.6
C(8)–C(9)–C(10)	122.1(11)	C(18′)–C(19′)–C(20)	117.7
C(9)–C(10)–C(5)	118.4(10)	C(19′)–C(20)–C(15)	121.6

value due to the increased repulsion between the lone pair of electrons and the bonding electrons. In Me_3Te^+ BPh_4^- the (unconstrained) C–Te–C angles are 90.4 and 93.0 ° [6]. Assessment of the stereochemical activity of the tellurium lone pair in the title compounds would, however, be difficult because of the constraints imposed by the ring systems.

Bond lengths in the cations are unexceptional. The Te–C bonds range from 2.074(13) to 2.172(10) Å, mean 2.12 Å in good agreement with the single-bond covalent radii, sum 2.14 Å [9] and with previous results [1,2,6]. As was found previously [1], the 3,4-benzo-1-telluracyclopentane ring system of I is nearly planar (to within ±0.02 Å), apart from Te which is displaced by a small amount (0.29 Å) from the mean plane of the C atoms (in the direction of C(9)). The 1-telluracyclopentane ring of II has a twist conformation with C(2) and C(3) displaced on opposite sides of the plane through Te, C(1) and C(4). The phenyl rings of the anions of I and II, and of the cation of II are planar to within the limits of experimental error.

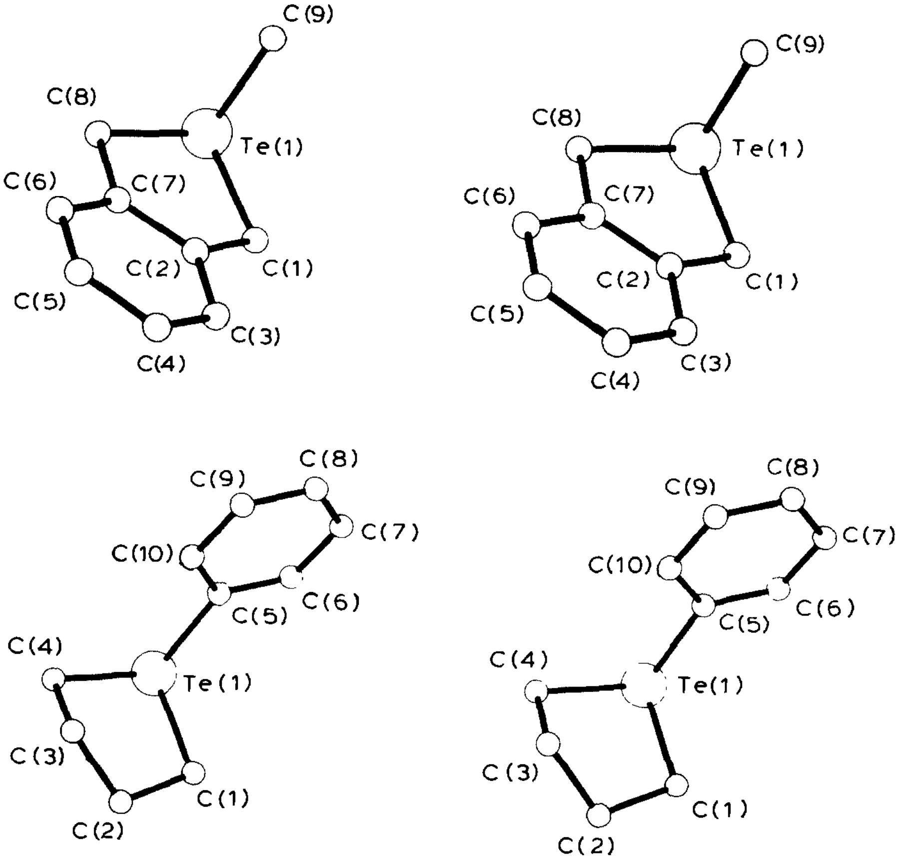

Fig. 1. Stereoscopic views of the tellurium coordination; upper diagram I, lower diagram ordered cation of II.

The bond angles at boron in the tetraphenylborate anions are close to the tetrahedral value, average 109.5° in I and in both anions of II. In each case, however, two angles are relatively small, 103–105° and the other four are larger,

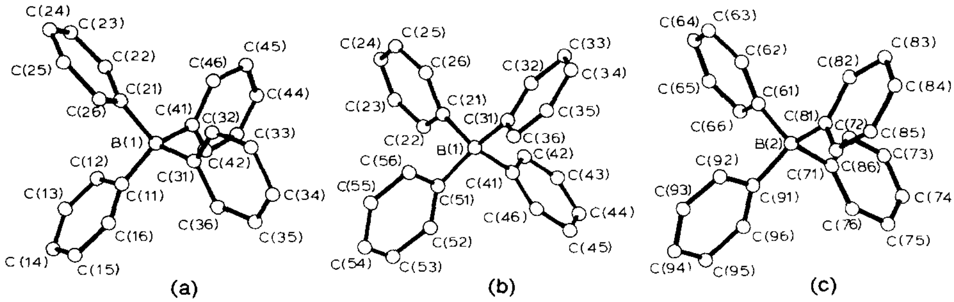

Fig. 2. The tetraphenylborate anions, (a) in I, (b) and (c) in II.

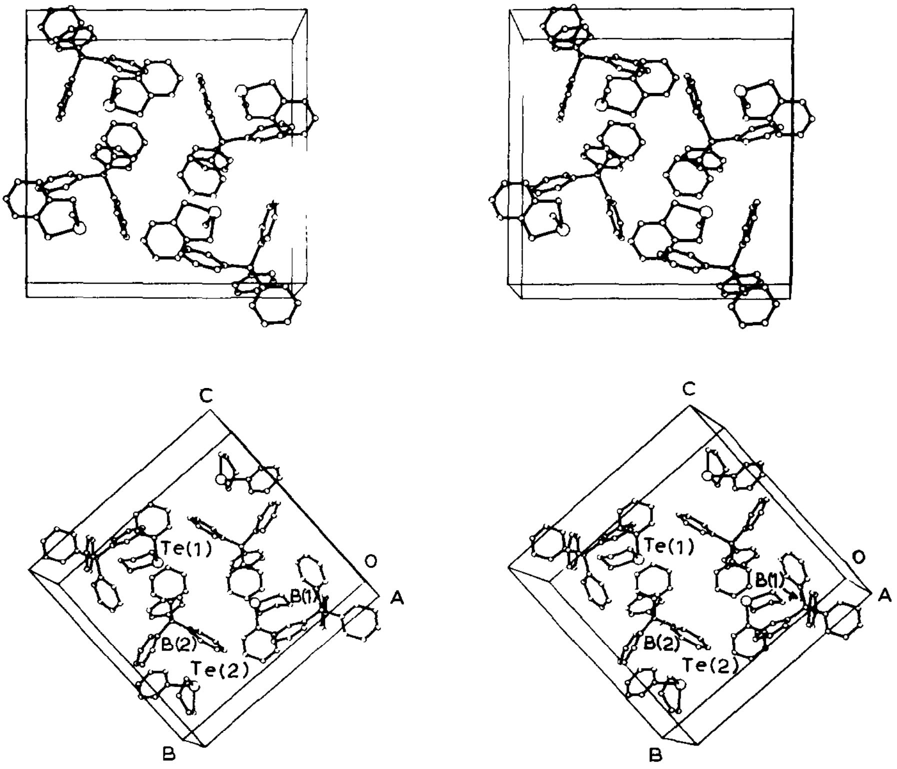

Fig. 3. Stereoscopic views of the packing; upper diagram I, lower diagram II (major occupancy site of disordered cation shown).

range 111–114°. In Me_3Te^+ BPh_4^- the C–B–C angles range from 103 to 112°. The boron atoms are displaced out of the planes of the phenyl rings by amounts varying from 0.060 to 0.167 Å, mean 0.133 Å. Similar deviations were noted in other tetraphenylborate salts [6,10,11,12]. The displacements seem to be such as to move further apart those phenyl rings for which the C–B–C angles are less than tetrahedral. A characteristic distortion of the endocyclic phenyl bond angles with values of ca. 114–116° at the carbon atom bonded to boron, noted previously [6,10–14], is also evident here *. Di Vaira and Orlandini [13] and, later, other workers [6,11,14] suggested that the distortion of the phenyl rings originated from steric hindrance between the substituents at the boron atom. An alternative explanation [15], based on rehybridization or VSEPR effects, induced by the electron-releasing nature of the negatively charged boron atom would, however, also account for the observed geometry of the phenyl rings. It would seem likely that both steric and electronic effects are operative.

The B–C bond lengths, 1.61(1)–1.68(2) Å, mean 1.64 Å agree well with values in the literature [6,10–14]. The angles between the phenyl-ring planes follow a similar pattern in the three anions; in each, there are two angles in the range 85.8–89.6°,

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* Only angle C(42)–C(41)–C(46) at 118.5° in I falls outside this range.

overall mean 87.7 ° and four in the range 52.0–64.6 °, mean 58.7 °. A similar pattern of dihedral angles has been reported [6,10,11] for the BPh_4 anion in a number of other structures.

Although the coordination of tellurium is essentially three-fold, in both I and II short contacts (< 3.55 Å) occur between tellurium and carbon atoms of the BPh_4^- anions (Fig. 3). Two adjacent carbon atoms are involved, C(15) and C(16) at distances of 3.47(1) and 3.51(1) Å in I and C(65), C(66) at 3.44(1), 3.52(1) Å in II *. These distances are shorter than the sum of the Van der Waals radii of tellurium and carbon, 3.9 Å according to Pauling [9], or 3.76 Å if the Van der Waals radius given by Bondi [16] for tellurium is used, but much longer than the sum of the covalent radii (2.14 Å). If these contacts are considered to involve secondary bonding, then this can only be quite weak, but may nevertheless provide an explanation for the low conductivity of I in solution [4] and for the pyrolysis reactions noted in the Introduction.

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* The disordered cation is also involved in short contacts; higher occupancy site: Te(2′) ··· C(43) 3.52 Å, lower occupancy site: Te(2″) ··· C(73) 3.42 Å, Te(2″) ··· C(74) 3.47 Å.