Effect of the Counter-ion on the Structures of Tetraphenylantimony(v)–Stibonium Compounds: Crystal and Molecular Structures of Tetraphenylantimony(v) Bromide, Perchlorate, and Tetraphenylborate†

George Ferguson *
Department of Chemistry and Biochemistry, University of Guelph, Guelph, Ontario, Canada N1G 2W1
Christopher Glidewell, Douglas Lloyd,* and Shirley Metcalfe
Department of Chemistry, University of St. Andrews, St. Andrews, Fife KY16 9ST

Crystals of Ph_4SbBr are monoclinic, $a = 16.293(3)$, $b = 10.616(3)$, $c = 12.507(2)$ Å, $\beta = 105.60(1)°$, space group $P2_1/n$. The structure consists of trigonal bipyramidal molecules in which the apical Sb–Br bond is very long [2.965(1) Å]; the apical and mean equatorial Sb–C distances are 2.151(9) and 2.102(9) Å, respectively. The perchlorate [tetragonal, $a = 12.670(2)$, $c = 6.711(2)$ Å, space group $I\bar{4}$] crystallises with isolated ions of almost perfect tetrahedral local symmetry; in the cation, the Sb–C distance is 2.095(2) Å. The structures of a range of tetraphenylantimony(v) derivatives Ph_4SbX are discussed in terms of the basicity/nucleophilicity of X. Crystals of Ph_4SbBPh_4 are tetragonal, $a = 16.272(3)$, $c = 13.703(3)$ Å, with an I lattice: structure solution was attempted, without success, in all possible space groups. The $SbPh_4^+$ and BPh_4^- ions are scrambled.

Following the structure determinations[1,2] of two stibonium ylides[3] (**1**) and (**2**), in which the lengths of the unique ylidic Sb–C bonds were found to be 2.042(3) Å and 2.049(4) Å, respectively, significantly shorter than the corresponding Sb–aryl bonds, it was necessary to establish, for comparative purposes, the Sb–C distance in an unperturbed tetrahedral Ph_4Sb^+ cation as a benchmark structural parameter.

Nearly all compounds of stoicheiometry Ph_4SbX, the structures of which have been reported, have been found to contain five-co-ordinate antimony; these include derivatives with X = OH,[4] OMe,[5] OC(O)H,[6] Cl,[7] OSO_2Ph,[8] and $ON{=}C(CH_3)NO$.[9] The carbonate $(Ph_4Sb)_2CO_3$ (**3**) contains both five- and six-co-ordinate antimony.[10]

The use of a poorly nucleophilic counter-ion of high symmetry offers the best chance of observing an unperturbed Ph_4Sb^+ unit of regular tetrahedral configuration: the $[Cu_2Cl_6]^{2-}$ ion fulfils the first condition, but not the second and the cations in $(Ph_4Sb)_2[Cu_2Cl_6]$ are[11] accordingly somewhat distorted from the regular tetrahedral arrangement.

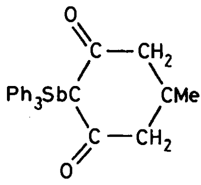
In the present work we have studied three derivatives Ph_4SbX [X = BPh_4 (**4**), Br (**5**), or ClO_4 (**6**)], which are all capable of at least tetrahedral symmetry. Our initial study of Ph_4SbBPh_4 (**4**) showed evidence of scrambling of the BPh_4^- anions and $SbPh_4^+$ cations. Subsequent study of Ph_4SbBr (**5**) revealed geometrical characteristics intermediate between the fully ionic tetraphenylstibonium bromide $Ph_4Sb^+Br^-$ and the fully covalent bromotetraphenylstiborane, $BrPh_4Sb$. The perchlorate salt (**6**) proved to contain isolated tetrahedral cations and anions. Here we report in detail the structural results for these compounds.

Experimental

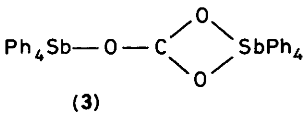
The bromide Ph_4SbBr was prepared[12] from Ph_3Sb and PhBr: Ph_4SbBPh_4 and Ph_4SbClO_4 were prepared from Ph_4SbBr by metathesis. Crystals suitable for *X*-ray examination were grown from solutions in nitromethane [for (**4**)], water [for (**5**)], or acetone [for (**6**)].

$Ph_3SbC(SO_2Ph)_2$

(**1**)



(**2**)



(**3**)

Ph_4SbBPh_4

(**4**)

Ph_4SbBr

(**5**)

Ph_4SbClO_4

(**6**)

Crystal Data.—(**4**), $C_{48}H_{40}BSb$, $M_r = 749.36$. Tetragonal, $a = 16.272(3)$, $c = 13.703(3)$ Å, $V = 3\,268.3$ Å^3. Laue symmetry $4/mmm$, and systematic absences (in hkl, $h + k + l \neq 2n$; in $00l$, $l \neq 4n$) define the space group uniquely as $I4_122$ (No. 98), but almost all $00l$ reflections are very weak. $Z = 4$, $D_x = 1.38$ g cm^{-3}, $\mu(\text{Mo-}K_\alpha) = 8.06$ cm^{-1}, $\lambda = 0.710\,73$ Å, $F(000) = 1\,536$.

(**5**), $C_{24}H_{20}BrSb$, $M_r = 510.09$. Monoclinic, $a = 16.293(3)$, $b = 10.616(3)$, $c = 12.507(2)$ Å, $\beta = 105.60(1)°$, $V = 2\,083.7$ Å^3. Space group $P2_1/n$ (No. 14). $Z = 4$, $D_x = 1.63$ g cm^{-3}, $\mu(\text{Mo-}K_\alpha) = 32.4$ cm^{-1}, $\lambda = 0.710\,73$ Å, $F(000) = 1\,000$.

(**6**), $C_{24}H_{20}ClO_4Sb$, $M_r = 529.63$. Tetragonal, $a = 12.670(2)$, $c = 6.711(2)$ Å, $V = 1\,077.3$ Å^3. Space group $I\bar{4}$ (No. 82). $Z = 2$, $D_x = 1.63$ gm cm^{-3}, $\mu(\text{Mo-}K_\alpha) = 14.4$ cm^{-1}, $\lambda = 0.710\,73$ Å, $F(000) = 528$.

Data Collection.—For all three compounds accurate cell dimensions and crystal orientation matrices were determined with a CAD4 diffractometer by least-squares treatment of the setting angles of 25 reflections in the ω–2θ range $8° \leqslant \theta \leqslant 16°$. Data were collected in the ω–2θ scan mode with ω scan width

---

† *Supplementary data* (see section 5.6.3 of Instructions for Authors in the January issue). Full lists of bond lengths and angles, temperature factors, hydrogen co-ordinates, and least-squares planes have been deposited at the Cambridge Crystallographic Data Centre.

Table 1. Details of measured reflections and R factors

	(4)	(5)	(6)
Crystal dimensions (mm)	0.30 × 0.30 × 0.50	0.12 × 0.37 × 0.45	0.14 × 0.21 × 0.45
Range of reflections measured:			
h	0—20	0—22	0—22
k	0—25	0—14	0—22
l	0—17	−17—17	0—11
$2\theta_{max.}/°$	54	60	80
No. of reflections measured	2 316	6 536	2 007
No. of unique reflections	1 158	6 048	1 874
No. with $F_o \geqslant 3\sigma(F_o)$	986	1 660	1 647
Max. and min. transmission coefficients for absorption correction		0.702, 0.483	0.837, 0.710
p[a]		0.07	0.04
R		0.044	0.025
R_w		0.058	0.030

[a] Weighting scheme: $w = 1/[\sigma^2(F_o) + p(F_o)^2]$.

Table 2. Positional parameters for Ph_4SbBr and their estimated standard deviations

Atom	x	y	z	$B/Å^{2\,a}$
Sb	−0.009 97(4)	0.178 71(6)	0.228 81(5)	3.82(1)
Br	0.136 45(7)	0.193 4(1)	0.130 75(8)	5.98(3)
C(11)	−0.120 4(5)	0.156 8(7)	0.290 3(7)	3.5(2)
C(12)	−0.175 5(6)	0.257 2(11)	0.285 7(8)	5.4(2)
C(13)	−0.243 7(6)	0.244 2(12)	0.326 5(9)	6.4(3)
C(14)	−0.261 6(6)	0.134 8(12)	0.371 4(9)	6.8(3)
C(15)	−0.209 7(6)	0.034 5(10)	0.376 7(7)	6.1(3)
C(16)	−0.138 5(6)	0.043 7(9)	0.338 5(7)	5.0(2)
C(21)	0.060 5(6)	0.293 5(7)	0.358 8(7)	4.0(2)
C(22)	0.116 8(6)	0.384 7(10)	0.343 5(8)	5.5(3)
C(23)	0.160 0(7)	0.457 9(10)	0.435 6(10)	6.8(3)
C(24)	0.151 2(8)	0.436 5(12)	0.537 4(10)	8.2(3)
C(25)	0.093 6(9)	0.348 3(14)	0.552 4(9)	9.7(4)
C(26)	0.048 5(7)	0.275 6(12)	0.463 4(8)	6.7(3)
C(31)	0.024 2(6)	−0.013 1(9)	0.238 1(7)	4.4(2)
C(32)	−0.020 7(6)	−0.097 3(10)	0.160 8(8)	6.0(3)
C(33)	−0.002 6(8)	−0.225 4(11)	0.176 4(10)	7.4(3)
C(34)	0.056 4(8)	−0.262 1(12)	0.268 9(10)	8.1(4)
C(35)	0.102 8(9)	−0.182 2(11)	0.343 3(11)	8.5(4)
C(36)	0.086 4(7)	−0.054 4(10)	0.329 7(8)	6.4(3)
C(41)	−0.076 7(6)	0.269 6(11)	0.082 8(7)	4.9(2)
C(42)	−0.135 2(8)	0.208 9(13)	0.004 0(9)	9.8(4)
C(43)	−0.185 3(7)	0.273 0(16)	−0.085 1(11)	12.9(4)
C(44)	−0.175 0(6)	0.395 2(15)	−0.099 3(8)	9.0(4)
C(45)	−0.115 9(7)	0.458 5(11)	−0.024 6(8)	7.6(3)
C(46)	−0.066 4(7)	0.393 5(11)	0.067 0(7)	6.1(3)

[a] Anisotropically refined atoms are given in the form of the isotropic equivalent thermal parameter defined as (4/3) $[a^2B_{1.1} + b^2B_{2.2} + c^2B_{3,3} + ab\,(\cos\gamma)\,B_{1.2} + ac(\cos\beta)B_{1,3} + bc(\cos\alpha)\,B_{2,3}]$.

Table 3. Positional parameters for Ph_4SbClO_4 and their estimated standard deviations

Atom	x	y	z	$B/Å^{2\,a}$
Sb	0.0	0.0	0.0	2.262(2)
Cl	0.0	0.5	0.25	3.74(2)
O	0.087 5(4)	0.485 2(6)	0.364 5(5)	12.7(1)
C(1)	−0.075 0(2)	0.112 2(2)	−0.180 3(3)	2.62(3)
C(2)	−0.043 0(2)	0.216 9(2)	−0.175 3(4)	3.30(4)
C(3)	−0.089 6(3)	0.288 2(2)	−0.304 6(5)	4.30(5)
C(4)	−0.167 9(3)	0.255 7(3)	−0.433 2(5)	4.71(5)
C(5)	−0.202 1(3)	0.152 2(3)	−0.431 0(5)	4.64(5)
C(6)	−0.155 1(2)	0.079 4(2)	−0.306 1(4)	3.74(4)

[a] Anisotropically refined atoms are given in the form of the isotropic equivalent thermal parameter defined as (4/3) $[a^2B_{11} + b^2B_{22} + c^2B_{33} + ab(\cos\gamma)B_{12} + ac(\cos\beta)B_{13} + bc(\cos\alpha)B_{23}]$.

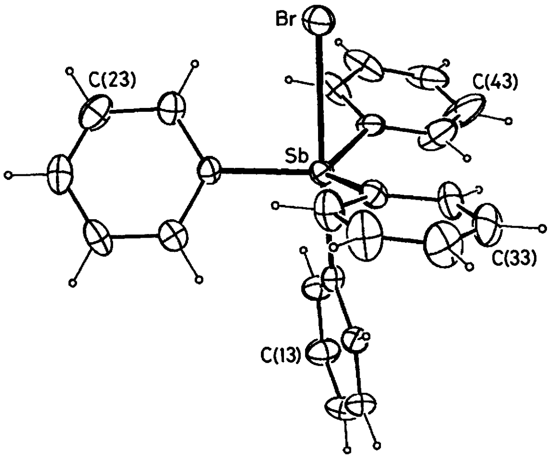


Figure 1. Perspective view of the molecule of Ph_4SbBr, showing the atom numbering scheme

(0.60 + 0.35 tanθ), using graphite-monochromatised Mo-K_α radiation: details of crystal size and reflections measured are given in Table 1. For (**5**) intensities of three reflections measured every 4 h decayed by 10.7% of the course of the data collection; this was allowed for by appropriate scaling. Data were corrected for Lorentz, polarisation, and absorption effects.

Structure Solution and Refinement.—Co-ordinates of Sb and Br in (**5**) were determined by Patterson methods: co-ordinates of Sb and Cl in (**6**) were deduced from a consideration of the space group. Positions of other non-hydrogen atoms were obtained by the heavy-atom method. Refinement was carried out by full-matrix least-squares techniques. Positions of all non-hydrogen atoms were refined with anisotropic temperature factors: hydrogen atoms were visible in difference maps and were included in calculated positions as riding atoms with C–H 0.95 Å, and B_{iso} 7.0 Å^2 [for (**4**)] or 5.0 Å^2 [for (**5**)]. Parameters p in the weighting scheme $w = 1/[\sigma^2(F_o) + p(F_o)^2]$ and final R factors are in Table 1. All calculations were performed with a PDP11/73 computer using the program SDP-Plus;[13] scattering

Table 4. Selected molecular dimensions (distances in Å, angles in degrees)[a]

(a) Ph_4SbBr			
Sb–Br	2.965(1)	Sb–C(31)	2.106(9)
Sb–C(11)	2.151(9)	Sb–C(41)	2.092(9)
Sb–C(21)	2.107(8)		
Br–Sb–C(11)	175.5(2)	C(11)–Sb–C(31)	96.3(3)
Br–Sb–C(21)	87.5(3)	C(11)–Sb–C(41)	94.2(3)
Br–Sb–C(31)	81.0(3)	C(21)–Sb–C(31)	115.8(3)
Br–Sb–C(41)	84.4(3)	C(31)–Sb–C(41)	124.2(4)
C(11)–Sb–C(21)	96.9(3)	C(41)–Sb–C(21)	117.0(4)
(b) $Ph_4Sb^+ClO_4^-$			
Sb–C(1)	2.095(2)	C(1)–Sb–C(1^{i})	109.44(8)
		C(1)–Sb–C(1^{ii})	109.49(8)
Cl–O	1.361(5)	O–Cl–O^{iii}	111.3(2)
		O–Cl–O^{iv}	108.6(4)

[a] Roman numerals refer to atoms at the following equivalent positions: i, $-x,-y,z$; ii, $y,-x,-z$; iii, $-x,1-y,z$; iv, $-\frac{1}{2}+y,\frac{1}{2}-x,\frac{1}{2}-z$.

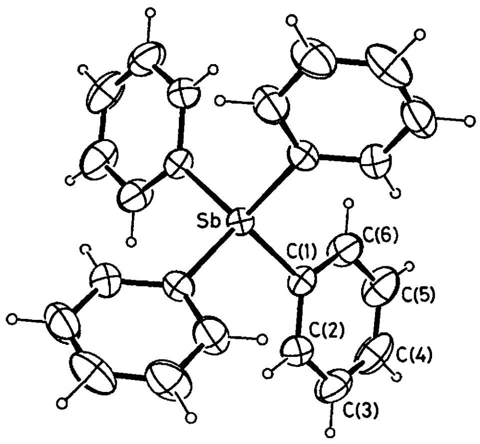


Figure 2. Perspective view of the cation Ph_4Sb^+ in Ph_4SbClO_4, showing the atom numbering scheme

factors and anomalous dispersion corrections were taken from ref. 14. Final difference maps were devoid of chemically significant features.

Atomic co-ordinates for (**5**) and (**6**) are in Tables 2 and 3 respectively, and selected molecular dimensions in Table 4. Figures 1 and 2 show perspective views of (**5**) and the cation of (**6**). Figure 3 is a view of the unit cell of (**6**), showing the independent cations and anions. The Figures were all prepared using ORTEP-II.[15]

Results and Discussion

Tetraphenylstibonium Bromide (**5**).—The structure consists of isolated trigonal bipyramidal molecules with no significant intermolecular contacts. The bromine atom occupies an apical site, just as chlorine occupies an apical site in Ph_4SbCl[7] and as oxygen occupies an apical site in Ph_4SbOH,[4] Ph_4SbOMe,[5] $Ph_4SbOC(O)H$,[6] Ph_4SbOSO_2Ph,[8] and $Ph_4SbON{=}C(CH_3)NO$.[9] As usual (Table 5) the apical Sb–C distance [2.151(9) Å] is longer than the equatorial Sb–C distance [mean value 2.102(9) Å]; the difference Δ (0.049 Å) is near the lower end of the range of Δ [0.110 Å in Ph_5Sb[16] as its hemi-cyclohexane solvate, to 0.024 Å in $Ph_3SbC(SO_2Ph)_2$[1]].

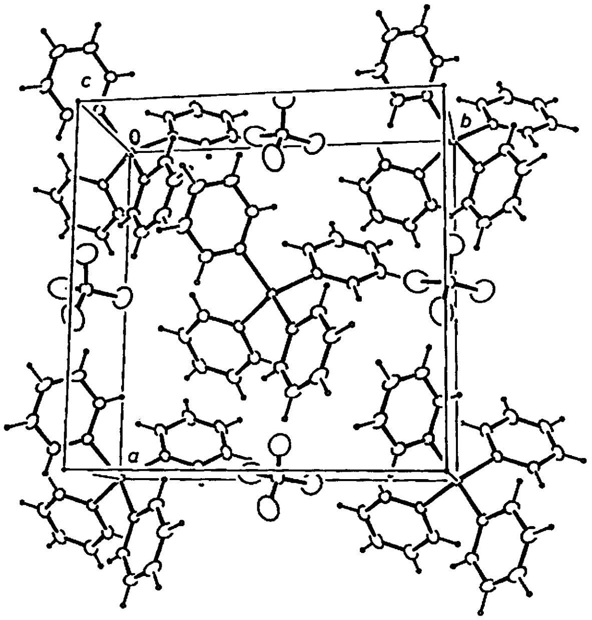
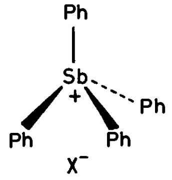
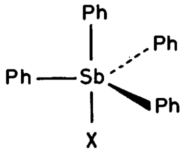


Figure 3. View of the unit cell of Ph_4SbClO_4, viewed approximately down the *c* axis, showing the independent cations and anions



(**5a**)



(**5b**)

Although the Sb–C distances found here are typical of Sb–aryl bonds, the Sb–Br distance [2.965(1) Å] is much longer than the values found in $SbBr_3$ (2.490 Å[17]) and in $Ph_2SbBrCl_2$ and Ph_2SbBr_3[18] (Table 5), although it is nevertheless substantially less than the sum of the van der Waals' radii for Sb and Br.[19] At the same time the mean C_{eq}–Sb–C_{ap} angle is 95.8°, representing a significant deviation of the equatorial SbC_3 fragment from the planar arrangement of a regular trigonal bipyramid. The distortion of the SbC_4 towards tetrahedral and the very long Sb–Br bond indicate that the structure should be represented as a hybrid of (**5a**; X = Br) and (**5b**; X = Br), a salt and a stiborane respectively, although with (**5b**) dominant.

Similar very long apical Sb–X bonds are found also in Ph_4SbCl, where the Sb–Cl distance is 2.74 Å[7] (*cf.* 2.333 Å in $SbCl_3$[20]), and in Ph_4SbOSO_2Ph), where the Sb–O distance is 2.506 Å[8] (typical Sb–O distances are *ca.* 2.00—2.10 Å; see Table 5). In $Ph_4SbOC(O)H$, the Sb–O distance is 2.222 Å,[6] again longer than the typical Sb–O value. If normal Sb–O, Sb–Cl, and Sb–Br distances are taken as 2.05 Å (Table 5), 2.33 Å,[20] and 2.49 Å,[17] respectively, the percentage elongations of Sb–O bonds in Ph_4SbX for X = OMe, OC(O)H, and OSO_2Ph are 0.5, 8.3, and 22.4%, respectively. When X = ClO_4 (see later) the separation of antimony and oxygen is complete. These elongations can be associated with a steadily increasing contribution from the canonical form (**5a**) at the expense of (**5b**).

The ordering of the Sb–O bond elongations: OMe < OC(O)H < OSO_2Ph < ClO_4 follows the same pattern as the pK_a values for the corresponding acids HX: HOMe, 15.5; HCO_2H, 3.8; $HOSO_2Ph$, −6.5; $HClO_4$, −10. Likewise the elongations in Ph_4SbCl and Ph_4SbBr (17.6% and 18.9%, respectively) reflect

Table 5. Comparison of mean distances in trigonal bipyramidal antimony compounds (Å)

	$d(\mathrm{SbC})_{ap}$	$d(\mathrm{SbC})_{eq}$	Δ†	$d(\mathrm{SbX})_{ap}$	$d(\mathrm{SbX})_{eq}$	Ref.
Ph_4SbOH	2.128	2.131	0.087	2.048[a]		4
Ph_4SbOMe	2.199	2.119	0.080	2.061[a]		5
$Ph_4SbOC(O)H$	2.176	2.109	0.068	2.222[a]		6
Ph_4SbOSO_2Ph	2.131	2.108	0.023	2.506[a]		8
Ph_5Sb	2.243	2.133	0.110			16
$(p\text{-}CH_3C_6H_4)_5Sb$	2.26	2.16	0.10			*b*
$(Ph_3SbO)_2$	2.162	2.127	0.035	2.077[a]	1.935[a]	*c*
(1)[d]	2.124	2.100	0.024	2.844[a]	2.042[e]	1
(2)[d]	2.111	2.005	0.106	2.856[a]	2.049[e]	2
Ph_2SbBr_3		2.149		2.614[f]	2.478[f]	18
$Ph_2SbBrCl_2$		2.128		2.491[g]	2.446[f]	18
Ph_4SbCl[d]	2.15	2.10	0.05	2.74		7
Ph_4SbBr[d]	2.151	2.102	0.049	2.965[f]		This work

† $\Delta = d(\mathrm{Sb{-}C})_{ap} - d(\mathrm{Sb{-}C})_{eq}$.

[a] X = O. [b] C. Brabant, J. Hubert, and A. L. Beauchamp, *Can. J. Chem.*, 1973, **51**, 2592. [c] G. Ferguson, C. Glidewell, B. Kaitner, D. Lloyd, and S. Metcalfe, *Acta Crystallogr., Sect. C*, 1987, **43**, 824. [d] Geometry at Sb intermediate between tetrahedral SbC_4 and trigonal bipyramidal SbC_4X. [e] X = ylidic C. [f] X = Br. [g] X = Cl.

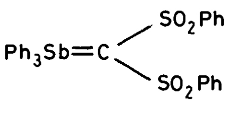
the pK_a values: HCl, −2.2; HBr, −4.7. Hence the detailed structures of compounds Ph_4SbX having structures in the solid state intermediate between stibonium salts and stiboranes are readily understood in terms of the basicity/nucleophilicity of the substituent X^-.

On the other hand, in acetonitrile solution, conductance data for the series Ph_4SbX (for X = F, Cl, Br, or I) indicate[21] that for X = F and X = Cl the compounds are molecular and non-conducting in solution, for X = I the compound is fully ionised in solution, while for X = Br the conductance is intermediate between the values for X = Cl and X = I. Hence although the hybrid structure (**5a**) $\longleftrightarrow$ (**5b**) is reflected in the solution behaviour for X = Br, this is not so for X = Cl. An earlier deduction that Ph_4SbX was molecular in the solid state for X = Cl and Br was based[22] upon an assignment of the Raman spectrum, which in turn depended on the assumption of 'normal' Sb–X bonds, and hence unshifted ν(Sb–X).

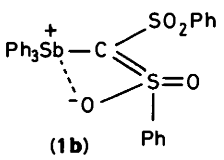
The behaviour of Ph_4SbX as X varies thus resembles that of tropylium salts, which also show a range of properties varying according to the counter-ion.[23] Thus, those having anions of low nucleophilicity, such as perchlorate or tetrafluoroborate, are colourless, of high melting-point, stable in air, and sublime only with difficulty, whereas those with more nucleophilic anions, such as the halides, may be coloured, sublime readily, and are not stable in the atmosphere.[24] It has been shown that tropylium salts with anions derived from a strong acid, for example the perchlorate, are completely dissociated, but if the anion is derived from a weak acid such as acetic or hydrocyanic the compounds are only feebly dissociated.[25] Thus C_7H_7CN exists largely as cyanocycloheptatriene.

Tetraphenylstibonium Perchlorate (**6**).—The structure comprises isolated tetrahedral ions. The cations lie at the vertices and the body-centre of the tetragonal cell, and the anions on the rectangular faces A and B (Figure 3), with the antimony and chlorine atoms occupying the special positions, of $\bar{4}$ (S_4) symmetry, of types *a* and *c* respectively in the space group $I\bar{4}$. The two independent C–Sb–C angles in the Ph_4Sb^+ cation are identical, so that the central SbC_4 core of this cation has exact $\bar{4}3$ (T_d) local symmetry, although the symmetry of the whole cation is only $\bar{4}$. The salt is thus isomorphous with Ph_4M^+ ClO_4^- (M = As[26] or Bi[27]) and with $Ph_4As^+I^-$.[28]

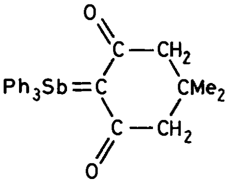
The unique Sb–C bond distance is 2.095(2) Å. The Sb–C distances in the species of unambiguous five-co-ordination in Table 5 are all longer than 2.095 Å: however the ylidic Sb–C distances in the stibonium ylides (**1**) and (**2**) are significantly shorter than the 2.095 Å found for Ph_4Sb^+, confirming the importance[1,2] of the canonical forms (**1a**) and (**2a**); the quasi-penta-co-ordination of antimony in these ylides points to the contribution also of the canonical forms (**1b**) and (**2b**).



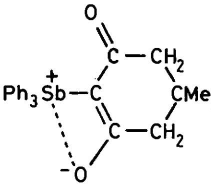
(**1a**)



(**1b**)



(**2a**)



(**2b**)

Tetraphenylstibonium Tetraphenylborate (**4**).—This compound crystallises in a body-centred tetragonal lattice with 4/*mmm* Laue symmetry. The 00*l* reflections were all weak or absent, but those having *l* = 4*n* were weakly present. If this is systematic, then the space group is defined uniquely as $I4_122$ (No. 98). Attempts at structure solution in $I4_122$ were consistent with total scrambling of the Sb and B atoms, but gave no clear location for the phenyl carbon atoms. Attempts in other possible space groups (made disregarding the 00*l* reflections) always led to the same conclusion of disorder. No further work is contemplated on this system.

References

1 G. Ferguson, C. Glidewell, D. Lloyd, S. Metcalfe, and B. L. Ruhl, *J. Chem. Res.*, 1987, (*S*) 32, (*M*) 0458.
2 G. Ferguson, C. Glidewell, I. Gosney, D. Lloyd, H. Lumbroso, and S. Metcalfe, *J. Chem. Soc., Perkin Trans. 2*, in the press.
3 C. Glidewell, D. Lloyd, and S. Metcalfe, *Tetrahedron*, 1986, **42**, 3887.

4 A. L. Beauchamp, M. J. Bennett, and F. A. Cotton, *J. Am. Chem. Soc.*, 1969, **91**, 297.

5 K. Shen, W. E. McEwen, L. J. LaPlaca, W. C. Hamilton, and A. P. Wolf, *J. Am. Chem. Soc.*, 1968, **90**, 1718.

6 S. P. Bone and D. B. Sowerby, *J. Chem. Res.*, 1979, (*S*) 82, (*M*) 1029.

7 V. A. Lebedev, R. I. Bochkova, E. A. Kuzmin, V. V. Sharutin, and N. V. Belov, *Dokl. Akad. Nauk SSSR*, 1981, **260**, 1124.

8 R. Ruether, F. Huber, and H. Preut, *J. Organomet. Chem.*, 1985, **295**, 21.

9 J. Kopf, G. Vetter, and G. Klar, *Z. Anorg. Allg. Chem.*, 1974, **409**, 285.

10 G. Ferguson and D. M. Hawley, *Acta Crystallogr., Ser. B*, 1974, **30**, 103.

11 A. Bencini, D. Gatteschi, and C. Zanchini, *Inorg. Chem.*, 1985, **24**, 704.

12 J. Chatt and F. G. Mann, *J. Chem. Soc.*, 1940, 1192.

13 B. A. Frenz, 1983, SDP-Plus Program System, Frenz and Associates, College Station, Texas 77840; Enraf-Nonius, Delft, Holland.

14 'International Tables for *X*-ray Crystallography,' Vol. IV, Kynoch Press, Birmingham, 1974.

15 C. K. Johnson, ORTEP-II, Report ORNL 5138, Oak Ridge National Laboratory, Oak Ridge, TN, U.S.A., 1976.

16 C. Brabant, B. Blanck, and A. L. Beauchamp, *J. Organomet. Chem.*, 1974, **82**, 231.

17 S. Konaka and M. Kimura, *Bull. Chem. Soc. Jpn.*, 1973, **46**, 413.

18 S. P. Bone and D. B. Sowerby, *J. Chem. Soc., Dalton Trans.*, 1979, 718.

19 A. Bondi, *J. Phys. Chem.*, 1964, **68**, 441.

20 S. Konaka and M. Kimura, *Bull. Chem. Soc. Jpn.*, 1973, **46**, 404.

21 G. S. Harris and A. Khan, personal communication.

22 J. B. Orenberg, M. D. Morris, and T. V. Long, II, *Inorg. Chem.*, 1971, **10**, 933.

23 See D. Lloyd, 'Non-benzenoid Conjugated Carbocyclic Compounds,' Elsevier, Amsterdam, 1984, p. 74.

24 K. M. Harmon, F. E. Cummings, D. A. Davis, and D. J. Diestler, *J. Am. Chem. Soc.*, 1962, **84**, 120, 3449.

25 M. E. Vol'pin, I. S. Akhrem, and D. N. Kursanov, *Zh. Obshch. Khim.*, 1958, **28**, 330.

26 M. C. Couldwell, *Cryst. Struct. Commun.*, 1979, **8**, 469.

27 J. Bordner and L. D. Freedman, *Phosphorus*, 1973, **3**, 33.

28 R. C. L. Mooney, *J. Am. Chem. Soc.*, 1940, **62**, 2955.

Received 7th May 1987; *Paper* 7/807